Experimental and Theoretical Investigation of Catalyst Poisoning and Regeneration During Biogas Steam Reforming on Nickel

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The Degree of Doctor of Philosophy

Department of Chemical Engineering

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Declaration

I declare that this written submission represents my ideas in my own words, and where ideas or words of others have been included, I have adequately cited and referenced the original sources. I also declare that I have adhered to all principles of academic honesty and integrity and have not misrepresented or fabricated or falsified any idea/data/fact/source in my submission. I understand that any violation of the above will be a cause for disciplinary action by the Institute and can also evoke penal action from the sources that have thus not been properly cited, or from whom proper permission has not been taken when needed.

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Finally, I would like to thank the ALMIGHTY for providing this opportunity and helped me in countless ways.

Srinivas Appari
DEDICATION

To

MY BELOVED PARENTS
**Nomenclature**

- $a_k$: Pre-exponential constant in sticking coefficient expression
- $a_{k}^{eq}$: Equilibrium activity
- $A_v$: Active surface area (m$^2$)
- $A_i$: Pre-exponential constant in Arrhenius expression (varies)
- $A_{CH_4}$: Chromatograph area of CH$_4$ (mm$^2$)
- $A_{N_2}$: Chromatograph area of N$_2$ (mm$^2$)
- $A_s$: Specific area (m$^{-1}$)
- $b_i$: Temperature exponent in sticking coefficient expression
- $B_{1/2}$: X-Ray diffraction angle (degrees)
- $C_p$: Specif heat (J kg$^{-1}$ K$^{-1}$)
- $c_A$: Concentration of A (mol m$^{-3}$)
- $D$: Mean size of crystallite (nm)
- $D_A$: Gas phase dissociation energy of molecule A (kJ mol$^{-1}$)
- $D$: Diffusivity (m$^2$ s$^{-1}$)
- $D_{km}$: Axial dispersion coefficient of species k (m$^2$ s$^{-1}$)
- $D_{kj}$: Binary diffusivity of species k in j (m$^2$ s$^{-1}$)
- $D_0$: Initial dispersion in sintering rate expression (m$^2$ s$^{-1}$)
- $E_f$: Activation energy for forward reaction (kJ mol$^{-1}$)
- $E_r$: Activation energy for reversed reaction (kJ mol$^{-1}$)
- $F$: Molar flow rate (mol min$^{-1}$)
- $k$: Thermal conductivity (J m$^{-1}$ s$^{-1}$ K$^{-1}$)
- $r_{Ai}$: Reaction rate of in reaction A (mol m$^{-3}$ sec$^{-1}$)
- $k$: Constant in Debye-Scherrer equation
- $k_{AB}$: Rate constant (varies)
- $k_{obs}$: Observed sintering rate constant
- $k_B$: Boltzmanns constant (J K$^{-1}$)
- $K_b$: Total number of bulk species
- $K_{ci}$: Equilibrium constant in concentration units for reaction i (varies)
- $K_g$: Total number of gas-phase species
- $K_p$: Equilibrium constant in pressure units for reaction i
- $K_s$: Total number of surface species
- $k_f$: Forward rate constant (varies)
- $k_r$: Reverse rate constant (varies)
- $K$: Equilibrium constant
- $G$: Gibbs free energy (J mol$^{-1}$)
- $G^0$: Standard Gibbs free energy (J mol$^{-1}$)
- $\Delta G$: Free energy change (J mol$^{-1}$)
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H$</td>
<td>Enthalpy (J mol$^{-1}$)</td>
</tr>
<tr>
<td>$\Delta H$</td>
<td>Enthalpy change (J mol$^{-1}$)</td>
</tr>
<tr>
<td>$m$</td>
<td>Sintering constant</td>
</tr>
<tr>
<td>$\dot{m}$</td>
<td>Mass flow rate (kg s$^{-1}$)</td>
</tr>
<tr>
<td>$N$</td>
<td>Total number of species</td>
</tr>
<tr>
<td>$N_T$</td>
<td>Total number of active sites</td>
</tr>
<tr>
<td>$n$</td>
<td>Sintering order</td>
</tr>
<tr>
<td>$n_{CH_4}$</td>
<td>Moles of CH$_4$</td>
</tr>
<tr>
<td>$n_{N_2}$</td>
<td>Moles of N$_2$</td>
</tr>
<tr>
<td>$p$</td>
<td>Pressure (Pa)</td>
</tr>
<tr>
<td>$p^0$</td>
<td>Standard state pressure (Pa)</td>
</tr>
<tr>
<td>$p_{H_2}$</td>
<td>Partial pressure of H$_2$ (Pa)</td>
</tr>
<tr>
<td>$p_{H_2S}$</td>
<td>Partial pressure of H$_2$S (Pa)</td>
</tr>
<tr>
<td>$Q$</td>
<td>Chemisorption energy (kJ mol$^{-1}$)</td>
</tr>
<tr>
<td>$r$</td>
<td>Interbody distance (m)</td>
</tr>
<tr>
<td>$R$</td>
<td>Gas constant (J mol$^{-1}$ K$^{-1}$)</td>
</tr>
<tr>
<td>$\dot{s}_k$</td>
<td>Molar production rate of species $k$ due to surface reaction (mol m$^{-2}$ s$^{-1}$)</td>
</tr>
<tr>
<td>$S_0$</td>
<td>Sticking coefficient</td>
</tr>
<tr>
<td>$S^0$</td>
<td>Standard state of entropy (J K$^{-1}$)</td>
</tr>
<tr>
<td>$\Delta S$</td>
<td>Entropy change (J K$^{-1}$)</td>
</tr>
<tr>
<td>$t$</td>
<td>Time (s)</td>
</tr>
<tr>
<td>$T$</td>
<td>Temperature (K)</td>
</tr>
<tr>
<td>$T^0$</td>
<td>Reference temperature (K)</td>
</tr>
<tr>
<td>$T_m$</td>
<td>Melting point of the metal (K)</td>
</tr>
<tr>
<td>$S$</td>
<td>Surface area of the catalytic bed (m$^2$)</td>
</tr>
<tr>
<td>$S_{F_{cal}}$</td>
<td>Calculated stoichiometric factor</td>
</tr>
<tr>
<td>$V_s$</td>
<td>Volume of sample adsorbed (m$^3$)</td>
</tr>
<tr>
<td>$x$</td>
<td>Co-ordinate direction</td>
</tr>
<tr>
<td>$W$</td>
<td>Molecular weight</td>
</tr>
<tr>
<td>$X_{CH_4}$</td>
<td>Conversion of CH$_4$</td>
</tr>
<tr>
<td>$X_k$</td>
<td>Mole fraction of species $k$</td>
</tr>
<tr>
<td>$[X]$</td>
<td>Concentration (mol m$^{-3}$) for gaseous species, (mol m$^{-2}$) for surface species</td>
</tr>
<tr>
<td>$Y_{CH_4}$</td>
<td>Mole fraction of CH$_4$</td>
</tr>
<tr>
<td>$Y_{N_2}$</td>
<td>Mole fraction of N$_2$</td>
</tr>
<tr>
<td>$z$</td>
<td>Axial length (m)</td>
</tr>
<tr>
<td>$Y_k$</td>
<td>Mass fraction of species $k$</td>
</tr>
<tr>
<td>$Z$</td>
<td>Rate of collision (mol m$^{-2}$ s$^{-1}$)</td>
</tr>
</tbody>
</table>

**Greek Letters**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha_{CH_4}$</td>
<td>Response factor of CH$_4$</td>
</tr>
<tr>
<td>$\alpha_{CO}$</td>
<td>Response factor of CO</td>
</tr>
<tr>
<td>$\alpha_{CO_2}$</td>
<td>Response factor of CO$_2$</td>
</tr>
<tr>
<td>$\alpha_{H_2}$</td>
<td>Response factor of H$_2$</td>
</tr>
<tr>
<td>$\beta$</td>
<td>Temperature exponent in Arrhenius expression</td>
</tr>
</tbody>
</table>
\( \epsilon \) Porosity
\( \varphi \) Deactivation function
\( \nu' \) Stoichiometric coefficient of reactants
\( \nu'' \) Stoichiometric coefficient of products
\( \rho \) Density (kg m\(^{-3}\))
\( \eta \) Effectiveness factor
\( \tau \) Tortuosity
\( \theta \) Angle of incidence (degrees)
\( \theta_k \) Fractional coverage of adsorbed species \( k \)
\( \theta_s \) Fractional sulfur coverage
\( \phi \) Total surface coverage
\( \lambda \) X-Ray wave length (A\(^0\))

**Subscripts**
- \( g \) Gas-phase species
- \( i \) Reaction index
- \( k \) Species index
- \( s \) Surface species

**Superscripts**
- \( 0 \) Standard conditions
- \( d \) Diffusive
- \( e \) Effective
<table>
<thead>
<tr>
<th>Abbreviations</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>AES</td>
<td>Auger electron spectroscopy</td>
</tr>
<tr>
<td>ATR</td>
<td>Autothermal reforming</td>
</tr>
<tr>
<td>CD</td>
<td>Condenser</td>
</tr>
<tr>
<td>CVD</td>
<td>Chemical vapor deposition</td>
</tr>
<tr>
<td>CPOX</td>
<td>Catalytic partial oxidation</td>
</tr>
<tr>
<td>DFT</td>
<td>Density functional theory</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier transform infrared</td>
</tr>
<tr>
<td>GLS</td>
<td>Gas liquid separator</td>
</tr>
<tr>
<td>HREELS</td>
<td>High resolution electron energy loss spectroscopy</td>
</tr>
<tr>
<td>HTS</td>
<td>High temperature shift</td>
</tr>
<tr>
<td>ID</td>
<td>Inner diameter</td>
</tr>
<tr>
<td>LEED</td>
<td>Low energy electron diffraction</td>
</tr>
<tr>
<td>LHHW</td>
<td>Langmuir-Hinshelwood-Hougen-Watson</td>
</tr>
<tr>
<td>LTS</td>
<td>Low temperature shift</td>
</tr>
<tr>
<td>MARI</td>
<td>Most abundant reactive intermediate</td>
</tr>
<tr>
<td>MCFC</td>
<td>Molten carbonate fuel cell</td>
</tr>
<tr>
<td>OD</td>
<td>Outer diameter</td>
</tr>
<tr>
<td>PAFC</td>
<td>Phosphoric acid fuel cell</td>
</tr>
<tr>
<td>PEMF</td>
<td>Proton exchange membrane fuel cell</td>
</tr>
<tr>
<td>QSS</td>
<td>Quasi steady state</td>
</tr>
<tr>
<td>RDS</td>
<td>Rate determining step</td>
</tr>
<tr>
<td>SC</td>
<td>Sensitivity coefficient</td>
</tr>
<tr>
<td>SOFC</td>
<td>Solid oxide fuel cell</td>
</tr>
<tr>
<td>SR</td>
<td>Steam reforming</td>
</tr>
<tr>
<td>TC</td>
<td>Thermocouple</td>
</tr>
<tr>
<td>TPD</td>
<td>Temperature programmed desorption</td>
</tr>
<tr>
<td>TPR</td>
<td>Temperature programmed reduction</td>
</tr>
<tr>
<td>TST</td>
<td>Transitional state theory</td>
</tr>
<tr>
<td>UBI-QEP</td>
<td>Unit Bond Index-Quadratic Exponential Potential</td>
</tr>
<tr>
<td>UHV</td>
<td>Ultra high vacuum</td>
</tr>
<tr>
<td>WGS</td>
<td>Water gas shift reaction</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
</tr>
<tr>
<td>XRD</td>
<td>X-Ray diffraction</td>
</tr>
</tbody>
</table>
Abstract

Biogas is an important source of renewable energy produced by the anaerobic digestion of biomass. The composition of biogas depends on the biomass source and duration of the digestion process. Biogas is an ideal fuel for distributed power generation using Solid-Oxide Fuel Cells (SOFCs), especially in areas that are not grid connected. Biogas may be combusted to produce electricity or can be converted to synthesis gas by reforming over Rh or Ni catalyst. However, the presence of H₂S or other sulfur containing compounds is a major problem for reforming of biogas because sulfur poisons most transition metals.

The goal of this research is two fold; i) experimental investigation of catalyst deactivation and regeneration, and ii) development of a comprehensive predictive microkinetic model for biogas steam reforming on Ni based catalysts. The kinetic model is developed based on experimental data and further validated by simulating the experiments reported in the literature. The kinetic model is able to capture the performance of a fixed bed reactor used to reform model biogas with and without H₂S in the feed gas.

The objective of the experimental study is the deactivation and regeneration of Ni catalysts supported on γ-Al₂O₃ during steam reforming of biogas containing ppm levels of H₂S. In order to ensure that the catalyst does not lose activity over time in a non-poisoning atmosphere (without H₂S), reforming experiments are performed at 700 and 800 °C for 22 hrs and no loss in activity of the catalyst is observed during this period. Catalyst deactivation experiments are then performed for two different temperatures (700 and 800 °C) and three different H₂S concentrations (20, 50, and 100 ppm). A low S/C ratio is employed to ensure the participation of CO₂ in reforming reactions. Low temperature operation (700 °C) lead to full deactivation of the catalyst whereas at higher temperature (800 °C) the catalyst maintained some residual activity. In certain cases, catalyst regeneration is also performed by removing H₂S from the feed gas and by increasing the reforming temperature. The fully poisoned catalysts are then regenerated by steam treatment followed by reduction in H₂. The regenerated catalyst is tested for its activity by performing steam reforming reaction without H₂S in the feed stream. The regenerated catalyst showed stable operation for more than 13 hrs.

The fresh and spent catalysts are characterized by various techniques. XRD studies confirms the absence of coke formation during the reforming reactions with and without H₂S in the feed stream. This also asserts that the catalyst deactivation by introducing H₂S to the feed gas is purely due to sulfur poisoning. The N₂ adsorption/desorption isotherms are of type IV, which is typical for mesoporous materials. TPR results indicate a strong interaction of NiO with the support. The pulse chemisorption result shows that the Ni is well dispersed on the support, and the particle size of Ni crystal is very close to the value calculated using Scherrer equation.

The experimental data are then utilized to develop a detailed elementary kinetic mechanism for biogas reforming with and without H₂S in the feed gas. A comprehensive mechanism of the plausible elementary reaction steps of sulfur are added to an existing methane steam reforming mechanism on Ni. Using established theories, the kinetics of each of the elementary reaction steps on Ni metal catalysts are calculated. The Unity Bond Index-Quadratic Exponential Potential Method (UBI-QEP) is used to calculate the activation energies for both the forward and reverse direction of each step based solely on heats of chemisorption and bond dissociation energies of the species involved. Transition state theory (TST) is used to predict the pre-exponential factors for each reaction step. However, pre-exponential factors are further adjusted to make
the entire surface reaction mechanism thermodynamically consistent. A one dimensional fixed bed reactor model is used to simulate the experiments. Sensitivity analysis is carried out to understand the influence of pre-exponential factors on surface coverage of sulfur. The mechanism is then validated using experimental data in the temperature range of 600-950 °C for biogas free from H₂S and 700-900 °C for biogas containing 20-108 ppm H₂S. The model is capable of predicting deactivation of the catalyst in presence of H₂S in the feed mixture. Moreover, it qualitatively predicts the recovery of the catalyst activity on the removal of H₂S as well as temperature enhancement. The model also predicts saturation coverages of adsorbed sulfur that are comparable to experimental observations.
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Chapter 1

Introduction

1.1 Background

The global energy demand is growing rapidly, and majority of the present demand is met by fossil based fuels such as coal, oil, and natural gas. Since the industrial revolution, our increased dependence on fossil based fuels has resulted in various airborne emissions leading to serious climatic, environmental, and health effects. These emissions are at alarming levels and require immediate actions to counter severe future problems. Moreover, the world’s oil and gas reserves are concentrated in a small number of geographic regions, dominated by the Middle East. Any geopolitical uncertainties in these regions can lead to price fluctuations and scarcity in oil supply. The above few factors have led to an increased attention on renewable energy sources.

Renewable energy production is a key objective across the world. According to US Energy information and administration (EIA), the energy demand will increase during this century by a factor of two or three [1]. The European Commission has set legally binding targets for Europe to increase energy production from renewable sources from the current level of 7% to 20% by 2020 [2].

In the recent past, biogas systems have received considerable attention as an attractive source of renewable fuel that is clean, environment friendly, and cheap. Biogas is produced by anaerobic digestion of a variety of organic wastes. This technology offers a very attractive route for decentralized applications in rural areas for meeting the energy needs. Biogas energy is typically used for small to medium scale combined heat and power production, and also receives increasing attention as a renewable feed stock for chemical industry. An increased usage of biogas as a fuel reduces the dependence on fossil based fuels, and has important advantages for both environment and long term energy security. The production of biogas is considered to be a carbon neutral process [3]. Plants produce oxygen and carbohydrates from carbon dioxide by photosynthesis. So even if the organic matter produces carbon dioxide in the course of biogas formation, there is a good balance between the exhaustion of carbon dioxide into the atmosphere and absorption of carbon dioxide from the atmosphere.

Germany is the biggest biogas producer in Europe and has 5,905 plants in operation with an installed power generation capacity of 2,291 MW. The resultant electricity supply is approximately 12.8 TWh, which
The Ministry of New and Renewable Energy, Government of India, has initiated a scheme on biogas based Distributed/Grid Power Generation Programmes in 2006. The main objectives of these programmes are proper utilization of animal wastes and wastes from forestry, rural based industries (agro/food processing), kitchen wastes, etc. India has a total of 348 biogas plants that produce a total capacity of 6,617 KW from 65,287 m$^3$ of biogas. Biomass energy and co-generation programmes are also promoted for optimum usage of India’s biomass resources. These programmes have the potential to deliver 19,500 MW. At present a total of 437 MW of renewable electrical energy is produced from these biomass sources [5].

1.2 Feedstocks for biogas

A wide variety of biomass can be used as substrates for biogas production as long as they contain carbohydrates, proteins, fats, cellulose, and hemicelluloses as main components. Other technologies that produce fuel from biomass sources require very specific feed stocks. For example, ethanol technology requires high fermentable carbohydrate levels in corn and sugarcane, while biodiesel production requires feed stocks with high oil content, waste vegetable oils or virgin vegetable oil from oil seed crops [6]. In contrast, biogas can be made from most biomass and organic wastes regardless of the composition and over a large range of moisture contents, with limited feedstock preparation. In fact, biogas can even be made from the left over organic matter from both ethanol and biodiesel production.

The facility required for the production of biogas is called an anaerobic digester. A great variety of organic materials such as biological wastes of cattle dung, vegetable wastes, animal manure, municipal solid waste, industrial waste water, landfill, etc. can be used in anaerobic digesters depending on the design. A basic biogas digester consists of a tank in which the organic material is digested, combined with a system to collect and store the biogas produced. The digester can be quite simple, and the details vary depending on available materials and the needs of the community. For household purposes a floating dome design enjoys wide acceptance. Anaerobic digestion comprises mainly of four steps. The first step is the decomposition (hydrolysis) of plant or animal matter to break down complex organic materials into simple organic substances such as sugars and amino acids. A number of intermediate products are formed in the second and third steps that include alcohols, fatty acids and hydrogen. In the fourth step a unique group of microorganisms collectively referred to as methanogens convert matter into methane and organic acids [6].

The process temperature plays a key role in biogas digesters that affects the rate of digestion. These digesters are operated at three conventional temperature levels depending on the species of methanogens in the digesters; psychrophilic (below 25 °C), mesophilic (30–40 °C with an optimum of 35 °C) and thermophilic range (55–65 °C). Apart from temperature, the rate of biogas production also depends on factors such as the carbon to nitrogen ratio, solid concentration, pH, hydraulic retention time and nature of the feed stocks [7].

The composition of biogas depends heavily on the nature of the feedstock and process conditions, but the
main components are methane and carbon dioxide, with smaller amounts of hydrogen sulfide and ammonia. Trace amounts of organic sulfur compounds, halogenated hydrocarbons, hydrogen, nitrogen, carbon monoxide, and oxygen are also occasionally present. The gas mixture is saturated with water vapor and may contain dust particles. Table 1.1 shows the biogas composition from different feedstocks [8, 9].

<table>
<thead>
<tr>
<th>Components</th>
<th>Municipal waste</th>
<th>Waste water</th>
<th>Agricultural /animal waste</th>
<th>Waste from agro food industry</th>
<th>Landfill</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄</td>
<td>50-60</td>
<td>61-65</td>
<td>55-58</td>
<td>68</td>
<td>47-57</td>
</tr>
<tr>
<td>CO₂</td>
<td>34-38</td>
<td>36-38</td>
<td>37-38</td>
<td>26</td>
<td>37-41</td>
</tr>
<tr>
<td>N₂</td>
<td>0-5</td>
<td>2</td>
<td>1</td>
<td>3-5</td>
<td>-</td>
</tr>
<tr>
<td>O₂</td>
<td>0-1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>-</td>
</tr>
<tr>
<td>H₂</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0-5</td>
<td>-</td>
</tr>
<tr>
<td>CO</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>H₂S (ppm)</td>
<td>60-750</td>
<td>700-2800</td>
<td>2100-7000</td>
<td>280</td>
<td>36-115</td>
</tr>
</tbody>
</table>

### 1.3 Applications

Biogas can be used for all applications designed for natural gas with sufficient purification. The main difference between natural gas and biogas is the carbon dioxide content. Natural gas contains very low levels of CO₂ whereas biogas may contain up to 40% CO₂. Moreover, natural gas also contains small fractions of heavier hydrocarbons. These two differences result in a lower energy content of biogas compared to natural gas. The percentage of methane in the gas determines its calorific value as the other constituents do not contribute to the energy content. The methane content of biogas is appreciably high (∼ 60%). This provides a high calorific value sufficient to find its use in many energy applications, including power generation. Table 1.2 shows the calorific values for different fuels [10].

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Calorific Value (kcal/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural gas</td>
<td>8600</td>
</tr>
<tr>
<td>LPG</td>
<td>10,800</td>
</tr>
<tr>
<td>Kerosene</td>
<td>10,300</td>
</tr>
<tr>
<td>Diesel</td>
<td>10,700</td>
</tr>
<tr>
<td>Biogas</td>
<td>5000</td>
</tr>
</tbody>
</table>

### 1.3.1 Electricity generation

Raw biogas can not be used directly in engines or heaters because of H₂S content and other trace amounts of acidic compounds. The following upgrading techniques are widely used to get atleast 95% methane for certain applications [11].

- Physical absorption (scrubbing with liquid)
- Chemical absorption (chemical reaction with a liquid)
- Pressure swing adsorption (adsorption on material like activated carbon)
- Membrane separation
- Cryogenic separation (cooling at low temperature)
- In-situ enrichment (sludge treatment)

The biogas plants usually provide gas for cooking and lighting through specially designed mantles. In principle, the chemical energy of the combustible gases is converted to mechanical energy in a controlled combustion system using heat engine. This mechanical energy then activates a generator to produce electrical power. The most common heat engines used for biogas energy conversion are gas turbines and combustion engines. Combustion engines can be either internal combustion engine (e.g. reciprocating engine) or external combustion engine (e.g. Stirling engine) [12, 13].

1.3.2 Fuel for vehicles and fuel cells

There is a growing interest in the transport sector for replacing natural gas with upgraded biogas. Like natural gas, biogas can also be compressed and used in motor vehicles [14]. Upgraded biogas with >95% methane is required in order to be used in normal vehicles. Biogas can be used in both light and heavy duty vehicles. Light duty vehicles can normally run both on natural gas and biogas, whereas heavy duty vehicles require minor modifications. Sweden is the first country that used biogas as a transportation fuel and currently 11,500 vehicles are running with natural gas and biogas [15]. Biogas as vehicle fuel is also used in Switzerland, and other countries including Germany, Austria, France, Spain, India, China and USA are following the trend [16, 9, 5].

Low temperature fuel cells such as Polymer Electrolyte Membrane Fuel Cell (PEMFC) and Phosporic Acid Fuel Cell (PAFC) operate on pure hydrogen. Today 90% of hydrogen is produced by the catalytic reforming of light hydrocarbons and naphtha [17]. A viable alternative, for near and short term, is generating hydrogen from biogas. Biogas reforming can be used for on-demand production of hydrogen for automotive and distributed power generation applications. Catalytic reforming for biogas either by a dry reforming or by combination of dry and steam reforming using appropriate catalysts such as Ni, Rh or bimetallic catalysts produce synthesis gas. The synthesis gas can be used directly in various applications such as a fuel for Solid-Oxide Fuel Cell (SOFC), Molten Carbonate Fuel Cell (MCFC) or Fisher-Tropsch synthesis to produce synthetic liquid fuel. Fisher-Tropsch process uses a \( \frac{H_2}{CO} \) ratio 2:1 depending on the desired product [18]. These ratios can be tuned by adjusting steam to carbon ratio in biogas steam reforming. Fuel cells operating with biogas offer higher electrical conversion efficiency (> 50%) compared to internal combustion engines or gas turbines that operate on biogas, and produce less pollutants and greenhouse gases. Fuel cells are very sensitive to trace amounts of \( H_2S \) so necessary precautions should be taken if biogas is used as a fuel. Table 1.3 shows the tolerance levels for \( H_2S \) and CO for various fuel cell types [19].
Table 1.3: Tolerance levels of H$_2$S and CO in ppmv levels.

<table>
<thead>
<tr>
<th>Fuel Cell</th>
<th>H$_2$S</th>
<th>CO</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEMFC</td>
<td>&lt;1</td>
<td>&lt;10</td>
</tr>
<tr>
<td>PAFC</td>
<td>&lt;20</td>
<td>&lt;10</td>
</tr>
<tr>
<td>MCFC</td>
<td>&lt;10</td>
<td>Fuel</td>
</tr>
<tr>
<td>SOFC</td>
<td>&lt;1</td>
<td>Fuel</td>
</tr>
</tbody>
</table>

### 1.4 Catalyst deactivation

Catalyst deactivation is a major problem for heterogeneous catalytic reactions. It is defined as loss of catalytic activity with time on stream. The deactivation process is inevitable in most processes but it may be slowed down or even be reversed with certain techniques [20, 21]. Interruption of the process for either replacement or regeneration results in loss of production and revenue.

The deactivation process may be physical and/or chemical in nature and occurs simultaneously with the main reaction. Generally the causes of deactivation are poisoning, fouling, phase transformation, and thermal degradation or sintering [20]. The deactivation time varies from seconds to years depending on the process. For example, entrained flow reactor with continuous regeneration deactivates within seconds (catalytic cracking and polymerization reactions), whereas the iron based catalysts in ammonia synthesis reactors deactivates over timespan of 5-10 years [20, 21].

Deactivation by poisoning occurs due to the strong adsorption of the poisoning species on active sites and thus blocks the adsorption or alters the adsorption energy of other species [22]. The poisoned catalysts may be regenerated and its activity can be partially restored by certain techniques [23, 24]. The best way to reduce catalyst poisoning is to decrease the amount of poisons in the fuel to more acceptable levels. Fuel/gas mixtures that contain sulfur compounds in ppm levels (>4) are considered to be poisonous to most catalytic reactors, and leads to the formation of inactive compounds on the surface and also to the morphological changes in the catalyst. Nickel catalyst reactor systems are more susceptible to sulfur compounds due to the strong chemisorption of sulfur species on Nickel active sites. The process of chemisorption is almost irreversible at lower temperatures and reversible at higher temperatures. Other compounds such as lead, phosphorous, zinc, calcium and magnesium are also considered to be catalyst poisons [20].

Fouling is another catalyst deactivation process in which carbonaceous materials form on the surface thus physically covering the active sites. Generally this is more severe in the dry reforming of hydrocarbons. Coke deposits may amount to 15% or even 20% (w/w) of the catalyst, and they may lead to deactivation of the catalyst either by covering active sites, and/or by pore blocking [20].

Catalyst sintering is another mechanism that refers to the loss of active surface area via structural modification of the catalyst. Generally sintering happens at higher operating temperature and leads to agglomeration and coalescence of small metal crystallites into larger ones with lower surface-to-volume ratio [20]. Solid-state transformation is another process and can be viewed as an extreme form of sintering at high temperatures and leads to the transformation of one crystalline phase into another one. For example active Nickel on alumina support forms an inactive Nickel Aluminate (NiAl$_2$O$_4$) at above 800 °C [20, 25].
1.5 Desulfurisation techniques

Most of the applications of biogas are discussed above are successful only in the absence of or at low \( \text{H}_2\text{S} \) concentration in the feed gas mixture. Hydrogen sulfide is typically the most problematic contaminant because of its toxicity and high corrosiveness. Additionally, combustion of \( \text{H}_2\text{S} \) leads to sulfur dioxide emissions, that are harmful to the environment and society. Hence it is necessary to remove hydrogen sulfide before the gas is taken into any process equipment. Biogas normally contains 100-10,000 ppmv \( \text{H}_2\text{S} \) depending on the feedstock. Hydrogen sulfide is formed when the reduction of sulfur-containing proteins under anaerobic conditions by sulfate reduction microorganisms. Inorganic sulfur, particularly sulfates, can also be biochemically converted to \( \text{H}_2\text{S} \) [26]. Table 1.4 shows the \( \text{H}_2\text{S} \) tolerance for various applications if biogas is used as fuel [11, 27].

<table>
<thead>
<tr>
<th>Technology</th>
<th>( \text{H}_2\text{S} ) tolerance (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Engines</td>
<td></td>
</tr>
<tr>
<td>Heating boiler and</td>
<td>&lt; 1000</td>
</tr>
<tr>
<td>Stirling engines</td>
<td></td>
</tr>
<tr>
<td>Kitchen Stoves</td>
<td>&lt; 10</td>
</tr>
<tr>
<td>Internal combustion</td>
<td>&lt; 500</td>
</tr>
<tr>
<td>engines</td>
<td></td>
</tr>
<tr>
<td>Turbines</td>
<td>&lt; 10,000</td>
</tr>
<tr>
<td>Micro turbines</td>
<td>&lt; 70,000</td>
</tr>
</tbody>
</table>

A variety of technologies are available to remove \( \text{H}_2\text{S} \) from fuel streams. These methods are used depending on the final use, the volume of the gas to be treated, the concentration of \( \text{H}_2\text{S} \) present, and the absolute quantity of \( \text{H}_2\text{S} \) to be removed. Additionally, to achieve higher \( \text{H}_2\text{S} \) removal two or three process are combined. The \( \text{H}_2\text{S} \) removal methods are classified into physical-chemical, and \textit{in-situ} biotechnological methods. Generally biotechnological methods are cheap and give higher efficiency and do not require any secondary treatments compared to the physical-chemical methods.

1.5.1 In-situ methods

In in-situ methods, iron chlorides, phosphates or oxides are directly added into the digester slurry. The addition of \( \text{FeCl}_2 \) is commonly practiced and iron hydroxide (\( \text{Fe(OH)}_2 \)) in solid form is also used. They react with \( \text{H}_2\text{S} \) and form insoluble iron sulfate salts. These salts are precipitated and thus stripping of \( \text{H}_2\text{S} \) into the biogas is prevented. These methods generally achieve 100-200 ppm \( \text{H}_2\text{S} \) in the final stream.

\[
\text{Fe}^{2+} + \text{S}^{2-} \rightarrow \text{FeS} \quad (1.1)
\]

Another simple in-situ method is the addition of 2-6% oxygen or air directly to biogas digester or storage tank. In this process \( \text{H}_2\text{S} \) is converted to elemental sulfur or sulfates by biological aerobic oxidation in the presence of thiobacillus bacteria [28]. The removal of \( \text{H}_2\text{S} \) depends on the process temperature, hydraulic retention time and amount of air introduced, and \( \text{H}_2\text{S} \) may be reduced to 20-100 ppm in biogas stream [29]. The disadvantages in this method is that the supply of oxygen may effect the anaerobic fermentation process and yellow clusters of sulfur are deposited on surfaces, which may lead to corrosion. Biogas is also explosive.
in the presence of air depending on the methane content. Another disadvantage is accumulation of O\textsubscript{2} and N\textsubscript{2} in the biogas, which are very difficult to remove in the biogas upgradation process [30].

### 1.5.2 Adsorption techniques

Physical and chemical adsorption techniques are widely used to remove H\textsubscript{2}S from the biogas streams. The adsorption process is carried out at different temperatures with high surface area adsorbing materials such as activated carbon, copper, iron, aluminium, zinc, titanium or mixtures of these are used to achieve ultra low level H\textsubscript{2}S concentrations. The main disadvantages of this process are high energy consumption due to the higher temperature operation, growing environmental concern over appropriate waste disposal methods, and expensive regeneration techniques [31].

**Adsorption on activated carbon**

The adsorption on activated carbon is widely used among the processes to achieve very low concentrations of H\textsubscript{2}S. In addition to physical adsorption, activated carbon provides a catalytic surface for oxidation to elemental sulfur and sulfate. The sulfur is trapped on the internal surface of the activated carbon, which significantly enhances the removal capacity of H\textsubscript{2}S. In presence of oxygen the following reaction takes place

\[
\text{H}_2\text{S} + \text{O}_2 \rightarrow 2\text{S} + 2\text{H}_2\text{O}
\] (1.2)

Generally the activated carbon adsorption technique is carried out at 50–70 °C and at a pressure of 7–8 bar. The removal capacity of activated carbon process can be significantly improved by impregnation with alkaline or oxide coatings on the activated carbon. Most commonly used coatings are potassium iodide, sodium hydroxide, sodium carbonate, potassium hydroxide, or metal oxides. The removal capacity is enhanced from normal 10-20 kg H\textsubscript{2}S/m\textsuperscript{3} carbon to 120 -140 kg H\textsubscript{2}S/m\textsuperscript{3} carbon by impregnation. The major drawback in activated carbon process is the spent carbon disposal. The spent carbon must either landfilled or regenerated [29].

**Adsorption on iron oxides**

Adsorption on iron oxides is one of the oldest method, generally impregnated on wood chips (iron sponge) and pellets. In this method, H\textsubscript{2}S is reduced to insoluble iron sulfides, which is converted into elemental sulfur by air in regeneration techniques. The following reactions take place during the adsorption and regeneration process.

**Adsorption:**

\[
\text{FeO} + \text{H}_2\text{S} \rightarrow \text{FeS} + \text{H}_2\text{O}
\] (1.3)

\[
\text{Fe}_2\text{O}_3 + 3\text{H}_2\text{S} \rightarrow \text{Fe}_2\text{S}_3 + 3\text{H}_2\text{O}
\] (1.4)

**Regeneration:**

\[
\text{FeS} + \frac{1}{2}\text{O}_2 \rightarrow \text{FeO} + \text{S}
\] (1.5)

\[
\text{Fe}_2\text{S}_3 + \frac{3}{2}\text{O}_2 \rightarrow \text{Fe}_2\text{O}_3 + 3\text{S}
\] (1.6)

The optimum operating temperature is 20 -50 °C and removal capacity of H\textsubscript{2}S from 1000 ppm to 1 ppm is achieved in this process. The general drawbacks of the process are that it is chemical intensive, the operating
costs are high and a continuous stream of spent waste material is accumulated [30].

Using iron oxide impregnated on wood chips (iron sponge) is a mature technology. Generally this is carried out at 18-46 °C, and 140 kPa. The time should be greater than 60 seconds for optimum removal of \( \text{H}_2\text{S} \) from the streams [29]. Iron oxide pellets are also made from redmud, which is a waste product from aluminium industry that has a higher surface to volume ratio than iron sponge. These pellets are impregnated with iron oxide or hydroxides and can remove 50 gm of \( \text{H}_2\text{S} \) per 100 gm of pellets. However, the pellets are more expensive than iron sponge. The major drawback on usage of iron oxide is safe disposal of spent iron oxide, which is considered as hazardous waste and requires special disposal procedures. Furthermore, the regeneration process is highly exothermic and requires accurate control of air flow and temperature, and if not controlled properly the wood chips may self-ignite [29].

ZnO supported on silica is gaining interest in the removal of \( \text{H}_2\text{S} \) at low temperatures. These systems have, however, low capacity and require large volumes of adsorbed bed. Recently modified mesoporous silica has received attention and is used as support materials for metal oxides and metals, due to a combination of good accessibility, uniform pore size, and high surface area. For example, MCM-41 (Mobil Composition of Matter No. 41), KIT-6 silica (ACS material mesoporous silica molecular sieve) and SBA 15 (Santa Barbara Amorphous) structures received considerable attention of many researchers for \( \text{H}_2\text{S} \) removal applications [26].

**Adsorption on molecular sieves**

Molecular sieves (zeolites) are used to separate different compounds in the gas streams. The adsorption selectivity of different compounds depends on the mesh size and gas pressures. Generally polar compounds such as water, \( \text{H}_2\text{S} \), \( \text{SO}_2 \), \( \text{NH}_3 \), carbonyl sulfide, and mercaptans are strongly adsorbed and can be removed from methane gas. Zeolites are thermally and chemically inactive, however, the main drawbacks are high investment cost and limited capacity.

### 1.5.3 Absorption techniques

In absorption techniques, solvents are used to remove the \( \text{H}_2\text{S} \), which alters the solubility of \( \text{H}_2\text{S} \) by making water alkaline or by its oxidation to make it more water soluble. The solvents like methanol, polyethylene glycol ethers, and amine solutions are used for this purpose. Generally absorption column and stripper column (for regeneration) are operated simultaneously to achieve higher removal efficiency (> 99%). This process can handle wide range of pollutants, but the major drawbacks are high initial investment cost and large volumes of water and/or chemicals that are required for processing [29].

**Caustic scrubbing**

The absorption of \( \text{H}_2\text{S} \) on sodium hydroxide is the oldest method. In this method NaOH reacts with \( \text{H}_2\text{S} \) to form salts of sodium sulfide or sodium hydrogen sulfide. The formed salts are insoluble, that may precipitate in the scrubber. To avoid the formation of salts on the scrubber, spent caustic must be removed on regular basis. The major drawbacks are high investment cost and handling of caustic soda. Caustic soda is considered as poisonous material, and causes severe skin burns and eye damage [29].
Catalytic oxidation with chelated-iron salt solutions

In this method, the oxidation of \( \text{H}_2\text{S} \) into elemental sulfur is formed by the reduction of a soluble \( \text{Fe}^{3+} \) into a \( \text{Fe}^{2+} \). The chelated agents helps in preventing the precipitation of iron sulfide or iron hydroxide, and ferrous ions can be re-oxidized to ferric ions in the presence of air. The chelated ferric iron (\( \text{Fe}^{3+} \)) is acting as a catalyst which improves the rate of chemical oxidation process. The following reactions take place during the absorption and regeneration [29].

Absorption:

\[
\text{H}_2\text{S} + 2[\text{Fe}^{3+}] \rightarrow \text{S} + 2[\text{Fe}^{2+}] + 2\text{H}^+ \tag{1.7}
\]

Regeneration:

\[
2[\text{Fe}^{2+}] + 0.5\text{O}_2 + 2\text{H}^+ \rightarrow 2[\text{Fe}^{3+}] + \text{H}_2\text{O} \tag{1.8}
\]

Sulfur removal efficiencies of 99.99% or higher can be achieved with this technology. There are many commercially available chelated ferrous iron catalysts in the market for this process namely LO-CAT®, MINI-CAT® redox chemistry technology (Gas Technology ProductsMerichem), SulFerox® (shell) and Sulfothane® (Biothane Corporation).

Biofilters and Biotrickling filters

In these systems the biogas is forced through a moist, packed bed that contains microorganisms. Microbes grow on the surface and crevices of the support, forming a biofilm. The \( \text{H}_2\text{S} \) in the biogas is transferred into the biofilm, where it is used as energy source by the microorganisms producing mainly sulfur if the oxidation is partial or sulfate if it is total. The \( \text{H}_2\text{S} \) removal efficiency depends on the medium, temperature, pH, nutrient and oxygen levels. The difference between biofilters and biotrickling filters is the nature of the carrier material: organic carriers in biofilters and inorganic carriers in biotrickling filters. The nutrients are not available in the inorganic carrier material, which are supplied by recirculating the liquid phase through the reactor. This liquid phase provides the moisture and in turn controls the pH or other operating parameters. The major problem found in biofilters is the acidification of the media due to sulfuric acid formation by the degradation of \( \text{H}_2\text{S} \). This problem is avoided in biotrickling filters due to the fact that the acid reaction products are washed out continuously from the media [29].

Several commercial biofilters and biotrickling filters are available to remove \( \text{H}_2\text{S} \) with efficiency up to >99% such as Biopuric process (Biothane Corporation, Germany), BioSulfurex® (DMT Environmental technology), Biodox® (Closen B V, Dutch company), QSR® (Quick Sludge Removal), BiogasCleaner®.

Bioscrubber

Bioscrubbers are used for treating hydrogen sulfide containing gases from a wide variety of sources such as biogas, off-gases from wastewater treatment plants, livestock farms, etc. The biofilter medium is inexpensive and may contain sufficient micronutrients for the microbial growth. This process is operated simultaneously in two reactors. The first column is an absorption column in which the pollutants are absorbed in a liquid phase and liquid phase goes into a second unit, which acts as a activated sludge unit. In the sludge unit, microorganisms grow in suspended flocks of water degrading pollutants. The effluent is recirculated to the
first unit to increase the inoculation of microorganisms. This process usually removes 99.9% H₂S from the
gas streams [32].

1.6 Objective and scope of thesis

Syngas gas production from various sources have been studied extensively by several research groups [33, 34, 35, 36, 37, 38]. The severe operating conditions during the reforming such as high pressure and high temperature, leads to several challenges concerning to the loss of catalytic activity. Catalyst deactivation is a complex phenomenon and it is affected by several known and even unknown factors [20, 39, 40, 41, 42].

The main objective of this thesis is to develop elementary steps of the surface reactions for biogas steam reforming in the presence of H₂S, and to determine kinetic parameters for them. The developed detailed kinetic model can be further used in reactor simulations under various conditions to understand the poisoning and regeneration of the catalyst at different operating temperatures. The work can be divided in two parts:

- Experimental study of catalyst deactivation and regeneration during biogas steam reforming on Ni catalyst.
- Development of a detailed kinetic model by means of Unity Bond Index-Quadratic Exponential Potential (UBI-QEP) calculations and reactor simulations.

The experimental study deals with the catalyst preparation, its characterization and quantification of poisoning. Various techniques such as XRD, BET, TPR, and pulse chemisorption are used for characterization of catalyst samples. The modeling study deals with the development of a detailed kinetic scheme for biogas reforming and its validation with the experimental data. The UBI-QEP method is used in this thesis to calculate the reaction energetics and a one dimensional fixedbed reactor model is used to simulate the experiments.

This thesis is organized as follows: a review on biogas and its applications related to the electricity generation and fuel cell is given in Chapter 1. An extensive literature survey on biogas reforming technologies and catalyst regeneration methods are also reviewed in Chapter 1. The fundamentals of catalyst deactivation mechanisms are presented in Chapter 2. In particular, the deactivation mechanisms and modeling studies that are relevant to this thesis are examined. Chapter 3 describes the reactor and mainly focuses on the preparation and characterization of catalysts by various techniques. In Chapter 4, a review of micro-kinetics, transport and thermodynamics related to this research is presented. In Chapter 5, the UBI-QEP method, which is used to determine the activation energies and reaction enthalpies of the elementary reaction is described. In addition, thermodynamic consistency of elementary surface reaction mechanism is addressed in Chapter 5. Chapter 6 deals with numerical simulations of the fixed bed reactor using a one dimensional model by applying the kinetic model developed in this work. Finally, in Chapter 7, overall conclusions are drawn and suggestions are made for possible future extensions of the current research.

1.7 Biogas reforming- earlier studies

Effendi et al (2003), reported biogas steam reforming reactions on Ni/ Al₂O₃ in fluidized bed and fixed bed reactors [43]. They have shown that higher conversions of CH₄ and CO₂ can be achieved in fluidized bed
reactors with slow deactivation compared to the fixed bed reactors. Fixed bed reactors with lower steam to carbon ratio resulted in massive carbon formation causing reactor blockage. In general, reducing the steam in the feed increases the selectivity towards CO production and enhanced CO₂ conversion in both types of reactors. The H₂/CO ratios depend strongly on steam concentration and increases with increasing steam to carbon ratio. In addition, the carbon deposition was dramatically reduced with ratios greater than 0.75 at 750 °C. For ratios less than 0.75, the reaction indicated critical conditions for carbon formation. Furthermore, it was observed that the catalyst fluidization was very poor owing to the massive carbon deposition. Increase in temperature resulted in higher conversions of CH₄ and CO₂. Moreover, enhanced selectivity towards H₂ and CO were observed with increasing temperature suggesting that water gas shift reaction is not favorable thermodynamically at higher temperatures.

In another study Efendi et al., [44] incorporated two CO shift reactors (fixed bed) to maximize hydrogen yield from fluidized bed biogas steam reforming. CO acts as a poison to low temperature PEM fuel cells even in the 10 ppm range and results in carbon formation through the disproportionation reaction. An increase in steam to biogas ratio resulted in slight increase in CH₄ conversion and steep decrease in CO₂ conversion at 850 °C. The increased CH₄ conversion leads to a selectively lower CO concentration and higher selectivity towards H₂ in the product stream. The H₂ in product stream remained constant for S/G (G-biogas) ratios above 0.8 and reached a maximum of 60% corresponding to an almost complete conversion of CH₄ at 850 °C. CH₄ conversion, H₂ and CO concentrations in the product stream very closely followed thermodynamic predictions. The CO₂ conversion, however, does not appear to follow the thermodynamic prediction at high S/G ratios. In the series of experiments at 850 °C, carbon deposition was identified at steam to biogas ratios less than 0.3. A limited amount of carbon (less than 0.1wt%) was identified during the biogas reforming with S/G ratios above 0.67.

Kolbitsch et al., reported biogas steam reforming on commercial nickel catalyst on CaO/Al₂O₃ support in a fixed bed reactor [45]. They reported increasing CH₄ and CO₂ conversions with temperature and maximum H₂ production between 700- 800 °C. Above 800 °C the H₂ yield decreased due to the reverse water gas shift reaction, which was favorable at higher temperatures. CH₄ conversion and H₂ yield increased with increasing S/C but the CO₂ conversion was zero at S/C ratio of 2.9, above this value CO₂ was produced and below this value CO₂ was consumed.

Araki et al., studied the biogas autothermal reforming on Ni catalyst supported on a cordierite monolith with fluctuating CH₄ concentration in biogas [46]. They found CH₄ conversion to be about 70% in the absence of steam with an oxygen to methane ratio of 0.5. About 95% of CH₄ conversion was achieved at S/C = 2 and O₂/C = 0.5. They observed that S/C ratios above 3 adversely effects the methane conversion, and continuously decreased over time, due to the formation of NiO and Ni₂O₃ in the presence of steam. They extended their studies on startup procedures for catalytic partial oxidation and autothermal reforming of biogas [47], and found that the carbon free operation can be obtained by supplying oxygen below 427 °C for partial oxidation of biogas. Auto thermal reforming was possible only when steam was supplied at temperatures higher than 450 °C, below which the catalytic activity decreased due to the formation of NiO. They reported that the formation of NiO can be prevented by supplying steam at temperature higher than that is required for catalytic partial oxidation. The Ni metal may be oxidized to NiO during steam reforming, dry reforming, catalytic partial oxidation, and auto thermal reforming. However, NiO is reduced to nickel by
CH<sub>4</sub> or H<sub>2</sub> which is produced during the above reactions.

Xu et al., developed catalysts for carbon free operation for biogas dry reforming at 800 °C [48, 49]. They have used CH<sub>4</sub>/CO<sub>2</sub> ratio of 1.0 on Ni-Co bimetallic catalyst supported on γ-Al<sub>2</sub>O<sub>3</sub> modified with La<sub>2</sub>O<sub>3</sub> in a fixed bed reactor. It is a known fact that addition of promoters inhibits carbon formation. Lanthanum oxide is an excellent promoter which can strengthen CO<sub>2</sub> adsorption. The addition of cobalt also improves the anti coking and catalytic activity. The excellent performance of Ni-Co bimetallic catalyst is due to the high metal dispersion, strong metal support interaction, and formation of stable strong solution. The conversions of CH<sub>4</sub> and CO<sub>2</sub> on Ni/La<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub> are improved by addition of cobalt.

Sun et al., reported the tri-reforming of biogas on nickel based SBA-15 (mesoporous silica supported) in fixed bed micro reactor [37]. They observed improved conversions of CH<sub>4</sub> with the addition of oxygen but no significant effect on CO<sub>2</sub> conversion for O<sub>2</sub>/CO<sub>2</sub> ratio less than 0.6. However, CO<sub>2</sub> conversions decreased with O<sub>2</sub>/CO<sub>2</sub> ratio greater than 0.6, which may be due to the added oxygen that promotes CH<sub>4</sub> conversion.

Reforming of a model biogas on nickel and rhodium-nickel catalysts with addition of lanthanum was reported by Lucredio et al., in a fixed bed reactor [50]. Higher CH<sub>4</sub> conversion was achieved in Rh-Ni and Rh-NiLa than Ni and Ni-lanthanum catalysts. They found that Ni and Ni-lanthanum catalysts converts more CO<sub>2</sub> than CH<sub>4</sub>. This may be due to the reverse water gas shift reaction which occurs simultaneously with dry reforming reaction. They concluded that formation of carbon was suppressed by addition of lanthanum oxide to nickel catalysts and addition of synthetic air to the biogas.

Bereketitodou et al., reported [38] that the addition of CeO<sub>2</sub> improves the nickel dispersion on the support resulting in improved catalytic activity and resistance towards the carbon deposition. The conversions are increased by the addition CeO<sub>2</sub> to the Ni/Al<sub>2</sub>O<sub>3</sub> catalysts at temperature above 800 °C. However, the conversions of CH<sub>4</sub> and CO<sub>2</sub> were less in the temperature range 700- 800 °C on Ni/CeO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>. They concluded that ceria based catalysts enhances the water gas shift reaction because of their strong interactions with the metal due to the transition between Ce<sup>3+</sup> and Ce<sup>4+</sup>. Moreover, CeO<sub>2</sub> has a high oxygen storage capacity, which helps in water gas shift activity.

Izquierdo et al., reported tri-reforming of biogas on Ni and Rh-Ni catalysts supported on magnesia or alumina modified with CeO<sub>2</sub> and ZrO<sub>2</sub> [51]. They found higher hydrogen yields on Rh-Ni/Al<sub>2</sub>O<sub>3</sub> catalysts than Ni/ MgO catalysts in dry reforming. The low hydrogen yield on Ni/MgO catalyst may be due to the reverse water gas shift reaction. Interestingly on Rh-Ni/Al<sub>2</sub>O<sub>3</sub> catalysts increasing S/C ratio, resulted in low CO<sub>2</sub> conversions and H<sub>2</sub> yield. This could be related to the water gas shift reaction which is favourable at higher S/C ratios. They have concluded that for biogas tri reforming reactions the highest CO<sub>2</sub> conversion and hydrogen yields were achieved at O<sub>2</sub>/CH<sub>4</sub> =0.25 and S/C=1.0. The same trend was observed in Ni/Ce-Zr-Al<sub>2</sub>O<sub>3</sub> micro reactors.

Much of the work has been done on steam reforming and/or dry reforming of biogas in the absence of hydrogen sulphide. The presence of H<sub>2</sub>S in the biogas adversely affects the activity of the nickel based catalysts. Although desulphurization technologies can decrease the amount of hydrogen sulphide present in the biogas, the remaining minor concentrations of sulfur cannot be tolerated by nickel-based catalyst even the if
fuel processor is operated at higher temperatures (>700 °C) [23].

Asharfi et al., [23] reported the biogas steam reforming in the presence of H2S on commercial nickel based catalyst. They have tested biogas steam reforming with different concentrations of H2S in the feed at different operating temperatures and concluded that the H2S poisoning proceeds quickly depending on the H2S concentration in the feed gas and operating temperature. It is important to note that the poisoned Ni catalyst keeps an appreciable residual activity at 900 °C, but at 700 °C the catalytic activity decreases rapidly even for low concentration of H2S. They have also found that H2S poisoned catalysts can effectively be recovered by temperature enhancement. Furthermore, extent of catalyst regeneration by H2S removal increases with increasing temperature.

1.8 Regeneration of poisoned catalysts

The chemisorption of hydrogen sulphide on a supported nickel catalyst is reversible [52], but the driving force is extremely small. The sulfur deactivated catalyst can be regenerated in a reducing environment at higher temperatures. However, temperature increase may be difficult in some cases because of the temperature limitations of the reactor system or due to sintering of the catalyst.

Wang et al., [53] carried out DFT studies on the regeneration of sulfur poisoned catalysts. They claimed that O2 is more effective than H2O in removing the adsorbed sulfur atoms from nickel surface. However, exposure to the large amounts of O2 or H2O can lead to excessive oxidation of the nickel metal, resulting in adsorption of oxygen atoms (O(s)) and formation of NiO. While O(s) species can be readily removed by H2 or other fuels, the formation of bulk NiO will significantly deactivate the Ni catalyst, mostly due to the volume change associated with the redox reaction of Ni. They finally concluded that H2O is a better candidate for removing surface sulfur without over-oxidizing the Ni surface because of its broader pressure range.

Shawal Nasri et al., reported poisoning and regeneration of precious metals catalys during CH4 decomposition in the presence of H2S [54]. FTIR spectroscopic investigations indicated that the nature of the metal species on the catalysts is different for the freshly reduced and regenerated catalysts. The catalytic activity for fresh catalysts followed the order of Pd > Rh > Pt. Regenerated Pd catalytic showed less activity than the fresh catalyst, but regenerated Rh and Pt showed higher activity than fresh catalyst. They claimed that the differences in catalytic activity is due to the changes in metallic structure caused by H2S exposure. In the case of Rh/Al2O3, the regenerated catalyst shows an increased Rh+/Rh0 ratio compared to the fresh catalyst. They observed that the catalytic activity for regenerated catalysts is reduced in the order of Rh > Pt > Pd.

Conventionally sulfur-poisoned steam reforming catalysts are regenerated by sequential treatment with steam, steam-air mixture, and steam-hydrogen mixture (H2O/H2 molar ratio of 100) [55]. Steam has been shown to have no influence on the chemisorption equilibrium but, according to the results by Rostrup [52], steaming of sulfur poisoned catalysts results in complete oxidation of the metallic nickel to nickel oxide. Sulfur can be removed easily at temperatures above 600 – 650 °C if the catalyst is unpromoted. However, If the catalyst is promoted with magnesium or calcium, temperatures above 700 °C are required. The sulfur on the catalytic surface is removed in the form of SO2 and H2S. The following reactions take place during the
regeneration process

\[ \text{Ni} - \text{S} + \text{H}_2\text{O} \rightleftharpoons \text{NiO} + \text{H}_2\text{S}, \] (1.9)

\[ \text{H}_2\text{S} + 2\text{H}_2\text{O} \rightleftharpoons \text{SO}_2 + 3\text{H}_2, \] (1.10)

\[ \text{Ni} + \text{H}_2\text{O} \rightleftharpoons \text{NiO} + \text{H}_2. \] (1.11)

If the catalyst is promoted with potassium or sodium, treatment with steam and steam-air mixture may result in a nearly complete conversion of chemisorbed sulfur to alkali sulphate. Owing to the high stability of alkali sulphates (\(\text{NiSO}_4\)), regeneration of alkali promoted catalysts becomes difficult. \(\text{NiSO}_4\) may be decomposed into \(\text{H}_2\text{S}\) according to the following reaction.

\[ \text{NiSO}_4 + 4\text{H}_2 \rightleftharpoons \text{NiO} + \text{H}_2\text{S} + 3\text{H}_2\text{O} \] (1.12)

The major disadvantages of conventional regeneration process are slow sulfur removal rate, which declines exponentially with time. These process also requires large volume of sulfur-free reducing gas. Recently Li et al. [24], developed faster regeneration methods to remove adsorbed sulfur on Ni based steam reforming catalysts. The regeneration method proposed by Li et al., has the following steps. Initially the adsorbed sulfur is oxidized in the presence of low flow 1\% \(\text{O}_2\) into \(\text{SO}_2\) and \(\text{NiSO}_4\) at 750 °C, \(\text{NiSO}_4\) is decomposed into \(\text{O}_2\), \(\text{SO}_2\), and \(\text{NiO}\) in the inert argon atmosphere at 900 °C, the nickel oxide is reduced into metallic nickel with 2\% \(\text{H}_2\) at 900 °C, and finally the trace amounts of sulfur is removed at 900 °C with steam reforming. They claimed that after regeneration by this method, the reforming performance of the the deactivated catalyst is fully regained to its initial activity.
Chapter 2

Catalyst Deactivation

Catalytic deactivation inherently occurs during the fuel processing of hydrocarbons, which is due to the process conditions and impurities present in the feed. It may be physical and/or chemical in nature, and occurs simultaneously with the main reaction. The deactivation process depends on nature of the process and varies on time scales from few seconds to years. For example, catalytic cracking reactions may take few seconds for deactivation, while ammonia synthesis process takes 5-10 years for iron catalyst deactivation. It costs to the industry billions of dollars per day for catalyst replacement and process shutdown. The deactivation process is inevitable but can be slowed down or may be compensated with certain techniques [23, 24].

Catalyst deactivation can generally be classified into physical and chemical. Physical deactivation is caused by the blocking of pores by entrained solids, loss of active sites due to agglomeration (site sintering), closure of pores by internal collapse (support sintering), and the reversible loss of active sites by physical adsorption of impurities. Chemical deactivation includes the irreversible loss of active sites through chemisorption of impurities, loss of sites due to coking, and pore blockage due to coking. The deactivation mechanisms can be classified as, coking or fouling, poisoning, phase transformation, and thermal degradation or sintering [20]. Other deactivation mechanisms include masking and loss of active elements via volatilization, erosion and attrition [21].

2.1 Deactivation by Coking

Catalyst deactivation due to the coking or fouling is caused by the formation of carbonaceous material on surface of the catalyst, thereby blocking the pores of the catalyst. This phenomena is generally observed in hydrocarbon catalytic reactions with steam and dry reforming reactions. The deactivation process by coking is more severe for dry reforming reactions of alkanes. Several authors have investigated the coke formation on Ni supported catalysts [56, 57, 21, 58, 59, 60] and concluded that the different routes to carbon formation affect the morphology of the carbon and the way it is gasified. Three types of carbon are observed during the steam reforming reactions such as, whisker like, encapsulating, and pyrolytic carbon. Whisker like carbon is formed at temperatures greater than 450, encapsulating carbon films are formed by slow polymerization of \( \text{C}_n\text{H}_m \) radicals on Ni surface at temperatures below 500 °C, and pyrolytic carbon is formed during thermal cracking of hydrocarbons [33, 60]. The following main reactions are responsible for the coke
formations [59, 61].

\[
\begin{align*}
\text{CH}_4 & \rightleftharpoons C + 2\text{H}_2 & \Delta H^0 = 75 \text{kJ/mol} & \text{(2.1)} \\
2\text{CO} & \rightleftharpoons C + \text{CO}_2 & \Delta H^0 = -172 \text{kJ/mol} & \text{(2.2)} \\
\text{CO} + \text{H}_2 & \rightleftharpoons C + \text{H}_2\text{O} & \Delta H^0 = -131 \text{kJ/mol} & \text{(2.3)} \\
\text{C}_n\text{H}_m & \rightleftharpoons n\text{C} + \frac{m}{2}\text{H}_2 & \text{(2.4)} \\
\text{C}_n\text{H}_m\text{(higher hydrocarbons)} & \Rightarrow \text{Olefins} \Rightarrow \text{coke} & \text{(2.5)} \\
\text{C}_n\text{H}_m\text{(higher hydrocarbons)} & \Rightarrow (\text{CH}_2)_n \Rightarrow \text{gum} & \text{(2.6)}
\end{align*}
\]

The above equations are reversible, and the basis to removal of carbon by gasification [60, 62]. The formation of coke via exothermic reactions 2.2 and 2.3 become less favorable as the temperature increases, and coke formation via endothermic reaction 2.1 becomes important at higher temperatures, which can rapidly deactivate the catalyst. Moreover, the decomposition of CO also forms carbon films on the surface. Depending on their reactivity and temperature of formation, carbon films can be classified into five types; adsorbed atomic carbon(C_a), amorphous carbon (C_β), vermicular carbon (C_v), bulk nickel carbide (C_γ), and graphitic carbon( C_c) [21]. Table 2.1 shows the different forms of carbon during CO disproportionation reaction.

<table>
<thead>
<tr>
<th>Structural type</th>
<th>Temperature(°C)</th>
<th>name</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adsorbed, atomic (surface carbide)</td>
<td>200 – 400</td>
<td>C_a</td>
</tr>
<tr>
<td>Polymeric, amorphous films</td>
<td>250 – 500</td>
<td>C_β</td>
</tr>
<tr>
<td>Vermicular filaments, fibers</td>
<td>300 – 1000</td>
<td>C_v</td>
</tr>
<tr>
<td>Nickel carbide (bulk)</td>
<td>150 – 200</td>
<td>C_γ</td>
</tr>
<tr>
<td>Graphitic (crystalline) platelets</td>
<td>500 – 550</td>
<td>C_c</td>
</tr>
</tbody>
</table>

Coking is one of the major factors to be controlled for industrial steam reforming applications. The operating conditions are chosen to increase \( \text{H}_2\text{O}/\text{C} \) or \( \text{CO}_2/\text{C} \) ratio to favor the reverse of reactions 2.2 and 2.3 for carbon free operation [60]. Although, high temperature steam is expensive, any measures to reduce coke formation have significant economic advantage for the process [63]. Table 2.2 shows the critical parameters for the coke formation reactions.

In extreme cases, strong carbon filaments may build-up in pores to the extent that they stress and fracture the support material, ultimately causing disintegration of catalyst pellets and plugging of reactor voids. Some forms of carbon result in loss of catalytic activity and some do not. For example, at low temperature (< 300-375 °C) condensed polymer films and at high temperatures (> 650 °C) graphitic carbon films encapsulate the metal surfaces of methanation and steam reforming catalysts. In the intermediate temperature range of 375 - 650 °C, carbon filaments are formed by precipitation of dissolved carbon at the rear side of metal crystallites causing metal particles to grow away from the support. Filament growth ceases when sufficient carbon accumulates on the free surface to cause encapsulation by a carbon layer. However, encapsulation of the metal particles does not occur if \( \text{H}_2/\text{CO} \) or steam/carbon ratios are sufficiently high. Thus, carbon filaments from CO hydrogenation and steam reforming may not necessarily cause intrinsic loss of catalytic activity unless
Table 2.2: Type of carbon formation.

<table>
<thead>
<tr>
<th>carbon type</th>
<th>reaction</th>
<th>phenomena</th>
<th>critical parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Whisker carbon</td>
<td>2.1 – 2.4</td>
<td>Catalyst pellet breakup</td>
<td>Low H₂O/C ratio, high temperature, Presence of olefins, and aromatics</td>
</tr>
<tr>
<td>Pyrolytic</td>
<td>2.5</td>
<td>Encapsulation on catalyst surface</td>
<td>High temperature, high residence time, presence of olefins</td>
</tr>
<tr>
<td>Gum</td>
<td>2.6</td>
<td>Blocking of Ni surface</td>
<td>Low H₂O/C ratio, absence of H₂, lower temperature</td>
</tr>
</tbody>
</table>

they form in sufficient quantity to cause plugging of pores [58, 64].

The chemical nature of the carbonaceous material depends on the temperature, pressure, the age of the catalyst, nature of the feed, and products formed. An important principle is that the rate of deactivation greatly depends on the difference in rates of formation and gasification of carbon or coke precursors. In steam reforming reactions, carbon formation rate is a function of hydrocarbon structure. For example, carbon formation decreases in the order of acetylenes, olefins and paraffins. Hydrogen acceptors presence in acetylenes and olefins accelerate the carbon formation [65]. Moreover, the carbon formation rate greatly depends on the catalyst structure, metal crystallite size, promoter and catalyst support. For example, Ashcroft et al., reported methane partial oxidation using CO₂ on Ni, Pd, Rh, Ru and Ir catalysts with γ-Al₂O₃ support. They found carbon formation on Ni and Pd, but not on Rh, Ru and Ir catalysts at temperature of 1050 K. They have also observed that Ni is more susceptible to carbon formation than Pd [66]. In another significant work Rostrup-Nielsen and Bak Hansen on methane dry reforming with Ni, Ru, Rh, Pd Ir and Pt as catalysts, demonstrated large differences. Ni alone showed carbon formation at a temperature of 775 K, whereas at 925 K, the carbon formation rates were increased enormously for some of the noble metals. The formation of carbon increases in the order ofRu < Pt < Ir < Rh < Pd < Ni, and Ru is the best suitable catalyst for dry reforming of methane [61].

The addition of noble metal to the base metal can also significantly reduce formation of carbon. For example, bimetallic catalyst Ni- Pt reduces the carbon formation in methanation, and Cu-Ni and Co-Ni bimetallic catalysts substantially reduce the carbon in steam reforming as well as dry reforming reactions [65]. In addition to this, promoters and inhibitors also enhance the gasification rate of adsorbed carbon or coke precursors, and suppress the carbon formation reactions on the catalytic surface. Moreover, the coke formation rate is proportional to the acid strength of the support. For example, potassium is used in Ni based steam reforming reaction, that neutralizes the acid sites, and enhances the gasification of adsorbed carbon [67]. Different types of coke are formed based on bi functional metal or acidic oxide support. In case of Pt catalyst soft coke is formed and bimetallic Pt- Re catalyst results in hard coke formation on γ-Al₂O₃ support in the catalytic reforming [68].

Rostrup-Nielsen et al., reviewed the deactivation process due to the coking from hydrocarbon reforming. They postulated that the coke is formed from different sources. However, irrespective of the sources, the initial mechanistic step involves the dehydrogenation and formation of unsaturated species, that may migrate
to gaseous phase or adsorbed phase. One of the source for coke formation is high temperature gas phase reactions, in which intermediate carbonaceous material may form from the free radicals, and condenses on the catalyst surface. A highly accepted mechanism for the formation of carbon in reforming reactions is the dissociation of hydrocarbon on nickel catalyst to produce highly reactive carbon, in which most of the carbon is gasified and the remaining is less reactive due to the polymerization and rearrangement [69]. The less reactive carbon may encapsulate the Ni surface, and may dissolve in the Ni crystallite. The dissolved carbon may diffuse through nickel and precipitate at the rear side of the crystallite. This process leads to the formation of whisker like carbon. This is one of the few cases where carbon formation does not lead to deactivation, but it results in pressure build up in industrial applications. Rostrup- Nielsen reported that unsaturated olefins and aromatics are highly susceptible to the coke formation. In general formation of coke increases with unsaturation, molecular weight, and aromaticity.

2.1.1 Modeling of deactivation due to coking

Froment developed catalyst deactivation models for different levels such as, catalyst active site, the particle site, and reactor level. These models are developed based on mechanistic approach of coke formation [70]. The deactivation models at active site and particles site level are used to develop the deactivation model at the reactor level.

**Deactivation at active site level**

The deactivation by coking at active site level model is developed based on Hougen- Watson approach for a reaction \( A \rightleftharpoons B \). The model is based on the assumption of single site adsorption, no diffusional resistance, and surface reaction as the rate determining step [70]. The deactivation functions for the main reaction and coke formation are given by

\[
\frac{r_{Ai}}{r^0_{Ai}} = \varphi_{Ai},
\]

where \( r_{Ai} \) is rate of reaction \( i \) for reactant \( A \), \( r^0_{Ai} \) is initial rate, i.e, in the absence of coke, and \( \varphi_{Ai} \) is the deactivation function of reactant \( A \) in \( i \)’th reaction. For the coke formation

\[
\frac{r_C}{r^0_C} = \varphi_C,
\]

where \( \varphi_C \) is the sum of the coking rates. The above rate equations are intrinsic, i.e, free of diffusional limitations. Coke formation is not a simple one step transformation of chemical species. It proceeds through a sequence of steps gradually leading to a carbonaceous residue. The deactivation function has to be expressed in terms of the deactivating agent: for coking obviously the coke precursor, for poisoning the true poison. This means that the local amount of coke (or poison) on the catalyst site has to be known and this requires a rate equation for the formation of the coke precursor. The reaction rate (surface reaction controlled) \( r_{AB} \) is given by

\[
r_{AB} = \left( \frac{c_t - c_{C1}}{c_t} \right) \frac{k_{AB}K_{AC}(c_A - (c_B/K))}{1 + K_Ac_A + K_Bc_B},
\]

where \( c_t \) is the total active sites concentration, \( c_{C1} \) is coke concentration at active site, \( K \) is the reaction equilibrium constant, \( k_{AB} \) is rate coefficient, \( c_A \) and \( c_B \) are the concentrations of reactants and products respectively, \( K_A \) and \( K_B \) are adsorption equilibrium constants. The fraction \( (c_t - c_{C1})/c_t \) gives the free active
sites ($\varphi_A$) after coking.

The reduction of active sites information and coke formation rates are required for the actual rate of reaction $r_{AB}$. The coke may be formed from the reactants (parallel coking) or from the products (consecutive coking); for parallel coking

$$r_C = \frac{\varphi_C k_{CA}^0 c_A c_A}{1 + K_A c_A + K_B c_B} = \frac{r_0}{1 + K_A c_A + K_B c_B} \varphi_C,$$

(2.10)

and for consecutive coking

$$r_C = \frac{\varphi_C k_{CB}^0 c_B c_B}{1 + K_A c_A + K_B c_B} = \frac{r_0}{1 + K_A c_A + K_B c_B} \varphi_C,$$

(2.11)

where $k_{CA}^0$ and $k_{CB}^0$ are the rate coefficient for coke from $A$ and $B$ components respectively, $\varphi_C$ equals $\varphi_A$ only at coking at the same site and equal number sites. The above equations are valid only for single site coking. When $n_A$ sites are involved in the rate determining step of the main reaction and $n_C$ sites in the coking, then

$$\varphi_A = \left(\frac{c_t - c_{C1}}{c_t}\right)^{n_A}; \quad \text{and} \quad \varphi_C = \left(\frac{c_t - c_{C1}}{c_t}\right)^{n_C}.$$

(2.12)

**Deactivation at the particle level**

The active sites are distributed throughout the pores of the catalyst particle. Initially coke is formed on the active sites by formation of coke precursors and coke molecules grow up and lead to the pore blockage. In this model rate determining step is single site surface reaction $A \leftrightarrow B$. The model is developed based on three steps: the formation of coke precursors from the adsorbed species, precursors of coke grows on the active sites, and termination of the growing coke [70]. The reaction rate for the main reaction $r_{AB}$ is

$$r_{AB} = \frac{k_{AB} K_A c_A(1 + K_A c_A K_B c_B)}{\phi},$$

(2.13)

where $\phi$ is the accessible fraction of active sites for the reaction, and is given by $1 - (c_{1,acc}/c_t)$. The total coke formation during the deactivation at the particle level is given by

$$c_{C,global} = \frac{3}{R^3} \int_0^R r^2 c_C(r)dr.$$

(2.14)

**Deactivation at the reactor level**

A plug flow reactor model is used to develop the deactivation model with the assumption of no interfacial diffusion limitations. The continuity equation for $A$ component for pseudo steady state is given by [70]

$$- \frac{dF_A}{dz} = N_A S \frac{V}{V},$$

(2.15)

where

$$N_A = \left| - D_{eff} \left( \frac{\partial c_A}{\partial r} \right) \right|_{r=R},$$

(2.16)

where $D_{eff}$ is the effective diffusivity, which is a combination of molecular and Knudson diffusivities in the straight pore, and $S/V$ is the ratio of external surface area to volume of the bed. This model is used for the simulation of isothermal plug reactor by Beyne and Froment [71] and concluded that in the case of parallel coking, the coke formation is higher at the reactor inlet as time proceeds, and large fraction of reactant is converted as the reactor length increases. In consecutive coking, the formation of coke increases with the
reactor length as a result the fraction of reactant conversion decreases.

### 2.2 Thermal degradation and Sintering

Catalyst sintering is another mechanism that refers to the loss of active surface area via structural modification of the catalyst. Generally sintering happens at higher operating temperature and leads to the formation of agglomeration and coalescence of small metal crystallites into larger ones with lower surface-to-volume ratio [20].

Two different sintering mechanisms have been proposed by Gruber et al., i) atom migration, and ii) particle migration and coalescence [72]. Atom migration refers to the process where metal atoms are emitted from one metal particle and captured by another metal particle. In particle migration process, the particles themselves move over the support and collide and coalesce to form larger particles. The driving force for both processes is the difference in surface energy, which varies inversely with the particle size.

Sintering process is accelerated by high temperature and presence of water vapor. Sintering in steam reforming reactions is mainly caused by the atomic migration of nickel particles at above 600 °C. [20, 21]. There are many parameters that can also affect the sintering, which include atmosphere, metal type, metal dispersion, promoters/impurities, support surface area, texture, and porosity. Sintering rate increases exponentially with temperature and in the presence of O₂, and relatively low in H₂ atmosphere [21].

Sintering temperature generally depends on the melting temperature of metals. The ideal operating temperature for dry reforming reaction is 0.5\(T_m\), and (1/3)\(T_m\) for steam reforming reactions, where \(T_m\) is the melting temperature of the metal. The limit for the steam reforming is lower due to the presence of steam, as it facilitates reorganization of many metals, alumina and silica. Table 2.3 shows the sintering temperatures for the different metals in steam reforming reactions [73].

<table>
<thead>
<tr>
<th>Metal</th>
<th>Sintering temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>360</td>
</tr>
<tr>
<td>Fe</td>
<td>500</td>
</tr>
<tr>
<td>Ni</td>
<td>500</td>
</tr>
<tr>
<td>Pt</td>
<td>570</td>
</tr>
<tr>
<td>Pd</td>
<td>500</td>
</tr>
</tbody>
</table>

Sintering can be prevented by adding stabilizers like chromium, alumina, or magnesia to the catalysts that may have a high melting point, and prevent agglomeration of small crystals. There is evidence that adding trace amounts of chlorinated compounds to the gas phase prevents the platinum catalyst sintering [73]. Metal crystallite stability generally decreases with decreasing metal melting temperature in reducing atmosphere in the order Ru > Ir > Rh > Pt > Pd > Ni > Cu > Ag, but this order may be affected by the strong metal support interactions [20]. For example, platinum stability decreases in the order Pt/ Al₂O₃ > Pt/ SiO₂ > Pt/C. In oxidizing atmosphere, metal crystallite stability depends on the volatility of metal oxides and strength of
metal support interactions. For example, crystallite stability decreases in the order Rh > Pt > Ir > Ru [21].

Baker and Trimm et al., [74] reported on sintering of catalyst support materials. Single phase oxide carriers may sinter by one or more combinations of surface diffusion, solid state diffusion, evaporation/condensation of volatile atoms or molecules, and grain boundary diffusion. They claimed that γ-Al₂O₃ and silica supports in oxidizing atmosphere, and carbon carriers in reducing atmosphere are the most thermally stable carriers. Doping of additives and impurities can also improve the thermal stability of the supports, which occupy the defective sites or form new phases. For example, by adding calcium, barium, nickel or lanthanum oxides to alumina supports may form thermally stable spinel phases [73]. In steam reforming reactions water vapor accelerates the support sintering by forming mobile surface hydroxyl groups which are volatile at higher temperatures.

2.2.1 Modeling of sintering

The kinetics of sintering is a function of temperature, time, pressure and concentrations. The sintering kinetics are developed from active metal surface area versus time measurements at constant temperature [20]. A simple sintering kinetics can be fitted with simple power law expression

\[
-\frac{d}{dt} \left( \frac{D}{D_0} \right) = k_s \left( \frac{D}{D_0} \right)^n,
\]

where \(k_s\) is the sintering rate constant, \(D_0\) is the initial dispersion, and \(n\) is the sintering order

\[
k_s = k_{s0} \exp \left( \frac{-E_a}{RT} \right),
\]

where \(k_{s0}\) is the initial rate constant, \(E_a\) is the activation energy, \(R\) is the gas constant, and \(T\) is temperature. The sintering order varies from 3 to 15, lower \(n\) values indicates atomic migration, and larger values of \(n > 4\) indicates particle migration. This equation is not valid for sintering processes because it assumes that surface area or dispersion ultimately reaches zero given sufficient time, when in fact, for a given temperature and atmosphere, a non-zero or limiting dispersion is observed after long sintering times. Moreover, the use of this equation is further questionable because variations in sintering order are observed as a function of time and temperature for a given catalyst in a fixed atmosphere.

Bartholomew and co-workers [20] have proposed an expression for the sintering rates that considers the effects of temperature, atmosphere, metal, promoter, and support. This is developed by fitting sintering data to general power law expressions

\[
-\frac{d}{dt} \left( \frac{D}{D_0} \right) = k_s \left( \frac{D}{D_0} \right) - \frac{D_{eq}}{D_0} \right)^m
\]

the additional term \(D_{eq}/D_0\) accounts for the asymptotic nature of dispersion versus time curve to a limiting \(D_{eq}\) at infinite time, \(m\) is the order of the sintering which is either 1 or 2.
2.3 Catalyst poisoning

The presence of impurities in the feed have a tremendous effect on the performance of the catalyst. The most important poison for catalytic steam reforming is sulfur. Sulfur compounds in the feed are converted into $\text{H}_2\text{S}$ under reforming conditions, and leads to the total deactivation of the catalyst. Catalyst poisoning occurs due to the strong adsorption of sulfur or other poisons on active site, and consequently blocks or alters the adsorptivity of the other species by electronic effect [75]. Moreover, poisons may modify the chemical nature of the active site due to the strong adsorption or reconstruction of the catalytic surface [33].

Catalytic poisons are classified based on the chemical structure, selectivity, and nature of reactions poisoned. Table 2.4 shows the catalyst poisons classification based on chemical structure [20].

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Examples</th>
<th>Type of interaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>VA and VIA group</td>
<td>N, P As, Sb, O, S, Se, Te</td>
<td>Shielded structures with s and p orbitals</td>
</tr>
<tr>
<td>VII A</td>
<td>F, Cl, Br, I</td>
<td>Formation of volatile with s and p orbitals</td>
</tr>
<tr>
<td>Toxic metals and ions</td>
<td>As, Pb, Hg, Bi, Sn, Zn, Cd, Cu, Fe</td>
<td>May form alloys with d orbitals</td>
</tr>
<tr>
<td>Molecules with multiple adsorption bonds</td>
<td>CO, NO, HCN, $\text{C}_6\text{H}_6$, $\text{C}_2\text{H}_2$, unsaturated HCs</td>
<td>Chemisorption through multiple bonds and back bonding</td>
</tr>
</tbody>
</table>

Poisons can be classified as selective, anti-selective, and non-selective. The difference between these three are related to the nature of the surface, and the degree of interaction of the poison with the surface. The strongest active sites are poisoned first in selective poisoning, lesser active sites are blocked initially in anti-selective poisoning. In the both cases the catalyst activity depends on the amount of poison chemisorbed. In non-selective poisoning, the less active sites are poisoned in a uniform manner and net loss of catalytic activity is a linear function of chemisorbed poison [21, 20]. An example for selective poisoning is deactivation of platinum by CO for the para-$\text{H}_2$ conversion, Pb poisoning on platinum for CO oxidation is anti-selective, and arsenic poisoning of cyclopropane hydrogenation on Pt is non-selective.

Selective poisoning is preferred for certain reforming reactions and hydrocracking reactions to adjust the selectivity. Sulfur compounds are strongly chemisorbed on the active sites and thus reduces the number of active sites for the reaction. For example, the sulfur passivated nickel catalysts are used for carbon free methane dry reforming [76] and Pt-Re/ $\text{Al}_2\text{O}_3$ is pretreated with low concentrations sulfur to limit the hydrocracking activity [77].

Poisoning of catalytic reactions may be reversible or irreversible. In reversible poisoning, the poisons are weakly adsorbed on the surface, and the catalyst activity is regained by simply removing the poisons from the feed. For example, $\text{H}_2\text{O}$ and CO are considered as poisons for iron based catalyst in ammonia synthesis,
these compounds affect the adsorption capacity of N₂ on the catalyst. Whereas in irreversible poisoning, the poisons are strongly chemisorbed on the surface, and the catalyst activity is not regained by removing the poisons from the feed, but it may be regained with some other techniques. For example, Ashrafi et al., regained the initial catalyst activity of poisoned catalyst by temperature enhancement [23]. Table 2.5 shows the list of industrial catalytic reactions that are susceptible to poisonous compounds.

<table>
<thead>
<tr>
<th>Process</th>
<th>Catalyst</th>
<th>Poison</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonia synthesis</td>
<td>Fe</td>
<td>CO, CO₂, H₂O, C₂H₂, S, Bi, Se, Te, P</td>
</tr>
<tr>
<td>Steam reforming</td>
<td>Ni/ Al₂O₃</td>
<td>H₂S, As, HCl</td>
</tr>
<tr>
<td>Methanol synthesis</td>
<td>Cu</td>
<td>H₂S, AsH₃, PH₃, HCl</td>
</tr>
<tr>
<td>Catalytic cracking</td>
<td>SiO₂ - Al₂O₃, zeolites</td>
<td>Organic bases, NH₃, Na, heavy metals</td>
</tr>
<tr>
<td>CO hydrogenation</td>
<td>Ni, CO, Fe</td>
<td>H₂S, COS, AS, HCl</td>
</tr>
<tr>
<td>Oxidation</td>
<td>V₂O₅</td>
<td>As</td>
</tr>
<tr>
<td>Automotive catalytic converters (oxidation of CO and HC, NO reduction)</td>
<td>Pt, Pd</td>
<td>Pb, P, Zn</td>
</tr>
<tr>
<td>methanol oxidation to HCHO</td>
<td>Ag</td>
<td>Fe, Ni, carbonyls</td>
</tr>
<tr>
<td>Ethylene to Ethylene oxide</td>
<td>Ag</td>
<td>C₂H₂</td>
</tr>
<tr>
<td>many</td>
<td>transition metals</td>
<td>Pb, Hg, As, Zn</td>
</tr>
</tbody>
</table>

A number of researchers focused on poisoning of nickel metal catalysts by H₂S [76, 78, 79, 80, 52, 81, 82]. The studies on methane reforming on nickel catalysts by Rostrup-Nielsen suggests improvements against catalyst deactivation. A process named SPARG (Sulfur Passivated Reforming) has been commercialized against Haldor Topsoe A/S to protect catalyst from deactivation by coke deposition in natural gas steam reforming. In SPARG process, the formation of carbon is reduced by ensemble control, i.e., sites for carbon formation are blocked by sulfur species, while sufficient sites for steam reforming reactions are maintained. It has also been suggested that sulfur in liquid feed allows competition for metal sites between adsorbing sulfur atoms and coke precursors [83]. Studies on sulfur passivated catalysts of Pt, Pt-Ir, and Pt-Re on Al₂O₃ support indicates that the catalyst life can be improved by lowering the coke deactivation rate. Sulphur is adsorbed on the hydrogenolysis sites of platinum surface, later these sites are occupied by coke precursors. They have also concluded that the addition of small amounts of Ir or Re to Pt improves the sulfur tolerance [77].

### 2.3.1 Modeling of catalyst poisoning

In general the catalytic activity is proportional to the number of active sites [84]

\[
k_{obs} = N_T k_{int} \eta,
\]

where \( k_{obs} \) and \( k_{int} \) are the observed and intrinsic rate constants for the reaction, \( N_T \) is the total number of active sites, and \( \eta \) is the effectiveness factor. Catalyst deactivation is caused by the decrease in number of active sites \( (N_T) \), a decrease in quality of active sites \( (k_{int}) \), and a degradation in accessibility of the pore space. During the catalyst poisoning the the number of active sites are reduced by the strong adsorption of impurities on the active sites, which is given by

\[
N_T = N_T (1 - 0),
\]

23
where \( \theta \) is the fraction of sites occupied by the poisons. The intrinsic rate constant is affected by the presence of poisons in the feed. For example, the interaction of \( \text{H}_2\text{S} \) with transition metals leading to the formation of surface sulphides with a different activity than the fresh catalyst. The effectiveness factor is also influenced by poisoning.

### 2.4 Deactivation by solid phase transformations

Deactivation by phase transformations occurs at very high temperature and this can be viewed as extreme form of sintering. In this process phase crystallite is transformed into another. This phenomena can be observed in metal supported catalysts as well as metal oxide supports. In the first case, active metal on the support is transformed into inactive. For example, Nickel on \( \text{Al}_2\text{O}_3 \) is transformed into inactive nickel aluminate phase (\( \text{NiAl}_2\text{O}_4 \)) at above 800 °C, and reaction of \( \text{Rh}_2\text{O}_3 \) with \( \text{Al}_2\text{O}_3 \) forms inactive \( \text{Rh}_2\text{Al}_2\text{O}_4 \). In the second case, the conversion of \( \gamma\text{-Al}_2\text{O}_3 \) with surface area 100- 200 m\(^2\)/gm is transformed into \( \alpha\text{-Al}_2\text{O}_3 \) with low surface area 5 m\(^2\)/g. Table 2.6 shows the transformations of boehmite (Alumina oxide) to \( \alpha\text{-Al}_2\text{O}_3 \) with respect to the temperature, \( \alpha\text{-Al}_2\text{O}_3 \) is the non porous, which is the most stable phase of alumina with less surface area 5m\(^2\)/gm.

The solid phase transformations are also limited by rate of nucleation and occurs due to the presence of some foreign compounds in the lattice or even on the surface. For example, \( \text{V}_2\text{O}_5 \) support accelerates the sintering process of titanium catalysts. \( \text{TiO}_2 \) on \( \text{V}_2\text{O}_5 \) support transforms the anatase phase into inactive rutile phase of \( \text{TiO}_2 \), but the addition of \( \text{WO}_3 \) support effectively increases the surface area for \( \text{TiO}_2 \) catalysts [21].

### 2.5 Other forms of deactivation

Other forms of catalyst deactivation include masking or pore blockage caused by the presence of poisonous substances in the feed. The deactivation occurs due to the physical deposition of substances on the external surface of the catalyst. This is observed in nickel and vanadium catalytic reactions, and deposition of phosphorus and silica on automotive exhaust converters.

Active metal loss through the formation of volatile compounds is another deactivation mechanism. Volatile compounds like metal carbonyls, oxides, sulfides and halides are formed in the presence of gas phase environment. This process is significant over a wide range of conditions. For example, loss of nickel in the presence of \( \text{CO} \) form nickel carbonyls at relatively low temperature, and at high pressures of \( \text{CO}(> 20\text{kPa}) \), ruthenium oxide is formed in the presence of oxygen environment, and volatile \( \text{CuCl}_2 \) is formed with copper catalyst in
the presence of chlorides. Bartholomew has proposed the following mechanism for the formation of volatile compound from the metal surface.

Finally, the loss of catalytic material is observed in different forms such as crushing of catalysts due to the load, produce fines due to the attrition in moving or fluidized beds, erosion of catalyst particles or monolith coatings occur at higher gas velocities, and sudden changes in temperature. The changes in temperature also leads to differences in thermal expansion between the washcoat and monoliths, which results in washcoat peel off from the surface.

2.6 Hydrogen sulfide chemisorption studies

The chemisorption of H$_2$S on Ni surface is extensively studied by variety of techniques such as LEED, Auger experiments, TPD/TPR, HREELS, XPS, and AES [85, 79, 86, 80, 87]. Most of these methods deal with structural, electronic and vibrational properties of chemisorbed sulfur on different metals.

Zhou et al., reported the chemisorption of H$_2$S on clean and pre-adsorbed sulfur on Ni(100) by AES and TPD. They have found that the desorption of hydrogen from the surface is a strong function of H$_2$S exposure. At low H$_2$S exposure, H$_2$S is totally dissociated and H$_2$ is desorbed from the surface. But in the case of pre-adsorbed sulfur, the dissociation of H$_2$S is inhibited and also shifts the H$_2$ desorption to lower temperature [88]. The study by Hedge et al [89], on chemisorption of H$_2$S on clean and sulfur covered Rh(100) also led to the same conclusions as Zhou et al., and claimed that the initial sticking coefficient of sulfur on rhodium(100) surface is greater than 0.5 and constant up to 0.6 langmuir exposure. Langmuir (L) is unit of exposure or dosage to a surface. The high sticking coefficient indicates the involvement of a kinetically important weakly held molecular precursor state in adsorption process.

Alfonso et al., studied H$_2$S adsorption and dissociation on different metal surfaces using DFT calculations. They found that H$_2$S molecule is weakly adsorbed on the on-top sites and dissociates into S, SH, and H species on the surface. In contrast to the H$_2$S, species H, SH, and S strongly interact with the surfaces. SH is preferentially adsorbed on bridge site, where as S and H are adsorbed on hollow sites. The dissociation of H$_2$S on all the metals is exothermic and energy barrier for dissociation is higher for Ag(111) and Au(111), intermediate for Cu(111) and lower for Ir(111), Ni(111), Pd(111), Pt(111).

Oliphant et al., reported on chemisorption of H$_2$S on different metals and concluded that supported Ni catalysts have strong affinity for H$_2$S chemisorption than unsupported Ni, Ru, Ni-Co, and Ni-Pt bimetallic
catalysts. \( \text{H}_2\text{S} \) chemisorption is strong and dissociative at lower coverages and non dissociative at higher sulfur coverages. If the surface is saturated with sulfur it may form nickel sulfide or bulk sulfide [79]. Maraeëcot et al., observed two types of sulphides on Ni catalyst surface at 323 K. They found that after the formation of superficial metallic sulphides, sulfur quickly forms polysulphides on the surface or slowly attacks deeper layers and forms bulk sulphides. Furthermore, the relative amounts of these two sulfur species strongly depends on the ability of the nickel catalyst to dissociate the poison molecule and to form superficial polysulfides or bulk sulfides.

The earlier studies by Besten et al., [91], suggested that \( \text{H}_2\text{S} \) forms four chemisorption bonds with the nickel at lower coverages, and two nickel atoms are required at higher coverages. They found that hydrogen desorption from the catalytic surface depends on the sulfur coverages. If the coverage is low, the dissociated hydrogen is quickly adsorbed on bare sites, but at high coverage the dissociated hydrogen is forced out to the gas phase as the sulfur atoms are adsorbed. If the Ni surface is completely saturated with sulfur, it is found that about two-thirds of the total hydrogen may be removed, even at 400 °C. These results are confirmed with deuterium exchange experiments and suggested that two different types of chemisorption bonds are formed with Ni surface depending on the sulfur coverage. At higher coverages, it appears that the hydrogen cannot be removed below the sulphide layer, as it acts as a barrier and prevents diffusion of hydrogen to, and from the surface.

at lower coverages

\[
\text{H}_2\text{S} (g) + \text{Ni} \rightarrow \text{Ni-S-H}
\]

at higher coverages

\[
\text{H}_2\text{S} \rightarrow \text{Ni-S-Ni} + \text{H}
\]

Most of the previous chemisorption studies discussed above are carried out at low temperatures and they concluded that \( \text{H}_2\text{S} \) requires two or four nickel atoms for chemisorption. Rostrup-Nielsen et al., [80] reported the chemisorption studies of \( \text{H}_2\text{S} \) on nickel catalyst at higher temperatures (550- 645 °C). They found that sulfur uptake depends on \( p_{\text{H}_2\text{S}} \) and \( p_{\text{H}_2} \) as well as on the \( p_{\text{H}_2\text{S}}/p_{\text{H}_2} \) ratio. A saturation layer is obtained at \( p_{\text{H}_2\text{S}}/p_{\text{H}_2} \) ratios above \( 5 \times 10^{-6} \), which is independent of the amount of sulfur added. Furthermore, it is indicated that an abrupt increase in the sulfur uptake occurs when the \( \text{H}_2\text{S}/\text{H}_2 \) ratio exceeds the value for the formation of bulk sulphide (\( \text{Ni}_2\text{S}_3 \)), which is predicted from thermodynamics (\( p_{\text{H}_2\text{S}}/p_{\text{H}_2}=10^{-3} \)), and also identified by X-ray analysis. The following chemisorption mechanism involving of one nickel site is proposed by Rostrup-Nielsen for temperatures above 400 °C.

\[
\text{H}_2\text{S}(g) + \text{Ni} \leftrightarrow \text{Ni-S} + \text{H}_2(g) \tag{2.22}
\]

The saturation sulfur coverage and equilibrium coverages are dependent on the \( \text{H}_2\text{S}/\text{H}_2 \) ratio and temperature [80]. In another study by Alstrup et al. [81], sulfur chemisorption isobars were measured in the temperature range of 773 - 1023 K with \( \text{H}_2\text{S}/\text{H}_2 \) ratio 7-50 ppm. They have indicated that for up to 90% of saturation,
the H$_2$S/H$_2$ ratio can be calculated using simple expression relating entropy, coverage, and enthalpy (or heat of adsorption)

$$\frac{p_{H_2S}}{p_{H_2}} = \exp \left[ \frac{\Delta H_0^0 (1 - \alpha \theta) RT - \Delta S^0}{R} \right],$$

(2.23)

with $\Delta H_0^0 = -289$ kJ/mol, $\Delta S^0 = -19$ kJ/mol and $\alpha = 0.69$, $\theta = s/s_0$ where $s$ and $s_0$ are actual and saturation amounts of sulfur respectively. The high temperature data of the published sulfur chemisorption measurements are well described by Eq. 2.23. It is suggested that the absence of coverage dependence in the entropy term is due to the subsurface chemisorption. Constant entropy resembles gas/solid solution equilibrium or bulk-like behavior of the chemisorbed layer. Eq. 2.23 can be rearranged to give the surface coverage of sulfur as

$$\theta_s = 1.45 - 9.53 \times 10^5 T + 4.17 \times 10^5 T \ln \left( \frac{p_{H_2S}}{p_{H_2}} \right)$$

(2.24)

This expression is not valid for $\theta_s$ close to zero and one. Changes in the saturation level are very small at the higher temperatures but become significant at the lower temperatures. So, as the poisoning process is represented by a simple exothermic adsorption process, the sensitivity of the reforming catalyst to poisoning increases at lower operating temperatures. For example, while poisoning of the (nickel) catalyst occurs with about 5 ppm of sulfur in the feed gas at a temperature of 800 °C, concentrations of the order of 0.01 ppm poisons the catalyst at 500 °C [92, 21].

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Chapter 3

Biogas steam reforming: Experimental investigation

The objective of this chapter is to examine experimentally the biogas steam reforming in the presence of hydrogen sulphide. Model biogas with different levels of H$_2$S is subjected to reforming reaction over supported Ni catalyst in fixed bed reactor at 700 and 800°C. In order to understand the poisoning effects of H$_2$S the reactions are initially carried out without H$_2$S in the feed stream. Three different H$_2$S concentrations (20, 50, and 100 ppms) are considered in the study. The H$_2$O to CH$_4$ ratio is maintained in such a way that CO$_2$ also participates in the reforming reaction. After performing the poisoning studies, regeneration of the catalyst is attempted by three different techniques.

3.1 Basic reactions

The major reactions that occur during biogas reforming are i) steam reforming

$$\text{CH}_4 + \text{H}_2\text{O} \rightleftharpoons \text{CO} + 3\text{H}_2 \quad \Delta H_{298}^0 = +206 \text{ kJ/mol}$$

(3.1)

$$\text{CH}_4 + 2\text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + 4\text{H}_2 \quad \Delta H_{298}^0 = +165 \text{ kJ/mol},$$

(3.2)

ii) water gas shift reaction

$$\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2 \quad \Delta H_{298}^0 = -41 \text{ kJ/mol},$$

(3.3)

and iii) dry reforming reaction with CO$_2$

$$\text{CH}_4 + \text{CO}_2 \rightleftharpoons 2\text{CO} + 2\text{H}_2 \quad \Delta H_{298}^0 = +247 \text{ kJ/mol},$$

(3.4)

which plays a minor role when enough H$_2$O is available. Even though the dry reforming reaction tends to form coke, it can be suppressed by adding small amounts of H$_2$O. The syngas composition that results from reforming of biogas at a fixed temperature depends on S/CH$_4$ ratio as well as CO$_2$/CH$_4$ ratio.
3.2 Catalyst preparation

Initially the $\gamma$-Al$_2$O$_3$ (Alfa Aesar) supports are calcined in air at 800 °C and held for 4 h to remove any volatile components present in the supports. The physical properties of $\gamma$-Al$_2$O$_3$ as received are shown in table 3.1. The nickel metal catalysts supported on $\gamma$-Al$_2$O$_3$ are prepared by wet impregnation method using nickel (II) nitrate hexahydrate (Ni(NO$_3$)$_2$·6H$_2$O, Merck, 98.9% purity) as nickel precursor. Measured quantities of metal precursor equivalent to the desired metal loading (15 wt%) is first dissolved in distilled water of volume equal to or slightly excess of the total pore volume of the support. The precursor solution is slowly added to the $\gamma$-Al$_2$O$_3$ supports and stirred continuously for two hours to ensure uniform mixing. The wet material is subsequently dried overnight at 100 °C for 12 hours in a hot air oven, and followed by calcination at 800 °C in presence of air for about 6 hours. Enough catalyst is prepared in one batch and used throughout the experiments to ensure consistency in the results. The 15% nickel loading is calculated according to the following equation.

$$\text{Amount precursor required} = \frac{0.15}{1 - 0.15} \times \frac{W_{\text{Ni(NO}_3)_2\text{6H}_2\text{O}}}{W_{\text{Ni}}} \times \text{weight of support}.$$  \hspace{1cm} (3.5)

where $W_{\text{Ni(NO}_3)_2\text{6H}_2\text{O}}$ and $W_{\text{Ni}}$ are the molecular of weights of nickel nitrate hexahydrate and nickel respectively. The amount of distilled water to be added to the precursor salt is calculated according to

$$\text{Amount of water required} = \text{pore volume} \times \text{weight of support}$$  \hspace{1cm} (3.6)

3.3 Catalyst characterization

The fresh and spent catalysts are characterized by various techniques, including surface area and porosity analyzer, temperature programmed reduction (TPR), pulse chemisorption, and powder X-Ray diffraction (XRD).

3.3.1 X-ray powder diffraction (XRD)

X-ray powder diffraction (XRD) is a rapid analytical technique primarily used for phase identification of a crystalline material and can provide information on unit cell dimensions. It is also possible to roughly estimate the average crystallite size. XRD analysis of catalysts are performed on the Philips Xpert Pro instrument (X-Pert PRO PANalytical) between 10–90 degrees using CuK$_\alpha$ radiation ($\lambda =0.15418$ nm) at 40 kV and 30 mA, with a scanning rate of $2\theta = 0.067^\circ$. The crystallographic phases are identified by using the software PDFWIN. This software is based on diffraction data from International Centre for Diffraction Data (ICDD).
The crystal size of the catalysts is calculated using the Debye–Scherrer equation and the XRD spectra. The mean size (D) of the crystallite in the catalyst is determined using the following equation

$$D = \frac{k\lambda}{B_{\frac{1}{2}}\cos(\theta)}$$

(3.7)

where $k$ is a constant ranging between 0.9 to 1.0, $\lambda$ is the wave length of X-Ray (Å), $\theta$ is the angle of incidence in radians, $B_{\frac{1}{2}}$ is measured angle from the diffraction pattern figure obtained at the different 20 angles (degrees), as it can be approximated as line broadening at half of the maximum intensity. In general, a broader peak means that the corresponding crystallite present is of relatively small particles and a sharp peak usually is attributed to crystallites of relatively large size.

### 3.3.2 Surface area and porosity measurement

Micrometrics ASAP 2020 analyzer is used to measure the BET surface area, average porosity, and pore size distribution of fresh catalyst sample and spent catalysts. This analysis is essentially an adsorption-desorption phenomena.

Before the analysis, the sample needs to be degassed to remove impurities, such as air and other gases. The sample is degassed under high vacuum at 250 °C and for 1 hour. After degassing the amount of the catalyst in the cell is weighed and loaded to the analysis port of the equipment. Dewar flask is filled with liquid nitrogen and kept under analysis port to maintain the cell temperature at $-196$ °C. The amount of nitrogen gas adsorbed at various relative pressures is measured. From the obtained data a plot of $p/p_0$ vs $1/[w((p_0/p) - 1)]$ is drawn and surface area is calculated using BET equation. The linear relationship of this equation is maintained only in the range of $0.05 < p/p_0 > 0.35$, where $p$ and $p_0$ are the equilibrium and the saturation pressure of adsorbates at the adsorption temperature, and $w$ is the quantity of volume adsorbed.

Similarly, a sample of porous material is characterized by its distribution of pore sizes. Each pore size contributes to the total adsorption isotherm in proportion to the fraction of the total area of the sample. Isotherms of mesoporous materials are measured over a pressure range of 1 torr to approximately 760 torr. Once details of the isotherm curve are accurately expressed as a series of pressure vs. quantity adsorbed data pairs, a number of different methods (theories or models) can be applied to determine the pore size distribution. Barrett, Joyner and Halenda method (BJH), and T-Plot analysis is used to calculate the pore size.

### 3.3.3 Temperature programmed reduction

Temperature programmed reduction (TPR) is employed mainly to study the reduction behavior of metals present on the support. The data obtained from TPR is useful to estimate reduction temperatures, degree of reduction, metal-support interactions and any important findings related to the interaction of metal with other metals and support. The reduction temperature depends on the degree of interaction between the active metal and the support. Stronger interactions lead to higher reduction temperatures. TPR studies are carried out in a AutoChem II 2920 (Micrometrics, USA). A measured amount of fresh catalysts is loaded in a quartz tube supported on the quartz wool. Sample preparation includes heating the catalyst to 200 °C with a ramp rate of
10 °C/min, and holding it at that temperature for 1 h in argon stream with a flow rate of 30 ml/min to remove any absorbed moisture, after which the catalyst is cooled to 50 °C. After sample preparation, the catalyst is heated to 900 °C at a ramp rate of 10 °C/min in 10% H₂ in argon mixture. The consumption of hydrogen is monitored with a thermal conductivity detector (TCD).

### 3.3.4 Pulse chemisorption

Pulse chemisorption measures the metal dispersion in the catalyst support. Dispersion is the fraction of active metal atoms exposed or is accessible to the reacting species. It is a critical parameter for catalyst activity since only atoms which are exposed can take part in the surface catalyzed reactions. Due to the high temperatures encountered in different steps (calcination, reduction, reaction) during the catalyst preparation, some of the metal particles may become inaccessible to the reactants due to migration into the support bulk, formation of a new product, sintering, etc. 10% H₂ in argon mixture is used to carry out the experiment and the amount of H₂ chemisorbed is used to determine the exposed metal atoms in the catalyst. A measured amount of fresh catalysts is loaded in a quartz tube supported on the quartz wool. The catalyst is reduced with 10 vol% H₂ in argon with a flowrate of 30 ml/min. After completion of reduction, the sample is cooled down to ambient temperature with argon carrier gas and the flow is continued for another 30 min to remove any traces of hydrogen. Pulses of the 10% H₂ in argon mixture are dosed repeatedly until the catalyst surface is saturated (Fig. 3.1).

![Figure 3.1: Pulse chemisorption trend for 15% Ni reduced catalyst.](image)

The total amount of H₂ chemisorbed is measured using a thermal conductivity detector (TCD) and the metal dispersion can be calculated as [93],

$$\text{Percent metal dispersion} = \frac{M(V_s S F_{cal})}{S_w V_{ideal}} \times 100, \quad (3.8)$$

where $M$ is the molecular weight of Ni, $V_s$ is the volume adsorbed in cm³ at STP, $S F_{cal}$ is the calculated stoichiometry factor, $S_w$ is the sample weight, and $V_{ideal}$ is the molar volume of an ideal gas (22414 cm³)
3.4 Experimental rig

A schematic representation of the experimental rig used for biogas steam reforming is shown in Fig. 3.2. The following sections briefly explain the system configurations.

![Figure 3.2: A schematic representation of reactor used for experiments. The abbreviations used are as follows: Thermocouple (TC), Gas-Liquid separator (GLS), Condenser (CD), Gaschromato- graph (GC).](image)

3.4.1 Reactor

The reactor section consists of a high temperature tubular reactor inside a furnace and a temperature controller to control the temperature of the catalyst bed. A 40 cm long quartz tube having 18 mm ID and 22 mm OD forms the reactor. The two ends of the quartz reactor are fitted with stainless steel clamps with the help of graphite gaskets. Two Ni-Cr thermocouples are inserted into the catalyst bed at the top and bottom through 0.32 cm bored-through fittings. The furnace used in the reactor set-up has three split zones (Series 3220, Applied Test Systems, USA). The first zone serves as a preheating section, second zone maintains the isothermal conditions for the catalyst bed, and third zone maintains the reactor temperature to avoid condensation within the reactor. The three zones of the furnace heater are controlled using digital controllers, and the temperatures of the three zones are adjusted based on the bed temperature at the top and the bottom. By maintaining these temperatures the entire quartz reactor is maintained at a desired reaction temperature.

Initially the reactor is heated to the desired reaction temperature with a ramp rate of 10 °C per minute under inert $\text{N}_2$ flow (99.999% pure, Prax air). Prior to the reactions the nickel catalysts are reduced in pure $\text{H}_2$ flow.
20 ml/min at a temperature of 800 °C for about 5 hours. Before starting the reaction, water is fed using a calibrated HPLC pump through a preheating zone heater for 5 min to fill the liquid line. Pure gases of CH₄ (99.999%) and CO₂ (99.995%) are fed to the reactor using calibrated mass flow controllers with N₂ dilution. The gas mixture is heated to 250 °C in a preheating zone before entering the reactor hot zone.

3.4.2 Catalyst loading
Maintaining the location of the catalyst bed within the reactor is critical for reproducible data. For obtaining consistent reading the length of the bed is kept constant and so is the distance of the bed from one of the ends of the reactor. In this work, the reactor is loaded with 1.5 g of catalyst pellets diluted with quartz beads (3 mm to 5 mm diameter) and total length of the bed is maintained at ~6 cm and it is placed exactly at middle zone of the furnace. The catalyst bed is placed such that the temperature measurements are possible at the top and bottom of the bed. Care must be taken to obtain an ideal fixed bed reactor system. The ideal fixed bed configuration requires the catalyst bed to be placed on top of a flat surface and also to have a flat top. For this reason, the catalyst bed is placed in between the fine quartz wool.

3.4.3 Flow controllers
An HPLC pump (Series I, Lab alliance, USA), and calibrated mass flow controllers (Bronkhorst High Tech, The Netherlands and Alborg, USA) respectively controls the flow of liquid water and gases into the reactor. The HPLC pump for liquid water has a flow range of 0 to 5 ml/min with an accuracy of 0.01ml/min. The water flow rate is maintained at 0.036 ml/min throughout the experiments. The outlet of the HPLC pump is connected to microbore tubing in order to create sufficient pressure drop so that selected amount of liquid flow can be injected. The gases and water enter the reactor through different lines. 1/4 inch lines are used for gases and 1/8 inch line for liquid. Each line is fitted with a non-return valves to avoid any back flow due to pressure build up in the system. Pressure gauges are installed on each line to monitor the pressure. The inert gas feed lines have 7 µm size filters installed between the gas cylinder and the mass flow controller. Initially the mass flow controllers are calibrated with actual gas reactants. The range of mass flow controllers for CH₄, N₂, H₂ and CO₂ is 0-200 ml/min with minimum accuracy of 1%, while H₂S/N₂ mixture mass flow controller range is 0-20 ml/min with an accuracy of 1%. The inert gas N₂ served both as the internal standard for the gas chromatograph and as a carrier gas through the reactor system.

MFC calibrations
The mass flow controllers are calibrated in the range of flow necessary for the desired feed conditions. Actual flow rates are measured at the out let of the MFC with the help of manual soap bubble meter as well as digital soap bubble meter (Smarttech instruments, India). The following Table 3.2 gives actual flowrate equation constants from respective mass flow controller in the form of \( F_{act} = aF + b \), where \( F_{act} \) is actual flow from MFC in ml/min, \( F \) is the set point of MFC, and \( a \) and \( b \) are the constants for the respective controller.

3.4.4 Steam generation and gas preheating
Vaporization of water is accomplished using heating tape wrapped around the feed lines. Sufficient length of the water line wrapped with heating tapes ensure the complete vaporization of water before entering into the
Table 3.2: MFC actual flow equation constants in the form of $F_{act} = a F + b$.

<table>
<thead>
<tr>
<th>Species</th>
<th>a</th>
<th>b</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄</td>
<td>0.8373</td>
<td>2.0242</td>
</tr>
<tr>
<td>CO₂</td>
<td>1.1181</td>
<td>-1.8987</td>
</tr>
<tr>
<td>N₂</td>
<td>1.0611</td>
<td>6.9020</td>
</tr>
<tr>
<td>H₂S</td>
<td>1.0860</td>
<td>-0.3759</td>
</tr>
</tbody>
</table>

preheating zone of furnace heater. The temperature of all the feeding lines are maintained at 250°C, which is controlled by a K-type thermocouple and a controller. The vaporized water and preheated gases are mixed together in a cross connection near the reactor inlet.

3.4.5 Condenser and gas liquid separator

A condenser is required to condense any unreacted water that comes out of the reactor. The condenser is made of stainless steel with inside spiral coil of surface area 160 cm². The shell side of the condenser is maintained at 0°C using a chiller (Zulabo, Germany) and the effluent coming out from the bottom of the reactor is passed through a coiled section of the condenser using 1/4 inch OD SS 316 line. The gases and condensed water are separated in one side torispherical head closed gas liquid seperator. The left over uncondensed water vapor from the condenser is condensed in the gas liquid separator, which also has a provision to maintain shell side temperature at 0°C by using a chiller. The effluent gases leaving this section are passed through a moisture trap to remove trace amounts of water vapor. The dry gases are then directed to online GC for analysis.

3.4.6 Gas analysis

The gases leaving the reactor system mainly contains H₂, CO, CH₄, CO₂ and N₂. These gases are directed to the online GC 2014 (Shimadzu Corporation) equipped with a thermal conductivity detector (TCD) for analysis. The sampling is done with gas sampling valve (MGS-5, Shimadzu). The gas sampler is used to introduce gas samples through manual operation, under ambient temperature conditions. The sample volume is selectable in 1, 2, or 5 milliliters by valve operation. In our experiments 1 ml loop is operated throughout the experiments. Carboxane packed column of inner diameter 3.17 mm and length 4.5 m is used for gas separation. The injector port temperature, column temperature, and TCD temperature are maintained at 150°C with TCD current of 60 mA. Argon is used as a carrier gas for GC for detecting all the components. The product gas sample is injected for every 15-30 mins until steady state is reached. i.e., constant chromatogram areas for all the components.

3.4.7 Process automation

SCADA software is used for online control of system for gas flow, liquid flow, reactor furnace temperature, reactor upstream and down stream pressures, pressure control system, and catalyst bed temperature.
3.5 Catalyst testing

This section briefly explains the different sets of experiments carried out just for the sake of explaining the results of catalyst characterization. Three sets experiments are carried out for biogas steam reforming.

(i) Catalyst stability test at 700°C and 800°C in the absence of H₂S in the feed gas

(ii) Catalyst poisoning with 20, 50, 100 ppm of H₂S in the feed stream.

(iii) Catalyst regeneration by different techniques.

Table 3.3 shows the actual flow rates of reactants which are maintained throughout the experimental studies.

<table>
<thead>
<tr>
<th>Species</th>
<th>Flow rate (ml/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄</td>
<td>23.794</td>
</tr>
<tr>
<td>CO₂</td>
<td>15.99</td>
</tr>
<tr>
<td>N₂</td>
<td>102.4</td>
</tr>
<tr>
<td>H₂O</td>
<td>0.036 (liquid)</td>
</tr>
</tbody>
</table>

The above flow rates gives CH₄/CO₂ ratio is 1.487. This composition corresponds approximately to mean values of the biogas (CH₄/CO₂ ratio is ~1.5).

\[ \text{S/C ratio} = \frac{n_{H_2O}}{n_{CH_4}} \]  

\[ (3.9) \]

where \( n_{H_2O} \) and \( n_{CH_4} \) are the molar flow rates of steam and CH₄ respectively. Biogas mainly contains CH₄ and CO₂, while calculating S/C only organic carbon is considered. A low S/C = 2.02 is employed throughout the experimental studies to ensure the participation of CO₂ in reforming reactions.

Catalyst stability tests are carried out at temperature of 700°C and 800°C. The main purpose of the stability test is to evaluate the catalyst performance during reforming of H₂S free biogas. The reaction is carried out for \( \sim 12 \) h at 700°C and for \( \sim 22 \) h at 800°C. In second set of experiments, the biogas steam reforming reaction is performed with out H₂S until steady state and once the steady state is reached H₂S is introduced into the reactor from a cylinder containing 1052 ppm H₂S diluted with N₂. All the experiments with H₂S are repeated to ensure reproducibility of the results. The reforming reactions are continued in the presence of H₂S and sampling is done for every 15-30 min until a new steady state is reached. In regeneration experiments, the totally poisoned catalyst is regenerated by.

- removing of H₂S from feed stream
- temperature enhancement
- steam treatment followed by reduction in H₂
3.6 Calculations

The gas chromatograph calibrations are performed using a constant flow rate of ∼100 sccm of different concentrations of individual gases diluted in nitrogen. Response factors of each species are generated from the GC chromatographs. For example CH₄ response factor is calculated based on the following.

Chromatographs of different compositions of CH₄ balanced with N₂ are generated and corresponding areas are measured. Once the areas are known at different compositions the response factor for individual composition is calculates as

\[
\frac{Y_{\text{CH}_4}}{Y_{\text{N}_2}} = \alpha_{\text{CH}_4} \times \frac{A_{\text{CH}_4}}{A_{\text{N}_2}}
\]  

(3.10)

where \( Y_{\text{CH}_4} \) and \( Y_{\text{N}_2} \) represents the mole fractions of CH₄ and N₂ respectively, \( \alpha_{\text{CH}_4} \) is the response factor CH₄, and \( A_{\text{CH}_4} \) and \( A_{\text{N}_2} \) are the chromatogram area of CH₄ and N₂ respectively. The above equation can be written as

\[
\alpha_{\text{CH}_4} = \left( \frac{n_{\text{CH}_4}}{n_{\text{N}_2}} \right) \times \left( \frac{A_{\text{CH}_4}}{A_{\text{N}_2}} \right)
\]  

(3.11)

where \( n_{\text{CH}_4} \) and \( n_{\text{N}_2} \) represents the moles of methane and nitrogen. The above procedure is repeated for all the compositions and average response factor of CH₄ is calculated. The similar procedure is adopted for all other reactant and product gases. The response factor of each component is listed in Table 3.4.

<table>
<thead>
<tr>
<th>Species</th>
<th>( \alpha )</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄</td>
<td>0.382137</td>
</tr>
<tr>
<td>H₂</td>
<td>0.085576</td>
</tr>
<tr>
<td>CO</td>
<td>0.833152</td>
</tr>
<tr>
<td>CO₂</td>
<td>1.324115</td>
</tr>
</tbody>
</table>

N₂ component calibration is done by injecting different volumes of N₂ into the GC and measuring corresponding chromatogram areas. The generalized equation is developed for unknown moles of N₂ in the gas mixture given by

\[
n_{\text{N}_2} = 7 \times 10^{-11} \times A_{\text{N}_2}
\]  

(3.12)

The unknown moles of CH₄ in the gas mixture is then calculated according to

\[
n_{\text{CH}_4} = \alpha_{\text{CH}_4} \times \left( \frac{A_{\text{CH}_4}}{A_{\text{N}_2}} \right) \times n_{\text{N}_2}
\]  

(3.13)

The conversion of methane is calculated as

\[
X_{\text{CH}_4} = 1 - \frac{n_{\text{CH}_4}}{n_{\text{CH}_4,0}}
\]  

(3.14)

where \( n_{\text{CH}_4,0} \) is the initial moles of methane in the reaction mixture and \( n_{\text{CH}_4} \) is the moles of methane in the product stream.
3.7 Mass balance

Here, it is assumed that the reaction of inlet gases produces a mixture of CO, CO$_2$, H$_2$, CH$_4$, H$_2$O and solid C. The calculations of all outlet flow rates are based on the assumption that carbon, oxygen and hydrogen mass balance equations are given by equations that are presented in the following.

**Carbon balance**

\[
[\text{CH}_4]_{\text{in}} + [\text{CO}_2]_{\text{in}} = [\text{CO}]_{\text{out}} + [\text{CO}_2]_{\text{out}} + [\text{Carbon}]_{\text{out}}
\]  \hspace{1cm} (3.15)

**Oxygen mass balance**

\[
[\text{H}_2\text{O}]_{\text{in}} + 2[\text{CO}_2]_{\text{in}} = [\text{CO}]_{\text{out}} + 2[\text{CO}_2]_{\text{out}} + [\text{H}_2\text{O}]_{\text{out}}
\]  \hspace{1cm} (3.16)

**Hydrogen balance**

\[
2[\text{CH}_4]_{\text{in}} + [\text{H}_2\text{O}]_{\text{in}} = 2[\text{CH}_4]_{\text{out}} + [\text{H}_2\text{O}]_{\text{out}} + [\text{H}_2]_{\text{out}}.
\]  \hspace{1cm} (3.17)

Where \([ ]_{\text{out}}\) and \([ ]_{\text{in}}\) are outlet flow rates [mol/h] and inlet flow rates [mol/h], respectively.

The outlet gas from the reactor passes through the condenser and gas liquid separator to remove unreacted H$_2$O. Thus, the gas passing the gas analyzer contains only H$_2$, CO, CO$_2$, and unreacted CH$_4$. These components are related by the following equation:

\[
[\text{H}_2]_{\text{out}}^{\text{mf}} + [\text{CH}_4]_{\text{out}}^{\text{mf}} + [\text{CO}]_{\text{out}}^{\text{mf}} + [\text{CO}_2]_{\text{out}}^{\text{mf}} = 1.
\]  \hspace{1cm} (3.18)

Where \([ ]_{\text{out}}^{\text{mf}}\) are water free mol fractions (dry mole fractions) of the outlet stream and are given through gas analyzer results.

Carbon deposition is one of the main factors of catalyst deactivation. The deposited carbon amount can be calculated using the mass balance equations above. Since no carbon deposition and catalyst deactivation was observed during the stability at 700 °C and 800 °C, carbon$_{\text{out}}$. Formation of carbon is assumed to be zero throughout the calculations.

3.8 Results and discussion

3.8.1 XRD- phase identification

The γ- Al$_2$O$_3$, the catalyst calcined at 800 °C, and fresh reduced catalyst with hydrogen are characterized to get an insight into the phases present. XRD is also useful in estimating the crystallite sizes of the different phases using the Scherrer equation. The XRD patterns of these catalysts are shown in Fig. 3.3. The calcined catalyst shows NiO peaks at 37.26 and 66.12 degrees, and NiAl$_2$O$_4$ is observed at 45.62 degrees. The formation of nickel aluminate is attributed to the close interaction between NiO and Al$_2$O$_3$ support at a high temperatures (>800 °C) according to

\[
\text{NiO} + \text{Al}_2\text{O}_3 \rightleftharpoons \text{NiAl}_2\text{O}_4
\]  \hspace{1cm} (3.19)

The presence of NiAl$_2$O$_4$ in Fig 3.3 indicates strong metal support interaction. However, a careful examination of the γ- Al$_2$O$_3$ and calcined samples reveals that there is an intensity increase at the 2θ values slightly
lower than the 2θ of the γ-Al₂O₃ peak. It has been reported that γ-Al₂O₃ has a pseudospinel structure and its lattice parameters are very close to that of NiAl₂O₄, with 2θ shifted slightly to higher values [94]. After reduction of the Ni/γ-Al₂O₃ at 800 °C for 5 hr, nickel shows (1 1 1), (2 0 0) and (2 2 0) faces and are clearly visible respectively at 2θ of 44.6, 51.90 and 76.42 degrees. The peak intensity of NiAl₂O₄ is reduced compared to the calcined catalyst. Alumina crystallite phase is also observed at 2θ of 67.24 degrees. The absence of NiO indicates that NiO is completely reduced to metallic nickel during reduction with H₂.

Spent catalysts are characterized using XRD analysis and the results are shown in Fig. 3.4 The figure shows the XRD patterns of catalyst after stability at 800°C without H₂S, reforming in the presence of H₂S with temperature enhancement (catalyst regeneration), and complete catalyst poisoning at 700°C with H₂S.
A nearly identical set of XRD patterns are observed for the fresh and spent catalysts. It is observed that support alumina unchanged position at 2θ value for different spent catalysts as well as in fresh catalysts. It also shows that these peaks remain intact even after reaction, indicating the stability of the support during reactions at high temperatures. The peak at 37.26 degrees corresponds to NiO, observed for all Ni-containing catalysts, which indicates that metallic Ni is oxidized into NiO in the presence of steam that is not observed in XRD pattern of fresh reduced catalyst. The diffraction patterns for NiS and NiS$_2$ are not observed for the spent catalyst at 700 °C with 100 ppm H$_2$S exposure even though the catalyst is almost fully poisoned. A similar XRD pattern is also observed by Kuhn et al., for Ni-YSZ sample exposed to 100 ppm H$_2$S [95]. The absence of stable compounds of NiS or Ni$_3$S$_2$ in the XRD pattern is not surprising as these are expected to form only at high concentrations of H$_2$S in the feed. The diffraction peak for graphite carbon at 26.50 degrees is not observed for spent catalyst at 700 °C and 800 °C, which confirms the absence of coke formation during the reforming reactions.

### 3.8.2 BET area and pores size distribution

Figure 3.5 shows the N$_2$ adsorption/desorption isotherms of the fresh and spent catalyst at 1073 K. The N$_2$ adsorption/desorption isotherms are of type IV; they are presented as a hysteresis loop H$_2$ type, which is typical for mesoporous material. Figure 3.6 shows the the pore size distribution of the fresh and spent catalysts; both follows a normal distribution and that the mean pore size is less than 20 nm. The maximum value on the pore size distribution of the spent catalyst shifts from 15 nm to 18.3 nm and is about 3.3 nm larger than the fresh catalyst. The distribution of pores larger than 20 nm is similar for both the fresh and the spent catalysts.

![Figure 3.5: N2 adsorption-desorption isotherms of reduced catalyst and spent catalysts.](image)
Figure 3.6: Pore diameter distribution of fresh and spent catalysts.

The BET surface area of calcined $\gamma$-Al$_2$O$_3$, reduced catalyst, and spent catalysts are shown in Table 3.5. The calcined and reduced catalysts show lower surface area compared to $\gamma$-Al$_2$O$_3$. The reduction in surface area is probably due to pore blockage. Moreover, the fresh reduced catalyst shows lower surface area than the calcined catalyst. This may be due to sintering of nickel metal particle during reduction at 800 °C for 5 h. It is also observed that spent catalysts shows less surface area than the fresh reduced catalyst. The pore volume is lower in the case of calcined and reduced catalysts compared to the $\gamma$- Al$_2$O$_3$ support. This may be due to the blockage of pores with metallic nickel particle.

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET surface area (m$^2$g$^{-1}$)</th>
<th>Pore volume (cm$^3$g$^{-1}$)</th>
<th>Average pore Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcined $\gamma$-Al$_2$O$_3$ at 800 °C</td>
<td>206</td>
<td>0.793</td>
<td>11.34</td>
</tr>
<tr>
<td>Calcined Ni/$\gamma$-Al$_2$O$_3$</td>
<td>151</td>
<td>0.626</td>
<td>12.09</td>
</tr>
<tr>
<td>Reduced Ni/$\gamma$-Al$_2$O$_3$</td>
<td>106</td>
<td>0.585</td>
<td>17.30</td>
</tr>
<tr>
<td>Spent catalyst after stability test at 800 °C</td>
<td>86</td>
<td>0.581</td>
<td>21.11</td>
</tr>
<tr>
<td>Spent catalyst at temperature enhancement</td>
<td>93</td>
<td>0.573</td>
<td>9.54</td>
</tr>
<tr>
<td>Spent catalyst at 700 °C</td>
<td>76</td>
<td>0.433</td>
<td>17.66</td>
</tr>
</tbody>
</table>

### 3.8.3 TPR studies

Fig 3.7 shows the TPR profile for 15% Ni loaded catalyst. The peak temperature is observed in the range of 780-800 °C. The higher reduction temperature indicates strong interaction NiO with $\gamma$-Al$_2$O$_3$ support. This is also normally attributed to the reduction of Ni aluminate (NiAl$_2$O$_4$), a surface spinel species formed by the diffusion of NiO into the support alumina. Similar type of TPR behavior is observed by Chen et al., [96]. Formation of NiAl$_2$O$_4$ occurs at calcination temperatures higher than 700 °C with NiO diffusing into the surface of support. There are no low temperature peaks found around 400–450 °C, which indicates that the sample is deprived of any free NiO dispersed on the support.
3.8.4 Pulse chemisorption

Nickel metal dispersion and metallic surface area are determined by assuming an adsorption stoichiometry Ni/H ratio of 1 [97]. The mean size of the nickel particles is calculated from hydrogen adsorption [98]. H₂ pulse chemisorption results for Ni/Al₂O₃ reduced at temperature of 800 °C for 15 wt% Ni loading gave 3% metal dispersion, metallic surface area of 19.9 m²/g.metal and cubic crystallite size of 28.1 nm.

3.9 Activity tests

3.9.1 Stability tests

In order to ensure that the catalyst does not lose activity over time in non poisoning atmosphere (without H₂S) reforming experiments are performed for 22 h at 800 °C. Fig. 3.8 shows the conversion of CH₄ and CO₂ on dry basis during the catalyst stability test at 800 °C. All data reported in this thesis is on dry basis and the lines are just drawn to guide the eye. The reactor exit compositions for the stability test are shown in Fig. 3.9. The constant conversion and product composition implies that the catalyst is stable and the activity remains constant under non-poisoning gas atmosphere. The H₂ to CO ratio in the product gas for the given inlet composition is ~3.

The stability test is also carried out at 700 °C and the conversions of CH₄ and CO₂ are shown in Fig. 3.10. The exit product mole fractions are shown in Fig. 3.11. The H₂ to CO ratio at 700 °C is ~ 2.72 and CO₂ conversion is lower compared to 800 °C, which can be attributed to the shifting of the thermodynamic equilibrium of the reactions involved.
Figure 3.8: Time on stream conversion of CH$_4$ and CO$_2$ during catalyst stability test at 800°C.

Figure 3.9: Time on stream mole fraction of H$_2$ and CO during catalyst stability test at 800°C.

Figure 3.10: Time on stream conversion of CH$_4$ and CO$_2$ during catalyst stability test at 700°C.
Table 3.6: Comparison between equilibrium prediction and experiments

<table>
<thead>
<tr>
<th>Reactants/Products</th>
<th>Equilibrium</th>
<th>Experiments</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>800 °C</td>
<td>700 °C</td>
</tr>
<tr>
<td>CH₄ Conversion (%)</td>
<td>99.86</td>
<td>98.08</td>
</tr>
<tr>
<td>CO₂ Conversion (%)</td>
<td>22.85</td>
<td>7.03</td>
</tr>
<tr>
<td>H₂ dry moles fraction (%)</td>
<td>32.23</td>
<td>32.6</td>
</tr>
<tr>
<td>CO dry moles fraction (%)</td>
<td>13.06</td>
<td>11.5</td>
</tr>
</tbody>
</table>

Figure 3.11: Time on stream mole fraction of H₂ and CO during catalyst stability test at 700 °C.

Equilibrium calculations are performed with DETCHEM\textsuperscript{EQUIL} \cite{99} and Table 3.6 shows a comparison between equilibrium predictions and the experimental data. It can be seen that the conversions and product mole fractions agree well with the equilibrium calculations. The increase in CO₂ conversion with temperature shows that the methane dry reforming reaction takes place. At higher temperatures (800 °C), this endothermic reaction is favored and therefore CO₂ is consumed. Since all the catalysts used in the experiments are prepared in the same batch and since they are stable under non-poisoning gas atmosphere, we can assert that the catalyst deactivation by introducing H₂S to the feed gas is purely due to sulfur poisoning, at least for the time on stream considered in this study.

Mass balances of carbon and hydrogen are carried out for stability test at 800 °C based on equations of Eqs. 3.15 and 3.16.

Table 3.7: Carbon moles balance

<table>
<thead>
<tr>
<th>Species</th>
<th>In (mol/hr)</th>
<th>Out (mol/hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄</td>
<td>0.05938</td>
<td>172.2 x 10⁻⁶</td>
</tr>
<tr>
<td>CO₂</td>
<td>0.03991</td>
<td>0.03066</td>
</tr>
<tr>
<td>CO</td>
<td>0.0</td>
<td>0.0663931</td>
</tr>
<tr>
<td>Total</td>
<td>0.09930</td>
<td>0.09723</td>
</tr>
</tbody>
</table>

3.9.2 Deactivation studies

Catalyst deactivation experiments are performed for two different temperatures and three different H₂S concentrations. Fig. 3.12 shows the deactivation of the catalyst for 20, 50, and 100 ppm H₂S with respect to
Table 3.8: Hydrogen moles balance.

<table>
<thead>
<tr>
<th>Species</th>
<th>In (mol/hr)</th>
<th>Out (mol/hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 x CH₄</td>
<td>0.11877</td>
<td>0.00034</td>
</tr>
<tr>
<td>H₂O</td>
<td>0.11978</td>
<td>0.07252</td>
</tr>
<tr>
<td>H₂</td>
<td>0.0</td>
<td>0.15859</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>0.23855</strong></td>
<td><strong>0.23646</strong></td>
</tr>
</tbody>
</table>

CH₄ + CO₂ concentration at 700 °C. All H₂S concentrations led to almost complete deactivation (98%) of the catalyst, however, the rate at which deactivation occur varies. Higher H₂S concentrations lead to faster deactivation.

![Figure 3.12](chart1.png)

Figure 3.12: CH₄ conversion at 700 °C as a function of time for three different H₂S concentrations.

Figure 3.13 shows drop in CH₄ conversion as a result of deactivation at 800 °C for different H₂S concentrations. In all cases the catalyst activity dropped, however, did not deactivate fully. The residual activity retained by the catalyst depends on the concentration of H₂S in the feed gas. 100 ppm H₂S concentration in the feed gas led to a final steady state of 34% CH₄ conversion, 50 ppm to 43%, and 20 ppm to 48%.

![Figure 3.13](chart2.png)

Figure 3.13: CH₄ conversion at 800 °C as a function of time for three different H₂S concentrations.

Deactivation versus time on stream for 20, 50, and 100 ppm for the two temperatures studied are shown.
respectively in Fig. 3.14, 3.15, 3.16. It is interesting to notice that for both the temperatures the rate of activity loss (the slope of the curve) before reaching steady state is same for 50 and 100 ppm whereas for 20 ppm the rate of deactivation is much slower at 800 °C compared to 700 °C. For both the temperatures CH₄ conversion is ~98-99% in the absence of H₂S in the feed gas. Therefore, the catalyst deactivation is purely due to sulfur poisoning.

Figure 3.14: Comparison between CH₄ conversions achieved at 700 and 800 °C for 20 ppm H₂S in the feed gas.

Figure 3.15: Comparison between CH₄ conversions achieved at 700 and 800 °C for 50 ppm H₂S in the feed gas.

The H₂ and CO mole fractions from the reactor exit at 700 °C during deactivation for different H₂S concentrations are shown in Figures 3.17, 3.18. Examining Figure 3.12 and Fig. 3.17, 3.18 leads us to the conclusion that the final activity of the catalyst is independent of the H₂S concentration. In all cases the catalyst retained ~2% of its activity. However, the same is not true for high temperature operation.
Figures 3.16 and Fig. 3.20 shows the exit mole fractions of H\textsubscript{2} and CO at 800 °C. Higher ppm level of H\textsubscript{2}S results in low CH\textsubscript{4} conversion and hence low H\textsubscript{2} mole fraction in the product stream. That is at low operating temperatures, the saturation coverage of sulfur on Ni is independent of H\textsubscript{2}S concentration. All the H\textsubscript{2}S concentrations considered in this study lead to saturation coverages at 700 °C whereas at high temperature,
the mechanistics of H$_2$S adsorption and recombination reaction involving sulfur leads to different saturation coverages of sulfur for different H$_2$S concentrations.

![Graph showing mole fraction vs time for different H$_2$S concentrations](image1)

Figure 3.19: H$_2$ mole fraction from the reactor exit at 800°C.

![Graph showing mole fraction vs time for different H$_2$S concentrations](image2)

Figure 3.20: CO mole fraction from the reactor exit at 800°C.

### 3.9.3 Regeneration by H$_2$S removal

Since chemisorption is a reversible process, surface adsorbed sulfur can be removed by decreasing the sulfur content in the feed stream [100]. For 100 and 50 ppm we have performed the regeneration experiments by removing H$_2$S from the feed gas after reaching their steady state residual activity. For both 100 and 50 ppm the catalyst activity again reached another steady state after H$_2$S removal (Fig. 3.12). However, full regeneration could not be achieved. In the case of 50 ppm 95% activity could be recovered, whereas for 100 ppm recovery is only 90%. The time required for regeneration is $\sim$10 h, which is very short compared to the time required for conventional regeneration methods reported by Li et. al [1]. We could not perform regeneration experiments for 20 ppm due to periodic power outages after every 24 h. The rate of regeneration is same as rate of deactivation in all cases. For instance from Fig. 3.13 the deactivation for 100 ppm H$_2$S takes about 8 h and the regeneration also takes approximately the same duration. These results are consistent with the report of Ashra et al., [23]. The catalyst activity loss is mainly due to dissociative adsorption of H$_2$S on Ni leading
to the active sites being covered with sulfur. At high temperature each sulfur atom occupies one adsorption site on Ni [80]. To recover the activity the adsorbed sulfur needs to be removed from the active sites of the catalyst. The surface adsorbed sulfur can participate in recombination reactions with a number of other surface adsorbed species such as H, O, and OH. The recombination products can then desorb from the surface, leaving the surface again capable of promoting surface reactions. The partial recovery of activity would then imply that the adsorbed sulfur is not fully removed by the recombination reactions. Some possible reaction mechanisms for recombination reactions are given below.

\[
S^+ + H^+ \rightleftharpoons SH^+ + \cdot \cdot \cdot \\
\text{(3.20)}
\]

\[
SH^+ + H^+ \rightleftharpoons H_2S^+ + \cdot \cdot \cdot \\
\text{(3.21)}
\]

\[
S^+ + O^+ \rightleftharpoons SO^+ + \cdot \cdot \cdot \\
\text{(3.22)}
\]

\[
SO^+ + O^+ \rightleftharpoons SO_2^+ + \cdot \cdot \cdot \\
\text{(3.23)}
\]

### 3.9.4 Regeneration by temperature enhancement

At 800 °C the catalyst activity is recovered by removing H\(_2\)S from the feed gas. However, at 700 °C the catalyst activity could not be recovered in the same manner. This means that the kinetics of desorption and/or recombination reactions are not favored at low temperatures. This is further confirmed by temperature stepping at 700 °C which lead to recover the activity. Fig. 3.21 shows the gain in catalytic activity when the temperature is increased from 700 to 800 °C. 100 ppm H\(_2\)S concentration at 700 °C leads to almost complete deactivation of the catalyst. However, when the temperature is increased to 800 °C, the catalyst started regaining activity and stabilized at 32% CH\(_4\) conversion, very close to the steady state activity at 800 °C for 100 ppm reported in Fig. 3.13. This also reconfirms the reproducibility of our experiments. Since chemisorption is exothermic an improved sulfur removal is naturally expected by increasing the temperature [100]. Higher temperature favors the kinetics for desorption reactions and recombination reactions involving adsorbed sulfur species. After reaching the steady state, H\(_2\)S is completely removed from the feed gas and the catalyst is allowed to regain its activity further. 92% of the activity is recovered by this process. This again corresponds very well with the final activity reported in Fig. 3.13 for 100 ppm case.

![Figure 3.21: Effect of temperature and H\(_2\)S concentration on regaining catalyst activity.](image-url)
The mole fractions of various gases from the reactor exit for the same case are shown in Fig. 3.22. At steady state before introducing H$_2$S into the reactor, CH$_4$ is fully converted and the reactor exit contains 33% H$_2$, 9% CO, 9% CO$_2$ and remaining N$_2$. As soon as H$_2$S is introduced to the reactor, the reactants mole fraction starts to (CH$_4$ and CO$_2$) increases and stabilized respectively at 15% and 10%. These values corresponds very well to dry inlet mole fraction of CH$_4$ (16.7%) and CO$_2$ (11.2%). The 3% H$_2$ and 1.5% CO at the reactor exit is due to the residual activity (2%) of the catalyst.

![Figure 3.22: Mole fraction of various gases out of the reactor during the activity regeneration by temperature enhancement.](image)

3.9.5 Regeneration by steam treatment

Conventionally, the sulfur poisoned Ni is regenerated by sequential steam, steam air, and steam hydrogen treatment. Since the removal of adsorbed sulfur can be easily achieved by steaming above 650 °C we have attempted the regeneration by treating with H$_2$O. Once the catalyst is fully deactivated at 700 °C, the feed stream is replaced with H$_2$O (0.036 ml min$^{-1}$) diluted in N$_2$ (102.4 ml min$^{-1}$) flow for ~5 h. Since steam treatment leads to the formation of NiO the catalyst is further reduced under H$_2$ flow (20 ml min$^{-1}$) at 700 °C for 5 h. Total regeneration time is 10 h, which is far shorter than the regeneration time reported by Li et al. and Nielsen [24, 100]. The regenerated catalyst is tested for its activity by performing reforming reaction without H$_2$S in the feed stream. CH$_4$ conversion after regeneration is shown in Fig. 3.23. The catalyst showed stable operation for more than 10 h whereas Li et al. observed fall in activity of the catalyst regenerated using conventional sequential technique after 10 h of operation. Its very likely that the steam treatment regenerates the catalyst by forming SO$_2$ according to reactions 3.22 and 3.23. The oxygen atoms are formed by the dissociative adsorption of H$_2$O on Ni surface.
3.10 Conclusions

Ni Catalyst poisoning due to H$_2$S during the reforming of biogas is studied. The experiments are performed at 700 and 800 °C and for three different H$_2$S concentrations (20, 50, and 100 ppm w.r.t CH$_4$ + CO$_2$ concentration). At 700 °C, the saturation sulfur coverage is independent of H$_2$S concentration in the feed gas. However, at 800 °C, the saturation coverage of sulfur is dependent on the concentration of H$_2$S. Generally, higher H$_2$S concentrations lead to faster deactivation of the catalyst. The deactivation and regeneration showed exponential behavior on time on stream. At higher H$_2$S concentrations (50 and 100 ppm), the rate of deactivation is found to be independent of the temperature. At 800 °C, the activity of the catalyst is partially recovered just by removing H$_2$S from the feed gas. However, this method did not recover the catalyst activity at 700 °C. Regeneration of the poisoned catalyst at 700 °C required either temperature enhancement or steam treatment. The activity of the catalyst which is almost completely poisoned by exposure to 100 ppm H$_2$S at 700 °C is regenerated partially by enhancing the temperature to 800 °C and the catalyst is almost completely regenerated by removing H$_2$S from the feed gas. The same catalyst may also be regenerated by steam treatment. Five hours of steam treatment followed by reduction in H$_2$ for 5 h led to almost complete recovery of the catalyst activity. This regeneration time is far shorter than the ones reported in previous literature.
Chapter 4

Heterogeneous Catalysis

In heterogeneous catalysis, the reactants and the catalyst are in different phases, usually the catalyst is a solid and the reactants are either gases or liquids. These reactions proceed at the interface between the solid catalyst surface and the adjacent gas phase. The catalyst provides an alternate reaction pathway between reactants and products by lowering the activation energy for the reaction as shown in Fig. 4.1. Heterogeneous catalysis is of paramount importance in many areas of the chemical and energy industries.

Figure 4.1: Activation energy for catalytic and non-catalytic pathway for a chemical reaction [101].

The reaction conditions for a specific reaction is defined by the thermodynamics of the system. The catalyst facilitates the adsorption of the reactants and their subsequent conversion into products. However, the products of heterogeneous catalyst reaction must be removed rapidly from the catalyst surface to generate free active sites. In general heterogeneous catalysis consists of various physico-chemical processes such as [102]:

- Chemisorption
• Dissociation/activation
• Diffusion
• Recombination
• Desorption

After diffusion from the gas-phase to the catalyst surface, the reactants adsorb on the surface, and the adsorbed species further undergoes dissociation, disproportionation, and recombination. The reaction rates of surface reaction and desorption depend on the surface coverage and reaction temperature. Moreover, the catalytic reaction rate is specific to the catalyst formulation, catalyst support, catalyst type, and method of catalyst manufacturing. Therefore, the description of heterogeneous reaction rates is more complex compared to gas-phase kinetics. Due to this complexity, global rate expressions and reaction rates used to be the model for heterogeneous reactions. The reaction rate has often been based on catalyst mass, catalyst volume, reactor volume, or catalyst external surface area.

Most of the global reaction kinetics are developed based on some assumptions, and the validity of these assumptions cannot be verified a priori by changing the operating conditions. Most frequently Langmuir-Hinshelwood-Hougen-Watson (LHHW) method is used to develop the rate expressions for heterogeneous systems, which is based on Langmuir adsorption. Furthermore, rate expressions are developed by assuming that both reactants and products are equilibrated with surface species and that rate controlling step can be identified. LHHW kinetics cannot account for the complex variety of phenomena mentioned above and that the rate parameters must be evaluated experimentally for each new catalyst and various external conditions. The advantage of micro-kinetic model is that there are no initial assumptions during the mechanism development like rate determining step (RDS), most abundant reaction intermediate (MARI), quasi steady state (QSS) and partial equilibrium. A key advantage of the micro-kinetic analysis is that it captures system features under significantly different conditions.

### 4.1 Mean-field approximation

Heterogeneous reactions on solid surfaces can be principally treated by drawing analogy with gas phase reactions if mean-field approximation is applied. In mean-field approximation, the surface adsorbed species are assumed to be randomly distributed on surface, which is viewed as being uniform. The state of the surface is described by the temperature \( T \) and the fractional coverages of adsorbates \( \theta_k \). Fractional coverage \( \theta_k \) is the fraction of the surface covered by the surface adsorbed species \( k \). Moreover, it is assumed that the adsorption is limited to a mono atomic layer, and an uncovered surface is treated as the \( k \)’th surface species. This means, there are only \( K_s - 1 \) surface adsorbed species. The surface temperature and coverage depend on time and the macroscopic position in the reactor, but are averaged over microscopic local fluctuations. Under these assumptions a chemical reaction can be defined in a way similar to gas-phase reactions [103],

\[
\sum_{k=1}^{K_s} v'_{ki} X_k \Rightarrow \sum_{k=1}^{K_s} v''_{ki} X_k
\]  

where \( X_k \) is the species involved in the reaction and \( v'_{ki} \) and \( v''_{ki} \) are the stoichiometric coefficients of the \( k \)’th species for the \( i \)’th reaction.
Steric effects of adsorbed species and various configurations are taken into account in the surface structure. The surface structure is associated with surface site density $\Gamma$ in mol/m$^2$ that describes the maximum number of species that can adsorb on a unit surface area [104]. The number of sites required for the species to adsorb on the surface is given by the coordination number $\sigma_k$. In the following analysis it is assumed that the total number of surface sites is conserved for each reaction, i.e.,

$$\sum_{i=1}^{K_i} \nu_{ki} \sigma_k = 0$$

(4.2)

The above equation means that if the reactants occupy two surface cites then the products should also occupy two surface sites. Here $\nu_{ki} = \nu_k' - \nu_k''$. However, the scenario could be different in case of Chemical Vapor Deposition processes (CVD), where the surface sites are not conserved.

Under these assumptions a multistep reaction mechanism can be developed. The net molar production rate $\dot{s}_k$ of a gas phase species or a surface adsorbed species due to heterogeneous reactions on the solid surface is given by

$$\dot{s}_k = \sum_{i=1}^{N} \nu_{ki} k_{fi} \prod_{k=1}^{K_g+K_s} [X_k]^{\nu_k'}$$

(4.3)

where $N$ is the number of surface reactions, $[X_k]$ are the species concentrations, which are given in mol/m$^2$ for the $K_g$ adsorbed species, and mol/m$^3$ for the $K_g$ and $K_b$ gaseous and bulk species. A modified Arrhenius expression is used for the reaction rate constant based on mean field approximation and is given by

$$k_{fi} = A_i \left( \frac{T}{T_0} \right)^{\beta_i} \exp \left( \frac{E_{ai}}{RT} \right) \prod_{k=K_g+1}^{K_g+K_s} \theta_k \exp \left( -\varepsilon_{ki} \sigma_k \right)$$

(4.4)

where, $k_{fi}$ is the forward rate constant for the $i$'th reaction, $\mu_{ki}$ and $\varepsilon_{ki}$ are the parameters modeling the surface coverage dependency of rate constant for $i$'th reaction and the $\theta_k$ is the surface coverage of the $k$'th chemical species. The rate constant for the reverse reaction can be calculated from the thermodynamic data as

$$K_{ri} = \frac{k_{ri}}{k_{fi}} = K_{ri} \left( \frac{p^0}{RT} \right)^{\sum_{i=1}^{K_g} \nu_k} \prod_{k=K_g+1}^{K_g+K_s} \sigma_k^{\nu_k'}$$

(4.5)

where $p^0$ is the standard state pressure and $K_{ri}$ is the equilibrium constant calculated by

$$K_{ri} = \exp \left( \frac{\Delta S_i^0}{R} - \frac{\Delta H_i^0}{RT} \right)$$

(4.6)

The relationship between surface coverages and the surface concentrations are given by

$$\theta_k = \frac{[X_k] \sigma_k}{\Gamma}$$

(4.7)

and the temporal variations of surface coverages are given by

$$\frac{d\theta_k}{dt} = \frac{\dot{s}_k \sigma_k}{\Gamma}, \quad k = K_g + 1, \ldots, K_g + K_s,$$

(4.8)
Here $\Gamma$ is the available site density in mol/m$^2$ and $\sigma_k$ is coordination number i.e., the number of sites the species takes to adsorb. At steady state the above equation becomes

$$\dot{\gamma}_k = 0, \quad k = K_g + 1, \ldots, K_g + K_s,$$

(4.9)

for surface adsorbed species indicating that the surface composition is invariant in time (although varying spatially). Since the surface coverages are referred to a single mono-layer, the sum of coverages obeys the condition

$$\sum_{k=1}^{K_s} \theta_k = 1.$$  

(4.10)

Since the reactor temperature and concentrations of the gases vary along the axial position in the reactor, and surface coverages vary with position, the lateral interactions of surface species are neglected in the above model. This assumption is valid due to the fact that the computational cells used in reactor simulations are much larger than the range of lateral interactions of the surface processes. The detailed implementation of kinetics is published elsewhere [105, 106, 107].

The change of entropy $\Delta S_i^0$ and enthalpy $\Delta H_i^0$ for $i$ is given by

$$\frac{\Delta S_i^0}{R} = \sum_{k=1}^{k=K_g+K_s} v_k \frac{S_k^0}{R},$$

(4.11)

and

$$\frac{\Delta H_i^0}{RT} = \sum_{k=1}^{k=K_g+K_s} v_k \frac{H_k^0}{RT}.$$  

(4.12)

### 4.2 Adsorption and sticking coefficients

Heterogeneous reactions occur by collision of gas phase molecule on a catalytically active solid adsorbent. According to kinetic theory of gases the rate $Z$ at which these collisions occur is given by

$$Z = \sqrt{\frac{k_B T}{2 \pi W}} \left( \frac{N}{V} \right),$$

(4.13)

where $k_B$ is Boltzmann’s constant, $T$ is the absolute temperature, $W$ the molar mass, and $N/V$ is the number density of gas molecules. The kinetic gas theory expression assumes that the gas molecules are in continuous random motion, with a Maxwellian velocity distribution that is determined by the temperature [104]. However, these surface collisions are only one of the several processes that occur during surface reactions. For example the surface adsorbate can be mobile, there can be interactions between the surface adsorbates, dissociative adsorption, and desorption from the surface and so forth. However, for a simple sticking reaction, the reaction rate is just the rate of collision multiplied with the probability that the collision results in the formation of a surface adsorbate. The probability of such a process, or in other words the ratio of the rate of adsorption to the rate at which the adsorptive strikes the total surface can be expressed in terms of sticking coefficient $S_i^0$. Furthermore, the sticking coefficient in general depends on temperature and the temperature dependency is expressed as [101]

$$S_k^0 = S_i^0 = a_k \left( \frac{T}{T_0} \right)^b e^{-c_i/RT}$$

(4.14)
Since sticking coefficient is a probability factor, its value should lie between 0 and 1. \(a_k\) and \(b_k\) are dimensionless constants and \(c_k\) has units compatible with gas constant \(R\). The expression for reaction rate while using sticking coefficient can be written as

\[
\dot{s}_k = S^0_k \sqrt{\frac{RT}{2\pi W}} [X_k] \theta_{\text{free}}^n \tag{4.15}
\]

Here \(\theta_{\text{free}}\) is the available free surface coverage for collision \(\tau = \sum K_{ki} v'_{ki}\). Equation 4.15 can be written as

\[
\dot{s}_k = k_f [X_k][X_{\text{free}}]^{\frac{1}{2}} \tag{4.16}
\]

where

\[
k_f = S^0_k \Gamma \sqrt{\frac{RT}{2\pi W}} \tag{4.17}
\]

### 4.3 Development of multistep surface reaction mechanism

Development of heterogeneous reaction mechanisms is a complex process and the inputs come from various sources. A schematic of the same shown in Fig. 4.2. Initially a tentative mechanism is proposed based on the surface studies, analogy to gas phase kinetics, and organo metallic compounds. This mechanism contains all possible paths for the formation of chemical species, which are in the form of elementary kinetics [103]. Generally surface science techniques are used to study the surface properties of a single crystal surface. The experimental techniques such as AES, XPS, LEED, and some direct probe methods are used to

![Figure 4.2: Methodology of the development of a surface reaction mechanism [103].](image-url)
get information on elemental, chemical, or structural composition/properties of the catalytic surface. Temperature programmed desorption/reaction/reduction techniques gives information on surface reaction kinetics and mechanisms. Sophisticated modulated molecular beam-scattering techniques are conducted at very low pressures for surface science studies. Since most of these techniques uses ultra high vacuum, extrapolation of these results to higher pressures may be questionable. For example, CO can dissociate on platinum at high pressure and temperature, while this reaction pathway could not be observed in UHV experiments [108]. In-situ measurements are required for surface reaction investigations at technically feasible pressures and temperatures on catalyst surfaces.

In mechanism development, rate expressions have to be developed for the proposed mechanism. A range of theoretical techniques such as \textit{ab-initio} electronic structure calculations and semi-empirical approximations, transition state theory, quantum mechanical reactive scattering, and classical trajectory methods are used in the mechanism development. The developed mechanism should be thermodynamically consistent in enthalpy as well as in entropy. The consistency of the surface mechanisms will be discussed in chapter 5.

Kinetic data of common facets such as (111), (110), (100) are used as initial guesses for real catalysts, especially for the estimation of sticking coefficients for the adsorption steps, and desorption energies. Density functional theory (DFT), or experiments (microcalorimetry) has to be used to determine heats of chemisorption for all the species that are presumed to be present on the surface. Using this information as an input, UBI-QEP makes possible the computation of thermodynamically consistent, coverage-dependent activation energies for all the proposed reactions, through analytical equations. The calculations of activation energies for the surface reactions by using UBI-QEP will be discussed more in detail in chapter 5.

Based on the available theories, a tentative reaction mechanism is initially proposed. The tentative reaction mechanism is then coupled with reactor models that may include appropriate gas-phase kinetics and transport phenomena. These models are to be simulated with actual experimental conditions of numerous experiments. The numerical data need to be compared with experimental data such as conversions, selectivities, etc. The deviations between experimentally derived and numerically predicted data can now be used for fine tuning the mechanism, which even can be done using optimization techniques [109]. Sensitivity analysis is a widely used technique to fine tune elementary reaction mechanisms [110, 105]. Sensitivity analysis allows for an identification of the individual reaction steps that are most influential to the system. Several methods can be used in order to calculate the sensitivity of the solution, i.e., the time behavior of the different species profiles with respect to the rate coefficients. Generally sensitivity analysis involves perturbation of pre-exponents from their nominal, initial value, and estimation of the corresponding change in the model response. Although this technique is very simple, it has the disadvantage of requiring a large amount of computational power if the number of parameters involved are large. Furthermore, appropriate reactor models need to be used and experimental uncertainties have to be taken into consideration.
Chapter 5

Kinetic modeling

5.1 UBI-QEP

The theoretical approaches to surface reactivity are based on the estimation of energetics (enthalpies and activation barriers). Determination of adsorption energies and activation barriers of surface reactions is a complex task. The reaction energetics are determined by using quantum mechanical methods such as ab-initio wave function methods and density functional calculations [111]. These methods are useful for structural predictions such as calculations of bond lengths and angles, vibrational frequencies, charge moments, etc. than for thermochemical properties due to their computational demands. As a result accurate calculations of bond energies and activation barriers for surface reactions are still an enormous challenge [112].

The simulation of adsorption and surface reaction on a metal surface is commonly accomplished by modeling the catalyst surface as a finite cluster of limited size. A fundamental dilemma, with both DFT and ab initio, is designing or assembling the cluster of a size such that it accurately represents the atoms on the bulk surface. It is a theoretical paradox: the clusters must be large enough to adequately represent a geometric and electronic structure of a surface; yet, the size of the cluster must also be small enough that it may be accurately treated by the available methods [112].

A reasonable agreement between the cluster and slab-type calculations, with experiments are achieved by using ad hoc parameters [112]. However, the use of ad hoc parameter values blurs the conceptual picture. Because of the challenge with both first-principle and semi-empirical methods, another practical alternative is considered: the phenomenological approach. The phenomenological approach differs from empirical- or heuristic-based approaches because it employs phenomenological quantities, i.e., observable thermodynamic quantities, as input parameters and analytically calculates quantities relevant to phenomenological, observable thermodynamic properties of surface adsorption and reactive systems. The greatest advantage of an analytic phenomenological model is that it provides a direct conceptual understanding through its explicit interrelations among its parameters. Because our interest is with surface energetics, the model should be based on thermodynamics. An informative analytic model should have a rigorous and rigid mathematical formalism which provides well-defined rules [112].

Bond Order Conservation– Morse Potential (BOC– MP) method was developed by Shustorovich. Fur-
ther developments resulted in the renaming of the method, now known as the Unity Bond Index–Quadratic Exponential Potential (UBI–QEP) method. This method is unique due to its success with complex reactions, whose mechanisms may be extensive both in terms of number of intermediates and number of elementary reactions. This method requires only a few basic inputs such as atomic heats of adsorption and gas phase molecular bond energies to calculate heats of chemisorption of diatomic, polyatomic molecules, as well as the reaction activation barriers of dissociation, recombination, and disproportionation reactions. Typically, the accuracy of the calculated values of heats of adsorption and activation barriers is within 1-3 kcal/mol. This method has been successfully applied to several reaction systems including direct conversion of methane to methanol [113], methanol synthesis [114], hydrogen peroxide synthesis [115], ammonia synthesis [116], NO reduction and decomposition [117], and Fischer-Tropsch synthesis [118, 119], sulfur oxide chemistry [120], and many more.

BOC–MP was initially based on three postulates, the modified UBI-QEP method is now based on four main postulates. First, the two-body interaction energy is spherical and depends only on the interbody distance \( r \). Second, the two-body interaction energy poses a single minimum and approaches zero monotonically as the distance between them increases and is described by Morse potential (MP) as

\[
E(x(r)) = a(x(r) - 2x(r)) \tag{5.1}
\]

Third, as shown above, the two-body interaction is expressed as a polynomial function of an exponential variable called the bond index and can be written as

\[
x(r) = \exp \left[ \frac{- (r - r_0)}{b} \right] \tag{5.2}
\]

where \( r \) is the distance of the bond of interest, \( a \) is the bond energy, \( r_0 \) is the equilibrium distance corresponding to the minimum interaction energy, and \( b \) is a distance scaling constant. In a many body system, the total bond order, \( X \), of all interacting two-center bonds is conserved at unity

\[
X = \sum_i x_i = 1 \tag{5.3}
\]

Fourth, the multi-body, where body is defined as an atom or group of atoms that may be treated as a single entity, potential energy is formed by summing the nearest neighbor pair-wise interactions [111], i.e.,

\[
E(X) = \sum_i a_i \left[ x_i^2 - 2x_i \right] \tag{5.4}
\]

The bond index function should be defined such that: a one-to-one correspondence between \( x(r) \) and \( r \) exists; \( x(r) \) is non-negative and greater than zero; \( x(r) \) monotonically decreases to zero as \( r \) increases without bound; and, at the equilibrium distances, \( x_0 = x(r_0) = 1 \).

The unity bond index (UBI) condition at equilibrium requires that, at the equilibrium distance, \( r_0 \), any bond index will be unity, regardless of the system. In addition, the total bond index \( N \) of a multi-body system is conserved, stipulating that \( N = x_0 \). Bond indices are the same regardless of changing multiplicities.
of states, therefore \( N \) may be considered a normalization constant where

\[
N = \sum_i x_i(r_i) \tag{5.5}
\]

The value of the equilibrium bond index is the value to which the bond index is conserved [111]. As a result, the unity bond index condition may be written as

\[
X = \sum_i x_i(r_i) = N = 1. \tag{5.6}
\]

\( N = 1 \) condition has been verified by \textit{ab initio} calculations with exponential bond index functions for linear, three-center bonds. This condition is verified for adsorption and dissociation of diatomic molecules \( \text{H}_2, \text{O}_2, \) and \( \text{F}_2 \) on closed packed metal (Hg) surface (111).

Therefore, the UBI-QEP principle of chemisorption states “The sum of the two-body bond indices of the active bonds along any minimum energy path of a metal surface reaction is conserved and equal to unity” [111].

The total energy of a many-body system can be expressed as a summation of additive two-body bond energies governed by the UBI condition. For example, UBI constraint for a diatomic \( \text{AB} \) adsorption is written as

\[
x_{\text{AB}} + x_A + x_B = 1. \tag{5.7}
\]

For practical reasons, the sum over pairwise interaction energies is limited to nearest neighbors within a metal surface unit mesh or bonding site. Within the UBI-QEP method, the heats of chemisorption \( (Q) \) and reaction activation barriers \( (E_{\text{fsc}} \) and \( E_{\text{rev}} \) ) are independent of the choice of the bond index; they only contain energy parameters which are thermodynamic observables that are obtained from atomic chemisorption energies \( (Q_A) \) and gas-phase molecular bond energies \( (D_{\text{AB}}) \).

### 5.1.1 Atomic heats of adsorption

The heats of atomic chemisorption is determined from the energy function \( E \) which is the sum of the \( n \) pairwise interactions between the adatom, and the \( n \) metal atoms of the surface (M), that form the \( M_n \) binding site or unit mesh

\[
E = Q_0 \sum_i \left[ x_i^2(r_i) - 2x_i(r_i) \right]. \tag{5.8}
\]

where \( Q_0 \) is the strength of the M-A interaction, independent of the crystal plane. The summation in the above equation is limited to the nearest neighbor metal atoms, or the number of metal atoms defining the binding site. For example \( n=1 \) for on-top, \( n=2 \) for bridge type, \( n=3 \) for fcc (111) hollow, \( n=4 \) for fcc (100) hollow, \( n=5 \) for bcc(100) hollow.

The atomic binding Eq. 5.8 is optimized under the unity bond index constraint Eq. 5.7, and the resulting
The equation represents the binding energy of $n$ M-A interactions

$$Q_{nA} = -E(n) = Q_{0A} \left( 2 - \frac{1}{n} \right)$$

(5.9)

The value of $Q_{0A}$ in the above equation can be found from the experimental heat of atomic chemisorption $Q_A$,

$$Q_{0A} = \frac{Q_A(n)}{2 - 1/n}$$

(5.10)

The heats of chemisorption for diatomic molecules are based on the type of binding. Weakly bound molecules such as closed shell molecules CO, $N_2$ or molecular radicals with strongly delocalized unpaired electrons such as $O_2$, NO tend to have heats of chemisorption in the range 10-35 kcal/mol. The heat of chemisorption for mono-coordination of weakly bound diatomics over a $n$-fold site is given by

$$Q_{AB,n} = \frac{Q_{0A}^2}{Q_{0A}/n + D_{AB}}$$

(5.11)

where $D_{AB}$ is the gas phase dissociation energy of AB molecule. Eq. 5.11 gives higher values for higher coordination number than for on-top coordination. This may be due to neglecting the repulsive M-B interactions. Another reason for neglecting the M-B repulsive interactions may be because it is particularly inaccurate for mono-coordination of homonuclear diatomics. For mono-coordinated closed shell molecule with on-top binding, the chemisorption energy is given by

$$Q_{AB} = \frac{Q_{0A}^2}{Q_{0A} + D_{AB}}$$

(5.12)

The heat of energy for on-top site with di-coordination of diatomic molecule $AB$ is given by

$$Q_{AB} = \frac{ab(a + b) + D_{AB}(a - b)^2}{ab + D_{AB}(a + b)}$$

(5.13)

where

$$a = \frac{Q_{0A}^2(Q_{0A} + 2Q_{0B})}{(Q_{0A} + Q_{0B})^2}$$

(5.14)

and

$$b = \frac{Q_{0B}^2(Q_{0B} + 2Q_{0A})}{(Q_{0A} + Q_{0B})^2}$$

(5.15)

Eq. 5.13 for a homonuclear diatomics, $A_2$ can be written as

$$Q_{A_2} = \frac{9Q_{0A}^2}{(6Q_{0A} + 16D_{A_2})}$$

(5.16)

The chemisorption for a AB molecule positioned parallel to a surface and across the M-M bridge is given by

$$Q_{AB} = \frac{2[a(b + b) + 2D_{AB}(a - b)^2]}{ab + 2D_{AB}(a + b)}$$

(5.17)

where

$$a = 3Q_{0A}/4,$$

(5.18)
For a homonuclear $A_2$ Eq. 5.17 reduces to

$$Q_{A_2} = \frac{9Q_0^2}{(3Q_{0A} + 16D_{A_2})}.$$  \hspace{1cm} (5.20)

Strong binding typically occurs with radicals that have localized unpaired electrons (i.e. OH, SH and CH). In this case, the heat of chemisorption is given by

$$Q_{AB,n} = \frac{Q_A^2}{Q + D_{AB}},$$  \hspace{1cm} (5.21)

and the chemisorption energies of these molecules are in range of $\sim 35$-$120$ kcal/mol. The chemisorption energies of medium binding are in the range of $\sim 10$-$120$ kcal/mol and is given by

$$Q_{AB} = 0.5 \left[ \frac{Q_{0A}^2}{Q_{0A/n} + D_{AB}} + \frac{Q_A^2}{Q + D_{AB}} \right].$$  \hspace{1cm} (5.22)

Once the chemisorption energies are determined, the enthalpy change for each reaction, as it occurs on the surface, may be calculated as

$$\Delta H = \sum_r Q_r - \sum_p Q_p + \sum_b D_b - \sum_f D_f$$  \hspace{1cm} (5.23)

where $Q_r$ and $Q_p$ are respectively chemisorption energies of reactants and products, $D_b$ and $D_f$ are the binding energies that are broken ($b$) and formed ($f$) respectively. The net enthalpy change of a reaction is written as the sum of the enthalpies of the steps of the thermodynamic cycle:

- adsorbed reactants $\rightarrow$ gas-phase reactants $\Delta H_1 = \sum_r Q_r$
- gas-phase reactants $\rightarrow$ gas-phase products $\Delta H_2 = \sum_b D_b - \sum_f D_f$
- gas-phase products $\rightarrow$ adsorbed products $\Delta H_3 = -\sum_p Q_p$

The net enthalpy change is $\Delta H_1 + \Delta H_2 + \Delta H_3$.

In the case of the disproportionation reaction, $A(s) + BC(s) \rightleftharpoons AB(s) + C(s)$, the direction of the reaction is defined such that the condition $D_{BC} > D_{AB}$ is satisfied. If it is not, the direction of the reaction should be reversed for the analysis [121].

### 5.1.2 Activation energy barriers

The activation energy ($\Delta E_{AB}^\ast$) of the reaction in the forward direction (dissociation reaction), corresponding to the appropriate form of the reaction, may be written as

$$\Delta E_{AB}^\ast = \frac{1}{2} \left[ \Delta H + \frac{Q_A Q_B}{Q + Q_B} \right].$$  \hspace{1cm} (5.24)
The recombinations reaction is the reverse of dissociation reaction and therefore the activation barrier for recombination reaction ($\Delta E_{AB,rev}^*$) is written as

$$\Delta E_{AB,rev}^* = \Delta E_{AB} - \Delta H.$$  \hspace{1cm} (5.25)

In the case where the numerical result for either the forward or reversed activation energy is negative, both activation energies are shifted such that the negative activation energy is forced to zero and the enthalpy change for the reaction remains unchanged [121].

The dissociation barrier relative to gas phase reactants is obtained from the difference between activation barrier relative to surface adsorbed reactants and the heat of adsorption of dissociating molecule ($Q_{AB}$):

$$\Delta E_{g,f}^* = \Delta E_{f,s}^* - Q_{AB}$$ \hspace{1cm} (5.26)

The reverse activation energy for this type of reaction may be determined from the following equations, depending on the sign of the forward activation barrier

$$\Delta E_{f,s}^* = \Delta E_{g,s} = Q_A + Q_B - D_{AB} + \Delta E_{g,s}^*,$$ \hspace{1cm} if $\Delta E_{g,s} > 0$ \hspace{1cm} (5.27)

or

$$\Delta E_{f,s}^* = \Delta E_{g,s} - \Delta E_{f,g} = Q_A + Q_B - D_{AB},$$ \hspace{1cm} if $\Delta E_{g,s} < 0$ \hspace{1cm} (5.28)

where $D_{AB}$ is defined as the difference between total bond energies of the reactants and products. This definition is valid for both atomic and molecular adsorbates [122]. Table 5.1 shows the heats of chemisorption and gas phase dissociation energies for species involved in biogas steam reforming.

Table 5.1: Chemisorption energies (Q) and gas-phase dissociation energies (D) [123, 111, 124, 125, 121, 120].

<table>
<thead>
<tr>
<th>Species</th>
<th>Q (kcal/mol)</th>
<th>D (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_4$</td>
<td>6</td>
<td>398</td>
</tr>
<tr>
<td>CH$_3$</td>
<td>48</td>
<td>293</td>
</tr>
<tr>
<td>CH$_2$</td>
<td>83</td>
<td>183</td>
</tr>
<tr>
<td>CH</td>
<td>116</td>
<td>81</td>
</tr>
<tr>
<td>C</td>
<td>171</td>
<td>–</td>
</tr>
<tr>
<td>CO</td>
<td>27</td>
<td>257</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>6.35</td>
<td>384</td>
</tr>
<tr>
<td>HCO</td>
<td>50</td>
<td>274</td>
</tr>
<tr>
<td>O</td>
<td>115</td>
<td>–</td>
</tr>
<tr>
<td>H</td>
<td>63</td>
<td>–</td>
</tr>
<tr>
<td>OH</td>
<td>61</td>
<td>102</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>17</td>
<td>220</td>
</tr>
<tr>
<td>H$_2$S</td>
<td>19</td>
<td>173</td>
</tr>
<tr>
<td>SH</td>
<td>65</td>
<td>82</td>
</tr>
<tr>
<td>S</td>
<td>112</td>
<td>–</td>
</tr>
<tr>
<td>SO</td>
<td>17</td>
<td>125</td>
</tr>
<tr>
<td>SO$_2$</td>
<td>36</td>
<td>132</td>
</tr>
</tbody>
</table>

As an example of the application of the UBI-QEP method, consider one of the reaction $\text{H}_2\text{S} + \text{Ni}(s) \rightleftharpoons \text{SH}(s) + \text{S}(s)$ on a Ni(111) catalyst. Where “(s)” represents the species on the surface. Using the information provided in Table 5.1, the enthalpy change of the elementary reaction step is calculated using Eq. 5.23
\[ \Delta H = \sum_r Q_r - \sum_p Q_p + \sum_b D_b - \sum_f D_f \]
\[ = Q_{H, S(0)} - (Q_{SH(0)} + Q_{S(0)}) + D_{H, S} - D_{SH} \]
\[ = (19) - (65 + 63) + (173 - 82) \]
\[ = -18 \text{ kcal/mol}. \]

Forward activation energy of the elementary reaction step using Eq. 5.24 can be written as
\[ \Delta E_{\text{for}}^* = 1/2 \left[ \Delta H + \frac{Q_{SH(0)}Q_{S(0)}}{Q_{SH(0)} + Q_{S(0)}} \right] \]
\[ = 0.5 \left[ -18 + \frac{65 \times 63}{65 + 63} \right] \]
\[ = 6.996 \text{ kcal/mol}. \]

Next, the activation energy for reverse reaction can be determined using Eq. 5.25
\[ \Delta E_{\text{rev}}^* = \Delta E_{\text{for}} - \Delta H \]
\[ = 6.996 - (-18) \]
\[ = 25 \text{ kcal/mol}. \]

### 5.1.3 Pre-exponential factors

A variety of methods are available to estimate the pre-exponential factors, but this is a challenging task for surface reactions. Generally transition state theory is used to predict the pre-exponential factors for each elementary surface reactions. The critical assumption of the transition state theory is that quasi equilibrium is established between the reactants and an activated complex. Cortright and Dumesic [126, 127] provides the guidelines from which the pre-exponential factors may be estimated using transition-state theory through an order-of magnitude analysis of partition functions for a variety of surface reactions, including adsorption and desorption reactions.

For a bimolecular reaction \( \Lambda^+ + B^+ \rightleftharpoons \Lambda B^+ \rightarrow \Lambda^+ + \Lambda^+ \), the forward rate constant for formation of the activated complex is given by [128]
\[ k_{AB} = \frac{k_B T}{h} \cdot R^* = \frac{k_B T}{h} \cdot \exp \left[ \frac{\Delta S^0}{k_B} \right] \cdot \exp \left[ \frac{\Delta H^0}{k_B T} \right] \]
\[ (5.29) \]
where \( k_B \) is the Boltzmann constant, \( T \) is the temperature, \( h \) is the Planck constant. \( \Delta S^0 \) and \( \Delta H^0 \) are the entropy and enthalpy change for formation of activated complex \( \Lambda B^+ \), respectively. The activation energy for the forward reaction \( E_{AB} \) can be calculated from \( \Delta H^0 \) and Eq. 5.29 can be written as
\[ k_{AB} = A_{AB} \cdot \exp \left[ \frac{-E_{AB}}{k_B T} \right], \]
\[ (5.30) \]
where $A_{AB}$ is the pre-exponential factor for the forward reaction, given by

$$A_{AB} = \frac{k_BT}{\hbar} \exp \left[ \frac{\Delta S^{0^\ddagger}}{k_B} \right] \quad (5.31)$$

The standard entropy change for formation of the activated complex $AB^\ddagger$ from A and B in Eq. 5.31 is

$$\Delta S^{0^\ddagger} = S_{AB}^{0^\ddagger} - \left( S_A^0 - S_B^0 \right) \quad (5.32)$$

where $S_{AB}^{0^\ddagger}, S_A^0$, and $S_B^0$ are the total standard entropies of the individual species. The total standard entropy ($S_{tot}^0$) of a gas phase species is a summation of contributions from translational, rotational, and vibrational modes.

Generally, a thumb rule for assigning the pre-exponential factors for mono and bi-molecular surface reactions are respectively in the order of $10^{13}$ sec$^{-1}$ and $10^{21}$ con$^{-1}$sec$^{-1}$. Dumesic, et al., [127] provides a more detailed examination of the transition state theory applied to the estimation of the pre-exponential factor for several other types of reactions under various conditions.

## 5.2 Thermodynamic consistency

Thermodynamic consistency of surface reaction mechanism is a key problem for many of the surface reactions. The main reason for this problem is the lack of thermochemical data for surface species. The rate parameters of forward and backward reactions are chosen in ad hoc fashion without maintaining the thermodynamic constraints. This issue has been addressed in many instances [127, 128, 129, 130, 109].

If the reversible surface reaction mechanism is thermodynamically consistent, then any reversible $i$’th reaction in the complex network must follow the enthalpy as well as entropy (Eq. 5.33) consistency given by

$$\Delta H = E_f - E_r,$$

$$\Delta S = \frac{R}{A_r} \ln \left( \frac{A_f}{A_r} \right). \quad (5.33)$$

where $\Delta H$ is enthalpy change of reaction, $E_f$ and $E_r$ are the activation energies of forward and reverse reactions respectively, and $\Delta S$ is the entropy change. $A_f$ and $A_r$ are the pre-exponential factors of forward and reverse reactions respectively.

Mechanisms that are not consistent in enthalpy results in incorrect solutions of temperature, and in turn wrong predictions in heat exchange and conversion/ selectivity in nonisothermal simulations. Errors can propagate in isothermal simulations as well. Entropy inconsistency is due to the incorrect pre-exponential of surface reactions. Both inconsistencies distorts the underlying thermodynamic principle, which affects the prediction of equilibrium constants and equilibrium states. A previously published alogorithm [131, 105] address the above issues and makes the complex surface reaction mechanism thermodynamically consistent in enthalpy as well as in entropy.
The equilibrium of a chemical reaction is defined as
\[
\sum_k v_{ki}' = \sum_k v_{ki}'' A_k
\]  
(5.34)
for any reaction mixture to exist at equilibrium, the rates of the forward and backward (reverse) reactions must be equal. The equilibrium constant \( K_{pi} \) is defined as
\[
K_{pi} = \prod_k (d_k^{co})^{v_{ki}'} = \exp\left(-\frac{\Delta G^0}{RT}\right)
\]  
(5.35)
\( d_k^{co} \) is the equilibrium activity, \( R \) is the gas constant, \( T \) is the absolute temperature. The change of free enthalpy \( \Delta G^0 \) at normal pressure \( p_0 \) is given by
\[
\Delta G^0 = \sum_k v_{ki} G_0^0(T).
\]  
(5.36)
Once the specific heat is known, the other thermodynamic properties can be evaluated in terms of the specific heat. The standard state enthalpy is given as
\[
H_0^0_k = \int_{T_0}^T C_0^0(T')dT'
\]  
(5.37)
and the standard state entropy by
\[
S_0^k(T) = \int_{T_0}^T \left(\frac{C_0^0(T')}{T'}\right)dT'.
\]  
(5.38)
When heat capacity is expressed as fourth order polynomial is given by
\[
C_p^0 = R \sum_{n=1}^5 a_n T^{n-1} = R(a_1 + a_2 T + a_3 T^2 + a_4 T^3 + a_5 T^4)
\]  
(5.39)
then the standard free enthalpies \((G = H - TS)\) can be expressed in terms of seven coefficients, \(a_0, ..., a_6\) as
\[
G_0^k = a_{0,k} + a_{1,k} T + a_{2,k} T^2 + a_{3,k} T^3 + a_{4,k} T^4 + a_{5,k} T^5 + a_{6,k} T \ln T
\]  
(5.40)
The equilibrium of reversible reaction can be written in terms of forward and reverse reaction rates as
\[
\frac{k_{fi}}{k_{ri}} = K_{pi} \prod_k \left(\frac{c_k^0}{\sigma_k}\right)^{v_{ki}'}
\]  
(5.41)
where \( v_{ki} \) is the difference of stoichiometric coefficients of reactants and products of \( i \)’th reaction, \( c_k^0 \) are the reference concentrations at normal pressure, i.e.,
for gas-phase species
\[
c_k^0 = \frac{P_k^0}{RT}
\]  
(5.42)
for surface species
\[
c_k^0 = \frac{\Gamma_0 \theta_k}{\sigma_k}
\]  
(5.43)
where \( \Gamma \) is the total surface site density and \( \sigma_k \) is the site occupancy number of species \( k \).
One problem in calculating the equilibrium constant by Eq. 5.35 is unknown thermo-chemistry data for intermediate species. The forward and reverse reaction rates are then defined separately with their own rate laws. Nevertheless, these rates cannot be chosen independently.

Assuming an initial guess for the rate parameters of a surface reaction mechanism, the rate coefficients for the forward and reverse reactions may be adjusted separately to make the entire mechanism thermodynamically consistent.

The free energy change for the \(i\)'th reaction is calculated based on the initial guess values of rate constants by using Eqs. 5.33

\[
\Delta_i G = -RT \ln K_{pi}
\]  

Eq. 5.44 can also be written by using thermo-chemistry data of participating species in the \(i\)'th reaction as

\[
\Delta_i G = \sum_{k=1}^{N} v_{ki} G_0^k(T)
\]  

The above equation includes the free energies of gas phase species and surface species in \(i\)'th reaction. Eq. 5.45 can be written as

\[
\Delta_i G_0 = \sum_{k=1}^{N_a} v_{ki} G_0^k(T) + \sum_{k=N_a+1}^{N} v_{ki} G_0^k(T),
\]  

which is a linear equation system for the known \((G_0^k)\) and unknown free enthalpies \((\tilde{G}_0^k)\). In the above equation, thermo-chemical properties of \(1, \ldots, N_u\) out of \(N\) species are unknown. For each pair of a reversible reactions we can calculate the equilibrium constant according to Eq. 5.41 and, Eq. 5.44 yields change of free enthalpy. Since most of the surface species are involved in more than one reaction, this system is usually over-determined. Equation 5.40 for several temperatures \(T_j\) gives a system of linear equations in the unknown coefficients \(\tilde{a}_{ik}\):

\[
\sum_{k=1}^{N_a} \sum_{l=0}^{6} v_{ki} t_{lj} \tilde{a}_{ij} = g_{ij},
\]  

the unknown free enthalpy can be found from Eq. 5.46

\[
g_{ij} = \Delta_i G_0^j(T_j) - \sum_{k=N_a+1}^{N} v_{ki} G_0^k(T_j)
\]  

where

\[
t_{lj} = \begin{cases}  
T_j^l & \text{if } l < 6 \\
T_j \ln T_j & \text{if } l = 6
\end{cases}
\]  

An optimal set of parameters \(\tilde{a}_{ik}\) are determined by a weighted least square approximation for each unknown surface species. These weights can be chosen individually for each pair of reactions according to a sensitivity analysis. This guarantees that the equilibrium of crucial reaction steps will be shifted less than others after the adjustment.

The newly calculated polynomials are used to calculate the free enthalpy change for each pair of reaction,
equilibrium constant, and the rate coefficient for the reverse reaction. In case the reverse reaction shall be expressed in terms of Arrhenius coefficients, another least-square approximation using the rate constants at the discrete temperatures, \( T_j \), is performed.

Since the surface reactions are written as pairs of irreversible reactions, this procedure has to be repeated during the mechanism development after modification of any rate coefficients in the reaction network. Fig. 5.1 shows the schematic representation of the adjustment algorithm to setup thermodynamically consistent surface reaction mechanism. Mahedeshwar et al., [109] proposed a mechanism based on the linear base and linear combinations. The main advantage of previously proposed algorithm [131, 105] is that it is not required to select linear combinations and all reactions are treated equally by solving the linear problem using a least-squart fit.

![Figure 5.1: Illustration of the adjustment algorithm to set up thermodynamically consistent surface reaction mechanisms.](image)

Figure 5.1: Illustration of the adjustment algorithm to set up thermodynamically consistent surface reaction mechanisms.
Chapter 6

Modeling of experiments

This chapter deals with the development and validation of a detailed kinetic model for steam reforming of biogas with and without H2S. The presence of H2S in the feed is the root cause for catalyst poisoning during reforming. In order to account for catalyst deactivation, H2S adsorption, dissociation, desorption, and disproportionation reactions are incorporated into a previously published mechanism of CH4 steam reforming on Ni. The activation energies for the elementary step reactions are calculated by UBI-QEP method and the entire mechanism is made thermodynamically consistent using algorithm that are discussed in the chapter 5. The developed kinetic model is validated by comparing the model predictions with our experiments and the experiments reported by other research groups. These experiments are performed in isothermal fixed bed reactors. Therefore, a one dimensional fixed bed reactor model is used to simulate the experiments.

6.1 Kinetic model

The main set of the kinetic model is a previously published mechanism for steam reforming of CH4 on Ni by Janardhanan et al., [132]. Additional reactions are incorporated into this mechanism to account for sulfur adsorption, desorption, disproportionation, and recombination reactions. The UBI-QEP method is adopted to calculate the forward and reversed activation energies of biogas steam reforming reactions. Table 6.1 shows the forward ($E_{for}$) and reverse ($E_{rev}$) activation energies for reactions involving sulfur species. The reversible activation energies are forced to zero in Table 6.1 when the activation barrier $E_{rev}$ is negative [121].

6.2 Reactor model

A one-dimensional transient fixed bed reactor model is used for the simulations presented in this thesis. Assuming ideal gas behavior and constant pressure, the partial differential equation that describes the species transport in a fixed bed reactor with constant mass flow rate is:

$$\rho \frac{\partial Y_k}{\partial t} = -\dot{m} \frac{\partial Y_k}{\partial x} + \frac{\partial}{\partial x} \left( D_{km} \frac{\partial Y_k}{\partial x} \right) + A_k W_k \dot{s}_k, \quad k = 1, \ldots, N_g. \quad (6.1)$$
Table 6.1: Activation barriers for forward and reversed reactions with sulfur involving reactions.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$E_{\text{fwd}}$ (kJ/mol)</th>
<th>$E_{\text{rev}}$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_2S(Ni) + (Ni) \rightleftharpoons SH(Ni) + H(Ni)$</td>
<td>29.31</td>
<td>104.67</td>
</tr>
<tr>
<td>$SH(Ni) + (Ni) \rightleftharpoons S(Ni) + H(Ni)$</td>
<td>25.79</td>
<td>143.02</td>
</tr>
<tr>
<td>$H_2S(Ni) + O(Ni) \rightleftharpoons SH(Ni) + OH(Ni)$</td>
<td>27.84</td>
<td>40.40</td>
</tr>
<tr>
<td>$S(Ni) + O(Ni) \rightleftharpoons SO(Ni) + (Ni)$</td>
<td>296.82</td>
<td>0.00</td>
</tr>
<tr>
<td>$SH(Ni) + O(Ni) \rightleftharpoons SO(Ni) + H(Ni)$</td>
<td>206.05</td>
<td>0.00</td>
</tr>
<tr>
<td>$S(Ni) + OH(Ni) \rightleftharpoons SO(Ni) + H(Ni)$</td>
<td>229.02</td>
<td>0.00</td>
</tr>
<tr>
<td>$SO_2(Ni) + (Ni) \rightleftharpoons SO(Ni) + O(Ni)$</td>
<td>106.31</td>
<td>0.00</td>
</tr>
<tr>
<td>$S(Ni) + H_2O(Ni) \rightleftharpoons SH(Ni) + OH(Ni)$</td>
<td>143.37</td>
<td>0.00</td>
</tr>
<tr>
<td>$SH(Ni) + CO(Ni) \rightleftharpoons SO(Ni) + CH(Ni)$</td>
<td>206.12</td>
<td>0.00</td>
</tr>
<tr>
<td>$S(Ni) + CO(Ni) \rightleftharpoons SO(Ni) + C(Ni)$</td>
<td>206.12</td>
<td>0.00</td>
</tr>
</tbody>
</table>

Here, $\rho$ is the density, $Y_k$ is the mass fraction of species $k$, $t$ is the time, $\dot{m}$ is the mass flux, $D_{km}$ is axial dispersion coefficient of species $k$ in the mixture, $A_v$ is the active area available for chemical reactions per unit volume, $\dot{s}_k$ is the molar production rate of gasphase species $k$, $W_k$ is the molecular weight of species $k$, $N_g$ is the number of gasphase species, and $x$ is the axial coordinate. The density $\rho$ is calculated from the ideal gas equation:

$$p\bar{M} = \rho RT,$$

where $\bar{M}$ is the average molecular weight, $R$ is the gas constant, and $T$ is the temperature. The axial dispersion coefficient of species $k$ in the mixture $D_{km}$ is calculated according to

$$D_{km} = \frac{1 - Y_k}{\sum_{j=1}^{N_g} X_j / D_{jk}}.$$

Here $X_j$ is the mole fraction of species $j$, and the binary diffusion coefficient $D_{jk}$ is calculated according to Chapman-Enskog theory [133]. Since the catalyst poisoning is mainly due to loss in active surface area $A_v$ is not a constant and changes with sulfur coverage. In the present calculations, we assume a linear dependence of $A_v$ on the sulfur coverage [84]. i.e.,

$$A_v = A_{v0}(1 - \theta_s),$$

where, $A_{v0}$ is the active area available before poisoning and $\theta_s$ is the surface coverage of sulfur. When the surface is fully covered with sulfur, the active area becomes zero. Assuming surface diffusion to be negligible, the fractional surface coverage $\theta$ of various species is calculated from [105]

$$\frac{d\theta_k}{dt} = \frac{\sigma_k \dot{s}_k}{\Gamma}, \quad k = N_g + 1, \ldots, N_g + N_s.$$

Here $\sigma_k$ is the number of sites occupied by adsorbed species $k$, $\Gamma$ is the total site density, $\dot{s}_k$ is the molar production rate of surface adsorbed species $k$, and $N_s$ is the number of surface species. Calculation of $\dot{s}_k$ from an elementary like reaction mechanism is described in Chapter 4. Method of lines is applied to solve equations 6.1 and 6.5 simultaneously by using the ODE solver CVODE [134]. The entire model is implemented in C++. 72
6.3 Results and discussion

The detailed kinetic model developed for reforming of biogas on Ni is given in Table 6.2. The mechanism contains 68 reactions among 8 gasphase species, 17 surface adsorbed species, and the catalytic surface. While solving 6.5, the catalytic surface is also considered as a surface species. i.e., \( N_s \) includes the surface adsorbed species and the free catalytic surface. The adsorption of gas phase species on the catalytic surface is expressed as sticking reactions. It is generally well accepted that, \( \text{H}_2\text{S} \) chemisorbs dissociatively on Ni surface. However, there is no consensus on the number of Ni sites required for dissociative adsorption or the number of active sites that a sulfur atom may occupy. It is likely that at low temperature, the dissociative adsorption involves two Ni sites and at high temperature it involves only one Ni site. Although Rostrup-Nielsen [135] postulates the following scheme

\[
\text{H}_2\text{S}(g) + \text{Ni} \rightleftharpoons \text{Ni} - \text{S} + \text{H}_2(g) \tag{6.6}
\]

for the adsorption of \( \text{H}_2\text{S} \) on Ni at high temperature, Rostrup does not make a final claim on this. Nevertheless, his data fitting to Langmuir isotherm leads to the conclusion that sulfur occupies only one site at high temperature. Since the mechanism developed here is for use at high temperature, sulfur is assumed to occupy only one site. Formation of bulk sulfide is not considered in this study as they form only at significantly high \( \text{H}_2\text{S} \) partial pressures [135]. For the disproportionation and recombination reactions the activation energies are calculated by applying UBI-QEP method. The pre-exponential factors are adjusted to reproduce the experimental observations and the entire reaction mechanism is made thermodynamically consistent by using the method described in Chapter 5. Sensitivity analysis is performed to elucidate the effect of various reaction parameters on sulfur coverage. In the analysis presented here, the sensitivity coefficients are defined as follows

\[
\text{SC} = \frac{\phi - \phi_0}{\phi_0}, \tag{6.7}
\]

where

\[
\phi = \frac{1}{\tau} \int_0^\tau \theta_s \, dt, \quad \phi_0 = \frac{1}{\tau} \int_0^\tau \theta_s^0 \, dt. \tag{6.8}
\]

Here \( \phi \) is the total surface coverage of sulfur for \( \pm 5\% \) change in pre-exponential factors and \( \phi_0 \) is the total surface coverage of sulfur for pre-exponential factors as noted in Table 6.2. Figure 6.1 shows the scaled value of the sensitivity coefficient with respect to absolute maximum for major reactions that affect the formation of sulfur on Ni. The most sensitive reactions for the formation of adsorbed sulfur is the \( \text{H}_2\text{S} \) sticking reaction (R7) and \( \text{H}_2\text{S} \) desorption reaction (R45). An increase in sticking coefficient results in higher sulfur coverage, whereas an increase in \( \text{H}_2\text{S} \) desorption pre-exponential factor results in lower sulfur coverage. The sticking coefficient of \( \text{H}_2\text{S} \) is generally found be higher than 0.5 [85]. Therefore, in this mechanism we used a sticking coefficient of 0.6 for \( \text{H}_2\text{S} \). In addition to these reactions, hydrogen abstraction reaction from \( \text{H}_2\text{S} \) and the reaction between adsorbed \( \text{H}_2\text{S} \) and O atom are also found to be influencing the formation of adsorbed sulfur. A positive change in R52 leads to the formation of SH, which further dissociates to give adsorbed sulfur. Since surface coverage of O facilitates the formation of SH from adsorbed \( \text{H}_2\text{S} \) through R52, a positive change in R16 also results in more adsorbed sulfur. Increasing the pre-exponential factor of R52 and R47 also results in faster deactivation.
The kinetic model presented in 6.2 is developed by fine tuning the pre-exponential factors to reproduce our own experiments. The only adjustable parameter in the modeling results presented below is $A_v$. To check the predictive capability of the mechanism we have simulated the experiments reported by other research groups [136, 45, 23] in addition to our own experiments. In addition to predicting catalyst deactivation, the mechanism is also capable of predicting the product composition under non poisoning conditions.

### 6.3.1 Model predictions without sulfur poisoning

Comparison between model predictions and experimental observations made by Ashrafi et al. [136] for CH$_4$ and CO$_2$ conversions are shown respectively in Fig. 6.2 and Fig. 6.3. The experiments were performed in a fixed bed reactor with S/C ratio of $\sim$2.7 and CH$_4$ to CO$_2$ ratio of 1.5. The reactor model described above is used for the simulations. The steady state model predictions for CH$_4$ conversions are in good agreement with the experimental observations and are well within the limits of equilibrium predictions. Deviation from experimental observation is present only at low temperatures (873 K), which are not anyway practically
Figure 6.3: Comparison between CO\textsubscript{2} experimental data (Exp), equilibrium predictions (Eql), and model predictions (Sim). The experimental data is from [136]. The S/C ratio employed is \( \sim 2.7 \) and CH\textsubscript{4}/CO\textsubscript{2} ratio is 1.5.

useful for biogas reforming. As far as CO\textsubscript{2} conversions are concerned, the experimental observations violate thermodynamic predictions. Thermodynamics predicts the maximum possible conversion or production. Although the experimentally observed CO\textsubscript{2} production (negative conversion in Fig. 6.3) is within the thermodynamic limits, the observed conversions are above that predicted by thermodynamics. The increase of CO\textsubscript{2} conversion in Fig. 6.3 with temperature shows that the methane dry reforming reaction takes place. At higher temperatures, this endothermic reaction is favored and therefore CO\textsubscript{2} is consumed. At temperature below 700°C, CO\textsubscript{2} is negative due to the water gas shift reaction. The Nevertheless, the model predictions are well within the thermodynamic limit. The comparison between model predictions and experimental observation for CO selectivity and H\textsubscript{2} yield are shown respectively in Fig. 6.5 and Fig. 6.4.

Figure 6.4: Comparison between H\textsubscript{2} experimental data (Exp) and model predictions (Sim). The experimental data is from[136]. The S/C ratio employed is\( \sim 2.7 \) and CH\textsubscript{4}/CO\textsubscript{2} ratio is 1.5.
Figure 6.5: Comparison between CO experimental data (Exp) and model predictions (Sim). The experimental data is from [136]. The S/C ratio employed is ~2.7 and \( \text{CH}_4/\text{CO}_2 \) ratio is 1.5.

In both cases the model predictions are in very good agreement with the experimental observations. For the given S/C ratio \( \text{CO}_2 \) participates in the reforming reaction only at temperatures higher than 1050 K. However, at 1050 K \( \text{CH}_4 \) conversion is almost 97% and therefore, the \( \text{CO}_2 \) production below 1050 K is probably due to water gas shift reaction. When the temperature exceeds 1050 K, the \( \text{H}_2 \) yield starts decreasing and the \( \text{CO}_2 \) conversion becomes positive; this indicates the occurrence of reverse water gas shift reaction. The reverse water gas shift reaction at high temperature is also confirmed by the increasing CO selectivity (Fig. 6.5).

The kinetic model also able to reproduce the experiments reported by Kolbitsch et al., [45]. The experiments are performed in a fixed bed reactor with S/C ratio 2.2 and \( \text{CH}_4 \) to \( \text{CO}_2 \) ratio of 1.5. Figures. 6.6 and 6.7 shows the steady state model predictions and experimental observations of \( \text{CH}_4 \) and \( \text{CO}_2 \) conversions respectively. Again very good agreement is observed between the model predictions and the experimental observations of \( \text{CH}_4 \) conversions at temperatures above 1023 K. Deviations are observed in \( \text{CO}_2 \) conversions, but model predictions of \( \text{CO}_2 \) conversions are within the thermodynamic equilibrium limits. Figure 6.7 shows an increase in \( \text{CO}_2 \) conversion with temperature, which indicates dry reforming reaction. At higher temperatures, this reaction is favored and therefore \( \text{CO}_2 \) is consumed. For all these simulations CO and H atoms are found to be the major surface adsorbed species.

6.3.2 Model predictions with sulfur poisoning

Comparison between the model predicted and experimentally observed deactivation at 973 K and 1073 K is shown respectively, in Fig. 6.8 and Fig 6.9. The initial inlet mixture to the reactor contains 12.5\% \( \text{CH}_4 \), 8.4\% \( \text{CO}_2 \), 25.2\% \( \text{H}_2\text{O} \) and 53.9\% \( \text{N}_2 \) and the gas hourly space velocity is \( 3.35 \times 10^4 \) h\(^{-1} \). \( \text{H}_2\text{S} \) (20 and 50 ppm) is introduced after 1 hr into the experiments during which the reactor reaches steady state operation. The experiments simulated in this work represent the catalyst activity loss in terms of drop in \( \text{CH}_4 \) conversion. The 6 cm long fixed bed reactor is simulated using the reactor model resented earlier. At 973 K, the model very well captures the experimentally observed deactivation profile for 20 ppm \( \text{H}_2\text{S} \) in the feed gas, but an early deactivation for 50 ppm (Fig. 6.8). Nevertheless, the qualitative nature of the deactivation profile and steady state conversions are well predicted. At 1073 K, the model-predicted deactivation matches very well with the experimental observation (Fig. 6.9). Active surface area \( A_{v0} = 18 \times 10^4 \) m\(^{-1} \) is used at 973 K and \( A_{v0} \)
Figure 6.6: Comparison between CH$_4$ experimental data (Exp) and model predictions (Sim). The experimental data is from [45]. The S/C ratio employed is $\sim 2.2$ and CH$_4$/CO$_2$ ratio is 1.5.

Figure 6.7: Comparison between CO$_2$ experimental data (Exp) and model predictions (Sim). The experimental data is from [45]. The S/C ratio employed is $\sim 2.2$ and CH$_4$/CO$_2$ ratio is 1.5.

$= 15 \times 10^4 \text{ m}^{-1}$ is used at 1073 K.

Figure 6.8: Comparison between the model predicted deactivation and experimental observations made at 973 K.
The product composition from the reactor exit (on dry basis) during deactivation of the catalyst for 20 ppm and 50 ppm H$_2$S in the feed gas at 973 K is shown respectively in Fig. 6.10 and Fig. 6.11.

The model predictions are in excellent agreement with the experimental measurements. At steady state the product mixture mainly contains H$_2$, CO, CO$_2$ and N$_2$, however, N$_2$ mole fractions are not shown in the figure. As soon as H$_2$S is introduced, the mole fractions of H$_2$ and CO starts to decrease and CO$_2$ and CH$_4$ starts to increase. This means that CO$_2$ also participated in the reforming reactions for the S/C ratio employed here (S/C=2.02). Generally CO$_2$ does not participate in reforming reactions at high S/C ratio; however, this is temperature dependent. For instance at 1023 K, CO$_2$ participates in reforming reaction only at S/C ratio below 2.5 [45]. The product mole fractions on dry basis for 20 ppm and 50 ppm H$_2$S at 1073 K are shown in Fig. 6.12 and Fig. 6.13. As observed at 973 K and 20 ppm, the mole fractions of H$_2$ and CO start to decrease after introducing H$_2$S. Due to 100% CH$_4$ conversion there is no significant difference in the steady state mole fractions of CO and H$_2$ before introducing H$_2$S compared to operation at 973 K. However, higher operating temperature is beneficial in maintaining catalytic activity. Unlike operating at 973 K, the catalytic activity is not fully compromised at 1073 K even with higher H$_2$S content in the feed gas (Fig. 6.9). This low
degree of activity loss at high temperature is due to the exothermic nature of chemisorption reactions. This leads to higher CH₄ conversion and hence higher H₂ and CO mole fractions, after achieving the saturation sulfur coverage at 1073 K. However, at 1073 K there is a slight disagreement with the model predictions and experimental observation for the mole fractions of H₂ and CO₂ at steady state after poisoning. The model slightly under predicts H₂ and CO₂ for 20 ppm at steady state (Fig. 6.12). Similar behavior is observed for 50 ppm H₂S in the feed gas at 1073 K 6.13.

The average fractional surface coverage of various surface adsorbed species and free surface along the length of the reactor as a function of time for 973 K and 1073 K with 20 ppm H₂S in the feed mixture is shown respectively in Fig. 6.14 and Fig. 6.15. The major surface adsorbed species before introducing H₂S into the feed are CO and H atom and most of the surface remains open for adsorption. As soon as H₂S is introduced, sulfur starts to occupy most of the surface and the coverages of CO and H starts to decrease. After poisoning at 973 K, adsorbed sulfur occupies 92.0% of the surface with 4% open surface. CO and H atoms still remain as the other major species on the surface. The average fractional surface coverage of sulfur increases linearly and then reaches the steady state asymptotically. At 1073 K, sulfur occupies only 66% of
Figure 6.13: Comparison between the model predicted product composition during catalyst deactivation and experimental observations made at 1073 K for 50 ppm H$_2$S in the feed.

the surface with 16% open surface.

Figure 6.14: Average fractional coverage along the length for major surface adsorbed species and the free coverage as a function of time at 973 K. The inlet mixture contains 20 ppm H$_2$S.

Figure 6.15: Average fractional coverage along the length for major surface adsorbed species and the free coverage as a function of time at 1073 K. The inlet mixture contains 20 ppm H$_2$S.
However along the length of the reactor, the poisoning is not uniform. Figures 6.16 and 6.17 shows the buildup of sulfur coverages at 973 K and 1073 K along the length of the reactor. At both temperatures, the poisoning occurs from inlet towards the exit of the reactor as time proceeds. In fact as the poisoning proceeds, the location of the methane reforming reaction moves downstream through the reactor length. This sort of wave behavior is typical for parallel poisoning [70].

The predictive capability of the model is further explored by simulating the deactivation experiments reported by Ashrafi et al. [23]. The simulations are again performed using the fixed bed reactor model with CH$_4$ to CO ratio of 1.5 and S/C ratio is of ~3.0, for these simulations active surface area $A_{v0} = 5520 \times 10^3$ m$^{-1}$ is used. Figure 6.18 shows the model predictions against the experimentally observed CH$_4$ conversions for two different H$_2$S concentrations (31 ppm and 108 ppm) in the feed gas for reactor operating at 1073 K. The model very well predicts the experimentally observed CH$_4$ conversion for 31 ppm H$_2$S. However, for the 108 ppm case, the CH$_4$ conversions are over predicted. The model predicts 37% conversion, while the experimentally observed conversion is only 18%. This may be attributed to the inconsistencies in the reported experimental data. A careful examination of CH$_4$ conversions reported by Ashrafi et al. for 1073 K reveals some discrepancy in their data. In one case they report steady state CH$_4$ conversion of 32% at 1073 K with
Figure 6.18: Comparison between the model prediction and experimental observation for CH4 conversion at 1073 K. Initial inlet mixture to the reactor contains CH4 to CO2 ratio of 1.5 and S/C ratio of ~3.

145 ppm H2S in the feed mixture. In another case they report 18% conversion for 108 ppm H2S in the feed gas. These two are contradictory results, if 108 ppm H2S results in 18% CH4 conversion, then 145 ppm must result in a lower CH4 conversion. Therefore, it is most likely that the error is in the data reported at 108 ppm and in fact 108 ppm must result in higher CH4 conversion, which is consistent with the predictions of the present model. At 1173 K, the model predictions are in good agreement with experimental observations. Figure 6.19 shows the comparison between the model predictions and the experimentally measured data.

Figure 6.19: Comparison between the model prediction and experimental observation for CH4 conversion at 1173 K. Initial inlet mixture to the reactor contains CH4 to CO2 ratio of 1.5 and S/C ratio of ~3.

The model predicts 82% CH4 conversion at 1173 K with 108 ppm H2S in the feed gas, while the experimentally observed conversion is 86%. For 31 ppm, the model predicted conversion (91%) is very close the experimentally observed conversion of 93%. One may notice that the inlet composition used by Ashrafi et al. is different from the ones used in our own experiments. Thus, the model that is developed based on experiments conducted at one fixed composition, is able to predict catalyst deactivation at other conditions as well. Although the model predicts the deactivation profile for 108 ppm H2S reported by Ashrafi et al. [23], it failed to predict the deactivation profiles with 100 ppm H2S in the feed gas for our own experiments. Therefore, we can say that the confidence interval for the model is 20 to 50 ppm H2S in the feed gas for 973-1123 K.
6.3.3 Model predictions with catalyst regeneration

Catalyst regeneration by H₂S removal

Experimentally it was possible to regenerate the catalyst by removing H₂S from the feed gas. The same is attempted in the simulations by removing H₂S from the feed gas at 1073 K. Figure 6.20 shows CH₄ conversion with time on stream for 20, 50, and 100 ppm H₂S. As observed in the experiments, the model predicted recovery in the catalyst activity. However, the model predicts slow regeneration compared to the experimental observations. The recovery in catalyst activity on removal of H₂S from the feed stream is due to the reversible nature of chemisorption reactions. Figure 6.21 shows for predicted mole fractions at reactor exit during the deactivation and regeneration. Before introducing H₂S in the feed CH₄ is completely converted by steam and dry reforming reactions. As soon as H₂S is introduced to the reactor, the reactants mole fraction starts to increase and the products mole fraction starts to decrease. The mole fraction of CH₄ and CO₂ increases and stabilizes respectively at 8.7% and 9.3%. After removing the H₂S from the feed, the reactants mole fractions starts to decrease and products molefractions starts to increase slowly. This indicates that the adsorbed sulfur is slowly oxidized by surface species and desorbed as SO₂ to the gas phase and more free surface becomes available to the steam and dry reforming reactions.

![Graph showing methane conversion vs time for different H₂S concentrations]

Figure 6.20: Comparison between the model prediction and experimental observations made at 1073 K. Different concentrations (ppm) of H₂S are introduced after reaching steady state.

Figures 6.22, 6.23, 6.24, and 6.25 shows the surface coverages along the length of the reactor at various time instances for the reactor operating at 1073 K with 50 ppm H₂S in the feed stream. The major surface adsorbed species before introducing H₂S in to the feed are CO and H atom and 50% of the surface remains open for reactions (Fig. 6.22). During the initial stages of poisoning (15 min after introducing H₂S), sulfur coverage is high near the reactor inlet (Fig. 6.23) and CO and H occupies most of the remaining surface. Figure 6.24 shows steady state poisoning, and adsobed sulfur occupies 74% of the surface with 2% open surface. Figure 6.25 shows the surface profiles after 10.30 hrs catalyst regeneration. As soon as H₂S is removed from the feed stream the sulfur coverages start to decrease and CO and H occupy the most of the surface. The kinetic model predicts slow recovery of the catalyst as opposed to experimental observation.

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Figure 6.21: model predictions of reactor exit molefractions during catalyst deactivation and regeneration at 1073 K for 50 ppm H$_2$S in the feed.

Figure 6.22: Fractional coverages of various surface adsorbed and free surface along the length of the reactor before introducing H$_2$S.

Figure 6.23: Fractional coverages of various surface adsorbed and free surface along the length of the reactor 15 min after introducing H$_2$S.

The fractional surface coverages of major species during the poisoning and regeneration is shown in Fig. 6.26. As soon as H$_2$S is introduced, sulfur starts to occupy most of the surface and the coverages of CO
and H starts to decrease. After poisoning, adsorbed sulfur occupies 74% of the surface with 2% open surface. CO and H atoms still remain as the other major species on the surface. As soon as H$_2$S is removed from the feed stream the sulfur coverage starts to decrease. As sulfur coverages starts to decrease, CO and H begins to occupy most of the surface.

**Catalyst regeneration by temperature Enhancement**

Since the chemisorption is exothermic, the activity of the catalyst can also be recovered by increasing the temperature [100]. Figure 6.27 shows the model predicted and experimentally observed CH$_4$ conversion during temperature enhancement from 973 K to 1073 K. The initial mixture contains 100 ppm H$_2$S and catalyst is fully poisoned at the first steady state. Although, the model predicts early loss in activity the steady state is well predicted. The second steady state is achieved by increasing the temperature from 973 K to 1073 K. The model slightly under predicts the CH$_4$ conversion at second steady state. When the model predicted only 25% conversion, the experimentally observed conversion is 30%. From the second steady state, the catalyst activity is further recovered by removing H$_2$S from the feed gas. The model predicted very slow regeneration compared to the experiments. The corresponding model predicted and experimentally observed mole frac-
Figure 6.26: Average fractional coverage along the length for major surface adsorbed species and the free coverage as a function of time at 1073 K. The inlet mixture contains 50 ppm H\textsubscript{2}S.

Figure 6.27: Comparison between the model prediction and experimental observation for catalyst regeneration by temperature enhancement.

### 6.3.4 Effect of steam to carbon ratio

The simulations are extended to study the deactivation behaviour at 50 ppm H\textsubscript{2}S by varying steam to carbon ratio (S/C). Figure 6.29, 6.30 shows the conversion of methane as a function of time at different S/C ratios. An increase in S/C ratio has no effect on methane conversion at 700 °C but has a positive effect at 800 °C. At 700 °C, the addition of steam may not effect the chemisorption equilibrium of sulfur [100]. Furthermore, the deactivation profile and steady state conversions are similar at various S/C ratios. The steady state conversion of CH\textsubscript{4} after poisoning increases with increase in S/C ratio at 800 °C. The methane conversion at S/C = 2.02 is 37%, and at S/C = 4.0 is 55%. High steam concentration in the feed may produce sufficient OH(Ni) and O(Ni) species on the surface, and oxidize the adsorbed sulfur to SO\textsubscript{2}. This may be further confirmed from Fig. 6.31, which shows decrease in average fractional sulfur coverages with increasing S/C ratios. For example, at S/C = 2.02 and 4.0, the average sulfur coverages are 72% and 67% respectively.
Finally the saturation coverages predicted by the model at different temperatures are shown Fig. 6.32. These linear trends are very much similar to the experimental observation by Nielsen et al. [137]. Although a direct comparison is not possible due to the difference in composition of the feed gas that is reported in dry basis, a qualitative agreement can be observed between the model predictions and experimental observations reported in [137]. The dry gas composition reported in [137] contains all the chemical species considered in this work. The authors report saturation sulfur coverages higher than 90% at 973 K for 50, 10 and 2 ppm H₂S in the feed gas, and our model also predicts saturation coverages higher than 90% at 973 K. Similar to the experiments, the model also predicts a linear decrease in sulfur coverage with increase in temperature.
6.4 Conclusions

A detailed kinetic model for simultaneous dry and steam reforming of biogas on Ni based catalyst is developed and validated against experimental data. The model can be used for simulating reforming of biogas...
with and without H$_2$S. The catalyst deactivation is represented in terms of loss in CH$_4$ conversion at different temperatures and H$_2$S concentrations. The model is developed by fine tuning the pre-exponential factors to reproduce the experimental observations. The entire mechanism is made thermodynamically consistent by using method described in Chapter 5. Brute force sensitivity analysis is carried out to understand the influence of various reaction parameters on the formation of sulfur. It is found that the sticking and desorption reactions of H$_2$S are the most influential ones. An increase in sticking coefficient and decrease in the pre-exponential factor for desorption reaction facilitates the formation of surface adsorbed sulfur. The only adjustable parameter used in the simulations is the surface area available per unit volume $A_{v0}$. The model is able to predict accurately the time on stream drop in CH$_4$ conversions and the product mole fractions at the reactor exit. At high temperature, the deactivation profiles are very well predicted. Analysis of the fractional coverages along the reactor length reveals that during the initial stages of poisoning, the sulfur coverages are high near the reactor inlet. However, during the later stages, the surface coverage of sulfur increase towards the reactor exit. Since our experiments are conducted at one fixed composition the predictive capability of the kinetic model is further confirmed by simulating the experiments reported by Ashrafi et al. [23], which are performed for a different composition. The model also qualitatively predicts the recovery of the catalyst activity on removal of H$_2$S and temperature enhancement. At high temperature, the deactivation profiles are very well predicted, however, predicts slow recovery of the catalyst as opposed to experimental observation. In general the model is capable of predicting reforming of H$_2$S free biogas in the temperature range from 873-1200 K. However, the transients of deactivation are validated only in the temperature range of 973-1173 K and H$_2$S compositions from 20-50 ppm in the feed stream. Finally, although for a different composition, the model predicted saturation coverages are comparable to experimentally observed values.
Table 6.2: Detailed kinetic model for reforming of Biogas

<table>
<thead>
<tr>
<th>R No</th>
<th>Reaction</th>
<th>( A(\text{cm}^2\text{mol}^{-1}\text{s}^{-1}) )</th>
<th>( \beta )</th>
<th>( E_a^a )</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1</td>
<td>( \text{H}_2 + (\text{Ni}) + (\text{Ni}) \rightarrow \text{H}(\text{Ni}) + \text{H}(\text{Ni}) )</td>
<td>0.01(^b)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>R2</td>
<td>( \text{O}_2 + (\text{Ni}) + (\text{Ni}) \rightarrow \text{O}(\text{Ni}) + \text{O}(\text{Ni}) )</td>
<td>0.01(^b)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>R3</td>
<td>( \text{CH}_4 + (\text{Ni}) \rightarrow \text{CH}_4(\text{Ni}) )</td>
<td>0.006(^b)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>R4</td>
<td>( \text{H}_2\text{O} + (\text{Ni}) \rightarrow \text{H}_2\text{O}(\text{Ni}) )</td>
<td>0.1(^b)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>R5</td>
<td>( \text{CO}_2 + (\text{Ni}) \rightarrow \text{CO}_2(\text{Ni}) )</td>
<td>( 1 \times 10^{-05b} )</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>R6</td>
<td>( \text{CO} + (\text{Ni}) \rightarrow \text{CO}(\text{Ni}) )</td>
<td>0.5(^b)</td>
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<td>0</td>
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<tr>
<td>R7</td>
<td>( \text{H}_2\text{S} + (\text{Ni}) \rightarrow \text{H}_2\text{S}(\text{Ni}) )</td>
<td>0.6(^b)</td>
<td>0</td>
<td>0</td>
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<tr>
<td>R8</td>
<td>( \text{SO}_2 + (\text{Ni}) \rightarrow \text{SO}_2(\text{Ni}) )</td>
<td>0.02(^b)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>R9</td>
<td>( \text{H}(\text{Ni}) + \text{H}(\text{Ni}) \rightarrow (\text{Ni}) + (\text{Ni}) + \text{H}_2 )</td>
<td>( 2.676 \times 10^{19} )</td>
<td>81.40</td>
<td></td>
</tr>
<tr>
<td>R10</td>
<td>( \text{O}(\text{Ni}) + \text{O}(\text{Ni}) \rightarrow (\text{Ni}) + (\text{Ni}) + \text{O}_2 )</td>
<td>( 4.143 \times 10^{23} )</td>
<td>0</td>
<td>474.93</td>
</tr>
<tr>
<td>R11</td>
<td>( \text{CH}_4(\text{Ni}) \rightarrow (\text{Ni}) + \text{CH}_4 )</td>
<td>( 8.386 \times 10^{15} )</td>
<td>0</td>
<td>37.46</td>
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<td>R12</td>
<td>( \text{H}_2\text{O}(\text{Ni}) \rightarrow (\text{Ni}) + \text{H}_2\text{O} )</td>
<td>( 3.823 \times 10^{12} )</td>
<td>0</td>
<td>60.78</td>
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<td>R13</td>
<td>( \text{CO}_2(\text{Ni}) \rightarrow (\text{Ni}) + \text{CO}_2 )</td>
<td>( 6.483 \times 10^{07} )</td>
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<td>25.95</td>
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<td>R14</td>
<td>( \text{CO}(\text{Ni}) \rightarrow (\text{Ni}) + \text{CO} )</td>
<td>( 3.677 \times 10^{11} )</td>
<td>0</td>
<td>111.39</td>
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\( ^a \) Arhenius parameters for the rate constants written in the form: \( k = A T^\beta \exp(-E_a^a/RT) \). The units of \( A \) are given in terms of moles, centimeters, and seconds. \( E_a^a \) is in kJ/mol.

\( ^b \) Sticking coefficient. Total available surface site density is \( \Gamma = 2.66 \times 10^{-5} \text{ mol/cm}^2 \)

\( ^c \) Coverage dependent activation energy.
<table>
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<tr>
<th>Reaction</th>
<th>Stoichiometry</th>
<th>Change</th>
<th>Free Energy Change</th>
<th>Activation Energy</th>
<th>Barrier Height</th>
</tr>
</thead>
<tbody>
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<td>R34</td>
<td>CH(Ni) +H(Ni) → CH2(Ni) +Ni</td>
<td>4.001×10^{24}</td>
<td>0</td>
<td>79.11</td>
<td></td>
</tr>
<tr>
<td>R35</td>
<td>CH(Ni) +Ni → C(Ni) +H(Ni)</td>
<td>3.7×10^{21}</td>
<td>0</td>
<td>18.80</td>
<td></td>
</tr>
<tr>
<td>R36</td>
<td>C(Ni) +H(Ni) → CH(Ni) +Ni</td>
<td>4.529×10^{22}</td>
<td>0</td>
<td>161.06</td>
<td></td>
</tr>
<tr>
<td>R37</td>
<td>O(Ni) +CH4(Ni) → CH3(Ni) +OH(Ni)</td>
<td>1.7×10^{24}</td>
<td>0</td>
<td>88.30</td>
<td></td>
</tr>
<tr>
<td>R38</td>
<td>CH3(Ni) +OH(Ni) → O(Ni) +CH2(Ni)</td>
<td>9.728×10^{22}</td>
<td>0</td>
<td>30.35</td>
<td></td>
</tr>
<tr>
<td>R39</td>
<td>O(Ni) +CH3(Ni) → CH2(Ni) +OH(Ni)</td>
<td>3.7×10^{24}</td>
<td>0</td>
<td>130.10</td>
<td></td>
</tr>
<tr>
<td>R40</td>
<td>CH2(Ni) +OH(Ni) → O(Ni) +CH3(Ni)</td>
<td>4.538×10^{21}</td>
<td>0</td>
<td>23.60</td>
<td></td>
</tr>
<tr>
<td>R41</td>
<td>O(Ni) +CH2(Ni) → CH(Ni) +OH(Ni)</td>
<td>3.7×10^{24}</td>
<td>0</td>
<td>126.80</td>
<td></td>
</tr>
<tr>
<td>R42</td>
<td>CH(Ni) +OH(Ni) → O(Ni) +CH2(Ni)</td>
<td>1.435×10^{23}</td>
<td>0</td>
<td>47.05</td>
<td></td>
</tr>
<tr>
<td>R43</td>
<td>O(Ni) +CH(Ni) → C(Ni) +OH(Ni)</td>
<td>3.7×10^{21}</td>
<td>0</td>
<td>48.10</td>
<td></td>
</tr>
<tr>
<td>R44</td>
<td>C(Ni) +OH(Ni) → O(Ni) +CH(Ni)</td>
<td>1.624×10^{21}</td>
<td>0</td>
<td>128.60</td>
<td></td>
</tr>
<tr>
<td>R45</td>
<td>H2S(Ni) → H2S +Ni</td>
<td>1.108×10^{10}</td>
<td>-0.8</td>
<td>69.47</td>
<td></td>
</tr>
<tr>
<td>R46</td>
<td>SO2(Ni) → SO2 +Ni</td>
<td>2.709×10^{09}</td>
<td>0</td>
<td>102.50</td>
<td></td>
</tr>
<tr>
<td>R47</td>
<td>H2S(Ni) +Ni → SH(Ni) +H(Ni)</td>
<td>5.5×10^{4}</td>
<td>1.2</td>
<td>29.31</td>
<td></td>
</tr>
<tr>
<td>R48</td>
<td>SH(Ni) +H(Ni) → H2S(Ni) +Ni</td>
<td>1.291×10^{13}</td>
<td>0</td>
<td>106.19</td>
<td></td>
</tr>
<tr>
<td>R49</td>
<td>SH(Ni) +Ni → S(Ni) +H(Ni)</td>
<td>7.9×10^{11}</td>
<td>0</td>
<td>25.79</td>
<td></td>
</tr>
<tr>
<td>R50</td>
<td>S(Ni) +H(Ni) → SH(Ni) +Ni</td>
<td>6.375×10^{15}</td>
<td>0</td>
<td>142.94</td>
<td></td>
</tr>
<tr>
<td>R51</td>
<td>SH(Ni) +OH(Ni) → H2S(Ni) +O(Ni)</td>
<td>1.053×10^{13}</td>
<td>0</td>
<td>29.72</td>
<td></td>
</tr>
<tr>
<td>R52</td>
<td>H2S(Ni) +O(Ni) → SH(Ni) +OH(Ni)</td>
<td>8×10^{11}</td>
<td>-0.5</td>
<td>27.84</td>
<td></td>
</tr>
<tr>
<td>R53</td>
<td>S(Ni) +O(Ni) → SO(Ni) +Ni</td>
<td>1×10^{18}</td>
<td>1</td>
<td>296.82</td>
<td></td>
</tr>
<tr>
<td>R54</td>
<td>SO2(Ni) +Ni → SO(Ni) +O(Ni)</td>
<td>1.775×10^{12}</td>
<td>0</td>
<td>0.00</td>
<td></td>
</tr>
<tr>
<td>R55</td>
<td>SH(Ni) +O(Ni) → SO(Ni) +H(Ni)</td>
<td>1×10^{14}</td>
<td>-1</td>
<td>206.05</td>
<td></td>
</tr>
<tr>
<td>R56</td>
<td>SO(Ni) +H(Ni) → SH(Ni) +O(Ni)</td>
<td>2.115×10^{5}</td>
<td>0</td>
<td>0.00</td>
<td></td>
</tr>
<tr>
<td>R57</td>
<td>S(Ni) +OH(Ni) → SO(Ni) +H(Ni)</td>
<td>1×10^{21}</td>
<td>1</td>
<td>229.02</td>
<td></td>
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<tr>
<td>R58</td>
<td>SO(Ni) +H(Ni) → S(Ni) +OH(Ni)</td>
<td>3.352×10^{23}</td>
<td>-2.0</td>
<td>0.00</td>
<td></td>
</tr>
<tr>
<td>R59</td>
<td>SO2(Ni) +Ni → SO2(Ni) +O(Ni)</td>
<td>1×10^{18}</td>
<td>-0.5</td>
<td>106.31</td>
<td></td>
</tr>
<tr>
<td>R60</td>
<td>SO(Ni) +O(Ni) → SO2(Ni) +Ni</td>
<td>9.029×10^{09}</td>
<td>1.5</td>
<td>0.00</td>
<td></td>
</tr>
<tr>
<td>R61</td>
<td>S(Ni) +H2O(Ni) → SH(Ni) +OH(Ni)</td>
<td>1×10^{10}</td>
<td>0</td>
<td>143.37</td>
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</tr>
<tr>
<td>R62</td>
<td>SH(Ni) +OH(Ni) → S(Ni) +H2O(Ni)</td>
<td>1.652×10^{5}</td>
<td>0</td>
<td>0.00</td>
<td></td>
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<tr>
<td>R63</td>
<td>SH(Ni) +CO(Ni) → S(Ni) +HCO(Ni)</td>
<td>1.0×10^{4}</td>
<td>0</td>
<td>61.82</td>
<td></td>
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<tr>
<td>R64</td>
<td>S(Ni) +HCO(Ni) → SH(Ni) +CO(Ni)</td>
<td>1.991×10^{12}</td>
<td>0</td>
<td>54.55</td>
<td></td>
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<tr>
<td>R65</td>
<td>SH(Ni) +CO(Ni) → SO(Ni) +CH(Ni)</td>
<td>1×10^{23}</td>
<td>0</td>
<td>223.41</td>
<td></td>
</tr>
<tr>
<td>R66</td>
<td>SO(Ni) +CH(Ni) → SH(Ni) +CO(Ni)</td>
<td>3.066×10^{28}</td>
<td>0</td>
<td>0.00</td>
<td></td>
</tr>
<tr>
<td>R67</td>
<td>S(Ni) +CO(Ni) → SO(Ni) +C(Ni)</td>
<td>1×10^{13}</td>
<td>0</td>
<td>206.12</td>
<td></td>
</tr>
<tr>
<td>R68</td>
<td>SO(Ni) +C(Ni) → S(Ni) +CO(Ni)</td>
<td>4.651×10^{15}</td>
<td>0</td>
<td>0.00</td>
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Chapter 7

Summary and outlook

Conventional fossil fuel reserves are limited and are being depleted at a faster rate, and the production and use of conventional fuels have adverse environmental impacts. Researchers are striving hard to replace conventional fuels with renewable fuels. In the recent past biogas systems have received considerable attention as an attractive source of renewable fuel, that is clean, environment friendly, and cheap. Biogas technology offers a very attractive route for decentralized applications in rural areas for meeting the energy needs. Biogas is an ideal gas for distributed power generation using Solid-Oxide Fuel Cells (SOFC). However, one of the major challenges in utilizing biogas for any applications is presence of H$_2$S. For example, the presence of H$_2$S or other sulfur containing compounds is a major problem for reforming of biogas due to its poisoning effect on most transition metals.

In this study, catalyst deactivation and regeneration during the biogas reforming on Ni catalyst was investigated. For consistent results, the catalysts were prepared in one batch and used throughout the experiments. In general, Ni catalysts showed better activity and stability during biogas steam reforming in non-poisoning atmosphere. No obvious catalyst deactivation or carbon formation was observed during the stability experiments at 700 and 800 °C.

The deactivation studies were performed at three different H$_2$S concentrations (20, 50, and 100 ppm) and two different temperatures (700 and 800 °C). It was found that even low concentration (20 ppm) of H$_2$S in the feed can completely poison the catalyst at 700 °C, whereas at 800 °C the catalyst maintained some residual activity. It was found that the rate of deactivation depends on the H$_2$S concentration in the feed and operating temperature. Lower operating temperature and higher H$_2$S concentration leads to faster deactivation of the catalyst. At 800 °C, the activity of the catalyst was partially recovered just by removing H$_2$S from the feed gas. However, this method did not recover the catalyst activity at 700 °C. The activity of the poisoned catalyst at 700 °C can be effectively recovered by increasing the temperature or steam treatment. In conclusion, within the scope of this thesis, application of high temperatures was identified as the only effective means to enhance the sulphur resistance of nickel catalysts.

The experimental results were further used to develop a micro-kinetic model of biogas steam reforming in the presence of H$_2$S. The detailed kinetic model contains 68 reactions among 8 gas-phase species and 18 surface adsorbed species including the catalytic surface. The model can be used to simulate reforming
of biogas with and without $H_2S$ in feed gas. The model was developed by fine tuning the pre-exponential factors to reproduce the experimental observations and entire mechanism was made thermodynamically consistent by using method described in Chapter 5. Brute force sensitivity analysis was carried out to study the influence of various kinetic parameters on formation of sulfur. The most sensitive reactions for the formation of adsorbed sulfur were the $H_2S$ sticking reaction and $H_2S$ desorption reaction. An increase in sticking coefficient resulted in higher sulfur coverage, whereas an increase in $H_2S$ desorption pre-exponential factor resulted in lower sulfur coverage. In addition to these reactions, hydrogen abstraction reaction from $H_2S$ and the reaction between adsorbed $H_2S$ and O atom were also found to be influencing the formation of adsorbed sulfur. Increasing the pre-exponential factors of above reactions also resulted in faster deactivation.

The kinetic model was able to capture the time on stream behaviors of drop in $CH_4$ conversions and product mole fractions at the reactor exit. The model predicted that during the initial stages of poisoning sulfur coverages are high near the reactor inlet, however, as the reaction proceeds further sulfur coverages increase towards the reactor exit. At steady state the sulfur coverage increases asymptotically towards the reactor exit. The predictive capability of the kinetic model was further confirmed by simulating the experiments reported in the literature. In general the model was capable of predicting reforming of $H_2S$ free biogas in the temperature range from 873-1200 K. However, the transients of deactivation were validated only in the temperature range of 973-1173 K and $H_2S$ compositions from 20-50 ppm in the feed stream. Although, the kinetic model successfully predicts the deactivation on time on stream, it failed to predict the catalyst regeneration. The kinetic model model also predicted a linear decrease in sulfur coverage with increase in temperature, which were consistent with the experimental literature.

**Future scope**

The experiments were conducted at a fixed $S/C$ ratio of 2.02. Due to the constant $S/C$ ratio employed, it was not possible to assess the effect of $H_2O$ on sulfur poisoning. Although, the kinetic model can be used to predict the influence of $H_2O$ on saturation sulfur coverage, it needs to be validated. Therfore, one may extend these studies with varying $S/C$ ratio. At a low $S/C$ ratio and in the presence of $H_2S$ catalyst may be deactivated simultaneously by carbon and sulfur species. Experiments were carried out only in the range of 20-100 ppm $H_2S$ in the feed gas. This work may be further extended to study the Ni catalyst deactivation in the range of 1-20 ppm. Experiments at very low concentration of $H_2S$ (1 ppm or even less) may be more useful to evaluate the performance of industrial reformers. Finally, In-situ studies concerning the interaction of sulfur with well defined metal and oxide surfaces should be conducted to elucidate changes in the structural, morphological, and electronic properties. Such studies will help in the better scientific design of catalysts, resistant to sulfur poisoning during the biogas reforming.

The present kinetic model has to be improved to capture regeneration in the concentration ranges studied. At present the model very well predicts catalyst deactivation in the range of 20-50 ppm $H_2S$ concentration and qualitatively predicts the catalyst regeneration. One may extended this model to predict catalyst deactivation simultaneously with formation of carbon and sulfur species on the catalytic surface. It is worth mentioning that during the simulations it was found that, increasing the pre-exponential factor of the reaction $S + CO \rightleftharpoons SO + C$ leads to carbon and sulfur species formation on the catalytic surface.
References


List of Publications

Refereed journal papers


International conference papers

