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Water Gas Shift Reaction Catalysis Promoted by Selective Sorption of Carbon Dioxide: Microreactor Experiments

Ramanjaneyulu Katta

**Thesis submitted to the College of Engineering and Mineral Resources at
West Virginia University**

**In partial fulfillment of the requirements
for the degree of**

**Master of Science
in
Chemical Engineering**

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Morgantown, West Virginia

2011

**Keywords: WGS reaction, HTS catalyst, kinetics, CaO sorbent, SEWGS
reaction, sorption capacity**

Abstract

Water Gas Shift Reaction Catalysis Promoted by Selective Sorption of Carbon Dioxide: Microreactor Experiments

Ramanjaneyulu Katta

Production of hydrogen via the water-gas shift (WGS) reaction normally requires multiple reaction steps followed by CO₂ separation. However, *in-situ* removal of CO₂ via the carbonation reaction between CaO and CO₂ provides the opportunity to combine WGS and separation reactions into a single unit. Consequently, the need for heat exchangers between catalyst beds as well as the absorption and stripping units for CO₂ removal can be eliminated.

In this study, a commercial high-temperature-shift (HTS) catalyst, Fe₂O₃/Cr₂O₃/CuO is used. Calcium oxide (CaO) and calcium oxide incorporated with calcium aluminate (Ca₁₂Al₁₄O₃₃) are used as sorbents for CO₂ capture. The CaO/Ca₁₂Al₁₄O₃₃ sorbent is synthesized in 75/25 and 50/50 ratios.

Initially, the performance of HTS catalyst alone is studied. The results indicate that the CO conversion increases as the temperature and H₂O/CO ratio increase. From these experiments, the forward and reverse kinetic parameters are calculated. The activation energy and pre-exponential factor are found to be 79.01 KJ/mol and 2.44×10^3 mol/gcatalyst/sec/atm² respectively.

Subsequently, the activity of sorbents towards the WGS reaction is measured. The sorbents exhibit minute activity towards WGS and the CO conversions obtained are negligible.

Finally, the combined shift and carbonation reactions are conducted. Conditions are 500 °C and 1 atm with a H₂O/CO ratio of 2. Two different modes are used: catalyst and sorbent particles well mixed (sorption-enhanced WGS, SEWGS), and catalyst and sorbent particles separated by quartz chips. The SEWGS will proceed in three phases: sorbent enhancement, sorbent breakthrough, and post-breakthrough. For the HTS-CaO, no CO₂ is detected in the reactor outlet till after the 6th minute. This is the sorbent enhancement period. For HTS-CaO/Ca₁₂Al₁₄O₃₃ (75/25), the sorbent enhancement period lasts for 5 mins. For HTS-CaO/Ca₁₂Al₁₄O₃₃ (50/50), this period lasts for only 4 mins. The sorbents CaO, CaO/Ca₁₂Al₁₄O₃₃ (75/25), and CaO/Ca₁₂Al₁₄O₃₃ (50/50) reach their post-breakthrough period at approximately 35, 29, and 20 minutes respectively. The sorbents CaO and CaO/Ca₁₂Al₁₄O₃₃ (75/25) show better performance in the SEWGS than does the CaO/Ca₁₂Al₁₄O₃₃ (50/50) sorbent.

The presence of any sorbent (CaO, CaO/ Ca₁₂Al₁₄O₃₃ whether 75/25 wt % or 50/50 wt %) in the reactor as a separate bed does not affect the CO conversion, and the values obtained are same as that of HTS catalyst alone. The CaO, CaO/Ca₁₂Al₁₄O₃₃ (75/25), and CaO/Ca₁₂Al₁₄O₃₃ (50/50) adsorb all the CO₂ formed for the first 7, 6, and 3 mins respectively, and finally reach their post-breakthrough period at approximately 45, 36, and 28 minutes respectively.

Sorption capacities are calculated based on both the total weight and on a CaO basis. The CO₂ sorption capacities of CaO, CaO/Ca₁₂Al₁₄O₃₃ (75/25), and CaO/Ca₁₂Al₁₄O₃₃ (50/50) sorbents on the total weight basis in the separated mode are 8.27, 6.33, and 3.92 mol/Kg respectively. In the mixed mode, the corresponding values are 8.54, 6.36, and 4.16 mol/Kg respectively. The sorption capacity is found to remain relatively constant for each sorbent in the two different modes. On the CaO basis, the CO₂ capture capacities of CaO/Ca₁₂Al₁₄O₃₃ (75/25) and CaO/Ca₁₂Al₁₄O₃₃ (50/50) in the separated mode are 8.43 and 7.84 mol/Kg respectively. In the combined mode, the corresponding values are 8.48, 8.31 mol/Kg respectively. Hence, the CO₂ capture capacities of all the sorbents are found to be approximately the same on the CaO basis. From these results, it is concluded that the calcium aluminate (Ca₁₂Al₁₄O₃₃) acts as a binder only and does not necessarily participate in the carbonation reaction.

***Dedicated to my uncle
Late Polineni Yellamandarao.***

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CHAPTER 1 INTRODUCTION

1.1 Background

Over the years, the hydrogen economy has received a great deal of attention. This arises from the fact that some kinds of fossil fuels such as petroleum and natural gas are likely to be exhausted in the near future.¹ Nowadays, there is an increasing interest in hydrogen as an energy carrier since hydrogen is important in the attainment of a low-emission, environmental–benign, cleaner and more sustainable energy system.² As a transportation fuel, hydrogen has some special properties, such as a rapid burning speed, high octane number, and no toxicity or ozone-forming potential. Hydrogen has a high energy yield (122KJ/g), which is 2.75 times more than an average hydrocarbon fuel.² In addition, unlike wind or solar energy, hydrogen can be stored and transported. It is therefore, considered as a viable energy carrier. Recently, there is a development in fuel cells, which can be used for transportation and primary power generation; hydrogen is a main fuel in the fuel cells.¹ However the need for hydrogen is not limited to use as a source of energy.² Hydrogen is also used as a feedstock in ammonia synthesis, alternative fuel synthesis by Fischer-Tropsch synthesis, methanol production, hydrogenation of hazardous wastes and fats, desulphurization, and reformulation of gasoline in refineries.²

However, despite of all these advantages, hydrogen is not a freely available primary energy source in nature.² It is a secondary form of energy that has to be manufactured. Hydrogen is present in a combined form with other elements.² Water, natural gas, crude oils, hydrocarbons, coal, and biomass are the major sources of

hydrogen. Hydrogen is produced on a large scale mainly by steam reforming, partial oxidation, and gasification of coal or biomass.² Other possible methods of hydrogen production include electrolysis, thermochemical water decomposition, photo-biological processes, and photo-electrochemical technology.^{2,6} Among all the current commercial hydrogen production methods, steam reforming is the most cost-effective method, followed by partial oxidation of residual oil and gasification of coal or biomass.² After the generation of synthesis gas (syngas, CO+H₂) from steam reforming and gasification of coal or biomass, the hydrogen contained in the syngas is further increased through the water-gas-shift reaction:

$$\Delta H^\circ = -41.2 \text{ KJ/mole}, \Delta G = -28.6 \text{ kJ/mole}$$

In this reaction, the oxygen in steam can be used to convert CO into CO₂, thus transforming steam into hydrogen.

Hydrogen global production share by source and comparison of different hydrogen production methods are given in Table 1 and Table 2 respectively.

Table 1. Annual global hydrogen production share by source.²

Source	(Billion cubic meters/year)	Share (%)
Natural gas	240	48
Oil	150	30
Coal	90	18
Electrolysis	20	4
Total	500	100

Table 2. Comparison of various hydrogen production methods. ^{1, 2, 4, 5}

Process Type	Advantages	Disadvantages
Steam Reforming	Most mature technology Most cost-efficient processes High hydrogen concentrations	Finite resource (natural gas) Rising natural gas prices Not CO ₂ neutral Slow start up
Coal gasification	Inexpensive coal Abundance of coal around the world.	Produces more CO ₂ than other technologies Purification and separation of hydrogen at high temperatures is challenging Centralized production Complex and expensive process
Biomass gasification	CO ₂ -neutral Decreased dependence on conventional energy sources	Very inefficient Large amounts of land required
Electrolysis	No CO ₂ production However the emission of pollutants depends on the source of power Pure H ₂ production	Expensive Huge amount of electricity required

1.2 Statement of the problem

The water-gas shift (WGS) reaction plays a vital role in increasing the production of hydrogen from fossil fuels. However, because of the reversibility and the moderate exothermicity of the reaction, WGS is thermodynamically unfavorable at elevated temperatures at which kinetics are favorable. In order to overcome this thermodynamic limitation while maintaining high reaction rates, a sorption-enhanced reaction concept can be developed, in which the catalyst and high-temperature sorbent are mixed together. In this process, the use of the sorbent along with the catalyst captures the CO_2 produced from the WGS reaction. The loss of the product of the reversible reaction increases the forward reaction rate. However, the selection of sorbent plays a vital role.

The main purpose of this work is to develop a catalyst-sorbent mixture and a more-efficient process for in-situ removal of CO_2 during the WGS. The main objectives of this project are listed below:

1. To evaluate the activity of the catalyst alone for WGS in the temperatures range of 350-600 °C.
2. To study the performance of inexpensive sorbents CaO and $\text{CaO/Ca}_{12}\text{Al}_{14}\text{O}_{33}$ (75/25, 50/50 wt %) towards WGS reaction in the temperatures range of 350-600 °C.
3. To study the sorption-enhanced water-gas shift reaction (SEWGS) using a mixture of WGS catalyst and sorbent at a temperature of 500 °C.

CHAPTER 2 LITERATURE REVIEW

2.1 Introduction

The water-gas shift reaction (WGS) is a well-developed industrial process in which water (in the form of steam) is mixed with carbon monoxide to obtain hydrogen and carbon dioxide expressed by equation (1). The WGS reaction is reversible and exothermic ($\Delta H^\circ = -41.2$ KJ/mole).⁹ As the reaction is exothermic in nature, WGS is thermodynamically unfavorable at elevated temperatures and the equilibrium constant K_e of the reaction decreases with temperature, as shown in Figure 1.^{8, 9} In order to overcome this thermodynamic equilibrium limitation while maintaining high reaction rates, WGS is normally operated in multiple adiabatic stages with inter-cooling to obtain high overall conversion.^{8, 9} The high-temperature shift (HTS) reaction is carried out in the first stage, where the operation temperature ranges from 350-600 °C. The low-temperature shift (LTS) reaction is carried out in the later stages, within the temperature ranges of 150-300 °C.⁸ Different catalysts are used for WGS in these two stages. For example, iron-based ($\text{Fe}_3\text{O}_4/\text{Cr}_2\text{O}_3$) catalyst can be used for HTS, while copper-based ($\text{Cu}/\text{ZnO}/\text{Al}_2\text{O}_3$) and precious-metal-based catalysts can be used industrially for LTS.^{8, 9}

The dual-stage method is expensive as this method requires high steam, multiple reactors, heat exchangers, and a number of separate product purification units, all of which are capital intensive.⁷ For example, to lower the CO content of the typical fuel gas from 45% to 3%, a total of 1.18 kg steam is required per 1 m³ of CO at a total pressure of 60 bar and 410 °C.¹⁰ To overcome these limitations, a

sorption-enhanced reaction concept is developed, in which catalyst and sorbent are mixed together. The

Figure 1. Equilibrium constant vs temperature for WGS reaction

mixture enhances the net rate of the reaction, simultaneously adsorbing the CO_2 produced from WGS. The continuous removal of CO_2 product from the reactor constantly drives the equilibrium-limited reaction forward. This will ensure a high yield and purity of hydrogen, with near-stoichiometric amounts of steam needed for the reaction. Besides, the reaction now can be carried out at higher temperatures, at which kinetics are favorable in the forward direction. In general, the sorbents

currently tested for the removal of carbon dioxide are based on calcium oxide, hydrotalcites, potassium carbonate, lithium-oxide components, and alumina.

2.2 Mechanism of WGS reaction

The literature reports that the water-gas shift reaction probably occurs via one of the following mechanisms: ⁸

1. The redox mechanism.
2. The formate mechanism.
3. The associative mechanism.
4. The carbonate mechanism.

In the redox mechanism, the reactive catalyst surface undergoes successive oxidation and reduction cycles by water and carbon monoxide respectively. In oxidation, the reactive catalyst surface is oxidized by adsorbed oxygen from H_2O , and the reduction of reactive catalyst surface occurs by adsorbed CO , as CO is oxidized to CO_2 . In the formate mechanism, the reactants are adsorbed on the catalyst surface. Then the adsorbed water dissociates into an adsorbed hydroxyl group and atomic hydrogen. The hydroxyl group reacts with adsorbed carbon monoxide to form adsorbed formate, which finally decomposes into hydrogen and carbon dioxide. In the associative mechanism, adsorbed water dissociates into adsorbed OH and atomic hydrogen. Then the adsorbed hydroxyl will produce CO_2 and atomic hydrogen by oxidizing the adsorbed CO . Finally, in the carbonate mechanism, the water adsorbed on the catalyst surface is decomposed into a hydroxyl group and atomic hydrogen. The hydroxyl groups decompose into surface oxygen atom and hydrogen. The adsorbed carbon monoxide reacts with an oxygen

atom and form a carbonate intermediate. In the last step, the carbonate intermediate decomposes into carbon dioxide. The reactions of the various mechanisms are listed in Table 3.

Table 3. Various mechanisms for WGS reaction.⁸

Associative mechanism	Redox mechanism:	Formate mechanism
$\text{H}_2\text{O} + \text{S} \leftrightarrow \text{H}_2\text{O} \cdot \text{S}$	$\text{H}_2\text{O} + \text{S} \leftrightarrow \text{H}_2\text{O} \cdot \text{S}$	$\text{CO} + \text{S} \leftrightarrow \text{CO} \cdot \text{S}$
$\text{H}_2\text{O} \cdot \text{S} + \text{S} \leftrightarrow \text{OH} \cdot \text{S} + \text{H} \cdot \text{S}$	$\text{H}_2\text{O} \cdot \text{S} \leftrightarrow \text{OH} \cdot \text{S} + \text{SH}$	$\text{H}_2\text{O} + \text{S} \leftrightarrow \text{H}_2\text{O} \cdot \text{S}$
$\text{CO} + \text{S} \leftrightarrow \text{CO} \cdot \text{S} \leftrightarrow \text{CO}_2 \cdot \text{S}$	$2\text{OH} \cdot \text{S} \leftrightarrow \text{H}_2\text{O} + \text{O} \cdot \text{S}$	$\text{H}_2\text{O} \cdot \text{S} + \text{S} \leftrightarrow \text{OH} \cdot \text{S} + \text{H} \cdot \text{S}$
$\text{CO} \cdot \text{S} + \text{OH} \cdot \text{S} \leftrightarrow \text{CO}_2 \cdot \text{S} + \text{H} \cdot \text{S}$	$\text{OH} \cdot \text{S} + \text{S} \leftrightarrow \text{O} \cdot \text{S} + \text{H} \cdot \text{S}$	$\text{CO} \cdot \text{S} + \text{OH} \cdot \text{S} \leftrightarrow \text{HOCC} \cdot \text{S} + \text{S}$
$\text{CO}_2 \cdot \text{S} \leftrightarrow \text{CO}_2 + \text{S}$	$2\text{H} \cdot \text{S} \leftrightarrow \text{H}_2 + 2\text{S}$	$\text{HCOO} \cdot \text{S} \leftrightarrow \text{CO}_2 + \text{H} \cdot \text{S}$
$2\text{H} \cdot \text{S} \leftrightarrow \text{H}_2 + 2\text{S}$	$\text{CO} + \text{S} \leftrightarrow \text{CO} \cdot \text{S}$	$2\text{H} \cdot \text{S} \leftrightarrow \text{H}_2 + 2\text{S}$
	$\text{CO} \cdot \text{S} + \text{O} \cdot \text{S} \leftrightarrow \text{CO}_2 \cdot \text{S} + \text{S}$	
	$\text{CO}_2 \cdot \text{S} \leftrightarrow \text{CO}_2 + \text{S}$	
Carbonate mechanism		
$\text{CO} + 2\text{O} \cdot \text{S} \leftrightarrow \text{CO}_3 \cdot \text{S}_2$		
$\text{CO}_3 \cdot \text{S}_2 \leftrightarrow \text{CO}_3 \cdot \text{S} + \text{S}$		
$\text{CO}_3 \cdot \text{S} \leftrightarrow \text{CO}_2 + \text{S}$		
$\text{H}_2\text{O} + \text{S} \leftrightarrow \text{H}_2\text{O} \cdot \text{S}$		
$\text{H}_2\text{O} \cdot \text{S} + \text{O} \cdot \text{S} \leftrightarrow 2\text{OH} \cdot \text{S}$		
$2\text{OH} \cdot \text{S} \leftrightarrow 2\text{O} \cdot \text{S} + \text{H}_2$		

Note: S represents an active site

2.3 HTS and LTS catalysts for WGS reaction

In the absence of the catalyst, the water-gas-shift reaction is very slow at accessible industrial temperatures; therefore different catalysts are used to increase

the rate of water-gas-shift reaction. For example, iron- and copper-based catalysts, and precious-metal-based catalysts are industrially used for high-temperature shift (HTS) and low-temperature shift (LTS) reactions respectively.⁹

The HTS catalyst contains iron oxide, in the form of hematite (Fe_2O_3), as well as chromium oxide (Cr_2O_3), which acts as stabilizer, retards sintering, and inhibits the loss of specific surface area.¹¹ The HTS catalyst has high catalytic activity and excellent thermal stability. Iron oxide in the form of magnetite (Fe_3O_4) is believed to be the active phase in the reaction. Therefore, hematite is pre-reduced to magnetite before being used as a catalyst in the WGS reaction.¹² Since the HTS reaction is exothermic, the reaction should be controlled to avoid the production of metallic iron, which may catalyze undesirable reactions such as hydrocarbon generation.¹³ In industrial processes, large amount of steam are used to inhibit the metallic iron formation. However, this increases operational cost.¹¹

The effect of addition of transition metal oxides like CuO, CoO, and ZnO on the activity of the $\text{Fe}_2\text{O}_3/\text{Cr}_2\text{O}_3$ catalyst has also been studied. The addition of CuO and CoO in co-precipitated $\text{Fe}_2\text{O}_3/\text{Cr}_2\text{O}_3$ was found to enhance the reaction rate and shift the maximum of the conversion curve to a lower temperature, compared to unpromoted $\text{Fe}_2\text{O}_3/\text{Cr}_2\text{O}_3$ catalyst.¹⁴ Also, $\text{Fe}_2\text{O}_3/\text{Cr}_2\text{O}_3/\text{CuO}$ can work in more severe conditions, like lower steam-to-carbon monoxide ratios, without being reduced to metallic iron which will favor undesirable side reactions¹¹.

A series of $\text{Fe}_2\text{O}_3/\text{Cr}_2\text{O}_3$ catalysts promoted with 2 wt % B, Pb, Cu, Ba, Ag, or Hg were tested for WGS at 400 psig and various temperatures.¹⁵ Most of these dopants were found to increase the activity, except B which slightly poisons the

activity. Addition of Ba^{2+} , Ag^{2+} , and Hg^+ increases the catalyst activity above the promotion levels observed with Cu^{2+} across the temperature range studied [350-440 °C]¹⁵.

In view of environmental problems with chromium, one study¹² replaced the chromium of $\text{Fe}_2\text{O}_3/\text{Cr}_2\text{O}_3$ with alumina and a low amount of copper. The surface area of the catalyst increases after chromium is replaced with alumina. The Fe_2O_3 catalyst promoted with Al_2O_3 and CuO produces the active phase more easily. The promoters also resist the over-reduction of magnetite (Fe_3O_4) to iron oxide (FeO) or iron species (Fe)¹². The promoted catalyst was also found to perform well at low steam-to-process-gas (S/G) ratios (0.4) as well as at low temperatures. The activity shown by the iron catalyst promoted with Al_2O_3 and CuO was found to be closer to that of copper-doped iron-based commercial catalyst¹². Moreover, the $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3/\text{CuO}$ catalyst system can be discarded without any damage to the environment. However, studies of the stability of the aluminum-and copper-doped Fe_2O_3 catalyst system are needed for its commercial application. The chromium of iron-based commercial catalysts was also replaced with $\text{Al}_2\text{O}_3/\text{CeO}_2$ and activities tested¹. This catalyst has activity and thermal stability which are comparable to those of the commercial Fe-Cr catalyst.¹⁶

The Pb-doped iron catalyst shows similar catalytic performance to that of a commercial Fe-Cr based catalyst. However, the stability of the Fe/Pb-based catalyst is very low compared to that of Fe/Cr-based WGS catalyst, since the activity of the Fe-Pb catalyst is sensitive to the trace amounts of sulfur in the feedstock.¹⁷ Oxides like ZnO , MgO , SnO_2 , Al_2O_3 , TiO_2 , and SiO_2 have CO conversion rates 2 to 7 orders

of magnitude smaller than conversions over commercial iron-based catalyst.¹⁹ The WGS activity of Mg and Zn ferrites is also much lower than that of Fe-Cr based catalyst.¹⁸

Notably, not only the promoters, but also the activation process plays a crucial role in the activity and stability of the iron-based catalysts. The reduction of the iron-based catalysts in CO/CO₂ prior to the reaction increases the WGS catalytic activity. In contrast, the catalyst treatment in H₂/H₂O causes the growth of magnetite particles, leading to a decrease in catalytic activity.²⁰

Cu-based catalysts are generally used for low-temperature WGS reaction. Because of the relatively low melting point of the copper, the commercial LTS catalyst is more sensitive to deactivation caused by sintering than the HTS catalyst. This causes the maximum operating temperature to be around 250 °C⁸. The addition of ZnO/Al₂O₃ not only stabilizes the copper crystallites against thermally induced sintering, but also increases the strength of the catalyst.⁹ Also ZnO/Al₂O₃ minimizes the shrinkage during the reduction process.⁹ Copper-based-catalysts are easily deactivated by sulfur and chloride impurities. Hence gas streams must be cleaned before these catalysts can be used.²¹

Precious metals supported on ceria and zirconium oxide have also been used as catalysts for WGS reaction. Even though precious metals have shown better catalytic activity, when compared with iron-based and copper-based catalysts, precious metals are expensive and hence economically unfeasible. Also, the precious metal catalysts produce methane along with hydrogen.²² Methane causes a decrease in production of hydrogen and releases excess heat.²² In spite of being

Table 4. Comparison of various WGS catalysts.²³

Catalyst	HTS catalysts	LTS catalysts	Precious-Metal catalysts
Form	3-10mm pellets	3-6mm pellets	Monolith supported
Poisons	Low sensitivity to sulfur	Deactivates on exposure to sulfur and halogens	Tolerance to some poisons
Thermal stability	Thermal stability up to~500 °C	Loss of activity above 280 °C	Thermal stability >400 °C
Activity	Not active below~350 °C	High activity below 200 °C	High activity above 250 °C
Other Considerations	Self-heating material in the reduced state Inexpensive material Insensitive to sulfur up to certain level	Needs to be carefully reduced Self-heating material in the active state (reduced) Deactivates by water condensation and air exposure Need careful discharge from the reactor (self heating catalyst)	Insensitive to start-stop and air exposure No need for pre-reduction

expensive, the benefits of precious metal catalysts over iron- and copper-based catalysts can be accepted, if the durability (time for which the catalyst keeps sufficient level of activity) and redox resistance (resistance to oxidation and reduction) can be proven.²² A comparison of different WGS catalysts is given in Table 4.

2.4 Catalyst pretreatment

Pretreatment is a basic step in the activation of a WGS catalyst. Generally, pretreatment conditions (such as reduction temperature, reduction atmosphere, calcination temperature, and calcination atmosphere) strongly affect the active phase of the catalyst, which in turn, influences its performance. After the preparation step, WGS catalysts are pretreated by being calcined in the temperature range of 350- 450 °C, either in air or N₂ for 2-4 hours to convert the basic carbonates to oxides.

The calcination step for the chromium-containing HTS catalyst is very important, since the temperature of the catalyst must be carefully controlled to avoid the formation of chromic oxide (CrO₃) from the air oxidation of chromia expressed by

9

(2)

The presence of the Cr (VI) compound in the HTS catalyst is undesirable, not only because of the potential health hazards associated with that compound, but also because of the possible operating problems as the catalyst is reduced.⁹ For instance, leaching of chromium occurs when condensation of soluble hexavalent

chromium takes place on unreduced catalyst in the reactor. In addition, the exothermic conversion of hexavalent chromium to trivalent chromium during the reduction leads to considerable evolution of heat and a correspondingly large increase in bed temperatures.⁹

The catalytically active phase of the HTS catalyst is magnetite (Fe₃O₄). Therefore, commercial catalysts (which are normally supplied in the oxide form, Fe₂O₃-Cr₂O₃-CuO or prepared catalysts (via precipitation after the calcination step) need to be activated before use. The activation process comprises the partial reduction of hematite (Fe₂O₃) to magnetite (Fe₃O₄), and any CrO₃ present to Cr₂O₃.⁹

The WGS catalysts (commercial or prepared via precipitation) are reduced with H₂ /N₂ or process gas mixtures of H₂, CO, CO₂, and steam, within the temperature range of 300-500 °C, using a flow rate of 50-200 cc/min for 2-3 hours according to:^{9,12,20}

Approximately, 150 mg of the catalyst is used at this flow rates^{12, 20}.

It is very important to avoid over-reduction of the magnetite (Fe₃O₄) active material to iron oxide (FeO) or iron species (Fe) during this reduction process, since these compounds will promote methanation and carbon dioxide disproportionation.⁹ Moreover, even a relatively small degree of over-reduction can cause weakening and physical damage to the catalyst pellets. Therefore, the reduction conditions are

chosen so that they permit the required reactions to occur without further reduction of Fe_3O_4 to iron oxide (FeO) or metallic iron (Fe).

2.5 Side reactions in WGS reaction

In WGS, side reactions become important when a low $\text{H}_2\text{O}/\text{CO}$ ratio is used. For instance, in a gas system containing CO , CO_2 , H_2O , and H_2 , the following side reactions may occur.²¹

(10)

(11)

(12)

(13)

These reactions produce undesired products such as carbon or methane. The extent to which these reactions proceed depends mainly on the catalyst system used, reaction conditions like $\text{H}_2\text{O}/\text{CO}$ ratio, and the kinetics of the reaction. If these reactions occur at a high rate during the WGS reaction, a number of problems can arise. For example, the formation of carbon will cause blockage of the catalyst bed,

deactivation of the catalyst, an increase in the pressure drop across the catalyst bed, and plugging and fouling of the equipment, which finally leads to shut-down of the process.²¹ The formation of methane consumes hydrogen and alters the product composition.⁸

2.6 Carbon dioxide separation techniques

The most commonly used methods for CO₂ capture are absorption, adsorption and membrane gas separation. The currently preferred method for carbon dioxide capture is absorption using a chemical or physical solvent. Monoethanolamine (MEA), diethanolamine (DEA), and triethanolamine (TEA) are used for CO₂ capture in chemical absorption while glycol and methanol are used commercially for CO₂ capture in physical absorption.²⁴

In chemical absorption, CO₂ in the gas phase dissolves into a solution of water and amine compounds and forms protonated amine (AH⁺), bicarbonate (HCO₃⁻), and carbonate (ACO₂⁻). As these reactions take place, more CO₂ from the gas phase is driven into the liquid solution due to the lower chemical potential of the liquid phase compounds. Once the solution is saturated with CO₂, it is removed from contact with gas stream and heated to remove the absorbed carbon dioxide from the amine solution.²⁴

Although many alkanolamines are used industrially for CO₂ capture, MEA is the most extensively used solvent for CO₂ absorption because it has the highest alkalinity and, hence, reacts more rapidly with CO₂. In addition, MEA is inexpensive and has the highest CO₂ separation, which leads to relatively low overall costs.²⁵ However, despite these advantages, MEA has the problem that it requires a huge

amount of energy for regeneration.²⁵ Another major drawback of MEA solvent is that it has low cyclic absorption capacity. In addition, irreversible reactions of MEA with minor impurities result in solvent degradation and loss.²⁴ For example, MEA solvent reacts with NO_x , SO_x , CO, and O_2 which accompany the CO_2 in flue gas and forms heat-stable salts such as formates, acetates, oxalates, thiocyanates, and sulphates.^{25,26} The presence of these heat-stable salts in the absorption solution creates many adverse effects such as increase in corrosion, increase in foaming tendency of the solution and increase in solution viscosity.^{25,26}

Physical absorption occurs through mass transfer of CO_2 gas molecules into the solvent. The physical absorption process is governed by Henry's law, which states that the amount of absorbed gas is proportional to its partial pressure. Glycol, methanol, tributyl phosphate, propylene carbonate, and polyethylene glycol are commonly used solvents for physical absorption.⁶¹ All these solvents are non-corrosive and non-toxic and only require carbon steel construction for a simple cycle process. Physical absorption is favorable at high partial pressures of CO_2 (180-1200 psi) and low temperatures (-20-30°C).⁶¹ Therefore, physical absorption processes are notably suitable for the treatment of CO_2 -rich gas streams.

Since these solvents interact weakly with the dissolved CO_2 during physical absorption, the solvents are regenerated by depressurization. However, depressurization of the solvent results in a significant energy penalty. Also, these physical absorption solvents have low capacities for cyclic CO_2 absorption.¹⁰ Besides, the CO_2 capture capacity decreases as the temperature increases. The flue gas from power plants is at sub-atmospheric pressure and usually hot (800–

120°C). Further, the CO₂ concentration in flue gas is only about 10-15%.¹⁰ Therefore, the physical absorption requires compression and cooling of the flue gas. This makes physical absorption process energy intensive.¹⁰

CO₂ can also adsorb physically on a bed of adsorbents such as zeolites and activated carbon. Since adsorption of CO₂ occurs through weak interactions such as Van der Waals forces, these adsorbents have the advantages of low regeneration temperature and quick regeneration time.²⁴ However, these adsorbents have a high affinity towards water in the feed gas rather than CO₂ in the product, hence water is removed. The removal of water drives the WGS reaction backward and hence reduces the amount of hydrogen produced.²⁷ Another major problem associated with these physical adsorbents is that the adsorption capacity for CO₂ decreases as the temperature increases.²⁸ As a consequence, the use of physical adsorbents for in-situ removal of CO₂ during WGS reaction becomes inefficient as the reaction (WGS) is operated in the range of 300-600 °C. Physical adsorbents such as activated carbon and zeolites have adequate adsorption capacity for CO₂ at high pressures (1-10 atm) and ambient temperatures (25-100 °C). Various techniques like pressure-swing adsorption (PSA), vacuum-pressure-swing adsorption (VPSA) and thermal-swing adsorption (TSA) are used for CO₂ regeneration.¹⁰

Membrane gas separation uses the difference in interaction between the membrane material and various components of the product gas (CO₂, H₂, H₂O, and CO). This selective affinity for one gas component causes it to permeate faster than the others, thus achieving its separation.¹⁰ The efficiency of a membrane depends on its permeability (the flow rate of the gas through the membrane) and selectivity

(the ability of one component of the gas to permeate faster than others).²⁹ Some examples of membrane materials are polymer membranes, palladium membranes, inorganic microporous membranes, and ceramic porous membranes.¹⁰

Although the system for membrane gas-separation process is quite simple, there are a number of challenges: high cost, low CO₂ recovery rate, and high pressure requirement.²⁴ In addition, removal of impurities becomes inevitable. Impurities like H₂S, COS, and arsene react with membranes and have a deleterious effect on membrane performance.³⁰ Membranes usually cannot achieve high degrees of separation, so multiple stages of membranes and/or recycle of one stream are necessary.²⁹ This leads to increased complexity, energy consumption and costs.²⁹ Hence these membrane separation processes are generally not suitable for production of high-purity products.

2.7 Reaction-based systems for CO₂ removal

The use of a reaction-based CO₂ separation with facile kinetics will lead to:³¹

1. Lower sorbent requirements,
2. Smaller size reactors,
3. Lower pressure drop across the reactor,
4. Higher equilibrium carbon dioxide-capture capacity, and
5. Generation of pure CO₂.

2.7.1 Metal-oxide-based sorbents

In reaction-based sorption processes, metal oxides are the most important sorbents. As metal oxides are basic in nature and CO₂ is acidic in nature, metal

oxides have good CO₂ capture capacity.⁴⁴ The metal oxide (MO) sorbent reacts with CO₂ at high temperatures to produce the metal carbonates (MCO₃).³¹ The carbonation reaction can be given as

The metal carbonate formed is calcined at high temperature to regenerate the metal oxide, and pure CO₂ can in principle be generated via³¹:

This pure CO₂ can be economically compressed, cooled, liquefied, and transported for its sequestration.

Many metal oxides exhibit the carbonation and calcination reactions of Equations (9) and (10). However, metal carbonates that decompose above 1000°C are not suitable for CO₂ capture, because their high calcination temperatures will impose severe energy penalties.³¹ Therefore, metal oxides whose calcination temperatures are within the desired temperature range of 300-800 °C are used for CO₂ capture. These include CaCO₃ (~750 °C), MgCO₃ (~385 °C), ZnCO₃ (~340 °C), CuCO₃ (~290 °C), and MnCO₃ (~440 °C). However, carbonation of metal oxides other than CaO has not been widely studied in the literature.³¹

2.7.2 CaO-based sorbents

CaO sorbents are derived from precursors such as limestone (CaCO₃), calcium hydroxide (Ca(OH)₂), dolomite (MgCa(CO₃)₂), and huntite (Mg₃Ca(CO₃)₄). These sorbents have a high CO₂ capture capacity and react rapidly over a wide range of temperatures and pressures.³¹ Limestone is widely available and CaO from limestone has a higher theoretical CO₂ capture capacity (0.79g CO₂/g CaO) than

that of calcined dolomite (0.46 g CO₂/g CaO·MgO) and huntite (0.25g CO₂/gCaO·3MgO).^{32, 33} The decline of CO₂ capture of natural CaO sorbents over multiple carbonation-calcination cycles can be attributed to changes in the structure of the CaO particles during calcination at high temperatures (850-1000 °C).³⁴ Exposure of CaO particles to higher temperatures leads to a loss in surface area and porosity due to sintering, which reduces its reactivity. As the limestone cannot maintain a high CO₂ capture capacity beyond 20 cycles, large quantities of limestone make-up are required for CO₂ capture. Huntite has been found to give the highest fractional conversion and high CO₂ sorption capacity over multiple carbonation-calcination cycles, followed by dolomite and calcite.^{32,33} This property of huntite is due to the excess pore volume created by the initial decomposition of MgCO₃ during calcination at high temperatures (850-1000 °C). The MgO produced from the decomposition of MgCO₃ provides structural property stability, which in turn contributes to better performance over multiple carbonation-calcination cycles. Since huntite has a higher MgO-to-CaO molar ratio than dolomite or limestone, huntite shows better performance over multiple carbonation-calcination cycles.^{32,33} However the limited availability of huntite and its low theoretical CO₂ capacity (0.25g CO₂/g CaO·3MgO) probably eliminates its use in a commercial process.³³

Synthesized CaO sorbents have shown significantly improved CO₂ capture and reaction stability over multiple carbonation-calcination cycles when compared to limestone and dolomite.³⁴ For example, CaO supported on mayenite (Ca₁₂Al₁₄O₃₃) attains 41 wt% CO₂ capture at the end of 50 carbonation-and-calcination cycles.³⁵ The calcium oxide from precipitated calcium carbonate (PCC-CaO) captures 36 wt

% CO₂ after 100 carbonation-and-calcination cycles.³¹ The high reactivity of PCC-CaO is due to the predominant mesoporous structure, which allows the reactant gases to access the entire surface of the particles through large pores.³¹ The CaO/Ca₁₂Al₁₄O₃₃ sorbent also has a high reactivity, but the mechanism is different from that PCC-CaO. The high reactivity of CaO/Ca₁₂Al₁₄O₃₃ may be due to the formation of binder (Ca₁₂Al₁₄O₃₃) uniformly among the ultra-fine CaO particles, and this Ca₁₂Al₁₄O₃₃ may retard the sintering of the CaO particles.³⁵

Generally, the drawbacks associated with prepared or natural CaO-based sorbents are spalling induced by cycling and the need for high temperatures to carry out the regeneration.

2.7.3 Mechanism of carbonation of CaO-based sorbents

Calcium oxide will react with carbon dioxide and forms calcium carbonate represented by the reaction:

The carbonation of calcium oxides occurs through three regimes. In the first regime, carbonate is formed, and this could provide active sites for further growth of a calcium carbonate layer. The second regime involves a rapid chemical reaction between calcium oxide and carbon dioxide. Most of the initial carbonation occurs due to fast kinetics. In the final regime, the carbonation reaction occurs very slowly due to the formation of an impervious calcium carbonate layer that prevents the further exposure of unreacted calcium oxide with carbon dioxide. The kinetics of the third regime is controlled by the diffusion of the CO₂ through the formed calcium carbonate layer.²²

2.7.4 Lithium-oxide-based sorbents

Lithium-containing oxides have also been tested for the removal of carbon dioxide. Among these, lithium orthosilicate and lithium zirconate are the most favorable sorbents. The CO₂ sorption rate on pure lithium zirconate is very low³⁶, because an impervious shell of Li₂CO₃ is formed on the outer surface of the unreactive Li₂ZrO₃. But doped lithium zirconates have high CO₂ sorption capacities and fast sorption kinetics compared to those of pure Li₂ZrO₃.³⁶ These improvements are due to the formation of a eutectic carbonate layer composed of lithium carbonate (Li₂CO₃) and potassium carbonate (K₂CO₃) on the outer surface of the lithium zirconate particles. Since the diffusion of CO₂ through the molten carbonate layer occurs at a much faster rate than through the solid phase, the formation of the K₂CO₃/Li₂CO₃ eutectic layer helps in facilitating the transfer of gaseous CO₂ during the CO₂ sorption.³⁶

Compounds such as lithium ferrite (LiFeO₂), lithium nickel oxide (LiNiO₂), lithium titanate (Li₂TiO₃), lithium sulfate (Li₂SiO₄), and lithium metasilicate (Li₂SiO₃) have also been tested for CO₂ capture. Among these, Li₄SiO₄ is found to have the highest capacity (28% higher than Li₂ZrO₃) and sorption rate with CO₂. However, the increase in weight during the carbonation is only about 70% of the theoretical maximum capacity.³⁷ Li₄SiO₄ can absorb CO₂ faster than lithium zirconate at lower temperatures and even in low CO₂ concentrations.³⁸ Usually, adsorption of CO₂ on these sorbents is affected by the mechanism in which the Li₂O moves from Li₂ZrO₃ or Li₄SiO₄ to the surface and reacts reversibly with carbon dioxide. Since Li₂SO₄

contains many sites for lithium-ion hopping, the CO_2 absorption rate for Li_2SiO_4 is faster than that for Li_2ZrO_3 .³⁸

The main advantages of lithium-oxide-based sorbents over CaO-based sorbents are that the former require less energy for sorbent regeneration (calcination) and are unusually stable over multiple cycles.³⁹ But lithium is not abundant, and the cost is expensive when compared with other metal compounds.⁴⁰ Also, the CO_2 sorption capacity of lithium-based-sorbents is lower than that of CaO-based sorbents. Since lithium-based sorbents have less favorable thermodynamic properties, the product H_2 concentrations are lower than what can be obtained using calcium-based sorbents.⁴¹

2.7.5 Metal-carbonate-based sorbent

The sorption of CO_2 on K_2CO_3 depends on the type of the support and the temperature of the activation process. Sorption of CO_2 on K_2CO_3 impregnated on supports such as activated carbon, alumina, MgO, and TiO_2 has been reported in the literature^{42, 43, 8}. Sorbents like K_2CO_3 /activated carbon, $\text{K}_2\text{CO}_3/\text{TiO}_2$, $\text{K}_2\text{CO}_3/\text{MgO}$, and $\text{K}_2\text{CO}_3/\text{Al}_2\text{O}_3$, which show good CO_2 -capture capacity at low temperature (60 °C), can be completely regenerated above 130 °C, 130 °C, 350 °C, and 400 °C, respectively.⁴² The CO_2 -capture capacity of K_2CO_3 supported on Al_2O_3 and MgO, after regeneration at low temperatures (less than 200 °C), decreases due to the formation of intermediate compounds ($\text{KAl}(\text{CO}_3)_2(\text{OH})_2$, $\text{K}_2\text{Mg}(\text{CO}_3)_2$ and $\text{K}_2\text{Mg}(\text{CO}_3)_2 \cdot 4\text{H}_2\text{O}$), which are not completely converted to the original K_2CO_3 phase.⁴² But in the case of $\text{K}_2\text{CO}_3/\text{TiO}_2$ and K_2CO_3 /activated carbon, a KHCO_3

phase is formed during the adsorption. This phase can be easily converted into the original phase during the regeneration, even at low temperature (150 °C).

The total CO₂-capture capacities of K₂CO₃/TiO₂ and K₂CO₃/ZrO₂ are maintained constant during multiple CO₂ absorption /regeneration cycles, and their regeneration temperatures are the lowest relative to potassium carbonate supported on all other supports.^{42,43} Even though the potassium-based-carbonates have good adsorption/ desorption properties in the temperature range of 60-100 °C, they are not suitable for in-situ removal of CO₂ from the WGS and reforming reactions, because these reactions are operated within in the temperature range of 200-600 °C.⁸

2.8 Hydrotalcite compounds

Hydrotalcite compounds (HTCs) are also known as layered double hydroxides. They can be represented by the general formula $[(M^{2+}_{1-x} \cdot M^{3+}_x(OH)_2)]^{x+} \cdot (A^{n-}_{x/n} \cdot mH_2O)^{x-}]$, where M²⁺ represents Mg²⁺, Ni²⁺, Zn²⁺, Cu²⁺ or Mn²⁺; M³⁺ represents Al³⁺, Fe³⁺ or Cr³⁺; and Aⁿ⁻ represents CO₃²⁻, SO₄²⁻, NO₃⁻, Cl⁻ or OH⁻.⁴⁴ The CO₂ adsorption capacity of the HTCs is mainly affected by cation, anion, water/steam, temperature, and chemical modification. The low water content in the HTC and the presence of steam in feed gas are favorable for adsorption of CO₂ onto HTC at high temperature. The aluminum content in the substituted HTC strongly affects the adsorption capacity of carbon dioxide.⁴⁴ As the aluminum content increases in the HTC, the density of the layer charge in HTC increases, which is favorable for adsorption of carbon dioxide. Simultaneously, there is also a

decrease in the interlayer spacing of HTC, and this reduces the number of high-strength CO₂-adsorption sites. Therefore, there is an optimum aluminum content for adsorption of carbon dioxide. HTCs containing CO₃²⁻ show higher adsorption capacities than those of OH⁻ containing HTC sorbents. This is due to the presence of more void spaces in the interlayer of the CO₃²⁻-containing HTC sorbents.⁴⁴ Addition of K₂CO₃ enhances the adsorption capacity of the HTC by a factor of 3, when compared to non-impregnated HTC adsorbents.⁴⁵ As the HTC can be regenerated with low energy input and at low temperature, the sorbent durability is increased, avoiding sintering.⁴⁶ However, HTCs have lower CO₂-capture capacity than Ca-based sorbents, and are considerably more expensive.⁴⁶ The adsorption temperature, physical properties, advantages, and disadvantages of different sorbents discussed in Sections 2.5- 2.7 are given in Tables 5 & 6.

Table 5. Comparison of various sorbents.^{27, 38, 41, 44, 45, 57}

Sorbent type	Temperature (°C)	Surface area (m ² /g)	Advantages	Disadvantages
CaO-based-sorbents Dolomite (MgCa(CO ₃) ₂) Calcite (CaCO ₃) Huntite (MgCa(CO ₃) ₄) Lime Ca(OH) ₂ Carbonation: $\text{CaO} + \text{CO}_2 \leftrightarrow \text{CaCO}_3$ Regeneration: $\text{CaCO}_3 + \text{Heat} \leftrightarrow \text{CaO} + \text{CO}_2$	500-650	1-50	1. Large sorption capacity 2. Low cost 3. Wide availability 4. Fast sorption kinetics 5. Good kinetics	1. High regeneration temperature 2. Sulfur removal is often needed 3. Poor stability because of pore blocking and sintering
Hydrotalcite- based compounds $\text{Mg}_6\text{Al}_2(\text{CO}_3)(\text{OH})_{16} \cdot 4\text{H}_2\text{O}$	300-450	30-270	1. Low regeneration temperature 2. Good stability	1. Expensive and poor adsorption capacity
Lithium-zirconate-based sorbents $\text{Li}_2\text{ZrO}_3 + \text{CO}_2 \rightarrow \text{Li}_2\text{CO}_3 + \text{ZrO}_2$	400-500		1. Low regeneration temperature 2. Fair adsorption 3. Good stability 4. Attrition resistance in thermal cycling tests	1. Expensive and less abundance 2. Less favorable thermodynamic properties 3. Low sorption rate

Table 6. Comparison of various sorbents.^{27, 38, 41, 44, 45, 57}

<p>Lithium ortho silicate (Li_2SiO_4) $\text{Li}_4\text{SiO}_4 + \text{CO}_2 \rightarrow \text{Li}_2\text{CO}_3 + \text{Li}_2\text{SiO}_3$</p>	500-600	--	<ol style="list-style-type: none"> 1. Fair adsorption and stability 2. Low regeneration temperature 3. Attrition resistance in thermo cycles 4. Effective in the presence of H_2S 5. Fast kinetics 	<ol style="list-style-type: none"> 1. Less favorable thermodynamics properties 2. Expensive and less abundance
Carbon-based sorbents	25-75	600-3370	<ol style="list-style-type: none"> 1. Low cost 2. Easily modified structure 3. Low regeneration temperature 	<ol style="list-style-type: none"> 1. Adsorption of CO_2 decreases as the temperature increases 2. Low adsorption capacity 3. They have high affinity towards water rather than CO_2
Zeolite-based compounds	25-75	600-3370	<ol style="list-style-type: none"> 1. High surface area 2. Low cost 3. Low regeneration temperature 4. Quick regeneration temperature 	<ol style="list-style-type: none"> 1. Adsorption of CO_2 decreases as the temperature increases 2. Low adsorption capacity 3. They have high affinity towards water rather than CO_2

2.9 Summary

Among all the sorbents described in the literature and reviewed in Sections 2.5-2.7, CaO-based sorbents appear to be the best. Even though their regeneration temperature is very high (of the order of 800–950 °C), CaO-based sorbents are widely available and inexpensive and have a high adsorption capacity. Correspondingly, CaO-based sorbents are widely used for CO₂ capture from reforming reactions and WGS reactions.

2.10 Sorption-enhanced reaction process

The process in which in-situ separation of one or more products is performed in the reaction chamber is called sorption-enhanced reaction (SER). Generally, this SER process is used in equilibrium-limited reactions such as steam reforming and WGS. In the sorption-enhanced WGS process, the WGS catalyst and sorbent are admixed. The mixture containing the catalyst and the sorbent adsorbs the CO₂ and thereby enhances the rate of reaction. The advantages of SER process over the conventional methods of WGS are given below.⁴⁹

1. According to Le Chatelier's principle, removal of CO₂ from the reaction zone will drive the WGS reaction forward. This will allow (i) higher conversion of CO to H₂ than that obtained by thermodynamically limited conventional WGS reaction, (ii) enhancement of the reaction rate in the forward direction, (iii) the use of a lower H₂O/CO ratio in the feed gas and (iv) a relatively higher

operating temperature of the reactor (kinetics are favored at high temperature) without thermodynamic limitation.

2. This process also eliminates any subsequent separation process needed.
3. The simultaneous production of an essentially pure and compressed CO₂ by-product promotes subsequent CO₂ sequestration, and the sale of the CO₂ product.
4. Lower capital and energy costs due to simple equipment used in SER, in which there is no need to install a separate product purification unit.

2.11 Impurities from syngas

Synthesis gas can be obtained from the gasification of biomass and coal or from steam reforming of natural gas. In the gasification process, steam or oxygen is fed to a gasifier at high temperatures (greater than 700 °C) to convert coal, biomass or any carbonaceous material into CO, CO₂, and H₂. In addition to these primary products, the gasification of coal or biomass also produces varying levels of impurities such as NO_x, SO_x, chloride, sulfides, cyanide compounds, particulate matter, organic tar, and some hydrocarbon compounds.⁵⁰ The impurities produced differ by feedstock and gasification process.⁵¹ Coal gasification produces more NO_x and SO_x impurities, whereas biomass gasification produces more hydrocarbon impurities.^{52,53} The composition of synthesis gas produced from coal in different gasifiers is given in Table 7. The effect of impurities is given in Table 8. The main impurities in syngas produced from coal are sulfur, halides, and carbonyl sulfide compounds. These impurities affect the activity of the WGS catalysts. The

deactivation of the catalyst will depend on the concentration of impurities in the feed. The Cu/Zn-based catalysts are extremely sensitive to H₂S and completely deactivate in H₂S even at low concentrations (50ppm).^{21, 55}

Table 7. Synthesis gas composition (volume %) generated by different gasifiers.⁵⁴

Gasifier type (Coal)	Moving bed Lurgi (Illinois no.6)	Fluidized bed Winkler (Texas lignite)	Entrained bed Kopper- Totzek (Illinois no.6)
Ar	Trace	0.7	0.9
CH ₄	3.3	4.6	-
C ₂ H ₆	0.2	-	-
CO	5.8	33.1	43.8
CO ₂	11.8	15.5	4.6
COS	Trace	-	0.1
H ₂	16.1	28.3	21.1
H ₂ O	61.8	16.8	27.5
H ₂ S	0.5	0.2	1.1

The H₂S reacts with copper and zinc oxide to form Cu₂S and ZnS according to:⁹

But compared to Cu/Zn catalysts, the iron-chromium-based catalyst and precious metals supported on ceria or zirconia are less susceptible to sulfur, at least up to 50 ppm H₂S. However above 50 ppm, a decline in catalytic activity is observed.⁵⁵ The H₂S in the feed reacts with the active phase (Fe₃O₄) of the HT shift catalyst and forms FeS by:⁹

Any carbonyl sulfide present in the feed gas is converted to hydrogen sulfide (H_2S) according to:

The H_2S eventually deactivates the active phase (Fe_3O_4) of iron-chromium based catalyst. The sulfided catalyst also shows catalytic activity, but its activity is only about half that of the original iron catalyst. Therefore, the volume of catalyst needed is doubled.⁹ The WGS activities of various catalysts in the presence of H_2S are given in Table 9.

Table 8. Contaminants from syngas and their potential effects.^{49, 50}

Class	Contaminant	Potential effect
Sulfur compounds	H_2S , COS, CS_2 , $\text{C}_4\text{H}_4\text{S}$	Poisoning of the catalytic reaction sites Corrosion
Particulates	Coal fines, ash	Plugging of gas passages Deactivation of catalysts
Hydrocarbons	C_6H_6 , C_{10}H_8 , $\text{C}_{14}\text{H}_{10}$	Carbon deposition, which causes loss of surface area Lower the heat transfer from catalyst to gas
Halides	HCl, HF, HBr	Corrosion
Tar compounds	Refractive aromatics	Coke formation
Alkali metals	Sodium, potassium compounds	Hot corrosion Catalyst poisoning

Table 9. The WGS activities of various catalysts in the presence of H₂S.⁵⁶

Catalyst description	Temperature (°C)	CO conversions at different H ₂ S concentrations (ppm) in the feed			
		0	50	200	1000
Cu/Zn	240	80	0	0	0
Fe-Cr	300	3	2.4	2.4	1.8
Fe-Cr	350	17	14	11	7.5
Co-Cr	300	58-39	-	18-12	
Pt/ZrO ₂	300	44	25	14	12

CHAPTER 3 EXPERIMENTAL SETUP AND PROCEDURE

3.1 Reactor Setup description

The catalyst-testing unit used for the WGS reaction is shown in Figure 2. The unit is computer controlled using In Touch commercial software by Wonderware. The experimental setup consists of a stainless-steel reactor (from TW METALS), a high- pressure water syringe pump, a steam generator, a gas chromatograph (5890 HP-GC), and four mass-flow controllers (from Brooks Instruments). The reactor consists of a silica-lined stainless-steel tube of nominal diameter of 13 mm and nominal length of 0.6 m (25 in.), placed in a 0.45 m (18 in.) single-zone furnace (Applied Test Systems). A tube furnace capable of reaching 1100 °C was used as a heat source for the reactor. A K-type thermocouple of 1/16" nominal diameter and 24" nominal length with an inconel sheath ungrounded is inserted into the reactor to measure the temperature of the catalyst bed. The pressure in the reactor is monitored using a sensotec pressure transducer (model no. THE/743-011) with an operating range of 0-2000 psig. Water is pumped continuously to a preheater using an ISCO 2350 stainless-steel high-performance liquid chromatograph (HPLC) pump. The temperature of the preheater is maintained at 170 °C in order to vaporize the water. A thermocouple is inserted at the centre of the preheater and the temperature is controlled by a temperature program controller. All feed lines from the pump outlet are heat-traced and insulated to ensure vaporization of the water when it mixes with other feed gases (CO/He/Ar).

The reactant gases coming from the mass-flow controllers are well mixed with

Figure 2. Schematic diagram of experimental setup for WGS reaction.

steam in the preheater before being sent into the reactor. The feed lines between the preheater and the reactor inlet are maintained at 160 °C by wrapping the line with heating tapes.

The product from the reactor outlet consists of CO, CO₂, He, Ar, H₂ and H₂O. The product stream is analyzed using a six-port 0.5 ml external-volume gas-sampling valve (Valco instrumentation Co. Inc) as shown in Figure 3. With the valve in position “A”, sample flows through the external loop while the carrier gas (argon) flows directly to the chromatographic column. When the valve is in position “B”, the sample contained in the sample loop and valve flow passage is injected onto the column. The sampling valve is maintained at reaction pressure and, at a temperature of 130 °C. A chiller with water as coolant is used between the reactor outlet and sampling valve to decrease the temperature of the hot gases from the reactor outlet to the temperature of the sampling valve. The exit gas from the sampling loop is sent to the condenser through the back-pressure regulator, used to maintain the required pressure in the reactor. Water is condensed in the condenser while other gases are released through the scrubber to the vent.

3.2 HP 5890 Gas Chromatograph

The products from the reactor outlet are continuously analyzed using the HP5890 gas chromatograph. A HayeSep-D packed column of 9 m length and 3.1 mm diameter is used for analysis. The packed column is connected to a thermal-conductivity detector (TCD) to analyze the product gases quantitatively. The temperature of the GC oven is maintained at 150°C and the TCD temperature is maintained at 255 °C. Helium gas is used as internal standard gas while Ar is used

Figure 3. Schematic flow diagram of two-position six-port external volume sample injector (Valco Instruments Co. Inc).

carrier gas. The operating conditions of the GC are given in Appendix B. The feed line between the sampling loop and the GC injection port is heated by wrapping the lines with heating (Omega Engineering, Inc) and insulation tapes.

3.3 Calibrations

3.3.1 Calibration of Mass Flow Controllers

As mentioned earlier, the reactor system has four lines for feed gases, each one independently controlled by a Brooks mass-flow controller (MFC). The mass-flow controllers are enclosed in an insulated styrofoam container to minimize the effect of any change in the room temperature on the calibration process. Initially, the gas flow rate for particular MFC is set to the maximum value and the system is allowed to reach steady state. Then, the outlet flows for different set points on each mass-flow meter are measured using a bubble flow meter. The same procedure is repeated for the other MFCs. The process is repeated each time prior to each experiment at the reaction conditions. The equations obtained from MFC calibration curves are given in Table 10.

Table 10. MFC Calibration equations for gases used in WGS reaction

X = set value, Y = measure flow rate.

MFC	Gas	Equation	R ²
CH ₄	H ₂	Y= 1.3284 X- 41.947	0.9991
CO ₂	CO/He	Y= 1.2111X- 89.774	0.9999
Ar	Ar	Y= 1.0188X + 0.46666	1

3.3.2 Calibration of HP5890 Gas Chromatograph

As mentioned earlier, the products are analyzed online by the Hewlett-Packard 5890 GC, which provides quantitative analysis for He, CO, CO₂, H₂O, and H₂ using the thermal-conductivity detector (TCD). All the gases are calibrated by injecting standard gas mixtures of known composition into the injector port from the sampling loop using the auto-injector for the GC. The GC operating conditions are given in Appendix B, while the details of the calculation and the calibration curves are presented in Appendix C.

3.4 Catalyst and Sorbents

A commercial high-temperature-shift (HTS) catalyst comprises of Fe₂O₃/Cr₂O₃/CuO with a composition of 88%/12%/2.5% (weight basis) is used for WGS reaction. CaO, CaO/Ca₁₂Al₁₄O₃₃ (75/25 wt %), and CaO/Ca₁₂Al₁₄O₃₃ (50/50 wt %) sorbents are used for CO₂ adsorption in the present study. CaO is obtained from Alfa Aesar. The sorbent CaO/Ca₁₂Al₁₄O₃₃ in various ratios is synthesized.

3.4.1 Preparation of CaO/Ca₁₂Al₁₄O₃₃ sorbent in various ratios

The preparation of CaO/Ca₁₂Al₁₄O₃₃ requires CaO, aluminum nitrate (Al(NO₃)₃·9H₂O), 2-propanol, and water.

To prepare 40 g of the CaO/Ca₁₂Al₁₄O₃₃ (75/25 wt %) mixture, initially, 34.85 g of powdered calcium oxide is added to 760 ml of water. When CaO is added to water, the hydration of calcium oxide takes place according to:

Because of the volume increase from CaO (16.9 cm³/mol) to Ca(OH)₂ (33 cm³/mol) and the expansion caused by the large quantity of heat released in hydration, ultra-fine Ca(OH)₂ particles can be generated from the cracking and refining of CaO particles.⁵⁸ The formed solution of Ca(OH)₂ is stirred for 2 hours at 75 °C.

In the second step, a solution of aluminum nitrate and 2-propanol is prepared by adding 37.89 g of aluminum nitrate to 150 ml of 2-propanol solvent. Then the solution of aluminum nitrate and 2-propanol is added to the solution of Ca(OH)₂, stirred at a constant temperature of 75 °C. The addition of 2-propanol makes the particle size distribution of hydration product Ca(OH)₂ more uniform in the solution. The water in the sample is removed via drying in air at 120°C overnight. The resulting cake is calcined at 500°C. Calcination at 500 °C leads to the formation of large aggregates of a mixture of calcium oxide and aluminum oxide according to:

In the third step, wet paste is obtained by adding water to the mixture of large aggregates of CaO and Al₂O₃ produced by calcination at 500 °C. The addition of water leads to the hydration of CaO to Ca(OH)₂. Because of the volume increase from CaO to Ca(OH)₂ and the expansion caused by the exothermic hydration of CaO, the aggregates crack and swell, and the regular hexagonal crystalloids of Ca(OH)₂ are generated.⁵⁸

Finally, the formed paste is dried at 120 °C for 2 hours and calcined in air at 900 °C for 2 hours. During this calcination, regular hexagonal Ca(OH)₂ crystalloids

decompose into CaO and H₂O, and transform into a porous network. Then Al₂O₃ reacts with CaO proportionally and generates a new kind of binder, mayenite (Ca₁₂Al₁₄O₃₃) according to:⁵⁸

The binder mayenite (Ca₁₂Al₁₄O₃₃) is distributed uniformly among the CaO particles and a mixture of CaO/Ca₁₂Al₁₄O₃₃ (75/25 wt %) is formed.

To prepare CaO/Ca₁₂Al₁₄O₃₃ (50/50 wt %), a similar procedure is followed. The following amounts are used; 29.07 g of CaO, 75.79 g of Al(NO₃)₃·9 H₂O, 760 ml of distilled water, and 150 ml of 2-propanol.

3.5 Catalyst and sorbent characterization

The interpretation of catalyst performance depends on the study of physical, chemical, and structural properties of the catalyst and on measurement of correlations between these characteristics and catalyst performance. The important catalytic properties of the synthesized catalysts are the catalyst composition, the BET surface area and the pore size distribution, metal dispersion, reducibility, crystal structure, surface morphology and oxidation state of the metals. BET surface area measurements, pore size distribution measurements, temperature-programmed desorption /reduction (TPD/TPR), and X-ray diffraction (XRD) are used for characterization of the catalyst.

3.5.1 XRD measurement

XRD is mainly useful for the determination of change in crystallinity and phase transformation of species present in the HTS catalyst and sorbents during

calcination and reduction steps. X-ray diffraction analysis was performed at room temperature on a Rigaku X-ray diffractometer with rotating anode generators and a monochromatic detector using CuK α radiation (1.5418Å).

Figure 4 shows the XRD pattern of the commercial HTS (Fe₂O₃/Cr₂O₃/CuO) catalyst. Before XRD measurements, the HTS catalyst was calcined at 450 °C in the presence of air overnight. The peaks at 24.1378°, 33.1523°, 35.6112°, 40.8544°, 49.4791°, 54.0892°, 57.4276°, 62.449°, 63.9891°, and 72.2603° in the XRD pattern of the fresh HTS catalyst correspond well to the reference data of Fe₂O₃ from the International Centre for Diffraction Data (ICDD). The XRD result explains that the fresh HTS catalyst is primarily comprised of Fe₂O₃, Cr₂O₃ and CuO crystalline phases are not prominent in the XRD pattern of the calcined HTS catalyst. However, the Cu and Cr could exist in solid solution within the hematite (Fe₂O₃) lattice upon the catalyst preparation.

The XRD image of calcium oxide is shown in Figure 5. The peaks at 29.44°, 32.257°, 37.418°, 53.913°, 64.20°, 67.437°, and 88.590° match well to the reference data of calcium oxide from ICDD. No other phases are found.

The XRD patterns of the synthesized sorbents CaO/Ca₁₂Al₁₄O₃₃ in the ratios 75/25, and 50/50 are shown in Figures 6 & 7 respectively. The peaks at 32.18°, 37.319°, 53.817°, 67.296°, 79.627°, and 88.65° in Figures 6 & 7 match well to the reference data of CaO from ICDD, with the peak at 37.319° being the most prominent. The peaks at 18.09°, 20.91°, 23.46°, 27.79°, 28.741°, 33.396°, 36.073°, 38.227°, 41.21°, 46.64°, 55.21°, 56.40°, and 57.46° match well to the reference data of mayenite (Ca₁₂Al₁₄O₃₃), with the peak at 18.09° being the most prominent. The

Figure 4. XRD pattern of HTS (Fe₂O₃/Cr₂O₃/CuO) catalyst.

Figure 5. XRD pattern of calcium oxide.

Figure 6. XRD pattern of $\text{CaO}/\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ (50/50 wt %) sorbent.

Figure 7. XRD pattern of CaO/Ca₁₂Al₁₄O₃₃ (75/25 wt %) sorbent.

XRD patterns of the $\text{CaO}/\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ mixtures, both 75/25 wt % and 50/50 wt % indicate that they contain mainly calcium oxide and mayenite ($\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$). No other phases are found. The major peak for CaO (37.319°) is much more pronounced relative to the major peak for mayenite (18.09°) in Figure 7 relative to Figure 6, as expected.

3.5.2 Scanning electron microscopy

The surface morphology of the commercial HTS catalyst ($\text{Fe}_2\text{O}_3/\text{Cr}_2\text{O}_3/\text{CuO}$) is obtained using a Hitachi S-4700 scanning electron microscope (SEM), with X-ray energy dispersive spectroscopy (EDS) used to determine local elemental composition. The sample is placed on conductive double-faced tape and then placed in the Hitachi S-4700.

As shown in Figure 8, the HTS catalyst is highly porous, with a grain-like structure. The main elements present in the HTS catalyst are shown in Figure 9 as chromium, iron, copper, oxygen, and carbon. The peak corresponding to gold is due to the use of gold as conductive material for specimen coating.

3.5.3 Brunauer-Emmett-Teller (BET) Surface Area Measurement

The most common method for measuring the surface area of HTS catalyst is the Brunauer, Emmett and Teller (BET) method. The BET surface area and pore volume of the calcined HTS catalyst ($\text{Fe}_2\text{O}_3/\text{Cr}_2\text{O}_3/\text{CuO}$) are measured by the isothermal adsorption of N_2 77K in a Coulter Omnisorp 360 system. Prior to the adsorption measurements, the sample is degassed under a vacuum at 300°C for 2 hours. The surface area and pore volume of the HTS catalyst are given in Table 11.

Table 11. Morphological properties of HTS catalyst

HTS Catalyst HIFUELW210	Surface area (m ² /g)	Pore volume (ml/g)	Average pore diameter (Å°)
(Fe ₂ O ₃ /Cr ₂ O ₃ /CuO)	193.09	0.21	169

Figure 8. SEM image of HTS (Fe₂O₃/Cr₂O₃/CuO) catalyst.

Figure 9. EDS spectrum of HTS ($\text{Fe}_2\text{O}_3/\text{Cr}_2\text{O}_3/\text{CuO}$) catalyst.

3.6 Pelletization of HTS catalyst and sorbents

The powdered calcium oxide, $\text{CaO}/\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ (75/25 wt %, 50/50 wt %), and HTS catalyst ($\text{Fe}_2\text{O}_3/\text{Cr}_2\text{O}_3/\text{CuO}$) were each pelletized by applying a pressure of 10 tons for 5 minutes. The formed HTS catalyst pellets were crushed and sieved into grains of 0.84-0.042 mm (20-40 mesh) in size. Sorbents were crushed and sieved into particles of 0.42-0.25 mm (40-60) in size.

3.7 Pretreatment of the HTS ($\text{Fe}_2\text{O}_3/\text{Cr}_2\text{O}_3/\text{CuO}$) catalyst and sorbents

The commercial HTS ($\text{Fe}_2\text{O}_3/\text{Cr}_2\text{O}_3/\text{CuO}$) catalyst obtained from Alfa Aesar was calcined in air at 450°C for 3 hours. The reduction process used for the catalyst involves two steps. In the first step, the HTS catalyst was heated up to 120°C with a ramp rate of $5^\circ\text{C}/\text{min}$ in the presence of Ar. During this heating, any moisture content on the catalyst was evaporated. In the second step, the catalyst was

reduced in the presence of H_2/Ar (10/90 %) with a ramp rate of 5 °C/min up to 300 °C. The catalyst was held at 300 °C for 3 hours. A total flow of 170 sccm was used for reduction. Prior to each experiment, the catalyst was purged with a flow rate of 200 sccm for 2 hours in order to remove any traces of hydrogen on the surface of the catalyst.

The CaO sorbent is calcined in air at 600 °C for 2 hours while the $\text{CaO}/\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ (75/25 wt% and 50/50 wt %) sorbent is calcined in air at 900 °C for 1.5 hours.

3.8 Feed gas compositions

The gases used for all experiments are 100% ultrahigh-pure argon and CO/He (95/5%). The H_2O is pumped by using a HPLC liquid pump. The reaction mixture used for the WGS reaction alone comprised of CO , Ar , H_2O , and He with a ratio of 1:2:1.44:0.00055. A steam-to- CO ratio of 2 was used for the study of effect of temperature on CO conversions. A total flow of 200 sccm was used for each experiment.

For the combined WGS and carbonation reactions, the feed gas composition $\text{CO}/\text{H}_2\text{O}/\text{Ar}/\text{He}$ of 1/2/2.7/0.0524 was used. A total feed rate of 380 sccm was used for each experiment. The combined reactions are conducted in two modes. In the first mode, the HTS catalyst and sorbent are mixed together and placed in the reactor as a single bed. This concept is also called sorption-enhanced water-gas shift reaction (SEWGS). In the second mode, the HTS catalyst and the sorbent are kept as separate beds separated by quartz chips. This is to understand better the

role of the sorbent in the sorption-enhanced process. The schematic diagrams of the two modes are shown in Figure 10.

3.9 Reactor loading

The stainless-steel reactor tube was washed with soap solution and dried using air. For the WGS reaction, 200 mg of the catalyst was used for each experiment. For both modes of the combined WGS and carbonation reactions, a catalyst weight of 200 mg and a sorbent weight of 2.5 g are used. For these experiments, the amounts of catalyst and sorbent were not varied. The catalyst (and sorbent) were diluted with 1/32" quartz chips. Approximately 42 g of the 1/16" quartz chips were used for each experiment. The fresh quartz chips were washed and dried before loading into the reactor. About half of the quartz chips were inserted into the top of the reactor, over a plug of quartz wool (used because of its stability up to 1000°C and its inert nature). The catalyst system (0.2 g of catalyst and 0.8 g of fine quartz chips for the catalyst-alone set up, and 0.2 g catalyst, 2.5 g sorbent, and 5.8 g of quartz chips for the combined mode) was inserted into the centre of the reactor over quartz wool. A thermocouple was inserted into the reactor such that the end of the thermocouple touched the bed of the catalyst-chips system at the centre. The remaining part of the reactor was filled with rest of the quartz chips. The top end of reactor exit was covered with a second plug of the quartz wool and the reactor was placed into the furnace.

The reactor system was tested for leaks by flowing argon gas under a pressure of 40 psig at room temperature. To avoid the condensation of steam (H_2O) in the feed lines between the evaporator and reactor inlet, the lines

Figure 10. Schematic diagram of reactor with (1) HTS catalyst and sorbent mixture, (2) HTS catalyst and sorbent separated with chips.

were heat-traced and maintained at 150 °C using heating tapes with insulation into the reactor.

3.10 Blank tests

Blank tests were conducted to study the activity of WGS reaction in the absence of the catalyst or sorbent. In this case, the tube reactor was totally filled with 1/16" quartz chips without catalyst. The pressure in the reactor was maintained at 1 atm for all the blank runs.

3.11 Study of catalytic activity of sorbents towards WGS reaction

Experiments were conducted to study the catalytic activity of the sorbents CaO and CaO/Ca₁₂Al₁₄O₃₃, both 75/25 wt%, and 50/50 wt%, towards WGS and CO conversion without any HTS catalyst at 500°C. Sorbent particles of 40-60 mesh were used for each experiment. 2.5 g of the sorbent was used for each experiment. The pressure in the reactor was maintained at 1 atm for all the experiments.

3.12 Study of WGS reaction

The WGS reaction was conducted using the high-temperature shift (HTS) catalyst (Fe₂O₃/Cr₂O₃/CuO) obtained from Alfa Aesar. Catalyst particles of 20-40 mesh were used for all the experiments. 0.2 g of HTS catalyst was used for each experiment. The reactor outlet gas mixture comprised of CO, H₂O, CO₂, H₂, He, and Ar was continuously measured using the GC. The reactions were conducted at temperatures ranging from 350–600 °C, and with two different steam-to-CO ratios (H₂O/CO), 1:1 and 2:1. The pressure in the reactor was maintained at 1 atm for all the runs.

3.13 Combined WGS and carbonation reactions in two different modes

The combined WGS and carbonation reactions in two different modes (described in Section 2.6.3 and 2.10) were conducted using the same fixed-bed reactor setup described earlier. A commercial HTS catalyst comprised of $\text{Fe}_2\text{O}_3/\text{Cr}_2\text{O}_3/\text{CuO}$ was used. CaO and $\text{CaO}/\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ in various ratios (75/25 wt % and 50/50 wt %) were used as sorbents in this study. Typically, 0.2 g of the catalyst and 2.5 g of the sorbent were used for each experiment.

The experiments were conducted at 500 °C with a $\text{H}_2\text{O}/\text{CO}$ ratio of 2 at 1 atm pressure. A total gas flow rate of 380 sccm with a composition of CO -17.54%, He -0.92%, H_2O -34.67%, and Ar -46.87% was used for each experiment.

Before each experiment, the HTS ($\text{Fe}_2\text{O}_3/\text{Cr}_2\text{O}_3/\text{CuO}$) catalyst was reduced using a gas mixture of H_2/Ar (10/90%) for 2 hours. Then the system was flushed with argon (100%) with a flow rate of 200 sccm to remove any traces of hydrogen present on the catalyst surface.

3.14 Safety considerations

The safety requirements are continuously reviewed. The most important areas of concern deal with high operating temperatures, toxicity of chemicals, compressed cylinders, electrical connections, and flammability of gases. Since the reactions are operated at high temperature, safety goggles, lab coat, and gloves are used while working near the equipment. Latex gloves are used while handling chemicals. Compressed cylinders are always secured firmly and valve protective caps are kept in place when cylinders are not in use.

Chemicals are stored in proper conditions and the iron/ chromium/ copper catalyst used in this study is tightly sealed in a container and stored in a cool, dry place.

Hydrogen, carbon monoxide, and methane are highly flammable. Therefore, these gases are always kept away from a heat source. The computer continuously monitors flows of reactive gases, hood velocity, ambient hood temperature, reactor temperature, pressure, and electric power. The quality of air inside the laboratory area is controlled using gas sensors which are connected to the emergency alarms. The laboratory is provided with chemical hoods, fire extinguishers, chemical safety showers, chemical split kit, and eye wash stations. Material Safety Data Sheets (MSDSs) have been obtained for all the chemicals used in the laboratory and are placed in accessible place in the laboratory. Food and beverages are always avoided while working in the laboratory.

CHAPTER 4 RESULTS AND DISCUSSION

4.1 Thermodynamics of WGS reaction

The equilibrium constant (K_e) of the WGS reaction (1) is expressed by

$$K_e = \frac{X_e^2}{(1 - X_e)(M - X_e)} \quad (25)$$

where X_e is the equilibrium conversion, K_e is the equilibrium constant, and M is the number of moles of water per moles of CO at the inlet. The equilibrium constant (K_e) of the WGS reaction in the temperature range of 350-1000°C was calculated by using the CHEMEQ-BAS software and shown in Figure 11 (This is identical to Figure 1 and is reproduced here for convenience). Since the WGS reaction is reversible and slightly exothermic in nature, the equilibrium constant (K_e) of the WGS reaction decreases with increasing temperature. From Equation 25, the value of equilibrium conversion (X_e) also decreases with increasing temperature. On a thermodynamic equilibrium basis, it is desirable to perform the WGS reaction at low temperatures. However, the reaction kinetics are very slow at low temperatures. On the other hand, at high temperatures, the reaction kinetics are fast but the equilibrium constant and the equilibrium conversion are low. Consequently, the optimum conversion is obtainable at optimum temperature where the reaction kinetics and equilibrium are favorable.

4.2 Effect of the H₂O/CO ratio on equilibrium CO conversion (X_e)

The effect of inlet H₂O/CO ratio on equilibrium conversion (X_e) is shown in Figure 12. The calculation procedure for equilibrium CO conversions for various

Figure 11. Effect of temperature on equilibrium constant (K_e) of WGS reaction.

H_2O/CO ratios is given in Appendix E. From Figure 12, it can be observed that the equilibrium conversion of CO, and hence the H_2 yield, decreases with increase in temperature. This is consistent with Figure 11. For instance, a CO conversion of 82 % obtained at 350 °C is reduced to 69% at 450 °C for same H_2O/CO ratio ($H_2O/CO = 1$). The equilibrium CO conversion increases with the increase in the H_2O/CO ratio at the same temperature. Increasing the amount of H_2O increases the forward rate of reaction. For example, the conversion of CO is 73 % at 450 °C for a H_2O/CO ratio of 1 while it is 90% for a H_2O/CO ratio of 2:1. However, the use of very high steam-

to-CO ratios (greater than 5:1) has little effect on CO conversion. Also, the production of large amount of steam from water requires more energy. Therefore, a $\text{H}_2\text{O}/\text{CO}$ ratio of 2 to 3 is reasonable for the WGS reaction.

Figure 12. Effect of inlet $\text{H}_2\text{O}/\text{CO}$ ratio on CO conversion at thermodynamic equilibrium

4.3 Effect of sorbent presence on equilibrium CO conversion (X_e)

The effect of different levels of CO_2 capture on the equilibrium CO conversion of WGS reaction as a function of $\text{H}_2\text{O}/\text{CO}$ ratios at a temperature of 500 °C is shown in Figure 13. The calculation procedure for the effect of the sorbent on equilibrium

CO conversions is given in Appendix F. The removal of CO_2 from the reaction zone decreases the rate of the reverse reaction. This is equivalent to decreasing the value of $\text{H}_2\text{O}/\text{CO}$ ratio at the inlet. For example, a CO conversion of 90% is possible at 500 °C with a $\text{H}_2\text{O}/\text{CO}$ ratio of 2.5 while approximately the same equilibrium conversion (X_e) is obtainable at 500 °C with a $\text{H}_2\text{O}/\text{CO}$ ratio of 1 in the presence of a sorbent that can capture 75% of the CO_2 product. This is in accordance with Le Chatelier's principle, by which the removal of one product from the reaction zone will drive an equilibrium-limited reaction in the forward direction. Therefore, the steam usage may be greatly reduced,

Figure 13. Effect of CO_2 removal on equilibrium CO conversion of WGS reaction at 500 °C for various $\text{H}_2\text{O}/\text{CO}$ ratios.

resulting in less operating cost. The higher equilibrium conversion of CO to H₂, compared to that obtained in conventional WGS reactions without CO₂ removal, allows a higher operating temperature of the reactor, resulting in faster kinetics.

4.4 Activity of the blank reactor

Blank tests were conducted to study the activity of WGS reaction in the absence of the catalyst. In this case, the reactor was totally filled with quartz chips of size 1/16" without catalyst. The details of the reactor loading are given in Section 3.11. Experiments were carried out in the temperature range of 450-600 °C and a pressure of 1 atm. The stainless-steel reactor was pretreated using a gas mixture of H₂/Ar (10/90%) with a total flow rate of 170 sccm at 300°C for 3 hours. The pretreatment was performed at atmospheric pressure and was similar to that for catalyst testing. Subsequently, the temperature was increased with a ramp rate of 5 °C/min to the reaction temperature. The system was purged with 100% Ar with a flow rate of 200 sccm for 2 hours to remove any traces of hydrogen in the reactor. Then the feed gas comprised of CO, He, Ar, and H₂O was introduced into the reactor. The feed ratio used for each experiment was CO: H₂O: Ar: He = 1:2:1.44:0.0055 with a total flow rate of 200 sccm.

The effect of temperature on the activity of the stainless-steel reactor for WGS reaction in the range of 450-600 °C is shown in Figures 14 & 15. There is negligible activity of the WGS reaction between 450-500 °C and almost no products are observed. Between 550-600° C, carbon monoxide conversion and hydrogen flow rates are measurable but small, and of the order of GC measurement error.

Figure 14. Effect of reaction temperatures on the activity of the blank reactor for WGS reaction (Total pressure: 1 atm, H₂O/CO: 2, 22 % CO, total flow: 200 sccm).

Figure 15. Formation of H₂ gas in the blank reactor during the WGS reaction at different temperatures (550-600 °C) (Total pressure: 1 atm, H₂O/CO: 2, 22 % CO, total flow: 200 sccm).

4.5 Thermodynamics and kinetics of the WGS reaction

Experiments were carried out to study the activity of the HTS catalyst ($\text{Fe}_2\text{O}_3/\text{Cr}_2\text{O}_3/\text{CuO}$) for the WGS reaction in the temperature range of 350-600 °C at 1 atm pressure. The experiments were performed with a reaction gas mixture comprising of CO, He, CO_2 , Ar, and H_2O . The total feed ratio used was CO: H_2O : Ar: He = 1:2:1.44:0.0055, with a total feed rate of 200 sccm. Typically, 0.2 g of HTS catalyst of 20-40 mesh was loaded for each experiment.

The catalytic activity of the HTS catalyst (carbon monoxide conversion) was obtained from the difference between inlet and outlet compositions. The activity increases monotonically as the temperature increases which is evident from Figure 16. The CO conversion increases from 21% at 350 °C to 75 % at 500 °C. Beyond 500 °C, the conversion does not change much. This is due to the thermodynamic limitations imposed on the WGS reaction. These data were further analyzed to determine whether the system was operated within the range of thermodynamic equilibrium as determined in Figure 12.

The comparison of experimental and equilibrium CO conversions is shown in Figure 17. From the figure, it can be seen that the reaction system is operated in the region below the thermodynamic equilibrium. The equilibrium conversion (X_e) decreases continuously with increasing temperature. In contrast, the experimental conversion (X) increases with respect to temperature studied within the range of 350-600 °C. Thus at 600 °C, the experimental conversion (X) increases to 0.765 while the equilibrium conversion (X_e) decreases to 0.795. It is clearly evident from

Figure 16. Effect of reaction temperature on the CO conversion (0.25 g of HTS catalyst, P: 1 atm, 22.2 % CO, H₂O/CO: 2, total flow: 200 sccm).

Figure 17 that the system moves closer to equilibrium as temperature increases from 350° C to 600 °C.

Figure 17. Comparison of equilibrium and experimental CO conversions for WGS reaction in the temperature range of 350-600 °C (0.25 g of HTS catalyst, 22.2 % CO, P: 1 atm, H₂O/CO: 2, total flow: 200 sccm).

4.6 Effect of the reaction temperature on CO conversion for various

H₂O/CO ratios

The effect of reaction temperature on CO conversions for two different H₂O/CO ratios is given in Figure 18. The conversion increases with increase in the H₂O/CO ratio. For example, the conversion of CO is 58 % at 500 °C for a H₂O/CO ratio of 1, while it is 75 % for H₂O/CO ratio of 2. The increased concentration of reactant H₂O increases the rate of the forward reaction. From Figure 18, it is also

observed that, as the temperature increases, the CO conversions increase for both $\text{H}_2\text{O}/\text{CO}$ ratios. However, the effect of $\text{H}_2\text{O}/\text{CO}$ ratio is small at low temperatures, and increases with increase in temperature. Also, the comparison of equilibrium and experimental CO conversion for two different $\text{H}_2\text{O}/\text{CO}$ ratios at various temperatures is given in Figure 18.

4.7 Kinetics of WGS reaction

Assuming both sides of the WGS reaction to be of first order in each component, the forward and reverse kinetic parameters, k_f and k_r were calculated. The activation energy (E_a) and pre-exponential factor (k_0) of the WGS reaction were calculated using the Arrhenius equation. The calculation procedure is given in Appendix H.

Figure 18. Effect of $\text{H}_2\text{O}/\text{CO}$ ratio on CO conversion for various temperatures (0.25 g of HTS catalyst, 22.2 % CO, $\text{H}_2\text{O}/\text{CO}$: 1, 2, P: 1 atm, total flow: 200 sccm).

The rate equation for the WGS reaction is given below:

$$-r = k_f [P_{CO}][P_{H_2O}] - k_r [P_{H_2}][P_{CO_2}] \quad (26)$$

where,

$-r$ = rate of consumption of CO, H₂O

P_{CO} , P_{H_2O} , P_{CO_2} , and P_{H_2} , are the partial pressures of CO, H₂O, CO₂, and H₂

The parameters k_f and k_r are related to the equilibrium constant (K_e) by:

$$K_e = \frac{k_f}{k_r} \quad (27)$$

The rate constants k_f and k_r are related to the absolute temperature T by:

$$k = k_0 \exp(E_a / RT)$$

where,

k_0 = pre-exponential factor (mol/min/g catalyst/ (atm)²

E_a = activation energy (kJ/mol)

R = universal gas constant (J/mol.K)

The forward and reverse reaction constants, k_f and k_r of the WGS reaction over HTS catalyst are calculated and summarized in Table 12. The calculation procedure is given in Appendix H. From the table, as the temperature increases, the rate constants, k_f and k_r increase. The activation energy (E_a) and pre-exponential factor from the data in Table 12 are obtained from Figure 19 and given in Table 13.

Also shown in Table 13 are the corresponding values from the literature. The values obtained in the present work fall in the range of values obtained in the literature.

Table 12. Forward (k_f) and reverse (k_r) reaction constants of WGS reaction at different temperatures

T (K)	K_e	k_f (mol/sec/g catalyst/atm ²)	k_r (mol/sec/g catalyst/(am) ²)
623	20.44	4.48×10^{-4}	2.19×10^{-5}
673	11.73	1.92×10^{-3}	1.64×10^{-4}
698	9.17	3.82×10^{-3}	4.17×10^{-4}
723	7.31	7.52×10^{-3}	1.02×10^{-3}
773	4.87	1.40×10^{-2}	2.87×10^{-3}
823	3.43	1.60×10^{-2}	4.68×10^{-3}

Figure 19. Arrhenius plot for WGS reaction (T: 350-550 °C, catalyst weight: 0.2 g, 22 % CO, H₂O/CO: 2, P: 1 atm).

Table 13. Arrhenius parameters for the WGS reaction over various HTS catalysts

Catalyst name	E_a (kJ/mol)	$\ln k_0$	Reference
Fe ₂ O ₃ /Cr ₂ O ₃ /CuO (88%/8.1%/2.5%)	79.01	7.8	current work
Fe ₂ O ₃ /Cr ₂ O ₃ /CuO (80-90%/8-13%/1-2%)	111	6.55	58
Fe ₂ O ₃ /Cr ₂ O ₃ /CuO	85	5.5±0.1	60
Fe ₂ O ₃ /Cr ₂ O ₃	118±1	10.1±0.2	59

4.8 Study of sorbent activity for WGS reaction without catalyst

Experiments were conducted to study the catalytic activity of the sorbents CaO and CaO/Ca₁₂Al₁₄O₃₃ (75/25 wt % and 50/50 wt %) towards WGS and CO conversion without any HTS catalyst at 500°C. The CO conversions of WGS reaction over various sorbents are given in Figure 20. The product profiles are given in Figure 21.

The CaO sorbent does not show any catalytic activity. The CaO/Ca₁₂Al₁₄O₃₃, materials, both 75/25 and 50/50, show minute activity towards the WGS reaction at 500 °C. The CO conversion is around 2-3 % in this range.

Figure 20. Catalytic activity of sorbents towards WGS reaction (T: 500 °C, sorbent: CaO/Ca₁₂Al₁₄O₃₃ (75/25 and 50/50 wt %), sorbent weight: 2.5 g, Pressure: 1 atm).

Figure 21. Formation of hydrogen during WGS reaction over sorbents (T: 500 °C, sorbents: $\text{CaO}/\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ 75/25 wt % and $\text{CaO}/\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ 50/50 wt %, sorbent weight: 2.5 g, Pressure: 1 atm).

4.9 Combined WGS and carbonation reactions with HTS catalyst-sorbent system

The combined WGS and carbonation reactions were conducted in two different modes. In the first case, the catalyst and sorbent were mixed uniformly and kept in the reactor as single bed. This concept is also called sorption-enhanced WGS reaction. In the second case, the HTS catalyst and sorbent were kept as separate beds with separation by quartz chips.

4.9.1 HTS catalyst and sorbent mixture

The sorption-enhanced WGS reaction was carried out at 500 °C with an operating pressure of 1 atm. The following reactions take place during the sorption-enhanced WGS reaction:

Typically 0.2 g of HTS catalyst and 2.5 g of sorbent (CaO or CaO/Ca₁₂Al₁₄O₃₃) were mixed thoroughly and diluted with fine quartz chips with a ratio of 1:4. Then the catalyst-sorbent system was loaded into the reactor. Subsequently, the HTS catalyst-sorbent system was reduced at 300°C using H₂/Ar (10/90 %) with a total flow of 170 sccm for 2 hours. Then, the system was purged with argon for 2 hours to remove any trace amount of hydrogen on the surface of the HTS catalyst. Finally, the reaction gas mixture with a composition of CO-17.54%, He-0.92%, H₂O-34.67%, and Ar-46.87% was allowed to flow through the reactor-system.

The reaction was conducted for 3 hours. The GC continuously monitored the flow of product gases from reactor outlet with an interval of 8 min. Since CO₂ has retention time of 6.3 minutes, product analysis was carried out using gas chromatograph with a time interval of 8 minutes. For instance, if sample is injected at 8th min, the product data will be obtained at 8th, 16th, 24th, 32th minute etc. Similarly, if the sample is injected at 7th minute, the product data will be obtained at 7th, 15th, 23rd, 31th minute etc. Therefore, a series of experiments were conducted to get the product data at each minute in the time range.

The profiles of CO₂, CO, and H₂ from the reactor outlet for sorption-enhanced WGS over HTS-CaO, HTS-CaO/Ca₁₂Al₁₄O₃₃ (75/25 wt %), and HTS-CaO/Ca₁₂Al₁₄O₃₃ (50/50 wt %) are given in Figures 22-24 respectively. From the figures, it can be observed that the sorption-enhanced WGS reaction will proceed in three different phases: sorbent-enhancement (pre-breakthrough), sorbent breakthrough, and post-breakthrough steady-state operation.

Figure 22. Profiles of product gases for sorption-enhanced WGS reaction over HTS-CaO sorbent system (T: 500 °C, total flow: 380 sccm, H₂O/CO: 2, CO: 17.54 %, He: 0.92 %, Ar: 46.81 %, H₂O: 34.67 %).

During the sorbent enhancement phase, both WGS and the carbonation reactions are active, and hence the sorbent adsorbs nearly all of the CO₂ produced. The CO in the outlet stream is negligible, and the amount of H₂ produced is at its

maximum during this period. For instance, in the case of the HTS-CaO system shown in Figure 22, no CO is detected in the outlet for upto 5 mins during the sorbent enhancement period. Similarly, for the HTS-CaO/Ca₁₂Al₁₄O₃₃ (75/25 wt %) system, no CO is observed in the reactor outlet for upto 5 mins during this period. In the case of HTS-CaO/Ca₁₂Al₁₄O₃₃ (50/50 wt %) system, no CO is observed in the reactor outlet for upto 3 mins.

Figure 23. Profiles of product gases for SEWGS reaction over HTS catalyst-CaO/Ca₁₂Al₁₄O₃₃ (75/25 wt %) sorbent system (T: 500 °C, total flow: 380 sccm, H₂O/CO: 2, CO: 17.54 %, He: 0.92 %, Ar: 46.81 %, H₂O: 34.67 %).

Figure 24. Profiles of product gases for SEWGS reaction over HTS catalyst-CaO/Ca₁₂Al₁₄O₃₃ (50/50 wt %) sorbent system (T: 500 °C, total flow: 380 sccm, H₂O/CO: 2, CO: 17.54 %, He: 0.919 %, Ar: 46.808 %, H₂O: 34.67 %).

During the second, sorbent-breakthrough, phase, the activity of the carbonation reaction decreases due to the continuous use of sorbent. This leads to an increase in the CO outlet molar flow rate. For the HTS-CaO system, the CO outlet molar flow rate increases from approximately 0 to 0.72 mmol/min during the sorbent-breakthrough period which lasts approximately 35 minutes. The H₂ outlet molar flow rate decreases from approximately 3.04 mmol/min to 2.38 mmol/min, while CO₂

outlet molar flow rate increases from approximately 0 mmol/min to 2.34 mmol/min. This corresponds to a change in mole fraction for H_2 from approximately 27.0 mol % to 17.7 mol % (dry basis) and for the CO_2 from approximately 0 mol % to 17.2 mol % (dry basis).

For the HTS- $CaO/Ca_{12}Al_{14}O_{33}$ (75/25 wt %) sorbent system, the sorbent-breakthrough period starts at the 6th minute and ends approximately at the 29th minute. The CO outlet molar flow rate increases from approximately 0 to 0.69 mmol/min during this period. The H_2 outlet molar flow rate decreases from approximately 3.04 mmol/min to 2.35 mmol/min while the CO_2 outlet molar flow rate increases from approximately 0 mmol/min to 2.33 mmol/min. This corresponds to a change in mole fraction for H_2 from approximately 26.1 mol % to 17.5 mol % and for the CO_2 from approximately 0 mol % to 17.1 mol % (all dry basis).

For the HTS- $CaO/Ca_{12}Al_{14}O_{33}$ (50/50 wt %) system, the sorbent-breakthrough starts at the 4th minute and ends at the 20th minute. During this period, the CO outlet molar flow rate increases from approximately 0 to 0.70 mmol/min. The H_2 outlet molar flow rate decreases from approximately 3.04 mmol/min to 2.36 mmol/min while the CO_2 outlet molar flow rate increases from approximately 0 mmol/min to 2.34 mmol/min. This corresponds to a change in mole fraction for H_2 from approximately 26.9 mol % to 17.6 mol % and for the CO_2 from approximately 0 mol % to 17.3 mol % (all dry basis).

During the post-breakthrough period, the sorbent is nearly saturated, and hence there is little or no effect of sorbent presence on the CO conversion for WGS reaction. The comparisons of CO outlet molar flow rates for the WGS reaction over

the catalyst alone and over the catalyst-sorbent mixtures are given in Figures 25, 26, and 27 for sorbents CaO, $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ 75/25 wt %, and $\text{CaO}/\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ 50/50 wt % respectively.

Figure 25. Comparison of CO outlet molar flow rates for WGS reaction over HTS catalyst-CaO sorbent mixture and HTS catalyst alone (Catalyst: $\text{Fe}_2\text{O}_3/\text{Cr}_2\text{O}_3/\text{CuO}$, T: 500°C, $\text{H}_2\text{O}/\text{CO}$: 2, total flow: 380 sccm, P: 1 atm).

Figure 26. Comparison of CO outlet molar flow rates for WGS reaction over HTS catalyst- $\text{CaO}/\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ (75/25 wt %) sorbent mixture and HTS catalyst alone. (Catalyst: $\text{Fe}_2\text{O}_3/\text{Cr}_2\text{O}_3/\text{CuO}$, T: 500°C, $\text{H}_2\text{O}/\text{CO}$: 2, total flow: 380 sccm, P: 1 atm).

Figure 27. Comparison of CO outlet molar flow rates for WGS reaction over HTS catalyst-CaO/Ca₁₂Al₁₄O₃₃ (50/50 wt %) sorbent mixture and HTS catalyst alone. (Catalyst: Fe₂O₃/Cr₂O₃/CuO, T: 500°C, H₂O/CO: 2, total flow: 380 sccm, P: 1 atm).

The outlet flow rates in the presence of the sorbent are considerably lower in the first two stages and somewhat lower in the post-breakthrough period. It should be noted that, although Figures 22-27 extend only up to $t = 40$ minutes, the runs were carried out upto 120 mins. No significant changes were observed between 40-120 minutes.

The comparisons of CO₂ outlet molar flow rates of WGS reaction over catalyst alone and the catalyst-sorbent mixture using sorbents CaO, Ca₁₂Al₁₄O₃₃ 75/25 wt %, and CaO/Ca₁₂Al₁₄O₃₃ 50/50 wt % are given in Figures 28, 29, and 30 respectively.

Figure 28. Comparison of CO₂ outlet molar flow rates for WGS reaction over HTS catalyst-CaO sorbent mixture and HTS catalyst alone (Catalyst: Fe₂O₃/Cr₂O₃/CuO, T: 500°C, H₂O/CO: 2, total flow: 380 sccm, P: 1 atm).

Figure 29. Comparison of CO₂ outlet molar flow rates for WGS reaction over HTS catalyst-CaO/Ca₁₂Al₁₄O₃₃ (75/25 wt %) sorbent mixture and HTS catalyst alone. (Catalyst: Fe₂O₃/Cr₂O₃/CuO, T: 500°C, H₂O/CO: 2, total flow: 380 sccm, P: 1 atm).

Figure 30. Comparison of CO₂ outlet molar flow rates for WGS reaction over HTS catalyst-CaO/Ca₁₂Al₁₄O₃₃ (50/50 wt %) sorbent mixture and HTS catalyst alone. (Catalyst: Fe₂O₃/Cr₂O₃/CuO, T: 500°C, H₂O/CO: 2, total flow: 380 sccm, P: 1 atm).

4.9.2 HTS catalyst and sorbent separated with chips

Experiments were also conducted keeping the catalyst and the sorbents as different beds separated by quartz chips. HTS catalyst (0.2 g) was diluted with quartz chips with a ratio of 1:4 and sorbent (2.5 g) was diluted with a ratio of 1:2. Subsequently, the catalyst-sorbent system was reduced at 300°C using H₂/Ar (10/90 %) with a total flow of 170 sccm for 2 hours. Then the system was purged with argon for 2 hours in order to remove any trace amounts of hydrogen present on the surface of the HTS catalyst. Finally, the reaction gas mixture with a composition of CO-17.54%, He-0.92%, H₂O-34.67%, and Ar-46.87% was allowed to flow through the system.

The reaction was conducted for approximately 2 hours. The GC continuously monitored the flow of product gases from reactor outlet with an interval of 8 min. The

comparison of outlet molar flow rates of CO for WGS reaction over HTS catalyst alone with HTS-CaO sorbent separated by quartz chips is shown in Figure 31. The comparisons of outlet molar flow rates of CO for sorbents $\text{CaO}/\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$, (75/25 wt % and 50/50 wt %) are shown in Figures 32 and 33, respectively.

Figure 31. Comparison of CO outlet molar flow rates for WGS reaction during the HTS catalyst and CaO sorbent separated with chips and HTS catalyst alone (Catalyst: $\text{Fe}_2\text{O}_3/\text{Cr}_2\text{O}_3/\text{CuO}$, sorbent: CaO , T: 500°C , $\text{H}_2\text{O}/\text{CO}$: 2, total flow: 380 sccm, P: 1 atm).

Figure 32. Comparison of CO outlet molar flow rates for WGS reaction during the HTS catalyst and $\text{CaO}/\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ (75/25 wt %) sorbent separated with chips and HTS catalyst alone (Catalyst: $\text{Fe}_2\text{O}_3/\text{Cr}_2\text{O}_3/\text{CuO}$, T: 500°C, $\text{H}_2\text{O}/\text{CO}$: 2, total flow: 380 sccm, P: 1 atm).

Figure 33. Comparison of CO outlet molar flow rates for WGS reaction during the HTS catalyst and $\text{CaO}/\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ (50/50 wt %) sorbent separated with chips and HTS catalyst alone (Catalyst: $\text{Fe}_2\text{O}_3/\text{Cr}_2\text{O}_3/\text{CuO}$, T: 500°C, $\text{H}_2\text{O}/\text{CO}$: 2, total flow: 380 sccm, P: 1 atm).

From Figures 31, 32, and 33, it can be observed that the presence of sorbent in the reactor as a separate bed affects CO outlet flow rates to a negligible extent, compared to the HTS catalyst alone. According to Le Chatelier's principle, removal of the CO₂ product from the reaction zone should drive the reaction in the forward direction. But in the present case, the sorbent is not present in the reaction zone.

The corresponding product profiles are shown in Figures 34-36, respectively. From the figures, it is observed that the adsorption of CO₂ with sorbents will occur in three different phases similar to those for catalyst-sorbent mixture: the pre-breakthrough period, sorbent-breakthrough, and post-breakthrough steady-state operation.

During the pre-breakthrough period, the CaO sorbent adsorbs all the CO₂ formed for the first 7 minutes while the CaO/Ca₁₂Al₁₄O₃₃ (75/25 wt %) sorbent adsorbs all the CO₂ formed for the initial 6 minutes. The CaO/Ca₁₂Al₁₄O₃₃ (50/50 wt %) sorbent adsorbs all the CO₂ formed for the first 3 mins. The CO₂ breakthrough begins at the 8th minute for the CaO sorbent, at the 7th minute for CaO/Ca₁₂Al₁₄O₃₃ (75/25 wt %), and at the 4th minute for CaO/Ca₁₂Al₁₄O₃₃ (50/50 wt %) sorbent.

The CO₂ concentration increases rapidly for all three sorbents until the post-breakthrough steady state is reached. In the case of the CaO sorbent, the CO₂ outlet molar flow rate increases from 0 mmol/min to 2.81 mmol/min and finally reaches the post-breakthrough period approximately at the 45th minute. Similarly, the CO₂ outlet molar flow rate increases from 0 mmol to 2.33 mmol/min for the CaO/Ca₁₂Al₁₄O₃₃ (75/25 wt %) sorbent and reaches the post-breakthrough period at approximately the 36th minute. For the CaO/Ca₁₂Al₁₄O₃₃ (50/50 wt %) sorbent, the CO₂ outlet molar

flow rate increases from 0 mmol/min to 2.36 mmol/min during the sorbent-breakthrough period which ends approximately at the 28th minute. During the post-breakthrough period, the sorbents are completely saturated and the CO₂ moles obtained are approximately the same as that of HTS catalyst alone.

Figure 34. Profiles of product gases for HTS catalyst and CaO sorbent separated with chips (T: 500 °C, total flow: 380 sccm, H₂O/CO: 2, CO: 17.54 %, He: 0.92 %, Ar: 46.81 %, H₂O: 34.67 %).

Figure 35. Profiles of product gases for HTS catalyst and CaO/Ca₁₂Al₁₄O₃₃ (75/25 wt %) sorbent separated with chips (T: 500 °C, total flow: 380 sccm, H₂O/CO: 2, CO: 17.54 %, He: 0.92 %, Ar: 46.81 %, H₂O: 34.67 %).

Figure 36. Profiles of product gases for HTS catalyst and CaO/Ca₁₂Al₁₄O₃₃ (50/50 wt %) sorbent separated with chips (T: 500 °C, total flow: 380 sccm, H₂O/CO: 2, CO: 17.54 %, He: 0.92 %, Ar: 46.81 %, H₂O: 34.67 %).

4.9.3 Comparison of products with varying reactor contents

The CO₂ product profiles of WGS reaction over HTS catalyst, catalyst and sorbent (CaO, Ca₁₂Al₁₄O₃₃ (75/25 wt%, 50/50 wt %)) separated with chips, and the catalyst-sorbent mixture are given in Figures 37, 38, and 39 respectively. Similarly, the profiles of H₂ are given in Figures 40, 41, and 42.

From Figures 37-39, it is observed that the presence of the sorbent enhances the rate of formation of CO₂ at short times, in the pre-breakthrough period, by

simultaneously adsorbing the CO_2 produced from WGS reaction. This leads to production of high amount of pure hydrogen in the pre-breakthrough period, as shown in Figures 40-42. This trend is observed in all the three sorbents. Since the amount of reactive material in three sorbents is not the same, the pre-breakthrough period for three sorbents is different. However, the presence of sorbent in the reactor does not affect the production of CO_2 or H_2 in the post-breakthrough period, compared to HTS catalyst alone.

Figure 37. Profiles of CO_2 for WGS reaction over HTS-CaO in both modes and HTS catalyst alone (T: 500 °C, total flow: 380 sccm, $\text{H}_2\text{O}/\text{CO}$: 2)

Figure 38. Profiles of CO₂ for WGS reaction over HTS-CaO/Ca₁₂Al₁₄O₃₃ (75/25 wt %) in both modes and HTS catalyst alone (T: 500 °C, total flow: 380 sccm, H₂O/CO: 2).

Figure 39. Profiles of CO₂ for WGS reaction over HTS-CaO/Ca₁₂Al₁₄O₃₃ (50/50 wt %) in both modes and HTS catalyst alone (T: 500 °C, total flow: 380 sccm, H₂O/CO: 2).

Figure 40. Profiles of H₂ for WGS reaction over HTS-CaO in both modes and HTS catalyst alone (T: 500 °C, total flow: 380 sccm, H₂O/CO: 2)

Figure 41. Profiles of H₂ for WGS reaction over HTS-CaO/Ca₁₂Al₁₄O₃₃ (75/25) in both modes and HTS catalyst alone (T: 500 °C, total flow: 380 sccm, H₂O/CO: 2)

Figure 42. Profiles of H₂ for WGS reaction over HTS-CaO/Ca₁₂Al₁₄O₃₃ (50/50) in both modes and HTS catalyst alone (T: 500 °C, total flow: 380 sccm, H₂O/CO: 2)

4.10 Comparison of adsorption capacity of different sorbents for combined WGS and carbonation reactions

The CO₂ capture capacity of sorbent is defined as:

$$\text{Sorption capacity} = \frac{\text{Moles or grams of CO}_2 \text{ adsorbed}}{1000 \text{ grams of sorbent}}$$

The CO₂ capture capacities were determined from the results for both modes, SEWGS and separated beds, conducted at 500 °C with an operating pressure of 1 atm. The calculation procedure is given in Appendix I. The amount of CO₂ captured by the sorbents can be correlated with the time of CO₂ breakthrough and conversion of CO during the WGS reaction.

The CO₂ capture capacity of each sorbent studied is summarized in Table 14. The capacity is given based on the total sorbent weight and on a CaO basis. The breakthrough times are also noted. Among the three sorbents, the CaO sorbent has the largest CO₂ capacity, and CaO/Ca₁₂Al₁₄O₃₃ (50/50 wt %) has the smallest CO₂ capacity value, based on the total weight of the sorbent. This is because the pure CaO sorbent has the largest amount of CaO. As the quantity of Ca₁₂Al₁₄O₃₃ increases in the sorbent, the CO₂ sorption capacity of the sorbent decreases, as shown in Table 14. Also, all the three sorbents have approximately same CO₂ capture capacity in both modes based on CaO weight. From the results, it can be shown that the Ca₁₂Al₁₄O₃₃ in the sorbent acts only as a binder and does not take part in the carbonation reaction as discussed in Section.2.6.3.

In the separated mode, the CaO, CaO/Ca₁₂Al₁₄O₃₃ (75/25), and CaO/Ca₁₂Al₁₄O₃₃ (50/50) adsorb all the CO₂ formed for the first 7, 6, and 3 mins respectively, and finally reach their post-breakthrough period at approximately 45, 36, and 28 mins respectively. The corresponding CO₂ capture values are 8.27, 6.36, and 3.92 mol/Kg respectively. In the combined mode (SEWGS), the sorbent-enhancement period for CaO, CaO/Ca₁₂Al₁₄O₃₃ (75/25), and CaO/Ca₁₂Al₁₄O₃₃ (50/50) last for 6, 5, and 4 mins respectively. The sorbents CaO, CaO/Ca₁₂Al₁₄O₃₃

(75/25), and $\text{CaO}/\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ (50/50) reach their post-breakthrough at approximately 35, 29, and 20 mins respectively. The corresponding capture capacity values are 8.54, 6.36, and 4.16mol/Kg respectively.

The comparison of CO_2 capture capacities obtained in the present study with data in the literature is given in Table 15. The CO_2 capture capacities of sorbents obtained in the present study work fall in the range of values obtained in the literature. However, the CO_2 capture capacities of sorbents reported in the literature vary widely. This wide range may be attributed to the different operating conditions, equipments, and precursors.

The CO_2 sorption capacities with respect to time for three sorbents in the two different modes are given in Figures 43-45. From all three figures, the sorbents mixed with catalyst adsorb slightly more CO_2 than the sorbents kept apart from the catalyst. This increase may be because of the production of more moles of CO_2 in the former case. The capacities for the 75/25 and 50/50 mixtures are compared in Figure 46. The pre-breakthrough adsorption is the same. At larger times, the adsorption is greater for the 75/25 mixture.

Finally, note that the SEWGS reaction over multiple cycles with CaO and $\text{CaO}/\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ sorbents is required to find the best sorbent among them. Since the CaO particles are vulnerable to high calcination temperatures (900-1000°C), the CO_2 capture capacity of the CaO particles over multiple carbonation and calcination cycles decreases. On the other hand, the uniform distribution of $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ among CaO particles provides a stable framework inhibiting the sintering of CaO during the calcination.⁶⁸

Table 14. Capacity (weight basis and CaO basis), pre-breakthrough time, and post-breakthrough time for sorbents

sorbent	CaO		CaO/Ca ₁₂ Al ₁₄ O ₃₃ (75/25)		CaO/Ca ₁₂ Al ₁₄ O ₃₃ (50/50)	
combination	mixed with HTS	separated beds	mixed with HTS	separated beds	mixed with HTS	separated beds
total weight basis (mol/Kg)	8.54	8.27	6.36	6.33	4.16	3.92
CaO basis (mol/Kg CaO)	8.54	8.27	8.48	8.43	8.31	7.84
Pre-breakthrough time (mins)	6	7	5	6	4	3
Post-breakthrough time (mins)	35	45	29	36	20	28

Table 15. Comparison with literature values

Sorbent	Sorption capacity (mol/Kg)		Theoretical sorption capacity (mol/Kg)		Reference
	weight basis	CaO basis	weight basis	CaO basis	
CaO (Alfa Aesar)	8.27-8.54		17.863	17.863	current work
PCC-CaO (Section 2.7.1)	8.18-10.295		17.863	17.863	10
Linwood (LC)-CaO	5.0		17.863	17.863	10
CaO	6.25		17.863	17.863	62
CaO (10 μ m)	1.795		17.863	17.863	63
CaO (10 nm)	16.590		17.863	17.863	64
CaO/Ca ₁₂ Al ₁₄ O ₃₃ (75/25)	6.33-6.36	8.43-8.48	13.386	17.863	current work
CaO/Ca ₁₂ Al ₁₄ O ₃₃ (75/25)	9.545	12.72	13.386	17.863	65
CaO/Ca ₁₂ Al ₁₄ O ₃₃ (75/25)	10.227	13.63	13.386	17.863	67
CaO/Ca ₁₂ Al ₁₄ O ₃₃ (75/25)	8.1318	10.843	13.386	17.863	66
CaO/Ca ₁₂ Al ₁₄ O ₃₃ (75/25)	7.4	9.8	13.386	17.863	68
CaO/Ca ₁₂ Al ₁₄ O ₃₃ (65/35)	5	7.69	11.60	17.863	68
CaO/Ca ₁₂ Al ₁₄ O ₃₃ (50/50)	3.92-4.15	7.842-8.317	8.931	17.863	current work

Figure 43. Adsorption capacity of CaO sorbent with respect to time in different modes

Figure 44. Adsorption capacity of CaO/Ca₁₂Al₁₄O₃₃ (75/25 wt %) sorbent with respect to time in different modes

Figure 45. Adsorption capacity of sorbent CaO/Ca₁₂Al₁₄O₃₃ (50/50 wt %) with respect to time in different modes.

Figure 46. Adsorption capacity of sorbent CaO/Ca₁₂Al₁₄O₃₃ with respect to time in various ratios.

CHAPTER 5 SUMMARY AND FUTURE WORK

5.1 Summary

Based on the various experiments performed for WGS reaction alone and combined WGS and carbonation reactions in the fixed-bed reactor, the following conclusions can be drawn:

1. The commercial HTS catalyst used in the present study was characterized using BET, XRD, and SEM/EDS. The surface area and pore volume of the HTS catalyst are found to be $193.0 \text{ m}^2/\text{g}$ and 0.21 ml/g respectively. The SEM/EDS results show that the HTS catalyst is highly porous, with a grain-like structure, and contains iron, chromium, oxygen, and carbon. The XRD patterns of the HTS catalyst confirm the presence of Fe_2O_3 . However, Cr_2O_3 and CuO crystalline phases are not prominent in the XRD pattern. Perhaps the Cu and Cr exist in solid solution within the hematite lattice. The $\text{CaO}/\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ sorbent was synthesized in a 75/25 ratio following the literature. A 50/50 mixture was synthesized following an analogous procedure. The XRD patterns of the synthesized $\text{CaO}/\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ sorbent, both 75/25 and 50/50, confirm the phases of CaO and mayenite ($\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$). No other phases are found.
2. Blank tests were conducted to study the activity of WGS reaction in the absence of the catalyst or sorbent over a temperature range of 450-600 °C. A total flow of 200 sccm with $\text{H}_2\text{O}/\text{CO}$ ratio of 2 was used. There is negligible activity of the WGS reaction between 450-500 °C and almost no products are

detected. However, between 550-600° C, carbon monoxide conversion and hydrogen flow rates are measurable but small, and of the order of GC measurement error.

3. The WGS reaction was performed using the commercial HTS catalyst ($\text{Fe}_2\text{O}_3/\text{Cr}_2\text{O}_3/\text{CuO}$) alone. The effect of temperature and $\text{H}_2\text{O}/\text{CO}$ ratio on WGS reaction was examined. The CO conversion increases with temperature from 350 °C to 500°C and thereafter it is approximately constant. It is due to the thermodynamic limitations imposed on the WGS reaction. Also, the CO conversion increases with $\text{H}_2\text{O}/\text{CO}$ ratio. In all the cases, the reaction system was operated in the region below the thermodynamic equilibrium. The forward and reverse kinetic parameters, k_f and k_r , of the WGS reaction were determined at different temperatures. The activation energy (E_a) and pre-exponential factor (k_0) of WGS reaction over HTS catalyst were found to be 79.01 KJ/mol and $2.44 \times 10^3 \text{ mol/gcatalyst/sec/atm}^2$ respectively. The values obtained are consistent with reported data in the literature.
4. The CaO does not show any activity towards WGS reaction. The activity of the sorbent $\text{CaO}/\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ (both 75/25 wt% and 50/50 wt %) towards WGS reaction is very small. The CO conversion and hydrogen flow rates are measurable but small, and of the order of GC measurement error.
5. The combined WGS and carbonation reactions were conducted. Conditions are 500 °C and 1 atm with a $\text{H}_2\text{O}/\text{CO}$ ratio of 2. Two different modes were used: catalyst and sorbent well mixed (sorption-enhanced WGS, SEWGS), and catalyst and sorbent separated by quartz chips.

6. The SEWGS reaction proceeds in three phases: sorbent-enhancement, sorbent- breakthrough, and post-breakthrough. During the sorbent-enhancement period, the CO conversion obtained is very high and the amount of H₂ produced is at its maximum. For the HTS-CaO system, no CO₂ is detected in the reactor outlet till after the 6th minute. This period is the sorbent-enhancement period for HTS-CaO system. For the HTS-CaO/Ca₁₂Al₁₄O₃₃ (75/25) system, the sorbent enhancement period lasts for 5 minutes. For the HTS-CaO/Ca₁₂Al₁₄O₃₃ (50/50 wt %), this period lasts for only 4 minutes. The CO₂ is first observed in the reactor outlet for CaO and CaO/Ca₁₂Al₁₄O₃₃ (75/25 wt %), and CaO/Ca₁₂Al₁₄O₃₃ (50/50 wt %) at 7, 6, and 5 minutes respectively. The sorbents CaO, CaO/Ca₁₂Al₁₄O₃₃ (75/25), and CaO/Ca₁₂Al₁₄O₃₃ (50/50) reach their post-breakthrough period at approximately 35, 29, and 20 minutes respectively. The activity of the catalyst-sorbent combinations towards SEWGS decreases in the order of CaO, CaO/Ca₁₂Al₁₄O₃₃ (75/25 wt %), and CaO/Ca₁₂Al₁₄O₃₃ (50/50 wt %) sorbent. The CaO sorbent is found to show slightly better performance towards SEWGS reaction relative to CaO/Ca₁₂Al₁₄O₃₃ (75/25 wt %).
7. To understand the role of the sorbents better, experiments were carried out with the catalyst and each sorbent present in the reactor, but separated by a layer of quartz chips. The presence of any sorbent (CaO, CaO/Ca₁₂Al₁₄O₃₃ whether 75/25 wt % or 50/50 wt %) in the reactor as a separate bed does not affect the CO conversion. Hence, the values obtained are the same as that of HTS catalyst alone. The CaO, CaO/Ca₁₂Al₁₄O₃₃ (75/25 wt %), and

CaO/Ca₁₂Al₁₄O₃₃ (50/50 wt %) adsorb all the CO₂ formed for the first 7, 6, and 3 minutes respectively, and reach their post-breakthrough period at approximately 45, 36, and 28 minutes respectively.

8. The sorption capacities of CaO, CaO/Ca₁₂Al₁₄O₃₃ (75/25 wt %), and CaO/Ca₁₂Al₁₄O₃₃ (50/50 wt %) were determined based both on the total weight of sorbent and on a CaO basis in the sorbent. On the total weight basis, the CO₂ sorption capacities of CaO, CaO/Ca₁₂Al₁₄O₃₃ (75/25 wt %), and CaO/Ca₁₂Al₁₄O₃₃ (50/50 wt %) sorbents in the separated mode are 8.28, 6.33, and 3.92 mol/Kg respectively. In the mixed mode, the corresponding capacities are 8.54, 6.36, and 4.16 mol/Kg respectively. On the CaO basis, the CO₂ capture capacities in the separated mode are 8.43 and 7.84 mol/Kg respectively, while in the combined mode, the corresponding values are 8.48 and 8.31 mol/Kg respectively. Hence, in the mixed (SEWGS) mode, the CO₂ capture capacities of all the sorbents are found to be approximately the same on the CaO basis. From these results, it is observed that the calcium aluminate (Ca₁₂Al₁₄O₃₃) acts as binder and does not necessarily participate in the carbonation reaction. The CO₂ capture capacities of CaO and CaO/Ca₁₂Al₁₄O₃₃ sorbents obtained in the present study fall in the range of values reported in the literature.
9. The SEWGS reaction over multiple cycles with CaO and CaO/Ca₁₂Al₁₄O₃₃ sorbents is required to find the best sorbent among them. Since the CaO particles are vulnerable to high calcination temperatures (900-1000°C), the CO₂ capture capacity of the CaO particles over multiple carbonation and

calcination cycles decreases. On the other hand, the uniform distribution of $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ among CaO particles provides a stable framework inhibiting the sintering of CaO during the calcination.⁶⁸

5.2 Future Work

In the present study, the WGS reaction was studied over HTS catalyst at a specific space velocity and at atmospheric pressure. Future work could involve the study of the WGS reaction at different space velocities and pressure.

The type of catalyst used could also be changed. The Cr_2O_3 in the HTS catalyst creates some environmental problems. Therefore, the HTS catalysts can be prepared by replacing Cr_2O_3 with other oxides. Some examples of these catalysts are $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3/\text{CuO}$ and $\text{Fe}_2\text{O}_3/\text{MoO}_3/\text{CuO}$. Also the effect of catalyst pore size on the activity of WGS reaction can be studied.

In the present study, for all the experiments, the product analysis was carried out with a GC. However, the GC provides product data at times approximately 10 minutes apart. In order to get the product data at shorter intervals (approximately 1 min), a series of experiments had to be done. On the other hand, a mass spectrometer can provide the product analysis almost continuously. Therefore, use of a mass spectrometer can be recommended for future work.

The sorption-enhanced water-gas shift reaction over multiple cycles with HTS catalyst-sorbent mixture can be studied. In these studies, catalyst and sorbent in various sizes can be used, in order to separate catalyst and sorbent from each other once the sorbent is saturated. The sorbent can be calcined in various media, such

as nitrogen, H_2O , and vacuum. The effect of calcination medium on capture capacity can be studied. Also the effect of various $\text{H}_2\text{O}/\text{CO}$ ratios on the SEWGS reaction can be investigated.

The flue gas obtained from the gasifier typically contains impurities such as sulfur (in the form of H_2S) which deactivate the catalyst and also result in the sulfidation reactions with the sorbents. Therefore, the effect of impurities on catalyst and sorbent can be investigated.

APPENDICES

APPENDIX A: Mass Flow Controller calibration curves

The catalyst unit system has four lines for feed gases, each one independently controlled by a Brooks' mass-flow controller (MFC). The mass-flow controllers are enclosed in an insulated styrofoam container to minimize the effect of any change in room temperature on the calibration process. Initially, the gas flow rate for particular MFC is set to the maximum set value and the system is allowed to reach steady state. Then, the outlet flows for different set points on each mass-flow meter are measured using a bubble flow meter. The same procedure is repeated for the other mass-flow controllers. The procedure is repeated each time prior to each experiment at the reaction conditions. The calculations are as given below.

Volumetric flow rate of the gas as measured by bubble flow meter = V_1 cc/min

Ambient pressure = P_1 atm

Ambient temperature = T_1 K

Assuming ideal gas law holds good for all the gases:

Volumetric flow rate of the gas at STP conditions are:

$$V_2 = (P_1/P_2) * (T_2/T_1) * V_1 \text{ cc/min}$$

Where, V_1 is the volume of the gas "n" in the loop at STP conditions, cc

P_2 is the atmospheric pressure, 1 atm

T_2 is the temperature at STP conditions, 273 K

Hence, the molar flow rate of the gas, $n = V_2/22400$ (mol/min)

The MFC calibration curves for CO, CO₂, He, Ar, and H₂ are given below.

Figure 47. MFC Calibration curve for argon

Figure 48. MFC calibration curve for CO/He mixture

Figure 49. MFC calibration curve for hydrogen

Figure 50. Calibration curve for HPLC pump

APPENDIX B: Gas Chromatograph operating conditions

Gas chromatograph type: Hewlett-Packard 5890 II

Detector used: Thermal- conductivity detector (TCD)

Detector temperature: 255 °C

Carrier gas: Argon

Carrier gas inlet pressure: 70 Psig

Total carrier gas flow rate: 50.6 ml/min

Reference flow rate: 35.1 ml/min

Column flow rate: 15.5 ml/min

Column used: HayeSep-D packed column

Oven temperature: 150 °C

Injector A temperature: 150 °C

Period of analysis: 30 minutes, 60 minutes, 8 minutes

Chromatographs showing separation of different gases during WGS and SEWGS reaction at 500 °C are given in Figures 50 and 51 respectively.

Figure 51. A schematic chromatogram showing separation of different gases during the WGS reaction at 500 °C
Conditions: T: 500 °C, Catalyst: Fe₂O₃/Cr₂O₃/CuO, H₂O/CO: 2, P: 1 atm

Figure 52. A schematic chromatogram showing separation of different gases during the SEWGS reaction at 500 °C
Conditions: T: 500 °C, Catalyst: Fe₂O₃/Cr₂O₃/CuO, sorbent: CaO, H₂O/CO: 2, P: 1 atm

APPENDIX C: GC Calibration curves

For TCD calibration, 3 sets of standard gases are used and given below.

Set 1: CH₄ mixture+H₂ +Ar

Set 2: CH₄ mixture + Steam (H₂O) + Ar

Set 3: CO/He +H₂+Ar

The CH₄ mixture will contain He, CH₄, CO₂, and Ar with a ratio of 4:30:30:36 and the ratio of CO to He in CO/He mixture is 5.25: 94.75. A total flow of 150 sccm is used for each set. The Gas Chromatograph and operating conditions for calibration are given in the Appendix B.

For example, a stream of CO/He, is mixed with Ar and H₂. The amount of each gas in the mixture is determined before injection. The mixture is injected automatically into the GC injection port from the sampling loop using auto-injector. The temperature and pressure in the loop are noted. The GC output in the form of peak areas from the TCD is noted. The calculations are given below.

Volume of the GC sampling loop: 0.5 cc

Fraction of the gas species “X” in the injected sample, $f = \text{Volume of X} / (\text{Volume of the gas mixture})$.

Where “X” corresponds to CH₄, He, CO₂, H₂, and CO

Volume of the species “X” in the loop, $V_2 = (f \cdot 0.5) \text{ cc}$.

Temperature of the loop = $T_2 \text{ K}$

Absolute pressure in the loop = $P_2 \text{ atm}$

Assuming ideal gas law holds good for all the gas species,

$$V_1 = (P_2/P_1) \cdot (T_1/T_2) \cdot V_2$$

Where V_1 = volume of the species "X" in the loop at STP conditions, cc

P_1 = atmospheric pressure, 1 atm

T_1 = temperature at STP conditions, 273 K

The moles of species 'X' in the loop, $n_1 = V_1/22400$

For example, a peak of Area A1 is obtained for particular fraction of the gas in the mixture. Similarly, for different fractions of f, the area counts A are observed and corresponding moles are calculated. A plot of areas and corresponding moles is obtained as calibration curve. The slopes thus obtained from these plots are used for product analysis. The slope has a unit of area count.mole. The average slopes obtained for all the gases used are given in Table 16.

Table 16. Average slopes of calibration curves of TCD gases

Gas name	Slopes			Average slopes
	Set 1: CH ₄ mixture+H ₂ +Ar	Set 2: CH ₄ mixture +Steam	Set 3: CO/He mixture+ H ₂ +Ar	
He	27981401968	27004663292	28687166671	27891077310
H ₂	45826801293	—	45967971901	45897386597
CO	—		4538652505	4538652441
CH ₄	18809079364	18193567547		18501323456
CO ₂	5878063299	5676787424		5777425362
H ₂ O	26191920735			26191920735

Figure 53. Calibration curve for helium using CH₄ mixture diluted with steam.

Figure 54. Calibration curve for helium using CO/He mixture diluted with hydrogen, and argon.

Figure 55. Calibration curve for He using CH₄ mixture diluted with hydrogen and argon.

Figure 56. Calibration curve for H₂ using CH₄ mixture diluted with argon and hydrogen.

Figure 57. Calibration curve for hydrogen using CH₄ mixture and argon.

Figure 58. Calibration curve for CO₂ using CH₄ mixture diluted with hydrogen and argon.

Figure 59. Calibration curve for CO₂ using CH₄ mixture diluted with steam.

Figure 60. Calibration curve for CO using CO/He mixture diluted with hydrogen and argon.

Figure 61. Calibration curve for H₂O using CH₄ mixture diluted with hydrogen and argon.

APPENDIX D: Calculation procedure for Relative Response Factors

The relative-responsive factor, rRF, is a measure of the relative response of the instrument detector to an analyte compared to an internal standard. Helium gas was used as internal standard and based on Helium; relative response factors of gases were calculated. Since the gases have different thermal conductivities, they have various retention times on Thermal Conductivity Detector (TCD). In order to get accurate quantification of each gas, rRF was used. Known quantities of each gas are sent into the GC along with known quantities of internal standard. The rRF can be calculated using the formula:

$$(rRF)_x = \frac{\frac{A_x}{C_x}}{\frac{A_{He}}{C_{He}}} = \frac{\text{Slope of } x}{\text{Slope of He}}$$

where A_x is the area of x ($x = \text{CO}_2, \text{CO}, \text{H}_2\text{O}, \text{and H}_2$), A_{He} is the area of helium (internal standard). C_x is the known concentration of x ($x = \text{CO}_2, \text{CO}, \text{H}_2\text{O}, \text{and H}_2$) and C_{He} is the known concentration of helium. The relative responsive factor (rRF) of all the gases are calculates using average slopes from Table16 .The rRF and retention time of each gas is given in Table 17.

Table 17. Relative response factors of gases used for WGS reaction

Gas	Retention time (min)	Relative Responsive Factor
He	2.319	1
H ₂	2.708	1.645593
CO	3.461	0.16272
CO ₂	6.470	0.2071406
CH ₄	-	0.663341
H ₂ O	13.038	0.939

APPENDIX E: Calculation procedure for equilibrium conversions (X_e) of WGS reaction

The equilibrium constant (K_e) of the equi-molar water-gas shift reaction can be expressed as:

$$K_{eq} = \left[\frac{C_{A_0} X_e \times C_{A_0} X_e}{C_{A_0} (1 - X_e) \times C_{A_0} (M - X_e)} \right] \quad (1)$$

Where,

C_{A_0} = initial concentration of carbon monoxide (CO)

M = ratio of steam to carbon monoxide (H_2O/CO)

X_e = equilibrium conversion of WGS reaction

The equilibrium constant (K_e) can written as

$$K_{eq} = \frac{X_e^2}{[(1 - X_e) \times (M - X_e)]} \quad (2)$$

The equilibrium conversions X_e of WGS reaction are calculated within the range of 350-750 °C using corresponding K_e values.

Example calculation:

The value of equilibrium constant (K_e) at 500 °C = 4.878, H_2O/CO : 2:1

The equilibrium conversion of WGS reaction at 500 °C is calculated by substituting the values of H_2O/CO ratio and K_e at 500 °C in the equation 2

$$4.878 = \frac{X_e^2}{[(1 - X_e) \times (2 - X_e)]} \quad (3)$$

$$0.79499X_e^2 - 3X_e + 2 = 0 \quad (4)$$

By solving the quadratic equation, equilibrium (X_e) conversion is calculated to be:

0.8654

APPENDIX F: Calculation procedure for effect of sorbent presence on equilibrium CO conversion (X_e)

The equilibrium constant (K_e) of the equi-molar water-gas shift reaction can be expressed as below:

$$K_{eq} = \left[\frac{C_{A_0} X_e \times C_{A_0} X_e}{C_{A_0} (1 - X_e) \times C_{A_0} (M - X_e)} \right] \quad (1)$$

Where,

C_{A_0} = initial concentration of carbon monoxide (CO)

M = ratio of steam to carbon monoxide (H_2O/CO)

X_e = equilibrium conversion of WGS reaction.

For example, if the sorbent adsorbs 75 % of the carbon dioxide produced in the reaction, then the equation 1 can be written as

$$K_{eq} = \frac{C_{A_0} X_e \times (1 - 0.75) \times C_{A_0} X_e}{C_{A_0}^2 [(1 - X_e) \times (M - X_e)]} \quad (2)$$

$$K_{eq} = \frac{0.25 C_{A_0}^2 X_e^2}{C_{A_0}^2 [(1 - X_e) \times (M - X_e)]} \quad (3)$$

The equilibrium conversion X_e of WGS reaction in the presence of sorbent that can capture 75% of the CO_2 produced in the reaction is calculated at 500 °C for various H_2O/CO ratios.

Example calculation:

The value of equilibrium constant (K_e) at 500 °C = 4.878

The ratio of H_2O/CO used: 2:1

The equilibrium conversion of WGS reaction at 500 °C is calculated by substituting the values of H_2O/CO ratio and K_e at 500 °C in the equation 2

$$4.878 = \frac{0.25 X_e^2}{[(1 - X_e) \times (2 - X_e)]} \quad (4)$$

$$0.948749X_e^2 - 3X_e + 2 = 0$$

By solving the quadratic equation, equilibrium (X_e) conversion is calculated to be:

0.9552

APPENDIX G: Calculation procedure for preparation of $\text{CaO}/\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ sorbent in various ratios

Amount of precursors used for preparation of $\text{CaO}/\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ sorbent:

For $\text{CaO}/\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ (75/25 wt %)

Weight of CaO : 34.85 g

Weight of $(\text{AlNO}_3)_3 \cdot 9 \text{H}_2\text{O}$: 37.89 g

Distilled water: 760 ml

2-propanol: 150 ml

For $\text{CaO}/\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ (50/50 wt %)

Weight of CaO : 34.85 g

Weight of $(\text{AlNO}_3)_3 \cdot 9 \text{H}_2\text{O}$: 37.89 g

Molecular weights of precursors and products

Molecular weight of CaO : 56 g

Molecular weight of $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$: 1385.72 g

Molecular weight of $(\text{AlNO}_3)_3 \cdot 9 \text{H}_2\text{O}$: 374.98 g

The decomposition of aluminum nitrate is expressed as:

From the above equation 1, 4 moles of aluminum nitrate produces 2 moles of aluminum oxide or 749.96 (2×374.18) g of aluminum nitrate produces 101.96 g of Al_2O_3

Therefore 37.89 g of aluminum nitrate produces 5.153 g of Al_2O_3

Formation of mayenite ($\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$) expressed as:

From the equation 2, 713.72 g of Al_2O_3 requires 672 g of CaO to produce 1385.72 g of $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$.

Also, 713.72 g of Al_2O_3 or 672 g of CaO will produce 1385.72 g of $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$

Therefore, 5.15 g of Al_2O_3 requires 4.85 g of CaO to produce 10 g of $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$

Amount of unreacted CaO = 34.85092 - 4.85092 = 30 g

Amount of $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ formed = 10 g

Percentage of $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ in the total amount = $(10/40) \times 100 = 25\%$

Percentage of CaO in the total amount = $(30/40) \times 100 = 75\%$

The sorbent $\text{CaO}/\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ (50/50 wt %) is prepared using the same procedure described above.

APPENDIX H: Calculation procedure for determination of kinetic parameters of WGS reaction

Kinetics of WGS reaction

Assuming both sides of the WGS reaction to be of first order in each component, the forward and reverse kinetic parameters, k_f and k_r were calculated. The activation energy (E_a) and pre-exponential factor (k_0) of the WGS reaction are calculated using Arrhenius equation. The rate equation for the reverse WGS reaction given is:

$$-r = k_f [P_{CO}][P_{H_2O}] - k_r [P_{H_2}][P_{CO_2}] \quad (1)$$

where,

$-r$ = rate of reaction of CO, H₂O

P_{CO} , P_{H_2O} , P_{H_2} , P_{CO_2} are the partial pressures of CO, H₂O, H₂, and CO₂

The equilibrium constant of the WGS reaction in terms of forward and backward reaction constants is given below:

$$K_e = \frac{k_f}{k_r} \quad (2)$$

Therefore, by substituting k_r in equation 1 with $k_r = K_e \times k_f$, and rearranging, the expression obtained is:

$$-r = k_f [P_{CO}][P_{H_2O}] - (k_f / K_e) [P_{H_2}][P_{CO_2}] \quad (3)$$

The rate constant, k_f is related to the absolute temperature (T) by:

$$k = k_0 \exp \{-E_a/RT\}$$

K_0 = pre-exponential factor (mol/min/g catalyst/ (atm)²

E_a = activation energy (kJ/mol)

R = universal gas constant (J/mol.K)

T = reaction temperature (K)

Example calculation:

Total pressure of the reactor: 1 atm

Inlet flow rate of CO: 0.002075893 (moles/min)

Inlet flow rate of H₂O: 0.0039444 (moles/min)

Outlet flow rate F_X (mol/min) of products at steady state during the WGS reaction at 450 °C:

F_{CO} (mol/min): 0.00628645

F_{CO_2} (mol/min): 0.001447248

F_{H_2} (mol/min): 0.001422158

F_{H_2O} (mol/min): 0.0024971

Partial pressures of products obtained during the WGS reaction at 450 °C are calculated using the equation 4:

$$P_X = \left(\frac{F_X}{\sum_X (F_X)_{OUT} + (F_{He})_{IN} + (F_{Ar})_{IN}} \right) \times P_T \quad (4)$$

where,

P_X = partial pressure of CO, CO₂, H₂, and H₂O

F_X = outlet flow rate of CO, CO₂, H₂, and H₂O

F_{He} = inlet flow rate of the helium (mol/min)

F_{Ar} = inlet flow rate of the argon (mol/min)

By substituting F_X values in the equation 4, the corresponding partial pressures of product gases obtained are:

$$P_{CO} = 0.0700826 \text{ (atm)}, P_{Ar} = 0.31934 \text{ (atm)}, P_{He} = 0.01230 \text{ (atm)}$$

$$P_{CO_2} = 0.01447 \text{ (atm)}, P_{H_2} = 0.15854 \text{ (atm)}, P_{H_2O} = 0.27838 \text{ (atm)}$$

Equilibrium constant (K_e) of the WGS reaction at 450 °C: 7.31

$$\text{Rate of consumption of CO (mol/min}\cdot\text{g catalyst): } \frac{CO_{in} - CO_{out} \text{ (mol/min)}}{\text{catalyst weight(g)}}$$

$$= \frac{0.002075893 - 0.00628645}{0.2}$$

$$= 0.00723624 \text{ (mol/min} \cdot \text{g catalyst)}$$

By substituting partial pressures of all the gases in the product, equilibrium constant (K_e) at 450 °C, and rate of consumption of CO in the equation 1, the corresponding forward reaction constant (k_f) calculated is:

$$0.007524684 \text{ (mol/sec/ g catalyst/ atm)}^2$$

The backward reaction constant k_r is calculated as:

$$k_r = (k_f/K_e)$$

$$= (0.007524684/ 7.34644)$$

$$= 0.001024263 \text{ mol/sec/g catalyst / (atm)}^2$$

APPENDIX I: Calculation procedure for CO₂ sorption for CaO/Ca₁₂Al₁₄O₃₃ (75/25 wt %) and catalyst separated with chips

Step 1:

Moles of CO₂ adsorbed are calculated based on H₂ moles produced and CO reacted. Since WGS reaction is equi-molar, 1 mole of CO reacts with 1 mole of H₂O and gives 1 mole of CO₂ and 1 mole of H₂.

Therefore, moles of CO₂ adsorbed (mol/min) = moles of H₂ formed (mol/min) – moles of CO₂ from the reactor outlet (mol/min). Moles of CO₂ adsorbed with respect to time are calculated and given in Table 18.

Step 2:

The curve representing the moles of CO₂ adsorbed with respect to time is shown in Figure 62.

Step 3:

From this curve, the total amount of CO₂ adsorbed between consecutive time points is determined by calculating the area under the curve using Origin 6 software or trapezoidal rule.

Table 18. Moles of CO₂ adsorbed and corresponding time

Time (min)	Moles of CO ₂ adsorbed (mol/min)
3	0.002452313
4	0.002430254
5	0.002446539
6	0.002479130
7	0.000671289
12	0.000182099
13	0.000063176
14	0.000062747
15	0.000060863
20	0.000058983
21	0.000057637
22	0.000033996
23	0.000033105
28	0.000029559
29	0.000023098
30	0.000026855
31	0.000022228
36	0.000014671

Figure 62. Moles of CO₂ adsorbed with respect to time

Example calculation for Moles of CO₂ adsorbed (mol/kg)

1). Calculation of moles of CO₂ adsorbed for first 3 minutes:

The number of moles of CO₂ adsorbed at 0th minute will be “0” moles. Then, we assume that the CO conversion will vary linearly from 0 to 3 minutes. Therefore, the region below the straight line represents the CO₂ moles adsorbed up to 3 minutes.

Area of the rectangle ABCD is: height × width

$$: 0.002452313 \times 3$$

$$: 7.577742 \times 10^{-03} \text{ moles}$$

Therefore the area of the triangle ABC, which is equal to half of the area of the rectangle ABCD, gives the number of moles of CO₂ adsorbed.

So number of moles of CO₂ adsorbed up to 3 min will be:

$$: (7.577742 \times 10^{-03})/2 = 3.788871 \times 10^{-03}$$

Moles of CO₂ adsorbed (per/2.5 g of sorbent) up to 3 min will be equal to 4.851828×10^{-03} . So, the moles of CO₂ adsorbed per 1000 g will be equal to:

$$= (3.788871 \times 10^{-03} \times 1000)/(2.5)$$

$$= 1.51554 \text{ mol/Kg}$$

Figure 63. Moles of CO₂ adsorbed with respect time

At 4th min

Calculation for moles of CO₂ adsorbed (mol/2.5 g of sorbent) for the 4th minute:

To calculate moles of CO₂ adsorbed at the 4th minute, we need rate of moles of CO₂ adsorbed at the 3rd and the 4th minutes

Rate of moles of CO₂ adsorbed at the 3rd min: 0.002452313 (mol/min)

Rate of moles adsorbed at the 4th minute: 0.002430254 (mol/min)

Using trapezoid rule or origin 6 software

Area under the curve:

$$= ((\text{Height of the curve at } 3^{\text{rd}} \text{ min} + \text{Height of the curve at } 4^{\text{th}} \text{ min}) \times (t_4 - t_3)) / 2$$

$$= ((0.002452313 + 0.002430254) \times (4 - 3)) / 2$$

$$= 0.002478084 \text{ moles adsorbed per 2.5 gm of sorbent}$$

The calculated amount of CO₂ adsorbed corresponds to 2.5 g of sorbent used.

Hence, the amount of CO₂ adsorbed for 1000 g of sorbent is calculated.

Moles of CO₂ adsorbed per 1000 g of sorbent:

$$= (1000 \times 0.002434042) / 2.5$$

$$= 0.9912336 \text{ mol /kg}$$

Similarly, the moles of CO₂ adsorbed per 1000 g of the sorbent are calculated at each minute until the sorbent reaches its breakthrough curve. Then, the corresponding cumulative moles of CO₂ adsorbed at each minute is calculated and given in Table 19.

Table 19. Cumulative moles of CO₂ adsorbed per Kg

Time (minute)	CO₂ sorption capacity (mol/kg)	Time (min)	CO₂ sorption capacity (mol/kg)
3	1.5155	20	6.145134176
4	2.492013547	21	6.168458167
5	3.467372308	22	6.186784685
6	4.447680202	23	6.200204866
7	5.072938064	28	6.262869162
12	5.926326614	29	6.273400682
13	5.9753816	30	6.283391267
14	6.000566076	31	6.293207911
15	6.025287976	36	6.330107858

References

1. Chen, W. H., Hsieh, T. C. and Jiang, T. L. An experimental study on carbon monoxide conversion and hydrogen generation from water-gas shift reaction, *Energy Conversion Management*. 49 (2008) 2801-2808.
2. Balat, M. Potential importance of hydrogen as a future solution to environmental and transportation problems, *International Journal of Hydrogen Energy*. 33 (2008) 4013-4029.
3. Jeffrey, R. B., Michel, B. P. and Norman, K. O. An economic survey of hydrogen production from conventional and alternative energy sources, *International Journal of Hydrogen Energy*. 32 (2007) 3797-3810.
4. Mulur, L. F., Tzimas. E., Kaltschmit, M. and Peteves, S. Techno-economic assessment of hydrogen production processes for the hydrogen economy for the short and medium term, *International Journal of Hydrogen Production*. 32 (2007) 3797-3810.
5. Kothari, R., Buddhi, D. and Sawhney, R. L. Comparison of environmental and economic aspects of various hydrogen production methods, *Renewable and Sustainable Energy Reviews*. 12 (2008) 553-563.
6. Haryanto, A., Fernando, S., Murali, A. and Adhikari, S. Current status of hydrogen production techniques by steam reforming of ethanol: A Review, *Energy Fuels*. 19 (2005) 2098-2106.
7. Han, C. and Harrison, D. P. Simultaneous water-gas shift reaction and carbon dioxide separation for the direct production of hydrogen, *Chemical Engineering Science*. 49 (1997) 5875-5883.
8. Callaghan, C., Ilie, F., Ravindra, D., Michael, C., Matthew, C. and Anibal, L. An improved micro-kinetic model for the water-gas shift reaction on copper, *Surface Science*. 541(2003) 21-30.
9. Twigg, M. V. *Catalysis Handbook*, second edition, Manson Publishing.Ltd, London, 1996, ISBN: 1874545359.
10. Iyer, M. V., Gupta, H., Sakadjian, B. S. and Fan, L. S. High temperature CO₂ capture and hydrogen production using calcium oxide: Process development

- and economics for combustion and gasification systems. Proc. Int. Tech. Conf. Coal Utilization & Fuel Systems. 30 (2005) 419-426.
11. Quadro, E. B., Dias, M. L. R. and Amorim, A. M. M. Chromium and copper doped magnetite catalyst for the high-temperature shift reaction, Journal of Brazilian Chemical Society. 10 (1999) 51-59.
 12. Araujo, G. C. and Rangel, M. C. An environment friendly dopant for the high-temperature-shift catalysts, Catalysis Today. 62 (2000) 201-207.
 13. Newsome, D. S. Catalysis Reviews, Science and Engineering. 21 (1980) 275-281.
 14. Andreev, V., Idakiev, V., Mihajlova, D. and Shopov, D. Iron-based catalysts for the water-gas shift reaction promoted by first row transition metal oxides, Applied Catalysis. 22 (1986) 385-387.
 15. Rhodes, C., Williams, B. P., King, F. and Hutchings, G. H. Promotion of $\text{Fe}_3\text{O}_4/\text{Cr}_2\text{O}_3$ high-temperature WGS catalyst, Catalysis Communications. 3 (2002) 381-384.
 16. Liu, Q., Ma, W., He, R. and Mu, Z. Reaction and characterization studies of an industrial Cr-free iron-based catalyst for high-temperature water-gas shift reaction, Catalysis Today. 106 (2005) 52-56.
 17. Shirokov, Y. G. Khim. Tekhnol. 21 (1978) 1339-1345.
 18. Rethwisch, D. G. and Dumesic, Journal of Applied Catalysis. 21 (1986) 97-109.
 19. Kochloefl, K. Handbook of Heterogeneous Catalysis, part B, Wiley-VCH, Weinheim, 2008, ISBN: 9783527619474.
 20. Natesakhawat, S., Wang, X., Zhang, L. and Ozkan, S. U. Development of chromium-free iron-based catalysts for high-temperature water-gas shift reaction, Journal of Molecular Catalysis A: Chemical. 260 (2006) 82-94.
 21. Xue, E., Keeffe, M. O. and Ross, J. R. Water-gas shift conversion using a feed with low steam-to-carbon monoxide ratio and contains sulfur, Catalysis Today. 30(1996) 107-118.
 22. Ladebeck, J. R. and Wagner, J. P. Catalyst development for water-gas shift reaction, Handbook of Fuel Cells - Fundamentals, Technology and

- Applications, vol-3, John Wiley & Sons.Ltd, Chichester, 2003, ISBN: 0-471-49926-9.
23. Lee. S. Encyclopedia of Chemical Processing, third edition, Taylor & Francis. Ltd, New York, 2005, ISBN: 978-0-8247-5563-8.
 24. Jose, D. F., Timothy, F., Sean, P., Howard, M. and Rameshwar, D. S. Advances in CO₂-capture technology-The U.S. Department of Energy's Carbon Sequestration Program, International Journal of Greenhouse Gas Control. 2 (2008) 9-20.
 25. Bello, A. and Idem, R. O. Pathways for the formation of products of the oxidative degradation of CO₂-loaded concentrated aqueous monoethanolamine solutions during CO₂ absorption from flue gases, Industrial and Engineering Chemistry Research. 44 (2005) 945-969.
 26. Thitakamol, B., Veawab, A. and Aroonwilas, A. Environmental impacts of absorption-based CO₂ unit for post-combustion treatment of flue gas from coal-fired power plant, International Journal of Greenhouse Gases. 1(2007) 318-342.
 27. Readman, J. E. and Blom, J. The use of in-situ powder X-ray diffraction in the investigation of dolomite as a potential reversible high-temperature CO₂ sorbent, Physical Chemistry Chemical Physics. 7 (2005)1214-1219.
 28. Siriwardane, R. V., Shen, M. S. and Fisher, E. P. Adsorption of CO₂ on zeolites at moderate temperature, Energy & Fuels.19 (2005) 1153-1159.
 29. Coal generation technology & carbon capture and storage, National Association of Regulatory Utility Commissioners (NARUC), May 2009.
<http://www.naruc.org/Publications/NARUC%20CCTCCS%20Primer%20FINAL%206%2009.pdf>.
 30. Li, K. Ceramic membranes for separation and reaction, second edition, John Wiley & Son. Ltd, Chichester, 2007, ISBN: 978-0-470-01440-0.
 31. Gupta, H. and Fan, L. S. Carbonation-calcination cycle using high-reactivity calcium oxide for carbon dioxide separation from flue gas, Industrial and Engineering Chemistry Research. 41 (2002) 4035-4042.

32. Silaban, A., Narcida, M. and Harrison, D. P. Characteristics of the reversible reaction between $\text{CO}_2(\text{g})$ and calcined dolomite, *Chemical Engineering Communications*.146 (1996) 149-162.
33. Bandi, A., Specht, M., Sichler, M. and Nicoloso, N. In-situ gas conditions in fuel reforming for hydrogen generation, 5thInternational Symposium on Gas Cleaning at High temperature, NETL, Morgantown, WV, 2002, pp 17-20.
34. Li, Z., Cai, N. and Huang, Y. Effect of preparation temperature on cyclic CO_2 capture and multiple carbonation–calcination cycles for a new based CO_2 sorbents, *Industrial and Engineering Chemistry Research*, 45 (2006)1911-1917.
35. Li, Z., Cai, N., Huang, Y. and Han, H. Synthesis, experimental studies, and analysis of a new calcium-based carbon dioxide absorbent, *Energy & Fuels*. 19(2005) 1447-1452.
36. Nakagawa, K. and Ohashi, T. A. novel method for CO_2 capture from high temperature gases, *Electrochemical Society*.145 (1998) 1344-1346.
37. Kato, M. CO_2 separation techniques using lithium containing oxide, 6th International Conference on Green Gas Control Technologies, Kyoto, Japan, 2003, page 1579-1582.
38. Kato, M., Kakagawa, K., Essaki, K., Maezawa, Y., Takeda, S., Kogo, R. and Hagiwara, Y. Novel CO_2 Absorbents Lithium-Containing Oxide, *International Journal of Applied Ceramic Technology*. 2 (2005) 467-475.
39. Gauer, C. and Heschel, W. Doped lithium orthosilicate for absorption of carbon dioxide, *Journal of Materials Science*. 41 (2006) 2405.
40. Daniel, J. F., Elizabeth, A. F., James, S. H., Randall, P. R. and Henry, W. P, Eutectic salt promoted lithium zirconate: Novel high temperature sorbent for CO_2 capture, *Fuel Processing Technology*. 86 (2005) 1503-1521.
41. Fernandez, E. O., Haugen, G., Zhao, T., Ronning, M., Aartun, I. and Boresen, B. Process design simulation of H_2 production by sorption enhanced steam methane reforming: Evaluation of potential CO_2 acceptors, *Green Chemistry*. 9 (2007) 654-662.

42. Lee, S. C., Choi, B. Y., Lee, T. J., Ryu, C. K., Ahn, Y. S. and Kim, J. C. CO₂ absorption and regeneration of alkali-metal-based solid sorbents, *Catalysis Today*. 111(2006) 385-390.
43. Lee, S. C., Chae, H. J., Park, Y. H., Ryu, C. K. and Kim, J. C. Novel regenerable potassium-based dry sorbents, *Journal of Molecular Catalysis B: Enzymatic*, (2007), doi:10.1016/j.molcatb.2008.07.007.
44. Yong, Z. and Rodrigues, A. E. Hydrotalcite-like compounds as adsorbent for carbon dioxide, *Energy Conversion and Management*. 43 (2002) 1865-1876.
45. Hufton, J. R., Mayogra, S. G. and Sircar, S. Sorption enhanced reaction process for the production of hydrogen, *American Institute of Chemical Engineering*. 45 (1999) 248-256.
46. Douglas, P. H. Sorption enhanced hydrogen production: Review, *Industrial and Engineering Chemistry Research*. 47 (2008) 6475-6481.
47. Reijers, H. T. J., Schiermeier, S. E. A. V., Odden, P. D. and Van, R. V. Hydrotalcites as CO₂ sorbents for Sorption-Enhanced Reforming of Methane, *Industrial and Engineering Chemistry Research*. 45 (2006) 2522-2530.
48. Oliveira, E. L. J., Grande, C. A. and Rodrigues, A. E. CO₂ sorption on hydrotalcites and alkali-modified hydrotalcites at high temperatures, *Separation and Purification Technology*. 62 (2008) 137-147.
49. Lee, K. B., Beaver, M. G., Caram, H. S. and Sircar, S. Reversible chemisorptions of carbon dioxide: Simultaneous production of fuel-cell grade H₂ and compressed CO₂ from synthesis gas, *Adsorption*. 13 (2007) 385-397.
50. Holladay, J. D., Hu, J and Wang, Y. An overview of hydrogen production technologies, *Catalysis Today*. 139 (2009) 244-260.
51. Xuan. C., Zheng, S., Nancy, G., Haijiang, W. and Jun, S. A review of PEM hydrogen fuel cell contamination: impact, mechanism, and mitigation, *Journal of Power Sources*. 165 (2007) 739-756.
52. Kuo, K. K. Principles of combustion, second edition, John Wiley & Sons. Inc, Hoboken, New Jersey, 2005, ISBN: 0-471-04689-2.
53. McIlveen-Wright, D. R., Pinto, F., Armesto, L., Caballero, M. A., Aznar, M. P., Cabanillas, A., Huang, Y., Franco, C. and Gulyurtlu, I. A comparison of

- circulating fluidized-bed combustion and gasification power-plant technologies for processing mixtures of coal, biomass and plastic waste, *Fuel Processing Technology*. 87 (2006) 793-801.
54. Cayan, F. N., Zhi, M., Palaklapati, R. S., Celik, I. and Gemmen, N. R. Effect of coal syngas impurities on anodes of solid oxide fuel cells, *Journal of Power Sources*. 185 (2008) 595-602.
 55. Bohlbro, H and Jorgensen, M. H., *Chemical Engineering World*. 5 (1970) 46-54.
 56. Xue, E., O'Keeffe, M. and Ross, J. R. A study of Pt/ZrO₂ catalysts for Water-gas-shift reaction in the presence of H₂S, *Studies in Surface Science and Catalysis*. 130 (2000) 3813-3818.
 57. Arenillas, A., Smith, K. M., Drage, T. C. and Snape, C. E. CO₂ capture using some fly-ash-derived carbon materials, *Fuel*. 84 (2005) 2204-2210.
 58. San Shwe Hla, D. P., Duffy, G. J., Edwins, J. H., Roberts, D. J., Ilyushechkin, A., Morpeth, L. D and Nguyen, T. Kinetics of high-temperature water-gas shift reaction over two iron-based commercial catalysts using simulated coal-derived syngases, *Chemical Engineering Journal*. 146 (2009) 148-154.
 59. Collin, R. and Graham, J. H. Studies of the role of the copper promoter in the iron oxide/chromia high-temperature water-gas shift catalyst, *Physical Chemistry Chemical Physics*. 5 (2003) 2719-2723.
 60. Keiski, R. L., Tapio Salmi. and Veikko J. P. Development and verification of a simulation model for a nonisothermal water-gas shift reactor, *Chemical Engineering Journal*. 48 (1992) 17-29.
 61. Myer, K. *Environmentally conscious fossil energy production*, third edition, John Wiley & Sons, Inc, Hoboken, New Jersey, 2010, ISBN: 978-0-470-23301-6.
 62. Kato, Y., Harada, N. and Yoshizawa, Y. Kinetic feasibility of a chemical heat pump for heat utilization from high temperature process, *Applied Thermal Engineering*. 19 (1999) 239-254.

63. Barker, R. The reactivity of calcium oxide towards carbon dioxide and its use for storage, *Journal of Applied Chemistry and Biotechnology*. 24 (1974) 221-227.
64. Barker, R. The reversibility of the reaction $\text{CaO (s)} + \text{CO}_2 \text{ (g)} \leftrightarrow \text{CaCO}_3 \text{ (s)}$, *Journal of Applied Chemistry and Biotechnology*. 23 (1973) 733-742.
65. Zhen-shan, Li., Ning-sheng, C., Yu-yu, H. and Hai-Jin, H. Synthesis, experimental studies, and analysis of a new calcium-based carbon dioxide sorbent. *Energy & Fuels*. 19 (2005) 1447-1452.
66. Christina, S. M. and Angeliki, A. L. Parametric study of the $\text{CaO-Ca}_{12}\text{Al}_{14}\text{O}_{33}$ synthesis with respect to high CO_2 sorption capacity and stability on multiple operations. *Industrial Engineering and Chemical Research*. 47 (2008) 9537-9543.
67. Zhen-shan, Li., Ning-sheng, C. and Yu-yu, H. Effect of preparation Temperature on cyclic CO_2 capture and multiple carbonation-calcination cycles for a new Ca-based CO_2 Sorbent. *Industrial Engineering and Chemical Research*. 45 (2006) 1911-1917.
68. Christina, S. M. and Angeliki, A. L. Development of new CaO based sorbent materials for CO_2 removal at high temperature. *Microporous and Mesoporous Materials*. 110 (2008) 119-127.

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