

## Chapter 2: Literature review

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### 2.1. Introduction

In order to successfully complete this investigation, it is necessary to conduct a detailed literature survey regarding all aspects relevant to this study. This chapter contains applicable literature and background information required to obtain a better understanding of the research topic, catalytic gasification. Section 2.2 gives a brief overview of the origin and formation of coal, including South African coal. In Section 2.3, the composition of coal is discussed under the topics of microscopic constituents and macroscopic constituents. Section 2.4 contains a concise outline of general gasification technologies, as well as large particle gasification research. In Section 2.5 all necessary topics related to catalytic gasification, such as: advantages of catalytic gasification, factors influencing the catalytic effect, catalyst selection, catalyst addition methods and mechanisms associated with catalytic steam gasification are discussed. Mechanisms for steam and catalytic gasification are discussed in Section 2.6, while a summary of catalytic gasification research is given in Section 2.7.

### 2.2. Coal

By definition, coal is a combustible, carbonaceous, rock-like solid, which is black or brown in colour, and derived primarily from carbon enriched plant material (Osborne, 1988). Coal can be categorised as a sedimentary rock composed predominantly of organic compounds such as carbon, hydrogen and oxygen and only a small amount of mineral constituents (Osborne, 1988). The composition and properties of coal vary in agreement with the extent to which the original plant matter has been altered (Osborne, 1988). The significant variety of altered plant material from which coal is derived is responsible for the heterogeneity of coal (Schopf, 1966).

#### 2.2.1. Origin and formation of coal

The formation of coal originated during the first coal age, also known as the Carboniferous period, which occurred more than 290 million years ago (WCI, 2009). Coals are derived from a variety of plant matter, which have undergone significant transformations. Coals originating from different regions, such as the northern hemisphere and the southern hemisphere, were derived from different plant material. The variation in plant species can be

attributed to specific environmental conditions during the coal formation process, as well as the geological history of each region (England *et al.*, 2002). The main factors which influenced coal formation during plant accumulation and degradation include (Falcon, 1986):

- sedimentary environments and tectonic control;
- type and nature of plant life;
- climate; and
- geochemical conditions (water levels,  $E_h$ , pH, salinity).

The above-mentioned factors influenced the rate and degree of degradation, as well as the type and ratios of inorganic and organic compounds in the coal, during the maturation stage. These factors are largely responsible for differences between the northern hemisphere and southern hemisphere coals (Falcon, 1986). Northern hemisphere coals originated during the Carboniferous period, under hot and humid conditions. The northern hemisphere coals were formed from plants which underwent rapid and continuous growth, and flourished in wide coastal lowlands. The degradation of the plant material was very rapid and complete, which resulted in coal with a relatively high vitrinite content and low mineral matter content (Falcon, 1986). In contrast, the southern hemisphere coals were formed during the Permian period, in swamps which were exposed to cold conditions as a result of the ice age. Varying topographic and sedimentary environments resulted in evolving plant forms which were different to those found in the northern hemisphere. Cold and harsh conditions resulted in extremely slow degradation of accumulated plant matter, which resulted in a coal rich in inertinite, with a high mineral matter content and varying rank (Falcon, 1986). The main differences between northern hemisphere coals and southern hemisphere coals, is that southern hemisphere coals have a higher ash and inert organic matter content, and contain less sulphides, pyrite, chlorine and harmful trace elements (Falcon, 1986).

### **2.2.1.1. Coal formation**

Peat is the first carbonaceous product produced in the coal formation sequence. The formation of peat occurred in damp, swampy conditions, due to the biochemical transformation of plant matter. Under suitable conditions, beds of peat formed, which were then covered by sediments such as sandstone and shale. Over time, a series of peat beds formed, which is separated by the sediments (Bend, 1992; England *et al.*, 2002).

In order for the coal formation to occur, the peat beds had to become submerged in water and covered with layers of sand, clay and silt. Over time, increasing amounts of sediments

were deposited on the peat beds and eventually, the effect of pressure, increased temperature and time resulted in the second phase of the transformation of the original plant material. Coal formation occurred at a much slower rate than peat formation, and involved the decrease in the oxygen content of the coal, and reduction in the amount of water retained within the coal (England *et al.*, 2002).

The coal formation process consists of various stages, all of which are important to ensure that the coal progresses to maturity. A brief discussion regarding the coal formation stages follows:

### **Peat**

The decomposition of plant material obtained in swamps or marshes results in the formation of peat. Peat can be identified by its light to dark brown colour, as well as the many distinguishable plant remains visible on the surface. Peat has a characteristically high moisture content and low heating value. It should be emphasised that peat is not coal, but merely its precursor (Bend, 1992; England *et al.*, 2002).

### **Lignite (Brown coal)**

Lignite is the first stage of genuine coalification. Coalification can be defined as the formation of coal from buried plant matter through continuous exposure to pressure and heat. Lignite has a woody texture with an appearance which varies between light brown and blackish-brown. When compared to peat, lignite has a lower moisture content and a higher heating value (England *et al.*, 2002).

### **Sub-bituminous coal**

Sub-bituminous coal is a black coal, which has a lower moisture content and a higher heating value when compared to lignite. Sub-bituminous coal does not cake together when exposed to heat, but has a tendency to crumble and soften when exposed to excess moisture and temperature variations (England *et al.*, 2002).

### **Bituminous coal**

The bituminous stage of coal formation can be divided into three ranks, namely: low, medium and high rank. The specific rank of the coal indicates the maturity of the coal and depends on the age, geothermal temperature and depth of burial. The progressive nature of the coal formation process results in the variation of certain coal properties (England *et al.*, 2002).

As the coal rank increases from low rank to high rank, the volatile matter content decreases. The coal properties within each maturation class tend to change to some extent, due to the variation of the maceral or organic compound proportions. The inherent moisture content of bituminous coal usually decreases as the coal rank increases, and values can range from 8% to 2%. As the coal rank and maturity of the coal increase, the calorific value also increases. However, as the mineral matter and moisture content vary with maturation class, the calorific value also changes. An increase in mineral matter and moisture content will consequently result in a decrease in calorific value (England *et al.*, 2002).

The physical properties of coal, such as hardness and grindability, vary with rank. Less mature coals of lower rank are inclined to become brittle and crumble upon exposure to moisture and temperature deviations, due to their porous chemical and physical structure (England *et al.*, 2002).

### **Lean coal**

Lean coal is a high rank coal with a volatile matter content between that of bituminous coal and anthracite. Lean coal is a soft coal with no caking properties, and produces practically no smoke when alight (England *et al.*, 2002).

### **Anthracite**

Anthracite is the final stage of the coal formation process. Anthracite is a very hard coal with no caking properties and a volatile matter content of less than 10% (England *et al.*, 2002).

#### **2.2.2. South African coalfields**

It is estimated that the South African coalfields originated 250 million years ago, in the Permo-Carboniferous period (Smith and Whittaker, 1986). Coal is obtained in 19 different coalfields throughout South Africa. The major coalfields are located in KwaZulu-Natal, Mpumalanga, Limpopo and the Free State, while coalfields with smaller coal reserves are found in Gauteng, Eastern Cape and the North-West Province (Jeffrey, 2005). According to Smith and Whittaker (1986), the highest quality coals are situated in the Natal, Witbank, Soutpansberg, Pafuri and Wankie coalfields. These coals have relatively low ash contents and are higher in rank compared to coal from other coalfields (Smith and Whittaker, 1986).

South African coalfields are arranged horizontally, with irregular occurrences of dips and raises caused by slight rolls in the basin floor. The formation of the coalfields was limited by factors such as unfavourable environmental conditions which prevented coal formation and

the erosion of coal beds where elevation occurred. The coalfields situated in the Free State, Mpumalanga and Northern KwaZulu-Natal have a continuous pattern, while the Northern Province coalfields are obtained in isolated regions, since the surrounding coal measures were removed by erosion (England *et al.*, 2002). A brief discussion regarding the Highveld coalfield is included in the following section, since coal from this specific coalfield is used for this study.

#### **2.2.2.1. The Highveld coalfield**

The Highveld coalfield is situated in Gauteng, south of the Witbank coalfield, and stretches from Nigel and Greyling in the west to Davel in the east, with an approximate area of 7 000 km<sup>2</sup> (Jordaan, 1986). The Highveld coalfield is the second most productive coalfield in South Africa, after the Witbank coalfield (Jeffrey, 2005).

The Highveld coalfield is divided into various seams, much like the Witbank coalfield. The thickness of the seams, as well as the quality of coal in each seam, varies throughout the coalfield. Seams No. 1, 3 and 4A are very thin and discontinuous. Seam No. 2 is a thick coal seam (1.5 - 4 m), which is continuous throughout most parts of the coalfield. The No. 4 Coal Seam (1 – 12 m), which is also mostly continuous, is economically the most valuable coal seam, while No. 4 Upper Coal Seam is generally thin (1 – 4 m) and contains mostly poor quality coal. The No. 4 Seam and the No. 4 Upper Seam are separated by a parting which increases in thickness from 2 m to 15 m from north to south. The No. 5 Coal Seam is a thin coal seam with a thickness ranging between 1 m and 2 m, which extends over most of the Highveld coalfield. Mining takes place primarily in the No. 4 Coal Seam (Jordaan, 1986).

Now that an understanding of coal formation and the coalfields of South Africa (particularly the Highveld Coalfield) has been obtained, it is important to gain further insight into coal characteristics which impact on utilisation.

### **2.3. Coal composition**

The fundamental composition of coal consists of biochemically altered plant material, which has undergone significant chemical and physical transformations over time. Coal consists of various constituents which can be characterised into two main categories, namely microscopic constituents and macroscopic constituents.

### 2.3.1. Microscopic constituent of coal

On a microscopic level, the constituents of coal can be characterised into three different categories, namely macerals, mineral matter and microlithotypes. The discrete organic constituents in the coal are classified as macerals, while the minerals and inorganic constituents are generally known as “mineral matter” (Falcon and Snyman, 1986; Ward, 2002). Microlithotypes are layers which form when the macerals and minerals coalesce to create various compounds. The size range of macerals and minerals is between 1 and 50 µm, while the width of microlithotypes generally exceeds 50 µm (Falcon and Snyman, 1986).

#### 2.3.1.1. Macerals

Macerals are organic compounds derived from various components of the original plant matter. These organic constituents originated during the initial stages of biochemical transformation and maturation of the plant material (Falcon and Snyman, 1986). Macerals are essential in determining the nature of coal, such as type and rank. All the advantages associated with coal, specifically its energy related characteristics, originate from the macerals (Ward, 2002).

Although macerals are subject to progressive chemical, physical and optical alterations with increasing rank, the proportions and shape remain relatively unchanged. Therefore, macerals are differentiated from one another based on size, shape, colour, reflectance, morphology, and occasionally origin. The physical and chemical properties of the macerals depend on the coal rank. Macerals can either be classified together into group macerals, namely vitrinite, liptinite and inertinite; or characterised into further categories known as sub-macerals. Group macerals can be differentiated based on their reflectance, while sub-macerals are distinguished based on their physical structure (Falcon and Snyman, 1986). The group macerals are characterised as follows:

##### Vitrinite

Vitrinite is derived from cell wall material and the cell content of the wood-like tissue of vegetation (Falcon and Snyman, 1986). The structure of the vitrinite groups is difficult to identify, due to the extreme alteration processes (gellification or vitrination) through which the vitrinite was formed. The formation of vitrinite occurred in an anaerobic environment, which indicates that oxidation was not responsible for biochemical degradation (Falcon and Snyman, 1986). Vitrinite is medium grey in appearance, which differs from the darker grey appearance of lignites and the whitish grey colour of inertinites (Bend, 1992).

### **Inertinite**

Inertinite originated from plant material that underwent severe transformation during the peat stage of the coal formation process. Inertinite is also derived from the same wood-like plant matter as vitrinite, however, unlike vitrinite, inertinite was exposed to an aerobic environment during decay (Falcon and Snyman, 1986). Inertinite macerals have the highest carbon to hydrogen (C/H) ratio of all the macerals (Cloke and Lester, 1994). When compared to the other macerals, inertinite has the highest aromaticity and the lowest volatile matter and hydrogen content (Bend, 1992; Cloke and Lester, 1994).

### **Liptinite**

Liptinite, also known as exinite, is comprised of the residues of plant material and seeds which were the most resistant to biochemical degradation, and is therefore only somewhat altered from the original plant material. Liptinite consists of chemically distinct plant remains such as spores, leaf cuticles, waxes, resins, fats and oils (England *et al.*, 2002; Falcon and Snyman, 1986). In comparison with the characteristics of other maceral groups, liptinite has the highest volatile matter and hydrogen content, and the lowest reflectance and aromaticity (Cloke and Lester, 1994). The optical and chemical characteristics of liptinites vary significantly with increasing rank (Bend, 1992).

#### **2.3.1.2. Mineral matter**

The term mineral matter is a comprehensive term, which refers to the mineralogical phases in the coal as well as the inorganic constituents included in the coal (Harvey and Ruch, 1986). Mineral matter arises as distinct grains or flakes or a combination of the two, and is obtained in one of the following five physical states (Harvey and Ruch, 1986):

- disseminated particles included in the macerals;
- partings or layers, in which fine-grained mineral constituents dominate;
- nodules, which also include lenticular and spherical concretions;
- fissures, which include cleat, fracture and void fillings;
- rock fragments, as a result of rock substitution of coal caused by faulting, slumping or other disturbances.

The minerals obtained in coal occur in different forms, which vary in physical characteristics, as mentioned above, as well as chemical composition (Falcon and Snyman, 1986). The fundamentally different types of inorganic constituents obtained in coal, can be divided into the following categories (Ward, 2002):

- dissolved salts and other inorganic compounds in the pore water of the coal;
- inorganic constituents included within the organic composition of the macerals;
- distinct inorganic particles (non-crystalline and crystalline) signifying mineral components.

The first two types of mineral matter are defined as non-mineral inorganics, which are noticeably present in the mineral matter of low-rank coals, for example brown coals, lignites and sub-bituminous coal (Ward, 2002). The inorganic constituents in these lower-rank coals are also largely responsible for the formation of ash. The last type of mineral matter, the distinct inorganic particles, is obtained in lower-rank coals, as well as higher-rank coals, such as bituminous coals and anthracites (Ward, 2002).

The specific form in which minerals or inorganic constituents can occur in coal can be divided into two categories, based on the formation of the mineral matter. The first form is intrinsic mineral matter which was formed by the crystallisation of inorganic elements from the original plant matter (Falcon and Snyman, 1986; Harvey and Ruch, 1986). The second form of mineral matter obtained in coal is extrinsic mineral matter, also known as introduced minerals. The extrinsic mineral matter can either be primary (syngenetic) or secondary (epigenic) (Falcon and Snyman, 1986). Syngenetic extrinsic minerals were introduced during the initial peat accumulation stage by means of wind, water or precipitation. Epigenic extrinsic minerals were deposited by water which penetrated the peat beds long after early peat accumulation, most likely during the late lignite or initial sub-bituminous stages (Falcon and Snyman, 1986; Harvey and Ruch, 1986).

### 2.3.1.3. Microlithotypes

As previously mentioned, microlithotypes are an amalgamation of inorganic and organic compounds in varying combinations. The microlithotype layers can consist of pure macerals, or a combination of varying fractions of different macerals. If microlithotypes contain more than 20 % by volume of minerals, then it is characterised as carbominerite (Falcon and Snyman, 1986).

## 2.3.2. Macroscopic constituents

A sequence of microlithotypes forms bands that are known as lithotypes. Lithotypes can be identified on a macroscopic level, and have a width of 5 mm or more. The distinguishable

characteristics of lithotypes include the lustre, fracture pattern, colour of the coal, and the specific type and texture of stratification. Based on the above-mentioned characteristics, coal lithotypes can be divided into two categories, namely humic coals and sapropelic coals (Falcon and Snyman, 1986).

Sapropelic coals are generally characterised by their non-banded, dull appearance. These coal lithotypes have an even granular surface and contain sparsely distributed mineral matter. The coal lithotypes in sapropelic coals formed during plant decay under anaerobic conditions.

Humic coals are banded coals comprised of fine layers which vary in brightness. Unlike sapropelic coals, the lithotype layers in humic coals originated during the decay of the plant matter under aerobic conditions. Humic coal lithotypes are obtained in most coal types in banded coal seams (Osborne, 1988). The lithotypes found in humic coals can be divided into the following categories (Falcon and Snyman, 1986; Osborne, 1988):

- Vitrain
- Clarain
- Durain
- Fusain

The above-mentioned bands vary in texture and brightness, and correspond with the parallel bedding plain of the specific coal seam (England *et al.*, 2002).

## 2.4. Gasification

Gasification technology has been around for almost 200 years. The production of gas through the gasification of carbon-based solids and liquids dates back as far as the late eighteenth century. Gasification played a very important role in the nineteenth and twentieth centuries, and was primarily used to produce town gas for both industrial and residential use. However, the use of gasification for town gas production is no longer implemented, since the use of natural gas and oil proves to have become more economic (Stiegel and Maxwell, 2001). The continuous development of gasification technology has ensured that gasification still remains an important industrial process. Stricter environmental regulations and an increasing need for more efficient utilisation of low-value feedstock will ensure even further development of gasification technologies (Stiegel and Maxwell, 2001).

During the gasification process, solid or liquid hydrocarbon feedstocks are converted to synthesis gas, which consists mainly of hydrogen ( $H_2$ ) and carbon monoxide (CO). Gasification processes have the ability to process any carbon-based feedstock to produce synthesis gas. The most widely used feedstocks are coal and petroleum deposits, which account for more than 70 % of global synthesis gas capacity. Another important feedstock is natural gas, which is responsible for 20 % of the current synthesis gas capacity. Natural gas is primarily implemented as feedstock during the production of chemicals. Apart from the above-mentioned feedstocks, all carbon-containing material such as municipal solid waste, hazardous waste and biomass, etc., can be utilised for synthesis gas production, after suitable preparation (Stiegel and Maxwell, 2001). Gasification is the preferred technology for many industrial processes, specifically because of its ability to process low-value and low-cost feedstocks (Stiegel and Maxwell, 2001).

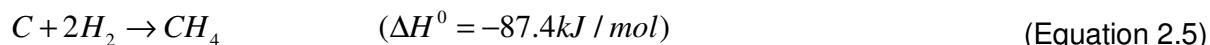
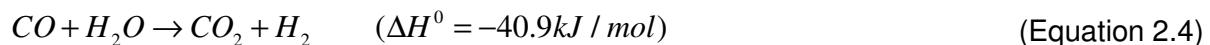
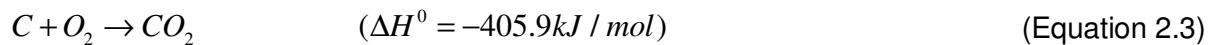
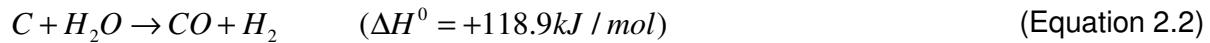
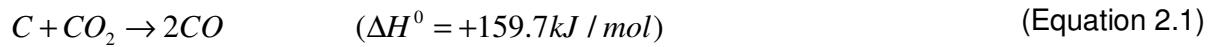
#### **2.4.1. Coal gasification process**

Gasification is described as the reaction of solid, carbonaceous fuel (in this case coal) with oxygen, air, steam, carbon dioxide, or a mixture of these gases to produce a gaseous product known as synthesis gas (Collot, 2006). Synthesis gas is a combustible gas consisting mostly of carbon monoxide and hydrogen, and can be further utilised in other industrial processes to produce electricity, chemicals, hydrogen or transportation fuels (Stiegel and Maxwell, 2001). The composition of the synthesis gas produced via coal gasification processes, varies due to its dependence on the following factors (Collot, 2006):

- coal rank and composition;
- coal particle size (coal preparation);
- gasification agents used (air, oxygen, carbon dioxide, etc.);
- and gasification operating condition such as temperature, pressure and heating rate.

The coal gasification process can be divided into two steps, namely devolatilisation and char gasification. Devolatilisation involves the release of the low molecular weight compounds, at temperatures as low as 300 °C (Hayashi and Miura, 2004). The compounds that are released during devolatilisation are primarily tars and non-condensable gases (Molina and Mondragon, 1998). The remains obtained from devolatilisation represents between 55% and 70% of the original coal sample (Molina and Mondragon, 1998).

At typical combustion and gasification temperatures, the devolatilisation reactions occur much faster than the gasification reactions (Molina and Mondragon, 1998). The following main reactions play an important role in the char gasification step (Molina and Mondragon, 1998):



The endothermic reactions (Equations 2.1 and 2.2) are considered to be the main reactions in the gasification process. Reaction 2.3 is an oxidation reaction, which provides the energy required to promote reactions 2.1 and 2.2. Reaction 2.4, also known as the shift reaction, mainly occurs in environments with high steam concentrations, while the importance of reaction 2.5 is emphasised in high pressure environments (Molina and Mondragon, 1998).

#### 2.4.2. Research on large particle gasification

For the purpose of this study, large coal particles are defined as particles larger than 1 mm in diameter. Previous research conducted on large particle gasification is summarised in Table 2.1, and is discussed subsequently.

**Table 2.1: Summary of large particle gasification research**

Investigators	Particle size studied (mm)
Hanson <i>et al.</i> (2002)	0.5-2.8
Huttinger and Natterman (1994)	2.0-3.0
Schmal <i>et al.</i> (1982)	0.8-1.4
Ye <i>et al.</i> (1998)	0.8-4.1
Huang and Watkinson (1996)	0.85-3.0

The effect of coal particle size on devolatilisation and steam gasification was studied by Hanson *et al.* (2002), for the purpose of power generation. The two different coals chosen for this study, La Jagua and Daw Mill coal, had ash contents of 3.2 wt.% and 10 wt.%, respectively. Various size fractions in the range of 0.5-2.8 mm were used for experimentation, and the devolatilisation and steam gasification experiments were carried out in a specially designed spouted bed reactor. Gasification experiments using CO<sub>2</sub> and air were conducted in a TGA. During this investigation it was observed that the devolatilisation and gasification results were not significantly influenced by particle size. The various size fractions used gave similar char yields during devolatilisation. The reactivity results obtained from the air, CO<sub>2</sub>, and steam experiments did not vary significantly between the different size fractions. It was concluded that for the specific particle size ranges, devolatilisation and gasification were relatively independent of particle size (Hanson *et al.*, 2002).

Huttinger and Natterman (1994) investigated the reactivity of six lignites and two high-volatile bituminous coals, with a particle size fraction of 2-3 mm. Steam and CO<sub>2</sub> experiments were conducted at 2.5 MPa in a fluidised bed reactor, at different partial pressures. They attempted to find a correlation between the reaction rates of various coals with the catalytically active components in the mineral matter. From the experimental results it was concluded that it is possible to predict coal reactivity based on the mineral matter content and distribution of catalytically active compounds in the coal (Huttinger and Natterman, 1994).

Schmal *et al.* (1982) studied the steam gasification kinetics using high-ash (> 50 wt.%) Brazilian sub-bituminous coal, and a particle size range between 0.8 mm and 1.4 mm. Isothermal runs were conducted in a thermobalance, at temperatures ranging from 800 °C to 1000 °C. It was found that the reactivity results were very temperature sensitive, which led to the conclusion that chemical reaction is the rate controlling step. Experimental results below 850 °C were accurately described by the homogeneous model, while the unreacted core model (SCM) successfully predicted the reactivity results above this temperature (Schmal *et al.*, 1982).

Ye *et al.* (1998) conducted a study on the kinetics and reactivity of CO<sub>2</sub> and steam gasification, using large coal particles. A low-rank South Australian coal (Bowmans) and a Victoria coal (Yallourn) were used for this study, and particle size fractions of 0.8-1.6 mm and 2.4-4.1 mm were selected for the steam gasification reactions. A single-particle reactor was used for the gasification experiments, which were performed at 765 °C. The reactivity

results showed that at a specific temperature, for CO<sub>2</sub> and steam gasification, the reaction rate was independent of particle size. The homogeneous model and SCM were fitted to the experimental data, and it was found that the homogeneous model accurately predicts the experimental results (Ye *et al.*, 1998).

Huang and Watkinson (1996) used two Canadian coals, Highvale and Coal Valley, to study the influence of various process variables on the steam gasification rate of the coals. Experiments were conducted in a stirred bed reactor, at 900 °C and atmospheric pressure. Size ranges of 0.85-1.4 mm, 1.5-2.0 mm and 2.36-3.0 mm were chosen for the Highvale chars, while size ranges of 1.0-2.0 mm, 2.0-2.36 mm and 2.36-3.0 mm were used for the Coal Valley chars. Results indicated that the reaction rate for the Coal Valley chars were particle size independent. However, it was found that the reaction rate of the Highvale chars decreased with increasing particle size. This was attributed to internal diffusional effects. According to the authors, the Highvale chars were far more reactive than the Coal valley char, and therefore experienced increased pore diffusion when compared to the Coal Valley chars at the same temperature and particle size (Huang and Watkinson, 1996).

## 2.5. Catalytic gasification

Gasification processes are receiving ever-increasing attention, and various methods are being studied in order to develop more efficient and environmentally friendly coal conversion technologies (Zhu *et al.*, 2008; Lee and Kim, 1995). One such method is catalytic gasification, which is considered to be an excellent optimisation method for gasification processes. Catalytic gasification has been studied extensively over the last few decades primarily because of the numerous advantages associated with the use of catalysts in gasification operations (Wang *et al.*, 2009; Jaffri and Zhang, 2008). The addition of a suitable catalyst to coal or char is known to increase reaction rates and to significantly reduce gasification operating temperature, which leads to moderate operating conditions (Zhang *et al.*, 2009; Zhu *et al.*, 2008).

Extensive research regarding the catalysis of coal gasification has two main purposes. Firstly, to understand and identify the gasification kinetics of coals which contain catalytically active compounds, and secondly, to develop and investigate the catalysis of gasification processes (Nishiyama, 1991).

### 2.5.1. Advantages of catalytic gasification

Numerous studies regarding catalytic gasification have focused on increasing reaction rates, decreasing operating temperature and improving synthesis gas production (Hippo and Tandon, 1996). As previously mentioned, the kinetic advantages of catalytic gasification are considered to be the most important (Wang *et al.*, 2009). The addition of a catalyst to coal samples increases the reactivity by at least one order of magnitude compared to uncatalysed coal samples (Hippo and Tandon, 1996). Catalytic gasification processes can be carried out at temperatures as low as 700 °C, while commercial gasification processes are generally conducted at temperatures exceeding 1000 °C (Sharma *et al.*, 2008).

Apart from the fundamental kinetic advantages associated with catalytic gasification, there are also various advantages regarding the operation of the process itself. These advantages include the following (Gallagher Jr. and Euker Jr., 1979): reduction of caking and swelling propensity of bituminous coal by using catalysts to coat the coal surface; the absence of oil and tar products, which streamlines water clean-up and removal of acid gas; and reduction in materials handling and mechanical problems due to moderate operating conditions (Yeboah *et al.*, 2003). Yeboah *et al.* (2003) also states that most or all of the disadvantages associated with coal conversion technologies, such as gasification, can be eliminated through the use of a suitable catalyst. The disadvantages of coal gasification which can possibly be eliminated by catalyst addition include: severe operating conditions, low methane yield, high oxygen consumption, and the incapability of handling caking coals (Yeboah *et al.*, 2003).

### 2.5.2. Factors influencing the catalytic effect

In order to acquire a better understanding of the exact influence a catalyst has on gasification reactions, it is important to recognize which factors influence the catalytic effect. According to Hippo and Tandon (1996), the catalytic effect of a catalysed system depends on the activity of the catalyst, de-activation of the active species, as well as the intrinsic activity of the active species. Nishiyama (1991) suggests that the increased reaction rates obtained when alkali metal catalysts are used can be explained by a possible increase in catalyst dispersion during burn-off, as well as an increase in the catalyst/carbon ratio in the final phase of gasification. Other possible explanations for an increase in gasification rates would be a change in surface area, a change in the chemical state of the catalyst and diffusivity caused by pore opening (Nishiyama, 1991). One of the major factors associated

with activity is the surface area of the char or coal. The enhancement of reaction rates by means of catalysis is determined mainly by the number of active sites which is influenced by the catalyst. The number of active sites is dependent on the available surface area which will be covered by the catalyst during impregnation. For nickel and calcium, which are immobile catalysts, the catalysts conversion for a fixed period is nearly proportionate to the initial surface area. However, for a mobile catalyst such as potassium, the activity is not directly related to surface area (Nishiyama, 1991).

The catalytic activity of a catalyst also largely depends on the substrate and gasification conditions. The main substrate characteristics which can influence the activity include the reactivity of the carbonaceous constituents, the effect of the mineral matter on the catalytic activity of the catalyst, and the catalytic effect of the mineral matter. The mineral matter in coal or char has a significant influence on catalysis. Some alkali and alkaline earth metals contained in the coal catalyse the reaction, while other minerals such as silica and alumina de-activate the catalyst. Previous studies indicate that the demineralisation of coal or char provides a noticeable increase in activity for potassium, while the activity for calcium and nickel only increases slightly (Nishiyama, 1991).

### **2.5.3. Catalyst selection**

The use of a catalyst to increase the rate of steam gasification of coal is considered to be decidedly advantageous. In order to achieve the desired results through catalyst addition, i.e. increased reactivity and lower operating temperature, it is crucial to select the best suitable catalyst for the system.

The catalysis of coal gasification processes by alkali-metal salts is a widely recognized phenomenon (Yeboah *et al.*, 2003). Numerous studies, based specifically on the activity of various catalysts, have also indicated that alkali and alkaline earth metallic species and Group VIII transition metals are efficient catalysts for gasification, specifically calcium and potassium based species (Suzuki *et al.*, 1984; Zhang *et al.*, 2009). Matsukata *et al.* (1992) established that alkali and alkaline earth metal compounds are efficient catalysts specifically for steam gasification of coal and petroleum deposits.

### 2.5.3.1. Influencing factors

When selecting a suitable catalyst to activate the coal particles, there are various aspects regarding catalyst reactivity, which have to be taken into consideration. These important aspects include:

- the order of the reactivity of alkali metals are specified in the periodic table, and are in the order of Cs > Rb > K > Na > Li (Moulijn *et al.*, 1984).
- the catalytic activity for equal amounts of catalysts are in the order of  $K_2CO_3/K_2SO_4 > Na_2CO_3 > KCl > NaCl > CaCl_2 > CaO$  (Liu and Zhu, 1986).

Nevertheless, catalyst selection should not be based solely on reactivity. Other aspects that should also be considered are: catalyst de-activation, catalyst mobility, catalyst behaviour under process conditions, and the catalysts' influence on process equipment. Iron and nickel are considered to be good commercial catalysts, due to their availability and relatively low cost. However, the rapid de-activation of these catalysts after 10 % carbon conversion is an enormous disadvantage (Hippo and Tandon, 1996). Calcium is also considered to be a promising catalyst, since it does not react with the mineral matter in the coal. But the selection of calcium as a catalyst is discouraged due to rapid deactivation and immobility (Hippo and Tandon, 1996). Previous studies indicate that alkali-salt catalysts like potassium and barium species distribute into the bulk of the coal during heat treatment in an inert atmosphere, and that these catalysts are extremely mobile in steam and  $CO_2$  gasification processes. Catalyst mobility is important for catalytic efficiency (Matsukata *et al.*, 1992; Hippo and Tandon, 1996; Yeboah *et al.*, 2003). Alkali-salts of weak acids perform well as catalysts, while those of strong acids are poor catalysts (Lang, 1986; Yeboah *et al.*, 2003). However, phosphates, borates and silicates of these alkali-salts will form glass-like, polymeric composites during gasification, which are unfavourable. The coal surface will be covered with a glassy layer, which will prevent it from reacting with the gaseous reagents (Yeboah *et al.*, 2003). The choice of catalyst is also crucial with regard to the process equipment, since some compounds can severely damage the construction materials. Catalysts containing chloride are responsible for severe corrosion under high steam pressure conditions, and might require the use of expensive materials for the construction of equipment (Sheth *et al.*, 2003).

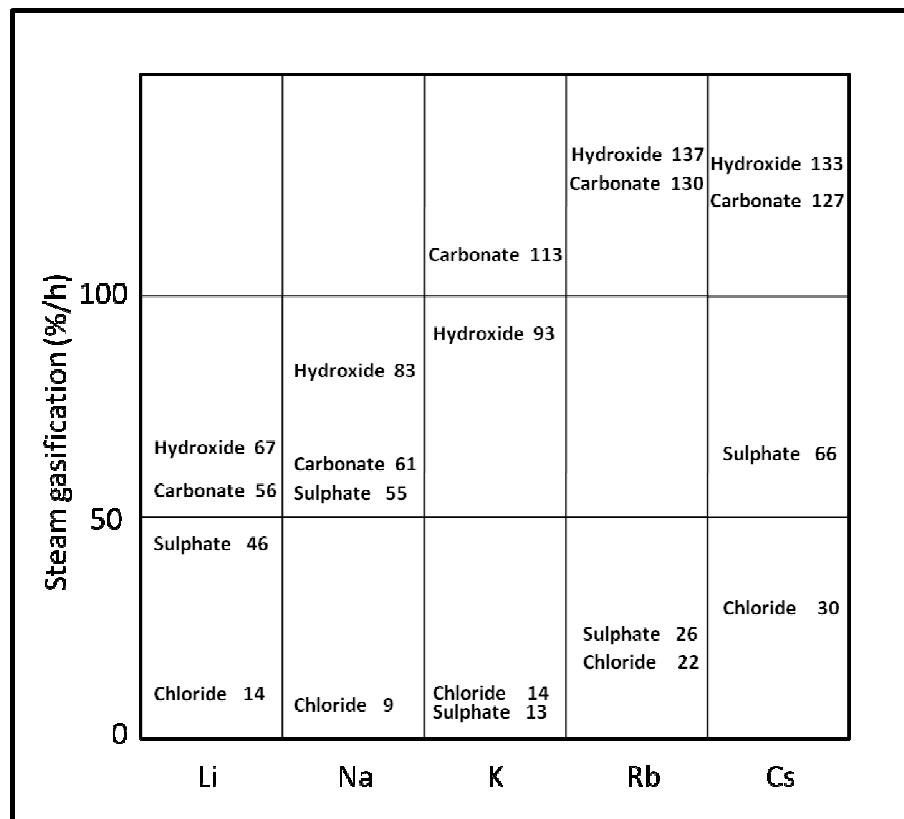
When selecting a catalyst for application in catalytic coal gasification studies, the behaviour of the catalyst under certain operating conditions should also be considered, since activity is largely dependent on the gasifying conditions. The operating temperature, gasifying agents

and the atmosphere inside the gasifier are the major factors which influence the catalytic activity of the catalysts (Nishiyama, 1991). The reaction rate of the catalysed process significantly increases in the vicinity of the melting temperature of the specific alkali metal carbonate catalyst (Yeboah *et al.*, 2003). However, at temperatures exceeding the catalyst melting temperature, agglomeration will occur which may cause severe operating problems. During gasification, the atmosphere within the gasifiers consists of varying concentrations of species including CO, H<sub>2</sub>, CO<sub>2</sub>, H<sub>2</sub>O and H<sub>2</sub>S. Research and literature indicate that the presence of gases such as CO and CO<sub>2</sub> inhibit the catalysis of C-H<sub>2</sub>O reactions by calcium, sodium and potassium, whereas H<sub>2</sub> negatively influences the catalysis by calcium. Therefore, the appropriate composition of the gas atmosphere is crucial in order to prevent catalyst inhibition or de-activation (Sheth *et al.*, 2003).

### **2.5.3.2. Anionic effect of catalysts**

Various studies regarding catalytic gasification have mainly focused on the activity of the metal ion (cation). The catalytic activity of the alkali metal salts generally increases with increasing atomic number and with increasing cation size. However, Lang (1986) reported that the associated anion can affect the activity of the catalyst more than the cation. It is believed that some anions can compete with the char for alkali cations and consequently inhibit the formation of alkali-carbon complexes, which are thought to be the active gasification sites (Lang, 1986).

Lang (1986) studied the gasification rates of coal char catalysed with various alkali metal salts, in order to determine the influence of the anions on the catalytic activity. As seen in Figure 2.1, the anions had a significant effect on the gasification rates. These experimental results confirmed that salts of weak acids, or salts which decompose to form weak acids, have the best activity overall.



**Figure 2.1: Comparison of gasification rates for coal char catalysed with various alkali metal salts (Adapted from Lang, 1986).**

As seen from Figure 2.1, the steam gasification rate is given as % carbon conversion per hour. With the addition of some alkali metal salt catalysts, complete conversion is achieved in less than an hour. Therefore, the gasification rates for these catalysed systems exceed a carbon conversion of 100 % per hour. Studies conducted on various potassium and sodium salts indicated an eight-fold variation in catalytic activity within each group of metal salts (Figure 2.1) (Lang, 1986). As presented in Figure 2.1, the hydroxides and carbonates of rubidium and caesium provided the highest gasification rates. However, these alkali metal salts are not as widely available as potassium and sodium, and such high gasification rates produce significant concentrations of CO<sub>2</sub>, which inhibit active sites (Lang, 1986). Chlorides of the alkali metals presented in Figure 2.1 produce highly corrosive HCl during gasification. Thus, potassium carbonate is the best alkali metal catalyst based on increased gasification rates. Experiments indicate that potassium carbonate has the most significant influence on the gasification rate, compared to other sodium and potassium salt catalysts (Lang, 1986).

Results obtained by Lang (1986) indicate that catalytic activity of a specific alkali metal salt is also influenced by the consequence of the competition, as seen in Figure 2.2. Figure 2.2 illustrates the competition of the potassium cation with the mineral matter in the ash, the active sites of the char and other anions (Lang, 1986).

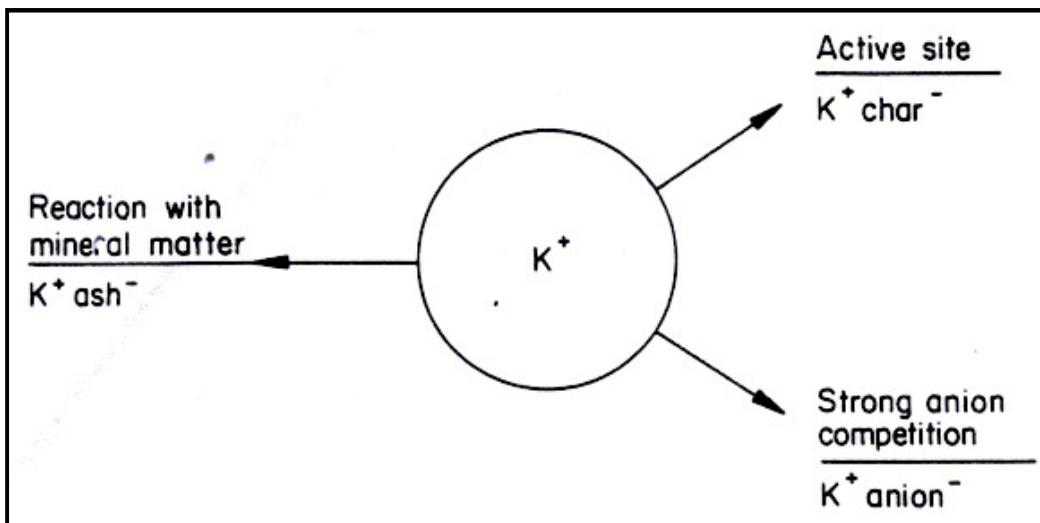


Figure 2.2: Competition of alkali cation (Taken from Lang, 1986).

The main factor responsible for increased gasification rates is the interaction of the alkali cation with the char. However, interactions with the mineral matter and other anions can prevent cation-char interaction. In the presence of mineral matter, potassium can react with pyrite or clays to form catalytically inactive compounds such as  $KFeS_2$  and  $KAISiO_4$ . This limits the amount of gasification sites, which are represented as an ionic association between the anionic coal char and the alkali cation (Lang, 1986). Suzuki *et al.* (1984) also observed that large amounts of ash decrease the catalytic effect of a catalyst. Therefore, in order to limit interactions between the alkali metal cation and the mineral matter, it is advantageous to use coal with a low ash content for catalytic gasification. The behaviour of coal char is thought to be similar to that of a weak-acid anion, and in the presence of strong-acid anions such as chlorides and sulphides, the  $K^+$ -char<sup>-</sup> interaction (Figure 2.2) is not favoured. This results in poor catalytic activity, unless the competing anion is altered or removed from the system (Lang, 1986). Thus, in order to promote the  $K^+$ -char<sup>-</sup> interaction, the amount of mineral matter and the strong-acid anions needs to be reduced.

### 2.5.3.3. Effectiveness of potassium carbonate as catalyst

Suzuki *et al.* (1984) investigated the catalytic effect of over 40 inorganic compounds and found that  $K_2CO_3$ ,  $KCl$  and  $Li_2CO_3$  are the most effective catalysts for steam gasification of coal or char. However, the catalytic activity of lithium salts is inhibited by CO and  $CO_2$  atmospheres, while potassium chloride is not favoured due to the chloride anion (Yeboah *et al.*, 2003). Therefore, potassium carbonate is the most favourable catalyst to enhance gasification reactions. Suzuki *et al.* (1984) also investigated the reaction kinetics for the gasification of char using steam, and the results signify that char impregnated with

potassium carbonate is almost a hundred times more reactive than uncatalysed char. The catalytic activity was significant for coal with low ash content (7.2-14.7 dry %) and high volatile matter content (31.1-46.0 dry %) (Suzuki *et al.*, 1984).

Numerous studies have concluded that  $K_2CO_3$  is one of the most effective catalysts for catalytic gasification, based on increased reaction rates. However, the reactivities of gasification reactions are influenced, to some extent by coal type. Since coal is a heterogeneous material, it is necessary to investigate various combinations of catalysts and coals in order to efficiently employ catalysts in coal gasification. Takarada *et al.* (1986) studied the effectiveness of  $K_2CO_3$  based on its dependence on coal rank in terms of reactivity and degree of catalyst dispersion obtained. This specific study investigated the catalytic effect of  $K_2CO_3$  on the reactivities of 34 coals with varying rank (Takarada *et al.*, 1986). The effectiveness of  $K_2CO_3$  was determined by the difference in reactivity of catalysed and uncatalysed samples. Results from this study indicated that the effectiveness of  $K_2CO_3$  as catalyst was significant for all coals examined and that the catalytic effect was not dependent on coal rank. An analysis of the dispersion of the catalyst showed that the entire char surface was covered with potassium. It is proposed that  $K_2CO_3$  disperses throughout the coal sample in two different ways. Firstly,  $K_2CO_3$  melts at the gasification temperature and forms a liquid film on the char surface, and secondly,  $K_2CO_3$  speciates to form K-O-C (surface intermediate) which is atomically dispersed on the carbon surface. This study concluded that good dispersion of  $K_2CO_3$  is not dependent on coal rank varying from anthracite to lignite. This is the reason for the exceptional effectiveness of  $K_2CO_3$  as catalyst and its independence on coal rank (Takarada *et al.*, 1986).

Based on the results from various studies which employed  $K_2CO_3$  as a catalyst for catalytic gasification experiments, it can be concluded that the following factors contribute to the exceptional effectiveness of  $K_2CO_3$  as catalyst for powdered coals:

- the ability of  $K_2CO_3$  to significantly increase the gasification reaction rates (Suzuki *et al.*, 1984);
- the mobility of  $K_2CO_3$  under gasification operating conditions, which leads to good dispersion throughout the coal sample (Liu and Zhu, 1986);
- the observation that coal rank does not influence the catalytic effectiveness of  $K_2CO_3$  (Takarada *et al.*, 1986);
- the observation that neither mechanical mixing or other impregnation methods influence the catalytic activity of  $K_2CO_3$  (Liu and Zhu, 1986).

Since potassium carbonate showed promising results when selected as catalyst for previous catalytic gasification studies, and also poses considerable advantages as mentioned above, it is selected as the catalyst for this study which focuses on the catalytic gasification of large coal particles (5 mm – 30 mm).

#### 2.5.4. Catalyst addition

The activity obtainable for catalysed reactions is greatly influenced by the method used for catalyst loading. The catalyst is most effective when sufficient contact is achieved between the catalyst and both the gaseous reactant and the solid substrate (Nishiyama, 1991). Catalyst distribution throughout the coal particle is important in order to obtain sufficient interaction between the catalyst and the coal sample. However, the dispersion of the catalysts throughout the coal particle remains a challenging topic in catalyst impregnation. The form of the specific catalyst, as well as the method of catalyst addition has an influence on the overall catalyst dispersion (Sommerfeld *et al.*, 1993). According to Sheth *et al.* (2003) it is required that the initial distribution of catalyst salts occurs homogeneously at ambient temperature, in order for the catalysts to infiltrate the coal matrix and be present at the active carbon sites at gasifier conditions. This can only be achieved if the proper catalyst impregnation method is used to obtain optimum catalyst distribution and penetration into the coal matrix (Sheth *et al.*, 2003).

With regards to selecting a suitable impregnation method, the following factors have to be considered (Nishiyama, 1991):

- Immobile catalysts, which do not sufficiently infiltrate the coal particle during devolatilisation, should be impregnated such that small catalyst particles form on the coal or char surface.
- When the catalyst is loaded in the form of an aqueous solution, a higher degree of dispersion is obtained for carbon surfaces with a hydrophobic nature, as opposed to carbon surfaces with a hydrophilic nature.
- A catalyst added before and after devolatilisation behaves similarly, which indicates that devolatilisation does not have a significant influence on the catalytic activity.

### 2.5.4.1. Catalyst addition methods

Various catalyst addition methods have been investigated in order to determine which method of catalyst addition provides the best catalyst distribution throughout the coal sample. As previously mentioned, catalytic activity is greatly influenced by the distribution of the catalyst on the pore surface of the coal particle. The catalytic effectiveness is not only dependent on the impregnation method, but also on the nature of the catalyst and the amount of catalyst added (Liu and Zhu, 1986). The conventional catalyst addition method involves physically mixing a catalyst with the coal to achieve a 10-20 wt % catalyst loading. However, alternative catalyst loading methods such as ion exchange and impregnation have been investigated, which may provide enhanced gasification rates at lower catalyst loadings (McCormick and Jha, 1995). According to Su and Perlmutter (1985), it is expected that solution impregnation will distribute the catalyst more uniformly throughout the coal sample than by physical mixing. Other catalyst impregnation methods used for catalyst addition include: wetness sequential impregnation (WSI), wetness co-impregnation method (WCIM), excess solution impregnation (ESI), and excess co-impregnation (ECI) (Rana *et al.*, 2007).

The main catalyst addition methods which will be discussed are mechanical mixing, incipient wetness impregnation, and excess solution impregnation (ESI). Mechanical mixing is a physical addition method, while the incipient wetness impregnation and excess solution impregnation (ESI) methods are considered to be impregnation methods. An impregnation method consists of the following three steps: (1) contacting the solid support material with the impregnation solution for a specific period of time, (2) drying the solid material to remove any absorbed liquid, and (3) activating the catalyst (Perego and Villa, 1997). According to McCormick and Jha (1995), the use of impregnation may result in the catalyst being deposited on the surface by means of precipitation, rather than ion-exchange or adsorption. Ion-exchange and adsorption/absorption are sorption processes by which the catalyst is incorporated in the coal structure during impregnation, and will also be discussed in this section (Kruger, 2008).

#### Mechanical mixing

The mechanical mixing method for catalyst addition may lead to particle size reduction, and is therefore not suitable for combining a catalyst with large coal particles (>1 mm). More efficient mixing and adequate catalyst distribution can be achieved when fine coal particles are used. The coal samples are usually pulverised to obtain <250 µm coal particles. A specific amount of catalyst salt is then physically mixed with the pulverised coal sample using a mortar and pestle (Yeboah *et al.*, 2003). The specific catalyst loading achieved with

physical mixing is more easily quantified than with other catalyst addition or impregnation methods. It should also be noted that the degree of contact between the catalyst and the coal is generally poor when the catalyst is simply mixed and introduced to the coal sample (Sheth *et al.*, 2003).

### **Incipient wetness impregnation**

According to Magee and Dolbear (1998), incipient wetness impregnation involves the addition of a sufficient amount of aqueous solution to a high surface area support substance to just fill all the pores. The volume of the aqueous catalyst solution is equal to or slightly less than the pore volume of the solid support, therefore the incipient wetness method of impregnation is also known as pore volume impregnation (PVI) (Dawes and Mazumber, 2006). For the incipient wetness method, the catalyst salt is weighed and dissolved in deionised water to form an aqueous catalytic solution, which is equal in volume to the pores of the solid support. The solution is then added to pulverised coal and shaken thoroughly to ensure sufficient mixing, after which the coal sample is dried (Yeboah *et al.*, 2003).

The catalyst added during incipient wetness will deposit into the pores when the coal sample is dried, as opposed to coating the outer surface area (Magee and Dolbear, 1998). PVI is not favoured when catalyst distribution is crucial, since the absorption of a volume of solution equal to the pore volume of the support results in poor catalyst distribution (Dawes and Mazumber, 2006).

### **Excess solution impregnation (ESI)**

Along with the pore volume impregnation method (PVI), the excess solution impregnation method is one of most well-known catalyst addition techniques (Dawes and Mazumber, 2006). The solid support is completely submerged in an excess amount of impregnation solution for a certain period of time. This impregnation method works on the principle of capillary pressure, which causes the impregnation solution to infiltrate the pores of the solid support and fill the available pore volume. After impregnation, the solid material is drained and dried (Perego and Villa, 1997; Dawes and Mazumber, 2006). A disadvantage of the excess solution method is that the different catalytically active materials have different chemisorption rates. This leads to preferential loading of specific metals over others if the impregnation solution contains a combination of metal salts (Perego and Villa, 1997).

### **Incorporation of catalyst in coal structure**

The catalyst cation can be incorporated in the coal structure by either ion-exchange, or by adsorption/absorption. During catalyst addition via ion-exchange, solution pH is used to

charge the coal surface positively or negatively, after which catalyst species of the opposite charge is ion-exchanged onto the surface. For example, at a certain pH value where the surface is negatively charged, positive ions are attracted to the surface to form surface carboxylate or phenolate salts (McCormick and Jha, 1995).

Absorption is a sorption process where solution molecules are taken up by a solid or liquid, and dispersed throughout that solid or liquid (Zarzycki and Chacuk, 1993). Adsorption on the other hand, is the term used to describe a process where a solid surface (adsorbent) concentrates solution molecules via physical and/or chemical forces, forming an atomic or molecular film known as the adsorbate (Fraissard, 1997). Adsorption can be divided into two categories, namely physical adsorption and chemical adsorption. During physical adsorption, or physisorption, solution molecules are bonded to the solid surface with Van Der Waals forces. During chemical adsorption, or chemisorption, the solution molecules chemically react with the solid surface and are bonded to the surface with strong chemical bonds. Chemical reactions taking place during chemisorption occur as a result of electron exchange between the adsorbent and adsorbate (Habashi, 1970).

As impregnation progresses and the molecules in the catalytic solution are taken up by the coal, the catalytic solution concentration decreases. Since the occurrence of both adsorption and ion-exchange will cause the catalytic solution concentration to decrease, it is difficult to determine exactly which of these processes takes place during impregnation.

#### **2.5.4.2. Factors influencing impregnation**

Apart from the impregnation method, factors such as time, temperature and solution pH are also thought to have an effect on the efficiency of catalyst impregnation. Liu and Zhu (1986) studied the effect of time and temperature on the efficiency of impregnation for various catalysts, specifically for  $K_2CO_3$  and CaO. Experimental results obtained indicate that the variation of the catalytic effectiveness of  $K_2CO_3$  with a change in impregnation time is negligible. However, for CaO the catalytic effectiveness and consequently the carbon conversion increased with increased impregnation time. This is due to a more uniform distribution of CaO obtained with prolonged impregnation (Liu and Zhu, 1986). The effect of impregnation temperature had little effect on the catalytic effectiveness of  $K_2CO_3$ . In the case of CaO the catalytic effectiveness is enhanced for impregnation temperatures exceeding 50 °C (Liu and Zhu, 1986).

McCormick and Jha (1995) also studied catalyst impregnation conditions, focusing mainly on solution pH. It was observed that the charge of the catalyst species and the charge of the carbon surface were directly responsible for the equilibrium catalyst loading achieved (McCormick and Jha, 1995). For example, at certain pH levels the carbon support is more negatively charged and will therefore attract more positive ions to the surface, which will consequently lead to increased catalyst loading. It was found that calcium catalysts could not be ion-exchanged onto coal in a pH range of 1-11, while potassium catalysts could be ion-exchanged sufficiently at pH levels greater than 7. Due to the varying nature of the carbon support and catalysts, the pH levels where optimum loading will be achieved will differ. McCormick and Jha (1995) found that a higher level of catalyst loading could be achieved for Illinois No. 6 coal at a pH of 3 than at pH 9, when impregnated with a calcium or sodium catalyst (McCormick and Jha, 1995).

## 2.6. Gasification mechanisms

Reactions between gases and porous solids play an important role in various industrial processes, and gas-solid reactions have been studied extensively in order to develop new processing operations and design criteria. The following equation illustrates the overall reaction sequence for the gasification of porous solids (Szekely, 1977):



The overall reaction (2.6) is comprised of various elementary reactions, collectively known as a reaction mechanism, which describe the behaviour of the coal particle in a certain gasification environment, i.e. H<sub>2</sub>O or CO<sub>2</sub>. Rate equation models used to describe the rate of gas-solid reactions depend largely on the reaction mechanism; therefore it is important to know which reaction mechanism is applicable under certain conditions.

### 2.6.1. Steam gasification mechanism

According to Sheth *et al.* (2003), the mechanism most commonly proposed for the steam gasification of coal is the Langmuir-Hinshelwood mechanism (Sheth *et al.*, 2003):





The overall steam gasification reaction is represented by reaction 2.7, while the individual elemental reaction steps are represented by reactions 2.8-2.11. Reaction 2.8 signifies the adsorption of a water molecule on the active sites of the coal surface. Consequently, the water molecule reacts with the carbon to produce adsorbed H<sub>2</sub> and CO. The H<sub>2</sub> and CO species are desorbed and released as gaseous product.

An important factor to consider when considering the Langmuir-Hinshelwood mechanism is reaction inhibition by H<sub>2</sub> and CO<sub>2</sub>. According to Molina and Mandragón (1998), the gasification reaction rate decreases by up to 42% when the H<sub>2</sub> concentration is the same as the H<sub>2</sub>O concentration. A further decrease in reaction rate is observed when CO and CO<sub>2</sub> are present during gasification (Molina and Mondragon, 1998). Everson and co-workers (2006) also studied the inhibiting effect of H<sub>2</sub> in steam gasification reactions, and reported that the reaction rate is significantly reduced in the presence of H<sub>2</sub> (Everson *et al.*, 2006).

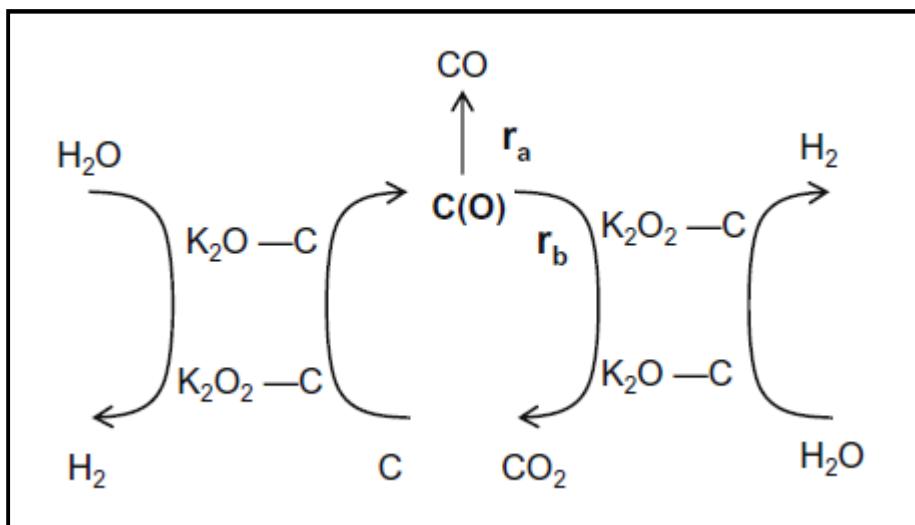
### 2.6.2. Catalytic gasification mechanism

Catalytic gasification reactions, specifically the complex mechanisms, have been studied extensively. Although the mechanism for such reactions is very complex, it has been concluded that the reaction follows a redox mechanism (Shadman *et al.*, 1987; Yeboah *et al.*, 2003; Wang *et al.*, 2009). This indicates that the alkali metal catalyst transitions between the oxidised state and reduced state. During this transition period, oxygen is transferred from the gaseous reactant to the coal surface by the catalyst, which results in the production of CO (Shadman *et al.*, 1987). The outcome of the catalytic process, specifically the mechanism, depends on the catalysts present, the gasification temperature and the nature of the reactant gas (Yeboah *et al.*, 2003).

The main catalysis mechanism when using alkali and alkaline earth metal salts in steam and CO<sub>2</sub> gasification involves the transport of oxygen from the catalyst to the carbon surface, possibly through the formation and decomposition of C-O complexes (Nishiyama, 1991). The following oxygen transfer mechanism for steam gasification reactions catalysed by potassium carbonate is widely recognized (Wang *et al.*, 2009):



In the redox cycle represented by equations 2.12-2.15, reaction 2.12 is essential for the formation of the active intermediate,  $KC_n$  (potassium carbide), involved in potassium-catalysed reactions (Wang *et al.*, 2009). The mechanism proposed in equations 2.12-2.15 does not explain the selectivity of the catalytic gasification reaction. Wang *et al.* (2009) proposed an oxygen transfer and intermediate hybrid mechanism for catalytic steam gasification reactions with potassium carbonate as catalyst. Figure 2.3 illustrates the mechanism as proposed by Wang *et al.* (2009):



**Figure 2.3: Oxygen transfer and intermediate hybrid mechanism (Taken from Wang *et al.*, 2009)**

As illustrated in Figure 2.3,  $K_2O-C$  represents the reducing form of the K-C-O intercalates, while  $K_2O_2-C$  represents the oxidising form. The K-C-O intercalates catalyse the gasification of carbon by means of a redox cycle. The most important aspect of this mechanism is the introduction of another intermediate into the reaction pathway, namely  $C(O)$ .  $C(O)$ , which is an oxygenated species or an adsorbed oxygen on the carbon surface, is regarded as the common intermediate in mechanisms proposed for both catalysed and uncatalysed gasification reactions. From the mechanism illustrated in Figure 2.3, it can be concluded that the reaction rate is dependent on the concentration of K-C-O, as well as the concentration of  $C(O)$ . The selectivity of the gasification reaction towards the formation of carbon monoxide (CO) and carbon dioxide ( $CO_2$ ) is governed by the competition between

reaction a ( $r_a$ ) and reaction b ( $r_b$ ), as seen in Figure 2.3. Reaction (a) illustrates the desorption of C(O), while reaction (b) illustrates the reaction between C(O) and  $K_2O_2\text{-}C$ . The overall gasification reaction equation can be illustrated by the following equation (2.16):



In equation 2.16,  $\alpha$  represents the ratio of the desorption rate of C(O) to the overall conversion rate C(O), namely  $r_a/(r_a+r_b)$ .

Since the mechanism of a catalytic gasification reaction largely depends on the type of catalyst used, as well as the operating conditions, it is difficult to predict which exact mechanism is followed during experimentation. Therefore, various researchers have extensively studied these reaction mechanisms to obtain a better understanding of catalysed gasification reactions. Veraa and Bell (1978) proposed a possible sequence for catalytic steam gasification reactions similar to the mechanism proposed by Wang (2009). According to Veraa and Bell (1978), the catalytic activity of  $K_2CO_3$  can be attributed to the following sequence:



In this sequence, the char reduces the  $K_2CO_3$  to metallic K and CO. K is then converted to KOH, as seen in reaction 2.18, and back to  $K_2CO_3$  in reaction 2.20. Freriks *et al.* (1981) proposed that reaction 2.17 is the rate limiting step. It was found that the free energy of reaction 2.17 is positive during gasification conditions (+198 kJ/mol at 1000 K), and literature suggests that the overall reaction rate depends on the degree of contact between the salt and the carbon, which increases as the carbonate phase melts and spreads on the carbon surface (Freriks *et al.*, 1981; Veraa and Bell, 1987). It was reported that the melting of the catalyst would cause a discontinuous catalytic effect on the reaction rate as the gasification temperature increased above the melting point of the catalyst (Freriks *et al.*, 1981). However, McKee and Chatterji (1978) have reported smooth Arrhenius plots for  $K_2CO_3$  catalysed graphite-steam reaction for temperatures between 850 °C and 1035 °C, while Veraa and Bell (1978) reported smooth Arrhenius plots for the  $K_2CO_3$  catalysed char-steam

reaction for a temperature range of 700-900 °C. These results indicate that the catalytic effect on the reaction rate is continuous throughout the gasification reaction, even at temperatures exceeding the melting point of the catalyst. This can be attributed to the fact that the potassium carbonate is unstable at temperatures above 700 °C, and decomposes to CO<sub>2</sub> and a potassium surface complex (Freriks *et al.*, 1981). According to Freriks *et al.* (1981), the active species is the potassium surface complex, which is not affected by the catalyst melting temperature.

A mechanism similar to that proposed by Veraa and Bell (1984), was presented by Shadman and Sams (1985), for catalysed CO<sub>2</sub> gasification reactions. The reduction of K<sub>2</sub>CO<sub>3</sub>, as shown in reaction 2.17, is presented as follows (Shadman and Sams, 1985):



In reaction 2.21, the CK represents the reduced form of potassium. The catalyst is first reduced during the initial reaction period, after which it is oxidised during the introduction of CO<sub>2</sub>, to produce CO. The oxidised potassium interacts with the carbon surface to release another CO and to return to the reduced form, which completes the cycle. Various researchers have suggested that the catalyst continually undergoes the reduction/oxidation cycle during catalytic gasification (Shadman and Sams, 1985). Moulijn *et al.* (1984) have described this cycle with the following reaction sequence (Moulijn *et al.*, 1984):



In reactions 2.22 and 2.23, K<sub>x</sub>O<sub>y</sub> represents the reduced form, while K<sub>x</sub>O<sub>y+1</sub> represents the oxidised form (Moulijn *et al.*, 1984). According to Moulijn *et al.* (1984), reaction 2.23 is the rate determining step. The reaction rate depends on the concentration of oxidised potassium species (K<sub>x</sub>O<sub>y+1</sub>), and is therefore controlled by the degree of oxidation obtained by the gas phase.

In addition to research conducted to study the mechanisms describing catalytic steam and CO<sub>2</sub> reactions, studies have also focused on the reaction between the carbon and catalyst at temperatures exceeding 700 °C, under inert conditions (Shadman *et al.*, 1987). The mechanism proposed by Shadman and Sams (1985) is expected to be valid for sodium and potassium carbonates:



In the above proposed mechanism, M can be either potassium or sodium. Reactions 2.24-2.26 show the reduction of the catalyst to form (-COM) and (-CO<sub>2</sub>M) and the production of CO. The CO produced during the reduction phase is only dependant on the initial catalyst concentration (Shadman *et al.*, 1987). After reduction of the catalyst has occurred, catalyst loss is observed due to vaporisation. The vaporisation of the catalyst is represented by reaction 2.27 (Shadman *et al.*, 1987). Shadman *et al.* (1987) states that reaction 2.27 is considerably faster than reaction 2.26, and that the amount of catalyst lost is always less than the amount of catalyst reduced.

## 2.7. Summary of previous catalytic gasification research

Table 2.2 contains a summary of research conducted in the field of catalytic gasification. Of specific importance is the particle size ranges used for catalytic gasification investigations, which indicate that the focus thus far has been on using small coal particles and powders.

**Table 2.2: Summary of catalytic gasification research**

<b>Author</b>	<b>Reactivity analysis</b>	<b>Catalysts used</b>	<b>Catalyst addition method</b>	<b>Particle size</b>	<b>Reaction models applied</b>
Yeboah <i>et al.</i> (2003)	CO <sub>2</sub> gasification (550-1000 °C)	Li <sub>2</sub> CO <sub>3</sub> , Na <sub>2</sub> CO <sub>3</sub> , K <sub>2</sub> CO <sub>3</sub> , KOH, NaNO <sub>3</sub> , CS <sub>2</sub> CO <sub>3</sub> , KNO <sub>3</sub> , LiNO <sub>3</sub> , K <sub>2</sub> SO <sub>4</sub> ,	-Physical mixing -Incipient wetness method	250 µm	-
Wang <i>et al.</i> (2009)	Steam gasification (750-1000 °C)	K <sub>2</sub> CO <sub>3</sub>	Physical mixing	-150 µm	-
Zhang <i>et al.</i> (2009)	CO <sub>2</sub> -gasification (850 °C)	Ca(COOH) <sub>2</sub> .H <sub>2</sub> O, KCOOH	Aqueous solution impregnation	-	Modified RPM
Sharma <i>et al.</i> (2008)	Steam gasification (650-775 °C)	K <sub>2</sub> CO <sub>3</sub>	Physical mixing	-75 µm	-
Lang and Neavel (1982)	Steam gasification (760 °C)	Ca(OH) <sub>2</sub> , K <sub>2</sub> CO <sub>3</sub>	-Aqueous solution impregnation -Ion-exchange	300-600 µm	-
Sheth <i>et al.</i> (2003)	Steam gasification (650-771 °C)	K <sub>2</sub> CO <sub>3</sub> , Na <sub>2</sub> CO <sub>3</sub> , Li <sub>2</sub> CO <sub>3</sub>	-Incipient wetness -Physical mixing	-595 +149 µm	Homogeneous and LH models
Sun <i>et al.</i> (2004)	CO <sub>2</sub> -gasification (850-950 °C)	Fe(NO <sub>3</sub> ) <sub>3</sub> , Ca(NO <sub>3</sub> ) <sub>2</sub> , KNO <sub>3</sub> , NaNO <sub>3</sub>	-Aqueous solution impregnation -Ultrasonic treatment	-74 µm	Distributed activation energy model (DAEM)
Yuh and Wolf (1983)	Steam gasification (700-800 °C)	K <sub>2</sub> CO <sub>3</sub>	Aqueous solution impregnation	88-105 µm	RCM
Guzman and Wolf (1982)	Steam gasification (695-800 °C)	K <sub>2</sub> CO <sub>3</sub>	Aqueous solution impregnation	120 µm	Grain model
Karimi <i>et al.</i> (2011)	Steam gasification (650-800 °C)	K <sub>2</sub> CO <sub>3</sub> , Na <sub>2</sub> CO <sub>3</sub>	Physical mixing	38-120 µm	SCM and LH models

Yeboah *et al.* (2003) investigated various eutectic salt mixtures, as well as different catalyst addition methods, for the gasification of Illinois No. 6 coal. CO<sub>2</sub> gasification experiments were performed in a TGA and fixed-bed laboratory scale reactor. It was found that eutectic catalysts increased reaction rates at lower temperatures, owing to their lower melting point (Yeboah *et al.*, 2003). During investigation, the 43.5% Li<sub>2</sub>CO<sub>3</sub>-31.5% Na<sub>2</sub>CO<sub>3</sub>-25% K<sub>2</sub>CO<sub>3</sub> and 39% Li<sub>2</sub>CO<sub>3</sub>-38.5% Na<sub>2</sub>CO<sub>3</sub>-22.5% Rb<sub>2</sub>CO<sub>3</sub> ternary catalysts were identified to be the most effective, while the best binary catalyst was found to be 29% Na<sub>2</sub>CO<sub>3</sub>-71% K<sub>2</sub>CO<sub>3</sub>. However, the ternary catalysts had a larger influence on the reaction rate when compared to the binary catalysts. TGA results showed that the use of the incipient wetness method gave better reactivity results than the physical mixing method, due to enhanced catalyst distribution and dispersion on the coal surface (Yeboah *et al.*, 2003). Sheth and co-workers (2003) studied the reaction kinetics of steam gasification with binary and ternary catalysts. A Langmuir-Hinshelwood rate equation was derived by incorporating the homogeneous model and only considering the catalytic gasification rates, thus neglecting thermal gasification rates. It was found that the LH type rate equation fitted the experimental data reasonably well at different pressures, temperatures and steam flow rates (Sheth *et al.*, 2003).

Steam gasification of K<sub>2</sub>CO<sub>3</sub>-catalysed char was investigated by Wang and co-workers (2009), by using a bench scale fixed-bed reactor. The effect of the catalyst on the gasification rate, as well as catalyst selectivity, was studied. It was found that K<sub>2</sub>CO<sub>3</sub> loadings of 10-17.5 wt.% drastically increased the gasification rate at temperatures ranging from 700 °C to 750 °C. It was reported that the addition of a catalyst significantly increased hydrogen formation, while low concentrations of CO and almost no CH<sub>4</sub> were produced (Wang *et al.*, 2009). Wang and co-workers (2009) also proposed an oxygen transfer and intermediate hybrid mechanism for describing catalytic selectivity.

Zhang *et al.* (2009) studied the kinetics of catalytic CO<sub>2</sub>-gasification reactions using coal char and carbon, and reviewed possible reaction models to describe the experimental data. Results obtained from TG-DTA analyses indicated that the calcium catalyst increased reactivity up to 40% conversion, while the reactivity increased with conversion for the potassium-catalysed experiments. Zhang and co-workers (2009) modified the random pore model specifically for catalytic CO<sub>2</sub>-gasification systems. It was found that this extended RPM accurately predicted the experimental reactivity, and that the empirical constants correlated well with the catalyst loading (Zhang *et al.*, 2009).

Australian Oaky Creek coal was used by Sharma *et al.* (2008) to study the production of H<sub>2</sub> and synthesis gas during catalytic steam gasification experiments. The coal was Catalytic steam gasification of large coal particles

demineralised to obtain an ash content of less than 0.05 wt.%, which is known as HyperCoal. Reactivity experiments were conducted in a TG-DTA, and the effect of temperature and steam partial pressure was investigated. The catalysed experiments were found to be four times faster than the uncatalysed experiments. The absence of mineral matter in the HyperCoal made it possible to recycle the catalyst up to four times without any variation in reactivity, since the formation of inactive potassium-compounds was eliminated, unlike for coal. The change in steam partial pressure did not have a significant effect on the reaction rate. Variations in experimental temperature indicated that the reactivity was temperature sensitive, and that the reaction rate decreased with decreasing temperature (Sharma *et al.*, 2008).

Lang and Neavel (1982) investigated the use of a calcium catalyst as a low-cost alternative to  $K_2CO_3$ , for catalytic steam gasification. Reactivity experiments were conducted with Illinois No. 6 coal, and were performed in a bench scale fluidised-bed reactor. It was observed that the calcium catalyst did not maintain its activity during the gasification reactions. The investigators also found that the calcium catalyst was not as mobile as the potassium catalyst, and concluded that unlike potassium it was not a suitable methanation catalyst (Lang and Neavel, 1982).

Sun *et al.* (2004) used Shenmu maceral chars to investigate  $CO_2$ -gasification kinetics with and without catalyst. All reactivity experiments were conducted using a TGA. Sun and co-workers (2004) reported that reactivity of the macerals significantly increased with catalyst loading. It was also seen that the type of catalyst addition method greatly influenced the reactivity of the chars. The gasification kinetics were analysed with the DEAM, and it was found that the addition of a catalyst reduced the activation energy while increasing the reaction rate (Sun *et al.*, 2004).

Yuh and Wolf (1983) and Guzman and Wolf (1982) conducted similar catalytic reactivity experiments using an electrobalance. Yuh and Wolf (1983) used supercritical extracted chars, while Guzman and Wolf (1982) used activated carbon and Illinois No. 6 coal char. Both of these studies investigated the kinetics of  $K_2CO_3$ -catalysed gasification reactions, and proposed suitable reaction models to describe experimental data. Yuh and Wolf (1983) found that the RCM accurately fit the experimental data of  $K_2CO_3$ -catalysed steam gasification reactions. In a separate study, also conducted by Yuh and Wolf (1984), it was found that sodium-catalysed reaction could also be accurately described by the RCM. Guzman and Wolf (1982) reported similar findings for the activation energies, but proposed a model which assumed that the reaction rate was proportional to the catalyst-solid contact

area. The grain model was used to derive a suitable model to describe catalysed systems (Guzman and Wolf, 1982).

Karimi and co-workers (2011) studied the kinetics of catalytic steam gasification using bitumen coke from Canada. Experiments were performed at atmospheric pressure in a TGA. The LH rate model was used to accurately describe the initial reaction rate at steam partial pressures between 60 kPa and 85 kPa. The reaction rates obtained later in the gasification process were successfully predicted with the SCM. Karimi and co-workers proposed that the reaction rate at different stages of gasification varied proportionally to the immediate surface catalyst loading at a particular conversion (Karimi *et al.*, 2011).