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## **A Review of the Water Gas Shift Reaction Kinetics**

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# A Review of the Water Gas Shift Reaction Kinetics

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## Abstract

The world's progression towards the Hydrogen economy is facilitating the production of hydrogen from various resources. In the carbon based hydrogen production, Water gas shift reaction is the intermediate step used for hydrogen enrichment and CO reduction in the synthesis gas. This paper makes a critical review of the developments in the modeling approaches of the reaction for use in designing and simulating the water gas shift reactor. Considering the fact that the rate of the reaction is dependent on various parameters including the composition of the catalyst, the active surface and structure of the catalyst, the size of the catalyst, age of the catalyst, its operating temperature and pressure and the composition of the gases, it is difficult to narrow down the expression for the shift reaction. With different authors conducting experiments still to validate the kinetic expressions for the shift reaction, continuous research on different composition and new catalysts are also reported periodically. Moreover the commercial catalyst manufacturers seldom provide information on the catalyst. This makes the task of designers difficult to model the shift reaction. This review provides a consolidated listing of the various important kinetic expressions published for both the high temperature and the low temperature water gas shift reaction along with the details of the catalysts and the operating conditions at which they have been validated.

**KEYWORDS:** water gas shift reaction, reaction kinetics

## 1. INTRODUCTION

The Water Gas Shift Reaction (WGSR) is a reaction traditionally used for the production of Hydrogen from synthesis gas which is further used for ammonia production in the fertilizer industry, petroleum refineries for a variety of operations and recently as fuel for power generation and transportation. The use of gasification for power generation has also increased the use of water gas shift reactors multifold. The earliest recording of the reaction dates back to 1888 [Rhodes et al., 1995], and its prominence came with the Haber ammonia synthesis process and development of catalyst by Bosch and Wilde in 1912 [Twigg, 1989]. The catalyst developed containing iron and chromium was capable of catalyzing the reaction at 400<sup>0</sup>C to 500<sup>0</sup>C and reduced the exit carbon monoxide content to around 2%.

Water gas shift reaction is a moderately exothermic reversible reaction and is expressed by



The equilibrium constant of the reaction decreases with increasing temperature. The reaction is thermodynamically favoured at low temperatures and kinetically favoured at high temperatures. Since there is no change in the volume from reactants to products, the reaction is not affected by pressure. The WGSR can be catalyzed by both metals and metal oxides. Historically, in the ammonia plant, the iron oxide chromium oxide catalyst in an adiabatic single reactor produced an exit composition of carbon monoxide at 2 – 4% as the temperature increases along the length of the reactor and approaches equilibrium [Twigg, 1989]. At lower temperatures, these catalysts lose their activity and hence to reduce the CO levels to less than 1 %, multiple beds with inter cooling was necessary. Since these catalysts could work in only high temperatures, the iron oxide – chromium oxide catalysts were called High Temperature (HT) shift catalysts. Later copper based catalysts were developed to operate at lower temperatures in the range of 200<sup>0</sup>C and these reactors could achieve exit CO concentrations of 0.1 to 0.3%. The temperature limitation is enforced due to the dew point of the gaseous mixture. These catalysts were known as Low Temperature (LT) shift catalysts. Commercially the water gas shift reaction is carried out in two adiabatic stages, namely the high temperature shift followed by low temperature shift with inter cooling to maintain the inlet temperatures [Twigg, 1989]. This configuration is necessitated because, the copper based catalyst can be easily poisoned by sulphur compounds which comes from coal or hydrocarbon sources whereas the iron based catalyst are sulphur tolerant. If sulphur is available in the feed, a guard bed should also be used to concentrate and remove the sulphur compounds to protect

the catalyst. Pasel et al. (2005) has suggested using isothermal reactors based on his experiments.

Both the high temperature and low temperature catalysts are available commercially and every vendor has a specific composition and characteristics for the catalysts. Active research is also carried out across the globe to develop better catalysts for the reaction. With the commercialization of fuel cell powered vehicles and fuel cell based power generation, the need for active water gas shift catalyst is felt as this reaction consumes the bulk space requirements in the power generation system. Moreover designing the reactor for this reaction requires the prediction of the rate of the reaction which in turn is predicted by the kinetics of the reaction. Hence it is imperative that the kinetics of the reaction be known to designers. Keeping in mind this requirement, a literature search was carried out to list the various kinetic expressions available in the open literature that could help in determining the rate of the reaction. Even though the focus was on the kinetic parameters, the details of the catalysts and the operating conditions on which these models were developed were also consolidated to help understand the reaction conditions.

## 2. HIGH TEMPERATURE SHIFT CATALYSTS

The high temperature catalyst can operate in the temperature range of 310<sup>0</sup>C to 450<sup>0</sup>C and are called ferrochrome catalysts because of their composition [Rhodes et al., 1995]. The reaction is operated adiabatically in the industrial scale where the temperature increases along the length of the reactor. Hence to prevent the catalyst bed temperature from going higher that damages the catalyst, the inlet temperature is normally maintained at 350<sup>0</sup>C. This inlet temperature can give a maximum temperature of approximately 550<sup>0</sup>C at the exit. Newsome (1980) has reported the typical composition of high temperature shift catalyst as 74.2% Fe<sub>2</sub>O<sub>3</sub>, 10.0% Cr<sub>2</sub>O<sub>3</sub>, 0.2% MgO and the remaining being volatiles. The Cr<sub>2</sub>O<sub>3</sub> acts as a stabilizer and prevents the sintering of the iron oxide and its optimal content in the catalyst is reported by Newsome (1980) to be 14%. To prevent the compromise on surface area, 8% is used industrially [Rhodes et al., 2002]. The high temperature reactor is capable of reducing the CO concentration to 3%, which is the equilibrium concentration at 450<sup>0</sup>C. The industrial reactors can operate from atmospheric pressure to 8375 kPa and varying compositions of gases with CO composition ranging from 3% to 80% [Newsome, 1980]. Rase (1977) has listed inorganic salts, Boron, Oils, Phosphorous compounds, liquid water (temporary poison) and sulphur compounds greater than 50 ppm as poisons for the iron chromia catalyst.

The pretreatment of HT shift catalyst is carried out by partially reducing the Hematite (Fe<sub>2</sub>O<sub>3</sub>) to Magnetite (Fe<sub>3</sub>O<sub>4</sub>) using the addition of the process gas

mixtures to activate the catalyst [Rhodes et al., 1995]. This also converts any  $\text{CrO}_3$  present in the catalyst to  $\text{Cr}_2\text{O}_3$ . The reactions are



This partial reduction process should be controlled by controlling the gas feed mixture concentrations of the constituent gases to achieve the required reduction. Over reduction of the catalyst can cause damage to the catalyst pellets. A convenient tool to control the reduction process is the reduction factor proposed by Rhodes et al. (2002). The typical value of the reduction factor (R) should be less than 1.2 and values more than 1.6 can cause over reduction.

$$R = (\{[\text{CO}] + [\text{H}_2]\} / \{[\text{CO}_2] + [\text{H}_2\text{O}]\}) \quad (4)$$

In high temperature shift reaction, the ratio of steam to CO is an important parameter and operating the reaction at low ratios could lead to formation of metallic iron, methanation, carbon deposition and Fischer Tropsch reaction [Twigg, 1989]. Callaghan et al. (2003) suggests a contact time of approximately 3-9 seconds for the reaction.

Publications on newer composition of the catalysts and newer catalysts are continuously emerging. Grenoble and Estadt (1981) analyzed the catalytic effect of group VIIB, VIII and IB metals coated on alumina, silica and carbon on WGS. They found that the support for the metal or metal oxide should be acidic in nature to help the reaction. The turnover number decreased in the order of Cu, Re, Co, Ru, Ni, Pt, Os, Au, Fe, Pd, Rh and Ir supported on alumina. Salmi et al. (1988) and Hakkarainen et al. (1993) have reported that the commercial cobalt – molybdenum oxide catalyst was capable of catalyzing the reaction above  $350^\circ\text{C}$  and can be sulphur tolerant. The studies by Rhodes and Hutchings (2003) using different promoters for the high temperature catalyst have shown higher conversions. The study involved addition of 2 wt% of B, Pb, Cu, Ba, Ag and Hg to the high temperature catalyst and studying the effect of the promoters on the conversion. The activity of the promoters obtained in the temperature range of  $350^\circ\text{C}$  to  $440^\circ\text{C}$  were,  $\text{Hg} > \text{Ag}, \text{Ba} > \text{Cu} > \text{Pb} > \text{unpromoted} > \text{B}$ . Various studies have showed the promotion by Cu, Au and Ru of the iron chromia catalyst as promising. The replacement of chromia by other less toxic component has not been so far commercially successful.

### 3. LOW TEMPERATURE SHIFT CATALYSTS

The low temperature shift reaction occurs at 200 °C to 250 °C and the catalyst is a mixture of ZnO, CuO and Cr<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> at varying composition depending on the manufacturer. The typical composition of the catalyst are 68 – 73 % ZnO, 15 – 20% CuO, 9 – 14 % Cr<sub>2</sub>O<sub>3</sub>, 2 – 5 % Mn, Al and Mg oxides [Newsome, 1980] and 32-33% CuO, 34-53% ZnO, 15-33% Al<sub>2</sub>O<sub>3</sub> [Callaghan et al., 2003 and Rhodes et al., 1995]. Recent catalysts can also be operated at medium temperatures of around 300°C. The active species in the catalyst is the copper metal crystallites. ZnO and Cr<sub>2</sub>O<sub>3</sub> provide the structural support for the catalyst and Al<sub>2</sub>O<sub>3</sub> is largely inactive and helps in the dispersion and minimizes pellet shrinkage. Copper is more susceptible to thermal sintering and hence should not be operated at higher temperature [Twigg, 1989]. The lower temperature of operation is restricted by the dew point of the mixture in industrial conditions. The catalyst is sulphur, Halogen and unsaturated hydrocarbon intolerant and hence needs to be protected from these compounds [Rase, 1977]. The ZnO is effective in reducing the poisoning of copper by sulphur [Twigg and Spencer, 2001]. To prevent the sulphur poisoning usually a guard bed of ZnO is always used before the low temperature shift reactor. The exit concentration of CO from the low temperature reactor will be 0.1% which is desirable in industrial practice. The advantages of the LT catalyst are its selectivity and fewer side reactions occurring at higher operating pressures. The normal life time of the low temperature catalyst is 2 – 3 years [Rase, 1977].

Similar to the HT catalyst, the LT catalyst needs to be activated and hence the catalyst is exposed to the process stream with dilute H<sub>2</sub> [Rhodes et al., 1995]. The CuO is reduced to copper by the following reaction and the catalyst gets activated.



Since the reduction reaction is exothermic, the catalyst should be exposed to the process stream at temperatures of 230°C and higher temperatures will lead to sintering of the catalyst [Callaghan et al., 2003]. Moreover the process stream should contain Hydrogen and steam is not preferable as condensation could affect the catalyst. Tanaka et al. (2003) found CuMn<sub>2</sub>O<sub>4</sub> and CuAl<sub>2</sub>O<sub>4</sub> mixed oxide catalyst having conversion of CO more than the commercial catalyst. Henrik Kusar et al. (2006) have found the copper ceria catalyst to be non-pyrophoric and stable. Studies on Mn promoted Cu/Al<sub>2</sub>O<sub>3</sub> by Dinesh et al. (2006) showed that with 8.55 wt% of Mn, 513 K and space time of 5.33 hour, CO conversion of 90% could be achieved. Many more studies on various modifications in the catalysts

are being proposed routinely in the literature. But the mainstay of all the catalysts still is copper.

#### 4. NOBLE METAL CATALYSTS

For compact fuel cell applications, several authors have listed the inherent disadvantages with the existing commercial catalysts and hence have tried the use of noble metals as catalysts. In the transportation sector, efforts are on to integrate reforming of fossil fuel and water gas shift reaction with the fuel cell technologies to improve modularity, reduce the emission and increase the efficiency of fuel utilization. The commercial Iron based catalysts are prone to coke formation in the presence of excess fuel from the reformer [Wheeler et al., 2004]. The use of the commercial copper based catalysts, due to kinetic limitations will occupy more volume. Moreover the Cu catalyst is pyrophoric in reduced state and gets deactivated in the presence of condensed water due to leaching of active component or formation of surface carbonates [Henrik Kusar et al.(2006), Wheeler et al.(2004), Mhadeshwar and Vlachos (2005)]. The catalysts should also be capable of withstanding thermal cycling and faster response during startup and shutdown. Hence the search for a better noble metal or promoted catalyst is still being carried out.

Hilaire et al. (2001) found the ceria supported transition metals acting as catalysts for the water gas shift reaction. Apanee et al. (2003) found the Pt/CeO<sub>2</sub> catalyst more active than Au/CeO<sub>2</sub> and Au/Fe<sub>2</sub>O<sub>3</sub>. Wheeler et al. (2004) studied the possibility of the WGSR using noble metals and metals with Ceria in the temperature range of 300<sup>0</sup>C to 1000<sup>0</sup>C and found the activity of the metals in the order, Ni>Ru>Rh>Pt>Pd. The measured frequency factor and activation energy are given in Table 4. Phatak et al. (2007) carried out experiments on Pt supported on alumina and ceria at varying compositions and reported their order of reactions and activation energy. Pt exhibited lower turnover rate than Cu.

Gonzaleza et al. (2010) studied the effect of Pt catalysts supported on TiO<sub>2</sub>, CeO<sub>2</sub> and Ce–TiO<sub>2</sub> and found the Pt supported on Ce-modified TiO<sub>2</sub> support exhibiting better activity than those corresponding to individual ceria and titania supported catalysts. Most of the recent studies have been directed in using any of the precious metals like Pt, Rh, Pd and Au deposited on Ceria, Zirconia, Alumina, Titania, Thoria or Magnesia supports [Andrea et al., 2010]. Latest research works have started using mixed oxides of the above supports with the precious metals dispersed in them to effect the low temperature water gas shift reaction. Ratnasamy and Wagner (2009) have recently published a comprehensive review on the latest developments on the catalysts for the water gas shift reaction.

## 5. REACTION KINETICS

The kinetic models provide the easiest way to represent the reaction and help the designers in determining the rate of the reaction and thus design the reactors. Basically the kinetic expressions can be classified as microkinetic approach and the empirical method. The microkinetic method is based on the knowledge about the elementary steps that are involved in the reaction and its energetics. This method explores the detailed chemistry of the reaction. Using this method it is possible to estimate the surface coverage, reaction order and activation enthalpy. This method provides the accurate pathway and prediction of the reaction, but is computationally intensive. On the other hand, the empirical models are based on the experimental results and are typically expressed in the Arrhenius model and provide an easy and computationally lighter way to predict the rate of reaction. Most of the design works use the empirical models. The WGSR has been explained through both the microkinetic approach and empirical approach.

### 5.1 Micro Kinetic Models

The WGSR mechanism over the metal oxide catalyst has been broadly classified as

1. Regenerative Mechanism and
2. Associative Mechanism

In the regenerative mechanism also known as the redox mechanism, the oxidation reduction cycle occurring on the catalyst surface is responsible for the reaction. In the redox mechanism it is proposed that the catalyst surface is oxidized by H<sub>2</sub>O, producing H<sub>2</sub> as by product followed by reduction of surface to convert CO to CO<sub>2</sub> as represented in equations 6 and 7.



The redox mechanism is used to explain the high temperature water gas shift reaction. The low temperature shift reaction has been explained by several authors using both the regenerative mechanism and the associative mechanism.

The mechanism for the water gas shift reaction has been elucidated from single copper crystal studies. Ovesen et al. (1992) proposed an eight step model based on surface redox mechanism using single crystal studies on copper. Citing his studies, he found the reaction structure sensitive with the reaction more on Cu (1 1 0) than Cu (1 1 1). Wang et al. (2003) investigated the kinetic properties for

both the forward and reverse reactions and supported the surface redox mechanism at low temperatures. In their energetic analysis they found the dissociation of water as the rate controlling step. They too supported the sensitivity of the reaction to Cu structure. Rhodes et al. (1995) has questioned the redox mechanism by showing that the reduction reaction as possible and raised doubt about the possibility of the oxidative step.

The associative mechanism is an adsorption - desorption model where the adsorbed species interact to form an adsorbed intermediate which then decomposes to form H<sub>2</sub> and CO<sub>2</sub> as explained in reaction step 8.



Even though many authors support this mechanism, there is still no convergence of idea on the nature of the intermediate. The conflict basically in the associative mechanism is based on the nature of the intermediate formed namely Formate intermediate mechanism and Carboxyl intermediate mechanism.

Rhodes et al. (1995) explained the associative mechanism of Cu – Chromite as a Langmuir Hinshelwood process with the reaction steps 9 to 13.



They found the intermediate species to be formate. Grenoble and Estadt (1981) proposed formic acid as the intermediate based on the fact that the principal decomposition pathways for formic acid involved both the reactants and products of the water gas shift reaction. Ovesen et al., (1996) further modified the 8 step microkinetic model he proposed in 1992 based on redox mechanism, by adding 3 more steps to account for the formate mechanism and suggested that the formate coverage was negligible at atmospheric conditions and was significant at higher pressures. He found the water dissociation and carbon monoxide oxidation as the rate limiting steps. Gideon Botes (2007) listed out three different mechanisms and applied them to the data generated from SASOL (South African Coal, Oil and Gas Corporation) and found the associative formate mechanism providing better fit for the data. Waugh (1999) using the microkinetic approach has questioned the

formate mechanism and supported the redox mechanism. Sun et al. (2005) studied the mechanism of precious metals for the water gas shift reaction and found the Langmuir Hinshelwood model giving better predictions.

Salmi et al. (1989) carried out transient studies on the water gas shift reaction and observed that  $H_2$  is liberated slowly which contradicted with the associative mechanism and put forth a mechanism with both adsorptive and regenerative reaction steps. Hakkarainen et al. (1994) found the reaction mechanisms different for the ferrochrome catalyst and the Co – Mo catalysts using transient response studies. Keiski et al. (1996) carried out stationary and transient studies on the high temperature water gas shift reaction and found that the CO adsorption,  $CO_2$  desorption and  $H_2$  formation were rate determining steps in the transient studies. Fishtik and Dutta (2002) found out that the formate and associative mechanisms were dominant in the low temperature region whereas the redox mechanism was dominant at higher temperatures.

Gokhale et al. (2008) has proposed the carboxyl mechanism as the intermediate route for the water gas shift reaction based on studies with Cu(1 1 1). They found the formate species non reactive and at high pressure contribute to blocking of active sites which explained the loss in activity with increase in  $CO_2$  concentration. Mao et al. (2008) using the Density Functional Theory investigation has reported that the formate mechanism had low probability whereas the carboxyl and the redox mechanisms had higher probability on copper catalyst. Grabow et al. (2008) carried out studies on low temperature water gas shift reaction on Pt (1 1 1) and found the carboxyl mechanism better suited than the formate mechanism. Tang et al. (2009) using density functional method and slab models studied the mechanism of the water gas shift reaction on Cu (1 1 1). They found the carboxyl and redox mechanisms feasible rather than the formate and associative mechanisms. Thus an undisputed conclusive mechanism is not available for the water gas shift reaction so far with many researchers taking sides for these mechanisms based on their studies. So to carry out the microkinetic simulation of the water gas shift reaction, the kinetics of the elementary steps can be used. The 18 step microkinetic model to explain the water gas shift reaction based on Cu (1 1 1) is given by Callaghan et al. (2003), Fishtik and Dutta (2002) is listed out in Table 1.

**Table 1 Microkinetic model for forward water gas shift reaction on Cu(1 1 1)**  
[Callaghan et al. (2003), Fishtik and Dutta (2002)]

Elementary Step	Ko	Ea (kcal/mol)
	Adsorption/desorption(1/atm s) Surface reaction (1/s)	
$\text{CO} + \text{S} \leftrightarrow \text{CO.S}$	$1.5 \times 10^6$	0
$\text{H}_2\text{O} + \text{S} \leftrightarrow \text{H}_2\text{O.S}$	$1.0 \times 10^6$	0
$\text{H}_2\text{O.S} + \text{S} \leftrightarrow \text{OH.S} + \text{H.S}$	$1.0 \times 10^{13}$	25.4
$\text{CO.S} + \text{O.S} \leftrightarrow \text{CO}_2.\text{S} + \text{S}$	$1.0 \times 10^{13}$	10.7
$\text{CO.S} + \text{OH.S} \leftrightarrow \text{HCOO.S} + \text{S}$	$1.0 \times 10^{13}$	0
$\text{OH.S} + \text{S} \leftrightarrow \text{O.S} + \text{H.S}$	$1.0 \times 10^{13}$	15.5
$\text{CO.S} + \text{OH.S} \leftrightarrow \text{CO}_2.\text{S} + \text{H.S}$	$1.0 \times 10^{13}$	0
$\text{HCOO.S} + \text{S} \leftrightarrow \text{CO}_2.\text{S} + \text{H.S}$	$1.0 \times 10^{13}$	1.4
$\text{HCOO.S} + \text{O.S} \leftrightarrow \text{CO}_2.\text{S} + \text{OH.S}$	$1.0 \times 10^{13}$	4
$\text{H}_2\text{O.S} + \text{O.S} \leftrightarrow 2\text{OH.S}$	$1.0 \times 10^{13}$	29
$\text{H}_2\text{O.S} + \text{H.S} \leftrightarrow \text{OH.S} + \text{H}_2.\text{S}$	$1.0 \times 10^{13}$	26.3
$\text{OH.S} + \text{H.S} \leftrightarrow \text{O.S} + \text{H}_2.\text{S}$	$1.0 \times 10^{13}$	1.3
$\text{HCOO.S} + \text{OH.S} \leftrightarrow \text{CO}_2.\text{S} + \text{H}_2\text{O.S}$	$1.0 \times 10^{13}$	0.9
$\text{HCOO.S} + \text{H.S} \leftrightarrow \text{CO}_2.\text{S} + \text{H}_2.\text{S}$	$1.0 \times 10^{13}$	14.6
$\text{CO}_2.\text{S} \leftrightarrow \text{CO}_2 + \text{S}$	$4.0 \times 10^{12}$	5.3
$\text{H.S} + \text{H.S} \leftrightarrow \text{H}_2.\text{S} + \text{S}$	$1.0 \times 10^{13}$	15.3
$\text{H}_2.\text{S} \leftrightarrow \text{H}_2 + \text{S}$	$6.0 \times 10^{12}$	5.5
$\text{H.S} + \text{H.S} \leftrightarrow \text{H}_2 + 2\text{S}$	$6.0 \times 10^{12}$	15.3

(S is the vacant site and X.S is the adsorbed X species)

## 5.2 Macro Kinetic Models

There are a number of kinetic expressions published since the use of WGS in the ammonia process. Since it is difficult to list out the variations in the models, only the commonly used models are listed out in Table 2. In general the associative mechanism is represented by the Langmuir Hinshelwood (LH) model and the Eley – Rideal type model.

The equilibrium constant for the WGS reaction is a function of temperature and various approaches are used to calculate the value at the required temperature of operation. Table 3 lists out the numerical values of the equilibrium constant at various temperatures in the regions of concern and a complete listing of equilibrium constants for the water gas shift reaction over a temperature range of 200°C to 1199°C is provided by Twigg (1989).

**Table 2 Kinetic Expressions for WGSR**

<i>Model</i>	<i>Kinetic Expression</i>
<b>High Temperature Shift [Ref. Twigg (1989)]</b>	
Kodama et al.	$r = \frac{k \left[ [CO][H_2O] - \frac{[CO_2][H_2]}{K} \right]}{(1 + K_{CO}[CO] + K_{H_2O}[H_2O] + K_{CO_2}[CO_2] + K_{H_2}[H_2])}$
Hulburt - Vasan	$r = \frac{k[H_2O]}{1 + K[H_2O]/[H_2]}$
Langmuir Hinshelwood Model	$r = \frac{kK_{CO}K_{H_2O} \left[ [CO][H_2O] - \frac{[CO_2][H_2]}{K} \right]}{(1 + K_{CO}[CO] + K_{H_2O}[H_2O] + K_{CO_2}[CO_2] + K_{H_2}[H_2])^2}$
Oxidation Reduction Model	$r = \frac{k_1k_2\{[CO][H_2O] - [CO_2][H_2]/K\}}{k_1[CO] + k_2[H_2O] + k_{-1}[CO_2] + k_{-2}[H_2]}$
Bohlboro et al.	$r = kP_{CO}^a P_{H_2O}^b P_{CO_2}^c P_{H_2}^d$
<b>Low Temperature Shift [Ref. Van Herwijnen and De Jong (1980)]</b>	
Campbell et al.	$r = k \frac{P_{CO}P_{H_2O}(1-\beta)}{(1 + K_{CO}P_{CO} + K_{H_2O}P_{H_2O} + K_{CO_2}P_{CO_2} + K_{H_2}P_{H_2})^2}$
Shchibrya et al.	$r = \frac{kP_{H_2O}P_{CO}(1-\beta)}{AP_{H_2O} + P_{CO_2}}$
Moe	$r = kP_{CO}P_{H_2O}(1-\beta)$
Kulkova and Temkin	$r = kP_{CO} \left( \frac{P_{H_2O}}{P_{H_2}} \right)^{0.5} (1-\beta)$
Goodgidge and Quazi	$r = kP_{CO}^a P_{H_2O}^b P_{CO_2}^c P_{H_2}^d$

The equation used by Twigg (1989) to calculate the equilibrium constants was

$$K_{eq} = \exp(Z(Z(0.63508 - 0.29353Z) + 4.1778) + 0.31688) \quad (14)$$

$$Z = (1000/T) - 1, \text{ Temperature (T) is in Kelvin} \quad (15)$$

**Table 3 Equilibrium constants for WGSR (Twigg, 1989)**

T (°C)	200	250	300	350	400	450	500	550
K <sub>eq</sub>	210.82	83.956	38.833	20.303	11.723	7.3369	4.9035	3.4586

The equilibrium constant for the reaction derived from thermodynamics is given in equation 16.

$$\ln(K_{eq}) = \frac{5693.5}{T} + 1.077 \ln(T) + 5.44 \times 10^{-4} T - 1.125 \times 10^{-7} T^2 - \frac{49170}{T^2} - 13.148 \quad (16)$$

Moe (1962) has derived a simple to use empirical model to represent the equilibrium constant which is sufficiently good for design computations and is given by

$$K_{eq} = \exp\left(\frac{4577.8}{T} - 4.33\right) \quad (17)$$

The detailed kinetic expressions for the high temperature, low temperature and noble metal catalysts were compiled and consolidated in Tables 4 and 5. In table 4, the kinetic parameters corresponding to the power law type kinetic expression are listed. These parameters are segregated based on the type of catalysts and similar catalysts are grouped together. Rhodes et al. (2003) has carried out a series of experiments on the high temperature catalysts and have reported their arrhenius parameters which are listed in Table 4. The table also lists the parameters put forth by Keiski et al. (1996) and San et al. (2009). The power law type reaction rates for the low temperature catalysts for different conditions are also listed in Table 4. Choi and Stenger (2003) and Koryabkina et al. (2003) have provided a comprehensive analysis of the previously published parameters. A good review of the noble metal catalysts was available in the work of Grenoble and Estadt (1981), Wheeler et al. (2004) and Phatak et al. (2004). By substituting the pre exponential factor, activation energy and the powers of the component gases, the rate of reaction can be computed for various catalysts.

Apart from the power law type of kinetic expression where the orders of the components are listed, complex kinetic expressions have also been developed to represent the water gas shift reaction. Podolski and Kim (1974) made a detailed study of the available models and concluded that their experimental data was reproduced by both the Langmuir Hinshelwood type model and the power law type model. The same is supported by Newsome (1980) where he has listed the

power law model by Bohlboro. This model was capable of predicting the rate in the presence of  $H_2S$ . Rase (1977) has provided a kinetic expression for both the high temperature and low temperature shift reactions in his book which has been used by Elnashaie and Elshishini (1993) in their modeling works on the shift reaction. Singh and Saraf (1977, 1980) extended the kinetics of laboratory catalysts for both low temperature and high temperature to industrial scale by using factors for diffusion limitation, age of catalyst, pressure correction and effect of exposure to  $H_2S$ . San et al. (2009) carried out the high temperature reaction for varying catalyst composition and derived two rate equations. Keiski et al. (1996) too has provided an expression for the high temperature shift reaction. Thomas and Barton (2009) have recently used the models of San et al. and Keiski et al. for modeling the heterogeneous reactor by introducing correction factors for porosity.

Earlier, the kinetic expressions for High temperature were applied to the low temperature shift also. Newsome (1980) has reported the Temkin model for the low temperature range. Van Herwijnen and De Jong (1980) have listed the various kinetic models for the low temperature WGS. Among them are the models by Campbell and Moe based on industrial data, Shchibrya, Kulkova and Temkin based on the redox mechanism and the power law model by Goodridge and Quazi. Ovesen et al. (1992) introduced a factor to account for the pressure correction in a power law expression. A pressure correction formulae is also provided by Rase (1977) to extrapolate the experimental data normally carried out at atmospheric pressure to industrial data. Amadeo and Laborde (1995) made an analysis of five model equation, 2 representing redox mechanism and 3 representing Langmuir Hinshelwood model. They found the LH model which included the adsorption of the four components and surface reaction controlling the reaction provided best fit to their experimental results. Based on their experimental results, they provided a modified LH model for the low temperature shift reaction.

Zhao et al. (1999) using the reduced rate method analyzed the pressure effects and found the LH model to be better than the other models. Choi and Stenger (2003) tested the validity of two adsorptive, two regenerative and one empirical model using  $Cu/ZnO/Al_2O_3$  catalyst and found that all the models giving good results with the best fit provided by the single step regenerative model. They also developed their own empirical equation which is listed in Table 5. Wei et al. (2008) has included the steam to CO ratio in the kinetic expression.

The noble metal catalysts are still evolving and have not reached the commercial stage. Hence a large number of newer catalyst combinations are being reported in the literature. The noble metal that shows more promise is platinum and the kinetic expressions derived for platinum has been reported by Ding and Chan (2008). Another expression is by Sun et al. (2005) for noble metals.

**Table 4 Power Law parameters for various WGSR catalysts and operating conditions**

Catalyst	Operating Conditions	Arrhenius Parameters		Order of reaction				Reference
		Ko	Ea	l	m	n	q	
<b>High Temperature Catalyst</b>								
Fe <sub>3</sub> O <sub>4</sub> /Cr <sub>2</sub> O <sub>3</sub> 8 wt% Cr <sub>2</sub> O <sub>3</sub>	1 atm, 350 <sup>0</sup> C - 440 <sup>0</sup> C	lnKo=11.5	112 (kJ/mol)	-	-	-	-	Rhodes et al ( 2003)
Fe <sub>3</sub> O <sub>4</sub> /Cr <sub>2</sub> O <sub>3</sub> 180 -250µm	1 bar, 380 <sup>0</sup> C – 450 <sup>0</sup> C	lnKo=10.1±0.2	118±1 (kJ/mol)	-	-	-	-	Rhodes et al ( 2003)
Fe <sub>3</sub> O <sub>4</sub> /Cr <sub>2</sub> O <sub>3</sub> 180 -250µm	6 bar, 380 <sup>0</sup> C – 450 <sup>0</sup> C	lnKo=12.0±0.2	124±1 (kJ/mol)	-	-	-	-	Rhodes et al ( 2003)
Fe <sub>3</sub> O <sub>4</sub> /Cr <sub>2</sub> O <sub>3</sub> 180 -250µm	27 bar, 380 <sup>0</sup> C – 450 <sup>0</sup> C	lnKo=7.4±0.1	111±1 (kJ/mol)	-	-	-	-	Rhodes et al ( 2003)
Fe <sub>3</sub> O <sub>4</sub> /Cr <sub>2</sub> O <sub>3</sub>	3 – 5 bar 573 <sup>0</sup> C - 633 <sup>0</sup> C	2.16 x 10 <sup>11</sup> (s <sup>-1</sup> ) (lnKo=26.1)	95 (kJ/mol)	1.1	0.53	-	-	Keiski et al. (1996)
89%Fe <sub>2</sub> O <sub>3</sub> , 9% Cr <sub>2</sub> O <sub>3</sub>	575 to 675 K	ln k0 = 14.78	E/R = 9598	0.74	0.47	-0.18	0	Keiski et al. (1992)
80-90%Fe <sub>2</sub> O <sub>3</sub> , 8-13% Cr <sub>2</sub> O <sub>3</sub> , 1-2%CuO,	1 atm, 450 <sup>0</sup> C 6mm x 6mm	10 <sup>2.845</sup> (mol/ gcat s)	111 (kJ/mol)	1	0	-0.36	-0.09	San et al. (2009)
80-95%Fe <sub>2</sub> O <sub>3</sub> , 5-10% Cr <sub>2</sub> O <sub>3</sub> , 1-5%CuO,	1 atm, 450 <sup>0</sup> C 6mm x 6mm	10 <sup>0.659</sup> (mol/ gcat s)	88 (kJ/mol)	0.9	0.31	-0.156	-0.05	San et al. (2009)
CuO/Fe <sub>3</sub> O <sub>4</sub> /Cr <sub>2</sub> O <sub>3</sub> 180 -250µm	1 bar, 380 <sup>0</sup> C – 450 <sup>0</sup> C	lnKo=2.0±0.1	75±1 (kJ/mol)	-	-	-	-	Rhodes et al ( 2003)
CuO/Fe <sub>3</sub> O <sub>4</sub> /Cr <sub>2</sub> O <sub>3</sub> 180 -250µm	6 bar, 380 <sup>0</sup> C – 450 <sup>0</sup> C	lnKo=5.5±0.1	85±2 (kJ/mol)	-	-	-	-	Keiski et al. (1992)
CuO/Fe <sub>3</sub> O <sub>4</sub> /Cr <sub>2</sub> O <sub>3</sub> 180 -250µm	27 bar, 380 <sup>0</sup> C – 450 <sup>0</sup> C	lnKo=4.0±0.1	85±1 (kJ/mol)	-	-	-	-	Keiski et al. (1992)

Power gas – pilot plant data	1/4" x 3/8" , 2.20 g/cm <sup>3</sup>	9.4 x 10 <sup>7</sup> (1/s)	21.4 (kCal/g mol)	-	-	-	-	Rase (1977)
Girdler – pilot plant data	1/4" x 1/4" 1.25 g/cm <sup>3</sup>	1.47 x 10 <sup>8</sup> (1/s)	23.8 (kCal/g mol)	-	-	-	-	Rase (1977)
ICI pilot plant data	11.3" x 8.5 mm, 1.36 g/cm <sup>3</sup>	4.5 x 10 <sup>9</sup> (1/s)	27.0 (kCal/g mol)	-	-	-	-	Rase (1977)
<b>Low Temperature Catalysts</b>								
ICI – CuO-ZnO-Al <sub>2</sub> O <sub>3</sub>	-	3.99 x 10 <sup>6</sup> (s <sup>-1</sup> ) (lnKo=15.2)	52.8 (kJ/mol)	1	1	-	-	Choi and Stenger (2003)
ICI 52-1 (Copper based catalyst) density= 5.83g/cm <sup>3</sup>	1 atm, 200 <sup>o</sup> C	k = 5.37 x 10 <sup>-7</sup> (mol/m <sup>2</sup> s)/atm <sup>1+m</sup>		0.45	0.07	-	-	Salmi and Hakkarainen (1989)
	1 atm, 250 <sup>o</sup> C	k = 4.40 x 10 <sup>-5</sup> (mol/m <sup>2</sup> s)/atm <sup>1+m</sup>		1.07	0.55	-	-	
CuO-ZnO-Al <sub>2</sub> O <sub>3</sub>	-	-	41.8 (kJ/mol)	0	1	-	-	Choi and Stenger (2003)
Cu-ZnO- Al <sub>2</sub> O <sub>3</sub> (EX-2248)Sud Chemie	200 -250 μm size, 120 – 250 <sup>o</sup> C, 1:2 CO-H <sub>2</sub> O	2.96 x 10 <sup>5</sup> (s <sup>-1</sup> ) (lnKo=12.6)	47.4 (kJ/mol)	1	1	-	-	Choi and Stenger (2003)
42% CuO-ZnO-Al <sub>2</sub> O <sub>3</sub> (G-66A) Sud Chemie	396 to 448K CO/H <sub>2</sub> O =1/3	4.9 x 10 <sup>6</sup> (s <sup>-1</sup> )	71 (kJ/mol)	-	-	-	-	Henrik et al. (2006)
Cu-ZnO- Al <sub>2</sub> O <sub>3</sub>	1 atm, 200 <sup>o</sup> C	-	67 (kJ/mol)	0.2	0.6	0	0	Koryabkina et al. (2003)
40%CuO-ZnO Al <sub>2</sub> O <sub>3</sub> (United Catalysts)	1 atm, 190 <sup>o</sup> C	-	79 (kJ/mol)	0.8	0.8	-0.9	-0.9	Koryabkina et al. (2003)

Cu-ZnO- Al <sub>2</sub> O <sub>3</sub>	1 atm, 180 <sup>0</sup> C-200 <sup>0</sup> C	-	86 (kJ/mol)	1	1.4	-0.7	-0.9	Koryabkina et al. (2003)
Cu/ Al <sub>2</sub> O <sub>3</sub>	-	-	69.3 (kJ/mol)	1	1.9	-	-	Choi and Stenger (2003)
10%Cu- Al <sub>2</sub> O <sub>3</sub>	1 atm, 130 <sup>0</sup> C	-	55 (kJ/mol)	0.3	0.38	-	-	Koryabkina et al. (2003)
8%CuO-Al <sub>2</sub> O <sub>3</sub>	1 atm, 200 <sup>0</sup> C	-	62 (kJ/mol)	0.9	0.8	-0.7	-0.8	Koryabkina et al. (2003)
CuO/MnO <sub>2</sub>	-	-	55 (kJ/mol)	1	1	-	-	Choi and Stenger (2003)
8%CuO-CeO <sub>2</sub>	1 atm, 240 <sup>0</sup> C	-	56 (kJ/mol)	0.9	0.4	-0.6	-0.6	Koryabkina et al. (2003)
8%CuO- 15%CeO <sub>2</sub> - Al <sub>2</sub> O <sub>3</sub>	1 atm, 200 <sup>0</sup> C	-	32 (kJ/mol)	0.7	0.6	-0.6	-0.6	Koryabkina et al. (2003)
Cu(111)	1 atm, 340 <sup>0</sup> C	-	71 (kJ/mol)	0	0.5-1	-	-	Koryabkina et al. (2003)
Cu(110)	1 atm, 340 <sup>0</sup> C	-	42 (kJ/mol)	0	1	-	-	Koryabkina et al. (2003)
<b>Noble Metal Catalysts</b>								
Ru	300 <sup>0</sup> C 1000 <sup>0</sup> C	-	1.6 x 10 <sup>7</sup> (s <sup>-1</sup> )	80 (kJ/mol)	-	-	-	Wheeler et al. (2004)
Ru/ceria	0.008 to 0.05 s contact time	-	5.0 x 10 <sup>7</sup> (s <sup>-1</sup> )	80 (kJ/mol)	-	-	-	Wheeler et al. (2004)
Ni		-	8.0 x 10 <sup>7</sup> (s <sup>-1</sup> )	85 (kJ/mol)	-	-	-	Wheeler et al. (2004)
Ni/Ceria	Coated on	-	1.7 x 10 <sup>8</sup> (s <sup>-1</sup> )	85	-	-	-	Wheeler et

	alumina support		(kJ/mol)					al. (2004)
Rh		$3.0 \times 10^9$ (s <sup>-1</sup> )	130 (kJ/mol)	-	-	-	-	Wheeler et al. (2004)
Rh/Ceria	5wt% loading	$1.5 \times 10^{10}$ (s <sup>-1</sup> )	130 (kJ/mol)	-	-	-	-	Wheeler et al. (2004)
Rh/ Al <sub>2</sub> O <sub>3</sub>	330 <sup>0</sup> C	$5.10 \times 10^6$ (molecules/s/ site)	23.0±1.3 (kcal/mole)	-0.10	0.44	-	-	Grenoble et al. (1981)
Rh/ SiO <sub>2</sub>	350 <sup>0</sup> C	$3.23 \times 10^5$ (molecules/s/ site)	22.8±2.5 (kcal/mole)	-0.24	0.53	-	-	Grenoble et al. (1981)
Pd	300 <sup>0</sup> C - 1000 <sup>0</sup> C	$4.0 \times 10^6$ (s <sup>-1</sup> )	100 (kJ/mol)	-	-	-	-	Wheeler et al. (2004)
Pd/Ceria	0.008 to 0.05 s contact time	$4.0 \times 10^7$ (s <sup>-1</sup> )	100 (kJ/mol)	-	-	-	-	Wheeler et al. (2004)
Pt	Coated on alumina	$1.0 \times 10^6$ (s <sup>-1</sup> )	80 (kJ/mol)	-	-	-	-	Wheeler et al. (2004)
Pt/Ceria	support 5wt% loading	$2.5 \times 10^7$ (s <sup>-1</sup> )	80 (kJ/mol)	-	-	-	-	Wheeler et al. (2004)
1%Pt/ Al <sub>2</sub> O <sub>3</sub>	1atm, 225 <sup>0</sup> C - 285 <sup>0</sup> C	-	68 (kJ/mol)	0.1	1.1	-0.07	-0.44	Phatak et al. (2007)
1%Pt/ Al <sub>2</sub> O <sub>3</sub>	1atm, 285 <sup>0</sup> C - 345 <sup>0</sup> C	-	84 (kJ/mol)	0.06	1	-0.09	-0.44	Phatak et al. (2007)
1.66%Pt/ Al <sub>2</sub> O <sub>3</sub>	1atm, 285 <sup>0</sup> C	-	81 (kJ/mol)	0.11	0.82	-0.06	-0.49	Phatak et al. (2007)
1.66%Pt/ Al <sub>2</sub> O <sub>3</sub>	1atm, 300 <sup>0</sup> C	-	81 (kJ/mol)	0.1	0.77	-0.08	-0.46	Phatak et al. (2007)
2%Pt/ Al <sub>2</sub> O <sub>3</sub>	1atm, 270 <sup>0</sup> C	-	82 (kJ/mol)	-0.21	0.75	-	-	Phatak et al. (2007)
0.9%Pt/ Al <sub>2</sub> O <sub>3</sub>	1atm, 100 <sup>0</sup> C	-		0.02	0.55	-	-0.22	Phatak et al. (2007)

0.4%Pt/ Al <sub>2</sub> O <sub>3</sub>	1atm, 544 <sup>0</sup> C	-	39 (kJ/mol)	0.45	0.37	0	-0.73	Phatak et al. (2007)
Pt/ Al <sub>2</sub> O <sub>3</sub>	270 <sup>0</sup> C	1.9 x 10 <sup>6</sup> (molecules/s/ site)	19.6±1.3 (kcal/mole)	-0.21	0.75	-	-	Grenoble et al. (1981)
1%Pt/ CeO <sub>2</sub>	1atm, 200 <sup>0</sup> C	-	75 (kJ/mol)	-0.03	0.44	-0.09	-0.38	Phatak et al. (2007)
1%Pt/ CeO <sub>2</sub>	1atm, 240 <sup>0</sup> C	-	46 (kJ/mol)	0	1	-	-	Phatak et al. (2007)
1% Pt/CeO <sub>2</sub>	-	-	91 (kJ/mol)	0.14	0.66	-0.54	-0.08	Thinon et al. (2009)
Pt/SiO <sub>2</sub>	340 <sup>0</sup> C	1.18 x 10 <sup>5</sup> (molecules/s/ site)	19.1±0.8 (kcal/mole)	-0.08	0.69	-	-	Grenoble et al. (1981)
Pt/C	340 <sup>0</sup> C	3.84 x 10 <sup>6</sup> (molecules/s/ site)	25.5±1.4 (kcal/mole)	0.13	0.35	-	-	Grenoble et al. (1981)
1% Pt/TiO <sub>2</sub>	-	-	59 (kJ/mol)	0.3	0.85	-0.67	0	Thinon et al. (2009)
1.4%Pt- 8.3% CeO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	1atm, 260 <sup>0</sup> C	-	86 (kJ/mol)	0.13	0.49	-0.12	-0.45	Phatak et al. (2007)
2%Pt- 1% Re/CeO <sub>2</sub> -ZrO <sub>2</sub>	1atm, 210 <sup>0</sup> C-260 <sup>0</sup> C	-	71 (kJ/mol)	-0.05	-0.32	0.85	-0.05	Phatak et al. (2007)
CuO.2CeO.8O <sub>2-y</sub> (Cu ceria)	473 K – 623K CO/H <sub>2</sub> O =1/3	1.8 x 10 <sup>3</sup> (s <sup>-1</sup> )	61 (kJ/mol)	-	-	-	-	Henrik et al. (2006)
CuO.1CeO.9O <sub>2-y</sub> (Cu ceria)	573 K – 623K CO/H <sub>2</sub> O =1/3	4.0 x 10 <sup>3</sup> (s <sup>-1</sup> )	78 (kJ/mol)	-	-	-	-	Henrik et al. (2006)
Ce(La)Ox	375 – 475 <sup>0</sup> C	-	58.5 (kJ/mol)	-	-	-	-	Li et al. (2000)
5 at.% Cu- Ce(10%La)Ox	175 – 300 <sup>0</sup> C CO/H <sub>2</sub> O=1.5	-	30.4 (kJ/mol)	0	1	-	-	Li et al. (2000)
5 at.% Ni- Ce(10%La)Ox	275 – 300 <sup>0</sup> C CO/H <sub>2</sub> O=1.5	-	38.2 (kJ/mol)	0	1	-	-	Li et al. (2000)

For Table 4, the rate is given by  $r = kP_{CO}^l P_{H_2O}^m P_{CO_2}^n P_{H_2}^q (1-\beta)$ , rate constant  $k = K_0 \exp(-E_a/RT)$ ,  $K_0$  is pre exponential or frequency factor,  $E_a$  is activation energy and  $\beta$  is the approach to equilibrium and is given by  $\beta = P_{CO_2} P_{H_2} / K_{eq} P_{CO} P_{H_2O}$

**Table 5 Macro kinetic Rate expressions for WGSR**

Catalyst information	Operating Conditions	Rate Expression
<b>High Temperature Catalysts</b>		
Girdler(G3-b)	particle size 0.62 cm equivalent diameter (1/4" x 1/4")	<p>Reference: Elnashaie and Elshishini(1993)</p> $r = k\psi \frac{X_A X_B - \frac{X_C - X_D}{K}}{379 \rho_b}, k = \exp(15.95 - 4900/T)$ <p> <math>\psi = 0.816 + 0.184P</math> for <math>P \leq 11.8</math>  <math>\psi = 1.53 + 0.123 P</math> for <math>11.8 &lt; P \leq 20</math>  <math>\psi = 4.0</math> for <math>P &gt; 20</math> </p> <p>r is rate of reaction (lb mol CO reacted/lb catalyst. hr ), <math>X_i</math> is the dimensionless concentration for component i (<math>C_i/C_{ref}</math>), T is temperature (K), P is Pressure (atm) and K is equilibrium constant, <math>\rho_b</math> is bulk density of catalyst (lb/ cu. ft), <math>\psi</math> is activity factor</p>

72% Fe <sub>2</sub> O <sub>3</sub> – 8% Cr <sub>2</sub> O <sub>3</sub>	Density 4.561 g/cm <sup>3</sup>	<p><i>Reference: Singh and Saraf (1977)</i></p> $r = \text{Eff} \times 2.32 \times 10^{13} (X_{\text{CO}} - X_{\text{CO}}^*) \exp(-27760/RT) \times \text{Ra} \times \text{Agf} \times \text{Pf} \times \text{fs}$ $\text{Keq} = \exp\left[\frac{9998.22}{T} - 10.213 + 2.7465 \times 10^{-3} T - 0.453 \times 10^{-6} T^2 - 0.201 \ln T\right] / R$ $\text{Ra} = \exp(-8.91 + (5.553 \times 10^4)/T)$ $\text{Log Agf} = (14.66 \times 10^{-4} - 2 \times 10^{-6}) \tau$ $\text{Pf} = P^{(0.5 - P/250)}$ $\text{fs} = -0.276 \log([\text{H}_2\text{S}] + 2.78) + 1.127$ $X_{\text{CO}}^* = X_{\text{H}_2} X_{\text{CO}_2} / X_{\text{H}_2\text{O}} \text{keq}$ <p>r is rate of reaction (cm<sup>3</sup>/gcat h), X<sub>CO</sub> is mole fraction of CO, X<sub>CO</sub><sup>*</sup> is mole fraction of CO in equilibrium condition P is pressure (atm), Keq is equilibrium constant, R is gas constant(cal/gmol K), T is temperature (K), Eff is effectiveness factor, Ra is relative activity, Agf is aging factor, Pf is pressure factor, fs is rate reduction factor due to H<sub>2</sub>S concentration, [H<sub>2</sub>S] is H<sub>2</sub>S concentration in ppm and τ is age of catalyst in days</p>
Sud Chemie SHT-4	Density = 7633.65 kg/m <sup>3</sup>	<p><i>Reference: Wei et al. (2008)</i></p> $r = k (P_{\text{CO}} P_{\text{H}_2\text{O}} - P_{\text{CO}_2} P_{\text{H}_2} / \text{keq})$ $k = 1.78 \times 10^{22} (1 + 0.0097 \delta - 1.1364 \delta^2) T^{-8} \exp(-70/RT)$ <p>r is rate of reaction, Pi is partial pressure of species ( kPa), Keq is equilibrium constant, R is gas constant, T is temperature (K) and δ is steam to CO ratio</p>

ferrochrome catalysts <i>Bohlboro</i> Power Law Model	0.8 to 1.2 mm particle size 330°C-500°C	<p>Reference: Newsome (1980), Elnashaie and Elshishini(1993)</p> $r = k [\text{CO}]^{0.9} [\text{H}_2\text{O}]^{0.25} [\text{CO}_2]^{-0.6} [\text{H}_2]^0 (1-\beta)$ $\beta = [\text{CO}_2][\text{H}_2] / K_{\text{eq}}[\text{CO}][\text{H}_2\text{O}]$ $E_a = 114.6 \text{ kJ/mol}$																				
	With H <sub>2</sub> S addition 380°C-500°C	<p>Reference: Newsome (1980), Elnashaie and Elshishini(1993)</p> <p>Average Equation <math>r = k [\text{CO}]^{0.8} [\text{H}_2\text{O}]^{0.45} [\text{CO}_2]^{-0.1} [\text{H}_2]^{-0.1} (1-\beta)</math></p> <p>For specific H<sub>2</sub>S concentrations l, m, n and q are powers of CO, H<sub>2</sub>O, CO<sub>2</sub> and H<sub>2</sub> respectively</p> <p>Ea at 2000 ppm H<sub>2</sub>S is 94.6 kJ/mol</p> <table border="1"> <thead> <tr> <th>ppm H<sub>2</sub>S</th> <th>l</th> <th>m</th> <th>n</th> <th>q</th> </tr> </thead> <tbody> <tr> <td>0</td> <td>1</td> <td>0.25</td> <td>-0.6</td> <td>0</td> </tr> <tr> <td>25</td> <td>0.75 – 0.8</td> <td>0.50</td> <td>-0.10</td> <td>-0.15</td> </tr> <tr> <td>2000</td> <td>0.85</td> <td>0.40</td> <td>-0.10</td> <td>-0.10</td> </tr> </tbody> </table>	ppm H <sub>2</sub> S	l	m	n	q	0	1	0.25	-0.6	0	25	0.75 – 0.8	0.50	-0.10	-0.15	2000	0.85	0.40	-0.10	-0.10
	ppm H <sub>2</sub> S	l	m	n	q																	
	0	1	0.25	-0.6	0																	
25	0.75 – 0.8	0.50	-0.10	-0.15																		
2000	0.85	0.40	-0.10	-0.10																		
For small Catalysts (crushed/experimental)	$r = k [\text{CO}]^{0.93} [\text{H}_2\text{O}]^{0.24} [\text{CO}_2]^{-0.31} [\text{H}_2]^0 (1-\beta):$ $E_a = 105.9 \text{ kJ/mol}$ <p>[ ] represents the species concentration</p>																					
For Large Catalysts (Commercial)	$r = k [\text{CO}]^{0.87} [\text{H}_2\text{O}]^{0.26} [\text{CO}_2]^{-0.18} [\text{H}_2]^0 (1-\beta)$ $E_a = 59.8 \text{ kJ/mol}$ <p>[ ] represents the species concentration</p>																					

80-90wt% $\text{Fe}_2\text{O}_3$ , 8-13 % $\text{Cr}_2\text{O}_3$ , 1-2% $\text{CuO}$  375 °C to 475 °C	<p><i>Reference: Boon et al. (2009)</i></p> $r = (3.2 \pm 1.3) \times 10^{-6} \exp\left[-\frac{(112 \pm 2) \times 10^3}{R}\right] \left[\frac{1}{T} - \frac{1}{678}\right] \times P_{\text{CO}}^{0.84 \pm 0.04} P_{\text{H}_2\text{O}}^{1.17 \pm 0.12} P_{\text{CO}_2}^{-0.36 \pm 0.05} P_{\text{H}_2}^{0.09 \pm 0.05} P_{\text{H}_2\text{S}}^{-0.3 \pm 0.03} (1 - \beta)$ <p>r is rate of reaction (mol/kg s), Pi is partial pressure of species (kPa) and T is temperature (K)  <math>\beta = P_{\text{CO}_2} P_{\text{H}_2} / K_{\text{eq}} P_{\text{CO}} P_{\text{H}_2\text{O}}</math></p>
<b>Low Temperature Catalysts</b>	
Temkin Model	<p><i>Reference: Newsome (1980)</i></p> $r = \frac{k P_{\text{H}_2\text{O}} P_{\text{CO}} (1 - \beta)}{A P_{\text{H}_2\text{O}} + P_{\text{CO}_2}}, \text{ Equilibrium Constant, } K_{\text{eq}} = \exp\left(\frac{4577.8}{T} - 4.33\right)$ <p>Rate Constant, <math>k = 6 \times 10^{11} \exp\left(-\frac{26800}{1.987 \times T}\right)</math> 1/atm s</p> <p>Constant, <math>A = 2.5 \times 10^9 \exp\left(-\frac{21500}{1.987 \times T}\right)</math></p> <p>r is rate of reaction (1/s), Pi is partial pressure of species (Pa), T is temperature(K)</p>

Langmuir Hinshelwood Model	<p>Reference: Criscuoli et al. (2000)</p> $r = \frac{kK_{CO}K_{H_2O} \left[ P_{CO}P_{H_2O} - \frac{P_{CO_2}P_{H_2}}{K_{eq}} \right]}{\left( 1 + K_{CO}P_{CO} + K_{H_2O}P_{H_2O} + K_{CO_2}P_{CO_2} \right)^2} \times \frac{\rho_{cat}}{60}$ <p>Equilibrium Constant <math>K_{eq} = \exp\left(\frac{4577.8}{T} - 4.33\right)</math></p> <p>Rate Constant <math>k = \exp\left(-\frac{29364}{1.987 \times T} + \frac{40.32}{1.987}\right)</math> mol/g cat. Min</p> <p><math>K_{CO} = \exp\left(\frac{3064}{1.987 \times T} - \frac{6.74}{1.987}\right)</math>, <math>K_{H_2O} = \exp\left(-\frac{6216}{1.987 \times T} + \frac{12.77}{1.987}\right)</math></p> <p><math>K_{CO_2} = \exp\left(\frac{12542}{1.987 \times T} - \frac{18.45}{1.987}\right)</math></p> <p>r is rate of reaction (mol/cm<sup>3</sup>s), Pi is partial pressure of species (Pa), ρ<sub>cat</sub> is density of catalyst(g cat/cm<sup>3</sup>), T is temperature(K)</p>
Empirical Model based on Industrial Data <b>Moe Kinetic Model</b>	<p>Reference: Seo et al. (2006)</p> <p><math>r = k P_{CO} P_{H_2O} \left[ 1 - \frac{P_{CO_2} P_{H_2}}{K_{eq} P_{CO} P_{H_2O}} \right]</math>,</p> <p>Equilibrium Constant, <math>K_{eq} = \exp\left(\frac{4577.8}{T} - 4.33\right)</math></p> <p>Rate constant <math>k = 1.85 \times 10^{-5} \exp\left(12.88 - \frac{1855.5}{T}\right)</math> mol/g.min</p> <p>r is rate of reaction (mol/g min), Pi is partial pressure of species (bar)</p>

Girdler(G3-b)	particle size 0.62 cm equivalent diameter (1/4" x 1/4")	<p><i>Reference: Elnashaie and Elshishini(1993)</i></p> $r = k\psi \frac{X_A X_B - \frac{X_C - X_D}{K}}{379 \rho_b}$ <p> <math>k = \exp(12.88 - 2002.6/T)</math>  <math>\psi = 0.86 + 0.14 P</math> for <math>P \leq 24.8</math>  <math>\psi = 4.33</math> for <math>P &gt; 24.8</math> </p> <p>r is rate of reaction (lb mol CO reacted/lb catalyst. hr ), <math>X_i</math> is the dimensionless concentration for component i (<math>C_i/C_{ref}</math>), T is temperature (K), P is Pressure (atm) and K is equilibrium constant, <math>\rho_b</math> is bulk density of catalyst (lb/ cu. ft), <math>\psi</math> is activity factor</p>
Catalyst composition, (%p/p) CuO (32.7), ZnO (47) and Al <sub>2</sub> O <sub>3</sub> (11)	1 atm, 453 K - 503 K	<p><i>Reference: Amadeo and Laborde (1995)</i></p> $r = \frac{0.92 \times e^{\left(\frac{-454.3}{T}\right)} P_{CO} P_{H_2O} (1 - \beta)}{\left[1 + 2.2e^{\left(\frac{101.5}{T}\right)} P_{CO} + 0.4e^{\left(\frac{158.3}{T}\right)} P_{H_2O} + 0.0047e^{\left(\frac{2737.9}{T}\right)} P_{CO_2} + 0.05e^{\left(\frac{1596.1}{T}\right)} P_{H_2}\right]^2}$ <p>r is rate of reaction (mol/g min), T is temperature (K), <math>P_i</math> is partial pressure of the components (Pa) and <math>\beta = P_{CO_2} P_{H_2} / K_{eq} P_{CO} P_{H_2O}</math></p>

Sud Chemie (EX-2248) Cu/ZnO/ Al <sub>2</sub> O <sub>3</sub>	1 atm, 120 °C - 250°C, particle size 200 – 250 μm, CO:H <sub>2</sub> – 1:2	<p>Reference: Choi and Stenger(2003)</p> $r = 2.96 \times 10^5 \exp\left(-\frac{47400}{RT}\right) \left(P_{CO}P_{H_2O} - \frac{P_{CO_2}P_{H_2}}{K_{eq}}\right)$ <p>r is the rate of reaction (mol/gcat h), Pi is partial pressure of component (atm), T is temperature (K), R is universal gas constant (J/mol K)</p>
Girdler/Sud Chemie (G66 b). unreduced wt% - CuO (32.2), ZnO(61.8) and Fe <sub>2</sub> O <sub>3</sub> (1.6)	0.35 – 0.42 mm particle size, Surface area 22.3(m <sup>2</sup> /g), pore diameter 12.5nm	<p>Reference: Van Herwignen and De Jong (1980)</p> $r = 25.9 \times 10^3 \exp\left(\frac{-16000}{RT}\right) \frac{P_{CO}P_{H_2O}}{(1+127P_{CO}P_{H_2O} + 26P_{CO})}$ <p>r is rate of reaction (mol/g s), Pi is partial pressure (atm), R is gas constant and T is temperature (K)</p>
CuO (33%) ZnO (66%)	5.09g/cm <sup>3</sup>	<p>Reference: Singh and Saraf (1980)</p> $r = E_{ff} \times 2.955 \times 10^{13} \exp(-20960/RT) \times A_{gf} \times P_t (X_{co} - X_{co}^*)$ <p>E<sub>ff</sub> is effectiveness factor  A<sub>gf</sub> is aging factor, log A<sub>gf</sub> = (4.66 × 10<sup>-4</sup> – 1.6 × 10<sup>-6</sup> T) τ  P<sub>t</sub> is effect of Pressure, P<sub>t</sub> = P<sup>(0.5 - P/250)</sup>  X<sub>co</sub><sup>*</sup> = X<sub>H<sub>2</sub></sub>X<sub>CO<sub>2</sub></sub> / X<sub>H<sub>2</sub>O</sub>keq  r is rate of reaction (cm<sup>3</sup>/gcat h), X<sub>CO</sub> is mole fraction of CO, X<sub>CO</sub><sup>*</sup> is mole fraction of CO in equilibrium condition, τ is age of catalyst in days, P is pressure (atm) and T is temperature(K)</p>

Sud Chemie MDC – 7 Cu-Zn based catalyst		<p><i>Reference: Wei et al. (2008)</i></p> $r = k (P_{CO}P_{H_2O} - k_{eq}^{-1}P_{CO_2}P_{H_2})$ $k = 1.74 \times 10^{17} (1 - 0.1540 \delta + 0.008 \delta^2) T^{-8.5} \exp(-35/RT)$ <p>r is rate of reaction, Pi is partial pressure (Pa), Keq is equilibrium constant, R is gas constant, T is temperature (K) and <math>\delta</math> is steam to CO ratio</p>																																			
General Empirical equation for Large Catalysts 4.5 x 4.5 mm, Bohlboro		<p><i>Reference: Newsome (1980)</i></p> $r = k [CO]^{0.8} [H_2O]^{0.5} [CO_2]^{-0.15} [H_2]^0 (1-\beta)$ <p>[ ] represents the species concentration</p>																																			
Cu/ZnO/Al <sub>2</sub> O <sub>3</sub> 40%Cu, 22%Zn, 5%Al	Copper surface area =10m <sup>2</sup> /g	<p><i>Reference: Ovesen et al. (1992)</i></p> $r = A \exp(-E_a/RT) P_{CO}^l P_{H_2O}^m P_{CO_2}^n P_{H_2}^q P_{tot}^\gamma (1-\beta)$ <p><math>\gamma</math> is fudge factor correcting total pressure dependence, <math>\beta = P_{CO_2}P_{H_2} / K_{eq}P_{CO}P_{H_2O}</math></p> <table border="1" data-bbox="772 841 1791 1029"> <thead> <tr> <th>Catalyst</th> <th>P(bar)</th> <th>Ea(kJ/mol)</th> <th>l</th> <th>m</th> <th>n</th> <th>q</th> </tr> </thead> <tbody> <tr> <td>Cu/ZnO/Al<sub>2</sub>O<sub>3</sub></td> <td>5</td> <td>86.5</td> <td>1</td> <td>1.4</td> <td>-0.7</td> <td>-0.9</td> </tr> <tr> <td>Cu/ZnO/Al<sub>2</sub>O<sub>3</sub></td> <td>20</td> <td>78.2</td> <td>1</td> <td>1.5</td> <td>-0.7</td> <td>-0.7</td> </tr> <tr> <td></td> <td></td> <td></td> <td></td> <td></td> <td></td> <td></td> </tr> <tr> <td>Cu/Al<sub>2</sub>O<sub>3</sub></td> <td>20</td> <td>59.3</td> <td>1</td> <td>1.9</td> <td>-1.4</td> <td>-0.9</td> </tr> </tbody> </table>	Catalyst	P(bar)	Ea(kJ/mol)	l	m	n	q	Cu/ZnO/Al <sub>2</sub> O <sub>3</sub>	5	86.5	1	1.4	-0.7	-0.9	Cu/ZnO/Al <sub>2</sub> O <sub>3</sub>	20	78.2	1	1.5	-0.7	-0.7								Cu/Al <sub>2</sub> O <sub>3</sub>	20	59.3	1	1.9	-1.4	-0.9
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<b>Noble Metal Catalysts</b>		
Platinum	Particle Size = 3.3 mm Surface area = 80 m <sup>2</sup> /g	<p><i>Reference: Ding and Chan (2008)</i></p> $r = \frac{k \left[ P_{CO}P_{H_2O} - \frac{P_{CO_2}P_{H_2}}{K_{eq}} \right]}{\left( 1 + K_{CO}P_{CO} + K_{H_2O}P_{H_2O} + K_{CO_2}P_{CO_2} + K_{H_2}P_{H_2} \right)^2}$ <p>K<sub>o</sub> (mol/kgcat s) = 748.824/bar<sup>2</sup>            E<sub>a</sub> (J/mol) = 53,821            K<sub>CO<sub>2</sub></sub>=0.036 (1/bar), K<sub>CO</sub>=2.222(1/bar)            K<sub>H<sub>2</sub></sub>=2.197 x 10<sup>-5</sup>(1/bar), K<sub>H<sub>2O</sub></sub>=2.006 x 10<sup>-5</sup>(1/bar)</p>
Precious Metals		<p><i>Reference: Sun et al. (2005)</i></p> $r = A \exp\left(\frac{-E_a}{RT}\right) \frac{P_{CO}P_{H_2O}(1-\beta)}{\left[ 1 + A_1 \exp\left(\frac{-\Delta H_1}{RT}\right) P_{CO} \right] \left[ 1 + A_2 \exp\left(\frac{-\Delta H_2}{RT}\right) P_{H_2} \right]}$ <p>A=9 x 10<sup>7</sup> mol/m<sup>3</sup>atm<sup>2</sup>s, E<sub>a</sub> = 44 kJ/mol, A<sub>1</sub>= 1 x 10<sup>-3</sup> 1/s, ΔH<sub>1</sub>=-46 kJ/mol,            A<sub>2</sub>=43 1/s, ΔH<sub>2</sub>=11 kJ/mol</p>

Almost similar kinetic expressions have been proposed for both the high temperature and low temperature catalysts. The kinetic models that have been endorsed by many authors from their experiments with various catalysts have been the Langmuir Hinshelwood model and the power law model. The recent literature publications use the kinetic expressions of Keiski et al. (1996), San et al. (2009) for high temperature and Choi and Stenger (2003) for low temperature water gas shift reaction.

The difference in opinion on the nature of kinetics for the water gas shift reaction has been attributed to the presence of impurities, mass transfer limitations, experiments carried out at atmospheric pressure and the use of integral reactor for kinetic studies rather than the differential reactor [Levent, 2001]. Since all the experiments were reported at atmospheric pressures, the kinetic models can be corrected for pressure using the modification recommended by Rase (1977) which also takes care of the diffusional effects of the catalysts or the pressure correction factor of Singh and Saraf (1977).

## 6. CONCLUSION

The use of water gas shift reaction is growing due to the shift towards the Hydrogen economy. This necessitated the need for designers to have kinetic expressions for the reaction to help them in designing the water gas shift reactors. A detailed view of the various catalysts used in the high temperature shift, low temperature shift and the noble metal catalysts was made. The microkinetic approach towards the WGSR was explained. A comprehensive listing of the various kinetic models for the high temperature shift, low temperature shift and noble metal shift reaction was provided in Table 4 and 5 along with the relevant numerical values. This consolidated table could provide a ready reference for computing the rate of the water gas shift reaction. Even though different authors have obtained different ranges of rates by these models for their experimental data, most of the works conform to the power law type of kinetic expression and hence can be conveniently used for design calculations.

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