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Kinetics of Ultrahigh Temperature Water-Gas Shift Reaction Catalysts Using Simulated Coal-Derived Syngas

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H_2 is currently being widely recognized as a possible energy carrier because of its high energy content and environmental compatibility. H_2 production from coal gasification has gained renewed interest because it is recognized as the most abundant fossil fuel. The coal-derived syngas consists mainly of CO and H_2. The CO can be further reacted with steam via the water-gas shift reaction (WGSR) to increase the H_2 concentration in the syngas. Development of catalyst that can be used at temperature higher than the traditional WGSR operating temperatures is an alternative way to enhance the overall coal-to-H_2 thermal efficiency and cost-effective design. With this high temperature catalyst two-stage shift reactors can be reduced to a single reactor and connected at the gasifier exit without the need for syngas cooling. In this study, catalyst performance of WGSR operated in ultrahigh temperature region (750 - 850 °C) was examined experimentally. Using syngas with various compositions and S/C ratios as feedstock, the chemical reaction kinetics of WGSR using 2.5 wt%Pt - 2.5 wt%Ni/5 wt%CeO_2/Al_2O_3 as catalyst can be established based on the experimental data and simple power law. It was found that the prepared catalyst promotes the rate of WGSR when the syngas consists of higher CO concentration and lower CO_2 concentration for the operation temperature range studied.

1. Introduction

The coal-derived syngas consists mainly of CO and H_2. The CO can be further reacted with steam via the water-gas shift reaction (WGSR) to increase the H_2 concentration in the syngas. At the same time, this reaction produces a concentrated CO_2 stream that can be sequestered to mitigate the greenhouse effect once the H_2 is removed.

The WGSR is an exothermic reaction limited by thermodynamic equilibrium,

$$CO + H_2O \leftrightarrow CO_2 + H_2 \text{ , } \Delta H_{298K} = -41.2 \ kJ/mol \tag{1}$$

That is, the conversion to H_2 and CO_2 decreases with increasing temperature (Fogler, 2006). However, a fast chemical reaction rate can be achieved at high temperatures. Moreover, for the case of coal-derived syngas where the CO concentration is relatively high (40 - 60 %), considerably higher degree of shifting is required. For these reasons the WGSR is carried out in two stages in practical applications: a high temperature (350 - 450 °C) shift reaction using Fe-Cr catalyst to increase the chemical reaction rate and low temperature (200 - 250 °C) shift reaction using Cu-Zn catalyst to increase the conversion efficiency. In general, the syngas produced from a gasifier has a higher temperature in comparison to the operating temperature range of practical reactors. The syngas must be cooled to perform the two-stage WGSR, which is capital intensive and incurs a loss of power production. Moreover, the traditional WGSR process is likely to deliver CO_2 at reduced pressure, which will have to be re-compressed for sequestration and storage.

To enhance the overall coal-to-H_2 thermal efficiency and cost-effective design, recent efforts have been devoted to develop catalysts that can be used at temperatures higher than the traditional high-temperature shift reactor and also exhibits high CO conversion capability. With this high temperature catalyst two-stage reactors can be reduced to a single reactor and connected at the gasifier exit without the need for syngas

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cooling. However, relatively few WGSR catalysts for operating temperatures higher than 450 °C were reported in the literature. Valsamakis and Flytzani-Stephanopoulos (2011) reported a high activity and stability of lanthanide oxysulphides catalyst for WGSR. With temperature higher than 750 °C, CO conversion can reach the equilibrium value. Aranifard et al. (2014) performed an analysis on the mechanism of WGSR at the three-phase boundary of Pt/CeO_2 catalysts. They showed that both the redox pathway and the associative carboxyl pathway with redox regeneration could operate on Pt/CeO_2 catalysts. Using Pt/TiO_2 as catalyst for WGSR, Panagiotopoulou and Kondarides (2011) showed that activity of alkaline earth metal-promoted catalysts depends appreciably on the nature and loading of the promoter, as well as on the calcination temperature employed for the preparation of doped TiO_2 supports. In the study of Palma et al. (2014), they focused on the preparation and testing of differently-supported Pt-based catalysts for WGSR and found that the $Pt/CeO_2/ZrO_2$ had a great potential for use in single-stage WGSR.

The objective of this study is to carry out the WGSR with reaction temperature at 750 °C which closes to the syngas temperature at gasifier outlet. Bimetal catalyst will be prepared and used for WGSR performance test using syngas with various compositions. Kinetics of WGSR will be established based on the measured experimental data.

2. Experimental

The 2.5 wt%Pt - 2.5 wt%Ni/5 wt%CeO_2/Al_2O_3 catalyst was prepared and used for WGSR in this study. The procedures for the catalyst preparation was in a similar way as that described in the study of Haryanto et al. (2007) except that spherical Al_2O_3 particles with an average diameter of 0.5 - 1.2 mm and specific surface area of 220 m^2/g were used as the catalyst support instead of alumina ceramic foam monoliths. A schematic diagram of the experimental setup is shown in Figure 1. The reactor was placed horizontally in a temperature-controlled furnace. The simulated syngas was made by mixing four gaseous species as shown in Figure 1. All the gaseous species flow was metered and regulated by a mass flow controller (Brooks 5850E, USA) and water was pumped through a HPLC pump (Simadzu LC-20AT, Japan) with the flow rate at designated steam to carbon (S/C) ratio. A preheater was used to vaporize the water before it mixed with the simulated syngas flow.

The WGSR was carried out using a conventional catalytic packed-bed tubular reactor operated isothermally at atmospheric pressure. A quartz tube with a diameter of 4 mm was used as the reactor in which the catalyst was loaded in the central section with two ends fixed using quartz wool. The catalyst with weight of 0.5 g was used and this results in a reaction zone length of 4.2 cm. Accordingly the ratio of catalyst bed length to catalyst particle size and the ratio of the inside diameter of the reactor to particle size are in the ranges of 35 - 84 and 3 - 8. This ensures that the back mixing and channelling effects can be minimized in the packed-bed reactor (Froment and Bischoff, 1990).

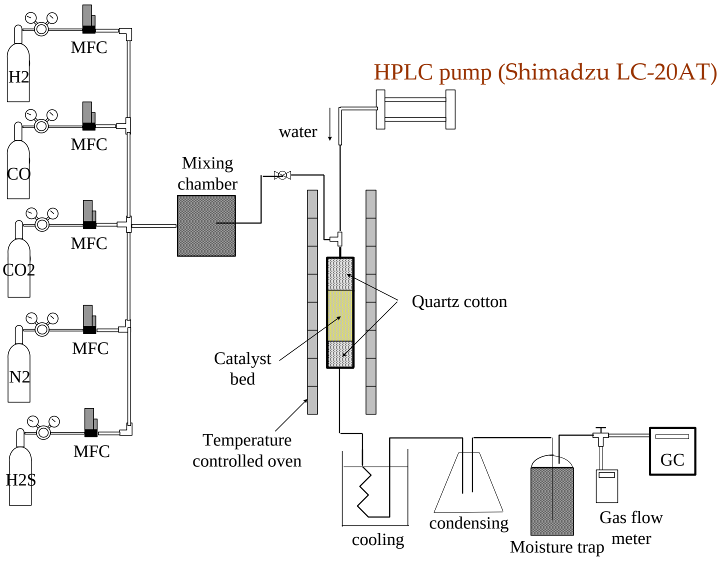

Figure 1: Experimental setup for WGSR test.

The experiments were carried out with reaction temperature at 750 °C. The reaction temperature was monitored by a K-type thermocouple placed at the top of the catalyst bed. Each experiment was carried out in 6 h after the reaction becomes steady. After removing the unused water by a condenser, the product gas was collected every 2 h to ensure stable performance of the catalyst under specified operating conditions. The product gases were analysed by gas chromatograph (Agilent 6890, USA). In this study, CO conversion rate is defined as,

$$R_{CO} = \frac{\dot{F}_{CO,in} - \dot{F}_{CO,out}}{W} \tag{2}$$

where $\dot{F}_{CO,in}$ and $\dot{F}_{CO,out}$ are the CO molar flow rate at reactor inlet and outlet. W is the catalyst weight used in the test.

3. Results and discussion

A power-law rate model is used to describe the kinetics of the catalyst. The power-law expression for the WGSR is generally of the form (Adams and Barton, 2009),

$$R_{CO} = kP_{CO}^{a}P_{H_2O}^{b}P_{CO_2}^{c}P_{H_2}^{d}(1-\beta) \tag{3}$$

In Eq(3), R_{CO} is the CO reaction rate (mol g_{cat}^{-1} s^{-1}), P_i is the partial pressure of gas component i (kPa), *a*, *b*, *c*, and *d* are the reaction orders of CO, H_2O, CO_2, and H_2. k is the rate constant defined as,

$$k = A\exp(-E/RT) \tag{4}$$

Where *A* is pre-exponential factor, *E* is the activation energy (kJ mol^{-1}), and *T* is the reaction temperature (K). β is the extent of the reverse reaction defined as,

$$\beta = \frac{1}{K_{eq}}\frac{P_{CO_2}P_{H_2}}{P_{CO}P_{H_2O}} \tag{5}$$

Where K_{eq} is the chemical equilibrium constant given as (Moe, 1962),

$$\begin{aligned} K_{eq} &= \exp\{z[z(0.63508 - 0.29353z) + 4.1778] + 0.31688\} \quad , \\ z &= (1{,}000/T) - 1 \end{aligned} \tag{6}$$

The simulated syngas compositions investigated in this study was chosen based on the study of Murgia et al. (2012) in which they reported a syngas produced from an air-blown updraft coal gasifier has the composition of 30 % CO, 18 % H_2, 22 % CO_2, and 30 % N_2. In this study, this syngas composition was used as the base syngas composition. To investigate the effect of CO, H_2O, CO_2, and H_2 concentrations, a syngas composition variation based on this base syngas composition was selected. Steam was added to syngas with S/C ratio varied from 3 to 5. The kinetic data measured for the WGSR at 750 °C was presented in Table 1. Experimental runs to examine the effects of CO, H_2O, CO_2 and H_2 were carried out by varying the composition of one component by replacing it with N_2 while all other components were held as close to constant as possible. The minor variations in these other gas compositions were caused by fluctuations in the total pressure of the system between each run. In Table 1, the value of β varied in 0.0188-0.1399 range indicating that the reaction was far from equilibrium.

Figure 2 presents plot of ln [R_{CO}/(1-β)] versus log of partial pressure of each component for WGSR at 750 °C. It is clear that all plots in Figure 2 are nearly linear, indicating that the kinetics of the WGSR can be expressed by using the empirical power-law model. The slope of each straight line is used to determine the reaction order with respect to the individual species and these values are also shown in Figure 2. As expected, Figure 2 shows that CO conversion rate increases with CO partial pressure under the conditions investigated. The reaction order for CO at 750 °C is found to be 0.8932. Figure 2 also shows that the reaction rate significantly depends on the H_2O concentration with reaction order of 1.7329 which is quite different from that obtained using Fe-Cr catalysts at 450 °C reported by Hla et al. (2009). The reaction order for CO_2 at 750 °C was found to be -0.2561 indicating that reaction rate decreases with the increase in CO_2 amount in syngas. A similar observation was also reported by Bohlbro (1961) and Hla et al. (2009) for their studies for the effect of CO_2 concentration on CO conversion rate over an Fe-Cr based catalyst in a temperature range of 380 - 500 °C. A small positive effect of H_2 concentration on CO conversion rate with reaction order of 0.1072 is observed, as shown in Figure 2 which is also different from that report by Hla et al. (2009). Further studies are needed to investigate the variation trend with H_2 concentration at other temperature for realizing the reason for this observation.

Table 1: Kinetic data for WGSR over 2.5 wt%Pt - 2.5 wt%Ni/5 wt%CeO_2/Al_2O_3 catalyst with simulated coal-derived syngas at 750°C.

P_{CO} (kPa)	P_{H_2O} (kPa)	P_{CO_2} (kPa)	P_{H_2} (kPa)	P_{N_2} (kPa)	β	R_{CO} ($\times 10^{-5}$ mol $g_{cat}^{-1}s^{-1}$)
CO varied (S/C=5)						
8.22	61.07	8.74	6.99	16.32	0.0973	0.94
12.31	60.99	8.6	7.01	12.4	0.0644	1.28
16.68	61.6	8.91	7.05	7.09	0.0489	1.88
H_2O varied (S/C=3, 4, 5)						
12.85	**36.28**	8.9	6.57	36.73	0.1002	0.5
12.46	**47.1**	8.69	6.41	26.67	0.0758	0.61
12.31	**60.99**	8.62	7.01	12.4	0.0644	1.28
CO_2 varied (S/C)=5						
12.36	60.54	**2.44**	7.19	18.8	0.0188	1.73
12.31	60.99	**8.62**	7.01	12.4	0.0644	1.28
12.32	60.87	**14.73**	6.96	6.46	0.1094	0.97
H_2 varied (S/C=5)						
12.31	60.99	8.62	**7.01**	12.4	0.0644	1.28
12.35	60.96	8.66	**11.04**	8.32	0.1015	1.27
12.41	60.66	8.73	**15.08**	4.45	0.1399	1.28

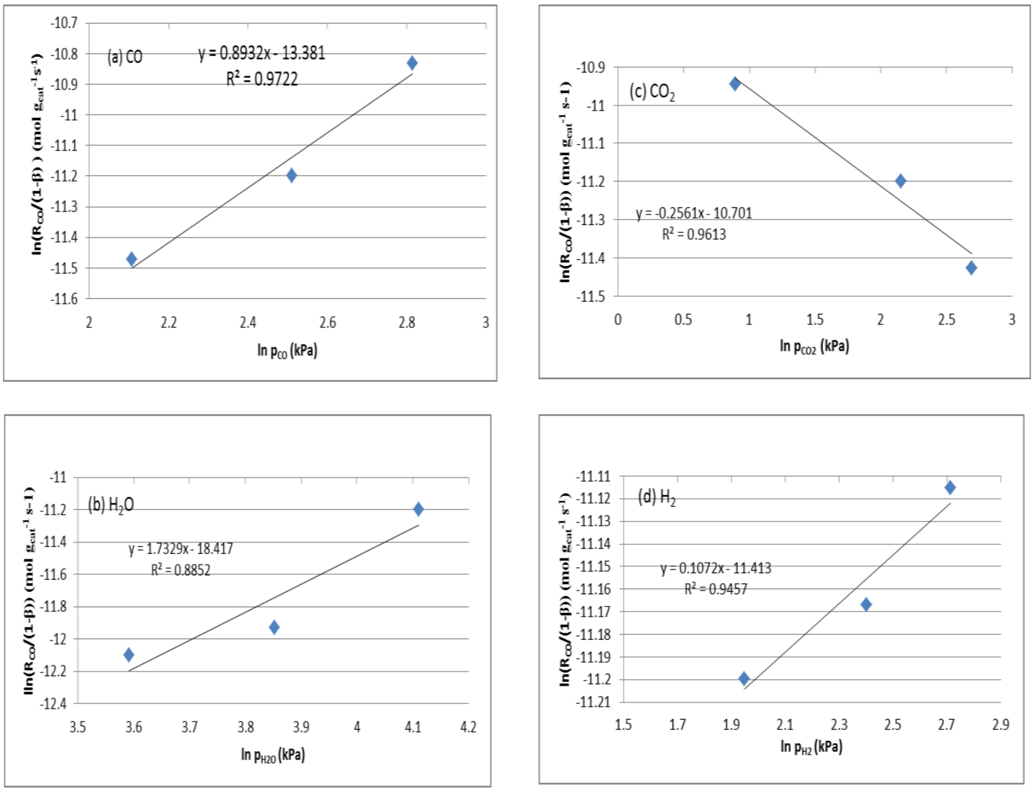

Figure 2: Determination of power-law rate model reaction orders: Log-log plots for the effect of CO, H_2O, CO_2 and H_2 partial pressure on reaction rates over 2.5 wt%Pt - 2.5 wt%Ni/5 wt%CeO_2/Al_2O_3 catalyst at 750 °C.

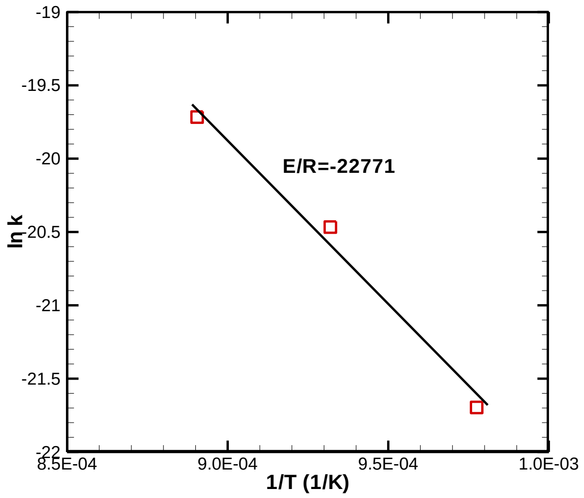

Figure 3: Arrhenius plot for the WGSR based on Eq(6) for temperature in the range of 750- 850°C.

Using the reaction rate orders obtained from the slopes of the plots in Figure 2, the rate constant can be calculated by rearranging Eq(3) as

$$k = \frac{R_{CO}}{P_{CO}^{a} P_{H_2O}^{b} P_{CO_2}^{c} P_{H_2}^{d} (1-\beta)} = A \exp\left(-\frac{E}{RT}\right) \tag{7}$$

Taking log on Eq(6), the Arrhenius plot can be generated and the activation energy can be evaluated. To be able to generate the Arrhenius plot, at least three points are needed. In addition to 750 °C, the CO conversion rates at 800 °C and 850 °C with base syngas composition and S/C=5 were also measured. Figure 3 shows the Arrhenius plot using the measured CO conversion rates for these three temperatures. Using the slope of the Arrhenius straight line in Figure 3, the value of -E/R is found to 22,771, which results in the activation energy of 183.322 kJ/mol. The corresponding pre-exponential factor A can also be determined from Arrhenius plot and has the value of $10^{1.063}$. Based on these calculated values, the power-law reaction rate under the operation conditions can be expressed,

$$R_{CO} = 10^{1.063} \exp\left(-\frac{183{,}322}{RT}\right) P_{CO}^{0.8932} P_{H_2O}^{1.7329} P_{CO_2}^{-0.2156} P_{H_2}^{0.1072} (1-\beta) \tag{8}$$

Comparison between reaction rates calculated using Eq(8) and experimental results are shown in Figure 4. It can be seen that the calculated rates correlate with experimental data very well. This power-law rate expression can be regarded as an intrinsic WGSR rate equation for 2.5 wt%Pt - 2.5 wt%Ni/5 wt%CeO_2/Al_2O_3 which can be used in reactor design to calculate either the amount of catalyst required to achieve a certain degree of CO conversion or the level of conversion that can be obtained with a given amount of catalyst at ultra-high temperature.

4. Conclusion

In this study, water-gas shift reaction performance at temperature of 750 °C with 2.5 wt%Pt - 2.5 wt%Ni/5 wt%CeO_2/Al_2O_3 as catalyst was tested using simulated coal-derived syngases. A power-law reaction kinetics was established based on the experimental data. At this high temperature, it was found that the reaction rate increases with the amounts of CO, H_2O, and H_2 while increasing the CO_2 amount results in decrease in CO reaction rate. Further studies will be needed to obtain more accurate rate constant and H_2 concentration dependence with more temperature variations.

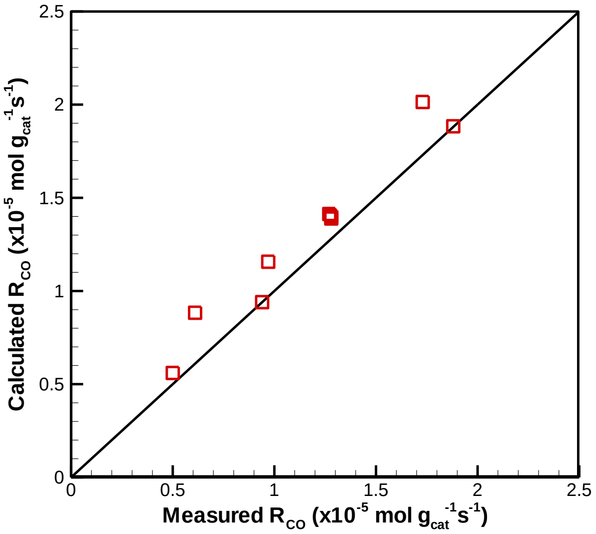

Figure 4: Measured reaction rate vs. calculated CO reaction rate for WGSR over 2.5wt%Pt-2.5wt%Ni/5wt%CeO_2/Al_2O_3 catalyst at 750°C under selected inlet gas compositions.

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