doi:10.1246/cl.2010.144

Derivation of Initial Rate Equations for Low-temperature Water Gas Shift Reaction over Pt–Re/ZrO_2 Catalysts

Hajime Iida,* Takumi Yamamoto, Masaru Inagaki, and Akira Igarashi

Department of Applied Chemistry, Faculty of Engineering, Kogakuin University, 2665-1 Nakano-machi, Hachioji, Tokyo 192-0015

(Received November 2, 2009; CL-090967; E-mail: iida@cc.kogakuin.ac.jp)

The effect of the partial pressure of CO and H_2O on the initial reaction rate of LT-WGS over a Pt–Re/ZrO_2 catalyst with superior catalytic activity was evaluated. As a result, the reaction order was approximately zero with respect to CO and ca. 0.6 with respect to H_2O, which indicates that CO is strongly adsorbed onto the catalyst surface in contrast to H_2O. The theoretical rate equation was derived from the Langmuir–Hinshelwood (L–H) mechanism and was in good agreement with the experimental data.

In the hydrogen production by steam reforming of hydrocarbons for polymer electrolyte fuel cells (PEFC), the water gas shift reaction at low temperature (LT-WGS) is used for the removal of CO, which deteriorates the Pt electrode of the PEFC. Although a Cu–Zn catalyst is conventionally used for LT-WGS, this catalyst is deactivated by daily start-up and shut down (DSS) operations under an oxidizing atmosphere.

Present authors reported that Pt–Re/ZrO_2 and Pt–Re/TiO_2 (R: rutile) catalysts have superior catalytic activities for LT-WGS,[1] which initiated further interest in Pt–Re catalysts as candidates for new LT-WGS catalysts.[2–4] Present authors have also reported that Pt–Re/ZrO_2 has superior durability under DSS operation with steam compared with Pt–Re/TiO_2(R).[5]

In this study, in order to collect some kinetic information about LT-WGS reaction over the Pt–Re/ZrO_2 catalyst, the effect of the partial pressure of CO and H_2O on the initial reaction rate was examined, deriving a power law equation for the initial reaction rate. Additionally, a Langmuir–Hinshelwood (L–H) equation for LT-WGS reaction was derived, based on the proposed reaction mechanism for LT-WGS over Pt–Re/ZrO_2.[6]

The Pt–Re/ZrO_2 catalyst was prepared using a conventional impregnation method as previously reported.[7] The ZrO_2 support was obtained by calcining a commercial zirconium hydroxide (Mitsuwa Chemical) at 500 °C for 1 h in a stream of air. The Pt precursor was platinum chloride hexahydrate, and the Re precursor was ammonium perrhenate. The impregnation of Re on ZrO_2 was carried out prior to the impregnation of Pt. Pt–Re/ZrO_2 was prepared with Pt and Re loading of 1.0 and 0.67 wt %, respectively.

LT-WGS was performed using a conventional fixed bed flow reactor, as previously described.[7] The catalyst was reduced at 500 °C for 1 h in a stream of H_2 prior to the reaction. Kinetic measurements were conducted under the differential reaction conditions. Reaction temperature was varied from 200 to 250 °C, time factor W/F_{CO} from 0.48 to 17.0 kg s mol^{-1}, steam to carbon ratio S/C from 1.45 to 5.84, and the catalyst particle size 0.5–1.0 mmϕ. The initial reaction rate r_0, can be determined as the slope of the curve at the origin in the plot of CO conversion, x_{CO} vs. W/F_{CO}.

The power law equation for the initial reaction rate can be written as

$$-r_0 = k_0 p_{CO}{}^{a} p_{H_2O}{}^{b} \tag{1}$$

and eq 1 can be written in logarithmic form;

$$\ln(-r_0) = \ln k_0 + a \ln p_{CO} + b \ln p_{H_2O} \tag{2}$$

To determine the kinetic order with respect to CO, the partial pressure of H_2O was held constant at 56.8 kPa while that of CO was varied between 9.7 and 39.2 kPa. To determine the kinetic order with respect to H_2O, the partial pressure of CO was held constant at 16.8 kPa, while that of H_2O was varied between 35.0 and 84.5 kPa. Argon was used as the balance gas.

Kinetic measurements should be performed under conditions without the influence of the film and pore diffusion resistance on the overall reaction rate. Generally, under the regime of strong pore diffusion resistance, the apparent activation energy is approximately one half that of the actual activation energy. Under the regime of film diffusion resistance, the apparent activation energy is approximately zero, because the temperature dependence of the mass-transfer coefficient is much smaller than that of the reaction rate constant.[8] Therefore, present authors examined the effect of the mass-transfer resistance on reaction rate using Arrhenius plots for the CO conversion x_{co} between 175 and 300 °C. As a result, it is confirmed that the reaction temperature for the kinetic measurements is included in the region of negligible mass-transfer resistance because the estimated activation energy was 88 kJ mol^{-1}.

Figure 1 shows logarithmic plots of the initial reaction rate and partial pressure of the reactants. From Figure 1, the reaction order with respect to CO was approximately zero while the reaction order with respect to H_2O was ca. 0.6. This infers that CO is strongly adsorbed onto the catalyst surface while the adsorption of H_2O onto the catalyst surface is weaker. Figure 2 shows Arrhenius plots for the initial reaction rate constant k_0. From Figure 2, the activation energy and pre-exponential factor were determined to be 65 kJ mol^{-1} and 5.35×10^2 mol kg^{-1} s^{-1} Pa$^{-0.52}$. The power law equation for the initial reaction rate is written as

$$-r_0 = 5.35 \times 10^2 \exp(-65 \times 10^3/RT) p_{CO}{}^{-0.08} p_{H_2O}{}^{0.60} \tag{3}$$

Figure 3a shows a comparison of the value calculated from eq 3 and the experimental data. The experimental data are in good agreement with the data calculated from the power law equation. The power law equations for the LT-WGS reaction rate over supported precious metal catalysts have been previously investigated;[3,9,10] the reaction order with respect to CO was from −0.24 to 0.5, the reaction order with respect to H_2O was from 0.4 to 1.0, and the activation energy was from 40 to 100 kJ mol^{-1}. The results of the present study are consistent with those reported for previous studies.

A typical LT-WGS reaction mechanism on the supported precious metal catalyst can be described as follows. Water is

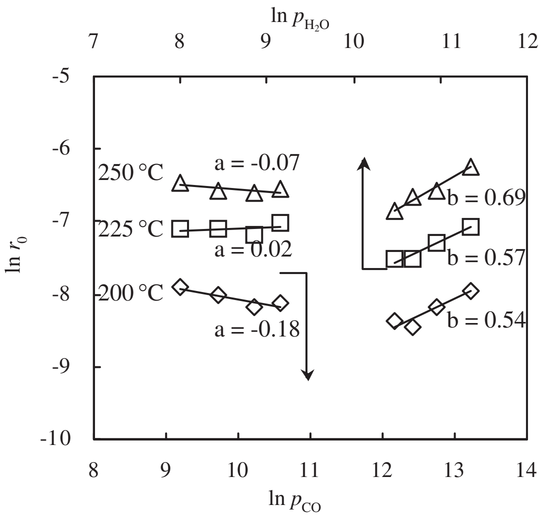

Figure 1. Logarithmic plots of the initial reaction rate and the partial pressures of reactants.

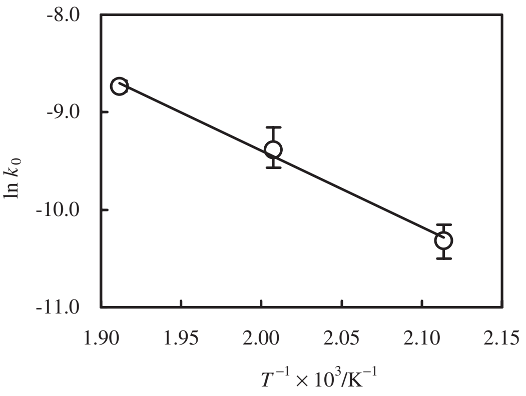

Figure 2. Arrhenius plot for the initial reaction rate constant k_0.

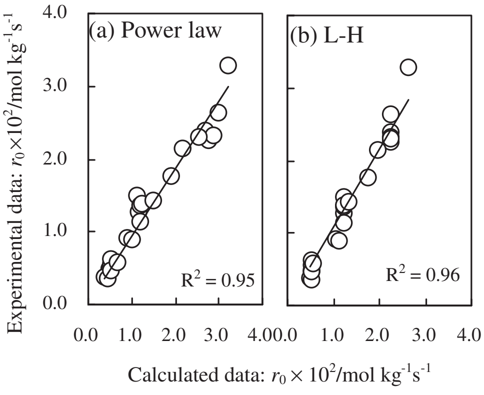

Figure 3. Comparison of the r_0 calculated from the power law and L–H equations with the experimental r_0.

Table 1. The calculated parameters for the L–H equation

	Temperature/°C		
	200	225	250
$k \times 10^4$/mol kg^{-1} s^{-1}	3.6	9.9	24.6
$K_{H_2O} \times 10^4$/Pa^{-1}	1.3	0.51	0.21
E_a/kJ mol^{-1}		79	

adsorbed onto the support surface as OH groups, and CO is adsorbed onto the precious metal surface. The activated CO and OH groups at the interface of the metal and support react to produce a formate species as an intermediate. The formate species is then converted to CO_2 and H_2. Present authors have previously characterized the CO–D_2O reaction over Pt–Re/ZrO_2 by in situ Fourier transform infrared (FT-IR) measurements. When CO was introduced into the IR cell at 250 °C after D_2O adsorption, the intensities of the bands assigned to the formate species gradually increased while the intensities of the bands assigned to active CO species and hydroxy (OD) species over ReOx and ZrO_2 decreased. The bands representing the formate species immediately disappeared upon exposure to D_2O.[7] Therefore, the overall surface reaction can be modeled as a surface reaction of two species adsorbed onto separate sites, and the formation of the formate intermediate can be assumed to be the rate-determining step. The L–H equation for this type of surface reaction process is written as;

$$\begin{aligned} -r_0 &= k(K_{CO}p_{CO}/(1 + K_{CO}p_{CO} + (K_{H_2}p_{H_2})^{1/2})) \\ &\quad \times (K_{H_2O}p_{H_2O}/(1 + K_{H_2O}p_{H_2O} + K_{CO_2}p_{CO_2})) \end{aligned} \quad (4)$$

In this case, the partial pressure of CO_2 and H_2 as products can be neglected at the initial stage of reaction, so that eq 4 can be rewritten as;

$$-r_0 = k(K_{CO}p_{CO}/(1 + K_{CO}p_{CO}))(K_{H_2O}p_{H_2O}/(1 + K_{H_2O}p_{H_2O})) \quad (5)$$

It is also inferred that CO is strongly adsorbed onto the catalyst surface because the reaction order with respect to CO for the power law equation was zero. Therefore, the adsorptive equilibrium constant of CO, K_{CO}, would be large.

$$\begin{aligned} &K_{CO}p_{CO} \gg 1, \text{ then } 1 + K_{CO}p_{CO} \approx K_{CO}p_{CO} \\ &-r_0 = k(K_{H_2O}p_{H_2O}/(1 + K_{H_2O}p_{H_2O})) \end{aligned} \quad (6)$$

Table 1 shows the calculated parameters for the L–H equation. The activation energy was determined to be 79 kJ mol^{-1}.

The L–H equation is written as

$$-r_0 = 1.9 \times 10^5 \exp(-79 \times 10^3/RT)(K_{H_2O}p_{H_2O}/(1 + K_{H_2O}p_{H_2O})) \quad (7)$$

Figure 3b shows a comparison of the values calculated from eq 7 and the experimental data, which indicates better agreement than that with the power law equation.

References

1 H. Iida, K. Tahara, H. Higashi, A. Igarashi, *Adv. Technol. Mater. Mater. Process. J.* **2002**, *4*, 62.
2 S. Y. Choung, M. Ferrandon, T. Krause, *Catal. Today* **2005**, *99*, 257.
3 R. Radhakrishnan, R. R. Willigan, Z. Dardas, T. H. Vanderspurt, *Appl. Catal., B* **2006**, *66*, 23.
4 K. G. Azzam, I. V. Babich, K. Seshan, L. Lefferts, *J. Catal.* **2007**, *251*, 163.
5 H. Iida, A. Igarashi, *Catal. Catal.* **2007**, *49*, 447.
6 H. Iida, A. Igarashi, *Appl. Catal., A* **2006**, *303*, 192.
7 H. Iida, A. Igarashi, *Appl. Catal., A* **2006**, *298*, 152.
8 O. Levenspiel, *Chemical Reaction Engineering*, 3rd ed., John Wiley & Sons, New York, USA, **1999**, p. 390.
9 D. C. Grenoble, M. M. Estadt, D. F. Ollis, *J. Catal.* **1981**, *67*, 90.
10 A. Phatak, N. Koryabkina, S. Rai, J. L. Ratts, W. Ruettinger, R. J. Farrauto, G. E. Blau, W. N. Delgass, F. H. Ribeiro, *Catal. Today* **2007**, *123*, 224.