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Kinetics of the water–gas shift reaction over a rhodium-promoted iron–chromium oxide catalyst

Yun Lei, Noel W. Cant, David L. Trimm [*]

School of Chemical Engineering and Industrial Chemistry, The University of New South Wales, Sydney, NSW 2052, Australia

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Abstract

The addition of a small amount of rhodium to a high temperature iron–chromia water–gas shift catalyst has been found to accelerate significantly the approach to equilibrium. The kinetics of the reaction have been studied in terms of the separate forward and backward reactions, and using a feed composition typical of those produced by steam reforming. It was found impossible to avoid the influence of mass transfer under relevant high-temperature operating conditions. A power rate law incorporating thermodynamic limitations best described the kinetic data for the reforming mixture. An equation based on forward and backward expressions was less satisfactory. Comparison of the observed kinetics with those reported in the literature for undoped catalysts indicates that the promoter has the greatest effect on the reactivity of carbon monoxide and hydrogen.

Keywords: Water–gas shift reaction; Iron–chromium oxides; Rhodium promotion; Kinetic models

1. Introduction

The use of catalysts based on Fe_3O_4–Cr_2O_3 to promote the water–gas shift (WGS) reaction:

$$CO + H_2O \rightleftharpoons CO_2 + H_2, \qquad \Delta H = -41.1\,\text{kJ/mol} \tag{1}$$

was first patented in 1911 [1]. However, the subsequent development of $Cu/ZnO/Al_2O_3$ catalysts that are more active at lower temperatures [2,3] resulted in the use of Fe–Cr based catalysts being confined to temperatures above 300 °C. The chromia acts to structurally stabilize the iron oxide, apparently by forming a solid solution [4,5].

The promotion of Fe_3O_4–Cr_2O_3 catalyst has been studied. Andreev et al. [6] have investigated the effect of small amount of CuO, CoO and ZnO, Edwards et al. [7] have added first row transition metal oxides and Rhodes et al. [8] have found that Hg, Ag, Ba, Cu and Pb improve performance. Copper, an effective promoter, appears to be dispersed in a solid solution throughout the catalyst but is present in a surface segregated state [7]. This suggests that, in agreement with the data of Topsoe and Boudart for a lead-promoted catalyst [4], copper provides electronic promotion of the Fe_3O_4–Cr_2O_3 rather than forming new active sites in an oxide matrix.

The kinetics of the high temperature WGS reaction have been studied extensively over the last 40 years and more than 20 kinetic expressions have been proposed. Newsome [9] provided an excellent review in 1980, but there is still some disagreement on various kinetic values. Twigg [2] reduced the plausible reaction models to five, of which the most relevant appeared to be based either on a Langmuir–Hinshelwood approach [2,10,11]:

$$r = \frac{kK_{CO}K_{H_2O}[[CO][H_2O] - [CO_2][H_2]/K]}{(1 + K_{CO}[CO] + K_{H_2O}[H_2O] + K_{CO_2}[CO_2] + K_{H_2}[H_2])^2} \tag{2}$$

where k is the rate constant, K_i the adsorption equilibrium constant of species i at concentration $[i]$ and K is the numerical value for the equilibrium constant for the WGS reaction, or on a power rate law basis [12,13] with the rate expressed as either

$$\text{rate} = k[CO]^m[H_2O]^n[CO_2]^p[H_2]^q \tag{3}$$

or

$$\text{rate} = k_1[CO]^a[H_2O]^b[CO_2]^c[H_2]^d(1-\beta) \tag{4}$$

$$\beta = \frac{[CO_2][H_2]}{K[CO][H_2O]} \tag{5}$$

The power rate law model was found to be sufficient for most reactor design studies.

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[*] Corresponding author. Tel.: +61 2 9385 4340.
E-mail address: d.trimm@unsw.edu.au (D.L. Trimm).

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The kinetic results were found to be fully in accord with a regenerative (oxidation–reduction) mechanism [12–14] in which water adsorbs and dissociates on reduced sites to produce hydrogen while oxidizing the site. In the following step, CO is oxidized to CO_2 and reduces the oxidized site to complete the cycle

$$H_2O + * \rightarrow H_2 + O* \tag{6}$$

$$CO + O* \rightarrow CO_2 + * \tag{7}$$

The effect of promotion by precious metals of a range of oxides, including Fe_3O_4–Cr_2O_3, has recently been studied [15]. Rhodium promotion of Fe_3O_4–Cr_2O_3 was found to be particularly effective. The present article reports measurements of the kinetics of the WGS reaction over Rh-promoted Fe_3O_4–Cr_2O_3.

2. Experimental

All kinetics experiments were carried out with the catalyst mounted in a tubular flow reactor. Gas supplies to the reactor were controlled using Brooks 5850 mass flow controllers; steam was generated in a preheater fed with water from an ISCO LC-260D stainless steel pump. The reactor (40 cm long × 1 cm i.d.) was built with a central thermocouple well and located in the constant temperature zone of an electric furnace.

Gases leaving the reactor were passed through an ice-cooled trap and a tube packed with Drierite to remove water before gas chromatographic analysis. One Shimadzu GC 8A chromatograph fitted with a thermal conductivity detector (TCD) was used to analyse carbon oxides, oxygen, nitrogen and methane after separation on a 1.8 m CTR-1 column (Alltech Associates). A second Shimadzu GC8A chromatograph, also with a TCD, was used to analyse hydrogen in an argon carrier stream using a 2 m molecule sieve 13X column.

The catalyst preparation involved precipitating $Fe(OH)_3$ from iron nitrate by adding 30% ammonia hydroxide to a pH of 7.5–8.0. The precipitate was filtered and washed before preparing a thick slurry. Chromium nitrate solution was then stirred into the slurry (pH 7.5–8.0) and the mixture was aged for 8 h. After filtration and washing the solid was dried (110 °C, 16 h) and calcined (500 °C, 3 h). Samples crushed and sieved to various particle sizes were impregnated with rhodium nitrate using the incipient wetness technique. The final catalysts were dried and calcined as above.

ICP analysis showed the catalyst contained 0.97 wt.% Rh; XRF measured 91.5% Fe_2O_3 and 7.36% Cr_2O_3 (residual trapped Na_2O). The surface area measured by the BET method was found to be 46 $m^2\,g^{-1}$. Metal surface area was too low to measure.

Catalyst (50 mg) was mixed with α-alumina of the same size and mounted in the reactor between quartz wool plugs. Initial reduction was carried out using 50 ml/min of a 10% H_2/90% N_2 mixture (400 °C, 2 h). Kinetics measurements were carried out using the Rh-promoted catalyst of particle size −250 + 150 μm. Reactants and products at the desired concentrations were then admitted to the reactor and the temperature adjusted to the starting temperature for the kinetics measurements. The system was then left running overnight. Subsequent measurements were stable and reproducible.

3. Results and discussion

Previous studies of the high temperature water–gas shift reaction have shown that promotion of the catalyst by the addition of small amounts of metals can be advantageous [15]. Comparison of the activities of different promoted catalysts showed that small amount of Rh was the best promoter. As a result, the present studies were initiated in order to quantify the advantage to be gained by promotion with this metal.

Some estimates of the advantages to be gained by the promotion are illustrated by the pseudo-Arrhenius plots in Fig. 1, which also illustrates the effect of mass transfer on the system. This plot demonstrates an interesting dilemma. The rate per gram of catalyst increases as the particle size decreases. This implies influence from mass transfer, but it proved impossible to decrease particle size to a value such that mass transfer effects were not significant. Extrapolation of the results would indicate that chemical kinetics control should predominate below 300 °C, but this is not the temperature range over which a high temperature water–gas shift catalyst is designed for use. As a result, a decision was made to investigate the kinetics of the reaction for the operating range, in the knowledge that there would be a small effect due to mass transfer that will affect the results.

Data was obtained for both the forward and backward WGS reaction and for the system operating under conditions close to those pertinent to the exit stream of a steam reforming reaction

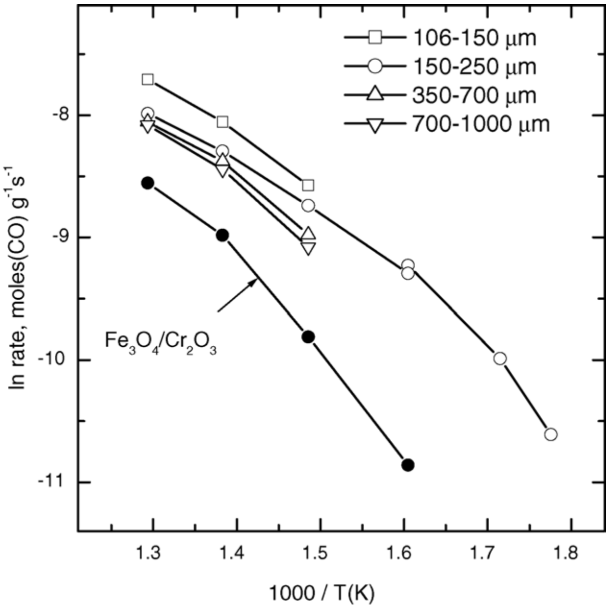

Fig. 1. Activities of unpromoted and Rh-promoted Fe_3O_4–Cr_2O_3 catalysts with different particle size for the forward gas shift reaction using conditions as per Table 1. All catalysts prepared as described in Section 2.

Table 1
Inlet pressures and temperatures employed

Reaction	CO (kPa)	H_2O (kPa)	CO_2 (kPa)	H_2 (kPa)	T (°C)	Parameter
Forward reaction	4–12	20	–	–	360	Order in CO
	10	5–30	–	–	360	Order in H_2O
	10	10	–	–	360–468	E_a[a]
Backward reaction	–	–	2–8.5	7	360	Order in CO_2
	–	–	8.3	3.9–11	360	Order in H_2
	–	–	8.4	8.4	360–448	E_a[a]
Reforming conditions	3–10	22	8.3	36	300–400	Order in CO
	7	5–22	8.5	36	300–400	Order in H_2O
	6.5	22	3–9	36	300–400	Order in CO_2
	6.5	22	8	5–36	300–400	Order in H_2

[a] Apparent activation energy.

[2]. In the latter case, the kinetics were expected to be affected by the presence of both reactants and products. In contrast, conversion was limited to less than 20% of the equilibrium conversion for the forward and backward reactions, in order to minimize the effect of reverse reactions. The range of operating conditions is summarised in Table 1.

Investigation of the forward reaction was first carried out and typical log–log plots for the dependence of rate on CO and H_2O are shown in Fig. 2. The apparent activation energy was determined separately for the temperature range 360–470 °C. The combined results could be expressed in terms of a power rate law:

$$-r_{CO} = 0.0041 \exp\left(\frac{-33\,600}{RT}\right) P_{CO}^{0.64} P_{H_2O}^{0.50} \tag{8}$$

where the apparent activation energy is ∼34 kJ/mol.

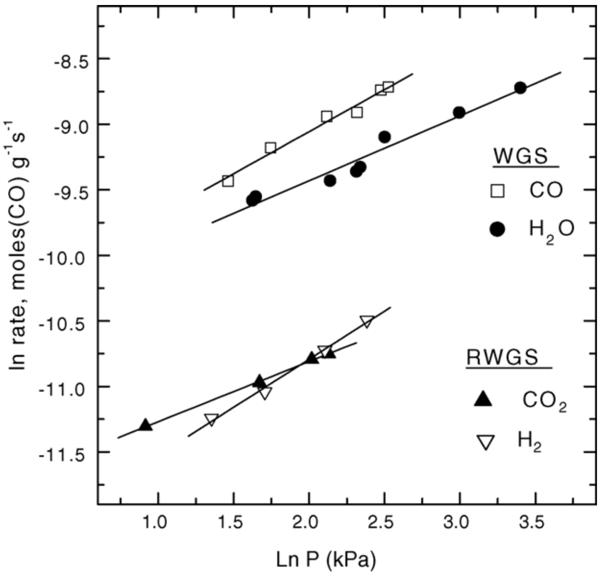

Fig. 2. Log–log plots of the effect of CO and H_2O partial pressures on the rate of the forward water–gas shift reaction (WGS) and of CO_2 and H_2 on the corresponding reverse shift reaction (RWGS) over $Rh/Fe_3O_4–Cr_2O_3$ at 360 °C. Conditions as per Table 1.

Similar studies were carried out for the backward reaction (Fig. 2), with the corresponding power rate law being:

$$-r_{CO_2} = 0.024 \exp\left(\frac{-50\,100}{RT}\right) P_{CO_2}^{0.46} P_{H_2}^{0.73} \tag{9}$$

where the apparent activation energy is ∼50 kJ/mol.

Finally the kinetics of the reaction under conditions pertinent to reforming (Table 1) were measured. Trial calculations showed that the measured rates could not be accurately described as the difference, Eqs. (8) and (9). This was somewhat unexpected, but results from competition of reactants and products for active sites on the catalyst. Studies of the initial rates of the forward and backward reaction would not reflect competition of all gases for adsorption sites, as would occur under reforming conditions. With this in mind, refinement of the kinetics equations using non-linear regression techniques with the apparent orders of reaction, rate constants and activation energies allowed to vary led to the expression

$$\begin{aligned} -r_{CO} = {} & 0.34 \exp\left(\frac{-63\,020}{RT}\right) P_{CO}^{0.87} P_{H_2O}^{0.40} \\ & - 0.55 \exp\left(\frac{-70\,420}{RT}\right) P_{CO_2}^{0.26} P_{H_2}^{0.66} \end{aligned} \tag{10}$$

The fit between predicted and observed rates was quite good with R^2 of 0.983 but the uncertainties in some parameters were rather large.

Several authors [3,9,16] have analysed kinetic data for the unpromoted catalyst in terms of Eq. (4), i.e.

$$\text{rate} = k_1 P_{CO}^{a} P_{H_2O}^{b} P_{CO_2}^{c} P_{H_2}^{d} (1-\beta) \tag{11}$$

In the present study, the experimental data involved measurements in which the partial pressure of one reactant was varied while the other partial pressures were constant (Table 1). This allowed estimation of reaction orders. Typical results for CO and H_2 as examples are shown in Fig. 3. It is apparent that orders vary little if any with temperature. Non-linear regression gave the best fit equation as

$$\text{rate} = 0.187 \exp\left(\frac{-63\,240}{RT}\right) P_{CO}^{1.45} P_{H_2O}^{0.44} P_{CO_2}^{-0.12} P_{H_2}^{-0.22} (1-\beta) \tag{12}$$

Table 2
Parameters for the water–gas shift reaction using reformate mixtures over $Rh/Fe_3O_4–Cr_2O_3$ catalysts compared with literature values for the unpromoted catalysts

Catalyst	T (K)	Apparent reaction orders				E_a (kJ/mol)	Reference
		CO	H_2O	CO_2	H_2		
$Rh/Fe_3O_4–Cr_2O_3$	573–673	1.45	0.44	−0.12	−0.22	63	This work
$Fe_3O_4–Cr_2O_3$	600–723	0.90	0.25	−0.6	0.0	60	[9]
						118	[3]
	653–723	0.93	0.33	−0.63	−0.02	106–114	[12]

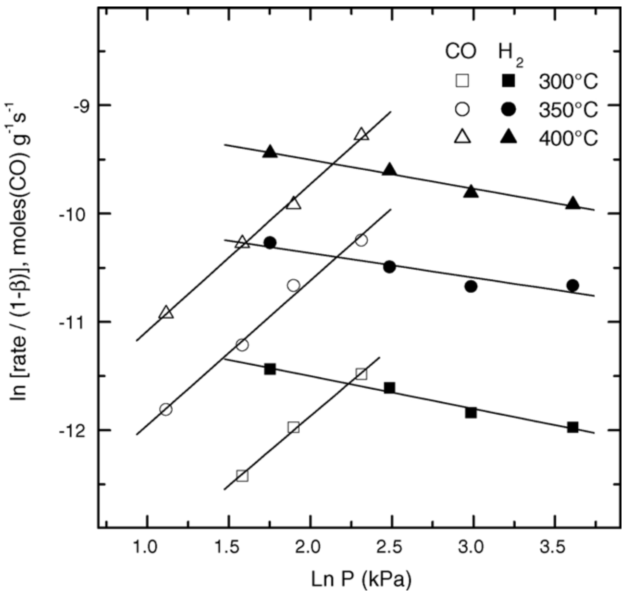

Fig. 3. Log–log plots for the effect of CO and of H_2 partial pressures on reaction rates over $Rh/Fe_3O_4–Cr_2O_3$ using reforming conditions (Table 1) at temperatures of 300, 350 and 400 °C.

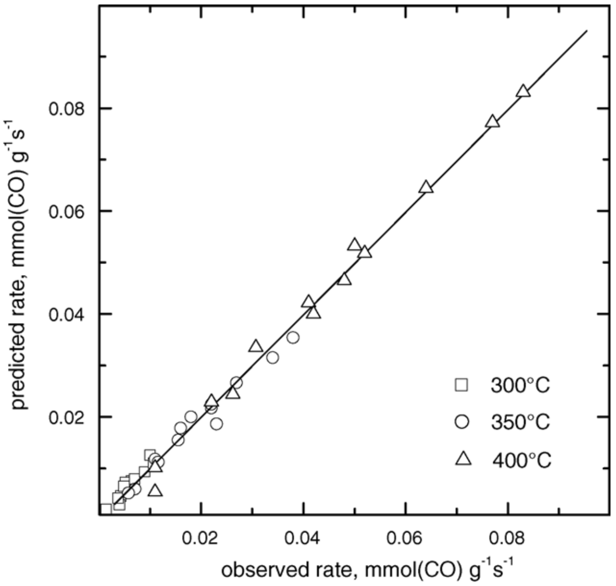

Fig. 4. Observed rates vs. predicted rates of water–gas shift over $Rh/Fe_3O_4–Cr_2O_3$ under reforming conditions based on Eq. (12).

The fit between predicted and observed rates (Fig. 4) was better than for Eq. (10) with R^2 of 0.993.

Comparison of parameters measured for catalysts containing Rh, with literature reported values for unpromoted catalysts (Table 2) gives some indications of the role of the promoter. Bearing in mind that the observed kinetics are affected to a small extent by mass transfer, the observed apparent activation energy is in reasonable agreement with values for $Fe_3O_4–Cr_2O_3$ ($E_a/2 = 63$ kJ/mol for $Rh/Fe_3O_4–Cr_2O_3$, cf. $E_a = 106–118$ kJ/mol for $Fe_3O_4–Cr_2O_3$ [3,12]). Reaction orders in CO and H_2 are higher, while that in CO_2 is less negative (Table 2). Although it is difficult to assess and compare reaction orders with and without Rh doping, due to the unknown influence of mass transfer in the two systems, it is interesting that the promoter has the greatest effect on the parameters for CO and H_2. This infers that Rh promotion involves the extent of adsorption of theses two gases. A mechanistic study designed to explore this is currently in progress.

4. Conclusions

It is clear that the above kinetic expressions (11) and to a lesser extent (10), give an accurate prediction of the observed rate and, as a result, are suitable for reactor design. Mass transfer does affect the results to a small extent, but the conditions under which the catalyst operates (high temperature) make such effects difficult to avoid.

Acknowledgement

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