Comparison of the Kinetics of the Fischer-Tropsch Synthesis Reaction Between Alumina and Silica Supported Cobalt Catalysts as a Function of Metal Loading

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Introduction

Water, as one of the main Fischer-Tropsch (FT) products, played important role in inhibiting active sites on the surface of the cobalt catalyst during FT reaction [1] consequently, it affected greatly the FT performance parameters of the catalyst. A kinetic method using an empirical kinetic model,

$$-r_{CO} = kP_{CO}^{a}P_{H2}^{b}/(1+ mP_{H2O}/P_{H2}) \qquad (1)$$

has proven to be reliable in quantifying a reversible H_2O effect in recent years [2-4]. In this paper, we conducted kinetic experiments over 15-25% Co/SiO_2 catalysts and a 25%Co/Al_2O_3 catalyst in order to quantitatively identify the effect of support type on the impact of water during FT, as well as the sensitivity of Co cluster size to the water effect.

Catalyst Preparation: Details of procedures for the preparation of a 25%Co/ Al_2O_3 and 15-25%Co/SiO_2 catalysts are reported elsewhere [4,5]. Briefly, a slurry phase method involving sequential impregnations (due to the solubility limit of cobalt nitrate) was used to load the desired amount of cobalt nitrate to the supports. Following cobalt addition, the catalyst was dried at 80°C and 100°C in a rotary evaporator. Finally, catalysts were calcined in flowing air at a rate of 1 liter per min for 4 hours at 350°C.

Catalyst pretreatment: The calcined 25%Co/Al_2O_3 and 15-25%/SiO_2 catalysts were ground and sieved to 80-325 mesh (8-10 g) before loading into a fixed-bed reactor for *ex-situ* reduction at 350°C and atmospheric pressure for 10 h using a gas mixture of H_2/He with the molar ratio of 1:3. The reduced catalyst was then transferred to a 1-L continuously stirred tank reactor (CSTR), under the protection of N_2 inert gas, which was previously charged with 315 g of melted Polywax 3000. The transferred catalyst was further reduced *in-situ* at 230 °C at atmospheric pressure using pure hydrogen for another 10 h before starting the FTS reaction.

Slurry phase catalyst testing: The catalyst was tested in a 1-L CSTR. The kinetics experiments were conducted on the air calcined 25%Co/Al_2O_3 and, 15 and 25%Co/SiO_2 catalysts through varying H_2 partial pressure between 1.27– 0.51 MPa while maintaining a constant CO partial pressure of 0.51 MPa, and conversely, by varying CO partial pressure between 0.32-0.81 MPa while holding a constant H_2 partial pressure of 0.81 MPa in the temperature range of 205-220 °C. Throughout the test, total reaction pressure was maintained at 2.03 MPa by adjusting the inert gas (N_2) flow to give a range of 12.5-50 vol.%. In total, four ratios of H_2/CO (2.5, 2.0, 1.5, and 1.0) were used in a space velocity range of 35- 3.3 Nl/gcat/h. After completing a set of space velocity for each ratio of H_2/CO, the reaction conditions were returned to a set of reference conditions of 220 °C, 2.03 MPa, H_2/CO = 2.5, N_2% =12.5, 10-25 Nl/gcat/h in order to measure the extent of deactivation of the catalyst. In general, the reaction period for each space velocity was 24 h to ensure that the data point was achieved at close to steady state.

Kinetic results on wide porous 25% Co/Al_2O_3 The reaction orders of *a* and *b* over a wide pore 25% Co/Al_2O_3 were calculated to be –0.24 and 0.50 based on the equation (1). These values are quite consistent with literature reports [2,6,7]. The *k* value obtained in this study is 0.0335 mol/g-cat/h/MPa$^{0.26}$, which is 25-65% higher than that of the medium porous and narrow porous Al_2O_3 supported Co catalysts [2,4], showing 25% Co on the wide porous Al_2O_3 is the most active among the three structured Al_2O_3 catalysts. Activation energy, E_a, is determined to be 76.9 kJ/mol on the catalyst, in good agreement with that of 25%Co on the medium porous Al_2O_3 catalyst [4] and is consistent with the literature values [8,9]. Water effect constant, *m*, was determined to be 1.02, clearly showing negative water effect of the Al_2O_3 supported catalysts. Comparing with the *m* value (0.91) of the medium porous Al_2O_3 catalyst, it is concluded that Cobalt catalyst in the wide pore Al_2O_3 is more sensitive to water. This might be mainly due to the effect of smaller Co particles present on the wide pore Al_2O_3, as characterized by hydrogen chemisorptions/pulse reoxidation. The inhibition rate by H_2O may be caused by adsorption inhabitation by water. This may in turn involve oxidation of a fraction of smaller crystallites strongly interacting with the support at high enough water partial pressures, as confirmed previously by EXAFS/XANES [1]. At low P_{H2O}/P_{H2} ratios, however, our previous results indicated that cobalt did not change oxidation state before/after H_2O co-feeding.

Table 1 Summary of kinetic parameter values on cobalt supported Al_2O_3 and SiO_2

Catalyst	Reaction order		Activation Energy	Water effect	Reaction rate constant
	a	*b*	E_a, kJ/mol	constant,*m*	*k*, mol/g-cat/h/MPa$^{(a+b)}$
25%Co/Al_2O_3	-0.24	0.5	78	1.02	0.0335
15%Co/SiO_2	-0.22	0.6	85.9	-0.33	0.0187
25%Co/SiO_2	-0.19	0.51	93.7	-1.11	0.0381

Kinetic results of 15%Co/SiO_2 and 25%Co/SiO_2 catalysts Table 1 also listed the kinetic results of 15, and 25%Co/SiO_2 catalysts. From Table 1, the orders of *a* and *b* for partial pressure of CO and H_2 in the current study (15%Co/SiO_2) are -0.22 and 0.6, respectively, which are in agreement with the values of -0.19 and 0.51 for 25% Co/SiO_2. The reaction kinetic rate constant is a function of the catalyst and can be used to effectively compare catalyst activity. The *k* value at 220 °C for the 15%Co/SiO_2 catalyst is 0.0187mol/gcat/h/MPa$^{0.38}$, which is less than half the value of 0.0381 obtained for the 25%Co/SiO_2 catalyst. This is consistent with the fact that higher per gram catalyst activities are observed with the more highly loaded Co catalysts. The activation energies of the 15%Co/SiO_2 and 25% Co/SiO_2 catalysts were calculated to be 85.9 and 93.7 kJ/mol, respectively, which are in the range of 60-100 kJ/mol as reported in literature [9]. Interestingly, the water effect constant, *m,* was calculated to be negative for each of the two SiO_2 supported catalysts (Table1), indicating a positive water effect for the Co/SiO_2 catalysts in terms of the empirical kinetic model (1). However, the *m* value of -0.33 for the 15%Co/SiO_2 differed significantly from the value of -1.11 obtained for the 25%Co/SiO_2 catalyst. This is clearly an indication of a stronger positive water effect during FTS for 25%Co/SiO_2. Co particles residing in the pores should be sensitive to this effect. It was reported [5] that the higher loading 25%Co/SiO_2 had an average Co cluster size of ~27 nm, while the 15%Co/SiO_2 catalyst was observed to have an average Co cluster size of ~38 nm. These results indicated that smaller Co particles on 25%Co/SiO_2 where the particles were small enough to fit inside pore of the support, were more sensitive to the effect of water. This finding is in agreement with the proposal that water may assist in displaying heavier hydrocarbons from the pore, thereby, preventing pore filling by the heavier hydrocarbons. As such, the catalyst with particles small enough to fit inside the pore will benefit from this effect more appreciably.

In summary, the kinetics of Fischer-Tropsch synthesis (FTS) for the 25%Co/Al_2O_3 and the 15 and 25% Co/SiO_2 catalysts were studied in a 1-L continuously stirred tank reactor (CSTR) in order to define the impact of water on the FTS rate and sensitivity of cobalt crystallite size to water effect. An empirical kinetic model, $r_{CO} = k\, P_{CO}^{a} P_{H2}^{b} / (1 + m\, P_{H2O}/P_{H2})$, was used in this study. The intrinsic kinetic parameters were identified using the kinetic data obtained under a wide range of experimental conditions of 3.3-35 Nl-gcat/h, H_2/CO ratio of 1.0-2.5, 205-220 ^{o}C and a fixed CO pressure of 0.51 MPa and a fixed hydrogen pressure of 0.81 MPa for the three Co catalysts. It is found that the support type governed whether the impact of H_2O on the rate was positive or negative, with less interacting Co/silica providing a positive kinetic effect, while the strongly interacting Co/alumina resulted in a negative impact on the CO conversion rate. Furthermore, the kinetic parameter values for the 15 and 25%Co supported on SiO_2 catalysts showed smaller Cobalt particles exerted greater negative water effect, indicating higher water sensitivity of smaller Co particles on FTS rate. This can be explained by water-assisted displacement of heavier hydrocarbons from the pores, resulting in higher CO conversion rates.

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References

1. Jacobs, G., Das, T.K., Patterson, P.M., Li, J.L., *Appl. Catal.,* 247, 335-343 (2003)

2. Das, T.K.; Zhan, X.D.; Li, J.L.; Jacobs, G.; Dry, M.E. and Davis, B.H., *Stud. Surf. Sci. Catal.,* 163, 289-314 (2007)

3. Das, T. K., Conner, W.A., Li, J.L., Jacobs, G., Dry, M.E., and Davis, B.H., *Energy & Fuels,* 19, 1430-1439 (2005)

4. Ma, W.P., Jacobs, G., Sparks, D.E., Spicer, R.L., Graham, U.M., Davis, B. H., *Preprints – Am. Chem. Soc. Div. Petro. Chem.,* 53, 99-102 (2008)

5. Jacobs, G., Ma, W.P., Ji, Y.Y., Khalid, S., Davis, B.H., *Preprints–Am. Chem. Soc. Div. Petro. Chem.,* 53, 79-83 (2008)

6. Ribeiro, F.H., Schach Von Wittenau, A.E., Bartholomew, C.H., Somorjai, G.A., *Catal. Rev. Sci. Eng.,* 39, 49-76 (1997)

7. Zennaro, R., Tagliabue, M., Bartholomew, C. H., *Catal. Today,* 58, 309-319 (2000)

8. Chang, J., Teng, B.T., Bai, L., Chen, J.G., Zhang, R.L., Xu, Y.Y., Xiang, H.W., Li, Y.W., and Sun, Y.H., *Cuihua Xuebao,* 26, 859-868 (2005)

9. Withers, H.P., Eliezer, K.F., and Mitchell, J.W., *Ind. Eng. Chem. Res.,* 29, 1807-1814 (1990)

Key words

Fischer-Tropsch, kinetic, water effect, Cobalt catalyst.