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Fischer–Tropsch synthesis. Effect of CO pretreatment on a ruthenium promoted Co/TiO_2

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The effect of pretreatment, using hydrogen or carbon monoxide, on the activity and selectivity of a ruthenium promoted cobalt catalyst (Ru(0.20 wt%)/Co(10 wt%)/TiO_2) during Fischer–Tropsch (FT) synthesis was studied in a continuous-stirred tank reactor (CSTR). The hydrogen reduced catalyst exhibited a high initial synthesis gas conversion (72.5%) and reached steady state after 40 h on stream, after which the catalyst deactivated slightly with time on stream. The carbon monoxide reduced catalyst reached steady state quickly and showed a lower activity and a good stability. Methane selectivity on the carbon monoxide reduced catalyst was 15–20% (carbon base), much higher than that on the hydrogen reduced catalyst (5–10%). Carbon monoxide regeneration increased the activity on the hydrogen reduced catalyst; however, it did not have significant effect on the carbon monoxide reduced catalyst.

Keywords: cobalt, ruthenium, titania, Fischer–Tropsch synthesis, synthesis gas conversion, CO pretreatment, continuous-stirred tank reactor

1. Introduction

Pretreatment conditions used for supported cobalt Fischer–Tropsch (FT) catalysts often have significant effect on the catalyst activity, selectivity and lifetime [1–9]. A number of researchers focused on the study of pretreatment of the catalyst with hydrogen, including the effects of calcination and hydrogen reduction temperatures. Calleja et al. [6] investigated the FT reaction over a Co/HZSM-5 catalyst, and found that the calcination and reduction temperatures did not have an effect on the catalyst activity. The results obtained by Rathousky et al. [8], however, revealed that the calcination and reduction temperatures have a significant effect on the catalytic properties of both Co/Al_2O_3 and Co/SiO_2 catalysts. The turnover frequency (TOF) for the FT reaction decreased with increasing calcination temperature for both Co/Al_2O_3 and Co/SiO_2. However, the total reaction rate increased for Co/Al_2O_3 while it decreased for Co/SiO_2 [7–9]. Belambe et al. [10] studied the pretreatment effects on the activity of a Ru-promoted Co/Al_2O_3 catalyst for the FT reaction. The calcination temperature was found to have a pronounced effect on the overall activity of the catalyst, but not on the TOF. The reduction temperature had only a negligible effect on the overall activity and TOF. A few studies on the effect of treatment with carbon monoxide or syngas for the supported cobalt catalysts has been reported. It has been reported that the supported cobalt catalyst pretreated with a gas containing carbon monoxide had increased activity and greater selectivity towards producing C_{5+} hydrocarbons [11]. Older work indicates that Co_2C is formed by low-temperature activation with CO [12]. Supported cobalt that were reduced in hydrogen, carburized with CO at 208 °C and then hydrogenated at 208 °C, the carbide was quickly converted to cobalt metal. Below about 240 °C, treatment of cobalt catalysts with CO led to Co_2C with little, if any, free carbon.

The present work was undertaken to investigate the effect of carbon monoxide pretreatment on the titania supported cobalt catalyst. The results obtained have been compared with these of catalyst pretreated with hydrogen. The catalyst chosen for the present study is Ru(0.20 wt%)/Co(10 wt%)/TiO_2. Our previous study [13] has shown that this catalyst had good catalyst activity and selectivity for Fischer–Tropsch synthesis.

2. Experimental

2.1. Catalyst preparation

The titania supported cobalt catalyst was prepared by pore volume impregnation of Degussa P-25 TiO_2 (72% anatase, 45 $m^2\,g^{-1}$, calcined at 673 K for 6 h before use) with a cobalt nitrate (Alfa) solution. The sample was dried at 393 K for 16 h and calcined at 573 K for 6 h. The ruthenium promoted catalyst was prepared by impregnating pretreated Co/TiO_2 with a solution containing ruthenium nitrosylnitrate (Alfa). The sample was dried at 393 K for 16 h and calcined at 573 K for 6 h. The ruthenium and cobalt contents were 0.20 and 10 wt%, respectively, corresponding to an atomic Ru/Co ratio of 0.012.

2.2. Reaction system and procedure

A 1 l autoclave, operated as a continuous-stirred tank reactor (CSTR), was used for the slurry FT reaction. Analyses of the gaseous, liquid, and solid (at room temperature) products was conducted using a variety of both on- and off-line gas chromatographs.

The catalyst was pretreated with pure hydrogen or with pure carbon monoxide at different temperatures. The hydrogen activation was first conducted *ex situ* and then *in situ* according to the following procedure. The catalyst (about 15 g) was put in a fixed-bed reactor and pure hydrogen was introduced at a flow rate of 60 Nl h^{-1} (298 K, 0.1 MPa); the reactor temperature was increased from room temperature to 373 K at a rate of 120 K h^{-1}, then increased to 573 K at a rate of 60 K h^{-1} and kept 573 K for 16 h. The catalyst was transferred under a helium blanket to the CSTR to mix with 300 g of melted polyethylene (PW 3000). The catalyst was then reduced *in situ* in the CSTR; the hydrogen was introduced to the reactor at atmospheric pressure with a flow rate of 30 Nl h^{-1} (298 K, 0.1 MPa). The temperature was increased to 553 K at a rate 120 K h^{-1} and maintained at this activation condition for 24 h.

The carbon monoxide activation was conducted *in situ* in the CSTR according to the following procedure. Approximately 15 g of catalyst was mixed with 300 g of melted polyethylene (PW 3000) in the CSTR. The reactor pressure was increased to 1.68 MPa with carbon monoxide at a flow rate 30 Nl h^{-1} (298 K, 0.1 MPa). The reactor temperature was then increased to 523 K at a rate of 120 K h^{-1}. These activation conditions were maintained for 24 h. In order to avoid any deposition of refractory carbon residues, a lower carbon monoxide pretreatment temperature (523 K) was chosen for this study.

After the activation period, the reactor temperature was decreased to 483 K and synthesis gas (2H$_2$/CO) was introduced to increase the reactor pressure to 2.35 MPa. The reactor temperature was then increased to 503 K at a rate of 10 K h^{-1}. During the entire run the reactor temperature was 503 K, the pressure was 2.35 MPa, and the stirring speed was maintained at 750 rpm.

The space velocity of the synthesis gas was 2 and 3 Nl g_{cat}^{-1} h^{-1} and the feed H$_2$/CO ratio was kept constant at 2. The conversion of carbon monoxide and hydrogen and the formation of products were measured during a period of 24 h at each condition. Test duration was 210 h on stream for the hydrogen reduced catalyst or 350 h on stream for the carbon monoxide reduced catalyst. A common gas supply and carbonyl removal (using Pb–Al$_2$O$_3$) system was used for five CSTRs that were utilized with a variety of cobalt catalysts. Since the methane selectivity and activity stability of the other catalysts utilized in the other four reactors were normal, the feed should not impact the runs. Furthermore, since CO pretreatment has been utilized in similar reactors for more than 100 runs without impact of metal deposition, the CO pretreatment should not impact the results. In this study, a PbO(20 wt%)–Al$_2$O$_3$ trap for metal carbonyls was used. Prior work with an alumina trap led to deposition of iron on cobalt catalysts; however, following installation of the PbO–Al$_2$O$_3$ trap, chemical analysis showed that the iron contamination was eliminated.

3. Results and discussion

3.1. Catalyst activity

The synthesis gas conversion is a rough measure of the overall Fischer–Tropsch activity of a supported cobalt catalyst. The synthesis gas conversions (mol%) for RuCo/TiO$_2$ catalysts reduced with hydrogen and with carbon monoxide as a function of time on stream are shown in figure 1 to illustrate the effect of pretreatment gas on catalyst activity. The space velocities used were 2 and 3 Nl g_{cat}^{-1} h^{-1}. Firstly, a space velocity of 2 Nl g_{cat}^{-1} h^{-1} was used. The hydrogen reduced catalyst exhibited a higher initial conversion of synthesis gas (73.5%), and it reached a steady state conversion at about 40 h on stream. After steady state, the catalyst deactivated slightly with time on stream. After 120 h on stream, the synthesis gas conversion had decreased to 66.7%, giving a deactivation rate of about 0.6% per day. When the space velocity was changed to 3 Nl g_{cat}^{-1} h^{-1}, the synthesis gas conversion decreased, reaching 45.0% at 140 h on stream.

The carbon monoxide reduced catalyst exhibited a very different catalytic performance compared with the hydrogen reduced catalyst. The synthesis gas conversion was lower and it reached a steady state value (32.0%) quickly. After 40 h on stream, the synthesis gas conversion increased slightly and then remained almost constant (34.0%) with time on stream during 250 h. When the space velocity was increased to 3 Nl g_{cat}^{-1} h^{-1}, the synthesis gas conversion decreased to 24.0%, lower than for the hydrogen reduced catalyst.

The rate of hydrocarbon production follows the same trend as the synthesis gas conversion, i.e., the hydrogen reduced catalyst exhibited a higher hydrocarbon production rate than the carbon monoxide reduced catalyst.

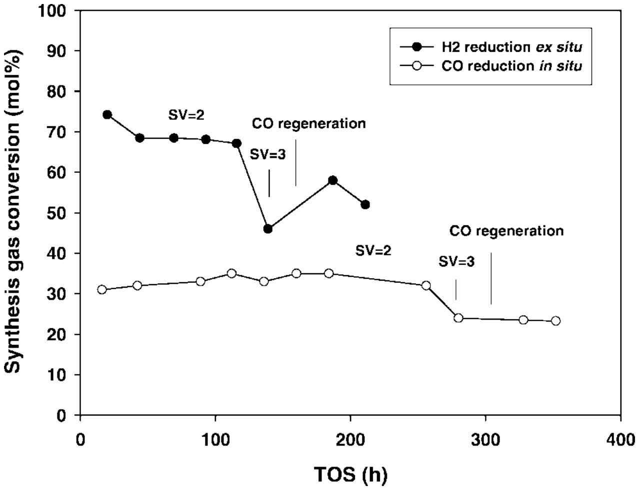

Figure 1. Effect of reduction gas on synthesis gas conversion of RuCo/TiO$_2$ catalyst.

3.2. Catalyst selectivity

Methane selectivities for the catalysts reduced with hydrogen or with carbon monoxide (calculated as $100 \times$(moles of CO converted to CH_4)/(total moles of CO converted − moles of CO converted to CO_2)) as a function of time on stream are shown in figure 2. Methane selectivity slightly changed between 15 and 20% with time on stream on the carbon monoxide reduced catalyst, and the values were higher than for the hydrogen reduced catalyst (5–10%). The higher methane selectivity on the carbon monoxide reduced catalyst may be due to some cobalt carbide phase that was produced by the carbon monoxide reduction. However, the methane selectivity varied with synthesis gas conversion, and even a small change on synthesis gas conversion could influence methane selectivity. From figure 3 it is seen that the same trend can be observed for the catalysts pretreated with hydrogen or with carbon monoxide; i.e., the methane selectivity decreased with increasing conversion for the two catalysts. As shown in figure 3, the H_2/CO ratio of the exit gas remained essentially constant over the CO conversion range where the methane selectivity underwent significant changes. Thus, the different methane selectivity cannot be due to different H_2/CO ratios. The alpha value, obtained from the Anderson–Schulz–Flory plot for the higher carbon number compounds, was essentially the same for the catalyst whether it was pretreated with H_2 or CO. Thus, the methane selectivity is not the result of widely varying FT selectivity.

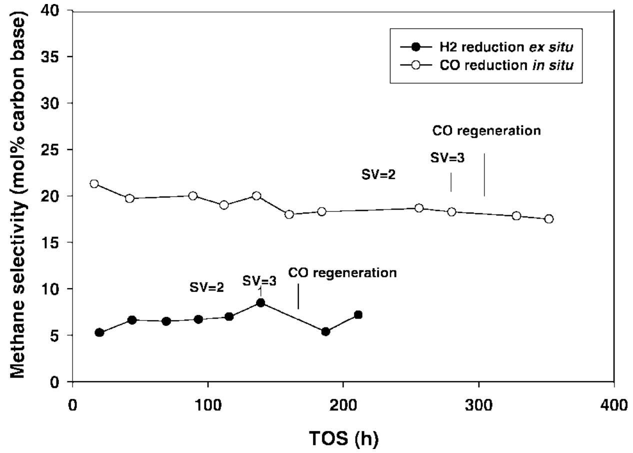

Figure 2. Effect of reduction gas on methane selectivity of RuCo/TiO$_2$ catalyst.

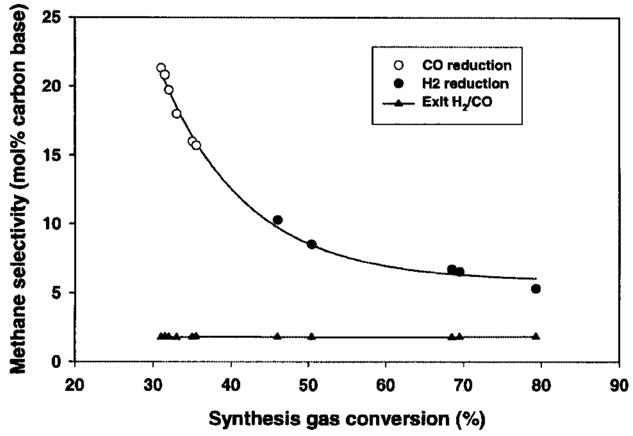

Figure 3. Methane selectivity vs. synthesis gas conversion.

One possible explanation is that a product is poisoning the methanation reaction relative to the FT reaction. Since water partial pressure increases with increasing CO conversion, it appears most likely that water selectively poisons the methane production. If this is the case, the most reasonable explanation is that there is a cobalt site that produces only methane, or low alpha FT products, that is poisoned by water. It does not appear that less methane could be produced as the CO conversion increases in a single conventional pathway that follows Anderson–Schulz–Flory (ASF) kinetics.

Another possibility is that surface cobalt carbide is formed when the catalyst is exposed to only CO. If this is the case, the cobalt carbide sites would produce predominantly methane while the carbide-free cobalt sites would produce typical ASF products. Based on preliminary data produced when adding water to the feed, it appears that the explanation involving surface cobalt carbide is more likely to be valid.

C_{5+} selectivity (expressed as a mass fraction of liquid and wax hydrocarbons in total hydrocarbons) exhibited a trend opposite to the methane selectivity. C_{5+} selectivity on the hydrogen reduced catalyst was between 71.5 and 77.8%, higher than on the carbon monoxide reduced catalyst (57.4–63.2%). However, similar alpha values were obtained for the two pretreatments.

Comparing the two pretreatment methods, the hydrogen pretreatment resulted in a higher Fischer–Tropsch activity, a lower methane selectivity and a higher C_{5+} selectivity.

3.3. CO regeneration effect

In order to investigate the effect of carbon monoxide treatment on the used catalysts, synthesis gas was switched off after 140 h on stream for the hydrogen reduced catalyst (after 280 h on stream for the carbon monoxide reduced catalyst) and only pure carbon monoxide was passed in an attempt to regenerate the catalysts. The regeneration was carried out at reaction temperature of 503 K and a pressure of 1.68 MPa for 24 h. It was found that the carbon monoxide treatment (regeneration) led to an improved catalytic performance in a subsequent FT reaction for the hydrogen reduced catalyst. After regeneration, the synthesis gas conversion increased from 45.0 to 58.0% (at 3 $\mathrm{Nl\,g_{cat}^{-1}\,h^{-1}}$) during the first 24 h and then gradually decreased to 52%. The methane selectivity firstly decreased from 9.8 to 5.6% and then gradually increased. However, the carbon monoxide regeneration did not have significant effect on the carbon monoxide reduced catalyst and the synthesis gas conversion remained essentially constant (at 3 $\mathrm{Nl\,g_{cat}^{-1}\,h^{-1}}$).

The methane selectivity was not influenced by the regeneration (figures 1 and 2).

4. Conclusions

The pretreatment gas (reductant) was found to have a remarkable effect on the performance of a ruthenium promoted cobalt catalyst during Fischer–Tropsch synthesis. The hydrogen reduced catalyst exhibited a higher initial synthesis gas conversion (72.5%) and reached steady state after 40 h on stream. The catalyst deactivated slightly with time on stream. The carbon monoxide catalyst reached steady state quickly, exhibiting lower activity and good stability. Methane selectivity for the carbon monoxide reduced catalyst was 15–20% (carbon basis), higher than that on the hydrogen reduced catalyst (5–10%). However, methane selectivity depends upon CO conversion and this can account for much of the differences in methane selectivity. Carbon monoxide regeneration increased the activity on the hydrogen reduced catalyst; however, it did not have a significant effect on the carbon monoxide reduced catalyst.

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References

[1] K.S. Chung and F.E. Massoth, J. Catal. 64 (1980) 320.
[2] R.L. Chin and D.M. Hercules, J. Phys. Chem. 86 (1982) 360.
[3] K.E. Yoon and S.H. Moon, Appl. Catal. 16 (1985) 289.
[4] S. Ihm, D. Lee and J. Lee, J. Catal. 113 (1988) 544.
[5] L. Fu and C.H. Bartholomew, J. Catal. 92 (1985) 376.
[6] G. Calleja, A. Lucas and R.V. Grieken, Appl. Catal. 68 (1991) 65.
[7] A. Lapidus, A. Krylova and J. Rathousky, Appl. Catal. 73 (1991) 65.
[8] J. Rathousky, A. Krylova and A. Zukal, Appl. Catal. 79 (1991) 167.
[9] A. Lapidus, A. Krylova, J. Rathousky and M. Jancakova, Appl. Catal. 80 (1992) 1.
[10] A.R. Belambe, R. Onkaci and J.D. Goodwin, Jr., J. Catal. 166 (1997) 8.
[11] B. Nay, M.R. Smith and C.D. Telford, US Patent 5 585 316 (1996).
[12] H.H. Storch, N. Golumbic and R.B. Anderson, *The Fischer–Tropsch and Related Syntheses* (Wiley, New York, 1951).
[13] J. Li, L. Xu, R. Keogh and B.H. Davis (1999), submitted.