Research Article

J. Li & N.J. Coville,
S. Afr. J. Chem., 2004, **57**, 49–52,
<http://journals.sabinet.co.za/sajchem/>.

Effect of Calcination and Reduction Temperatures on the Reduction and Activity of Boron-modified Co/TiO_2 Fischer-Tropsch Catalyst

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Received 5 December 2003; revised 25 April 2004; accepted 10 May 2004.

ABSTRACT

The effect of calcination and reduction temperatures on the reducibility, dispersion and Fischer-Tropsch activity of 10 wt% cobalt supported on titania catalyst modified by 0.1 wt% boron has been studied. The percentage reduction and percentage dispersion were found to decrease with increasing calcination temperature. The higher calcination temperatures decreased the total CO hydrogenation activity, but did not affect the turnover frequency. The decrease in CO hydrogenation rate with increasing calcination temperature is attributed to a decrease in the number of surface active sites. The higher reduction temperature also decreased the total activity. This may be due to the loss of the surface active sites, caused by blocking of the TiO_X phases produced at higher reduction temperatures. The higher calcination temperature shifted the F-T product spectrum to the lower weight hydrocarbons. The reduction temperature did not affect the product selectivity.

KEYWORDS

Fischer-Tropsch synthesis, carbon monoxide hydrogenation, syngas conversion, cobalt; titania, fixed-bed reactor.

1. Introduction

Supported cobalt catalysts have been widely employed for Fischer-Tropsch (F-T) synthesis of long-chain hydrocarbons from Syngas.[1] Cobalt has certain advantages over iron or ruthenium as a catalyst, such as longer catalytic life time, less water-gas-shift activity and production of a modified product. As with many supported transition metal catalysts, the structure and catalytic properties of supported cobalt catalysts can be affected by cobalt loading, support, preparation method and pretreatment conditions. Numerous studies have focused on the pretreatment effects on the supported cobalt catalysts.[2–10] Calleja *et al.*[7] investigated the pretreatment effects on the Fischer-Tropsch 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.*,[9] however, revealed that the pretreatment conditions had a significant effect on the catalytic properties of Co/Al_2O_3 and Co/SiO_2 catalysts. Turnover frequency (TOF) for the F-T 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.[8–10] Belambe *et al.*[11] studied the pretreatment effects on the activity of a Ru-promoted Co/Al_2O_3 catalyst for F-T reaction. The calcination temperature was found to have a pronounced effect on the overall activity of the catalyst, but not on TOF. The reduction temperature had only a negligible effect on the overall activity and TOF.

The pretreatment effects on cobalt supported on titania have not previously been reported in the literature. A previous investigation into the effect of boron on Co/TiO_2 catalysts indicated that boron decreases the reducibility of a Co/TiO_2 catalyst.[12] In parallel, the total CO hydrogenation rate was decreased by the addition of boron. The TOF, however, was not affected by boron. In this study, the pretreatment effects on the catalytic properties of the boron-modified Co/TiO_2 catalyst were investigated. TPR, H_2 chemisorption and O_2 titration have also been used to check the pretreatment effects on the reducibility and dispersion of the catalyst.

2. Experimental

2.1. Catalyst Preparation and Pretreatment

From a previous investigation, we found that the 10 wt% cobalt supported on titania modified by 0.1 wt% boron catalyst had good activity for the F-T reaction.[12] This catalyst also showed good resistance to sulphur poisoning.[13] This catalyst was thus used in this study. The titania modified by 0.1 wt% boron was prepared by pore volume impregnation of titania (Degussa P25, BET surface area: 50 $m^2 g^{-1}$; pore volume: 0.51 $mL g^{-1}$) with a boric acid solution. The sample was dried at 120°C for 16 h then calcined at 400°C for 6 h. Cobalt (10 wt%) was deposited on the boron-modified titania by pore volume impregnation with cobalt nitrate solution. The sample was redried at 120°C for 16 h before calcination. The catalyst was calcined at different temperatures (200–400°C) using flowing air (GHSV = 2000 h^{-1}) for 16 h. After calcination, the catalyst was cooled to room temperature and stored in a dry atmosphere. Before carrying out the F-T reaction, the catalysts were reduced for 16 h at various temperatures (200–450°C) under flowing hydrogen (GHSV = 2000 h^{-1}).

2.2. Characterization Techniques

Temperature Programmed Reduction (TPR), H_2 chemisorption and O_2 titration were used to characterize the catalysts. The methods used have previously been described.[12,13]

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2.3. Reactor Study

The catalysts, calcined and reduced at various temperatures, were tested for their activity and selectivity in the Fischer-Tropsch reaction in a fixed-bed flow reactor. The procedure has been described elsewhere[12,13] The catalyst amount (~2 g) used for various experiments was kept constant. The Fischer-Tropsch reaction was carried out at a pressure of 8 bar, a temperature of 250°C, GHSV of 350 h^{-1} and a CO/H_2 ratio of 1:2 for more than 400 h. Mass balances were carried out after the catalysts were on-line for >80 h. An on-line GC and two off-line GCs were used to analyse the composition of the product spectrum.

3. Results and Discussion

3.1. Effect of Pretreatment on the Extent of Reduction and Dispersion of $Co/B/TiO_2$

The TPR spectra of the catalysts calcined at various temperatures are shown in Fig. 1, and three reduction peaks can be observed for the catalyst calcined at 200°C. The first peak, ranging from 180–200°C, was attributed to the reduction of the NO_X group from $Co(NO_3)_2$. This peak became smaller when the catalyst was calcined at 300°C and it disappeared after calcination at 400°C due to the complete decomposition of nitrate. [9] Two peaks between 250–550°C were assigned to the reduction of Co_3O_4 supported on titania. The reduction of Co_3O_4 supported on titania proceeded in two stages,[14] namely a primary reduction of Co_3O_4 to CoO and a subsequent reduction of CoO to Co metal. It is apparent that the Co_3O_4 reduction peaks shift to higher temperature and the area of the reduction peaks decrease with increasing calcination temperature, suggesting that calcination decreases the reducibility of the catalyst.

The effects of pretreatment conditions on the percentage dispersion and percentage reduction of the catalysts were measured by H_2 chemisorption and O_2 titration. The results are shown in Tables 1 and 2. With the exception of the dried catalyst, the percentage dispersion and percentage reduction of catalysts were found to decrease with increasing calcination temperature. As the reduction temperature was increased, the percentage reduction also increased up to 300°C, after which there was little further effect.

The percentage dispersion increased initially and then decreased on increasing the reduction temperature. The maximum dispersion occurred for the catalyst reduced at 300°C.

The TPR and O_2 titration results revealed that the reducibility of the catalyst decreased with increasing calcination temperature. This may be due to (i) the smaller Co_3O_4 crystallite size (from XRD results, not shown) or (ii) the formation of surface cobalt compounds through metal-support interactions at higher calcination temperature.[2] Ho *et al.*[15] found a surface $CoTiO_3$-like phase in Co/TiO_2 catalysts, in addition to the Co_3O_4 phase, after calcination at 400°C. The amount of surface compound was dependent on the cobalt loading and calcination temperature. Surface compound formation has been reported by others for non-promoted Co/SiO_2, Co/Al_2O_3[2,3] and Ru-promoted Co/Al_2O_3 catalysts.[11] Our results revealed that the extent of reduction of the catalyst was not changed at the lower reduction temperatures (from 250 to 350°C) but that the higher reduction temperatures (400, 450°C) increased the extent of the reduction of the catalyst. This may be because the higher temperature causes the partial reduction of the titania support, resulting in a increase in the total reduction content, which was measured by total O_2 consumption.[15]

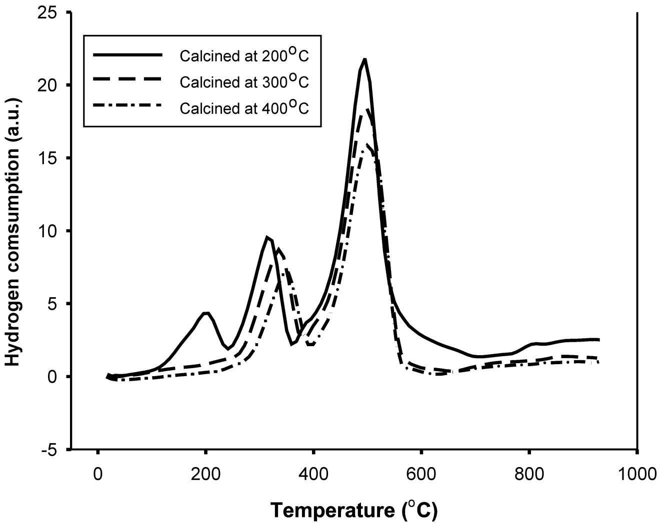

Figure 1 TPR profiles of $Co/B/TiO_2$ catalysts calcined at various temperatures.

The results shown in Table 1 reveal that the dispersion of the catalyst decreases with increasing calcination temperature. Hydrogen chemisorption has been reported to be suppressed for the catalysts which are poorly reduced.[4–6] Ho *et al.*[16] observed a decrease in chemisorption values with increasing calcination temperature for a Co/SiO_2 catalyst. Belambe *et al.*[11] also found the same effect for a Ru-promoted Co/Al_2O_3 catalyst. The results indicate that the higher reduction temperature gives a catalyst with a lower dispersion of catalyst, probably due to the strong metal-support interaction (SMSI). TiO_2 is a typical SMSI support. The higher temperatures can reduce TiO_2 to TiO_X which blocks the surface metal cobalt sites and can cause loss of dispersion.[17]

Table 1 Percentage dispersion and percentage reduction as a function of calcination temperature. [a]

Tc (°C)	Total H_2 uptake [b] (mL H_2 g^{-1} cat.)	Dispersion [b] (%)	Reduction [c] (%)
Uncalcined	0.11	0.9	40.5
200	0.36	1.95	51
300	0.32	1.71	42.5
350	0.31	1.69	40.9
400	0.25	1.42	37.6

[a] Catalysts were reduced at 300°C for 16 h after calcination.
[b] Obtained from H_2 chemisorption.
[c] Obtained from O_2 titration.

Table 2 Percentage dispersion and percentage reduction as a function of reduction temperature [a]

Tr (°C)	Total H_2 uptake [b] (mL H_2 g^{-1} cat.)	Dispersion [b] (%)	Reduction [c] (%)
250	0.28	1.5	35
300	0.32	1.71	42.5
350	0.31	1.65	40.9
400	0.26	1.41	43.3
450	0.23	1.2	45.6

[a] Catalysts were calcined at 300°C for 6 h before reduction.
[b] Obtained from H_2 chemisorption.
[c] Obtained from O_2 titration.

Table 3 Effect of calcination temperature on the Fischer-Tropsch synthesis.

Tc (°C)	Uncalcined	200	300	350	400
CO conversion (mol%)					
Intial [a]	32	65	58	54	47
Steady state [b]	28.5	49	43	39	35
Reaction rate (S-S) (μmole g^{-1} cat. s^{-1})	0.46	0.79	0.69	0.63	0.58
TOF (10^3 s^{-1}) [c]	24.5	25.9	24.2	24.9	26
Selectivity (%, by mass)					
C_1	15.6	11.2	11.5	13.2	19
C_2-C_4	14.2	12.7	9.4	11.5	15
C_5-C_{11}	48.7	47.6	52.3	49	46
C_{12}-C_{18}	16.3	17.5	19	18.5	15.5
C_{18+}	5.4	10.5	8.8	7.3	4.5
CO_2 selectivity (%, by mass)	0	0	0	0.8	1.5
α value	0.69	0.8	0.79	0.75	0.54

[a] Reduction temperature: 300°C; reaction conditions: T = 250°C, P = 8 bar, H_2/CO = 2:1, measured after about 30 min of reaction.
[b] Measured after 80 h of reaction.
[c] Based on total H_2 chemisorption.

Table 4 Effect of reduction temperature on the Fischer-Tropsch synthesis.

Tr (°C)	250	300	350	400	450
CO conversion (mol%) [a]					
Initial	53	58	57.2	40	35
Steady state	39	43	42.5	33	29
Reaction rate (S-S) (μmole g^{-1} cat. s^{-1})	0.65	0.69	0.68	0.57	0.47
TOF (10^3 s^{-1})	26	24.2	24.6	25.6	24.5
Selectivity (%, by mass)					
C_1	12	11.5	13	14.9	12
C_2–C_4	8.9	9.4	11	10.6	10.4
C_5–C_{11}	49	52.3	53	50	51
C_{12}–C_{18}	21	18.5	16	17	17.9
C_{18+}	9	8.8	7	6.9	8.6
α value	0.73	0.79	0.75	0.69	0.76

[a] Calcination temperature: 300°C; reaction conditions: T = 250°C, P = 8 bar, H_2/CO = 2:1.

3.2. Effect of Pretreatment on the Fischer-Tropsch Reaction of Co/B/TiO_2 Catalysts

The effect of calcination on the catalytic properties of the catalyst is shown in Table 3. The initial CO conversions were measured after about 30 min of reaction, while the steady-state CO conversions and the CO hydrogenation rates were measured after 80 h of reaction when the CO conversions are constant. The steady-state CO conversions decreased by about 25% from the initial conversions for all the calcination temperatures studied. Increasing calcination temperature was found to cause a linear decrease of both the steady-state CO conversion and total reaction rate for the F-T reaction. When the calcination temperature was increased from 200°C to 400°C, the reaction rate decreased by 30%. The product selectivity and α value were not affected by the lower temperature calcination. The higher temperature calcination shifted the product spectrum to the lower weight hydrocarbons. CO_2 was also found to be produced at the higher calcination temperatures. Turnover Frequency (TOF) was constant and independent of the calcination temperature. Table 4 shows the F-T reaction results obtained with the catalyst calcined at 300°C, but reduced at various temperatures. At this calcination temperature, the reduction temperatures have a significant effect on the F-T reaction rate. When the reduction temperature was increased up to 350°C, the total reaction rate almost remained constant. Further increase in the reduction temperature (400 and 450°C) resulted in a clear decrease in CO conversion. The reduction temperature, however, did not have an effect on the TOF and product selectivity.

The data in Table 3 show that the total CO hydrogenation rate decreases, and the TOF is almost constant with increasing calcination temperature. This suggests that the decrease in total rate is the result of a decrease in the number of cobalt active sites due to the lower reducibility of the catalyst at the higher calcination temperature. This is consistent with the results obtained by other researchers for SiO_2, and Al_2O_3-supported cobalt catalysts. Ho *et al.*[16] studied the effect of calcination temperature on the surface characteristics and CO hydrogenation activity of a Co/SiO_2 catalyst. They did not observe any change in TOF with calcination temperature. Belambe *et al.*[11] studied the effect of pretreatment on the activity of Ru-promoted Co/Al_2O_3 F-T catalyst. Their results indicated that the F-T activity decreased with increasing calcination temperature. TOF was constant and was independent of the calcination temperature and the extent of reduction of catalyst. By contrast, the results obtained by Rathousky *et al.*[9] exhibited an increase in total CO hydrogenation activity for a Co/Al_2O_3 catalyst at higher calcination temperatures. They indicated that cobalt-aluminium oxides formed due to a high calcination temperature, which favoured the increased yield of hydrocarbons.

Selectivity data and α-value data revealed that the higher calcination temperature favoured the lower weight hydrocarbons. Poorly-reduced catalysts contain a large fraction of stable surface oxide phases which are highly inactive for CO hydrogenation, but active for water-gas-shift reaction.[18] A higher H_2/CO ratio at the surface caused by the WGS reaction would promote the formation of lower weight hydrocarbons. The reduction temperature did not have a significant effect on the selectivity of the catalyst. This suggests that there is no change in the chemical properties of the active cobalt sites.[11] Calleja *et al.*[7] (for Co/HZSM-5 catalyst) and Fu and Bartholomew[6] (for Co/Al_2O_3 catalyst) obtained similar results.

4. Conclusions

Pretreatment conditions were found to have a significant effect on the reducibility and activity of 10 wt% cobalt supported on titania catalysts modified by 0.1 wt% boron. The percentage reduction and percentage dispersion decreased with increasing calcination temperature. The higher calcination temperatures decreased the total CO hydrogenation activity, but did not affect the turnover frequency. The decrease in CO hydrogenation rate with increasing calcination temperature is attributed to a decrease in the number of surface-active sites. The higher reduction temperature also decreased the total activity. This is the result of the loss of dispersion due to the TiO_X blocking the surface-active sites at the higher reduction temperatures. The higher calcination temperature shifted the product spectrum to the lower weight hydrocarbons; however, the reduction temperature did not affect the product selectivity.

Acknowledgements

This work was supported by Sasol and the South African National Research Foundation. J. Li gratefully acknowledges the financial support from National Natural Science Foundation of China (20373090) and Talented Young Scientist Foundation of Hubei (2003ABB013).

References

1 R.B. Anderson, *Fischer-Tropsch Synthesis,* Academic Press, New York, 1984.
2 K.S. Chung and F.E. Massoth, *J. Catal.,* (1980), **64**, 320.
3 R.L. Chin and D.M. Hercules, *J. Phys. Chem.,* 1982, **86**, 360.
4 K.E. Yoon and S.H. Moon, *Appl. Catal.,* 1985, **16**, 289.
5 S. Ihm, D. Lee and J. Lee, *J. Catal.,* 1988, **113**, 544.
6 L. Fu and C.H. Bartholomew, *J. Catal.,* 1985, **92**, 376.
7 G. Calleja, A. Lucas and R.V. Grieken, *Appl. Catal., A,*1991, **68**, 65.
8 A. Lapidus, A. Krylova and J. Rathousky, *Appl. Catal., A,* 1991, **73**, 65.
9 J. Rathousky, A. Krylova and A. Zukal, *Appl. Catal.,* 1991, **79**, 167.
10 A. Lapidus, A. Krylova, J. Rathousky and M. Jancakova, *Appl. Catal., A,* 1992, **80**, 1.
11 A.R. Belambe, R. Onkaci and J.D. Goodwin, *J. Catal.,* 1997, **166**, 8.
12 J. Li and N.J. Coville, *Appl. Catal.,* A, 1999, **181**, 201.
13 J. Li and N.J. Coville, *Appl. Catal.,* A, 2001, **208**, 177.
14 J.H. Martens and H.F.J. Van't Blik, *J. Catal.,* 1986, **97**, 200.
15 S.W. Ho, J.M. Cruz, M. Houalla and D.M. Hercules, *J. Catal.,* 1992, **135**, 173.
16 S.W. Ho, M. Houalla and D.M. Hercules, *J. Phys. Chem.,* 1990, **94**, 6396.
17 J. van de Loosdrecht, A.M. van der Kraan and A.J. van Dillen, *Catal. Lett.,* 1996, **41**, 27.
18 R.C. Reuel and C.H. Bartholomew, *J. Catal.,* 1984, **85**, 78.