Effect of Cobalt Source on the Catalyst Reducibility and Activity of Boron-modified Co/TiO$_2$ Fischer-Tropsch Catalysts

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ABSTRACT

The effect of cobalt precursor (nitrate, acetate and chloride salts) on the catalyst reducibility and dispersion, as well as the catalytic activity of the Fischer-Tropsch (FT) synthesis, of boron-modified titania-supported cobalt catalysts (0.1%B/10%Co/TiO$_2$) has been investigated. FT studies were performed on both calcined and uncalcined catalysts prepared from the three cobalt sources. The uncalcined nitrate catalyst showed a higher activity for FT synthesis compared to the uncalcined acetate and chloride catalysts. For the calcined catalysts, the acetate and nitrate catalysts exhibited higher FT activity. The low activity associated with the chloride catalyst related to poisoning by residual chloride ions. Calcination was found to enhance the extent of cobalt bulk reduction and FT activity for all three of the catalysts. The FT reaction rate increased with increasing percentage cobalt dispersion while the turnover frequency (TOF) was found be near independent of cobalt source.

KEYWORDS
Cobalt, boron, titania, Fischer-Tropsch synthesis.

1. Introduction

Supported cobalt catalysts are important in Fischer-Tropsch (FT) synthesis of high molecular weight parafinic waxes that can be hydrocracked to produce lubricants and diesel fuels. Although the effect of variation in support material has been previously explored for cobalt catalysts,[1–4] comparatively little systematic information has been reported on the corresponding influence of a cobalt *source* on the reducibility, dispersion and resulting catalytic behaviour of these materials.

Previous studies of other transition metal catalyst systems have demonstrated that the identity of the metal precursor employed in the catalyst preparation can have a significant effect on the catalyst structure and eventual catalytic behaviour of the reduced metal. Worley and coworkers[5,6] investigated the effect of Rh precursor materials on alumina-supported catalysts and found that the catalysts prepared by using Rh(NO$_3$)$_3$ were more easily reduced to metallic Rh^0 than samples prepared using RhCl$_3$. In the latter case, following reduction in hydrogen at 673 K, residual Cl$^-$ remained on the surface and stabilized a Rh^{1+} species. A study of supported nickel catalysts by Chauvin *et al.*[7] revealed that NiSO$_4$- and NiCl$_2$-derived materials on an alumina support had higher activities for alkene oligomerization than a catalyst prepared from Ni(NO$_3$)$_2$.

Recent studies have also described the effect of a cobalt precursor on FT catalysts. Van de Loosdrecht *et al.*[8] investigated the effect of cobalt precursors on the metal particle size, reduction and Fischer-Tropsch activity of an alumina-supported cobalt catalyst. It was shown that low-loaded cobalt catalysts (<2.5 wt%), prepared from cobalt EDTA and ammonium cobalt citrate precursors, produced very small cobalt oxide particles. The small oxide particles reacted easily with alumina to produce cobalt aluminate, which is neither an active nor a selective

catalyst for Fischer-Tropsch synthesis. However, high-loaded cobalt catalysts (>5.0 wt%) prepared using ammonium cobalt citrate exhibited a larger particle size, higher reducibility and a reasonable catalytic activity. Kraum and Baerns[9] found that titania-supported cobalt catalysts prepared by using oxalate, acetate and acetyl acetonate as cobalt precursor had higher Fischer-Tropsch activity compared to a catalyst prepared from cobalt nitrate. A silica-supported cobalt catalyst prepared by mixed impregnation of nitrate and acetate salts was found to have a higher activity than catalysts prepared separately from either mono-precursor.[10] The higher FT activities were suggested to arise from the increased metal cobalt dispersion.

Other cobalt complexes have also been used as precursors for the preparation of cobalt FT catalysts. Barbier *et al.*[11] found that a Co/SiO$_2$ catalyst prepared from Co$_2$(CO)$_8$ displayed both small cobalt clusters (~1 nm) together with big cobalt clusters (~4 nm) and these clusters produced either hydrocarbons (on big clusters) or alcohols (on small clusters) in the FT synthesis. Backman *et al.*[12] used Co(acac)$_3$ as a precursor to prepare Co/SiO$_2$ catalysts by gas phase deposition and found that the FT activity increased with increasing cobalt loading but that the turnover frequency (TOF) remained constant for all samples. Air calcination (450°C) of the Co/SiO$_2$ resulted in the preparation of difficult to reduce catalysts due to the formation of cobalt silicate.

In previous studies,[13,14] we found that boron-modified titania-supported cobalt catalysts showed moderate sulphur resistance during FT synthesis. Subsequent studies also revealed the effect of boron source on the physical properties and FT catalytic behaviour of a range of Co/B/TiO$_2$ catalysts.[15] In this study, we investigated the effect of cobalt precursors (nitrate, chloride and acetate salts) on titania-supported cobalt catalysts (boron-modified or boron-free). Comparative catalytic activities of these materials in FT synthesis were made.

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2. Experimental

2.1. Catalyst Preparation and Characterization

The 0.1 wt% boron-modified titania material 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) with a boric acid (H_3BO_3 in H_2O) solution. The sample was dried at 393 K for 16 h and then calcined in air at 673 K for 6 h. Cobalt (10 wt%) from different cobalt sources was deposited on the boron-modified (or boron-free) titania with cobalt salt solutions. Three different cobalt(II) salts were used to make the catalysts, *viz.* cobalt nitrate $Co(NO_3)_2.6H_2O$, cobalt chloride $CoCl_2.6H_2O$ and cobalt acetate $Co(CH_3COO)_2.4H_2O$. All were of analytical reagent grade (99% minimum purity) and purchased from SAARCHEM Chemical (Pty) Ltd. The cobalt acetate catalyst precursor was prepared by wet impregnation. The wet mixture was dried while being vigorously stirred. This procedure was necessary because of the low solubility of cobalt acetate. The other two salts were added by pore volume impregnation. All the catalysts were dried after impregnation at 393 K for 16 h. The catalysts prepared from cobalt nitrate, cobalt chloride and cobalt acetate are represented as $Co/B/TiO_2(N)$, $Co/B/TiO_2(C)$ and $Co/B/TiO_2(A)$, respectively.

The catalysts were characterized by BET, TPR , H_2 chemisorption and oxygen titration. BET measurements of the calcined catalysts were conducted using a Micromeritics ASAP 2010 system. Prior to the measurement, samples were slowly ramped to 433 K and evacuated for 4 h to approximately 50 mTorr.

Temperature programmed reduction (TPR) profiles of catalysts were recorded using equipment constructed in our laboratory.[13] Samples were first purged in flowing inert gas to remove traces of water. TPR studies were performed using a 5% H_2/Ar mixture referenced to Ar at a flow rate of 30 cm^3 min^{-1}. The sample was heated from 323 K to 1073 K using a heating ramp of 10 K min^{-1}.

The H_2 chemisorption and reducibility by re-oxidation were measured using the ASAP 2010 system, which incorporates a thermal conductivity detector (TCD). The sample weight was always 0.100 g. The catalyst was reduced (hydrogen at 573 K for 10 h) and cooled under flowing hydrogen to 373 K. The sample was held at 373 K under flowing argon to prevent adsorption of physisorbed and weakly bound species, before increasing the temperature slowly to the reduction temperature. At the required temperature, the catalyst was held under flowing argon to desorb the remaining chemisorbed hydrogen until the TCD signal returned to the baseline. The TPD spectrum was integrated and the number of moles of desorbed hydrogen determined by comparison with the area of calibration pulses of hydrogen in argon. Prior to the experiment, the sample loop was calibrated with pulses of N_2 in a helium flow and compared against a calibration line produced from using gas-tight syringe injection of N_2 into a helium flow. The volume of the loop was found to be 52 μL. After H_2 TPD measurements, the sample was reoxidized at the activation temperature by pulses of pure O_2 in helium carrier referenced to helium gas. The oxidation of the cobalt metal was then performed (where the entire O_2 pulse was observed by TCD), and the number of moles of O_2 consumed was determined, and the percentage reducibility was calculated assuming that Co^0 oxidized to Co_3O_4.

2.2. Reactor System and Procedure

FT reaction was performed in a fixed bed reactor on each of the three catalysts. The reactor system has been described previously.[13] The sample (about 2 g) was loaded and calcined at 573 K for 24 h at 2000 h^{-1} in flowing air, followed by reduction in pure hydrogen at 573 K for 24 h at 2000 h^{-1} before FT synthesis. The FT reaction was carried out at a pressure of 8 bar, a temperature of 523 K, a GHSV of 350 h^{-1} (of CO) and a CO/H_2 1:2 ratio. The H_2, CO and product composition were analysed by on-line and off-line GC.

3. Results and Discussion

3.1. Characterization of Oxidic Catalysts

The BET surface areas of the calcined catalysts, prepared by using cobalt nitrate, cobalt chloride and cobalt acetate are shown in Table 1. The cobalt chloride precursor on TiO_2 had the lowest BET surface area. This may be due to the formation of large cobalt oxide clusters produced on the support after calcination.

In order to obtain information about the effect of calcination on the bulk composition of the three catalysts, X-ray diffraction (XRD) patterns were measured for each calcined catalyst and the line width of the peak occurring at $2\theta = 36.9°$, due to the (311) reflection of Co_3O_4, was used to calculate the Co_3O_4 cluster size, using the Scherrer equation.[16] The cluster size of Co_3O_4 is about 31 nm for $Co/B/TiO_2(C)$ and 19 nm for $Co/B/TiO_2(N)$. The XRD peaks characteristic of Co_3O_4 for calcined $Co/B/TiO_2(A)$ were difficult to detect, indicating that poorly crystalline Co_3O_4 is present and that cobalt oxide is well dispersed on the surface of support.

Reduction of the Catalysts

The TPR profiles of *calcined* $Co/B/TiO_2$ catalysts are shown in Fig. 1. In order to ascertain the effect of boron on the reduction step, the TPR profiles of catalysts without boron were also recorded and are included in Fig. 1. The TPR profile of calcined $Co/TiO_2(C)$ without boron had only one broad peak with a maximum at 486°C, that was attributed to the reduction of Co_3O_4 clusters.[8] The TPR profile of the calcined boron complex $Co/B/TiO_2(C)$ was quite different to that of the TPR spectrum of the catalyst without boron (Fig. 1b). Two peaks were observed for the catalyst, which are due to the reduction of both Co_3O_4 and

Table 1 Percentage dispersion and percentage reduction of catalysts [a].

Catalyst	Cobalt salt	Tc [b] (K)	BET (m^2 g^{-1})	H$_2$ uptake (cm^3 gcat^{-1})	Dispersion (%)	Reduction (%)
Co/B/TiO$_2$(N)	Co(NO$_3$)$_2$	Uncalcined		0.22	1.17	27.0
Co/B/TiO$_2$(C)	CoCl$_2$	Uncalcined		0.04	0.21	40.2
Co/B/TiO$_2$(A)	Co(CH$_3$COO)$_2$	Uncalcined		0.13	0.71	39.0
Co/B/TiO$_2$(N)	Co(NO$_3$)$_2$	573	41.8	0.32	1.71	42.5
Co/B/TiO$_2$(C)	CoCl$_2$	573	34.6	0.15	0.80	61.0
Co/B/TiO$_2$(A)	Co(CH$_3$COO)$_2$	573	43.5	0.42	2.23	58.0

[a] Reduced at 573 K for 16 h.
[b] Calcination temperature.
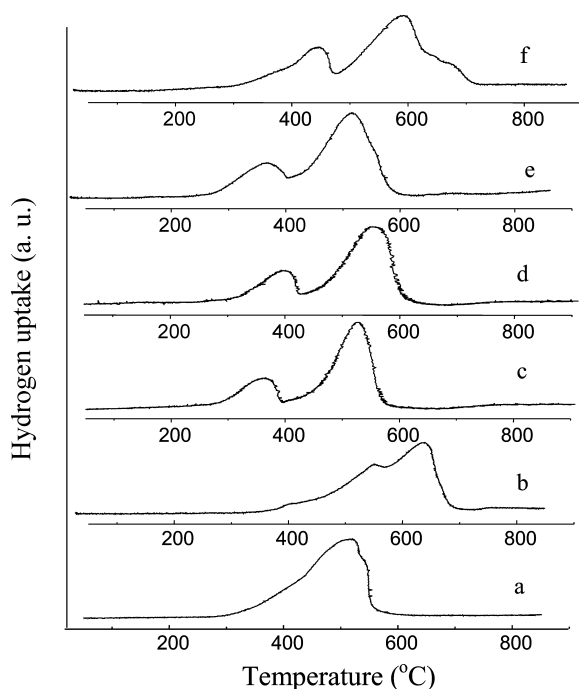
Figure 1 TPR profiles of calcined Co catalysts with and without boron [**a**, Co/TiO$_2$(C); **b**, Co/B/TiO$_2$(C); **c**, Co/TiO$_2$(N); **d**, Co/B/TiO$_2$(N); **e**, Co/TiO$_2$(A); **f**, Co/B/TiO$_2$(A)].

CoO. The shift of the peaks to higher reduction temperature indicated that the boron had made the reduction process more difficult.[13]

Two reduction peaks are observed in the TPR profiles for both calcined Co/TiO$_2$(N) and Co/B/TiO$_2$(N) (Fig. 1c,d). These peaks are attributed to the two-step reduction of Co$_3$O$_4$ supported on titania.[17] It is to be noted that boron, as expected, shifted the reduction peaks to higher temperatures.

The TPR profiles for the calcined acetate catalysts with or without boron were similar to those of the calcined nitrate catalysts (Fig. 1e,f). The peaks for the acetate salt catalysts, however, were broader than those of the nitrate salt-prepared catalysts. This indicates that cobalt oxide, prepared from cobalt

acetate is present as small clusters (range of sizes) that are well dispersed on the support.[8] Compared to the boron-free catalyst, the catalyst with boron had a higher reduction temperature and a broader reduction peak.

The extent of cobalt oxide reduction to cobalt metal was determined at 573 K using oxygen titration, assuming the formation of Co$_3$O$_4$ from Co during the oxidation.[18] Metal dispersions were determined at 373 K using hydrogen chemisorption after the catalysts were reduced in flowing hydrogen for 16 h at 573 K. Table 1 shows the percentage reduction and the percentage dispersion of the uncalcined and calcined catalysts. The percentage reductions of *uncalcined* Co/B/TiO$_2$(C) and Co/B/TiO$_2$(A) to metallic cobalt were 40.2% and 39.0%, respectively. These values are higher than found for the uncalcined Co/B/TiO$_2$(N) (27%).

For all three of the catalysts, calcination at 573 K prior to hydrogen treatment resulted in an increase in the extent of reduction relative to the uncalcined samples. The calcined Co/B/TiO$_2$(C) showed higher reducibility compared to the nitrate and acetate catalysts. This is presumably related to the larger Co$_3$O$_4$ cluster size in the calcined chloride catalyst (see XRD results). Previous studies have revealed that the cobalt oxide with larger cluster size is more easily reduced relative to small cobalt oxide clusters.[19] The percentage dispersion found for *uncalcined* Co/B/TiO$_2$(N) (1.17), was much larger than that found for uncalcined Co/B/TiO$_2$(A) (0.71) and Co/B/TiO$_2$(C) (0.21). The dispersion of these catalysts was increased by calcination. The increase was most pronounced for Co/B/TiO$_2$(A) (from 0.71% to 2.23%). The Co/B/TiO$_2$(C) had the higher reducibility and associated lower percentage dispersion. This must be due to the interaction of Co with residual chloride ions that are difficult to remove by calcination.

From the above we can conclude that the cobalt precursors significantly affect the Co$_3$O$_4$ cluster size produced on TiO$_2$, resulting in different catalyst reducibility. Further, the chloride ions have a deleterious effect on the cobalt metal dispersion.

3.2. Fischer-Tropsch Synthesis

The comparative catalytic behaviour in the FT reaction of the three catalysts was evaluated. Table 2 shows the catalytic

Table 2 Effect of cobalt source on Fischer-Tropsch synthesis of Co(10)/B(0.1)/TiO$_2$ catalysts[a].

Cobalt salt	Nitrate	Chloride	Acetate	Nitrate	Chloride	Acetate
Tc (K)[b]	–	–	–	573	573	573
CO conversion (%):						
Initial[c]	32.0	4.5	25.0	58.0	21.0	75.0
Steady-state[d]	28.5	3.9	20.0	43.0	18.6	62.0
Dispersion (%)	1.17	0.21	0.71	1.71	0.80	2.23
TOF (10^3 s^{-1})	23.1	20.3	27.5	26.3	22.5	28.6
Reaction rate[e]:						
(μmol CO gcat^{-1} s^{-1})	0.47	0.07	0.34	0.75	0.3	1.1
Selectivity (%, by mass):						
C$_1$	21.5	14.0	17.6	11.5	10.1	12.0
C$_2$–C$_4$	10.2	17.1	8.5	9.4	18.0	9.0
C$_5$–C$_{11}$	48.7	39.5	51.0	52.3	40.0	53.0
C$_{12}$–C$_{18}$	16.3	23.6	18.0	18.5	26.5	21.0
C$_{18+}$	3.5	5.8	5.0	8.8	5.7	5.1

[a] Reaction conditions: calcination: uncalcined or 573 K, 1 atm., 2000 h^{-1}, 24 h, flowing air; reduction: 573 K, 1 atm., 2000 h^{-1}, 24 h, 100% hydrogen; synthesis: 523 K, 8 bar, 350 h^{-1}, 2H$_2$:1CO.
[b] Calcination temperature.
[c] CO conversion was recorded after 30 min of reaction.
[d] CO conversion was recorded after 100 h of reaction.
[e] Steady-state reaction rate.

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activities and selectivities of both uncalcined and calcined catalysts for the Fischer-Tropsch synthesis.

The catalyst activity was significantly influenced by the cobalt salt precursors. The steady-state CO conversion and reaction rate of uncalcined Co/B/TiO$_2$(N) was higher than that obtained for uncalcined Co/B/TiO$_2$(A) and both values were higher than that obtained for uncalcined Co/B/TiO$_2$(C). There appears to be no direct relationship between catalytic activity and the extent of cobalt reduction among the various *uncalcined* catalysts. Calcination enhanced the activity of each of the three catalysts, since the catalyst reducibility was increased after calcination. The chloride-based catalyst, although it showed the highest reducibility, had a low activity. Bartholomew[20] pointed out that chloride is a severe poison for methane and FT synthesis because chloride ions are not all removed by calcination. The chloride ions could thus interact with a large fraction of the reduced cobalt sites and reduce their FT activity. The removal of adsorbed chloride from the supported catalysts is expected to occur relatively slowly, if at all, under the reaction conditions employed. Since the temperature used for FTS (523 K) was lower than the calcination temperature (573 K) employed, chloride ions should be present on the catalyst during FT reaction. Indeed, atomic absorption spectroscopy (AAS) data (not shown) revealed that all the chloride ions were not removed after the catalyst was calcined, even at 573 K for 16 h.

Table 2 lists the percentage dispersion, reaction rate and turnover frequency (TOF) data. It is clear that the reaction rate correlated with increasing percentage dispersion (see Fig. 2). However, the TOF remained almost constant and did not depend on the percentage dispersion for any of the uncalcined and calcined catalysts. The results are consistent with earlier literature reports.[9–11] Although the chloride-based catalyst showed a low reaction rate, the TOF of this catalyst was *similar* to that of the nitrate and acetate catalysts. It is to be noted that the chloride generated catalysts have a slightly smaller TOF for *both* the calcined and uncalcined catalysts. For all the catalysts (uncalcined and calcined), the activity increased with increasing Co dispersion.

The selectivities of the six catalysts are also presented in Table 2. Since the CO conversions were quite different for the different catalysts little can be said about the selectivity data. It has been reported that the presence of chloride ions can increase the selectivity towards higher molecular weight hydrocarbons.[20] Hagiwara *et al.*[21] found that during the hydrogenation of CO to
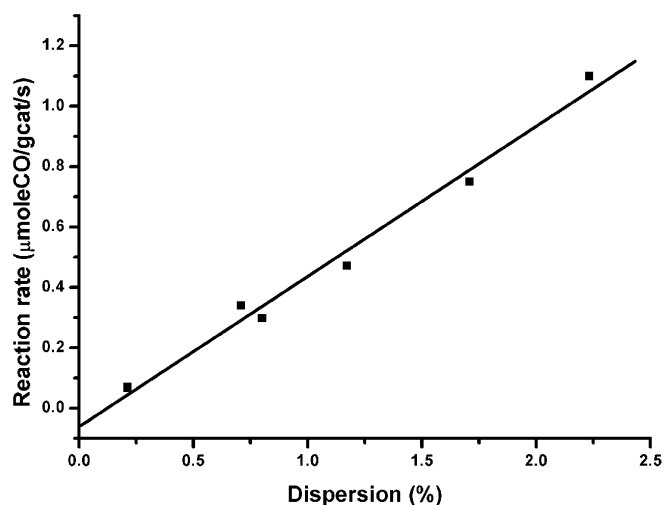
light olefins over a chloride-containing magnetite catalyst in a slurry phase reactor, the selectivity to C$_2$-C$_4$ olefins was increased to 48%, while that for CH$_4$ was decreased to 11%.

To date, no reasonable explanation has been given for the results.

Surprisingly the three calcined catalysts studied here exhibited similar selectivity values. However, the results show that the selectivity of cobalt-based FT catalyst is strongly influenced by calcination

4. Conclusion

The catalyst reducibility, dispersion and catalytic activity for the Fischer-Tropsch synthesis of boron-modified titania-supported cobalt catalysts were significantly influenced by both the identity of the cobalt salts used in the catalyst preparation and by calcination. As detected by TPR studies, the reduction of nitrate and acetate catalysts took place in two steps, while the reduction of the supported chloride salt catalyst occurs in a single step. Calcination enhanced the extent of cobalt dispersion and bulk reduction for all three of the catalysts. The reduced uncalcined nitrate catalyst showed a higher activity for Fischer-Tropsch synthesis compared to the corresponding acetate and chloride catalysts. The FT reaction rate increased with increasing percentage cobalt dispersion. The TOF remained relatively constant and is not dependent on cobalt dispersion. The three calcined catalysts showed almost the same selectivity even though the CO conversions were quite different.

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Figure 2 Relationship between FT reaction rate and Co dispersion.