The effect of cobalt and zinc precursors on Co (10%)/Zn (x%)/TiO$_2$ (x = 0, 5) Fischer–Tropsch catalysts

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Abstract

A series of Co (10%)/Zn (x%)/TiO$_2$ (x = 0, 5) catalysts were prepared from different nitrate and acetate precursors. TPR and chemisorption techniques revealed that a mixture of cobalt precursors (cobalt acetate and cobalt nitrate) on titania were more easily reduced when compared to Co (10%)/TiO$_2$ catalysts prepared from either cobalt acetate or cobalt nitrate alone. By contrast, after addition of zinc, catalysts prepared from zinc acetate and cobalt nitrate had the most highly dispersed cobalt species when compared to catalysts prepared from the other combinations of nitrate and acetate precursors of zinc and cobalt.

Mixed precursors of zinc and cobalt were also more active and had higher CO conversion in Fischer–Tropsch synthesis (FTS) when compared to catalysts prepared from: (i) both nitrate precursors or (ii) both acetate precursors of zinc and cobalt. However, the catalyst prepared from zinc nitrate and cobalt nitrate produced more wax ($>C_{16}$) when compared to the other catalysts studied (50% versus 12–32% wax). Data suggest that larger Co particles correlate with wax production as well as reduced CO conversion. CO chemisorption data correlated better with the FT activity data than did Co XPS data.
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1. Introduction

Supported cobalt catalysts have been extensively used in Fischer–Tropsch synthesis (FTS) when high molecular weight products are desired [1–3]. The particle size of the catalyst is one of the contributing factors that can affect the selectivity as well as activity of supported cobalt catalysts. One approach to the control of the ultimate particle size of cobalt catalysts is by varying the cobalt precursors. Surprisingly, only limited studies have been reported in which this variable has been systematically explored.

Van de Loosdrecht et al. [3] studied the influence of organic and nitrate precursors on the particle size of alumina-supported cobalt catalysts. Organic precursors were found to

result in the formation of small particles that were not easy to reduce and were not active towards FTS. However, nitrate precursors formed larger particles that reduced at lower temperatures and were active in FTS.

Similar results were obtained when different cobalt precursors (nitrate, chloride, acetate and acetylacetonate) were supported on silica SBA-15 and MCM-41 [2,4]. As with the study on alumina, superior performance towards FT synthesis was obtained for the cobalt nitrate precursor [2].

Kraum and Baerns [5] performed a similar study on cobalt catalysts supported on titania, zirconia and ceria. Temperature-programmed reduction (TPR) studies conducted on the Co/TiO$_2$ catalysts prepared from a nitrate precursor, indicated the presence of one shoulder and one peak at 328 and 395 °C in the TPR profiles, respectively, assigned to the stepwise reduction of Co$_3$O$_4$ to Co [5]. However, when titania supported cobalt catalysts were prepared from organic

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precursors (cobalt acetate and cobalt oxalate), only one peak was observed in the TPR profiles. The peak maximum was at 387 °C for the cobalt acetate precursor and at 383 °C for the cobalt oxalate precursor [5].

An increase in cobalt dispersion from 6.1 to 7.8% was also observed when cobalt acetate as compared to cobalt nitrate was added to titania [5]. Also, catalysts prepared from cobalt acetate gave higher CO conversions and lower chain growth when compared to catalysts prepared from nitrate precursors (CO conversion of 26.2% versus 14.7%; alpha value changed from 0.74 to 0.84).

An extensive TPR study of Co/SiO_2 catalysts prepared from different cobalt precursors (chloride, sulfate, nitrate, acetate) also revealed that the counter-ion dramatically affected the TPR profile [6].

Li and Coville [7] investigated the effect of cobalt nitrate, cobalt acetate and cobalt chloride on the reducibility and catalytic performance of boron modified cobalt FTS catalysts supported on titania. Catalysts prepared using nitrate and acetate precursors were found to reduce in two steps, whereas catalysts prepared, using chloride precursors, reduced in one step. Calcined acetate and nitrate catalysts showed higher activity towards FTS whilst chloride catalysts exhibited lower activity due to poisoning by chloride ions.

The effect of mixing organic and nitrate precursors to prepare Co/SiO_2 catalysts using an impregnation method has also been reported [8]. Mixed precursors displayed higher activity towards FTS when compared to single-cobalt source precursors. Large Co metal particles, resulting from nitrate precursors, were proposed to assist in the reduction of small, difficult to reduce particles that were obtained from organic precursors through a hydrogen spillover mechanism [8].

These results have prompted us to investigate the effect of: (i) different single cobalt sources, (ii) mixed cobalt sources and (iii) different zinc and cobalt sources on the properties and FT activity of a series of Co (10%)/Zn (x%)/TiO_2 catalysts ($x = 0, 5$). This publication continues on an investigation of the effect of zinc on Co/TiO_2 catalysts from our research group as described in earlier papers [9,10].

2. Experimental

2.1. Catalyst preparation

Co (10%)/TiO_2 catalysts were prepared by the incipient wetness method, using TiO_2 Degussa (P25) as the support. Cobalt nitrate and cobalt acetate were either impregnated separately to form a 10 wt.% Co/TiO_2 catalyst or were co-impregnated to form a nitrate/acetate (N/A) mixture in a 1:1 molar ratio on the TiO_2. In another series of experiments, various combinations of cobalt and zinc nitrates and acetates were used in the preparation of catalysts. In all the Co (10%)/Zn (x%)/TiO_2 ($x = 1, 5$) catalysts that were prepared, the zinc was always impregnated before the cobalt with drying (120 °C for 19 h) in-between the impregnation and calcination steps. All

catalysts were calcined at 300 °C for 19 h after the final impregnation step.

2.2. Catalyst characterization

2.2.1. X-ray photoelectron spectroscopy (XPS)

The percentage concentration of different species on the surface of the material was determined, using XPS, recorded with a Quantum 2000 Scanning ESCA microprobe (Physical Electronics Company). Monochromised Al Kα (1486.7 eV) was used as the X-ray source.

Different surface atoms observed include Co, Zn (where applicable), Ti, O and C. Carbon was observed on all the samples and originated from the instrument background and not from the catalysts. From the work done by Alstrup and co-workers [11] the binding energies of the Co $2p_{3/2}$ peaks of the clean cobalt metal are located at 778.5 and 793.6 eV. However, the Co $2p_{3/2}$ main peak of the oxidic cobalt is expected at 780.3 eV with the Co $2p_{3/2}–2p_{1/2}$ spin splitting equal to 15.1 eV [12].

2.2.2. TPR

TPR experiments were performed on the Co/Zn (x)/TiO_2 ($x = 0, 1$ and 5) catalysts. Sieved (1180–850 μm), calcined samples (100–200 mg) were placed in a quartz reactor and degassed with nitrogen at 150 °C. A reduction gas containing 5% hydrogen in argon was passed over the sample at a flow rate of 50 ml/min, while the temperature was linearly increased at a rate of 10 °C/min from 27 to 950 °C.

2.2.3. Chemisorption analysis

H_2 chemisorption was performed in a Micromeritics ASAP 2010 instrument. Calcined samples were first reduced at a temperature of 250 °C with 100% H_2 for 16 h and then evacuated under helium gas to remove all physisorbed hydrogen. Adsorption isotherms were extrapolated to zero pressure to obtain chemisorption uptake. The following equation was used to calculate dispersion:

$$D\% = \left[\frac{V_m / V_{mol}}{W\% / W_a} \right] F_s(100), \ (100)$$

where V_m is the total volume of hydrogen chemisorbed, V_{mol} the hydrogen molar volume, $W\%$ the percentage of cobalt by weight, W_a the cobalt atomic weight, and F_s is the stoichiometry factor ($F_s = 2$ for hydrogen).

2.2.4. pH measurement

The pH of different precursor solutions was determined prior to impregnation. Before impregnation to the support the cobalt ion concentration of the solutions from different precursors was 1.42 mol/L and the zinc ion concentrations were 0.638 mol/L. pH measurements were performed, using a Yokogawa Electric Corporation pH meter, model PH 8211-E. The pH meter was first calibrated, using buffer solutions

with pH 4, 7 and 9 and all measurements were carried out at room temperature.

2.3. CO hydrogenation

A system of three stainless steel fixed bed reactors was used to evaluate the activities and selectivities of catalysts towards FTS [13]. Catalysts were calcined at 300 °C for 19 h in an oven prior to loading in the reactors. Catalyst (2.0 ml–1.5 g) was loaded into each reactor. Catalysts were then reduced in situ under a flow of pure hydrogen at 250 °C for 16 h at a GHSV of 500 h^{-1}. After reduction, the reactor temperatures were decreased to 220 °C followed by the introduction of synthesis gas (10% Ar, 60% H$_2$, 30% CO) at a pressure of 8 bar and a GHSV of 400 h^{-1}. No additional gases were co-fed into the synthesis gas. Flow rates were controlled by Brookes flow meters and needle valves. The catalysts were allowed to stabilise over a period of 120 h and the mass balance was then performed over a period of 100–120 h.

The method used for mass balance calculations is similar to the one used by Nijis and Jacobs [14]. The calculations are based on carbon. The amount of carbon entering the reactor is equal to the amount of carbon reacted to form products plus unreacted carbon leaving the reactor, i.e. % mass balance $= (A + B)/C \times 100$, where A = mol carbon unreacted, B = mol carbon reacted and C = mol carbon entering the reactor.

A calibration gas containing hydrogen, carbon monoxide, carbon dioxide, methane, ethane and ethylene was used to calibrate the TCD and FID data. Response factors obtained were converted to molar compositions for different components, using the method described by Scanlon and Wills [15].

3. Results and discussion

3.1. XPS analysis

(a) *Zn/TiO$_2$:* XPS data were collected on Zn/TiO$_2$ samples prepared from both zinc acetate and zinc nitrate. Zinc acetate (pH 5.68) gives more surface zinc than does zinc nitrate (pH 2.76; an increase of about 20%), indicating that the size of the zinc particles is affected by the zinc

counter-ion. The counterion influences the pH of the solution and the bigger Zn particles formed from the nitrate solution are associated with the pH value being far removed from the zeta potential for TiO$_2$ (ca. 6–6.5)[16]. The closer the pH value of a precursor solution to the to the zeta potential of Degussa titania, the larger the amount of impregnated metal dispersed on the surface.

(b) *Co/TiO$_2$:* XPS data for Co/TiO$_2$ samples prepared from different Co precursors were recorded. A slight increase (approximately 20%) in the amount of cobalt species dispersed on the titania support was observed when cobalt acetate precursor salts were used in the catalyst preparation instead of cobalt nitrate salts (Table 1). Similar results were obtained by Kraum and Baerns [5]. The use of cobalt acetate as a precursor thus resulted in the formation of a more highly dispersed cobalt surface species. A significant increase in the surface cobalt species was also observed when mixed precursor salts of cobalt were co-impregnated on the titania support. The amount of cobalt increased from 2.07 to 2.98% (Table 1). These results show that mixed acetate and nitrate precursors of cobalt improves the dispersion of cobalt on TiO$_2$. Sun et al. observed similar results when mixed cobalt precursor salts were employed in the preparation of Co/SiO$_2$ [8]. Correlation was also established when considering the pH of different solutions prior to impregnation versus the isoelectric point of Degussa titania. The closer the pH of solution to the isoelectric point of the support, the more the cobalt is dispersed on the support (Tables 1 and 2).

(c) *Co (10%)/Zn (5%)/TiO$_2$ catalysts:* Table 1 shows the XPS data recorded on Co (10%)/Zn (5%)/TiO$_2$ samples in which the source of cobalt and zinc were varied. Cobalt was always impregnated after the addition of zinc to the titania support. In this set of experiments when the zinc and cobalt precursors were varied, the amount of cobalt dispersed on the surface (3.08–3.66%) was found to be less dependent on the zinc counterion than on the cobalt counterion used (3.08 and 3.12 for acetate and 3.66 and 3.49 for nitrate ions; Table 1).

Nevertheless, the catalysts prepared from cobalt nitrate and zinc acetate precursor had the highest amount of cobalt dispersed on the surface when compared to other counterions. These results show that the amount

Table 1
XPS results showing the effect of changing cobalt and zinc precursors on Co (10%)/Zn (5%)/TiO$_2$ catalysts

Cobalt and zinc precursor salts	%Ti 2p	%Co 2p$_{3/2}$	%Zn 2p$_{3/2}$	%Co/%Ti	%Co/%Zn	%Co/(%Ti + %Zn)
Co/TiO$_2$						
Cobalt acetate	18.6	2.59	0	0.139	–	13.93
Cobalt acetate + cobalt nitrate (1:1)	18.3	2.98	0	0.163	–	16.28
Cobalt nitrate	24.2	2.07	0	0.086	–	8.56
Co/Zn (5%)/TiO$_2$						
Cobalt acetate and zinc acetate	19.9	3.08	2.3	0.155	1.34	13.87
Cobalt acetate and zinc nitrate	18.5	3.12	1.54	0.169	2.04	15.57
Cobalt nitrate and zinc acetate	18.1	3.66	1.17	0.202	3.13	18.99
Cobalt nitrate and zinc nitrate	25.8	3.49	0.55	0.135	6.35	13.26

Table 2
Cobalt Chemisorption measurements

Cobalt and zinc precursor salts	pH data	Cobalt dispersion (%)	Metallic surface area (m^2/g) sample	Metallic surface area (m^2/g) metal
Co/TiO$_2$				
Cobalt acetate	6.69	1.82	1.19	11.92
Cobalt acetate + cobalt nitrate (1:1)	6.41	2.21	1.43	14.43
Cobalt nitrate	2.99	1.35	0.91	9.15
Co/Zn (5%)/TiO$_2$				
Cobalt acetate + zinc acetate		2.23	1.48	14.84
Cobalt acetate + zinc nitrate		2.31	1.59	15.96
Cobalt nitrate + zinc acetate		2.62	1.73	17.34
Cobalt nitrate + zinc nitrate		1.98	1.33	13.39

of cobalt in the surface is affected by more than one factor.

The presence of zinc in the catalyst is anticipated to improve the dispersion of cobalt by forming a 'sandwich layer' between the cobalt and the support [10]. In addition, cobalt dispersion is affected by the cobalt counterion used in the preparation of catalyst as well as the pH of the solution prior to impregnation. Cobalt nitrate precursors are expected to form bigger particles when compared to their organic counterparts. Further, formation of big cobalt particles on top of well dispersed zinc, is expected to improve the stablity of cobalt particle.

Changes were also observed in the amount of zinc detected on the surface due to the changes in the zinc and cobalt precursor salts. In particular: (i) zinc acetate yielded more surface zinc for similar cobalt salts than did zinc nitrate and (ii) cobalt nitrate gave a lower yield of surface zinc with cobalt nitrate.

The observed increase in cobalt dispersion when cobalt acetate is used as a precursor, is associated with smaller cobalt particles, as found for Co on SiO$_2$ [8]. This is also consistent with smaller zinc particles generated from acetate rather than nitrate. Cobalt oxide particles are expected to be more stable and zinc is also known to improve the stability of cobalt [12,17–20].

A change in the %Co/%Zn ratio is observed when changing from catalysts prepared from acetate precursors to catalysts prepared from nitrate precursors (Table 1). These results suggest that when nitrate precursors are used most of the zinc oxide is covered by cobalt oxide [9,10]. Thus, the source of cobalt plays a role in exposing zinc on the surface of the catalyst (Table 1).

3.2. Catalyst reduction study

Much work has been reported on the reducibility of supported cobalt catalysts [5,8,9]. Reduction of cobalt takes place in two reduction steps, which corresponds to the reduction of Co^{3+} to Co^{2+} and reduction of Co^{2+} to metallic cobalt, respectively [9].

(a) *Co/TiO$_2$ catalysts:* Both cobalt acetate and cobalt nitrate (Fig. 1a and c) gave similar TPR profiles and did not

show any significant effect on the reducibility of cobalt. The data are similar to that reported by Kraum and Baerns [5], but with different absolute values due to the different reaction/measurement conditions used. Sun et al. [8] also obtained similar results for the reducibility of Co^{3+} to Co^{2+} when working with Co/SiO$_2$ catalysts. However, a vast difference in the second cobalt reduction step was observed in the work reported by Sun et al., which was attributed to a metal support interaction [8].

When the nitrate precursor was combined with the acetate precursor more easily reducible species are obtained (Fig. 1b). These results correlate with the results obtained by Sun et al. on Co/SiO$_2$ catalysts [8]. The ease in the reducibility of cobalt prepared from mixed precursors was attributed to a spillover effect. Bigger particles resulting from nitrate precursors were thought to assist in the reduction of smaller particles prepared from acetate precursors [8].

(b) *Co (10%)/Zn (5%)/TiO$_2$:* We have previously reported on reducibility studies performed in Co (10%)/Zn (x%)/TiO$_2$ (x = 0, 1, 5) for catalysts prepared from nitrate
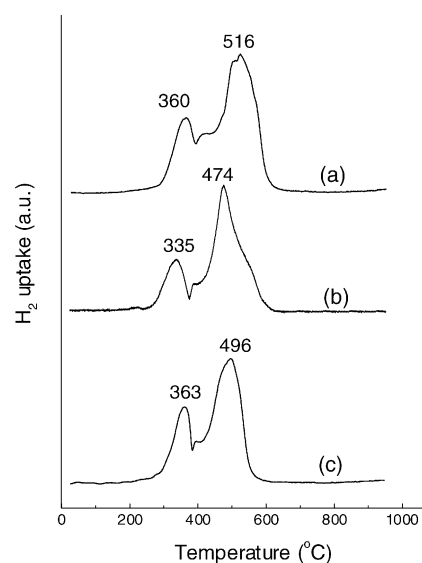

Fig. 1. TPR profiles showing the effect of adding different precursors of cobalt to generate Co/TiO$_2$ catalysts, (a) cobalt acetate, (b) cobalt acetate and cobalt nitrate (1:1 molar ratio) and (c) cobalt nitrate.

Table 3
Summary of the FT results

Metal precursors	Co Ac.	Co Ac. + Co nitr.	Co nitr.	Co Ac. + Zn Ac.	Co Ac. + Zn Nitr.	Co Nitr. + Zn Ac.	Co Nitr. + Zn Nitr.
CO conversion (%)	24.5	36.4	29.9	46.1	51.0	54.6	42.6
Activity (mmol/g/s)	0.43	0.96	0.64	1.30	1.58	1.72	0.89
Selectivities (% by mass)							
C_1	28.5	23.4	15.1	26.4	20.2	14.5	10.9
$C_2–C_4$	23.7	16.3	9.9	11.8	16.7	13.4	9.2
$C_5–C_{11}$	13.9	14.7	8.5	21.4	22.5	18.4	12.8
$C_{12}–C_{15}$	13.6	15.3	9.7	27.7	12.7	21.3	16.6
C_{16+}	19.6	31.8	56.8	12.8	27.5	32.4	50.6

Reaction conditions: calcinations, 300 °C, 1 atm, 19 h; reduction, 250 °C, 1 atm, 500 h^{-1}, 100% H_2 and synthesis, 220 °C, 8 bar, 400 h^{-1}, 200 h, 2H_2:1CO.

precursors and the results for $x = 0$ and 1% revealed no differences in the TPR profiles [9,10]. For the 5% loaded zinc, a combination of zinc acetate and cobalt nitrate resulted in the formation of easily reducible cobalt species when compared to zinc and cobalt salts with the same ions (zinc nitrate and cobalt nitrate, or zinc acetate and cobalt acetate) or the catalyst prepared from zinc nitrate and cobalt acetate [9]. These results correlate well with the results obtained from the XPS technique.

3.3. Chemisorption results

(a) *Co/TiO$_2$:* The use of cobalt nitrate as a cobalt catalyst precursor gave a cobalt dispersion of 1.35% (Table 2). When acetate precursors were used in the preparation of cobalt catalyst supported on titania, the amount of cobalt dispersed on the surface increased by approximately 25% (Table 2). A combination of cobalt nitrate and cobalt acetate added to TiO$_2$ resulted in an increase in dispersion (±39%) when compared to cobalt nitrate impregnated on titania (Table 2). These results correlate with the results obtained from the TPR technique where easily reducible cobalt oxide species were detected when mixed cobalt precursor salts were used.

(b) *Co (10%)/Zn (5%)/TiO$_2$:* In general the dispersion data showed a small range of values that correlated with the XPS data, except for the cobalt nitrate/zinc nitrate sample. The highest dispersion was also obtained when zinc acetate was impregnated with cobalt nitrate (Table 2). These results also show a correlation with the reducibility results obtained when using the TPR technique [9].

3.4. FTS

(a) *Co/TiO$_2$:* Catalysts prepared from the mixed cobalt precursor salts resulted in a higher CO conversion and a higher catalytic activity (Table 3) when compared to catalysts prepared from single-cobalt precursors. However, the cobalt catalyst prepared from the nitrate precursor resulted in higher selectivity towards the production of wax and lower methane selectivity when compared to the other Co/TiO$_2$ catalysts (Fig. 2; Table 3).

The cobalt acetate precursor gave a cobalt catalyst which has higher methane selectivity and lower wax selectivity when compared to the nitrate counterions, a result in agreement with earlier studies on TiO$_2$ [5] (Fig. 2; Table 3). These results are also similar to those observed by Sun et al. on SiO$_2$ [8]. It is thus clear that the Co counter-ion (via the solution pH) plays an important role in influencing particle size and consequently the FT activity of the Co catalysts. The FT results correlate with cobalt reducibility, particle size as well as dispersion as revealed by XPS, TPR and chemisorption techniques. Hydrogen spillover reactions during reduction, when mixed precursor salts are employed, have been suggested to be a contributing factor for the observed catalytic behavior [8].

(b) *Co (10%)/Zn (5%)/TiO$_2$:* Catalysts prepared from mixed precursor salts produced from diffferent metals (i.e. zinc and cobalt) were more active and have a higher CO conversion than catalysts prepared from single-precursors of zinc and cobalt (Table 3). The observed catalytic behavior of Co/Zn/TiO$_2$, when compared to Co/TiO$_2$ catalysts, could be attributed to the effect of zinc forming a 'sandwich' layer between cobalt and the support on the dispersion and stability of cobalt crystalline particles [10].

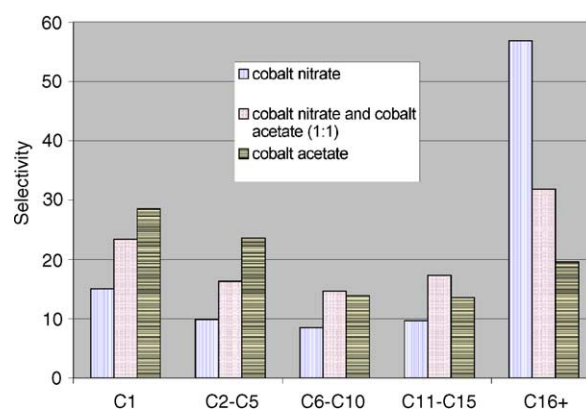However, exposure of zinc oxide particles on the surface was found to have detrimental effects with in-

Fig. 2. Effect on hydrocarbon selectivity of different cobalt precursors on Co/TiO$_2$ catalysts.
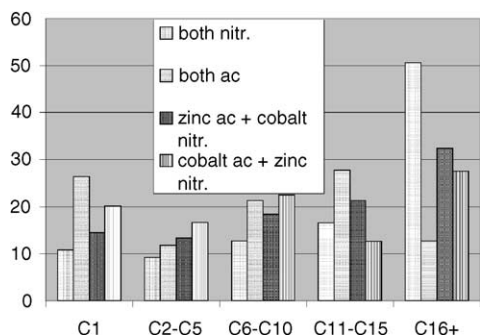
Fig. 3. Effect on the percentage hydrocarbon selectivity of adding different cobalt and zinc precursors on Co/Zn (5%)/TiO$_2$ catalysts.

creased methane selectivity and decreased amounts of high molecular weight products [10]. An increase in the amount of zinc (as revealed by XPS data) resulted in more methane production and less wax production.

Catalysts prepared from zinc acetate and cobalt acetate showed the highest methane selectivity as well as the most zinc exposed on the surface (Table 3). A similar behavior is also observed in catalysts prepared from zinc nitrate and cobalt acetate. Catalysts prepared from nitrates of zinc and cobalt have the lowest methane selectivities and the lowest amount of zinc on the surface (Table 3; Fig. 3). The wax production (fraction >C$_{16}$) is favoured by nitrate counterions. This suggests that large Co particles favour chain propogation over chain termination reactions.

Interestingly, the CO chemisorption data and not the XPS data correlate with the catalyst activity. While this is consistent with the general mechanism proposed in which the amount of reduced Co determines the FT activity, it also suggests that the secondary impact of Zn on the FT reaction is important.

4. Conclusion

Our study allows for the following conclusions to be drawn:

1. The use of acetate precursor salts, to prepare Co/TiO$_2$ catalysts resulted in the synthesis of highly dispersed crystalline cobalt particles which were easy to reduce when compared to their nitrate counter ions. However, these particles were less active towards FTS and resulted in higher methane selectivity.
2. Combinations of nitrate and acetate precursors used to prepare Co/TiO$_2$ catalysts resulted in better catalytic performance in terms of activity and CO conversion when compared to the use of their mono precursors.
3. The use of different cobalt and zinc precursor salts resulted in an increase in the amount of zinc exposed on the surface.
4. Catalysts prepared from mixed precursors of zinc and cobalt were more active and had higher CO conversion when compared to catalysts prepared from both nitrate precursors of zinc and cobalt and both acetate precursors of zinc and cobalt.
5. Exposure of zinc on the surface of Co/Zn/TiO$_2$ has a detrimental effect on the catalytic behavior of the catalysts. More methane was produced and this was accompanied by less wax production.
6. Nitrate precursors of zinc and cobalt gave better results in terms of wax selectivity when compared to the combination of all other precursors.

Acknowledgements

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