

A study of Co/Zn/TiO₂ catalysts in the Fischer–Tropsch reaction

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Abstract

A series of Co (10%)/Zn ($x\%$)/TiO₂ catalysts ($x = 0$ –10%) have been prepared by conventional incipient wetness techniques. TPR, BET, Raman Spectroscopy and XRD data reveal that the presence of the Zn has a minimal effect on the properties of the Co/TiO₂ materials. XPS data reveal that the surface cobalt (and Ti) concentration does not decrease after Zn addition (0% Zn–1.95% surface Co; 5% Zn–3.45% surface Co; 10% Zn–2.05% surface Co) suggesting that the Co covers the Zn ions on the TiO₂ surface. At high Zn coverage, the reducibility of the Co increases slightly. Fischer–Tropsch synthesis performed on Co (10%)/Zn ($x\%$)/TiO₂ ($x = 0, 5$ and 10%) reveals that the Zn enhances the Co activity, but changes the selectivity to lower mass hydrocarbons. The 5% Zn catalyst shows optimal methane production relative to the other two catalysts. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

The Fischer–Tropsch (FT) reaction is used to convert CO/H₂ (syngas) into chemicals and fuels [1]. The reaction is carried out in the presence of a transition metal catalyst, and the Fe and Co commercial catalysts are typically made by precipitation or deposition onto a support [1–8].

Syngas can be made from coal, oil or gas and in most instances the syngas contains impurities such as sulphur that are generally harmful to the catalyst [9–11]. However, various reports have appeared in the literature to suggest that small amounts of sulphur could be beneficial (activity, selectivity) to the catalyst [12–14]. Both the form of the sulphur (e.g. the

oxidation state) and the proximity of sulphur atoms to a metal site could influence the catalyst activity. These factors could be viewed as electronic and steric factors.

Supported cobalt catalysts are known to show activities in the FT reaction that are not influenced by support, dispersion, metal loading, etc., but are determined by the amount of reducible cobalt available to the reactants [15]. This would suggest that Co could be an ideal metal for assessing the role of S in the FT reaction.

To achieve this, the sulphur should be non-mobile and this suggests the use of metal sulphides as a source of sulphur. Zinc is a known sulphur scavenger which is used to extract sulphur (e.g. H₂S) from reactant gas streams, and ZnS has a high S binding constant [9,10,15]. Our objective is thus to synthesise cobalt-supported catalysts containing Zn and ZnS and evaluate the influence of S on the Co-catalysed FT reaction.

In this first report, we describe the effect of zinc on the properties and FT behaviour of Co/TiO₂ catalysts. While previous reports have appeared on the reaction

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of Co with Zn in precipitated catalysts, there appear to be no reports of the synthesis of Co/Zn-supported catalysts for FT studies [10].

2. Experimental

2.1. Catalyst preparation

TiO₂ (Degussa P25) was impregnated with zinc and cobalt precursors using the incipient wetness method to generate a series of Co (10%)/Zn (x%)/TiO₂ (x = 0, 0.01, 0.1, 1.0, 5.0 and 10.0%) catalysts. The catalysts were dried at 120 °C for 19 h after each impregnation step and then calcined at 300 °C for 19 h after the final impregnation step. Both the zinc and cobalt precursors as well as the order of zinc and cobalt impregnation varied.

2.2. Characterisation techniques

Temperature-programmed reduction (TPR). TPR experiments were performed to study the reduction behaviour of the calcined catalysts. Sieved (1180–850 μm), calcined samples (100–200 mg) were placed in a quartz reactor and degassed with nitrogen at 150 °C. A reducing 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°/min from 27 to 950 °C.

X-ray diffraction (XRD). A Phillips spectrometer (PW 1830 generator) equipped with a Cu radiation source was used to analyse powdered disc samples in the 0–70° 2θ range at a generator voltage of 40 kV and a generator current of 20 mA. A scan rate of 2° s⁻¹ per step was used.

Laser Raman spectroscopy. Laser Raman spectra were obtained with a Jobin-Yvon T 6400 Raman spectrometer that utilises holographic gratings. A 514.4 nm excitation source from a coherent argon ion laser was used. Samples were supported on KBr and pressed into pellets. Samples were rotated off-axis to prevent excessive heating.

Surface area determination. BET surface area results were obtained from a Micromeritics ASAP 2010 porosimeter. A sample of about 200 mg was degassed at 120 °C for 4 h prior to analysis. The surface area results were then obtained at –196 °C.

X-ray photoelectron spectroscopy (XPS). Percentage concentration of different species on the surface of the material were determined using XPS spectra recorded with a Quantum 2000 Scanning ESCA microprobe (Physical Electronics). Monochromised Al Kα (1486.7 eV) was used as the X-ray source. All spectra were referenced against the C peak at 285.00 eV [16].

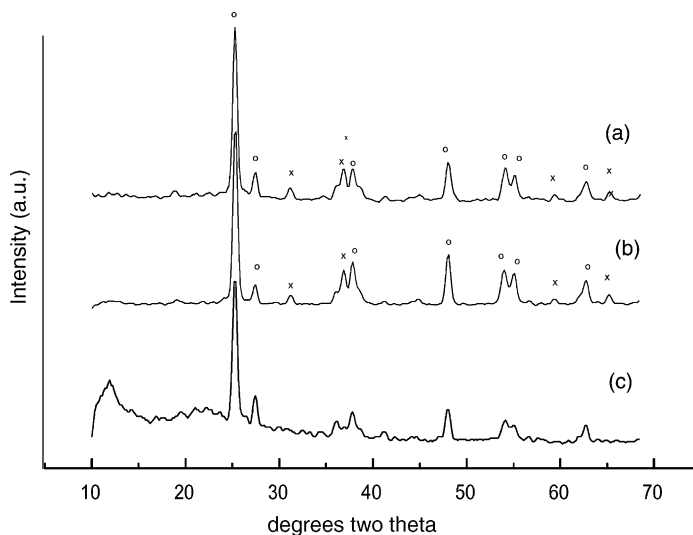


Fig. 1. XRD results showing the effect of changing cobalt and zinc precursors on Co (10%)/Zn (1%)/TiO₂ catalysts: (a) zinc acetate and cobalt nitrate; (b) zinc nitrate and cobalt nitrate; (c) Degussa titania P25. (×) Co₃O₄; (○) TiO₂.

From the work done by Alsstrup et al. [17], the binding energies of the Co $2p_{3/2}$ peaks of the clean cobalt metal have been 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 [11].

2.3. Results and discussion

2.3.1. Bulk characterisation of oxidic catalysts

Degussa titania contains about 70% of the anatase and 30% of the rutile phase. Results obtained from the XRD technique showed similar phase ratios, irrespective of the amount of zinc employed, the sequence of zinc and cobalt addition or the different precursors used (Fig. 1). The results imply that varying these parameters has no significant effect on the titania support.

Raman spectra did not show any significant differences when the zinc loading was changed from 0 to 1 wt.% (Fig. 2). However, peaks due to Co_3O_4 broadened in samples with 5 and 10 wt.% zinc (Fig. 2). This is associated with the presence of nitrate and organic residues which cause fluorescence [18]. In addition, changing the sequence of impregnation of the zinc and

Table 1
BET surface areas

	BET surface area (m^2/g)
Zinc (wt.%)	
0	43.2
0.01	42.9
0.1	43.1
1	42.5
10	40.4
Sequence	
Zinc first	42.5
Cobalt first	43.3
Zinc and cobalt together	42.8

cobalt precursors as well as pretreatment conditions did not have any significant effect on the Raman spectra (data not shown).

2.3.2. BET surface area measurements

Results obtained from BET surface area measurements show that zinc addition has no substantial effect on the surface area of the supported materials (Table 1). The BET surface areas of the samples were found to range between 40 and $43 \text{ m}^2/\text{g}$.

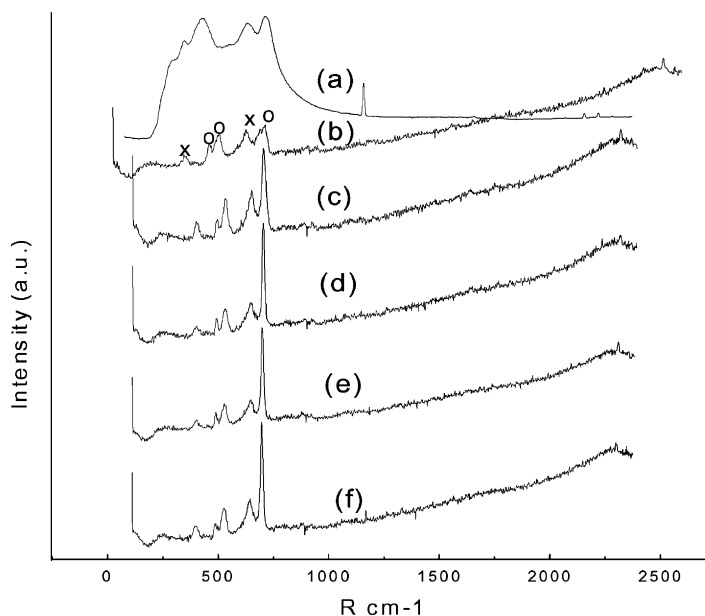


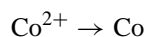
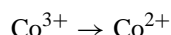
Fig. 2. Raman spectra showing the effect of adding different amounts of zinc to $\text{Co}_3\text{O}_4/\text{TiO}_2$: (a) 10, (b) 5, (c) 1, (d) 0.1, (e) 0.01 and (f) 0 wt.%. (x) Co_3O_4 ; (o) TiO_2 .

2.3.3. Catalyst reduction study

TPR was used to investigate the effect of varying synthesis parameters on the reducibility of the zinc/cobalt/TiO₂ catalyst. Analysis of a pure TiO₂ sample showed no hydrogen consumption.

1. Amount of zinc loaded onto the catalysts

Cobalt nitrate and zinc nitrate were used as precursors in this investigation. Results obtained from the TPR study showed very little or no change when the zinc loading was varied between 0 and 5% (Fig. 3). Two reduction peaks were observed in the spectra which correspond to the following chemical reactions [19]:



The 10% Zn/Co/TiO₂ revealed three peaks in the TPR profile. The first peak, due to the presence of nitrate ions, could be removed by further calcination at 350 °C for 19 h (Fig. 3d). The TPR peaks moved to lower temperature on addition of the 10%

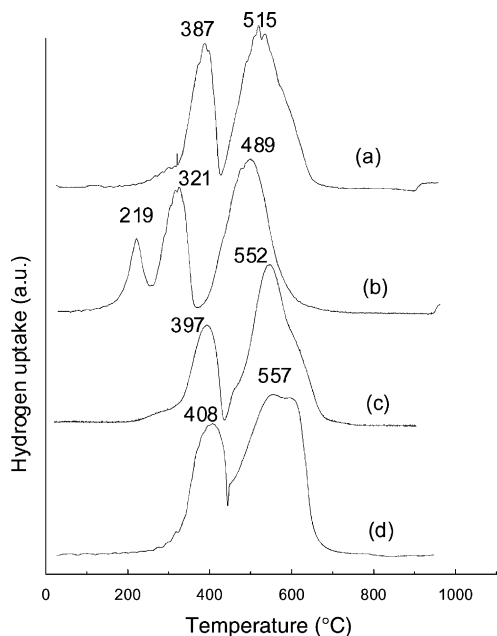


Fig. 3. The effect of % zinc on the reducibility of cobalt: (a) 10 wt.% (re-calcined at 350 °C), (b) 10 wt.% (calcined at 300 °C), (c) 5 wt.% and (d) 0 wt.%.

zinc (from 408 to 387 °C and from 557 to 515 °C for the first and second peaks, respectively).

Consequently, zinc has a minimal effect on the reducibility of cobalt when the zinc loading is ≤ 5 wt.%, but possibly enhances the reducibility when the Zn loading ≥ 5 wt.%.

2. Order of zinc and cobalt impregnation

A series of Co/Zn/TiO₂ catalysts were made in which the order of zinc and cobalt impregnated was varied, i.e. zinc was either impregnated before or after cobalt. Drying was done after each impregnation step and calcination was performed after the final impregnation step. Both zinc and cobalt were also impregnated simultaneously followed by drying and calcination. Both 1 and 5 wt.% zinc loadings were employed in the investigation of these materials. Results (not shown) revealed that there is no effect on the TPR profiles caused by changing the sequence of zinc and cobalt impregnation. Impregnating 5% zinc after cobalt seems to marginally assist the reducibility of cobalt.

3. Zinc and cobalt precursors

Various combinations of nitrates and acetates of cobalt and zinc were used in the preparation of catalysts. Both 1 and 5 wt.% zinc loading were employed in this investigation.

TPR experiments showed that the cobalt and zinc counterions (acetate and nitrate) had no effect on the TPR profiles when 1 wt.% loading of zinc was used. However, a significant effect of changing zinc and cobalt precursors on the profile was observed when a 5 wt.% zinc loading was used (Fig. 4). TPR results showed the formation of cobalt oxide species that reduce at lower temperatures when mixed precursors (combination of acetate and nitrate ions) were used as compared to mono-precursors (either nitrate or acetate ions) (Fig. 4). Similar results were obtained by Sun et al. [15] when cobalt acetate and cobalt nitrate were used as precursors in the preparation of Co/SiO₂ catalysts.

Sun found that the use of cobalt acetate as the only precursor gave formation of highly dispersed cobalt oxide species, which were not easy to reduce. However, when cobalt nitrate was employed as the sole precursor, cobalt oxide species with low dispersion (and that were easily reduced) were formed. Results obtained from mixed salts

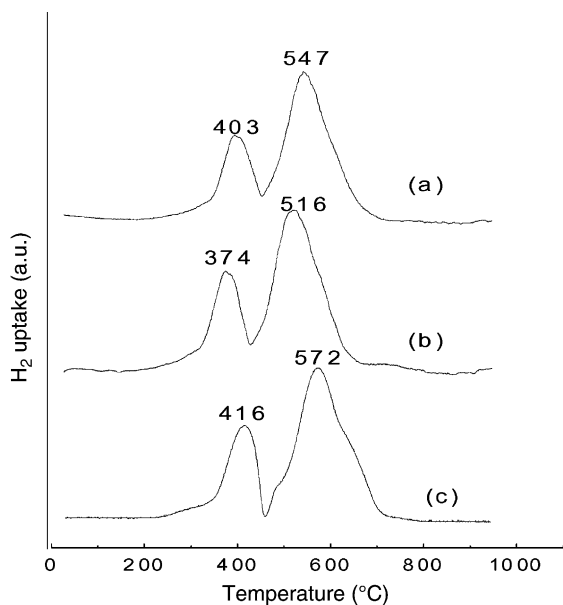


Fig. 4. The effect of precursors on the reducibility of cobalt (5 wt.% zinc loading): (a) zinc acetate and cobalt acetate; (b) zinc acetate and cobalt nitrate; (c) zinc nitrate and cobalt nitrate.

showed an increase in H_2 adsorption with increasing nitrate/acetate ratio. The CO conversion was found to be the largest when the nitrate/acetate ratio was unity [15].

4. Support pretreatment

Zinc before cobalt. The effect of titania-support calcination before impregnating zinc and cobalt and after impregnating zinc was investigated (5 wt.% zinc).

Un-pretreated titania support was impregnated with zinc followed by drying and calcination at 300 °C for 19 h. The Ti/Zn support was further impregnated with cobalt, dried and calcined at 300 °C for 19 h. Data are shown in Fig. 5b. The titania support was also calcined at 300 °C for 19 h and the resultant support was impregnated with zinc and cobalt followed by drying after each impregnation step and calcination after the final impregnation step (Fig. 5a). Finally, the material was calcined only after the impregnation of both Zn and Co (Fig. 5c). The TPR data suggest that pre-calcining the support (without Co) favours the formation of more easily reducible species.

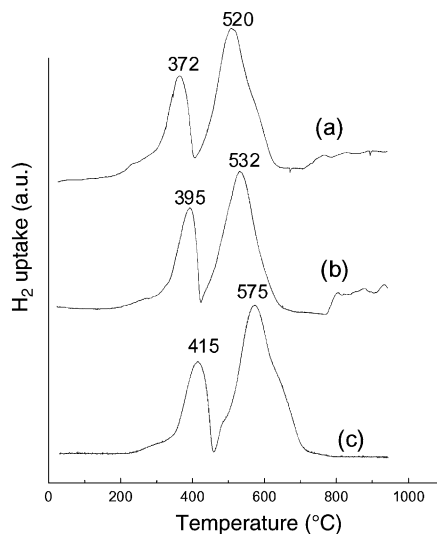


Fig. 5. TPR results showing the effect of support pretreatment (5 wt.% zinc addition before cobalt): (a) support calcined before zinc and cobalt impregnation; (b) support calcined after zinc impregnation, i.e. before cobalt impregnation; (c) calcination after Co and Zn impregnation steps.

Zinc after cobalt. Calcination of cobalt with the support before the impregnation of zinc shifted the reduction peaks towards higher temperature (403, 548 °C, Fig. 6a). During calcination ($T = 300$ °C), cobalt presumably interacts with the support surface to form cobalt–titania species, which are not as easy to reduce. Addition of zinc after calcination did not improve the dispersion of cobalt due to the already formed cobalt–titania species. However, when cobalt is dried with the support at 120 °C, little interaction is expected and this results in formation of cobalt oxide species that were easy to reduce (Fig. 6).

The general observation is thus that calcination of the Zn/TiO₂ favours formation of more easy to reduce Co.

2.3.4. XPS analysis

XPS was used in an attempt to obtain more insight into the surface composition of TiO₂/Co/Zn catalysts prepared by the incipient wetness method. Table 2 shows the binding energies of Co on the TiO₂ when different amounts of zinc were impregnated. Results confirm the presence of Zn²⁺ as well as Co²⁺ on the

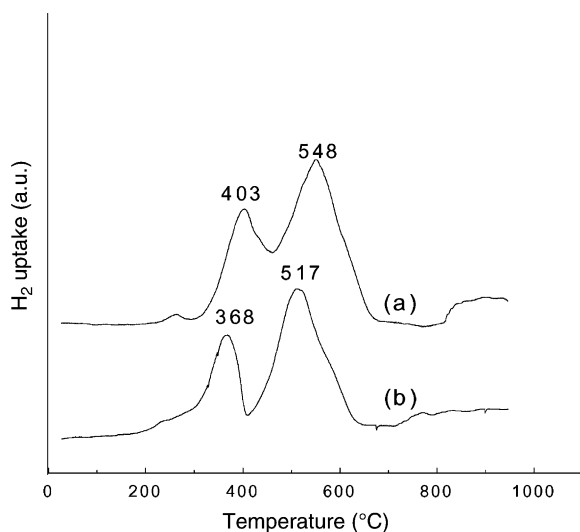


Fig. 6. TPR results showing the effect of support calcinations (5% zinc addition after cobalt): (a) calcination after the impregnation of cobalt and before zinc impregnation; (b) calcination after the impregnation of cobalt and zinc.

surface of the $\text{TiO}_2/\text{Co}/\text{Zn}$ catalysts [11,16] and that the cobalt oxidation state is unaffected by the presence of Zn. Also, based on the results, it is apparent that addition of 1% zinc does not affect the cobalt surface concentration. Remarkably, the addition of 5% zinc enhances the cobalt surface concentration, and the low zinc concentration detected suggests coverage of the zinc by cobalt. The Co/Zn ratio has actually increased at this Zn loading (Table 3), while the Ti surface concentration has remained unchanged. Addition of 10% Zn again reveals a low surface concentration of Zn on the catalyst surface (1.29%), but at this level the Co concentration has decreased to levels similar to that observed in the absence of zinc. These results suggest that the cobalt deposits on top of the zinc, i.e. the Zn is ‘sandwiched’ between the Ti and Co.

Table 2

XPS data for the Co (10%)/Zn (x%)/TiO₂ catalysts

Catalyst composition	Binding energy of cobalt	Binding energy of zinc	% of Co (2p _{3/2})	% of Zn (2p _{3/2})	% of Ti (2p _{3/2})
Co (10%)/Zn (0%)/TiO ₂	780.1	–	2.07	0	24.2
Co (10%)/Zn (1%)/TiO ₂	780.5	1022.1	1.95	0.45	24.1
Co (10%)/Zn (5%)/TiO ₂	779.8	1022.4	3.49	0.55	24.8
Co (10%)/Zn (10%)/TiO ₂	780.2	1022.3	2.18	1.29	22.1

Table 3

Surface element ratios for the Co (10%)/Zn (x%)/TiO₂ catalysts

Catalyst composition	% Co/% Zn	% Co/% Ti
Co (10%)/Zn (0%)/TiO ₂		0.086
Co (10%)/Zn (1%)/TiO ₂	4.33	0.081
Co (10%)/Zn (5%)/TiO ₂	6.35	0.14
Co (10%)/Zn (10%)/TiO ₂	1.68	0.099

The XPS data suggests that zinc improves the dispersion of cobalt on the surface for both 5 and 10% loaded samples. The increased dispersion of the cobalt in the presence of zinc will need to be confirmed by chemisorption techniques.

2.3.5. FT synthesis

Three catalysts (Co/TiO₂, 5% Zn/Co/TiO₂, 10% Zn/Co/TiO₂) were chosen for evaluation in the FT reaction. Table 4 and Fig. 7 show the results (selectivities and conversions) obtained for the different catalysts. Reaction conditions were kept constant in

Table 4

FT catalysis results for Co (10%)/Zn (x%)/TiO₂ catalysts (x=0, 5 and 10%)^a

	Zinc loading (wt.%)		
	0	5	10
CO conversion (%)	29.9	42.6	43.4
Activity (mmol/g/s)	0.64	0.70	0.92
Selectivities (% by mass)			
C ₁	15.3	10.9	18.3
C ₂ –C ₄	10.1	9.2	12.5
C ₅ –C ₁₁	7.8	12.7	11.5
C ₁₂ –C ₁₅	6.1	14.9	12.9
C ₁₆₊	60.6	52.3	44.8

^a Reaction conditions—calcination: 300 °C, 1 atm, 19 h; reduction: 250 °C, 1 atm, 500 h⁻¹, 100% H₂; synthesis: 220 °C, 8 bar, 400 h⁻¹, 200 h, 2H₂:1CO. Mass balance data = 100 ± 5%.

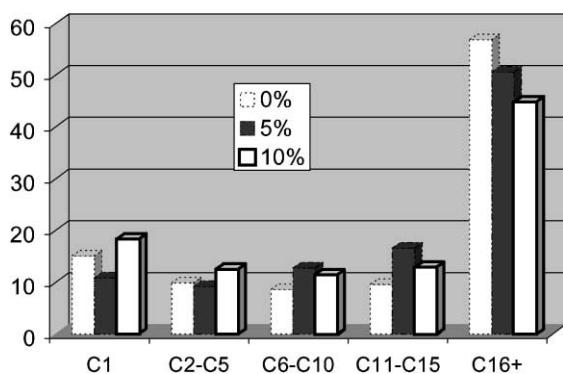


Fig. 7. The effect of different zinc loadings on the selectivities of Co/Zn/TiO₂ catalysts.

all these studies. It is apparent that increasing the amount of zinc increased the CO conversion of the catalyst although little difference is noted for the CO conversions of 5 and 10% zinc-loaded catalysts.

The changes noted in the TPR profiles of the three catalysts do not show an obvious correlation with the changes in activity. A greater change in activity might have been expected for the 10% zinc-loaded catalysts. This suggests that the degree of interaction of the zinc with the titania might be the critical issue in assessing catalyst performance.

Interestingly, the 5% zinc-loaded catalyst produces less methane (10%) than the pure Co/TiO₂ catalyst (15%) and suggests that the Zn addition has a positive effect on the Co in terms of selectivity. It is to be noted that very little alcohol was produced in the reaction (no CO₂), and thus the presence of the zinc does not affect the hydrocarbon producing reaction. The Zn addition did, however, leads to a decrease in the production of higher chain length hydrocarbons.

It is clear that excess zinc (e.g. at 10% loading) has a detrimental effect on the catalyst selectivity (poorer wax producer, more methane) when compared to the 5% Zn-loaded catalyst. The reason for this is currently not known, but further studies at high Zn loadings should permit an understanding of this finding.

3. Conclusion

This study of the influence of Zn on Co/TiO₂ FT catalysts reveals that:

1. The physical properties of the catalyst are little affected by Zn loadings of up to 10% as detected by BET, XRD, TPR and Raman studies. Some differences are noted at the higher zinc loadings. By contrast, the XPS studies reveal significant changes in the surface concentrations of Co and Zn with Zn loading. Chemisorption studies to evaluate the effect it has on the amount of reducible Co are still needed, although the TPR data suggests enhanced Co reducibility with increasing Zn content. Improvement in the reducibility of the cobalt could result from an increase in the cobalt dispersion.
2. The zinc has a positive effect on the activity and the selectivity of the Co/TiO₂ catalysts. This is reflected, in particular, by the increased activity and reduced methane content of the Co (10%)/Zn (5%)/TiO₂ catalyst.

The data thus suggest that the new Co (10%)/Zn (5%)/TiO₂ catalysts may be useful in the FT reaction when the reaction is performed in the presence of small amounts of sulphur-containing gases. Studies to investigate this possibility are planned.

Acknowledgements

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