

Fe:Co/TiO₂ bimetallic catalysts for the Fischer–Tropsch reaction Part 4: A study of nitrate and carbonyl derived FT catalysts

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Abstract

A series of Fe:Co bimetallic catalysts supported on TiO₂ were prepared by precipitation from nitrate salts and by impregnation from metal carbonyl complexes. These Fe:Co materials were characterized by a range of techniques including BET, temperature programmed reduction (TPR) and CO chemisorption, and their Fischer–Tropsch (FT) activity was evaluated in a series of fixed bed reactors (220 °C, 10 bar, 2H₂:1CO, 350 h⁻¹, 200 h). Important observations from the study are (i) both preparation technique yield catalysts in which the Fe:Co/TiO₂ has lower activity than the equivalent Co/TiO₂ catalyst and (ii) selectivity patterns are similar to a Co/TiO₂ catalyst but indicate the impact of Fe on the system. Methane levels produced with the precipitated catalysts are high (20 wt%) while levels for the most active carbonyl bimetallic catalysts are lower (10 wt%). The impregnated catalysts produced from metal carbonyl precursors proved to be the better long chain hydrocarbon producers and olefin producers than the precipitated catalysts produced from metal nitrate precursors.

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1. Introduction

The Fischer–Tropsch (FT) reaction has been comprehensively studied since the 1920s and numerous reviews are available that summarise key characteristics of the reaction [1–4].

The product distribution of the metal catalysed reaction can be described by an Anderson–Schulz–Flory (ASF) law [4]. The product spectrum can be modified within the ASF constraints and one method to achieve this is via the choice of the catalyst. However, only a limited number of catalysts (Fe, Co, Ru and Ni) have been found effective for the reaction and much work has thus been performed to modify the characteristics of the catalysts (typically Fe and Co) by use of supports and promoters [5–10].

The synthesis of supported catalysts is generally performed by precipitation [11] and solution adsorption [12]. Catalysts can also be produced by techniques such as plasma

coating [13], electroless plating [14], sintering [15], fusion [16], thermal decomposition [17] etc. The choice of catalyst preparation method is influenced by the reaction environment (e.g. temperature and pressure), the cost of the active phase, the support surface area [18] and the specific catalytic properties required of the catalyst for the reaction under consideration.

An alternative strategy to modify the properties of supported catalysts is by choice of the starting metal complex [19–22]. In this methodology the ligands/ions surrounding the metal affect the interaction of the support with the metal ion and hence the metal dispersion and loading. A variant of this approach is to use different *loading* procedures, e.g. by variation of reducing agents, pH etc. The ligands surrounding the metal ion will vary depending on the solution characteristics and again the metal ion will react differently with either the support or counterions leading to different metal loadings and dispersions.

We have recently reported on the FT activity and selectivity characteristics of a range of bimetallic Fe:Co/TiO₂ catalysts prepared by the incipient wetness method from metal

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nitrate salts [23–25]. These bimetallic catalysts have shown reactivity patterns that are different from equivalent Fe or Co single metal catalysts indicating that the intimate interaction between Fe and Co is important [26–34].

To further investigate the FT reactivity patterns of Fe:Co catalysts, we have chosen to investigate the effect of preparation procedure on the reaction by preparing a range of Fe:Co/TiO₂ catalysts by: (i) the precipitation method [12] and (ii) by impregnation from metal carbonyl precursors [12,17,35–42].

2. Experimental

Commercial TiO₂ (P25, Degussa; surface area 52 m² g⁻¹; anatase:rutile ratio, 79:21) was mixed with deionized water, dried at 120 °C for 1 h and calcined at 400 °C for 16 h. In every case the calcined material was crushed and sieved (0.5–1.0 mm) to produce the required supports. The [CpFe(CO)₂]₂ and Co₂(CO)₈ starting materials were purchased from Strem Chemicals and the iron and cobalt nitrates from Merck.

2.1. Catalyst characterization

Elemental analysis (Co, Fe) was determined by atomic absorption spectroscopy (AAS). BET surface area analysis, scanning electron microscopy (SEM), Mössbauer spectroscopy (MES), temperature programmed reduction (TPR), X-ray diffraction (XRD), and CO chemisorption were performed by classical procedures on apparatus described previously [23].

It is not possible with the techniques used in this study to assess from the reduction data whether Fe or Co has been predominantly reduced. A further difficulty relates to the determination of the catalyst dispersion.

Bartholomew has discussed this issue in some detail [43]. In this study dispersion values were ascertained by using CO as the probe gas and a “factor” of 1.175 was used in the calculation,

$$\% \text{Dispersion} = \frac{[\text{factor} \times (\mu\text{mol/g CO uptake})]}{[(\% \text{metal}) \times (\text{fraction reduced})]}$$

As described previously, this value is the average value for Fe (1.170) and Co (1.179) and will be assumed to hold for the 1:1 Fe:Co catalysts used in this study [23].

IR spectra were recorded on a Bruker FTS-85 Fourier transform IR spectrometer (CH₂Cl₂ solutions).

The DRIFTS study (CO adsorption) was carried out using a Nicolet Impact 420 IR Fourier Transform spectrometer. The diffuse reflectance IR spectra were recorded using a standard reflection accessory (Harrick Scientific), equipped with a flow cell into which the ground catalyst (100 mg) was loaded [44]. DRIFTS studies were performed on Cp(CO)₂FeCo(CO)₄/TiO₂. The catalyst was loaded into the DRIFTS cell and then heated in N₂ at 250 °C for 2 h

to remove unwanted surface species. The catalyst was then cooled to room temp and CO was passed over the catalyst for 15 min. Physisorbed CO was removed by purging with nitrogen (30 ml/min) for 15 min. IR spectra were then recorded at various stages after exposure to the CO. In the reduction study the catalyst was reduced in situ at 180 °C for 2 h in 100% H₂. Ex situ studies on the reduced samples were also performed (reduction at 250 and 300 °C for 2 h, at 1 atm in 100% H₂; 2000 h⁻¹). Thereafter the samples were reduced in situ at 180 °C for 1 h. The Fe:Co/TiO₂ materials were then placed in a DRIFTS cell and background IR spectra were recorded. Addition of CO to the unreduced Fe:Co mixture resulted in CO uptake.

2.2. Catalyst preparation

2.2.1. Catalysts prepared by precipitation

Seven precipitated catalysts (10:0, 0:10, 10:10, 5:5, 5:15, 5:10 and 10:5 Fe:Co/TiO₂) were prepared in this study, utilizing well known literature procedures [11]. In each case a co-solution (80 °C) of the required amount of Fe(NO₃)₃ and Co(NO₃)₂ was precipitated with a Na₂CO₃ solution (80 °C) until a pH of approximately 7 was obtained. Degussa TiO₂ powder was then stirred into the hot precipitate and mixed thoroughly until a homogeneous mixture was obtained. The resulting precipitate was then washed with hot distilled water until nitrates were no longer detected. The washed precipitate was dried at 120 °C for 16 h and then it was crushed to 0.5–1.0 mm particles.

2.2.2. Catalysts prepared by impregnation from nitrate salts

The preparation of these Fe:Co catalytic systems by a single co-impregnation of a hot (80 °C) solution of iron and cobalt nitrates onto pre-calcined TiO₂ by incipient wetness procedures was described in detail elsewhere [23–25].

2.2.3. Preparation of CpFe(CO)₂Co(CO)₄

The mixed metal carbonyl dimer, CpFe(CO)₂Co(CO)₄, was prepared via a literature procedure [45]. Reaction of [CpFe(CO)₂]₂ with I₂ in CH₂Cl₂ gave CpFe(CO)₂I. This complex was reacted with Ag(CF₃SO₃) to produce CpFe(CO)₂(CF₃SO₃). In another flask, air sensitive Co₂(CO)₈ was reacted with sodium/amalgam in tetrahydrofuran (THF) to produce Na[Co(CO)₄]. Reaction of equimolar amounts of Na[Co(CO)₄] with CpFe(CO)₂(CF₃SO₃) gave the required dimer. Each of the intermediate organometallic complexes was isolated and characterized by infra-red spectroscopy.

2.2.4. Catalysts prepared by impregnation from metal carbonyl complexes

Four carbonyl derived supported catalysts were prepared by impregnation. These were (i) 10% Fe/TiO₂, prepared from [CpFe(CO)₂]₂, (ii) 10% Co/TiO₂, prepared from Co(CO)₈. (iii) a bimetallic mixture consisting of a 5:5 Fe:Co/TiO₂ (10%

metal by weight) prepared from $[\text{CpFe}(\text{CO})_2]_2$ and $\text{Co}(\text{CO})_8$ and (iv) a 5:5 Fe:Co/TiO₂ (10% metal by weight) material prepared from $\text{Cp}(\text{CO})_2\text{FeCo}(\text{CO})_4$.

The preparation of the supported materials was achieved by dissolving both $[\text{CpFe}(\text{CO})_2]_2$ and $\text{Co}_2(\text{CO})_8$ in dry THF under nitrogen. This solution was impregnated in a single step via incipient wetness onto the pre-prepared TiO₂ support. The impregnated system was then dried under vacuum for 16 h. In an initial study, the dried catalyst was immediately exposed to atmospheric conditions but this material proved to be pyrophoric. The procedure was changed to one in which the dried catalyst was passivated for 16 h in a 30 ml/min nitrogen diluted N₂O mixture (5N₂:1N₂O) to produce an air-stable catalyst system that could be handled under oxidizing conditions.

The preparation of the supported $\text{CpFe}(\text{CO})_2\text{Co}(\text{CO})_4$ dimer was achieved in a single impregnation step using the procedure outlined above. In this instance the dimer was impregnated via the incipient wetness technique onto a TiO₂ support under nitrogen. The synthesized dimer is air sensitive and great care was taken during the impregnation step to avoid decomposition of the dimer.

2.3. Catalyst testing

Catalysts (about 2 g) were tested in a system comprising of three stainless steel reactors with two knockout pots each, one for wax and one for liquid hydrocarbon products. The reactors used were identical to those described previously [23]. The gas product fraction was analyzed by GC as

described previously [23]. All catalysts were reduced for 16 h in pure hydrogen (1 bar) at a temperature of 300 °C and space velocity of 2000 h⁻¹. After reduction the reaction system was cooled to below 200 °C. The reaction gas, 2H₂:1CO, was introduced and the pressure, unless otherwise specified, increased to 10 bar. The gas flow was set to a space velocity of 350 h⁻¹ and the temperature increased to 220 °C. All synthesis runs, without exception, ran for a stabilization period of ca. 120 h followed by a 100–120 h mass balance period. Thus, each run exceeded 200 h on line. Mass balance calculations, the water gas shift (WGS) extent (%mass CO₂/%mass (CO₂ + H₂O)) and olefin to paraffin ratio [%mass olefin/%mass (olefin + paraffin)] were determined as described previously [23]. The specific activity (mol CO converted per gram catalyst per second) was calculated as a function of the (CO + CO₂) conversion, and thus included the percent CO converted to CO₂. Mass balance data, collected after the full time on stream, of 100 ± 5% was accepted as adequate for comparison purposes.

3. Results and discussion

3.1. Catalyst characterisation

Table 1 contains characterization data (BET surface areas, metal analysis) for the various precipitated and carbonyl derived catalysts. For comparison the data for an optimum 5:5 Fe:Co catalyst prepared from metal nitrate sources by the incipient wetness technique is also shown [23]. It is clear from

Table 1
The influence of preparation method on BET surface area, $\mu\text{mole CO}_{\text{ads}}$, %reduction and %dispersion for the Fe:Co/TiO₂ bimetallic system^a

Catalyst	BET (m ² /g)	Metal loading (%)		CO _{ads} (μmole)	Reduction level (%)	Dispersion (%)	Reduction temperature (°C)
		Fe	Co				
Impregnated ^b							
5:5	51.0	5.2	5.1	5.8	94.6	0.6	300
Precipitated ^c							
10 Fe	86.6	8.5	0	5.0	9.4	5.9	270
10 Co	83.8	0	8.4	7.5	48.9	1.8	270
10:10	78.3	10.1	10.2	4.6	70.4	0.4	270
5:15	87.4	5.1	15.2	–	–	–	–
5:5	76.0	5.1	5.1	5.4	79.9	0.8	270
5:10	86.0	5.1	10.1	–	–	–	–
10:5	87.1	11.1	5.1	–	–	–	–
Carbonyl							
10 Fe	43.5	9.6	0	3.0	5.1 ^d	6.7	250
10 Co	47.2	0	10.3	13.0	37.4 ^d	4.1	250
5:5 (Fe + Co) ^e	48.7	4.7	4.6	8.0	2.8 ^d	32.8	250
5:5 (FeCo) ^f	47.8	4.8	4.5	4.2	3.8 ^d	16.3	250

^a Support calcination: 400 °C, 1 atm, 2000 h⁻¹, 16 h, flowing air.

^b Catalyst calcination: 200 °C, 1 atm, 2000 h⁻¹, 16 h, flowing air. Data taken from ref. [24].

^c Catalyst calcination: none.

^d Low values are due to the use of low oxidation state metal carbonyl complexes used in the synthesis.

^e Fe + Co: ($[\text{CpFe}(\text{CO})_2]_2 + \text{Co}_2(\text{CO})_8$)/TiO₂; catalyst calcination: none.

^f FeCo: $(\text{CpFe}(\text{CO})_2\text{Co}(\text{CO})_4)/\text{TiO}_2$; catalyst calcination: none.

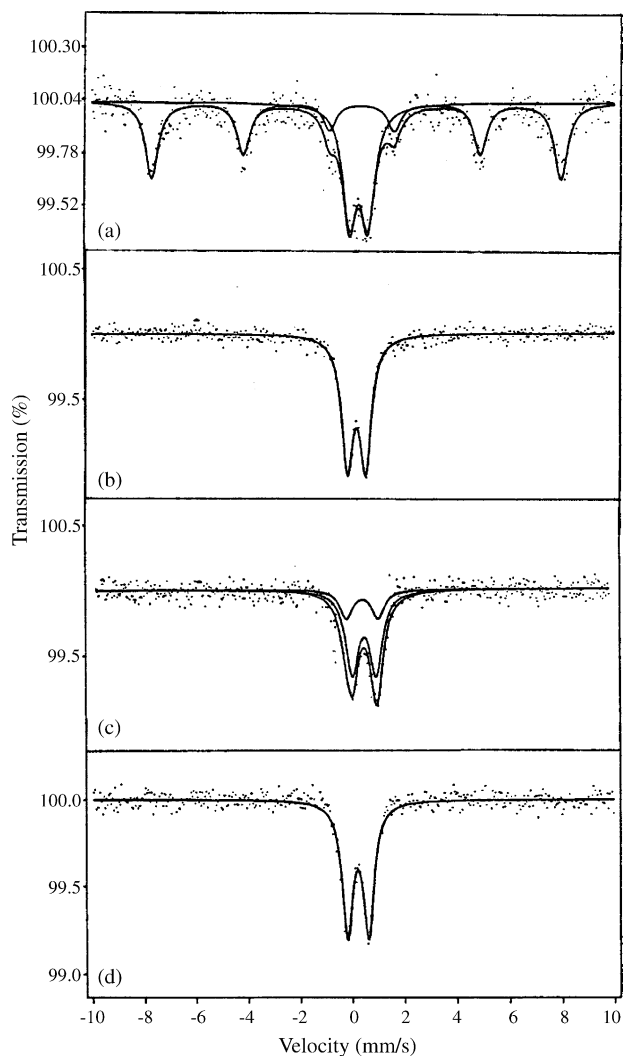


Fig. 1. Mössbauer spectra for 5:5 Fe:Co/TiO₂ systems prepared from: (a) impregnated metal nitrates, (b) precipitated metal nitrates, (c) mixed metal carbonyls (MMC) and (d) mixed metal cluster derived carbonyls (MMCC).

the AAS analysis that the required metal loadings and Fe:Co ratios were produced.

The BET surface area for the precipitated catalysts is much higher (approximately 84–87 m²/g) than that for the impregnated systems which have BET surface areas similar to those obtained for the TiO₂ support (52 m²/g). The catalysts derived from the metal carbonyls have BET surface areas in the range of 43–49 m²/g.

XRD spectra exhibited neither metal oxide nor metal peaks for the precipitated system or carbonyl derived systems (data not shown). This implies that small amorphous well-dispersed particles are formed on the titania. The carbonyl-derived systems should produce metals in a low oxidation state, due to the nature of the starting material, and would therefore not necessarily produce the expected metal oxide phases.

Fig. 1 displays the Mössbauer data (after calcination) for four different 5:5 bimetallic Fe:Co/TiO₂ (10%) ma-

terials that were synthesized: (a) impregnated Fe:Co nitrates [23–25], (b) precipitated Fe:Co nitrates, (c), impregnated [CpFe(CO)₂]₂/Co(CO)₈ and (d), impregnated Cp(CO)₂FeCo(CO)₄.

The sextet for the impregnated catalyst indicates the presence of ferromagnetic particles [46] that are not observed for the other samples. The other three samples reveal doublets, associated with superparamagnetic behaviour [47], with the precipitated and Cp(CO)₂FeCo(CO)₄ complexes giving remarkably similar spectra (see Fig. 1 and Table S1, Supplementary data). In contrast, the [CpFe(CO)₂]₂/Co(CO)₈ reveals two doublets suggestive of two different complexes or more specifically two different iron environments.

In an independent study the Mössbauer spectrum of 10% [CpFe(CO)₂]₂ on TiO₂ was measured and revealed a doublet with isomer shift = 0.22 mm s⁻¹. Further, the quadrupole splitting (0.92 mm s⁻¹) observed for the above doublet corresponds to that of the doublet observed for [CpFe(CO)₂]₂/Co(CO)₈ (Table S1, Supplementary data). Thus, the major component observed in Fig. 1 corresponds to a similar Fe derived complex, independent of the presence of Co. The origin of the second (minor) doublet is unknown but appears not to correspond to a Fe-Co supported material. (The Mössbauer spectrum of CpFe(CO)₂Co(CO)₄ has different parameters to that of the second dimer; Table S1, Supplementary data). Thus, prior to calcination the Co and Fe complexes do not interact substantially. It thus appears that the four complexes give a range of differently supported Fe (and Co) complexes.

The TPR profiles for the four Fe:Co are shown in Fig. 2. The impregnated nitrate catalysts were pre-calcined at 200 °C, while the carbonyl catalysts were used uncalcined (but passivated). The low temperature peaks (at ca 220 °C) shown in Fig. 2a and b are due to the presence of residual nitrate ions while the high temperature peak (>650 °C) is due to reaction with the support [48].

A comparison between the precipitated (Fig. 2a) and incipient wetness (Fig. 2b) catalysts reveals that the precipi-

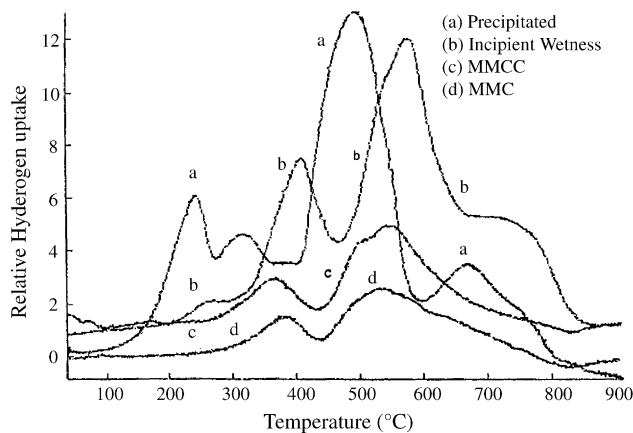


Fig. 2. TPR spectra for metal nitrate precipitated (a), nitrate impregnated (b), MMCC (c) and MMC (d) catalysts.

itated catalyst (i) contains larger quantities of nitrate ions (expected) and (ii) is easier to reduce (more porous). The shift in the two reduction peaks associated with Fe and Co metal reduction (300–600 °C) is lowered by about 100 ° (compare Fig. 2a and b).

The TPR profiles for the two titania supported metal carbonyl derived materials, namely $[\text{CpFe}(\text{CO})_2]_2/\text{Co}(\text{CO})_8$ (Fig. 2c) and $\text{Cp}(\text{CO})_2\text{FeCo}(\text{CO})_4$ (Fig. 2d) also can be compared. The presence of the reduction peaks is due partly to formation of oxidized metal in the passivation step used and also to some interaction between the support and the Fe/Co carbonyl complexes. The TPR profiles reveal that (i) no nitrate peaks are observed (nor expected) and (ii) the $[\text{CpFe}(\text{CO})_2]_2/\text{Co}(\text{CO})_8$ complex reduces at a slightly lower temperature than does $\text{Cp}(\text{CO})_2\text{FeCo}(\text{CO})_4$. Further the $\text{Cp}(\text{CO})_2\text{FeCo}(\text{CO})_4$ complex appears to interact more significantly with the support than does $[\text{CpFe}(\text{CO})_2]_2/\text{Co}(\text{CO})_8$ (broad peak at $T > 600$ °C).

In summary all four profiles reveal the presence of two major reduction peaks (between 300 and 600 °C as well as a metal support interaction ($T > 600$ °C)). It is clear that the different synthesis conditions do lead to different profiles suggestive of different Fe/Co interactions with the TiO_2 support. This is consistent with the Mössbauer data discussed above.

A SEM study of the precipitated and carbonyl derived system was performed and indicated that *both* the carbonyl derived materials had similar morphology (data not shown). As expected, the precipitated system displayed a more porous surface. This is consistent with the surface area data described above.

A reduction study was undertaken on the passivated TiO_2 impregnated $[\text{CpFe}(\text{CO})_2]_2/\text{Co}(\text{CO})_8$ and $\text{Cp}(\text{CO})_2\text{FeCo}(\text{CO})_4$ systems and data are shown in Table 2. The reduction levels for these systems were low (as expected) and increased with increasing reduction temperature. The data do suggest that the reduced particles sinter with temperature as indicated by chemisorption data and this is consistent with the reduced FT activity that is observed with increased reaction temperature (see below). While no comparable study was undertaken with the precipitated Fe:Co catalysts, simi-

lar results were obtained for the metal nitrate impregnated system [23–25].

IR studies complemented by thermal decomposition studies have been performed on numerous metal carbonyl systems, both supported and unsupported, to provide data on the formation of active catalyst centers [49,50]. Indeed DRIFTS and TPO/TPD studies have been performed on both $[\text{CpFe}(\text{CO})_2]_2$ and $\text{Co}_2(\text{CO})_8$ in the past. The decomposition of $[\text{CpFe}(\text{CO})_2]_2$ on alumina has been described and occurs with formation of ferrocene [40]. While this may provide a pathway for decomposition of the $\text{CpFe}(\text{CO})_2$ fragment its presence was not observed in this study when the materials were supported on TiO_2 [51].

CO absorption experiments were performed in this study by DRIFTS on a range of reduced metal carbonyl complexes supported on TiO_2 (10% metal loadings; see experimental section for details; Fig. 3). Interestingly within the accuracy of the experiment the $[\text{CpFe}(\text{CO})_2]_2$, $[\text{CpFe}(\text{CO})_2]_2/\text{Co}_2(\text{CO})_8$ and $\text{Cp}(\text{CO})_2\text{FeCo}(\text{CO})_4$ all gave similar IR spectra. All three spectra show a maximum absorption at $2002 \pm 2 \text{ cm}^{-1}$, a value that corresponds to CO adsorbed on a metal in the zero oxidation state. The results indicate that reaction with CO took place on the Fe and that the environment of the Fe atoms on the TiO_2 was similar for all three systems. Further, the IR spectrum recorded on $\text{Co}_2(\text{CO})_8/\text{TiO}_2$ (Fig. 3b) showed an IR spectrum more complex than that of the other spectra. While a peak was also observed at 2004 cm^{-1} (Co–CO) a further peak was observed at 2033 cm^{-1} (possibly due to Co with +1 oxidation state bonded to CO).

3.2. FT catalyst testing

3.2.1. Precipitated Fe:Co/ TiO_2

The results for the FT synthesis behaviour of a range of precipitated Fe:Co/ TiO_2 catalysts are reported in Table 3. The basic trends found are similar to those previously reported for incipient wetness systems [23–25].

The data reveal that the reactivity ranking for 10% loadings is $\text{Co} > 5:5 \text{ Fe:Co} > \text{Fe}$. However, in terms of metal reduction the order is $5:5 \text{ Fe:Co} > \text{Co} > \text{Fe}$ (Table 1).

Table 2

The effect of reduction temperature on the $\mu\text{mole CO}_{\text{ads}}$, %reduction and %dispersion for the carbonyl derived bimetallic systems

Catalyst (5Fe:5Co) ^a	Reduction temperature (°C)	CO_{ads} (μmole)	Reduction (%)	Dispersion (%)
Fe + Co ^b	250	8.0	2.8	32.8
	300	7.8	18.8	4.8
	400	6.9	32.0	2.5
FeCo ^c	250	4.2	3.8	16.3
	300	4.0	23.2	2.0
	400	3.4	48.2	0.8

^a Catalyst composition: 5Fe:5Co/ TiO_2 (total metal loading 10% by weight).

^b Fe + Co: ($[\text{CpFe}(\text{CO})_2]_2 + \text{Co}_2(\text{CO})_8$)/ TiO_2 ; catalyst calcination: none.

^c FeCo: $(\text{CpFe}(\text{CO})_2\text{Co}(\text{CO})_4)/\text{TiO}_2$; catalyst calcination: none.

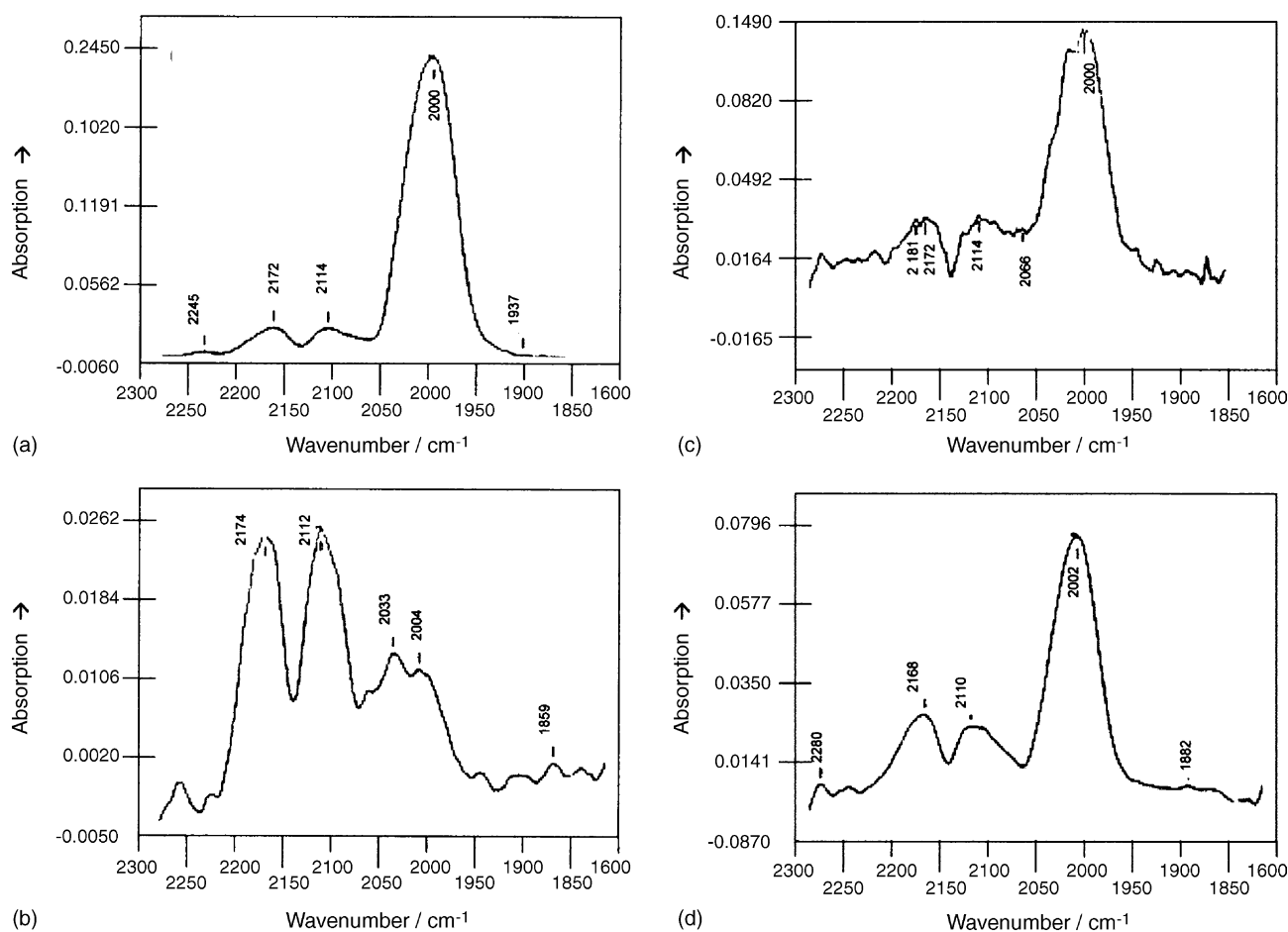


Fig. 3. DRIFTS spectra of reduced (100% H₂, 180 °C, 2 h) carbonyl catalysts: (a) 10% Fe/TiO₂, (b) 10% Co/TiO₂, (c) 5% Fe + 5% Co and (d) (5% + 5%) FeCo catalysts after CO adsorption at 25 °C. All percentage by weight.

There are indications that the improved level of reduction is a consequence of a decrease in the catalyst dispersion (Table 1, Fig. S1, Supplementary data) as discussed previously [23–25]. It is however clear that the improved level of reduction gives no improved effect on the activity of the 1:1 system when compared with the single metal Co system.

The %CO conversion, specific activity and TON all increase as the system contains more cobalt and less iron. Furthermore, the 10% Co catalyst is more active than the 5:5 Fe:Co catalyst. This indicates that, as for the impregnated systems [23–25], there is no advantage to be gained *with respect to activity* on mixing Fe and Co.

The effect of total metal loading, is shown from a comparison of the 5:5 and 10:10 Fe:Co/TiO₂ systems. Although the higher loaded material exhibited higher specific activity (0.24 versus 0.33 μmole/g/s) and the TON increased from $44.4 \times 10^{-3} \text{ s}^{-1}$ to $71.3 \times 10^{-3} \text{ s}^{-1}$, the effect was less than expected. As these catalysts appear to have similar BET surface areas (78.3 m²/g versus 76.0 m²/g) and the 5:5 system shows slightly better reduction (80% versus 70%) and dispersion levels (0.8 and 0.4%) it can be assumed that the loss in activity is due to a decrease in the amount of Co active phase.

A mixed Fe:Co catalyst does give important selectivity differences relative to the single metal catalysts. Thus, a very low selectivity towards methane is noted for Co/TiO₂ while mixtures of Fe:Co give enhanced methane formation. Indeed it appears that as the Fe content increases the methane content goes up (e.g. 10:10 Fe:Co has CH₄ content of 20% compared to 8% for the Co/TiO₂ catalyst).

The Fe/TiO₂ catalyst produces olefins and oxygenates and also exhibits a much higher activity for the WGS reaction (18%) when compared to the Co/TiO₂ system. The cobalt catalyst also exhibits better hydrocarbon chain growth probabilities as is evident from the alpha values ($\alpha = 0.90$ cobalt; $\alpha = 0.83$ iron). Mixing of the two metals gave similar results to that obtained for these systems prepared by the incipient wetness technique [23–25]. The data obtained in this study are indeed similar to results obtained by Nakamura et al. [52] on unpromoted Fe and Co/TiO₂ materials. In the Nakamura study the selectivity of the cobalt system towards methane at ca. 85% was much higher than that observed for iron at ca. 35%. The iron system was again the superior olefin producer.

The bimetallic system in many ways performs like a single metal cobalt system producing similar C₂–C₄ yield and paraffinity content. Comparison of catalysts with 5:10 and

Table 3

The Fischer–Tropsch^a performance of precipitated Fe:Co/TiO₂ bimetallic catalysts reduced at 270 °C

Metal ratio	10:0	5:10	10:10	5:15	5:5	10:5	0:10
Metal loading (% by mass)	10	15	20	20	10	15	10
CO conversion (%)	15.8	17.4	21.8	29.9	17.1	15.4	22.5
Specific activity ($\mu\text{mole CO s}^{-1} \text{ g}^{-1}$)	0.18	0.27	0.33	0.55	0.24	0.20	0.37
TON ($\times 10^{-3} \text{ s}^{-1}$)	36.0	–	71.7	–	44.4	–	49.3
Selectivity (% by mass)							
CH ₄	9.3	13.1	19.6	18.4	17.0	22.8	7.8
C ₂ –C ₄	25.8	16.1	21.4	13.7	13.0	31.9	6.8
C ₅ –C ₁₁	61.8	36.5	39.9	45.1	36.8	44.2	27.2
C ₁₂ –C ₁₈	2.7	7.9	6.9	15.2	12.6	tr	22.0
+C ₁₈	tr	25.9	2.3	7.4	20.1	tr	35.6
WGS extent	0.18	tr	0.05	0.05	0.07	0.09	tr
Paraffin (%)	55.6	88.7	89.7	92.8	89.5	81.3	92.4
Olefin (%)	39.2	9.5	9.1	6.4	9.2	12.0	6.5
Oxygenates (%)	5.2	1.9	1.3	1.0	1.3	6.6	1.0
Lower olefinit ^b							
C ₂	0.12	0.04	tr	0.04	0.05	0.04	tr
C ₃	0.84	0.40	0.49	0.44	0.52	0.35	0.60
C ₄	0.85	0.47	0.41	0.38	0.46	0.52	0.52
C ₅	0.34	0.30	0.21	0.03	0.13	0.27	0.33
ASF chain growth values							
A ₁	0.83	0.78	0.69	0.79	0.78	0.71	0.90
A ₂	–	–	0.77	–	–	–	–

^a Reaction conditions: calcination: none; reduction: 270 °C, 1 atm, 2000 h⁻¹, 16 h, 100% H₂; synthesis: 220 °C, 10 bar, 350 h⁻¹, 200 h, 2H₂:1CO.^b (Olefin/olefin + paraffin) ratio.

10:5 Fe:Co loadings revealed that these systems gave similar conversions and were comparable in terms of specific activity and product selectivity. The 10:5 system however gave the highest olefinic and oxygenate yields as well as higher WGS activity.

Comparison of the 5:15 and 10:10 Fe:Co catalysts (i.e. 20% total metal by mass) revealed similar trends (Table 3). The catalyst with the higher cobalt loading gave better hydrocarbon chain growth (alpha values of 0.79 and 0.69, respectively). Both catalysts showed similar selectivity towards methane while the higher iron containing system yet again displayed a preference for the production of olefins, oxygenates and WGS activity.

Fe:Co catalysts reported by Nakamura and co-workers [52], also showed that the product selectivities were associated with the most abundant metal.

A comparison of the 5:5 and 10:10 Fe:Co/TiO₂ systems revealed that the 5:5 system is the superior higher hydrocarbon producing catalyst. Similar selectivity towards olefins, oxygenates and WGS activity is observed for the 5:5 and the 10:10 Fe:Co catalysts. A comparison of the 5:5 Fe:Co system with, 10% Fe/TiO₂ and 10% Co/TiO₂ reveals that both the catalyst activity and product selectivity, with the exception of methane, is intermediate between the two single metal 10% loaded catalysts.

3.2.2. Impregnated Fe:Co carbonyl systems

The results for the FT synthesis behaviour of CpFe(CO)₂Co(CO)₄ and [CpFe(CO)₂]₂/Co₂(CO)₈ on TiO₂

is reported in Table 4. FT runs were recorded on each sample after the catalysts were reduced at three different temperatures (250, 300 and 400 °C). The most active catalysts were those reduced at the lowest reduction temperature (250 °C). The FT catalytic activity of [CpFe(CO)₂]₂ and Co₂(CO)₈ on TiO₂ was then recorded after the catalyst had been reduced at 250 °C to provided reference data for the study.

Under the reaction conditions used it was observed that the 10% Co/TiO₂ system possessed superior activity when compared to the 10% Fe/TiO₂ catalyst (1.161 $\mu\text{mole/g/s}$ compared to 0.133 $\mu\text{mole/g/s}$). This superior activity has previously also been observed for Co₂(CO)₈ supported on high surface area carbon [53,54] and Al₂O₃ [55] relative to Fe(CO)₅/Al₂O₃ and Fe₃(CO)₁₂/carbon systems. The cobalt catalyst yet again proved to be the better higher hydrocarbon producing system. The iron catalyst was found to be superior in the production of olefins and oxygenates, and also exhibited the highest WGS activity. These trends have also been confirmed by literature studies on related Fe(CO)₅/Al₂O₃ and Fe₃(CO)₁₂/carbon supported catalysts [53–55].

The effect of mixing the iron and cobalt on the activity and selectivity of the bimetallic catalyst activity is indicated in Table 4 (and Fig. S2, Supplementary data). Table 2 reveals that CpFe(CO)₂Co(CO)₄ and [CpFe(CO)₂]₂/Co₂(CO)₈ on TiO₂ show similar levels of reduction, i.e. 3.8 and 2.8%, respectively, with the latter containing the better dispersed metal. As the Fe:Co catalysts were already partially reduced no correlation between the catalyst performance and reducibility was expected [23–25] or found. However the

Table 4
The Fischer–Tropsch performance of carbonyl derived Fe:Co/TiO₂ bimetallic catalysts^a

Catalyst metal loading (% by weight)	[CpFe(CO) ₂] ₂ + Co ₂ (CO) ₈ (5% Fe + 5% Co = 10%)			Cp(CO) ₂ FeCo(CO) ₄ (5% Fe + 5% Co = 10%)			Fe (10%)	Co (10%)
	250	300	400	250	300	400	250	250
Reduction temperature (°C)								
CO conversion (%)	36.2	32.3	24.9	36.2	23.7	12.0	16.1	67.4
Specific activity (μmole CO s ⁻¹ g ⁻¹)	0.41	0.34	0.25	0.35	0.21	0.10	0.13	1.16
TON (× 10 ⁻³ s ⁻¹)	51.3	43.6	36.2	83.3	52.5	29.4	43.3	89.2
Selectivity (% by mass)								
CH ₄	9.8	11.2	12.2	9.1	20.0	18.1	9.2	15.6
C ₂ –C ₄	23.5	21.2	26.4	9.7	23.6	33.0	24.4	10.4
C ₅ –C ₁₁	48.8	50.9	53.9	37.1	43.3	48.1	38.8	36.6
C ₁₂ –C ₁₈	11.8	9.4	6.7	23.4	6.2	0.3	21.4	16.5
+C ₁₈	5.9	7.1	0.4	20.7	6.6	tr	6.0	20.3
WGS extent	0.05	0.06	0.04	0.07	0.05	0.04	0.22	0.04
Paraffin (%)	70.2	71.8	67.1	83.4	60.2	52.8	68.0	94.1
Olefin (%)	28.4	26.5	30.3	15.9	38.3	44.4	27.7	3.9
Oxygenates (%)	1.4	1.8	2.7	0.7	1.5	2.8	4.3	2.0
Lower olefinitiy ^b								
C ₂	0.09	0.10	0.10	0.12	0.21	0.20	0.20	0.01
C ₃	0.65	0.65	0.64	0.58	0.70	0.68	0.55	0.13
C ₄	0.62	0.64	0.64	0.52	0.75	0.87	0.83	0.22
C ₅	0.53	0.54	0.54	0.46	0.70	0.67	0.57	0.21
ASF chain growth values								
α ₁	0.75	0.71	0.79	0.85	0.67	0.70	0.72	0.75
α ₂	0.82	–	0.68	0.88	–	–	–	0.85

^a Reaction conditions: calcination: none; reduction: (see above) °C, 1 atm, 2000 h⁻¹, 16 h, 100% H₂; synthesis: 220 °C, 10 bar, 350 h⁻¹, 200 h, 2H₂:1CO.

^b (Olefin/olefin + paraffin) ratio.

% dispersion correlated with catalyst performance (TON) (see Supplementary data).

The selectivity data is displayed (or shown) Table 4 (and Fig. S3, Supplementary data) and indicates similar methane levels for the CpFe(CO)₂Co(CO)₄ and [CpFe(CO)₂]₂/Co₂(CO)₈ on TiO₂ catalysts. The selectivity data are also similar to data obtained for the iron system. The olefin and C₂–C₄ fractions for the [CpFe(CO)₂]₂/Co₂(CO)₈ on TiO₂ catalyst is comparable to that of the single metal iron system while the CpFe(CO)₂Co(CO)₄ on TiO₂ catalyst in general appears to have the better C₅⁺ selectivity.

A significant observation made for the CpFe(CO)₂Co(CO)₄ and [CpFe(CO)₂]₂/Co₂(CO)₈ on TiO₂ systems is the activity dependence on the temperature of reduction, i.e. decreasing activity with an increase in reduction temperature from 250 to 400 °C (Table 4). Both systems display the highest activity when reduced at 250 °C. Chen et al. [53–54] also observed the activity of carbonyl derived Fe:Co carbon supported bimetallic systems to be superior when reduced at 200 °C instead of 400 °C. The reverse behaviour was however found for the single metal systems. They attributed this increased reducibility for the bimetallic systems to the ability of cobalt to facilitate the reduction of the iron in the bimetallic system. As alternative explanation is that cobalt shows a tendency to sinter on a support when reduced at high temperatures [53,54] and this might apply to the carbonyl derived systems.

The two bimetallic systems, when reduced at 250 °C, have similar conversions, i.e. 36.2%, (Table 4) but the [CpFe(CO)₂]₂/Co₂(CO)₈ system proved to be mainly a petrol producer. The CpFe(CO)₂Co(CO)₄ system, in line with previous findings [56], displayed a strong tendency to produce higher molecular weight hydrocarbons. The [CpFe(CO)₂]₂/Co₂(CO)₈ system also proved to be the better olefin producer.

For both the [CpFe(CO)₂]₂/Co₂(CO)₈ and CpFe(CO)₂Co(CO)₄ systems, it is not possible to make deductions concerning the effect of reduction temperature on the product selectivity within the reduction series studied, as large differences in activity were observed. It is however clear that the catalyst displaying the highest activity had product selectivity trends similar to that of the Co system. The least active system mimicked the Fe system. It is also clear that both the carbonyl derived bimetallic systems yielded high selectivity towards olefin products which is much greater than that found for any of the incipient wetness and precipitated bimetallic systems [57].

These results furthermore differ markedly from those obtained by Chen and co-workers [53–55] for unpromoted Co₂(CO)₈ and Fe₃(CO)₁₂ and bimetallic mixtures of Fe and Co supported on high surface area carbons. These catalysts were evaluated at 225 °C, 3H₂:1CO and 1 atm pressure. Clusters synthesized from Co₂(CO)₈ and [CpFe(CO)₂]₂ and supported on Al₂O₃ were studied by Khomenko et al. [55]. They

also found that olefin production was inhibited by mixing of the metals. Differences observed between the systems studied by Khomenko and those evaluated here relates to the different supports and the level of metal loading (1–5% compared to the 10% in these studies).

Although the olefin selectivity for the bimetallic system is as high as that for the iron system, the WGS activities are very low, and similar to data observed for the cobalt system. This suggests that the resulting products are not just created from mixing two metals, but that a new catalyst with new catalytic features has been synthesized. Low CO₂ yield and selectivity to oxygenate compounds was also evident from studies performed by Armstrong and co-workers on [H_nFeCo₃(CO)₁₂]ⁿ⁻¹ systems supported on a partially dehydroxylated silica or aminated silica [56,58].

Finally, it is interesting to note that the [CpFe(CO)₂]₂/Co₂(CO)₈ catalyst is the only system which, on a selectivity basis, can be compared to that of a commercial potassium promoted fused Fe catalyst employed in the SASOL Synthol (high temperature Fischer–Tropsch) process [16]. This indicates the flexibility that is possible with Fischer–Tropsch catalysts.

3.2.3. Comparison of the different synthetic methodologies

A study of mixed metal catalysts containing Fe and Co from two different source materials, i.e. nitrates and carbonyls has revealed that both procedures produce materials with good Co–Fe interactions after pretreatment (calcination and reduction procedures). Indeed this is further revealed by the study entailing the use of metal carbonyl complexes involving CpFe(CO)₂Co(CO)₄. The results obtained were comparable to those obtained for nitrate based impregnated Fe:Co/TiO₂ bimetallic catalysts reported elsewhere [23–25]. The most important observations from the current study (and previous studies) can be summarized as follows:

Activity: Mixing iron and cobalt metals inhibits the total activity relative to a single metal cobalt catalyst (precipitation technique and impregnation methods using nitrates or carbonyl complexes). For all catalyst preparation methods the key issue relates to the Fe:Co catalyst ratio and appears to be independent of how the Fe and Co are mixed together.

Selectivity: The selectivity of the catalysts resembles Co rather than Fe. However, the selectivities are influenced by the Fe:Co ratios and the method of preparation. It is this behavior that clearly is influenced by the preparation techniques used to make bimetallic catalysts. For example, methane levels produced with the precipitated catalysts are high (20%), while values for the most active carbonyl bimetallic catalysts are much lower (10%). The carbonyl systems also proved to be the better lower olefin producers and also exhibited superior WGS activity.

4. Conclusions

The synergic effect found in mixed Fe:Co/TiO₂ catalysts is the common feature observed that is independent of the catalyst preparation route. The actual selectivity and activity observed for these materials is determined by the processing and preparation conditions, Fe:Co ratios and metal sources—but all in a predictable manner.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.molcata.2005.04.029](https://doi.org/10.1016/j.molcata.2005.04.029).

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