

# Fe:Co/TiO<sub>2</sub> bimetallic catalysts for the Fischer–Tropsch reaction Part 2. The effect of calcination and reduction temperature

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## Abstract

The effect of support calcination temperature as well as catalyst calcination and reduction temperature on the performance (activity and selectivity) of a Fe:Co/TiO<sub>2</sub> catalyst has been investigated. Various techniques (CO chemisorption, TPO, TPR, DSC, BET and Mössbauer Spectroscopy) have been utilized to relate the performance of the above catalyst system to the physical and chemical nature of the catalyst, surface structural stability and various other properties. It was found that a higher support calcination temperature increased the stability of the final catalyst while the catalyst calcination temperature played a lesser role in influencing catalyst performance. Catalyst reduction temperature increased the surface atom ratio, degree of reduction and CO chemisorption, and hence the active metal dispersion, and overall catalytic behaviour. © 2002 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

It has been reported in the literature that addition of a mixture of two active Fischer–Tropsch (FT) metals can produce catalysts with chemical, physical and catalytic properties that are not directly related to a knowledge of the properties of the separate metals. For example, addition of small amounts (<1%) of ruthenium to cobalt catalysts has given Co:Ru supported catalysts with activity much higher than expected from a knowledge of either the separate Co or Ru supported catalysts [1–3]. Numerous other reports have appeared in the literature, which highlight this interesting finding [4].

We have thus, commenced a series of studies to assess the range and generality of the influence of two catalytically active metals on each other in terms of their physical and chemical properties. In a recent study we reported on the synthesis, characterization and catalytic activity of a series of Fe:Co/TiO<sub>2</sub> catalysts (10–20% total metal loading) in which the Fe:Co ratio was varied [5]. In a continuation of these studies we now report on the influence of support calcination temperature and catalyst calcination/reduction temperatures on the performance of a 1:1 Fe:Co/TiO<sub>2</sub> catalyst. This 1:1 Fe:Co catalyst was noted in our previous study [5] to give optimal activity/selectivity catalyst characteristics when compared to other Fe:Co metal ratios.

Numerous other reports have appeared in the literature since our earlier publication [5] on the synthesis and use of both supported [6] and unsupported [7–11] Fe:Co catalyst mixtures.

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Table 1  
Effect of TiO<sub>2</sub> support calcination temperature on the Fe:Co/TiO<sub>2</sub> catalysts<sup>a</sup>

	Support calcination temperature (°C)		
	200	300	400
CO conversion (%)	29.8	34.9	36.3
Specific activity (μmol/(g/s))	0.33	0.43	0.40
TOF (× 10 <sup>-3</sup> /s)	88.0	78.0	70.0
Selectivity (% by mass)			
CH <sub>4</sub>	8.4	9.7	11.0
C <sub>2</sub> –C <sub>4</sub>	10.2	11.9	14.6
>C <sub>5</sub>	81.2	78.4	74.2
WGS extent	0.14	0.02	≈0.05
Paraffin (%)	84.6	77.0	82.9
Olefin (%)	13.4	20.5	15.8
Oxygenates (%)	2.0	2.5	tr
BET surface area (m <sup>2</sup> /g)			
Fresh	57.0	61.0	52.0
Used	55.0	58.0	54.0
Reduction (%)	84.9	86.5	90.0
Dispersion (%)	0.5	0.7	0.6
ASF chain growth values (α)	0.82 <sup>b</sup>	0.81	0.71

<sup>a</sup> Reaction conditions: calcination—200 °C, 1 atm, 2000 h<sup>-1</sup>, 16 h, flowing air; reduction—300 °C, 1 atm, 2000 h<sup>-1</sup>, 16 h, 100% H<sub>2</sub>; synthesis—220 °C, 10 bar, 350 h<sup>-1</sup>, 200 h, 2H<sub>2</sub>:1CO.

<sup>b</sup> α<sub>2</sub> value detected = 0.84.

Table 2  
The effect of support calcination temperature on the Mössbauer parameters of Fe:Co/TiO<sub>2</sub> bimetallic catalysts

T <sup>a</sup> (°C)	IS <sub>1</sub> <sup>b</sup> (mm/s)	QS <sub>1</sub> <sup>c</sup> (mm/s)	W <sub>1</sub> <sup>d</sup> (mm/s)	M <sup>e</sup> (%)	IS <sub>2</sub> <sup>f</sup> (mm/s)	QS <sub>2</sub> <sup>g</sup> (mm/s)	W <sub>2</sub> <sup>h</sup> (mm/s)	PM <sup>i</sup> (%)	Hi <sup>j</sup> (kOe)	PM/M(d)
Support calcination temperature <sup>k</sup>										
200	0.41	0.16	0.33	43.8	0.38	0.75	0.26	56.2	483	1.3
300	0.42	0.20	0.38	45.9	0.39	0.75	0.26	54.1	482	1.2
400	0.39	0.21	0.30	55.8	0.39	0.70	0.32	44.2	487	0.8
Catalyst calcination temperature <sup>l</sup>										
200	0.40	0.21	0.29	46.4	0.37	0.77	0.29	53.7	494	1.2
400	0.47	0.24	0.36	34.5	0.44	0.80	0.27	65.5	487	1.9
Error (±)	0.02	0.02	0.02	–	0.02	0.02	0.02	–	10	–

<sup>a</sup> Temperature.

<sup>b</sup> Isomer shift (doublet).

<sup>c</sup> Quadruple splitting (doublet).

<sup>d</sup> Half width (doublet).

<sup>e</sup> M: percent magnetic attribution.

<sup>f</sup> Isomer shift (sextet).

<sup>g</sup> Quadruple splitting (sextet).

<sup>h</sup> Half width (sextet).

<sup>i</sup> PM: percent paramagnetic attribution.

<sup>j</sup> Field strength.

<sup>k</sup> Catalyst calcined at 200 °C.

<sup>l</sup> Support calcined at 400 °C.

## 2. Experimental

Commercial TiO<sub>2</sub> (P25, Degussa) was mixed with deionized water, dried at 120 °C for 1 h and calcined. Standard calcination of the TiO<sub>2</sub> was performed at

400 °C for 16 h, but calcination at other temperatures (200, 300 °C) was also carried out. In every case the calcined support was crushed and sieved (0.5–1.0 mm) to produce particles for both characterization and reactor studies (Tables 1 and 2).

Table 3

Influence of catalyst calcination and reduction temperature on the Fe:Co/TiO<sub>2</sub> bimetallic systems (5% Fe:5% Co/TiO<sub>2</sub>)<sup>a</sup>

	Reduction temperature (°C)			
	250	300	350	400
Calcination temperature (200 °C)				
CO conversion (%)	16.01	36.25	25.77	14.09
Specific activity (μmol/(g/s))	0.272	0.397	0.242	0.117
Product selectivity (% by mass)				
CH <sub>4</sub>	19.01	10.96	19.90	23.15
C <sub>2</sub> –C <sub>4</sub>	14.97	14.62	24.58	25.12
+C <sub>5</sub>	65.85	74.15	54.95	51.73
Paraffins	87.62	82.87	65.22	88.86
Olefins	2.37	15.78	32.56	11.14
Oxygenates	10.01	1.35	2.22	tr
WGS extent	0.05	tr	tr	tr
ASF chain growth (α)	0.72 <sup>b</sup>	0.71 <sup>b</sup>	0.77	0.75
Calcination temperature (300 °C)				
CO conversion (%)	24.08	33.24	28.58	16.39
Specific activity (μmol/(g/s))	0.231	0.367	0.319	0.139
Product selectivity (% by mass)				
CH <sub>4</sub>	12.22	8.44	7.62	18.61
C <sub>2</sub> –C <sub>4</sub>	6.45	10.00	10.25	27.76
+C <sub>5</sub>	81.33	79.98	81.31	53.93
Paraffins	99.92	88.54	89.41	86.76
Olefins	0.08	9.50	9.41	13.24
Oxygenates	tr	1.96	1.18	tr
WGS extent	0.05	0.07	tr	tr
ASF chain growth (α)	0.85	0.78	0.84	0.65
Calcination temperature (400 °C)				
CO conversion (%)	23.27	33.77	28.79	19.18
Specific activity (μmol/(g/s))	0.206	0.317	0.250	0.200
Product selectivity (% by mass)				
CH <sub>4</sub>	20.48	17.53	15.67	11.72
C <sub>2</sub> –C <sub>4</sub>	14.66	16.89	22.04	18.83
+C <sub>5</sub>	64.86	65.59	62.29	69.45
Paraffins	100.00	93.11	91.81	89.36
Olefins	tr <sup>c</sup>	6.89	8.19	10.64
Oxygenates	tr	tr	tr	tr
WGS extent	tr	tr	tr	tr
ASF chain growth (α)	0.82	0.81	0.76	0.78

<sup>a</sup> Reaction conditions: calcination—1 atm, 2000 h<sup>-1</sup>, 16 h, flowing air; reduction—1 atm, H<sub>2</sub>, 2000 h<sup>-1</sup>, 16 h; synthesis—220 °C, 10 bar, 2H<sub>2</sub>:1CO, 350 h<sup>-1</sup>, 200 h.

<sup>b</sup> α<sub>2</sub> = 0.85.

<sup>c</sup> tr = trace.

Table 4

Temperature programmed analysis data for Fe:Co/TiO<sub>2</sub> bimetallic catalytic systems

	Reduction temperature (°C)		
	250	300	400
Calcination temperature (200 °C)			
CO chemisorbed (μmol/g catalyst)	6.0	5.8	5.0
Reduction (%)	66.0	94.6	96.7
Dispersion (%)	1.0	0.6	0.6
Specific activity (10 <sup>-3</sup> μmol/(g/s))	272	397	117
TOF (× 10 <sup>-3</sup> /s)	45	68	23
Calcination temperature (300 °C)			
CO chemisorbed (μmol/g catalyst)	9.1	9.2	5.1
Reduction (%)	58.0	90.5	96.9
Dispersion (%)	1.8	1.2	0.6
Specific activity (10 <sup>-3</sup> μmol/(g/s))	231	367	139
TOF (× 10 <sup>-3</sup> /s)	25	40	27
Calcination temperature (400 °C)			
CO chemisorbed (μmol/g catalyst)	7.3	7.0	8.5
Reduction (%)	39.8	77.5	82.0
Dispersion (%)	2.1	1.1	1.1
Specific activity (10 <sup>-3</sup> μmol/(g/s))	206	317	200
TOF (× 10 <sup>-3</sup> /s)	28	45	24

The supported Fe:Co catalyst was synthesized as described previously i.e. by co-impregnation of a hot (80 °C) solution of iron and cobalt nitrates into the pre-calcined TiO<sub>2</sub> by incipient wetness procedures. The impregnated particles of nominal composition 5% Fe:5% Co by mass were dried at 120 °C for 2 h and then calcined (16 h, air) and reduced (16 h, pure H<sub>2</sub>, 1 bar) at different temperatures prior to characterization and testing (Tables 3–6).

### 2.1. Catalyst characterization

Elemental analysis (Co, Fe) was determined by atomic absorption spectroscopy. BET surface area analysis, differential scanning calorimetry (DSC), temperature programmed reduction (TPR), temperature programmed oxidation (TPO), Mössbauer spectroscopy and CO chemisorption/desorption were performed by classical procedures on apparatus described previously [5].

### 2.2. Catalyst testing

Catalysts (~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 gas product fraction was analyzed by GC as described previously [5].

All catalysts were activated (reduced) for a 16 h period on line in pure hydrogen (1 bar) at temperatures specified in the tables and Section 3. After reduction the reaction system was cooled to below 200 °C. The

Table 5

Effect of reduction temperature on percent reduction (R), percent dispersion (D) and CO chemisorption<sup>a</sup>

Reduction temperature (°C)	CO adsorbed (μmol)	R (%)	D (%)
10% Co/TiO <sub>2</sub>			
250	2.9	57.1	0.6
300	5.1	74.0	0.8
400	16.9	85.5	2.4
10% Fe/TiO <sub>2</sub>			
250	6.6	12.3	6.0
300	5.2	35.4	1.6
400	4.7	33.3	1.6
10% Fe:Co/TiO <sub>2</sub>			
250	6.0	66.0	1.0
300	5.8	94.6	0.6
400	5.0	96.7	0.6

<sup>a</sup> Calcined at 200 °C.

Table 6  
Effect of catalyst reduction and calcination temperatures on BET surface areas

Calcination temperature (°C)	Reduction temperature (°C)	BET surface area (m <sup>2</sup> /g)
200	–	51
200	250	63
200	300	57
200	350	54
200	400	52
300	300	58
400	300	63

reaction gas, 2H<sub>2</sub>:1CO, was introduced and the pressure, unless otherwise specified, increased to 10 bar. The gas flow was set to a space velocity = 350 h<sup>-1</sup> and the temperature raised 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 CO<sub>2</sub>/% mass (CO<sub>2</sub> + H<sub>2</sub>O)) and olefin to paraffin ratio (% mass olefin/% mass (olefin + paraffin)) were determined as described previously [5]. The specific activity (mol CO converted per gram catalyst per second) was calculated as a function of the (CO + CO<sub>2</sub>) conversion, and thus included the percent CO converted to CO<sub>2</sub>. Mass balance data of 100 ± 5% was accepted as adequate for comparison purposes.

### 3. Results and discussion

#### 3.1. The effect of TiO<sub>2</sub> calcination temperature

Generally the effect of support calcination temperature is not considered in studies of supported FT catalysts [12–14]. To study this effect, TiO<sub>2</sub> was calcined at 200, 300 and 400 °C and then either analysed or loaded with 5% Fe:5% Co for analysis and use in the FT reaction.

##### 3.1.1. Anatase:rutile ratio

XRD spectra were recorded on the calcined TiO<sub>2</sub> (200–400 °C) and no changes in the anatase:rutile (A:R) ratio (72/28) were observed. Fe and Co were loaded onto the TiO<sub>2</sub> and XRD spectra were recorded

after both catalyst reduction and FT reaction. With one exception, the XRD A:R ratio did not change. The only change (to a 66/34 ratio) that did occur took place when a reduction and calcination temperature of 400 °C was used. TiO<sub>2</sub> converts from the anatase to the rutile phase at about 800 °C [15–22], but it has been reported that Fe<sup>2+</sup> can assist the phase transformation at temperatures of about 400 °C [23]. Our results thus, indicate that the A:R ratio does not change under the FT conditions used in this study.

##### 3.1.2. Surface area

The surface area measurements for a series of Fe:Co/TiO<sub>2</sub> samples in which the support calcination temperature was varied are given in Table 1. Some small variation in surface area between samples is to be noted. The data also reveal that no significant change in the surface area occurs during the FT reaction.

##### 3.1.3. Weight loss

A thermogravimetric analysis study of the weight loss of the support as a function of support calcination revealed a weight change of about 0.4% for all three samples (data not shown). A DSC study (not shown) also revealed a small endothermic peak due to water loss for the three samples

##### 3.1.4. Dispersion (Fe) and reduction

Mössbauer spectra were recorded on the Fe:Co/TiO<sub>2</sub> samples (different TiO<sub>2</sub> calcination temperatures) prior to reduction and use in the FT reaction and the data are given in Table 2 and Fig. 1. The data were fitted to a doublet and a sextet. Spectral analysis indicates a decrease in the super-paramagnetic features (56–44%) as the support calcination temperature increases from 200 to 400 °C. This corresponds to a change in the average Fe particle size shift from 5–10 nm (200 °C) to 50–80 nm (400 °C). Thus the dispersion of Fe has decreased with increased support calcination temperature. This is consistent with the proposals of Bickley et al. [16]. The larger particles should be suggestive of a higher degree of catalyst reducibility. Calculations based on CO chemisorption (see further) revealed an increase in reducibility (Table 1), consistent with this proposal.

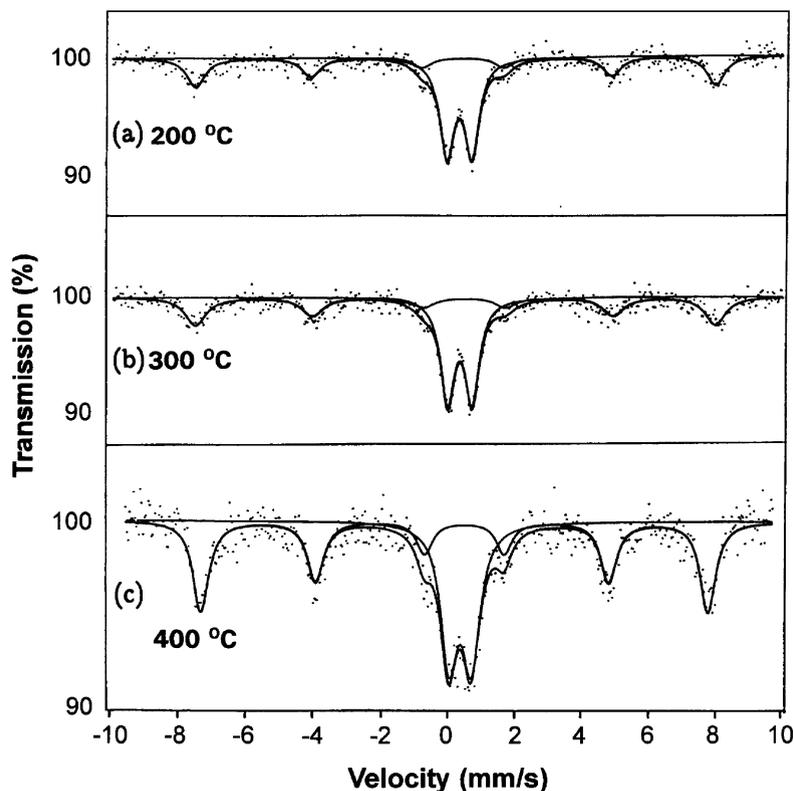


Fig. 1. The effect of support calcination temperature on the Mössbauer spectra of Fe:Co/TiO<sub>2</sub> bimetallic catalysts.

The variation of TiO<sub>2</sub> pre-calcination temperature thus leads to a possible method of producing catalysts with different particle sizes.

### 3.1.5. Fischer–Tropsch synthesis

FT synthesis was carried out over the catalysts on the three differently calcined supports under identical reaction conditions and the data are given in Table 1. The CO conversion increased from 29.8 to 36.3% as the support calcination temperature was increased (200–400 °C). This correlates with the catalyst dispersion (determined by TPO) and the degree of reduction of the catalyst [24]. Since the dispersion does not relate to a change in the A:R ratio, nor an increase in surface area, it suggests that the interaction between the metal salts and the surface OH groups is important. Although, the amount of water removed from the surface for all the catalysts is small, a more sensitive probe (e.g. DRIFTS) may be able to differentiate the surface changes suggested here. The surface Fe:Co

could also be affected by the surface–metal ion interaction.

The selectivity data (Table 1) revealed that the lower mass hydrocarbon fraction (C<sub>1</sub>, C<sub>2</sub>–C<sub>4</sub>) increased as the support calcination reaction increased, suggestive of a more efficient termination mechanism for the higher temperature calcined catalyst. The effect does not simply relate to chain termination via a hydrogenation reaction since the olefin/paraffin ratio does not follow the same trend.

Initial percent conversion data for the three catalysts after 50 h on line was 68, 63 and 47% for the 200, 300 and 400 °C support calcined samples, respectively. From this data it appears that the most stable catalyst is the one in which the support was calcined at the highest temperature.

In conclusion the data reveals that supports calcined at 400 °C (i) are more stable over the first ca. 200 h on line than those calcined at lower temperatures, and (ii) have a higher final activity, than supports calcined at

lower temperatures. They were thus used for further exploration in this study.

### 3.2. The effect of catalyst calcination and reduction: reactor studies

A catalyst batch was made up with nominal composition 5% Fe:5% Co on TiO<sub>2</sub> (calcined at 400 °C) which on AAS analysis revealed 5.2% Fe:5.1% Co on TiO<sub>2</sub>. The catalyst batch was divided into three equal portions and each portion was calcined at a different temperature (200, 300 and 400 °C). Each of these portions was again divided into four portions and each was reduced on line at four different reduction temperatures (250, 300, 350 and 400 °C). Thus, 12 different batches of catalysts were synthesized and tested for catalytic activity. The synthesis data obtained for these runs are given in Table 3.

#### 3.2.1. Catalyst stability

The deactivation pattern for the catalysts calcined at 200 °C and reduced at the four temperatures revealed that the lower the temperature of reduction, the higher the initial activity, but the more unstable the system over the first 50 h on line. This instability is indicated in Figs. 2 and 3. The large, but reproducible deactivation effect shown by the catalyst reduced at 250 °C appears to relate to the decomposition of the nitrate ion that takes place during the FT reaction. This would suggest that part of the initial catalyst instability is due to the incomplete decomposition of the cobalt and iron salts. However, the different final activities observed after 200 h on line are due to other factors e.g. Fe:Co surface ratios, metal–surface interactions, etc. The observed instability of the catalyst over the first 50 h on line stresses the importance of deriving data under steady state conditions.

The trends shown in Fig. 3 were similar for the systems calcined at higher temperatures, but the other samples showed less extreme deactivation with time on line. The dramatic effect noted for the 250 °C reduced sample was not observed.

#### 3.2.2. Catalyst activity

It is evident from Table 3 that the maximum percent CO conversion and highest specific activity at each of the calcination temperatures is observed at a reduction temperature of 300 °C. This is shown graphically in

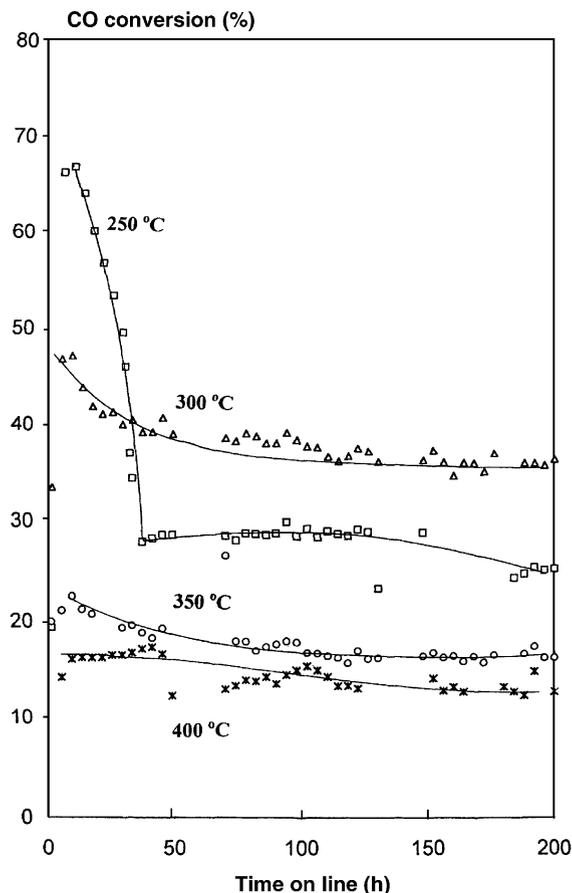


Fig. 2. The effect of reduction temperature on the deactivation profile for Fe:Co/TiO<sub>2</sub> systems calcined at 200 °C.

Fig. 4. The specific activity is found to be dependent on both the calcination and reduction temperature. Thus, at a low reduction temperature (250 and 300 °C) the specific activity decreases with increasing calcination temperature. At a reduction temperature of 350 °C the specific activity varies non-linearly with calcination temperature (going through a maximum at 300 °C). Finally, at a high reduction temperature (400 °C) the specific activity increases with calcination temperature [25]. An attempt to rationalize this data is given in Section 3.3.

#### 3.2.3. Catalyst selectivity

The different activation procedures produce catalytic systems having different product selectivities.

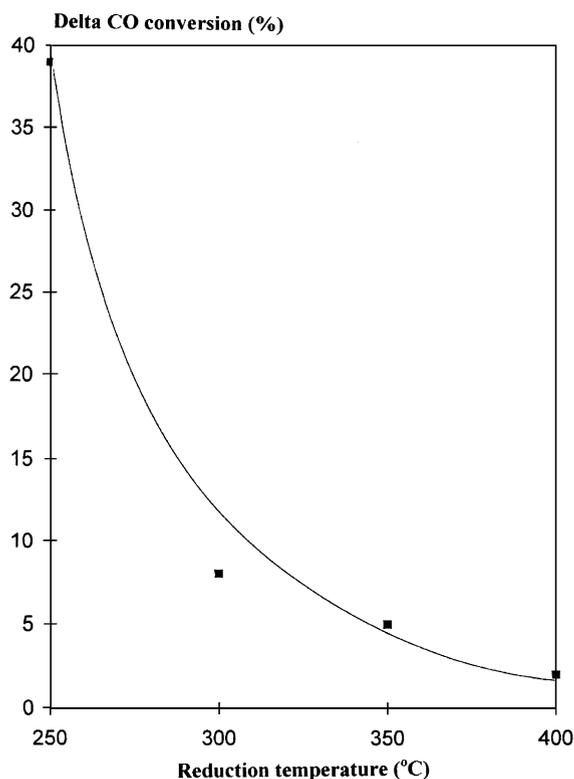


Fig. 3. The effect of reduction temperature on the change in activity over the first 50 h on line for Fe:Co/TiO<sub>2</sub> systems (200 °C calcination).

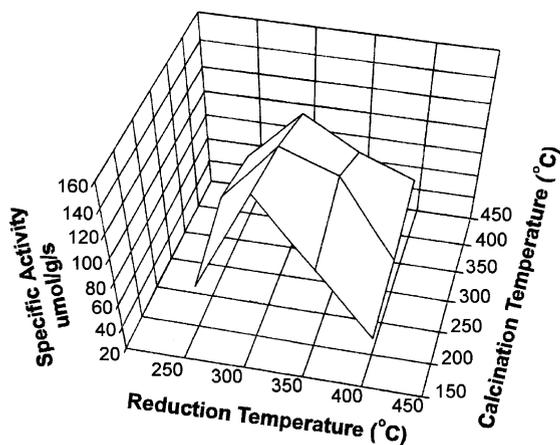


Fig. 4. The specific activity of the Fe:Co/TiO<sub>2</sub> bimetallic systems investigated.

Comparison of the product selectivity for catalysts calcined at the same temperature but reduced at different reduction temperatures must be treated with caution as the percent CO conversion varies over a wide range, i.e. 16–36%. However, meaningful trends can be assessed for catalysts reduced at the same temperature but calcined at different temperatures where the conversion data tend to be similar.

It is interesting to note that for FT data obtained at a calcination temperature of 200 °C, the level of methane production generally increases with reduction temperature, while the opposite is evident for the data obtained at a calcination temperature of 400 °C. The product fraction >C<sub>5</sub> indicates an opposite trend to methane production, an effect observed previously for both Co/Al<sub>2</sub>O<sub>3</sub> and Co/TiO<sub>2</sub> systems reduced between 380 and 530 °C [26]. Furthermore, an increase in olefin production is observed (Table 3) as the reduction temperature increases for catalysts calcined at the three temperatures, again consistent with literature reports on Co/TiO<sub>2</sub> [27]. It is also to be noted that the WGS activity is low and only observable at low calcination and reduction temperatures.

### 3.3. The effect of catalyst calcination and reduction: characterization studies

A range of characterization techniques (TPR, TPO, CO chemisorption/desorption, BET) were employed to investigate the relation between the active metal phase (Fe and Co), the support (TiO<sub>2</sub>) and the catalytic performance using the various catalyst calcination and reduction pre-treatment conditions [25,26,28,29].

#### 3.3.1. Correlation between CO chemisorption/desorption and the catalyst reducibility

A comparison has been made between the degree of dispersion, reduction and CO chemisorption/desorption for 10% Fe, 10% Co and 10% Fe:10% Co on TiO<sub>2</sub> reduced under equivalent conditions. (Table 5). The data indicate that the percent reduction (determined by TPO) increases with increasing reduction temperature for Fe and Co. Interestingly the Fe:Co catalyst resembles the Fe catalyst in CO chemisorption behaviour. However, the Fe:Co catalyst shows increased reducibility relative to Fe and Co [30].

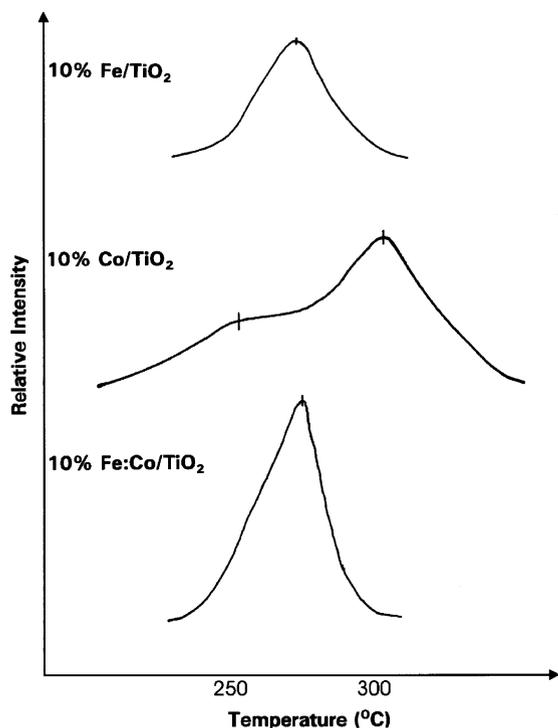


Fig. 5. The relation between CO-TPD spectra and catalyst type.

The CO desorption behaviour of the three catalysts also reveals that Fe:Co behaves more like Fe than Co (Fig. 5) [30]. It is also to be noted that the CO desorption from the Fe:Co catalysts occurs at a lower temperature than observed from the monometallic catalysts (Fig. 5). It has previously been noted that alumina and Kieselguhr supported Co catalysts desorb CO to generate two or even three peaks in the TPR, [31,32] while conventionally prepared iron on alumina desorbs to give only one peak [33].

TPR studies on both the Fe/TiO<sub>2</sub> and Co/TiO<sub>2</sub> systems and the bimetallic system Fe:Co/TiO<sub>2</sub> were performed (Fig. 6). All three TPR profiles reveal, not unexpectedly, that the three systems are more difficult to reduce after a high temperature calcination treatment. This implies that stronger interactions are induced between the active metal and the support with increasing calcination temperature [25]. A comparison of the Fe:Co profiles with the Fe and Co profiles shows that the Fe:Co complex is easier to reduce than the individual metals, in keeping with the TPO studies [5,30].

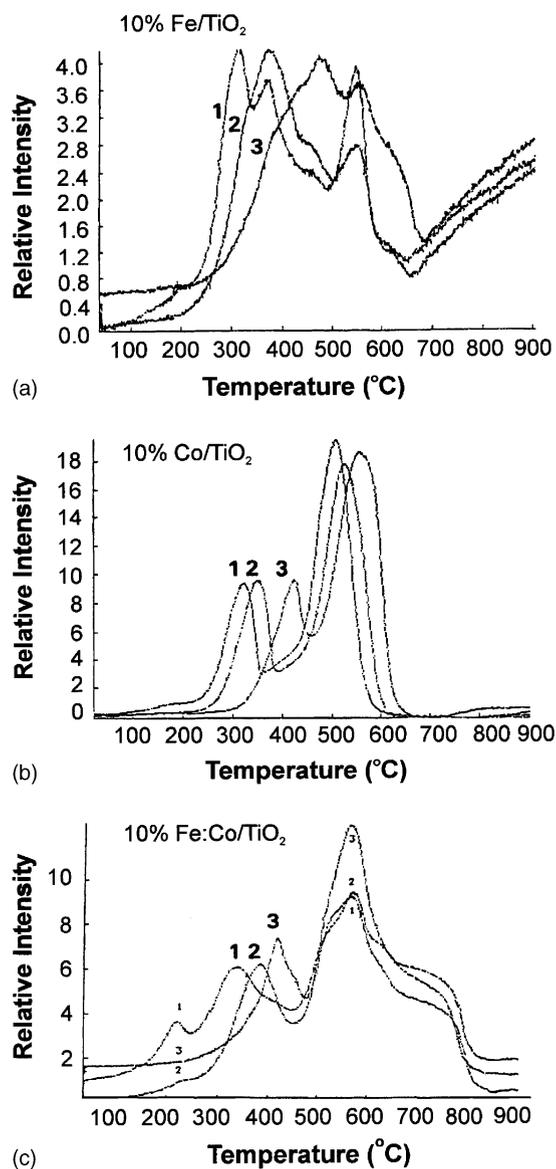


Fig. 6. TPR analysis of: (a) Fe/TiO<sub>2</sub>; (b) Co/TiO<sub>2</sub>; (c) Fe:Co/TiO<sub>2</sub> system calcined at 200 °C, 300 °C, and 400 °C.

The above data reveal that the Fe:Co system is different from the individual Fe and Co catalysts. More importantly the data suggests that the catalyst surface is more similar to Fe than Co. This is in agreement with earlier XPS studies [5] that indicated surface enrichment of Fe in related Fe:Co catalysts.

### 3.3.2. Correlation between CO chemisorption and catalytic performance

The amount of CO chemisorbed ( $\mu\text{mol/g}$  catalyst) varied non-linearly with increasing reduction temperature (within a set of calcined catalysts) or with increasing calcination temperature (within a set of similarly reduced catalysts) (Table 5). The catalytic activity did not correlate with the amount of CO chemisorbed onto the catalyst surface. The so-called SMSI phenomenon is not expected to be important at the low temperatures used [34–38]. The most likely explanation is that the Fe:Co surface atom ratio will vary with calcination and reduction temperature and this would lead to the different results [5].

Another possibility is that under the temperature conditions used a high temperature ilmenite ( $\text{FeTiO}_3$ ) phase (previously reported for a Fe/TiO<sub>2</sub> catalyst reduced for 16 h at 350 °C and identified by in-situ XRD and supported by TPR studies [5]) may inhibit the ad-

sorption of CO [5,24]. Other high temperature phases involving any combination of Fe, Co and TiO<sub>2</sub> could also inhibit the adsorption of CO.

### 3.3.3. Catalyst dispersion

Mössbauer studies on bimetallic catalysts calcined at 200 and 400 °C indicated that an increase in catalyst calcination temperature improved the metal Fe dispersion of the unreduced catalyst. The particle size changed from an average mean particle size of approximately 50–80 nm at 200 °C to particles of a mean average size in the range 5–10 nm at 400 °C (Fig. 7 and Table 2). From the table it is evident that a small increase in the paramagnetic (PM) feature relative to the magnetic (M) feature is observed and is reflected by the PM/M ratio changing from 1.2 to 1.9. This is coupled to a decrease in average particle size and subsequently a better dispersion of Fe is obtained [5], consistent with the data given in Table 5.

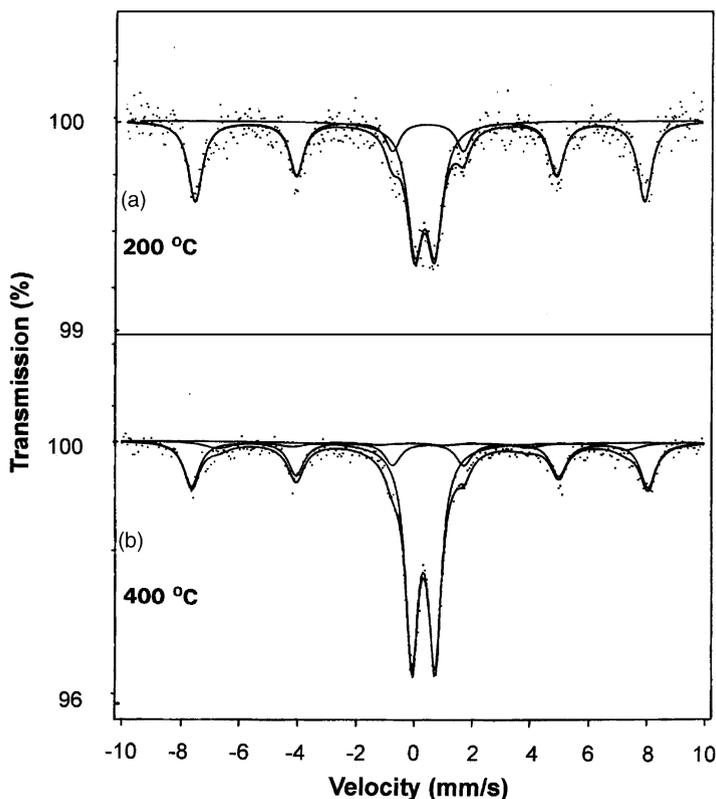


Fig. 7. Mössbauer spectra of Fe:Co/TiO<sub>2</sub> taken at different calcination temperatures.

Dispersion of the reduced catalysts was determined by CO absorption. The relationship between CO chemisorption and dispersion for monometallic complexes has been discussed in detail by Bartholomew and the advantages of using H<sub>2</sub> rather than CO to establish TOF has been enumerated [24]. Recently, the problems associated with the use of H<sub>2</sub> chemisorption have also been highlighted [39]. Because of difficulties associated with assessing the actual numbers of both Fe and Co atoms on the surface we have chosen, arbitrarily, to define our dispersion (and TOF data) from CO chemisorption data assuming both Fe and Co atoms are present on the surface in equal amounts. While the absolute data may not be correct, the data provide information on trends in dispersion.

### 3.3.4. Correlation between dispersion, reduction and catalytic performance

Our results for the Fe:Co/TiO<sub>2</sub> bimetallic system (Table 4) indicate at all calcination temperatures that the level of reduction (percent R) increased (and dispersion decreased) with increasing reduction temperature. This is consistent with earlier results reported in the literature [30]. The system with highest TOF (calcined at 200 °C and reduced at 300 °C) had one of the highest reduction levels values (94.6%).

A trend of decreasing specific activity and decreasing percent metal reduction with increasing calcination temperature is observed for both the 250 and 300 °C reduced catalysts. Thus, the catalysts with highest specific activity (those reduced at 300 °C) had high levels of reduction ca. 95, 91 and 78%, respectively. The low activities observed for the catalyst reduced at 250 °C can be explained [24,26,29,40] by the low reduction levels of 66, 58 and 40%. This is consistent with studies on Co catalysts where the activity is determined by the number of reduced Co surface atoms [3,24].

However, an opposite trend is evident for the catalysts reduced at 400 °C. Here reduction of almost 100% did not lead to an increase in activity. This is contrary to all available data on the reducibility/activity relationship for Co. A number of suggestions can be made to explain this observation

**3.3.4.1. Surface area changes.** The effect of various reduction and calcination procedures on the BET surface areas was investigated and minor trends were noted (Table 6). The increase (57–63 m<sup>2</sup>/g) with an in-

crease in calcination temperature (from 200 to 400 °C; catalysts reduced at 300 °C) is small and the corresponding decrease in activity cannot be explained by the small increase in metal dispersion that would result from a decrease in reducibility of such systems [34,41–44] (Table 4). The decrease in surface area (63–52 m<sup>2</sup>/g) on increasing the reduction temperature from 250 to 400 °C is to be contrasted to the influence of reduction temperature of group 8–10 metals on supports such as SiO<sub>2</sub> where an increase in surface area was observed [45]. In summary, the changes in BET of the material do not explain the activity changes.

**3.3.4.2. Fe:Co surface ratio.** The above characterization data and earlier studies (discussed above) are consistent with Fe migration to the surface of the Fe:Co catalysts. Thus, after the catalyst activation conditions Fe is the dominant surface atom on the catalyst and the Fe:Co will resemble Fe (rather than Co) in its behaviour. However, it is to be noted that the Fe in Fe:Co acts differently to that of pure Fe.

### 3.3.5. Relation between percent reduction, percent dispersion and product selectivity

As stated previously, the large differences in CO conversion for some of the reactions make comparison of selectivity data difficult. However, some trends can be detected.

It appears as if product olefinity generally increases with the level of reduction. High levels of olefins are produced at a calcination temperature of 200 °C (in particular at a reduction temperature of 350 °C; Table 3). Since Fe is known to preferentially produce olefins this observation suggests again that the activation conditions result in Fe migration to the surface.

A notable observation was the low level of the WGS reaction. This suggests that the Co has the ability to modify the behaviour of the Fe in the mixture.

A somewhat unexpected result was that an increase in high hydrocarbon molecular weight products (i.e. +C<sub>5</sub>) was found with a decreasing level of reduction (Tables 4 and 5) and higher dispersion for the bimetallic catalysts calcined at 200 and 300 °C. Thus, intermediate levels of metal oxidation result in systems with different product selectivities. More work is, however, needed to confirm this notion. Results for a Co/TiO<sub>2</sub> system [20], show an opposite trend in product distribution to that reported here.

#### 4. Conclusions

The TiO<sub>2</sub> support calcination temperature (200–400 °C) increased the stability of the final catalyst and suggests a method for controlling metal particle size.

The catalyst Fe:Co/TiO<sub>2</sub> calcination temperature (at constant reduction temperature) was not an important parameter in influencing the activity and product selectivity of the catalyst.

The reduction temperature (constant calcination temperature) of the Fe:Co/TiO<sub>2</sub> catalyst influenced the FT activity and selectivity. A low reduction temperature (250 °C) resulted in a highly dispersed and difficult to reduce catalyst. A high reduction temperature (400 °C) generated a catalyst with low dispersion and high reducibility, but poor activity. The higher reduction temperature generated catalysts with lowered BET surface area and increased surface Fe content.

The changes in reduction/calcination conditions used to generate the Fe:Co catalysts permits the methane and olefin yields to be manipulated within the constraints of the FT reaction.

Thus, there is a fine interplay between catalyst content, reduction and calcination temperature to obtain optimal activity and selectivity for the FT reaction of bimetallic catalysts. The catalyst properties are determined by the Fe:Co surface atom ratio.

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