

Fe:Co/TiO₂ bimetallic catalysts for the Fischer–Tropsch reaction

I. Characterization and reactor studies

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Abstract

The effect of different iron loadings (0.1%; 1%; 5%; 10%) on a 10% Co/TiO₂ catalyst was studied by a range of surface and bulk characterization techniques. The combination of techniques (B.E.T.; CO-chemisorption, desorption; DSC; XRD; XPS; TPR; TPD; SEM and Mössbauer Spectroscopy) revealed that an intimate interaction occurs between the Fe and Co atoms when compared to the pure metal components. Catalyst preparation and reduction procedures influenced both the bulk and the surface properties. The characterization studies revealed that the TiO₂ systems do not differ significantly from SiO₂ and Al₂O₃ supported, or alloy systems, reported elsewhere in the literature.

Keywords: Fischer–Tropsch; Bimetallic; Iron; Cobalt; Surface study; Mössbauer

1. Introduction

An important feature of the Fischer–Tropsch (F–T) reaction is that it can be viewed as a polymerisation reaction and that the product spectrum can broadly be predicted from the Anderson–Schulz–Flory (ASF) α value. The products produced in the F–T reaction can be manipulated within the constraints of this model by choice of catalyst, reactor and operating conditions [1,2]. Modification of the traditional F–T catalysts (Fe, Co, Ni, Ru) by means of promoters has provided one means of manipulating the F–T product spectrum and the literature abounds with examples in which this approach has been successful. Some years ago we were

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intrigued by a range of patents on F–T work in which the addition of two F–T active metals, when used together, did not simply give the additive properties (activity, selectivity) expected from a knowledge of the properties of the individual metals. We have thus undertaken a study of bimetallic catalysts, (in which both metals are F–T active metals), to explore this phenomenon.

Reports in the patent literature on the synthesis and study of a series of slurry phase unsupported Fe/Co F–T catalysts have indicated that the addition of small amounts of Co to Fe could influence the Fe catalyst quite dramatically [3–5]. Numerous other reports on the use of Fe/Co catalysts in the F–T reaction have also appeared in the literature [6–28]. Valuable information on Fe/Co catalysts has thus been obtained from the above studies, as well as related studies on the use of Fe/Co catalysts in the ammonia synthesis reaction [29]. A number of studies on the chemical and physical properties of Fe/Co systems have also been reported [30–37]. Notwithstanding the wealth of information reported, a review of these reports reveals a number of limitations with the collected data. These include:

1. time on line studies have generally been <24 h
2. conversions have generally been low (<10%) and
3. reaction conditions may have had little bearing on the F–T reaction as practised in industry.

We wish to report our investigation into a range of Fe/Co on TiO₂ catalysts [10–12,20] for use in the F–T reaction which will address the issues mentioned above. Characterization studies of the Fe/Co catalysts and preliminary reactor studies will also be described in this paper. The characterization studies have been carried out to assess the physical and chemical similarities/differences obtained on mixing the Fe and Co metals on TiO₂ and to compare the data with Fe/Co catalysts in other environments (SiO₂, Al₂O₃; as an alloy).

2. Experimental

2.1. Materials

Commercial Titandioxid P25 titania was supplied by Degussa. The oxide powder was mixed with deionised water, dried at 120°C for 1 h and thereafter calcined at 400°C for 16 h in an oven. The calcined support was crushed and sieved to between 0.5 mm and 1.0 mm particles for use as catalyst support. Fe(NO₃)₂·9H₂O and Co(NO₃)₂·6H₂O, obtained from SAARCHEM Chemicals, was used as obtained.

Catalysts were synthesised as follows. A hot, ca. 80°C, co-solution of the metal nitrates was impregnated to the point of incipient wetness onto TiO₂ pellets prepared as described by the method discussed above. The impregnated system was dried at 120°C for 2 h. Thereafter the catalyst was calcined in flowing air at

400°C for 16 h. The catalysts thus prepared (0.1%, 1%, 5% and 10% Fe added to 10% Co) give 1 : 100; 1 : 10; 1 : 2 and 1 : 1 ratios of Fe to Co. Catalysts with Fe : Co ratios of 2 : 1 (10% Fe : 5% Co); 1 : 3 (5% Fe : 15% Co) and 1 : 1 (5% Fe : 5% Co) were also prepared as well as 10% Fe and 10% Co on TiO₂. For simplification, reference to these catalytic systems will be made by referring to the metal loading, i.e. reference to a “10 : 10 system” will indicate a 10% Fe : 10% Co system supported on TiO₂. In each case the level of Fe is given first, followed by that of Co. The effect of preparation method was also studied. A bimetallic system was prepared by a dual impregnation procedure. During this procedure 10% cobalt was deposited by incipient wetness and then calcined for 16 h at 400°C. Thereafter the Co/TiO₂ system was impregnated with 1% Fe and re-calcined for 16 h at 400°C.

All gases employed were high purity special gases from AFROX, South Africa. Surface studies i.e. TPR, chemisorption and B.E.T. were performed with ultra high purity gases (99.997%) with oxysorb and hydrosorb utilities.

2.2. Catalyst characterization

A Du Pont 910 DSC was used for the DSC analysis. A small sample (10–20 mg) of catalyst was heated using a linear temperature program (10°C/min) in hydrogen (flowrate: 30 ml/min) and the corresponding measured changes in heat flow indicated the various metal reduction steps [38]. The data was correlated with temperature programmed reduction analysis data. A Du Pont 9900 TGA using linear temperature programming (heating rate: 10°C/min) under inert and oxygen atmospheres (flow rate: 30 ml/min) was used to measure catalyst weight loss (10–20 mg samples). A TPR apparatus constructed in our laboratory was used for reduction studies. A 100 mg sample size was found to give optimal results [39,40]. Calculations which permitted the determination of the metal dispersions at 1 atmosphere and temperatures ranging between 250°C and 400°C was previously described by Bartholomew and co-workers [41].

The reduction level was determined after reduction of the catalyst for 16 h followed by oxygen titration. The percentage reduction was calculated by assuming (mono-metal and bimetallic systems) total oxidation at 400°C by O₂ of the previously reduced Fe and Co sites to Fe₂O₃ and Co₃O₄ respectively had occurred. The % metal dispersion was calculated by determining the fraction of surface reduced sites as a function of the total metal atoms in the catalyst. The CO adsorption value obtained was accurate to about 10%, while the level of reduction was found to be accurate to about 5%.

The catalyst systems produced heavy hydrocarbon liquids and waxes, which were removed before the used catalysts was analyzed by TGA, B.E.T. surface area or SEM. The used catalyst samples were extracted with xylene for 16 h under reflux; thereafter the xylene was removed under a 2 h reflux period with a 1 : 1 mixture of methylethylketone and benzene.

SEM (JSM-840) characterization with a LINK analytical energy dispersive analysis facility was used to obtain information on the homogeneity of the catalyst surface. Samples subjected to these studies were used in granular form (0.5 mm–1.0 mm) and coated with gold for improved visibility. All samples were studied at a beam energy of 20 kV.

2.3. X-ray diffraction (XRD) analysis

2.3.1. *Ex situ* XRD study

A Philips (PW 1830 generator) spectrometer equipped with a Cu radiation source was used to analyze powdered disk samples (particle size: 100 micron) in the 9.5 to 150 2θ range at a generator voltage of 40 kV and a generator current of 20 mA. A scan rate of 2 sec per step (step size: $0.02^\circ 2\theta$) was used during a continuous scan in the above mentioned range.

2.3.2. *In situ* XRD study

This study was performed at the CSIR (Pretoria, South Africa), on a Rigaku Geigerflex D/max 111A computer controlled wide angle diffractometer. This system permitted *in situ* reduction and synthesis reactions of catalysts under real time conditions and permitted the study of phase changes during the activation and reaction stages for both the single metal and bimetallic systems. The equipment has previously been illustrated and discussed [42].

Approximately 1 g of sample was compacted onto a platinum mesh by means of a glass slide, firmly pressed by hand. The sample was then vertically mounted inside a small Khantal-wired furnace, whereafter it was aligned with the goniometer. The diffractometer parameters were: radiation: $\text{CuK}\alpha$; generator: 45 kV and 40 mA; goniometer: divergence slit = 1° ; receiving slit = 0.3 mm, scatter slit = 1° , $\text{K}\beta$ filter Ni; step scan: step-size $0.02^\circ 2\theta$ for fixed time of 4 s. The H_2 reduction was performed at 350 $^\circ\text{C}$ for 16 h at a flow rate of 40 ml/min and the H_2 :CO reaction at 220 $^\circ\text{C}$, with a gas flow ratio of 1 H_2 : 1CO at 40 ml/min.

2.3.3. X-ray photoelectron spectroscopy (XPS) analysis

This equipment permitted characterization of the catalyst surface during either catalyst activation or a catalytic reaction. The equipment used consisted of a VG MKII X-ray source with dual anode. The VG “Clam100” was attached to a “solar 300” UHV chamber. Pressures of 5×10^{-8} mbar were maintained during the study using a Leybold–Hereaus TMP 150 turbomolecular pump. The reaction setup and method of operation has been described previously [43]. During the study a pressed wafer, approximately 1 mm thick and 1 cm in diameter, was reduced in hydrogen at 350 $^\circ\text{C}$ for 16 h at a space velocity of 2000 h^{-1} . Spectra were recorded prior to reduction i.e. of the metal oxide, after reduction, and after reduction followed by bombardment with Argon.

2.3.4. Mössbauer spectroscopy (MBS) analysis

The equipment used consisted of an Austin Science Associated drive with Ortec electronics and a $^{57}\text{Co}(\text{Rh})$ γ -ray source. The isomer shift was obtained with reference to α -Fe. The source velocity was varied linearly and horizontally over a range of approximately 14 mm/s. A single channel discriminator was used to record only pulses of 14.4 keV [44].

For good statistical analysis of the Mössbauer spectrum at least 1 000 000 counts were required for each of the 1024 channels. Thus, in the experiment a sample of approximately 100 mg (approximately 15 mg Fe) was evaluated at 300 K for approximately 100 h. A computer program [45] utilizing a non-linear least squares method was used to fit a number of correlated Lorentzian peaks to the data. Reduced samples (from a glass reactor) were crushed under N_2 , loaded into the reactor and analyzed.

2.4. Catalyst evaluation

A simple system which permitted on line analysis of the gas fraction through a multiple G.C. column system and off-line analysis of both the liquid and wax fractions was used. The system comprised three stainless steel reactors with two knockout pots each, one for wax and one for liquid hydrocarbon products.

A Varian 3300 gas chromatograph equipped with a FID, TCD, splitter and cryogenic unit was used for product analysis, and employed hydrogen (flow rate: 30 ml/min) as carrier gas for optimum sensitivity. The day to day Ar, CO, CH_4 and CO_2 data were analyzed with a 2 m carbosieve IIS column on the TCD detector while the hydrocarbon gas fraction was simultaneously analyzed with a 2 m PPQ column on the FID detector. During the mass balance period the PPQ column was substituted for a 50 m megabore (BP1) column. This permitted analysis of the C_1 to C_{12} hydrocarbon gas fraction. Cryogenic temperature (-20°C) enabled adequate separation of methane and the C_2 paraffin and olefin fractions. Off-line analysis on the liquid (C_5 – C_{18}), wax and water fractions was performed on a classical OV-101 column.

All catalysts were activated (reduced) for a 16 h period in pure hydrogen at pressure and temperatures specified in the results section. After reduction the reaction system was cooled to below 200°C . The reaction gas, $2\text{H}_2 : 1\text{CO}$, was introduced and the pressure, unless otherwise specified, increased to 10 bar. The gas flow was set to S.V. = 350 h^{-1} and finally a suitable temperature was chosen (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 similar to those proposed by Nijs et al. [46] were used. The calculation entailed the conversion of gaseous inert and hydrocarbon products (TCD and FID data) to grams per component as detailed by Mikes [47], Diets [48], Purnell [49] and others [50,51].

The % of CO conversion was calculated as:

$$\text{CO}_{\text{in}} - (\text{CO}_{\text{out}} \times \text{gas contraction}) \times 100 \frac{\%}{\text{CO}_{\text{in}}},$$

where the gas contraction was determined from an $\text{Ar}_{\text{in}}/\text{Ar}_{\text{out}}$ calibration.

The product selectivity for hydrocarbons was calculated as:

$$\text{Selectivity of component } x_i = (\text{mass component } x_i / \sum x_i) \times 100\%.$$

The WGS extent was calculated as:

$$\% \text{ mass CO}_2 / \% \text{ mass (CO}_2 + \text{H}_2\text{O)},$$

While the olefin to paraffin ratio was given as:

$$\% \text{ mass olefin} / \% \text{ mass (olefin + paraffin)}.$$

The specific activity was expressed as μ mol CO converted per gram catalyst per second and was calculated as a function of the (CO + CO₂) conversion, and thus included the % CO converted to CO₂. Mass balance data of $100 \pm 5\%$ was accepted as adequate for comparison purposes. Finally, as already indicated, all product selectivity and product ratio results are reported as a function of % mass by mass of the total product spectrum for the particular catalytic system.

3. Results and discussion

3.1. Characterisation studies

3.1.1. Elemental analysis and B.E.T. surface areas

From AAS analysis of the loaded supports it is clear from Table 1 that the metal loading and metal ratios obtained are very close to those predicted from the catalyst preparation. B.E.T. surface analysis of the clean TiO₂-support (52.4 m²/g) compares favorably [52] with the values found for similar supports used by other researchers. As expected a small loss in B.E.T. surface area is observed as the total metal loading is increased viz. from ca. 46.6 m²/g at 10.0% loading to ca. 36.5 m²/g for 20.0% loading.

3.1.2. Differential scanning calorimetry (DSC) study

DSC studies were carried out using 100% H₂. For the Fe/TiO₂ (10%) catalyst significant reduction peaks were observed in the DSC spectra below 350°C with a large peak at ca. 250°C, while for Co/TiO₂ (10%) a solitary peak at ca. 300°C was detected. Use of 20% loaded samples did not result in significant shifts of the peaks indicating that diffusional (kinetic) effects were not important in influencing peak positions with 10–20% metal loadings.

Table 1
Elemental analysis and B.E.T. surface area measurements for Fe:Co/TiO₂ systems

Catalyst Fe : Co	Metal ratio (theoretical)	Metal loading (%) ^a		B.E.T. surface area (m ² /g) Fresh
		Fe	Co	
TiO ₂	—	0	0	52.4
10% Fe	—	10.3	0	44.0
10% Co	—	0	10.1	42.8
0.1% : 10%	1 : 100	0.7	11.5	46.6
1% : 10%	1 : 10	1.1	9.0	38.5
5% : 10%	1 : 2	5.1	9.7	40.5
10% : 10%	1 : 1	9.8	9.2	36.5 ^b
5% : 5%	1 : 1	4.9	5.0	45.0 ^c
5% : 5% ^d	1 : 1	5.1	5.0	46.0
5% : 15%	1 : 3	5.1	15.2	35.0
10% : 5%	2 : 1	9.8	5.1	41.8
1% : 10% ^e	1 : 10	1.0	10.1	40.8

^a as determined by AA spectroscopy.

^b Used: 23.6 m²/g.

^c Used: 47.0 m²/g.

^d On TiO₂ powder; all other additions to pellets.

^e Sequential addition of Fe to Co/SiO₂.

DSC spectra of TiO₂ loaded with different iron levels and 10% Co were compared as seen in Fig. 1. The spectra revealed the presence of two significant peaks; one between 250 ° and 350 °C and the other between 350 ° and 400 °C. From the figure it is clear that both peaks shift upwards as the Fe content of the mixture is increased. A third peak at 250 °C, associated with Fe, can only be observed at the highest Fe loadings (10 : 10 catalyst).

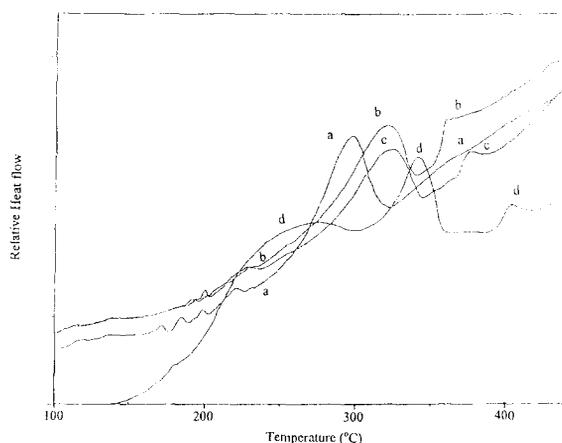


Fig. 1. DSC analysis of the x% Fe : 10% Co/TiO₂ catalyst (a) 0.1 : 10 bimetallic catalyst, (b) 1.0 : 10 bimetallic catalyst, (c) 5.0 : 10 bimetallic catalyst, (d) 10.0 : 10 bimetallic catalyst.

The DSC spectrum of the 1 : 10 catalyst prepared by stepwise (Co first) incipient wetness procedures was compared to that of the 1 : 10 system prepared by co-impregnation incipient wetness. A small shift (ca. 10°C) of the 300°C peak to a lower reduction temperature was observed after stepwise impregnation.

DSC spectra were also recorded on samples in which the metal loading was varied, but the metal ratio (1 : 1) remained constant. Data for Fe : Co ratios of 5 : 5 and 10 : 10 revealed a small shift (<10°C) in the Co (310°C) peak to higher value with increasing loading and the peak increased in size with increasing Fe and Co content. Similar observations were made for the 10 : 5 and 5 : 15 catalyst systems.

From the above we can conclude that the position of the reduction peak associated with cobalt (300°C) increases on addition of Fe but that the Co peak did not shift in a linear way as the Fe content was increased.

3.1.3. Temperature programmed reduction (TPR) study

A TPR spectrum recorded in hydrogen on Fe, Co and Fe : Co (5 : 5) supported on TiO₂ is shown in Fig. 2. The Fe/TiO₂ spectrum correlated with previous studies [12]. The relative hydrogen uptake of Fe/TiO₂ was lower than for the other systems and no pronounced peaks could be identified. The broad peak showing several shoulders is consistent with a difficult stepwise reduction of the metal oxide phase to metal ($\alpha\text{-Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4 \rightarrow \text{“FeO”} \rightarrow \text{Fe}$) [34]. On the other hand the Co catalyst shows two distinct peaks which are related to two different oxidation states (Co₃O₄, CoO) of the cobalt [53–57]. The TPR spectrum for Fe : Co/TiO₂ indicates a complex spectrum which is dominated by two absorptions at 400° and 550°C and shows some similarities to a previously reported TPR spectrum of Fe : Co on TiO₂ [20].

TPR studies have been reported for Fe : Co alloys [34] and Fe:Co supported on Al₂O₃ [29] and SiO₂ [20]. The general conclusion from the studies was that the Co assisted in reduction of the Fe. However, the effect of Fe on Co on the Fe : Co alloy is to *increase* the Co temperature of reduction [34]. In this study, and in keeping

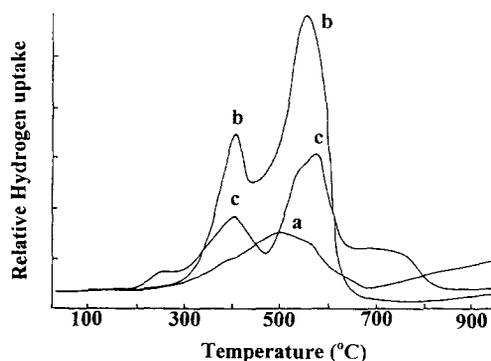


Fig. 2. TPR profile for (a) 10% Fe/TiO₂, (b) 10% Co TiO₂ and (c) 10% Fe :Co/TiO₂.

with the DSC data, there is also a small increase in the reduction temperature of the high temperature (ca. 575°C) Co peak in the Fe:Co/TiO₂ material.

The bimetallic system also reveals a broad absorption of H₂ between 700°C and 900°C, which is not present for the Co system. This absorption could be related to that of the high temperature peak obtained for the DSC analysis of the bimetallic catalysts. It appears that a very stable, difficult to reduce Fe rich phase is formed in the synthesis of the bimetallic catalyst.

3.1.4. CO Chemisorption and Desorption studies

CO Chemisorption studies were carried out on the range of Fe : Co/TiO₂ catalysts synthesized and the data are shown in Table 2 and Fig. 3. No attempt was made to optimize the reduction process; rather the emphasis was on an attempt to compare reduction data under a standard set of conditions. It is also not possible to assess whether Fe or Co has been predominantly reduced from the reduction data.

A further difficulty relates to the determination of the catalyst dispersion. Bartholomew has discussed this issue in some detail [58] and has proposed that H₂ be used as the probe gas for this determination. We have ascertained this value by using CO as the probe gas and came to the conclusion that the “factor” in the calculation,

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

of 1.175. This value is the average value for Fe and Co and will be assumed to hold for Fe, Co and Fe:CO on the surface. It is clear from both the table and the figure discussed that the % dispersion does not vary greatly (0.6–2.4) over the range of catalysts studied, and not unexpectedly generally follows the % reduction data.

Table 2
The effect of metal loading on CO_{ads}, % reduction and % dispersion

Catalyst	Loading (%)	CO chemisorption ^a	Reduction (%)	Dispersion (%)
TiO ₂ -support	0	–	–	–
10% Fe	10	7.6	9.5	8.9
10% Co	10	8.4	58.5	1.7
0.1% : 10%	10.1	13.4	63.0	2.4
1% : 10%	11	11.8	87.5	1.4
5% : 10%	15	12.8	88.7	1.1
10% : 10%	20	8.2	70.1	0.7
5% : 5%	10	9.5	92.4	1.2
5% : 5% ^b	10	7.3	86.4	1.1
5% : 15%	20	8.4	88.1	0.6
10% : 5%	15	7.5	73.6	0.8
1% : 10% ^c	11	10.0	56.7	1.9

^a μ mol CO/g Catalyst.

^b On TiO₂ powder; all other measurements on pellets.

^c Sequential addition of Fe to Co/SiO₂.

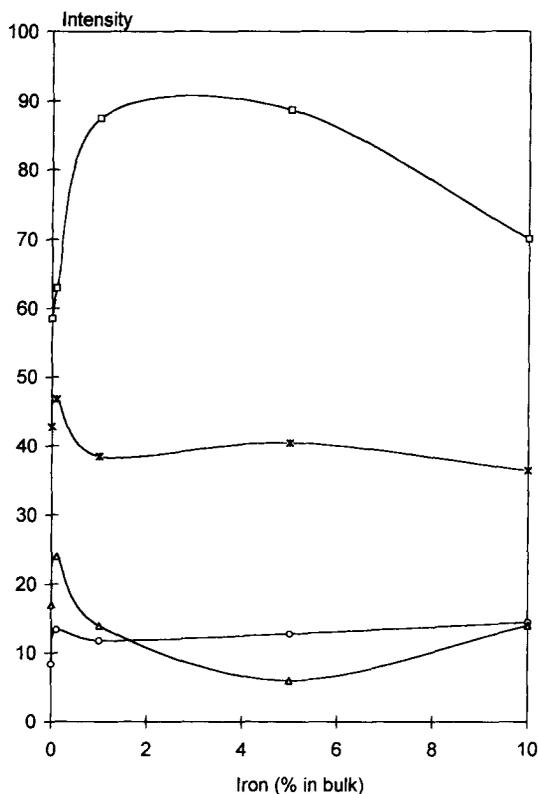


Fig. 3. Variation of Fe : Co/TiO₂ catalyst reduction (%), dispersion (% × 10, △), CO Chemisorption (μ mol/g, ○) and BET surface area (m²/g, *) with Fe content.

The data in the table and trends shown in the figure reveal that the presence of Fe has a significant effect on the reducibility of the bimetallic system. The Fe system has very low reducibility (ca. 9.5%). This could be attributed to the good dispersion of the metal oxide on the surface with subsequent inhibition of the reduction process [59]. Although Co is more reducible than Fe, it still shows incomplete reducibility (58.5%) under similar conditions. From the data it is thus clear that small amounts of Fe enhance the reducibility of the Fe : Co mixture but if Fe is present in high concentration then the catalyst takes on the properties of this metal. (The relationship between total metal loading and reduction for monometallic catalysts has been established [60]).

A comparison of the data for 11% loaded materials in which the Fe was either added with or after Co addition is revealing. Both the CO chemisorption and the degree of reduction are lowered by having Fe on the surface, in keeping with the data for monometallic catalysts. This is consistent with all the data discussed above, and suggests that the ratio of Fe to Co is important in achieving the benefit of the bimetallic system.

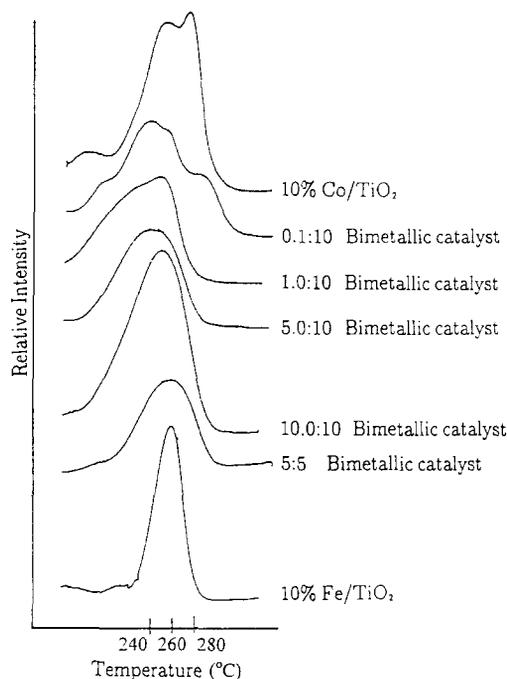


Fig. 4. CO-TPD spectra for Fe, Co and bimetallic systems.

CO desorption profiles of the Fe, Co and the bimetallic systems are shown in Fig. 4. Similar data have been reported [60–62] for Fe and Co supported on SiO_2 and Al_2O_3 , while Co has been known to give up to three CO peaks when supported on Al_2O_3 [59]. The desorption studies are also similar to reported data for Fe:Co alloys [15]. Addition of small amounts of Fe to Co (0.1% and 1%) reveals that CO desorption now occurs at lower temperatures. At higher Fe loadings a single broad desorption band is noted with a desorption peak close to that of Fe. The data would suggest that the surface has been dramatically affected by mixing of the Fe and Co and that the CO-metal interaction has properties more similar to that of Fe–CO than Co–CO.

3.1.5. X-ray diffraction (XRD) study

Powder X-ray diffraction studies on 10% Fe/ TiO_2 and 10% Co/ TiO_2 and the 10 : 10 bimetallic system revealed predictable results expected for the metal oxides. The TiO_2 (Degussa P25) revealed an anatase to rutile ratio of 71.4 : 28.5 which compared favorably with that reported by Sankar et al. [63] at 70 : 30. Powder XRD studies performed on these systems reduced for 16 h at 350°C in a glass reactor suggested complete reduction. This is consistent with data reported in the literature [12] for Co and Fe–Co systems.

An in situ XRD study revealed the above mentioned phases and other expected phases. Samples of the Fe and Co systems and 5 : 5 and 10 : 10 bimetallic systems

Table 3
Position of Fe(110) peak as determined by in situ XRD analysis

Sample	In situ XRD ^a [Fe(110)]
PDF# 6–696 ^b	2.0268
10 % Fe/TiO ₂	2.0267
10Fe : 10Co/TiO ₂	2.0174
5Fe : 5Co/TiO ₂	2.0169

^a d value precision: at 45° 2θ and CuK α wavelength of 1,540598 Å. Δd = 0.0002

^b International standard value as obtained from the “International Centre for Subtraction Data”.

were reduced in situ for 16 h at 350°C under hydrogen and cooled to 220°C. Thereafter a 1 : 1 mixture of H₂ : CO reaction gas was passed over the catalyst for at least 16 h. The catalysts were monitored for changes by taking eight spectra, one of the fresh sample at 20°C, one each after 5 h and 10 h reduction at 350°C in pure hydrogen, one after cooling to 220°C and one each after 5 h, 10 h and 15 h at 220°C in the reaction gas and finally one again at 20°C, at the end of the reaction.

The fresh samples for each of these systems revealed TiO₂, Fe₂O₃ and Co₃O₄ to be present. After reduction the Fe system revealed the presence of both Fe₂O₃ and reduced Fe (bcc phase) while the Co system displayed, as expected, fully reduced Co (fcc phase). The presence of unreduced Fe in the Fe/TiO₂ system is not surprising [11].

The XRD spectra for both the 5 : 5 and 10 : 10 systems revealed that all metal had been fully reduced to Fe : Co bcc alloys. This confirms previous results [7,64] on bimetallic systems and our ex situ XRD observations. As the ionic radii for Fe and Co are very similar, very small differences are shown in the XRD spectra of the bimetallic Fe and Co crystallites. Of particular importance is the relative position of the Fe(110) peak (Table 3).

It is clear that the single metal iron system (10% Fe/TiO₂) corresponds perfectly with the known standard value (PDF # 6–696). This peak shifts to a lower value for both the 5 : 5 and 10 : 10 system. Further the 5 : 5 and 10 : 10 peak positions show remarkable correspondence. There can be little doubt that an Fe–Co alloy of the bcc structure was formed on reduction of the Fe : Co systems. This low temperature Fe : Co alloy was previously observed and discussed by Nakamura et al. [15] and its presence is indicated by well documented Fe–Co phase diagrams [65].

After reaction with synthesis gas, the Fe system showed evidence of the presence of iron carbide phases while these phases were absent in the XRD study for both the Co and bimetallic systems. This is also consistent with reports on Fe : Co/SiO₂ systems [8,9], but could also be due to the amorphous nature of the species.

Finally, the Fe system also exhibited the presence of Ilmenite (FeTiO₃) during reduction. This metal-TiO₂ phase is not present in the bimetallic system. The presence of such a high temperature phase was recently identified by Mössbauer Spectroscopy and EXAFS on a Fe:Ru/TiO₂ catalyst [66].

Table 4
Mössbauer parameters for Fe and Fe:Co on TiO₂^a

Sample ^b	IS ₁ mm/s	QS ₁ mm/s	width mm/s	IS ₂ mm/s	QS ₂ mm/s	width ₂ mm/s	Hikoe
10%Fe/TiO ₂	+ 0.42	+ 0.18	0.36	+ 0.30	+ 0.34	0.33	493
5% Fe/TiO ₂	+ 0.37	+ 1.10	0.44	+ 0.34	+ 0.65	0.45	–
10 Fe:10Co/TiO ₂	+ 0.38	+ 0.22	0.38	+ 0.35	+ 0.52	0.35	483
5Fe :5Co/TiO ₂	+ 0.48	+ 0.24	0.35	+ 0.44	+ 0.52	0.28	487
^c	+ 0.04	+ 0.12	0.27	+ 0.50	+ 0.51	0.24	349
^d	+ 0.04	+ 0.11	0.21	–	–	–	341

^a Error ± 0.02 mm/s, ± 10 kOe.

^b Unreduced sample unless otherwise stated.

^c 5:5 Fe:Co sample reduced at 250°C.

^d 5:5 Fe:Co sample reduced at 400°C.

3.1.6. Mössbauer spectroscopy (MBS) study

Our results, for unreduced TiO₂-supported Fe (10%) and Fe : Co systems (Table 4) revealed the distribution of Hi fields that extended to ca. 500 kOe. The presence of a sextet for the 10% Fe/TiO₂ catalyst suggests the presence of ferromagnetic particles in the oxide [67]. A doublet with $I.S_1 = -0.22 \pm 0.02$ mm/s and $Q.S_1 = -0.02 \pm 0.03$ mm/s is characteristic of high spin Fe³⁺ ions which are highly dispersed (particle size between 5 nm and 10 nm and a smaller fraction with particle size of ca. 50 nm). Lowering the metal loading on the TiO₂ (5%) results in a loss of the species associated with the sextet. As a first estimate, this indicates a loss of magnetism. However, although no hyperfine field is identified, the sample is similar to the previous one and should therefore also consist of hematite. The lower loading suggests an increase in metal dispersion. As a consequence, the electron density decreases, the electron spin is influenced and a superparamagnetic feature [68] is observed.

Mixing of the metal oxides results in systems with similar Hi values as for the 10% Fe/TiO₂ system. It is however noted that a decrease in total metal loading from 20% to 10% by mass results in a better dispersed system with indication of smaller metal particles. The spectra obtained for these mixed Fe : Co oxides supported on TiO₂ correlates well with earlier studies of Fe : Co supported on SiO₂ [69] and Al₂O₃ [29].

Reduction of these catalysts (5 : 5 system) gives the results shown in Fig. 5 and Table 4. The results for the unreduced system are shown for comparative purposes. Low temperature reduction, i.e. at 250°C for 16 h at S.V.=2000 h⁻¹ and atmospheric pressure, resulted in a sample with Hi =349 kOe, which is characteristic of Fe⁰ (330 kOe) [30]. The shift from the reported 330 kOe for Fe⁰ to 349 kOe, indicates the possibility of alloy formation between the Fe and Co phases even at these low temperatures [69]. The effect of temperature on the shift of the hyperfine magnetic field for Fe : Co alloys has been discussed [70] and our values at room temperature are consistent with the literature values. Furthermore the large shift of

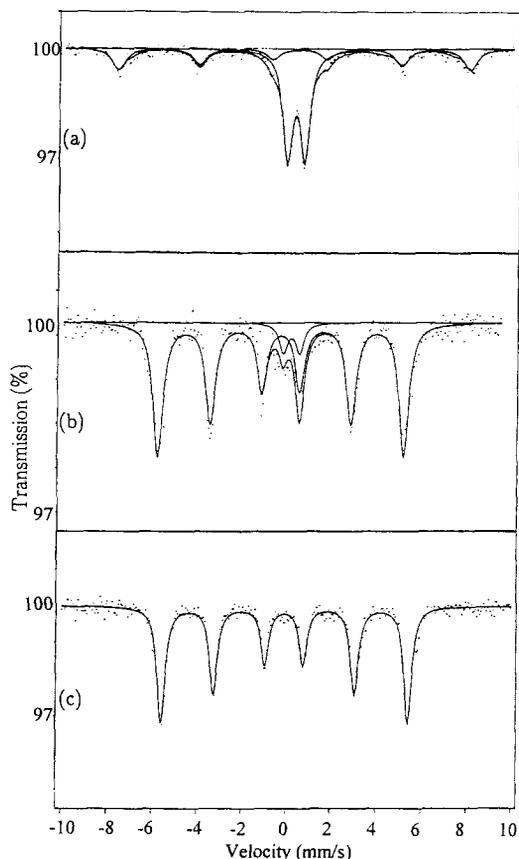


Fig. 5. Mössbauer spectra for 5% Fe : 5% Co/TiO₂ systems (a) unreduced; (b) reduced at 250°C and (c) reduced at 400°C.

$I.S_1$ towards 0 indicates the presence of metallic Fe while the presence of a component with $I.S_2 = 0.50$ reveals the presence of some unreduced Fe³⁺ species.

3.1.7. X-ray photoelectron spectroscopy (XPS) study

A number of studies have been reported in the literature in which enrichment or depletion of Fe at the surface of bimetallic catalysts containing Fe have been noted. For example Nakamura et al. [15] studied various precipitated unsupported Fe : Co bimetallic systems by Auger electron spectroscopy (AES). Ar⁺ bombardment revealed the concentration of Fe atoms to decrease slightly from the surface towards the bulk. Similar observations were made by Larkins and Khan [12] while studying the Kölbel–Engelhard synthesis reaction over TiO₂, SiO₂, Al₂O₃, MgO and ZrO₂ supported Fe–Co bimetallic systems. CO and H₂ desorption studies by Ishihara et al. [10] on Co/SiO₂, Fe/SiO₂ and Fe : Co/SiO₂ systems, also indicated that the desorption profile of Fe : Co/TiO₂ was similar to that of Fe/SiO₂. The

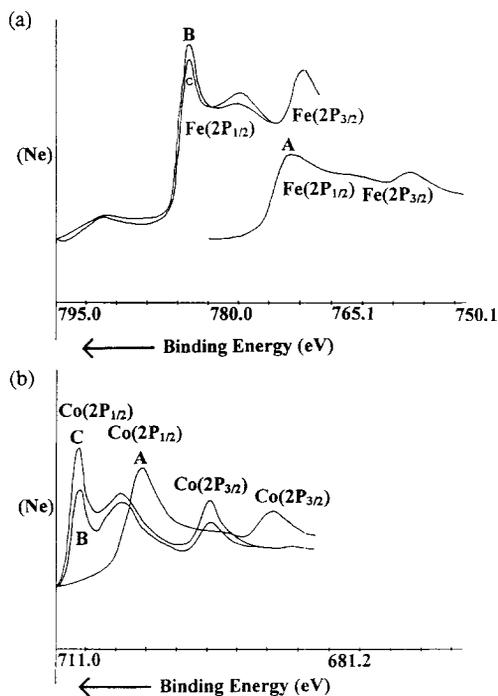


Fig. 6. XPS spectra of the 10% Fe : 10% Co bimetallic system. (a) Iron spectrum: A unreduced metal surface; B reduced metal surface before Ar^+ sputtering; C reduced metal surface after 20 min Ar^+ sputtering (b) Cobalt spectrum: A unreduced metal surface; B reduced metal surface before Ar^+ sputtering; C reduced metal surface after 20 min Ar^+ sputtering.

authors suggested that this arose from enrichment of the Fe phase in the surface of the bimetallic system. However, in contradiction to the above, Tricker et al. [33] observed Fe : Co/ Al_2O_3 spinel systems to be enriched with cobalt at the surface for both the 90 : 10 and 80 : 20 Fe : Co systems.

To assess whether Fe : Co/ TiO_2 would also show surface enrichment, XPS analysis was performed on the 5 : 5 and 10 : 10 materials. Spectra were recorded before and after reduction in hydrogen (400°C , 1 bar, S.V. = 2000 h^{-1} for 16 h) and after sputtering the sample for 30 min (see Fig. 6; 5 : 5 Fe : Co/ TiO_2). The spectra for both the 5 : 5 and the 10 : 10 systems after reduction showed little Co^{3+} phase to be present while the presence of a weak Fe $2p_{3/2}$ and $2p_{1/2}$ peak was evident. Argon sputtering for 5 min resulted in a decrease in the intensity of the Fe peak while the $2p_{3/2}$ and $2p_{1/2}$ peaks of Co became larger. The results are consistent with Fe enrichment at the surface. Further sputtering (5–30 min; 20 min, shown in the figure) gave further increases and decreases in the Co and Fe peaks respectively.

3.1.8. Scanning electron microscopy (SEM) study

Surface characterization by SEM and EDAX LINK analysis were also informative. Photographs of the 10% Fe and Co metals supported on TiO_2 ($500\times$

magnification) indicated that the Fe/TiO₂ system exhibited a smooth “molten like” surface with cracks while a granular “porous like” surface was observed for the Co/TiO₂ system. This observation of better porosity for the Co system is however not supported by B.E.T. surface area results.

Mixing the two metals reveals a different picture. The 1 : 10 system exhibited a uniform porous surface similar to that of the Co system. This is to be expected at this low level of mixing. However, the 5 : 10 and 10 : 10 systems displayed an increasing degree of non uniformity with an increase in Fe content. The higher the Fe content, the more the surface appeared to be like that of the Fe/TiO₂ system and EDAX analysis also suggested increasing surface segregation of the Fe in the bimetallic mixture towards the outer surface of the particles.

Another interesting observation from our studies is that the surface of a 1 : 10 system prepared by a stepwise impregnation method differs from that of the 1 : 10 system prepared by co-impregnation. The surface of the former, is in effect comparable to that of the 5 : 10 and 10 : 10 systems which display a rough inhomogeneous surface. The latter system exhibits smooth features similar to that of the single Co system. These two catalysts also display catalytic features similar to the catalysts with which they visually correspond (see Section 3.2).

3.2. Catalyst Evaluation

3.2.1. Activity and stability

The activity of the Fe : Co catalyst was evaluated as a function of % conversion, specific activity (μ mol CO/g/s) and activity per metal site (TON). It is a well known phenomenon that Fe/TiO₂ systems show low catalytic conversions [10]. Similar results are reflected in Table 5 for the 10% Fe/TiO₂ catalyst which shows CO conversions of 7.7% after 200 h on line. By comparison, the 10% Co/TiO₂ has a CO conversion of ca. 36% for the same time-on-line. The overall activity for the bimetallic systems, as seen in Fig. 7, decreases with an increase in Fe content. The results may be related to that of an inactive material being mixed with an active metal, resulting in some degree of dilution of the more active Co phase. This will subsequently result in a decrease in catalytic activity with an increase in Fe content. A similar observation was recently made for a Fe : Co/carbon bimetallic catalyst employed in benzene hydrogenation and thiophene desulphurization reactions [71]. A further decrease is expected due to Fe enrichment at the surface of the bimetallic system (see Section 3.18). The higher the iron loading the more severe will be this phenomenon.

All catalysts follow a similar loss in CO conversion with continued use, and are especially unstable over the first 50 h on line. Similar findings on Fe : Co supported catalysts were made by Butt and Schwartz [6] and Audier et al. [16]. Further, as the amount of Fe in the catalyst increases, the more pronounced will be the deactivation effect (see Fig. 8) The 10 : 10 system fails to reach moderate stability even after 200 h on line! The seemingly better catalyst stability obtained by Butt and

Table 5
The influence of Fe:Co ratios on the Fischer–Tropsch reaction^a

Catalyst : Fe : Co (%)	0 : 10	0.1 : 10	1 : 10	1.10B ^b	5 : 10	10 : 10	5 : 15	10 : 5	10 : 0	5 : 5
CO conversion (%)	36.0	36.9	35.7	14.5	22.3	19.7	28.9	9.0	7.7	14.7
Specific activity ($\mu\text{mol Co s}^{-1} \text{g}^{-1}$)	0.36	0.54	0.35	0.18	0.20	0.15	0.26	0.07	0.07	0.13
TON ($\times 10^{-3} \text{s}^{-1}$)	42.0	40.3	29.7	15.6	15.6	10.6	30.1	9.3	8.00	13.80
Selectivity (% by mass)										
CH ₄	14.5	14.5	11.8	15.0	10.1	8.0	15.3	28.6	5.40	19.20
LPG	7.4	9.1	12.5	12.8	16.6	23.0	24.5	40.2	22.80	17.20
Petrol	34.9	36.7	40.3	34.0	41.9	56.2	44.3	23.1	49.50	37.70
Diesel	25.9	24.5	19.9	14.9	17.0	5.5	13.00	5.1	14.20	12.90
Wax	17.2	15.2	15.6	22.9	14.0	7.4	2.5	3.1	8.10	13.10
WGS extent	trace	trace	trace	0.02	0.02	0.04	0.04	0.01	0.01	1.70
Paraffin (%)	93.9	95.5	92.2	95.5	85.7	77.1	86.1	90.40	100	86.60
Olefin (%)	0.3	0.8	4.0	3.4	12.3	14.3	11.9	5.00	–	12.60
Oxygenates (%)	0.8	2.3	3.9	1.2	2.0	4.7	2.1	4.60	–	0.90
ASF chain growth values										
α_1	0.79	0.85	0.84	0.87	0.74	0.56	0.74	0.65	0.81	0.77
α_2	0.88	–	–	–	0.88	0.85	–	0.84	–	0.89

^a Reaction conditions: Calcination: 400°C, 1 atm, 2000 h⁻¹, 16 h, flowing air; Reduction: 350°C, 1 atm, 2000 h⁻¹, 16 h, 100% H₂; Synthesis: 220°C, 10 bar, 350 h⁻¹, 200 h, 2H₂:1CO.

^b Fe added to Co/TiO₂

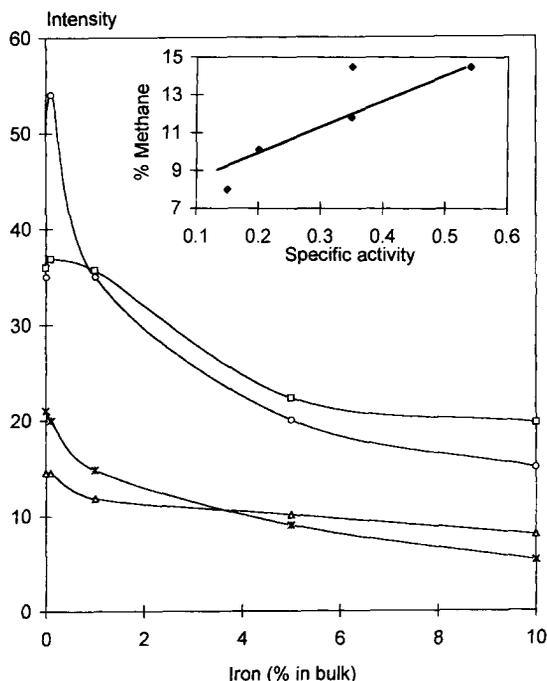


Fig. 7. The effect of iron content on the (a) % CO conversion □, (b) TON $2 \times 10^{-3} \text{ s}^{-1}$ △, (c) specific activity, $\mu \text{ mol CO g}^{-1} \text{ s}^{-1} \times 10^{-1}$ ○, (d) % CH₄ *.

Schwartz for a Fe : Co/SiO₂ bimetallic system could be related to the low CO conversions (ca. <10%) used in their studies.

Several studies have indicated that the activity of bimetallic catalysts is *enhanced* relative to the pure metals [11,15]. These results were for systems with constant metal loading (ca. 10%) and different metal ratios (ca. 6% Fe : 4% Co) and the results indicated *improved activity* upon alloying of the metals. This is not reflected in our results. Our observations are however similar to studies reported by Ishihara et al. [10] for Fe : Co/SiO₂ systems, where higher activity was observed for a higher (i.e. 2.5 : 7.5) Co loaded system when compared to a 5 : 5 system.

3.2.2. Methane selectivity

Methane selectivities are high (15% to 20% by weight) for the TiO₂-supported Fe : Co bimetallic systems. High methane selectivities were also obtained for unsupported [15], SiO₂ [7,8,10], zeolite [13,14] and carbon [11] supported Fe : Co bimetallic systems. The values obtained are however lower (15% by weight) than most of the values reported in the literature. It should however be kept in mind that most of the reported values are for systems evaluated at temperatures approximately 30°C higher than those reported here.

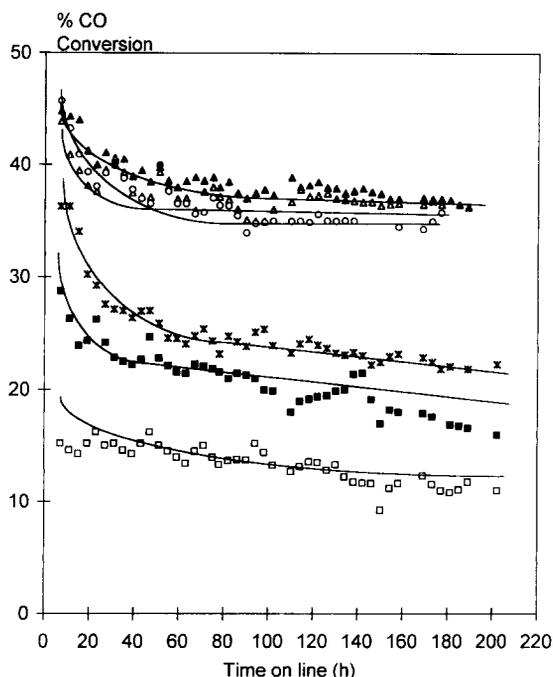


Fig. 8. The effect of Fe concentration on the deactivation profile of Fe:Co/TiO₂ bimetallic systems. (a) 10% : Fe □, (b) 0.1Fe : 10Co △, (c) 1Fe : 10Co ○, (d) 5Fe : 10Co *, (e) 10Fe : 10Co ■, (f) 10%Co ▲.

Increasing the Fe content of the bimetallic systems results in a decrease in methane formation. Fe catalysts are known for their low methane selectivities, and Co catalysts for their enhanced selectivities towards methane [72,73]. This decrease is related to the lower catalyst activity i.e. the lower the conversion the lesser will be the methane produced.

3.2.3. Light petroleum gas (LPG), petrol and diesel

From Table 5 it is clear that for all the bimetallic systems, i.e. 0.1 : 10; 1 : 10; 5 : 10 and 10 : 10 the C₅–C₁₁ fraction is the predominant product. The second most abundant product is dependent on the level of Fe loading. The higher the Fe level, the more will be the production of light petroleum gases (C₂–C₅). This product range is produced at the expense of the C₁₂–C₁₈ and > C₁₈ fractions. Care must be used in directly comparing the spectra, as the change in conversion is large, increasing with iron content, and decreasing activity. A comparison of the 0 : 10, 0.1 : 10 and 1 : 10 systems revealed that they have similar CO conversions at 35.6% to 36.0% and 37.0%. Here, the increase in iron content shifts the product spectrum to lower hydrocarbons, LPG and petrol fractions, indicating the influence of the bimetallic catalysts [74] on increasing lower hydrocarbons and olefinitivity.

Table 6
The effect of iron concentration on hydrocarbon selectivity for Fe : Co/TiO₂ systems

Catalyst	0:10	0.1 : 10	1 : 10	5 : 10	10 : 10	10 : 0	5 : 5
C ₂ olefin	–	0.03	0.85	0.14	0.21	–	0.30
C ₂ paraffin	–	1.03	1.77	1.78	2.70	2.19	2.38
o/(o+p) ^a	0.04	0.03	0.32	0.07	0.07	–	0.11
C ₃ olefin	–	0.95	1.74	2.16	3.36	–	5.06
C ₃ paraffin	–	2.21	2.65	2.45	3.53	8.55	2.90
o/(o+p) ^a	0.32	0.30	0.40	0.47	0.49	–	0.63
C ₄ olefin	–	1.09	1.93	2.95	3.12	–	3.24
C ₄ paraffin	–	3.63	3.07	2.59	3.52	11.88	3.64
o/(o+p) ^a	0.28	0.23	0.31	0.53	0.47	–	0.47
C ₅ olefin	–	0.91	1.38	2.66	2.60	–	0.19
C ₅ paraffin	–	4.97	4.53	3.37	3.95	12.59	5.70
o/(o+p) ^a	0.18	0.15	0.23	0.44	0.40	–	0.03
C ₂ C ₅ o/(o+p) ^a	0.28	0.20	0.32	0.44	0.40	–	0.37

^a olefin/(olefin+paraffin) ratio

3.2.4. Olefinity

As expected and previously documented [15], a decrease in paraffinity coincided with a slight increase in olefinity for the Fe : Co bimetallic systems. A breakdown of the C₂–C₅ spectrum (see Table 6) for the 0.1; 1.0; 5.0 and 10 : 10 systems shows the trends for the paraffins and olefins.

From the table it is clear that olefinity, especially for C₃ and C₄, increases with an increase in iron content and a decrease in activity. As observed by Arcuri et al. [7] for a SiO₂ supported system, nominal amounts of ethylene and pentene were also observed. The total C₂–C₅ olefinity increased to a maximum for the 5 : 10 system. The higher olefinity for this latter system is most probably [75] due to the lower residence time as indicated by the lower CO conversion.

Fig. 9 shows the effect of the time spent on line on the olefin production. From this Figure it is clear that the level of Fe present in the bulk of the catalyst influences the deactivation profile.

3.2.5. Oxygenate products

As expected, and portrayed in Table 5, an increase in oxygenate product formation was found with increase in Fe content in the bimetallic systems. These products were similar to those reported [6,10,11] for other bimetallic systems and consist mainly of C₁ to C₄ alcohols. Results observed for the 5 : 10 system are unexpectedly low, but this could be due to an analysis problem, as very low selectivities (less than 5%) were obtained for these catalysts. Gas chromatographic analysis of the water product fraction revealed trivial amounts

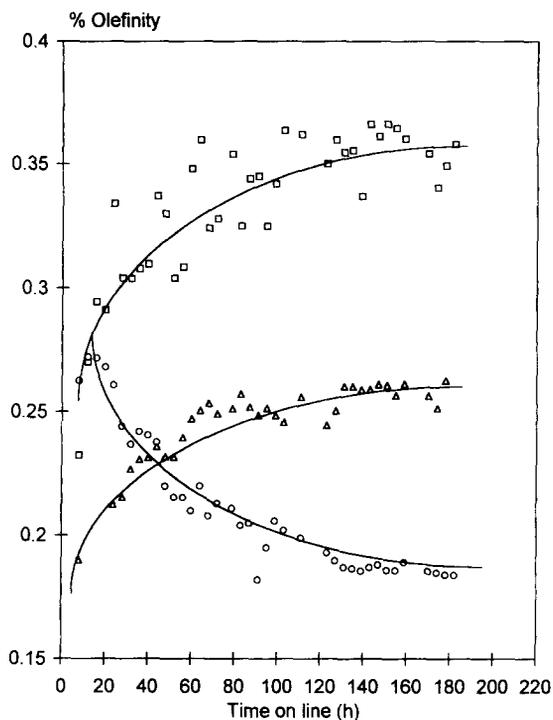


Fig. 9. The effect of Fe content on the C₂–C₅ olefins with time on line (a) 10Fe : 10Co □, (b) 5Fe : 10Co △, (c) 0.1Fe : 10Co ○.

of methanol, ethanol and propanol with ethanol being the most abundant of these products.

3.2.6. Water gas shift (WGS) activity

There are indications of the expected increase in WGS activity with higher Fe content, although a decrease in activity is observed for these catalysts (5 : 10 to 10 : 10 systems). The measured WGS activity was found to be very low, on average less than 5%, and consistent with that reported for other supported Fe : Co bimetallic systems [6]. The pure Co and 0.1% and 1% Fe content systems exhibited no WGS activity. That no WGS activity was observed for the Fe catalyst can be attributed to the very low overall activity obtained for this system. It was also observed, although the scatter is large, that the WGS activity decreased with time as observed for the 5 : 10 and 10 : 10 systems. A combination of medium pressure (10 bar), poor conversions (ca. 20%–25%) and low Fe metal loading contributed to this observed low WGS activity.

3.2.7. Higher hydrocarbon (wax) selectivity

From Table 5 it is clear that the selectivity to wax products decreased with an increase in Fe content (0% to 10%). It was initially thought that Fe, a known wax

producer [76], may have been stabilized by the presence of Co. Indeed, Ishihara et al. [10] found a 3 : 1 and a 1 : 1 Fe : Co/SiO₂ system to be superior higher hydrocarbon producers when compared with the single metal systems. We are however of the opinion that this effect is shortlived and that the selectivities will deteriorate with time. The catalyst used by Ishihara et al. was reduced for only one hour at 250°C and as the level of reduction is not reported it can be assumed that very low uneven levels of reduction would be obtained. Furthermore, although their synthesis evaluation conditions are similar to our own, their mass balance data are for systems that were examined for only 5 h to 7 h on line. As indicated, these catalytic systems exhibit very unstable behaviour over the first 24 h and stability is only achieved after 150 h on line.

3.2.8. *The effect of metal loading*

When the total loading for the 1 : 1 catalyst changed from 20% to 10%, the specific activity decreased from 0.151 μ mol g cat h to 0.131 μ mol g cat h (a 13% decrease). A decrease is expected as the total level of active metal is decreased. However, the drop in CO conversion is small and can be accounted for by an 18.9% increase in B.E.T. surface area (30.50 m²/g to 45.00 m²/g). It would seem that there is a better utilization of the amount of metal present in the 5 : 5 system. More importantly however, is the activity per metal site (TON) which decreased from 13.8 × 10⁻³ s⁻¹ for the 5 : 5 system to 10.6 × 10⁻³ s⁻¹ for the 10 : 10 system, confirming the previous statement.

3.2.9. *The effect of catalyst preparation method*

As discussed, the Fe in the Fe : Co/SiO₂ systems was found to segregate to the surface of the catalyst during either preparation, reduction or reaction, resulting in an Fe rich surface. Furthermore, the previous sections also revealed that Co is the most active phase when supported on TiO₂ even though the presence of Fe enhanced certain favorable catalytic features. In an effort to maximize catalytic activity, with similar selectivity shifts as observed for the 1 : 1 ratio system a 10% Co/TiO₂ system was impregnated with 1% Fe. This catalyst is referred to as 1 : 10 B. The 1 : 10 B system acted quite differently, particularly with respect to activity, when compared to the 1 : 10 co-impregnated system (Table 5). The 1 : 10 B system, in many ways mimicked that of the 5 : 5 system (especially activity data) discussed earlier while the 1 : 10 system acted like the pure Co/TiO₂ system. Clearly the issue relates to surface Fe and its impact on the reaction rate.

4. Conclusion

The issue of alloy formation for bimetallic catalysts and the evaluation of the physical and chemical properties of alloys with respect to electronic and steric effects has been well documented in the literature [77,78]. The objective of this

study was undertaken to assess whether alloys had been formed indeed on TiO₂ during a variety of reduction procedures and to compare the results with literature studies on other reports of supported and unsupported Fe/Co mixtures.

The following conclusions can be drawn from the work.

1. Fe/Co alloys are readily formed under mild conditions on TiO₂.
2. It thus appears that at sufficiently high loadings (>5%) Fe : Co alloys can form on TiO₂, Al₂O₃ and SiO₂. Alloys also form from unsupported Fe:Co mixtures.
3. Reduction procedures generate materials in which Fe is concentrated at the surface at the expense of cobalt.
4. Materials that have been prepared by sequential addition (Co then Fe) have surface properties similar to Fe : Co/TiO₂ catalysts in which the mixtures are Fe rich.

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