

Fe:Co/TiO₂ bimetallic catalysts for the Fischer–Tropsch reaction Part 3: The effect of Fe:Co ratio, mixing and loading on FT product selectivity

D.J. Duvenhage, N.J. Coville*

Molecular Sciences Institute, School of Chemistry, University of the Witwatersrand, Private Bag 3, Wits 2050, Johannesburg, South Africa

Received 21 December 2004; received in revised form 6 May 2005; accepted 9 May 2005

Available online 22 June 2005

Abstract

A series of catalysts, Fe:Co/TiO₂, were made with different total metal loadings (Fe:Co wt.% loading; 1:1–5:5), with different Fe:Co ratios (at 10% metal loading) and using different synthetic procedures (impregnation versus physical mixing). The catalysts were characterised by BET, CO-chemisorption and Mössbauer spectroscopy. Their Fischer–Tropsch (FT) activity/selectivity properties were also measured. The co-impregnated catalysts revealed that the 5:5 Fe:Co catalyst showed higher activity than catalysts prepared with either 2.5:7.5 or 7.5:2.5 Fe:Co ratios. Physically mixed samples of Fe/TiO₂ and Co/TiO₂ showed different selectivities and also gave better FT activity than equivalent co-impregnated Fe:Co samples. The reducibility behaviour and Mössbauer spectra of the Fe:Co samples suggested that the catalyst activity and selectivity changes related to the Co phase, Fe–Co alloy formation and the ability of the Co to enhance the reducibility of the Fe. A relationship between reduction level and activity was observed. The bimetallic systems also showed good stability and only modest changes in selectivity with time on line.

© 2005 Elsevier B.V. All rights reserved.

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

1. Introduction

The FT (Fischer–Tropsch) reaction entails the conversion of CO and H₂ to a spectrum of products mainly comprising alkenes and alkanes [1–4]. This product spectrum is very broad and consequently many studies have been carried out under FT conditions with the aim of controlling and limiting the product selectivity. The products most desired are those with (i) a low methane and low oxygenate content, (ii) a high alkene/alkane ratio and (iii) a high wax or C₅–C₁₀ content. This control is typically achieved by modification of the catalyst, the reactor and/or the reaction conditions [1]. As the catalyst activity impacts on the selectivity, the long term stability of a FT catalyst is also an important factor in controlling the catalyst selectivity.

Since the discovery of the FT reaction in the 1920s the industrial catalysts of choice have proven to be Co and Fe

[4]. While Ni and Ru have also shown FT activity, other metals have so far shown little propensity to catalyse the FT reaction to hydrocarbons.

Both Co and Fe are typically used when combined with a range of supports and promoters that permit further control over the product spectrum [5].

A viable methodology that has been developed for controlling the property of a metal is that of alloying [6–9]. Alloys (and their precursor oxides) have been used in the FT reaction and studies have shown that the selectivity of the FT product spectrum, relative to the single metal catalysts, can be modified using this type of catalyst [10]. In particular it has been reported that a mixture of the two most active catalysts, Fe and Co, have generated product streams in the FT reaction richer in olefins than expected from either Fe or Co catalysts [11–13].

Fe:Co catalyst mixtures, typically supported, have been synthesized by numerous routes [6,11–15]. Supports that have been used include alumina [6], silica [16], carbon [17,18], zirconia [19] and titania [10,20–22].

* Corresponding author. Fax: +27 11 717 6749.

E-mail address: ncoville@aurum.wits.ac.za (N.J. Coville).

Fe:Co materials are not only of interest in catalytic reactions (e.g. FT synthesis [10–16,19–22], NH_3 synthesis [17], carbon nanotube synthesis [23,24]) but because of their interesting magnetic properties the synthesis (e.g. by sol–gel [7], co-precipitated [6], hydrothermal procedures [9]) and characterization (e.g. Raman, XRD, TEM [6,11–13]) of these mixtures has been well documented.

In earlier studies we reported on the use of Fe:Co/TiO₂ catalysts in the FT reaction. In particular in these earlier studies we reported on preliminary metal loading effects [10], as well as reduction and calcination effects on the FT synthesis reaction [22]. Herein, we wish to further extend these studies to reveal the impact of combining the two metals, Fe and Co, on the FT reaction. In particular we wish to report on the role of Fe:Co ratio as well as mixing, loading and long term stability effects on the FT product activity and selectivity. Where possible we have compared our results with studies reported in the literature for similar Fe:Co systems.

2. Experimental

Commercial TiO₂ (P25, Degussa) was mixed with deionized water, dried at 120 °C for 1 h and calcined. Standard calcination of the TiO₂ was performed 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 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 onto the pre-calcined TiO₂ 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 (200 °C, 16 h, air) and reduced (300 °C, 16 h, pure H₂, 1 bar) prior to characterization and testing.

Two physically mixed systems, a 2.5:2.5 Fe:Co/TiO₂ (5% total metal loading) and a 5:5 Fe:Co/TiO₂ (10% total metal loading) were also prepared. This was achieved by mixing (i) 5% Fe/TiO₂ and 5% Co/TiO₂ and (ii) 10% Fe/TiO₂ and 10% Co/TiO₂ separately prepared samples. The two components were thoroughly mixed (in a slow tumble mixer) to produce a visually homogeneous physical mixture of Fe:Co/TiO₂.

2.1. Catalyst characterization

Elemental analysis (Co, Fe) was determined by atomic absorption spectroscopy. BET surface area analysis, scanning electron microscopy (SEM) and CO chemisorption were performed by classical procedures on apparatus described previously [10]. The equipment used to measure the Mössbauer spectra consisted of an Austin Science Associated drive with Ortec electronics and a ⁵⁷Co(Rh) gamma-ray source [10]. The isomer shift was obtained with reference to alpha-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. 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 utilizing a non-linear least squares method was used to fit a number of correlated Lorentzian peaks to the data.

2.2. 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 gas product fraction was analyzed by GC as described previously [10]. All catalysts were activated (reduced) for a 16 h period on line 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 [10]. 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 of 100 ± 5% was accepted as adequate for comparison purposes.

3. Results and discussion

In an earlier study it was observed that the best FT catalytic activity was obtained for a 10% total metal loaded Fe:Co (1:1) catalyst supported on TiO₂ that was calcined at 200 °C and reduced at 300 °C [10]. These conditions were thus used as the standard conditions in this study.

3.1. The variation of Fe:Co ratio (10% metal loading)

FT results generated under the standard set of conditions used are portrayed in Table 1 and Fig. 1. This study is related to an earlier study from our group [10,22] and to a study performed by Arai et al. [21]. While there are numerous differences both in the synthesis and conditioning between our catalysts and the Arai catalysts the key differences relate to their use of (i) short catalytic reaction times (8 h) and (ii) the use of a less reduced catalyst. Notwithstanding that the

Table 1
The influence of Fe:Co ratio at constant metal loading on the Fischer–Tropsch reaction^a

Catalyst sample	10:0	10:0 ^b	$\frac{10+10}{2}$	5:0	7.5:2.5	5:5 ^c	2.5:7.5	0:5	$\frac{5+5}{2}$	0:10	
Metal loading (% by mass)	10	10	10	5	10	10	10	5	5	10	
CO conversion (%)	11.4	7.7	45.7	11.0	18.3	36.3	30.9	42.5	28.7	63.9	
Specific activity ($\mu\text{mol CO s}^{-1} \text{g}^{-1}$)	0.10	0.10	0.59	0.10	0.17	0.40	0.34	0.58	0.32	1.15	
TON ($\times 10^{-3} \text{s}^{-1}$)	19.2	8.0	115.0	16.7	15.5	70.0	37.4	65.2	43.0	225.5	
Selectivity (% by mass)											
CH ₄		27.2	5.4	8.9	3.6	18.9	11.0	20.9	14.6	7.5	14.4
C ₂ –C ₄		72.8	22.8	6.0	29.8	45.9	14.6	14.5	13.7	6.6	9.3
+C ₅ fraction-total		0.0	71.8	85.0	66.7	34.7	74.2	64.2	71.7	86.0	76.1
C ₅ –C ₁₁		tr	22.8	35.7	66.7	34.6	51.3	34.5	33.6	24.3	30.8
C ₁₂ –C ₁₈		tr	49.5	28.9	tr	0.2	12.3	17.8	17.2	41.6	30.8
>C ₁₈		tr	14.2	20.5	tr	tr	10.6	11.9	20.9	20.1	14.5
WGS extent											
Paraffin (%)		tr	8.1	0.02	tr	<0.02	~0.05	tr	tr	tr	tr
Olefin (%)		100.0	100.0	95.1	100.0	68.5	82.9	96.6	100.0	92.2	95.9
C ₂ –C ₅ olefins (%)		tr	tr	4.8	tr	26.9	15.8	1.8	tr	7.8	3.8
CO ₂ (%)		tr	tr	–	tr	4.6	1.4	1.6	tr	–	0.2
Oxygenates (%)		tr	tr	0.04	tr	tr	1.5	tr	tr	0.01	tr
ASF chain growth values											
α_1		tr	0.81	0.86	na ^d	0.61	0.71	0.80	na ^d	0.83	0.80
α_2		tr	–	–	na ^d	–	0.85	–	na ^d	–	–
Surface characterization											
CO adsorbed (μmole)		5.2	8.8	5.2 ^c	6.0	11.0	5.8	9.1	8.9	7.5 ^c	5.1
Reduction (%)		35	9.5	55 ^c	9.0	42	95	49	60	35 ^c	74
Dispersion (%)		1.6	8.9	1.2 ^c	14.9	3.0	0.6	2.1	3.5	9.2 ^c	0.8
BET surface area (m^2/g)		48	48	48 ^c	51	–	51	–	51	51 ^c	47

^a Reaction conditions: calcination: 200 °C, 1 atm, 2000 h⁻¹, 16 h, flowing air; reduction: 300 °C, 1 atm, 2000 h⁻¹, 16 h, 100% H₂; synthesis: 220 °C, 10 bar, 350 h⁻¹, 200 h, 2H₂:1CO.

^b Values for Fe/TiO₂ system calcined: 400 °C, 1 atm, 2000 h⁻¹, 16 h, flowing air; reduction: 350 °C, 1 atm, 2000 h⁻¹, 16 h, 100% H₂; synthesis: same as (a).

^c D.J. Duvenhage, N.J. Coville, Appl. Catal. A: Gen. 233 (2002) 63–75.

^d Not analysed.

^e Value generated is an average from equal weights of the 10% and 5% single metal systems respectively.

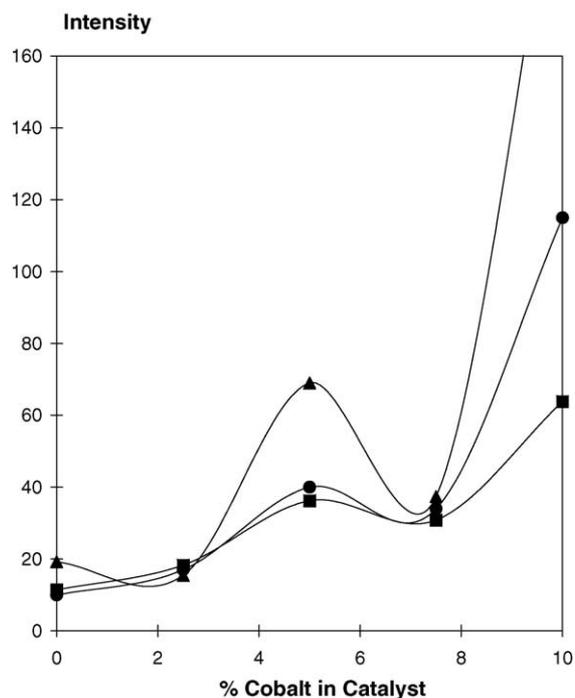


Fig. 1. The effect of cobalt loading on activity parameters of the 10% Fe:Co/TiO₂ catalysts ((●) specific activity ($\mu\text{mol/g/s} \times 10^{-2}$), (▲) TON ($\times 10^{-3} \text{s}^{-1}$), (■) % CO conversion).

experimental conditions used in the two studies were different, similarities in (i) compositional behaviour (Fig. 1) and (ii) FT product selectivities were observed.

Fig. 1 (and Table 1) shows that the CO conversion for the bimetallic systems goes through a maximum for the 5:5 Fe:Co/TiO₂ system while the 2.5:7.5 system has superior activity to the 7.5:2.5 system. Arai found similar behaviour in his system [21]. The 10% cobalt catalyst showed a factor of two higher activity than the 5:5 system, while the iron catalyst proved to have the lowest activity.

A comment on the low CO conversion for the Fe data is necessary. The 10% Fe/TiO₂ was calcined at both 200 and 400 °C but the activity remained low using the different calcination temperatures (11.4% and 7.7%, respectively; Table 1). Lower loadings of Fe (5%) also gave poor CO conversion data (11%). It is thus clear that the reduction conditions are insufficient to produce an active Fe catalyst, even though the %reduction data appears to be high enough for the 10% Fe/TiO₂ catalyst to generate better conversion data. This poor activity also impacts on the low olefin, WGS reaction and CO₂ yields.

Although the 5:5 system shows a CO conversion between that of the two single metal systems, it is clear that the higher iron content also inhibited the overall activity more than the cobalt enhanced the activity. Interestingly Arai found lower

CO conversions for both the single Co and Fe catalysts. A similar maximum in the +C₅ product and a minimum in CH₄ selectivity was also observed with the 5:5 Fe:Co catalysts in both our study and the Arai study.

The data from the two studies thus suggest that the time-on-line issue does not alter the relative trends in the data sets. Indeed, we also noted in our study, that although the absolute numbers changed, that the 10:0, 7.5:2.5, 5:5 and 2.5:7.5 systems studied showed similar trends in conversion and selectivity after being on line for both 8 and 250 h.

It can be speculated that the difference in absolute FT activity in the Arai and our study relates to experimental issues (e.g. intrinsic heat transfer problems associated with the use of powder pressed pellets and/or the lower degree of reduction used in the Arai study).

Of more significance is the finding that the relative activity rates (and the selectivity) in both studies are similar, suggesting that the rates relate to both metal–metal interactions and the effects of reducibility on performance (see below).

3.1.1. Reducibility effects

Since the 5:5 Fe:Co bimetallic system contains only 5% Co a comparison with a 5% loaded Co sample can also be made (Table 1). The data reveal that the 5% Co single metal system is similar to the 5:5 Fe:Co system in both CO conversion and TON. However, the catalyst selectivity is different as revealed by the olefin to paraffin ratio for the two catalysts. This indicates that while the activity data is dominated by Co, the selectivity data is influenced by the presence of the Fe.

The influence of the Fe is indicated by the correlation of total metal reduction with the TON (Table 1, Fig. S1 supplementary) [25,26]. It appears that the addition of Co to Fe aids in the reduction of Fe.

Mössbauer studies were performed on the Fe:Co catalysts (Fig. 2 and Table 2). As the Mössbauer data relate directly to the iron content in the catalyst, it can also be seen that the reduction of Fe is influenced by the Co. Indeed, the data are consistent with the reduction/activity relationship discussed above. This is shown by the pronounced sextet, which indicates very high magnetic properties for these catalysts (see Fig. 2d). The small quantity of paramagnetic particles found in this sample increased substantially from 16.8% to 80.1% with a decrease in iron content from 7.5% to 2.5%. The mean average Fe particle size was found to increase from approximately 5–10 to 50–80 nm, consistent with the increasing paramagnetic features found for the catalysts. The Mössbauer data thus confirms the poorer dispersion observed (as the cobalt content increases), and hence confirms the reduction behaviour discussed above. The Mössbauer data presented here are in line with data previously reported for Fe:Co/TiO₂ catalysts in which the support material was calcined between 200 and 400 °C [22] and in which decreasing metal content (from 20% to 10%)

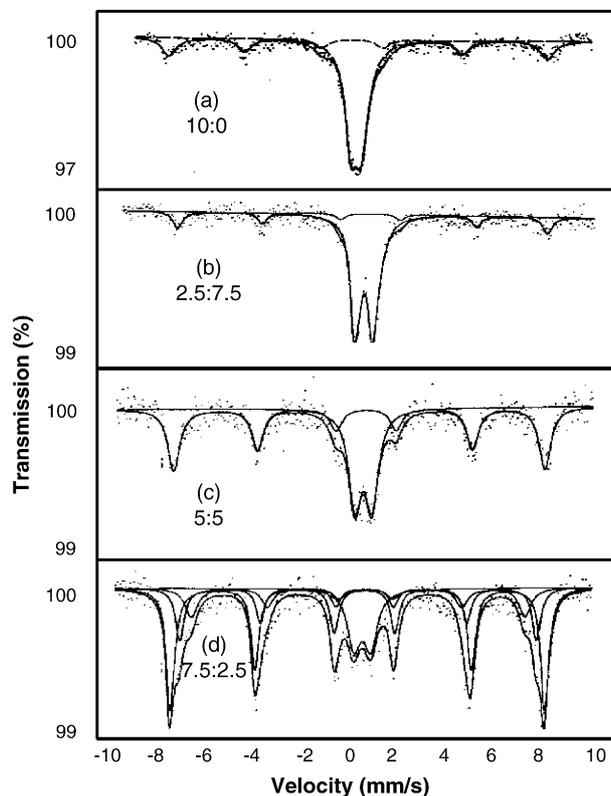


Fig. 2. Mössbauer spectra of different Fe:Co loaded catalysts, at fixed metal loading, supported on TiO₂, (a) 10Fe:0Co, (b) 2.5Fe:7.5Co, (c) 5Fe:5Co, (d) 7.5Fe:2.5Co.

resulted in better dispersed systems which were more difficult to reduce [10].

3.1.2. Metal–metal interactions

Cobalt can exist in a number of phases and the phase can be influenced by the Co:Fe ratio [17]. The active metal phases generally associated with good catalytic activity are the hcp/fcc phases [27]. This finding was also supported by an in situ XRD and Mössbauer study performed on our single metal Co/TiO₂ system [10]. Fe on the other hand exists in the bcc phase, results supported by our studies on a single metal Fe/TiO₂ system [10]. The 5:5 Fe:Co system forms an alloy and this alloy has the bcc structure [9,10,13,17], presumably by the Fe imposing its structure on the Co at high Fe concentrations. At low Fe concentrations the Co fcc structure is retained in the bimetallic system [10,17], and Fe segregates to the surface of the Fe:Co alloy system [17]. The latter effect is furthermore reported to be enhanced by increasing concentrations of cobalt [17]. Hence, these two effects will impact on the activity/selectivity as a function of Fe:Co ratio, giving rise to the unusual activity data seen in Fig. 1. In summary: (i) the 7.5:2.5 and 5:5 Fe:Co systems exist predominately in the bcc phase, (ii) the 2.5:7.5 Fe:Co system exists as a mixture of bcc, fcc and hcp phases, and (iii) the Fe reducibility is enhanced by Co. Further, as surface segregation of Fe is enhanced in the presence of Co, Fe

Table 2
Mössbauer parameters for bimetallic Fe:Co/TiO₂ catalysts with increasing Co content

Catalyst	IS ₁ ^a (mm/s)	QS ₁ ^b (mm/s)	W ₁ ^c (mm/s)	M ^d (%)	IS ₂ ^e (mm/s)	QS ₂ ^f (mm/s)	W ₂ ^g (mm/s)	PM ^h (%)	Hi ⁱ (kOe)	PM/M
100% Fe	0.23	0.20	0.36	29.2	0.10	0.45	0.33	70.8	493	2.4
7.5:2.5	0.40	0.25	0.30	83.2	0.39	0.69	0.34	16.8	438	0.2
5.0:5.0	0.39	0.21	0.30	55.8	0.39	0.70	0.32	44.2	487	0.8
2.5:7.5	0.43	0.25	0.24	19.9	0.37	0.74	0.27	80.1	486	4.0
Error (±)	0.02	0.02	0.02	–	0.02	0.02	0.02	–	10	–

^a Isomer shift (doublet).

^b Quadruple splitting (doublet).

^c Half width (doublet).

^d M: percent magnetic attribution.

^e Isomer shift (sextet).

^f Quadruple splitting (sextet).

^g Half width (sextet).

^h PM: percent magnetic attribution.

ⁱ Field strength

will be driven to the surface in the 2.5:7.5 system (more than in the 5:5 system) and the catalyst should be less active than the 5:5 system (as observed). The Fe–Co alloys on TiO₂ are therefore not as active as the single metal Co/TiO₂ catalysts.

While it is clear that a number of factors may be responsible for the observations, the relative importance of the effects cannot at this stage be evaluated.

As stated previously the large changes in CO conversion for these systems makes comparison of selectivity data difficult [28]. Table 1 does however indicate that the 7.5:2.5 and 5:5 bimetallic catalysts (i.e. with high iron content) produce more olefins, oxygenates and lower olefins (C₂–C₅) when compared to the catalysts with low Fe loading. The activity to WGS was minimal for all catalysts.

3.2. Physical mixture of salts: Fe:Co/TiO₂ catalysts with 5% and 10% metal loading

A series of catalysts were synthesized by physically mixing separately prepared Fe/TiO₂ (5% and 10%) and Co/TiO₂ (5% and 10%) samples containing different amounts (2.5% and 5%) of Fe and Co on TiO₂. These Fe:Co/TiO₂ bimetallic catalysts were characterized and their FT activity investigated (Table 1). Of the two sets of catalysts synthesized the 10% total metal loaded material has a similar total metal content to the solution co-impregnated 5:5 Fe:Co catalyst. Two reference catalysts (5% Co, 5% Fe) were also synthesized to permit correlation with the 2.5:2.5% Fe:Co physically mixed catalyst (Table 1).

Differences are observed for the activity values for the two differently prepared 5:5 Fe:Co catalysts. Indeed the physically mixed catalyst shows *higher* CO conversion and TON values than the co-impregnated sample (TON = 0.115 s⁻¹ for the physically mixed sample and 0.068 s⁻¹ for the co-impregnated sample). The activity values for the physically mixed sample are also closer to those observed for the 10% Co catalyst and suggests that the Co is acting independently of the Fe in the physically mixed 5:5 Fe:Co catalyst.

Differences are also observed in the selectivity data. In particular, the physically mixed catalyst shows (i) increased

+C₅ fraction, and (ii) a low paraffin/olefin ratio, relative to the co-impregnated sample. These are characteristics expected for Co catalysts. These product selectivity shifts are not due to the differences associated with changes in conversion. Co-impregnation of the active metals in a Fe:Co/TiO₂ catalysts thus inhibits activity but improves the selectivity to the lower hydrocarbon spectrum and the olefins.

A possible explanation for the inhibition of catalytic activity in the co-impregnated sample, which would also explain the shifts in selectivity in this sample, is that the close contact between Fe and Co (and new support interactions) yields (i) new Co–Fe bonds and (ii) affects the reducibility of the Fe. This in turn leads to weaker CO adsorption and bond dissociation capabilities by the metals and results in higher chain termination features. The evaluation of this interaction can in principle be done by TEM-EDX analysis, but the post-reaction analysis is non-trivial. SEM and EDAX analysis [10], as well as in situ XPS analysis [10] did suggest that Fe segregated to the surface of Fe:Co catalysts. Further Fe/TiO₂ has less ability to produce higher hydrocarbons when compared with the single metal Co/TiO₂ system.

3.3. The effect of varying the absolute metal loading on FT activity and selectivity

It was previously shown [10,22] that the 10:10 and 5:5 systems calcined at 400 °C displayed similar dispersions at 1.4 and 1.2%, but different levels of reduction, i.e. 70% versus 92%. It appeared that the higher metal loading inhibited the reduction process. To explore this phenomenon further, a range of 1:1 ratio Fe:Co/TiO₂ catalysts was studied with different metal loadings (≤10% by mass) to determine the effect of Fe:Co dispersion on the activity of the system.

Activity and selectivity data for a series of Fe:Co complexes containing equal amounts of Fe and Co but with variable metal loading, i.e. 2%, 4%, 6%, 8% and 10% were recorded and are given in Table 3. The corresponding chemisorption data were also measured and are also shown

Table 3

The effect of metal loading at constant metal ratio (1:1) on the Fischer–Tropsch^a performance of the Fe:Co/TiO₂ bimetallic system

Catalyst sample	5:5 ^b	4:4	3:3	2:2	1:1
Metal loading (% by mass)	10	8	6	4	2
CO conversion (%)	36.3	30.8	25.4	15.8	10.5
Specific activity ($\mu\text{mole CO s}^{-1} \text{ g}^{-1}$)	0.40	0.34	0.28	0.17	0.11
TON ($\times 10^{-3} \text{ s}^{-1}$)	70.0	46.6	42.4	22.7	18.6
Selectivity (% by mass)					
CH ₄	11.0	11.4	10.5	11.0	9.0
C ₂ –C ₄	14.6	14.5	12.6	14.1	19.5
+C ₅	74.2	73.8	76.8	74.3	72.6
WGS extent	~0.05	<0.02	tr	tr	tr
Paraffin (%)	82.9	85.0	78.7	82.7	74.5
Olefin (%)	15.8	14.2	20.7	17.3	25.5
CO ₂ (%)	0.5	~0.2	tr	tr	tr
Oxygenates (%)	1.4	0.9	0.6	tr	tr
ASF chain growth values					
α_1	0.71	0.80	0.81	0.65	0.71
α_2	0.85	0.89	–	–	–
Surface characterization					
CO adsorbed (μmole)	5.8	7.3	6.6	7.5	5.9
Reduction (%)	94.5	78.2	67.0	59.9	53.3
Dispersion (%)	0.6	1.4	3.3	6.0	6.4
BET surface area (m^2/g)	51	51	51	51	51

^a Reaction conditions: calcination: 200 °C, 1 atm, 2000 h⁻¹, 16 h, flowing air; reduction: 300 °C, 1 atm, 2000 h⁻¹, 16 h, 100% H₂; synthesis: 220 °C, 10 bar, 350 h⁻¹, 200 h, 2H₂:1CO.

^b D.J. Duvenhage, N.J. Coville, *Appl. Catal. A: Gen.* 233 (2002) 63–75.

in Table 3 (and Fig. S3). It is clear from the data that the CO conversion, specific activity and TON decrease with decreasing metal loading. From the trends for the % D and % R (Fig. S3) it is seen that decreasing the metal loading from 10% to 2% by mass results in a linear increase in dispersion from 0.6% to 6.4%, which seems to be responsible for the decrease in the level of reduction from 95% to 53%. It is again clear that the activity is directly related to the level of reduction, which is affected by the degree of metal dispersion on the catalyst support. This is in line with related studies by Bartholomew and co-workers [26].

It is interesting to note that the product slate (Table 3) for the series of catalysts are similar, with the +C₅ fraction being the major product. As expected [29] the olefinitiy increased with decreasing activity while the ASF values indicated an expected increasing trend in values with total metal loading. No WGS activity was observed for any of the systems.

3.4. Catalyst stability: the effect of synthesis conditions

FT catalysts are known to deactivate with time [30] and the impact of alloys on this issue has received limited attention in the literature. To study this effect, a series of experiments were performed in which the catalyst reaction conditions were varied.

In the study, three reactors were loaded with the optimized co-impregnated 5:5 Fe:Co/TiO₂ catalyst [22]. The catalysts were “bedded-in” for approximately 150 h at

220 °C, 10 bar, 350 h⁻¹ under 2H₂:1CO. Thereafter variable conditions of temperature (255–310 °C), pressure (5 and 2 bar) and space velocity (500 and 1150 h⁻¹) were studied in the three reactors. The reaction was studied for 48 h at any new set of reaction conditions before mass balance data were collected. The reactor conditions for the three catalysts were then returned to the initial sets of conditions to investigate the recovery and stability of the catalysts. Mass balance calculations were again carried out after the catalyst had been on line for 48 h. Finally the three reactors were subjected to different feed gas compositions to study the effect of the H₂:CO ratio on the synthesis performance and product selectivity of the Fe:Co/TiO₂ system. The effect of both 1H₂:1CO and 1H₂:2CO gas compositions were evaluated in a similar fashion to that described above. Conditions were then returned to the initial starting conditions. A study period of up to 480 h (ca. 20 days) on line was used for the total study.

As expected, specific activity increased with an increase in pressure, temperature and H₂:CO ratio and with a decrease in space velocity (Fig. S4, Table 4). The increase in specific activity with a decrease in CO conversion in the latter study is to be noted. In principle more moles of carbon are converted at a space velocity of 1140 h⁻¹ than at 350 h⁻¹ leading to the inverse variation of CO conversion and specific activity (Table 4). Remarkably the reaction selectivity did not change with space velocity, suggesting that even with the increased activity per site (specific activity) the chain termination reaction was not enhanced. It is interesting to note that Stoop [31] reported a similar shift

Table 4
The influence of Fischer–Tropsch reaction conditions on the performance of a 5:5 Fe:Co/TiO₂ catalyst

	4a Pressure (Bar) ^{a,b}			4b Temperature (°C) ^{a,c}			4c Space velocity (h ⁻¹) ^{a,d}			4d H ₂ :CO ratio ^{a,e}		
	2.0	5.0	10.0	220	255	310	1140	500	350	2:1	1:1	1:2
CO conversion (%)	17.7	28.3	36.5	37.3	72.6	90.3	15.9	23.6	35.5	36.8	12.1	7.1
Specific activity (μmole CO s ⁻¹ g ⁻¹)	0.131	0.278	0.375	0.372	0.964	1.014	0.589	0.378	0.350	0.356	0.167	0.125
Selectivity (% by mass)												
CH ₄	16.7	19.1	25.0	23.2	41.6	52.4	23.9	24.4	23.0	21.1	13.2	8.6
C ₂ –C ₄	26.6	28.3	25.7	26.4	24.3	29.1	23.0	25.2	25.9	26.9	28.4	19.6
+C ₅	56.4	52.4	48.8	49.9	33.6	17.8	52.7	50.2	50.6	51.6	57.9	71.3
WGS extent												
Paraffin (%)	65.3	69.2	74.3	64.5	82.6	78.9	57.8	59.6	62.9	62.6	41.5	28.4
Olefin (%)	33.5	29.7	24.2	34.0	16.6	20.0	41.1	39.7	35.8	35.9	57	70.1
CO ₂ (%)	tr	tr	1.5	1.7	17.0	56.0	tr	tr	1.5	1.5	tr	tr
Oxygenates (%)	1.2	1.04	1.6	1.5	0.8	1.1	1.1	0.7	1.3	1.4	1.5	1.5
Ratio: (olefin/olefin + paraffin)												
C ₂	0.10	0.08	0.07	0.09	0.02	0.05	0.22	0.14	0.11	0.08	0.83	0.65
C ₃	0.62	0.59	0.49	0.64	0.28	0.44	0.77	0.72	0.66	0.65	0.83	0.99
C ₄	0.66	0.60	0.53	0.63	0.45	0.63	0.72	0.69	0.64	0.64	0.79	0.88
C ₅	0.56	0.50	0.42	0.56	0.37	0.77	0.68	0.64	0.57	0.56	0.77	0.85

^a Reaction conditions: calcination: 200 °C, 1 atm, 2000 h⁻¹, 16 h, flowing air; reduction: 300 °C, 1 atm, 2000 h⁻¹, 16 h, 100% H₂.

^b Reaction conditions: variable pressure, 220 °C, 350 h⁻¹, 2H₂:1CO.

^c Reaction conditions: 10 bar, variable temperature, 350 h⁻¹, 2H₂:1CO.

^d Reaction conditions: 10 bar, 220 °C, variable space velocity, 2H₂:1CO.

^e Reaction conditions: 10 bar, 220 °C, 350 h⁻¹, variable feed gas ratio.

in specific activity for a Ru:Fe/SiO₂ system at space velocities between 0.2 and 2.0 × 10⁻² g cat/h for his system studied at 101 kPa, 550 K and 2H₂:1CO gas ratio.

The CO conversion changed over a large range, affecting the relevant partial pressures of the various reactants and products inside the reactor. Thus, an evaluation of selectivity evaluation is of limited value. This said it is not clear why the methane levels increase with an increase in pressure (Table 4). It can be speculated that the nature of the bimetallic catalyst surface results in modified adsorption/desorption behaviour relative to monometallic catalysts. Further studies are necessary to confirm such a notion. It is also possible that the 48 h stabilization time may have been insufficient to achieve stable catalyst activity for the reactions carried out at the different pressures.

However, it can be mentioned that with the exception of the variable temperature run the activity and selectivity of the catalyst, in each study (see Fig. S4a–d), had values similar to the initial performance values. This suggests a robust catalytic system. As expected the catalyst from the variable temperature study indicated a poorer activity after the study (temperature changed from 310 to 220 °C). This suggests sintering of the active phase, which is also supported by BET data (see below).

To further evaluate the stability of the catalyst, a reaction was carried out for 500 h on line (5:5 Fe:Co/TiO₂ catalyst at 220 °C, 10 bar, 2H₂:1CO and 350 h⁻¹). Three sets of data were obtained for the above study and the time on line data for one of these data sets is shown in Fig. 3 and Table 5. It is clear from the data that an initial loss of 24% (from 46% to 35%) CO conversion was observed over the first 120 h on

line. Thereafter, the catalyst proved to be stable in its activity up to 500 h on line.

A TGA study was performed on the above three catalysts after soxhlet extraction of the reactor wax present in the catalyst pores at the end of the reactions. No carbon formation (less than 0.5% carbon by mass of catalyst) was

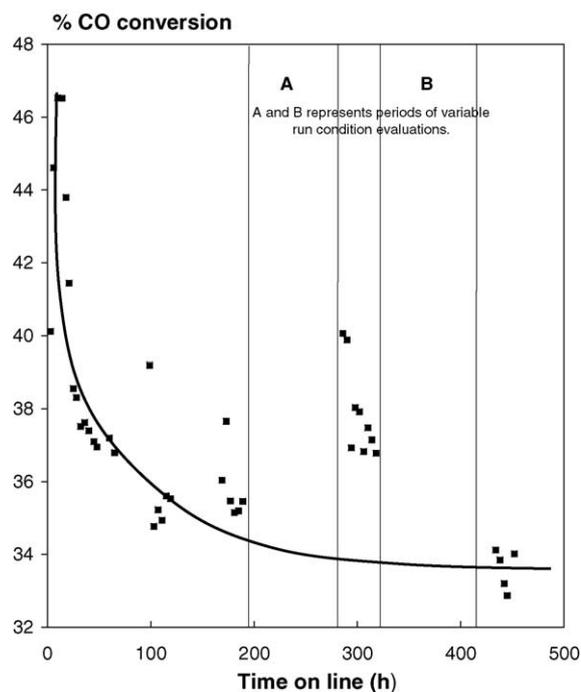


Fig. 3. The effect of time-on-line on the synthesis performance of a 5:5 Fe:Co/TiO₂ system.

Table 5
The influence of time-on-line on the Fischer–Tropsch performance^a of a 5:5 Fe:Co/TiO₂ catalyst

	Time on line (h)		
	195	330	460
CO conversion (%)	35.5	36.8	34
Specific activity ($\mu\text{mol CO s}^{-1} \text{g}^{-1}$)	0.350	0.356	0.344
Selectivity (% by mass)			
CH ₄	23.0	21.1	24.1
C ₂ –C ₄	25.9	26.9	25.5
+C ₅	50.6	51.6	50.0
WGS extent	~0.05	~0.05	~0.04
Gas product in total (%)	77.0	81.0	86.0
Paraffin (%)	62.9	62.6	60.2
Olefin (%)	35.8	35.9	38.3
CO ₂ (%)	1.5	1.5	1.4
Oxygenates (%)	1.3	1.4	1.4
Ratio: (olefin/olefin + paraffin)			
C ₂	0.11	0.08	0.12
C ₃	0.66	0.65	0.70
C ₄	0.64	0.64	0.66
C ₅	0.57	0.56	0.61

^a Reaction conditions: calcination: 200 °C, 1 atm, 2000 h⁻¹, 16 h, flowing air; reduction: 300 °C, 1 atm, 2000 h⁻¹, 16 h, 100% H₂; synthesis: 220 °C, 10 bar, 350 h⁻¹, 200 h, 2H₂:1CO.

detected on the catalyst after 500 h on line. The catalysts were also evaluated by SEM (pictures not shown here). The SEM pictures revealed that the catalyst that had been subjected to the study involving variation in pressure and space velocities had similar surface structures to the structures recorded before the FT reaction. The SEM images of the catalyst that had been heated to 310 °C displayed a very porous like structure when compared to the SEM images of the starting material. The BET surface area of this sample (35.2 m²/g) was also lower than the BET surface area (42.2 and 41.0 m²/g) of the used catalysts from the variable pressure and space velocity studies. This observation indicates that some degree of sintering took place at the higher temperatures that negatively impacted on the surface area.

The product selectivity measured over 500 h shows little if any variation – no substantial change was observed in the selectivity to olefins, oxygenates and WGS activity. There was a slight increase (ca. 12%) observed in the production of the gaseous components. This shift is also indicated by a decrease in the ASF α -value from 0.82 to 0.77. It thus appears that, without changing its activity, the catalyst system produces lighter products with time on line.

4. Conclusions

A series of catalysts containing Fe and Co on TiO₂ were prepared and FT studies revealed that the two metals, when intimately mixed together, had different catalytic characteristics when compared with catalysts containing the two

metals that were physically mixed together. Indeed, the Fe:Co catalysts acted more like Co containing catalysts in terms of selectivity, when the two starting metal salts were co-impregnated on TiO₂. Studies also revealed that when the Fe:Co ratio of the co-impregnated catalysts was varied (constant total metal loading of 10%), a non-linear relationship between metal content and catalyst FT activity and selectivity was observed. The enhanced activity of the 5:5 Fe:Co/TiO₂ catalyst relative to the 2.5:7.5 and 7.5:2.5 Fe:Co catalysts could be rationalized by Fe–Co interactions and enhanced reducibility of the mixtures as well as in changes to the Co phase with catalyst composition. The new 5:5 Fe:Co catalysts also showed good long term stability. The catalysts can be viewed as Co catalysts that have been promoted by Fe and that the promotion leads to varied activity and selectivity characteristics relative to reference Co/TiO₂ catalysts.

Acknowledgements

We wish to thank the University of the Witwatersrand, FRD/NRF and SASTECH for financial support. We also wish to express our thanks to Dr. H. Pollak (deceased) of the Physics Department, University of the Witwatersrand for assistance with obtaining the Mössbauer data.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.apcata.2005.05.008.

References

- [1] M.E. Dry, *Catal. Sci. Technol.* 1 (1981) 1159.
- [2] H. Schulz, *Appl. Catal. A: Gen.* 186 (1999) 3.
- [3] C.H. Bartholomew, in: L. Guzzi (Ed.), Chapter 5 - New Trends in CO Activation, Elsevier, Amsterdam, 1991.
- [4] R.B. Anderson, *The Fischer–Tropsch Synthesis*, Academic Press, London, 1984.
- [5] (a) M. Luo, R. O'Brien, B.H. Davis, *Catal. Lett.* 98 (2004) 17; (b) G. Jacobs, J.A. Chaney, P.M. Patterson, T.K. Das, B.H. Davis, *Appl. Catal. A: Gen.* 264 (2004) 203.
- [6] T.V. Reshetenko, L.B. Avdeeva, A.A. Khassin, G.N. Kustova, V.A. Ushakov, E.M. Moroz, A.N. Shmakov, V.V. Kriventsov, D.I. Kochubey, Yu.T. Pavlyukhin, A.L. Chuvilin, Z.R. Ismagilov, *Appl. Catal. A: Gen.* 268 (2004) 127.
- [7] (a) G. Ennas, M.F. Casula, A. Falqui, D. Gatteschi, G. Marongiu, G. Piccaluga, C. Sangregorio, G. Pinna, *J. Non-Crystal. Solids* 293 (2001) 1; (b) M.F. Casula, A. Corrias, G. Paschina, *J. Mater. Chem.* 12 (2002) 1505; (c) A. Corrias, M.F. Casula, A. Falqui, G. Paschina, *J. Sol–Gel Sci. Tech.* 31 (2004) 83; (d) A. Hutlova, D. Niznansky, J. Plocek, J. Bursik, J.-L. Rehspringer, *J. Sol–Gel Sci. Tech.* 26 (2003) 473.

- [8] (a) T. Caillot, G. Pourroy, D. Stuerge, *J. Solid State Chem.* 177 (2004) 3843;
(b) C. Liu, A.J. Rondinone, Z.J. Zhang, *Pure Appl. Chem.* 72 (2000) 37.
- [9] (a) G. Pourroy, A. Valles-Minguez, I.-S. Jurca, C. Meny, N. Viart, P. Panissod, *J. Alloys Compd.* 333 (2002) 296;
(b) G.B. Ji, S.L. Tang, S.K. Ren, F.M. Zhang, B.X. Gu, Y.W. Du, *J. Cryst. Growth* 270 (2004) 156.
- [10] D.J. Duvenhage, N.J. Coville, *Appl. Catal. A: Gen.* 153 (1997) 43.
- [11] F. Tihay, G. Pourroy, M. Richard-Plouet, A.C. Roger, A. Kiennemann, *J. Appl. Catal. A: Gen.* 206 (2001) 29.
- [12] F. Tihay, A.C. Roger, G. Pourroy, A. Kiennemann, *Energy Fuels* 16 (2002) 1271.
- [13] (a) F. Tihay, A.C. Roger, A. Kiennemann, G. Pourroy, *Catal. Today* 58 (2000) 263;
(b) C. Cabet, A.C. Roger, A. Kiennemann, S. Lakamp, G. Pourroy, *J. Catal.* 173 (1998) 64.
- [14] S.L. González-Cortés, S.M.A. Rodolfo-Baechler, A. Oliveros, J. Orozco, B. Fontal, A.J. Mora, G. Delgado, *React. Kinet. Catal. Lett.* 75 (2002) 3.
- [15] A.J. Dalai, N.N. Bakhshi, M.N. Esmail, *Fuel Processing Tech.* 51 (1997) 219.
- [16] V.A. de la Peña O'Shea, N.N. Menéndez, J.D. Tornero, J.L.G. Fierro, *Catal. Lett.* 88 (2003) 123.
- [17] S. Hagen, R. Barfod, R. Fehrmann, C.J.H. Jacobsen, H.T. Teunissen, I. Chorkendorff, *J. Catal.* 214 (2003) 327.
- [18] (a) C. Pham-Huu, N. Keller, C. Estournes, G. Ehret, M.J. Ledoux, *Chem. Commun.* (2002) 1882;
(b) R.K. Rana, I. Brukental, Y. Yeshurun, A. Gedanken, *J. Mater. Sci.* 13 (2003) 663.
- [19] Y. Bi, A.K. Dalai, *Can. J. Chem. Eng.* 81 (2003) 230.
- [20] D. Banerjee, D.K. Chakrabarty, *Ind. J. Technol.* 30 (1992) 81.
- [21] (a) H. Arai, K. Mitsuishi, T. Seiyama, *Chem. Lett.* (1984) 1291;
(b) T. Ishihara, K. Eguchi, H. Arai, *Appl. Catal.* 30 (1987) 225.
- [22] D.J. Duvenhage, N.J. Coville, *Appl. Catal. A: Gen.* 233 (2002) 63.
- [23] (a) Z. Kónya, I. Vesselényi, K. Lázár, J. Kiss, I. Kiricsi, *IEEE Trans. Nanotechnol.* 3 (1) (2004) 73;
(b) N. Nagaraju, A. Fonesca, Z. Konya, J.B. Nagy, *J. Mol. Catal.* 181 (2002) 57.
- [24] Hernadi, A. Fonseca, J.B. Nagy, B. Bernaerts, A.A. Lucas, *Carbon* 34 (1996) 1249.
- [25] M. Rameswaran, C.H. Bartholomew, *J. Catal.* 117 (1989) 218.
- [26] B.G. Johnson, C.H. Bartholomew, D.W. Goodman, *J. Catal.* 128 (1981) 231.
- [27] G.C. Bond, *Heterogeneous Catalysis – Principles and Applications*, 2nd ed., Oxford, New York, 1990, p. 23.
- [28] J.A. Amelse, PhD Thesis, Northwestern University, Evanston, Illinois, 1980.
- [29] M. Janardanarao, *Ind. Eng. Chem. Res.* 29 (1990) 1735.
- [30] D.J. Duvenhage, N.J. Coville, *Stud. Surf. Sci. Catal.* 88 (1994) 351.
- [31] F. Stoop, PhD Thesis, Technische Universiteit Eindhoven, Abblasterdam, 1986.