

Effect of K, Mn and Cr on the Fischer–Tropsch activity of Fe:Co/TiO₂ catalysts

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A range of 5% Fe/5% Co bimetallic catalysts supported on TiO₂ was promoted with 0.1%, 0.5% and 1.0% potassium, chromium and manganese respectively, and their physical properties and Fischer–Tropsch (FT) CO hydrogenation capabilities were evaluated. Low level promotion (0.1% and 0.5%) by K and Cr modestly improved the activity, decreased the selectivity to methane and increased the +C₅ fraction of the FT product while the Mn promoted catalysts retarded activity and reduced selectivity.

KEY WORDS: Fischer–Tropsch; Bimetallic; Iron; Cobalt; promoters.

1. Introduction

The study of promoters has been a common theme in the development of catalysts [1]. Promoters enhance both the selectivity and activity of the active catalyst phase in many reactions [2]. Studies have been driven by the economic issues associated with even small (<1%) changes in activity, while changes in selectivity can have a major impact on environmental and cost issues. The role of promoters is usually discussed in terms of electronic and structural effects and many different definitions of promoters have been given over the years. In summary, structural promoters increase the number of active catalyst sites while electronic promoters increase the intrinsic activity of the catalyst site [3].

The Fischer–Tropsch (FT) reaction is an example of a reaction in which the role of promoters has featured extensively [4–7]. Not only have the promoters led to the enhancement of economically important chemicals (olefins, petrol range hydrocarbons, long chain alkanes) but promoters have also reduced the non-economic products (e.g. methane).

The typical additives used to promote the iron FT catalysts include K [8], silica [9], Cu [10] and each plays a different role in the FT reaction. Thus, Cu enhances the Fe reducibility, K enhances the olefin content of the product and the silica acts as a structural promoter/binder in the reaction. Many other additives have also been investigated and these include Ca [11], S [12] and Mn [13].

Promoters have also been added to the other industrially important FT catalyst, cobalt. The main role of the promoter here appears to be that of assisting with

the metal reducibility and studies have been carried out with Re [14], Ru [15], Pd [16], Pt [17,18] etc. Attempts to add Zn, S and B [19–21] have met with less success.

Recently we have reported on the use of mixed Fe:Co/TiO₂ catalysts for the FT reaction [22]. It was found that the FT activity and selectivity results were dominated by the presence of the Co. To further investigate this reaction and to enhance the Fe behaviour in Fe:Co bimetallic catalysts we wished to evaluate the effect of promoters on the reaction.

This study thus provides an attempt to assess the *effect of a promoter on a mixed catalyst system*. The promoters chosen were those that are known to promote iron catalysts and to have less effect on cobalt catalysts [23]. The promoters/additives chosen for study were potassium, chromium and manganese.

2. Experimental

A large batch of a 10% metal loaded 5:5 Fe:Co/TiO₂ catalyst was prepared by a single metal addition incipient wetness procedure as discussed previously [22,24]. The TiO₂ support (Degussa P25) was calcined in air at 400 °C for 16 h, the active metals were added and the catalyst was then calcined in air at 200 °C for 16 h. The resulting Fe:Co/TiO₂ catalyst was divided into 10 fractions. One fraction was kept unpromoted while the remaining nine were impregnated with 0.1, 0.5 and 1.0% levels of potassium (KNO₃), chromium (Cr(NO₃)₃·9H₂O) and manganese (Mn(NO₃)₂) respectively. The promoter impregnated catalysts were all dried for 2 h at 120 °C before being calcined in air for 16 h at 200 °C (flowing air at a space velocity of 2000 h⁻¹). The impregnated catalyst was then sieved to the required particle size of 0.5–1.0 mm.

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2.1. Catalyst characterization

The catalysts were characterized by AAS to determine their exact composition, while the influence of promotion was evaluated by TPR, BET surface area analysis, CO-chemisorption, level of reduction and % dispersion. The experimental procedures are described in more detail elsewhere [22].

2.1.1. Catalyst testing.

Catalysts (about 2 g) were tested in a system comprising of three stainless steel reactors with two knock-out pots each, one for wax and one for liquid hydrocarbon products. The gas product fraction was analyzed by GC as described previously [22]. 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 [22]. Mass balance data of 100 ± 5% was accepted as adequate for comparison purposes.

3. Results and discussion

3.1. Catalyst characterisation

Table 1 contains characterization data for the various catalysts promoted by K, Cr and Mn. The promoter loadings, as determined by AAS, were very close to the predicted values of 5% Fe, 5% Co and 0.1%, 0.5% and 1.0% for the K, Cr and Mn catalysts.

It is also noted (Table 1) that the presence of the promoters increased the BET surface areas of the catalysts relative to the unpromoted material, but the changes are small.

TPR studies of each of the three sets of promoters (0.1% promotion) are shown in figure 1. Three peaks are observed. The first peak corresponds to nitrate decomposition while the latter two peaks at about 300 and 600 °C correspond to the reduction of both Fe and Co [22]. The broad tail to the peak at 600 °C is due to an interaction between the metal and the TiO₂. As can be seen from the three profiles the promoter has little effect on the metal reduction processes (peak position and intensity).

The reduction behaviour of the catalysts was also measured by reacting the catalyst with pure hydrogen followed by oxidation with an oxygen containing probe gas (5% O₂ in He) [25]. This data confirmed the TPR results. The K, Cr and Mn promoters *increased* the metal reduction level from approx. 84% to approx. 88–90%, 90–92% and 90–95% respectively (Table 1). It is also noted that the level of CO_{ads} decreased with increasing promoter content and that Mn promotion doubled the CO_{ads} when compared with the K and Cr promoted systems. The relatively low values obtained for CO_{ads} (between 6.2 and 11.8 μmole CO/g catalyst; ± 10% accuracy) could be indicative of a strong metal support interaction (SMSI) effect, not unexpected for TiO₂ supported catalysts. The decrease with increasing promoter content correlates with results reported by the Jensen group [26] for Fe catalysts promoted with Mn.

3.2. Synthesis evaluation

3.2.1. Potassium promotion

The promotion of the 5:5 Fe:Co/TiO₂ catalyst with 0.1, 0.5 and 1.0 potassium from a KNO₃ source gave the results shown in Table 2. It is clear from these results, that the catalyst promoted with 0.5% K has the highest specific activity, while decreased activity was observed at 1% K loading. The surface area also increased modestly on K promotion (45–53 m² g⁻¹). It is a well known phenomenon that very low levels of potassium increase the effective surface area of catalysts and as a consequence the activity [4]. Although promotion changes the degree of catalyst reduction by 4.8%, the reduction levels for the three promoted catalyst are similar. This leads to the notion that the loss in CO_{ads} capability must be a consequence of active surface site coverage by the excess promoter.

Addition of 0.1% K to Fe:Co:K/TiO₂ resulted in an increase in specific activity, oxygenate formation and olefinitiy (Table 2). This effect is even more pronounced at 0.5% K addition, but a reverse effect occurs at higher K loading (1% K). All these effects are the classic effects associated with potassium promoted Fe catalysts. It therefore appears that the promotion enhances behaviour expected for a traditional Fe catalyst [4,27].

While little evidence has been reported in the literature on K promotion of Co supported catalysts, the consensus appears to be that K poisons the catalyst [28]. Reports also indicate that K promoted Co catalysts on SiO₂ inhibits Co reducibility [29] while on C [30] the role of K (ratio 15/2 Co/K; very high) is to decrease FT activity and CH₄ selectivity and increase WGS activity. Another role for K promotion on Fe appears to be to enhance graphite and metal carbide formation [31,32]. Riedel *et al.* [33] reported that no CO₂ is formed during the FT synthesis over a cobalt catalyst and hence the catalysts exhibit no activity for the CO shift reaction.

Table 1

The influence of promoter addition on active metal and promoter loading, B.E.T surface area, $\mu\text{mole CO}_{\text{ads}}$, % Reduction and % Dispersion data for the potassium, chromium and manganese promoted Fe:Co/TiO₂ bimetallic systems

Characterization parameters obtained for K, Cr and MnO promoted (5%Fe: 5%Co)/TiO ₂ catalytic systems					
Catalyst	Promoter ^a (%)	BET ^b (m ² /g)	CO _{ads} ^c (μmole)	Reduction level ^d (%)	Dispersion ^e (%)
5Fe:5Co	None	45	6.2	84	0.9
5Fe:5Co:0.1K	0.08	49	5.5	88	0.7
5Fe:5Co:0.5K	0.47	53	4.6	89	0.6
5Fe:5Co:1.0K	1.13	53	4.0	90	0.5
5Fe:5Co:0.1Cr	0.09	55	6.7	90	0.9
5Fe:5Co:0.5Cr	0.60	50	6.1	91	0.8
5Fe:5Co:1.0Cr	1.04	49	5.5	92	0.7
5Fe:5Co:0.1Mn	0.07	47	10.8	93	1.4
5Fe:5Co:0.5Mn	0.45	45	11.8	95	1.5
5Fe:5Co:1.0Mn	0.97	46	8.7	90	1.1

^a As determined by AA analysis.

^b Classical N₂ adsorption procedure.

^{c, d, e} As per reference: M. Rameswaran & C.H. Bartholomew, J. Catal., 117 (1989) 218.

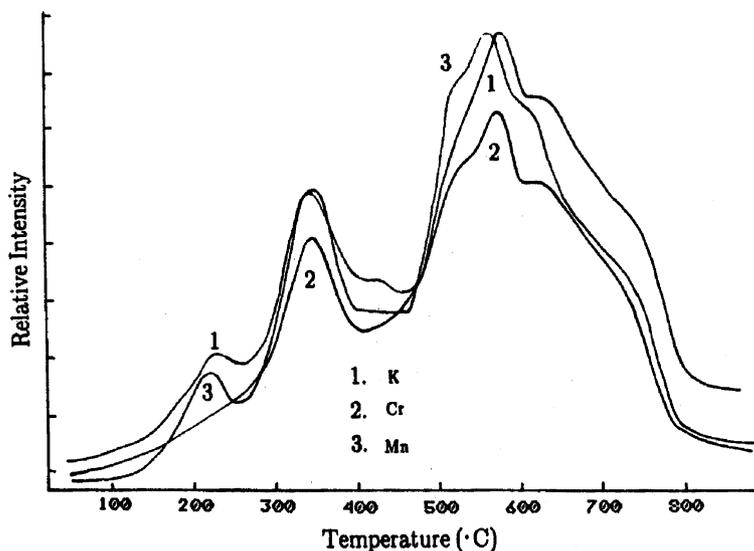


Figure 1. TPR profiles for 0.1% promoted potassium (1), chromium (2) and manganese (3) supported Fe:Co/TiO₂ bimetallic catalysts.

3.2.2. Chromium promotion

Promotion of the 5:5Fe:Co/TiO₂ bimetallic system with chromium revealed that low loadings of Cr (0.1%, 0.5%) enhanced the activity but that the activity decreased with a higher Cr loading (Table 2). It was noted in Table 1 that Cr addition increased the level of reduction slightly while a decrease in CO adsorption and % dispersion are also evident for these systems. The changed activity results could be explained by a combination of the assisted reduction of Fe and Co by Cr and by coverage of the active metal surface sites with the Cr, which is inactive in the classical Fischer–Tropsch reaction. It is clear from Table 2 that the methane levels in the promoted catalyst are similar (slight reduction) to the unpromoted system. This compares favourably with previous results [34] that

indicated large selectivity shifts to the unwanted methane in the presence of Cr promoters. The major influence of the Cr promoter in this study was on (i) the olefin content; this increased initially but decreased with Cr loading and (ii) the oxygenate content and water gas shift extent, that both increased slightly. These results appear to be consistent with that reported in the literature for Cr promoted Ni, Co and Fe systems [34–37]

Only a minor effect was noted on the chain length of the FT product at 0.5% Cr loading. This latter result is consistent with the Shell patent literature [35] that claims that the selectivity towards the C₁₀–C₂₀ range was increased with Cr promotion. It is however clear from our results that the above only holds for Cr levels <1.0%.

Table 2

The influence of potassium, chromium and manganese promoter addition on the synthesis performance^a of supported bimetallic Fe:Co/TiO₂ catalysts

Promoter loading (% by mass)	Unpromoted	Potassium			Chromium			Manganese		
		0	0.1	0.5	1.0	0.1	0.5	1.0	0.1	0.5
CO conversion (%)	34.2	38.8	28.7	25.8	39.6	37.4	31.4	32.3	31.6	25.6
Specific activity ($\mu\text{mole CO s}^{-1} \text{ g}^{-1}$)	0.381	0.442	0.575	0.239	0.481	0.436	0.339	0.350	0.331	0.242
TON ($\times 10^{-3} \text{ s}^{-1}$)	61.5	80.4	125	59.8	71.5	61.6	32.4	28.1	27.8	
<i>Selectivity (% by mass)</i>										
CH ₄	13	9	10	8	11	9	11	10	9	13
C ₂ –C ₄	12	10	19	12	12	9	13	14	12	14
+ C ₅	75	81	71	80	77	82	76	76	79	72
WGS extent	0.02	0.04	0.07	0.04	0.09	0.08	0.08	0.05	0.02	0.04
Paraffin (%)	91	83	64	84	83	84	89	81	83	92
Olefin (%)	9	16	35	15	17	16	10	18	16	7
Oxygenates (%)	0.3	0.5	0.6	0.6	0.6	0.5	0.7	0.9	0.6	0.5
<i>Lower olefinity^b</i>										
C ₂	0.06	0.11	0.18	0.34	0.10	0.08	0.20	0.09	0.07	0.28
C ₃	0.37	0.65	0.74	0.58	0.62	0.64	0.41	0.65	0.65	0.31
C ₄	0.44	0.63	0.71	0.59	0.62	0.63	0.47	0.63	0.64	0.35
C ₅	0.30	0.57	0.67	0.50	0.53	0.56	0.37	0.56	0.56	0.17
<i>ASF chain growth values</i>										
α_1	0.82	0.82	0.58	0.57	0.86	0.86	0.86	0.87	0.89	0.80
α_2	–	–	0.89	0.91	–	–	–	–	–	–

^a Reaction conditions: Calcination: (dual) 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 (olefin/olefin + paraffin) ratio.

3.2.3. Manganese promotion

Manganese, added as Mn(NO₃)₂ to the Fe:Co/TiO₂ gave the results portrayed in Table 2. It was found that as the promoter level increased from 0.1 to 0.5 to 1.0%, the CO conversion decreased. It is however interesting to note that the Mn promoter (see Table 1) more positively affected the reduction level than found with K and Cr promoted catalysts. It could be speculated that the presence of Mn limits the reducibility of the TiO₂ (which is associated with an SMSI effect) and hence give rise to better metal reduction levels. This notion however needs further investigation to obtain a clearer impression on the interaction between the active metal and the TiO₂ support and the effect of promoters thereon. The increased reduction level is accompanied by an unexpected slight increase in dispersion level. The results obtained are consistent with that reported for Co/MnO [38] and Fe/MnO [39] systems, but difficult to correlate with studies where high Mn loadings were used with unsupported Fe:Co catalysts [40]

In an effort to improve the performance of the system, the 0.1% Mn promoted Fe:Co/TiO₂ was reduced at two additional temperatures, i.e. 325 and 350 °C. The catalyst activity was found to significantly decrease while no significant selectivity changes were observed (see Supplementary Table; % CO conversion changed from 32.3 to 25.8 to 21.4% as the temperature increased from 300 to 325 to 350 °C).

Low level promotion with Mn (0.1% and 0.5%) resulted in a slight decrease in methane selectivity

(Table 2) while the olefinity increased two fold. Higher loadings (>0.1%) inhibit the lower olefin selectivity. Maiti and co-workers [41] also found that Mn reduced methane formation while enhancing the lower olefin content due to a lower catalyst hydrogenation activity. Jensen and Massoth [26] noted that low level Mn promotion (<5%) of Co showed more pronounced selectivity effects than higher levels of Mn promotion. Gonzalez-Cortes *et al.* [40] have reported on unsupported Mn promoted Fe:Co catalysts in the FT reaction (5:1 Fe:Co catalysts, >7% Mn) and showed that an increase in CH₄ and a slight decrease in olefin/paraffin ratio was generally observed.

Finally, our results indicate a slight increase in oxygenate production.

3.3. Impact of the promoters on the Fe:Co/TiO₂ catalysts

Since the bimetallic catalyst contains two active FT ingredients the promoter could preferentially promote one of the metals. From the data reported above and earlier data on single catalysts [4,23] the following conclusions can be drawn.

- It appears that the promoter effect of K resembles promotion of Fe rather than Co. For example, K promotion leads to improved FT and WGS activity and better olefin and oxygenate production as traditionally reported in the literature for single metal Fe systems. The site specific activity (TON) of K promotion also goes through a maximum with

K content, consistent with earlier literature reports [4]. Results for K promotion of Co are more ambiguous [30].

- (ii) Cr promotion effects on Fe:Co are also consistent with literature reports on Fe promotion.
- (iii) The Mn additive can be viewed as a catalyst poison.
- (iv) In general, the chain growth parameters, methane and +C₅ selectivities are not significantly altered by promotion with K, Cr and Mn.

From earlier studies it is known that Fe surface enrichment occurs in 5:5 Fe:Co catalysts [22,24] suggesting that the surface ratio Fe:Co >1. It had thus been hoped that promoter addition would enhance the catalyst activity substantially. The results do indeed reveal a predictable enhancement of activity/selectivity of Fe in the Fe:Co catalyst when promoted by K. What the data do not reveal is whether there is any synergistic effect of Co on the promoted Fe catalyst. This will require a future study of the catalytic species present on the surface of Fe:Co promoted catalysts.

4. Conclusions

Addition of small quantities of potassium, chromium and manganese promoters (0.1; 0.5; and 1.0%) to a Fe:Co/TiO₂ bimetallic catalyst has been investigated. The Mn was shown to be a poor promoter (olefin, WGS activity) for this catalytic system. On the other hand K and Cr exhibited some favorable promoting features. Low level promotion (0.1% and 0.5%) of K and Cr improved the activity, decreased the selectivity to methane and increased the +C₅ fraction of the product. Promotion with 0.5% K and 0.1 % Cr improved the lower olefin content substantially although the yield towards the C₂–C₅ fractions remained unchanged. Both the production of oxygenates and the activity towards the WGS reaction improved slightly with promotion. While reproducible, the chain growth parameters, methane and +C₅ selectivities are not significantly altered by the presence of the K, Cr and Mn promoters.

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