

## THE CONVERSION OF SYNGAS ON Fe/MnO

## I. Effects of Metal Modification on Product Distribution

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**Abstract** It has been found that Fischer-Tropsch catalysts based on Fe/Mn oxide give high selectivity for low molecular mass olefins. In this work, a series of modified manganese-rich Fe/MnO (*ca* 0.25) was prepared. In order to study the effects of promoter on product distribution, K, Cu, Co, Pd and Rh have been taken into account here. The reactions were performed under a moderate condition ( $T = 543$  K,  $p = 1.1$  MPa,  $GHSV = 215$  h<sup>-1</sup>). The 1% Cu- and 1% Co-modified catalysts have exhibited good promoter effect for both activity for CO hydrogenation and selectivity for C<sub>2</sub>~C<sub>4</sub> olefins. K increased the ratio of low molecular olefins/paraffins, but reduced the CO conversion slightly. Pd and Rh promoters benefited only the CO conversion. No increase of alcohol was observed in these catalyst systems. An extensive study of surface composition was made. Possible relation between activity and Fe<sup>0</sup> at the surface as well as coke deposit was obtained *via* XPS studies and CO<sub>2</sub> measurement from C-burning.

**Key words** FT-synthesis, Fe/MnO catalyst, CO hydrogenation, Olefin, XPS

In the last decade, the effects of active components and supports as well as promoters on the activity for CO hydrogenation have been studied rather extensively. The effects of metals in oxide catalysts on the production of different products in Fischer-Tropsch synthesis have been summarized<sup>[1]</sup>. It was suggested that Rh and Pd oxides as catalysts for FT-synthesis led to more alcoholic products, while Cu/ZnO and Pd oxide to methanol, and Ni, Co, Fe to hydrocarbons. Fe/Mn oxide was found to be a potential catalyst for selective production of short chain olefins in FT-synthesis<sup>[2]</sup>. Deviation from the normal products (Schulz-Flory-Anderson distribution) has been observed for Fe/MnO catalysts. It is indicated that the Schulz-Flory-Anderson distribution has a turning point<sup>[3]</sup>. Till now there was little work about promoter effects (other than potassium) on the Fe/MnO. In this paper, the catalytic properties of metal-modified Fe/MnO catalysts were investigated in order to observe the selectivity for C<sub>2</sub>~C<sub>4</sub> olefins and the activity for CO hydrogenation, compared with unloaded Fe/MnO. The results are discussed in combination with XPS surface studies.

Table 1 Composition of the catalysts

Catalyst	Composition* (%)					
	(Fe+Mn)**	K	Cu	Co	Pd	Rh
FT0	100					
FT1	99	1				
FT2	99		1			
FT3	99			1		
FT4	99				1	
FT5	99					1
FT6	99.9			0.1		

\* Based on all metal ions, \*\* Fe/Mn ratio *ca* 0.25

The results are discussed in combination with XPS surface studies.

## 1 Experimental

The Fe/Mn oxide (Fe/Mn ratio *ca* 0.25) was prepared by continuous coprecipitation from Fe-, Mn-nitrates and ammonia solution at 343 K and pH = 9.2,

followed by drying at 393 K and calcined at 773 K. The promoter ions were loaded by impregnating the calcined Fe/Mn oxide precursor, followed by drying at 393 K and calcining at 773 K in Ar once more. The composition of the catalysts is listed in Table 1. The catalytic reactions were carried out in a fixed bed tubular microreactor under the conditions:  $T = 543$  K,  $p = 1.1$  MPa,  $GHSV = 215$  h<sup>-1</sup>, and  $t = 48$  h. The reactant gas used in this reaction was a mixture of  $V_{CO}/V_{H_2} = 0.5$  in an aluminum cylinder to minimize carbonyl impurity. The gaseous products were analyzed on-line by a Carle AGC 111 gas chromatograph with 4 columns. The liquid effluent was sampled in 2 condensers, one at 373 K and the other was cooled by water. After completion of the reaction, the oil-phase and water-phase were separated and analyzed by a Perkin-Elmer Sigma 2B capillary gas chromatograph. The data to evaluate the catalysts were collected at steady state, *i. e.* at constant CO conversion. All catalysts studied were reduced at 673 K with H<sub>2</sub> for 24 h before reaction started. The composition of all catalysts was determined by chemical analyses and AAS, as well as XPS.

## 2 Results and Discussion

After reaction, the catalysts were taken out from the reactor and weighed for XPS-studies. The product distribution is summarized in Table 2.

The development of CO conversion and selectivity for C<sub>1</sub> ~ C<sub>4</sub> hydrocarbons with time on stream are shown in Fig 1. The activity was strongly affected by the addition of promoters. An increase in CO conversion was caused with the addition of promoter except for FT1 (K-containing catalyst). Among all the catalysts in this series, the 1% Rh-Fe/MnO (FT5) is the most active one, with a conversion of 98% at steady state. The catalysts FT2, FT3 and FT4 have comparatively the same activity (about 75%) for CO hydrogenation. K led to a slight decrease in CO conversion. The reasons will be discussed later. The product distribution was also

changed. The catalyst with potassium had much lower C<sub>1</sub> ~ C<sub>4</sub> selectivity than the K-free catalyst, especially still lower than 1% Rh-Fe/MnO, in which a great amount of CH<sub>4</sub> was found. The average molecular mass of products was increased by K, as mentioned in the literature. The selectivity for C<sub>2</sub> ~ C<sub>4</sub> olefins was differently affected by the promoters (Fig 2). The highest selectivity was found

Table 2 Product distribution over the catalysts

Promoter	$X_{CO}$ %	Selectivity (%)				
		C <sub>1</sub> ~ C <sub>4</sub>	OxO*	C <sub>5</sub> ~ C <sub>22</sub>	C <sub>23</sub> +	CO <sub>2</sub>
free	42.03	40.33	1.61	34.54	1.37	22.15
1% K	41.22	15.94	0.14	39.40	12.67	31.85
1% Cu	72.18	34.15	0.41	33.35	1.72	30.37
1% Co	72.92	32.74	-	34.32	2.14	30.80
1% Pd	77.10	30.98	0.28	31.56	0.83	36.35
1% Rh	98.30	53.41	0.22	7.95	0.25	38.17
0.1% Co	67.46	29.96	0.16	47.52	0.64	21.72

\* Alcoholic compounds

\*\* Described as carbon deposits

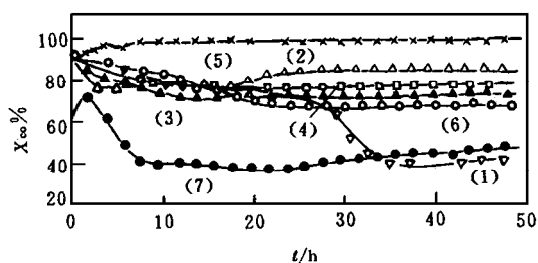


Fig 1 Synthesis activity as a function of time  
(1) FT1, (2) FT2, (3) FT3, (4) FT4,  
(5) FT5, (6) FT6, (7) FT0

with 1% Cu-(28%) and followed by 1% Co-Fe/MnO(25%) (both showed CO<sub>2</sub>-free selectivity). In contrast to this, 1% Pd- and 1% Rh-Fe/MnO had a negative effect on the production of olefins because of their strong hydrogenation ability. Only 1% olefins over 1% Pd- and almost nothing over 1% Rh-Fe/MnO were found. The unmodified Fe/MnO is itself a good catalyst for production of short chain olefins (21%), but the CO conversion over it is limited. The addition of potassium could not increase the selectivity for olefins, but obviously increased the ratio of C<sub>2</sub>~C<sub>4</sub> olefins to C<sub>2</sub>~C<sub>4</sub> paraffins. The selectivity ratio varied from 0 (1% Rh) to 3.96(1% K) (Fig 3). Kölbl *et al*<sup>[4]</sup> and Dry *et al*<sup>[5]</sup> suggested that the addition of alkali metal into Fe catalysts could intensify CO adsorption at the surface, as measured by the adsorption heat. This resulted in a poor hydrogenation function of the catalysts. It can also be proved by the strong coke formation which will be shown later.

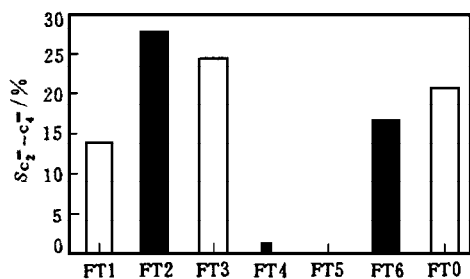


Fig 2 Selectivity for C<sub>2</sub>~C<sub>4</sub> olefins over different catalysts

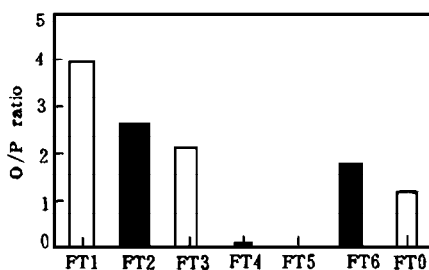


Fig 3 The olefins/paraffins ratio over different catalysts

The production of methane and carbon dioxide is unwanted reactions in FT-synthesis and should be suppressed. This is true for methane production on the Fe/MnO catalyst, in which a methane selectivity of 13.5% (CO<sub>2</sub>-free selectivity) was found. Still lower selectivity was found on K-, Cu-, Co- and Pd-promoted catalysts (below 12%). In contrast to this, the 1% Rh-Fe/MnO showed a very high selectivity for methane (65.5%).

Carbon dioxide is produced by the water gas shift reaction in the FT-synthesis. It was favored by the addition of promoter metals in this work. The selectivity increased from 21% over unloaded Fe/MnO to about 38% (1% Rh-Fe/MnO).

The XPS studies were performed for all catalysts after calcination, reduction/passivation, *in-situ* reduction and reaction. In the case of Co-containing catalyst, the XPS analysis was complicated by the fact that the Co lines overlapped with Auger peaks. Therefore, the Co content could not be detected. The Rh content after the reaction was too small to be determined. The surface composition and their valence states are listed in the Table 3.

The Fe in the catalysts is composed of Fe<sup>3+</sup>, Fe<sup>2+</sup>, and Fe<sup>0</sup> in different ratios after *in-situ* reduction. The Fe<sup>0</sup> was most favored by the addition of Pd and Rh, where initial activity of the catalysts is correlated with the amount of Fe<sup>0</sup> at the

Table 3 XPS surface analysis of the catalysts

Catalyst*	Com position (% (n/n))			Element content of various valence (% (n/n))						
	Fe	Mn	Prom oter	Fe <sup>3+</sup>	Fe <sup>2+</sup>	Fe <sup>0</sup>	Mn <sup>3+</sup>	Mn <sup>2+</sup>	Prom oter	
FT0	(1)	22.1	77.9	-	100	-	-	100	-	-
	(2)	17.3	82.7	-	100	-	-	100	-	-
	(3)	12.5	87.5	-	51	43	6	-	100	-
	(4)	12.1	87.9	-	100	-	-	60	40	-
FT1	(1)	21.0	76.1	2.9	100	-	-	100	-	K <sup>+</sup> 100
	(2)	10.1	75.8	14.1	100	-	-	20	80	K <sup>+</sup> 100
	(3)	6.5	81.5	12.0	37	41	22	-	100	K <sup>+</sup> 100
	(4)	10.8	81.9	7.2	77	23	-	-	100	K <sup>+</sup> 100
FT2	(1)	22.0	73.3	4.5	100	-	-	100	-	Cu <sup>2+</sup> 87 Cu <sup>+</sup> 13
	(2)	14.8	79.8	5.3	100	-	-	60	40	Cu <sup>2+</sup> 61 Cu <sup>+</sup> 4 Cu <sup>0</sup> 35
	(3)	9.6	89.5	0.9	44	40	16	-	100	Cu <sup>+</sup> 28 Cu <sup>0</sup> 72
	(4)	12.1	86.7	1.2	81	19	-	80	20	Cu <sup>+</sup> 23 Cu <sup>0</sup> 77
FT3	(1)	21.9	78.1	0	100	-	-	100	-	-
	(2)	16.8	83.2	0	100	-	-	100	-	-
	(3)	12.7	87.3	0	49	45	6	-	100	-
	(4)	13.3	86.7	0	72	25	3	60	40	-
FT4	(1)	17.8	78.5	3.6	100	-	-	100	-	Pd <sup>2+</sup> 100
	(2)	13.2	85.3	1.5	87	13	-	100	-	Pd <sup>2+</sup> 32 Pd <sup>0</sup> 68
	(3)	8.7	89.9	1.4	17	38	45	-	100	Pd <sup>0</sup> 100
	(4)	11.4	86.6	2.0	67	26	7	70	30	Pd <sup>2+</sup> 100
FT5	(1)	17.4	79.6	3.0	100	-	-	100	-	Rh <sup>3+</sup> 100
	(2)	14.0	81.8	4.2	100	-	-	60	40	Rh <sup>3+</sup> 100
	(3)	7.5	89.9	2.6	27	39	34	-	100	Rh <sup>0</sup> 100
	(4)	10.9	89.1	0	78	22	-	70	30	-
FT6	(1)	20.8	79.2	0	100	-	-	100	-	-
	(2)	10.7	79.2	0	89	8	3	80	20	-
	(3)	11.4	88.6	0	50	36	14	-	100	-
	(4)	12.1	87.9	0	100	-	-	60	40	-

Excitation: AlK $\alpha$  1 486.6 eV; Vacuum: 1 mPa

\* Pretreatment condition: (1) Calcination, (2) Reduction/passivation, (2) *in-situ* reduction, (4) After reaction

surface, as suggested by Grzybek *et al*<sup>61</sup>. It has also been proved by our results (see Fig 4). Except for the K-containing catalyst, Cu, Pd, Rh could be reduced easily by *in-situ* reduction. The valence of the promoters seemed not to play a decisive role for the activity, because after the reaction the promoters were fast fully oxidized, but the activity stayed at the same level and did not alter. It is worth to mention for FT1, which had the lowest activity after 48 h on stream. And the Mn was only in Mn<sup>2+</sup>, *i. e.* in the form of MnO, which was suggested as an “inactive” species by Das *et al*<sup>71</sup>.

The carbon deposits were also determined by XPS studies (for the surface) and C-burning (for the volume). The results are listed in Table 4.

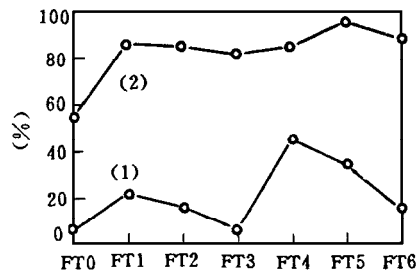


Fig 4 The initial activity of and Fe content on the reduced catalysts

(1) Fe content, (2) CO conversion

The potassium had a very strong influence on the carbon deposition during synthesis. The K-containing catalyst showed surface carbon content of 66%, while only about 20% ~ 25% was observed for the other catalysts. The concentration of bulk carbon was determined by C-burning. The catalyst FT1 contained carbon of 12%, *i. e.* much higher than the K-free catalysts (with carbon of below 4%).

The manganese-rich Fe/Mn oxide catalysts showed a good selectivity for low molecular olefins in the FT-synthesis and were stable with time on stream. The addition of 1% Cu and 1% Co caused an increase in selectivity for C<sub>2</sub> ~ C<sub>4</sub> olefins from 21% on unmodified Fe/MnO to 28% and 25% (CO<sub>2</sub>-free selectivity) respectively. Additionally, the activity was increased by impregnation with Cu, Co, Pd and Rh. In contrast to this, the modification with potassium had a negative influence on the activity of the catalysts and did not promote the production of olefins. The olefins/paraffins ratio was, however, raised over K-containing catalyst from 1.2 for unmodified Fe/MnO to 3.96 for the 1% K doped catalyst. The addition of potassium led to an increase in long chain hydrocarbons and a strong carbon deposition. The production of alcoholic compounds was very small on these catalysts (less than 2%). Methane formation was inhibited over these catalysts (apart from the 1% Rh-containing catalyst) and the methane selectivity was lower than 14% (CO<sub>2</sub>-free selectivity). The production of CO<sub>2</sub> was favored by the promoters and particularly by potassium.

After reaction, the Fe-content at the surface had reduced strongly, only about 10% left from the original 20%. In contrast, the Mn content increased by 5% ~ 10%. The Fe is composed of Fe<sup>3+</sup>, Fe<sup>2+</sup> and Fe<sup>0</sup> in various ratios after *in-situ* reduction. The reduction of Fe was most favored by the addition of Pd and Rh. The initial activity of the catalysts can be related to the content of metallic iron at the surface of the catalysts.

Table 4 Carbon content' after the reaction

Catalyst	Surface C (% (n/n))	Bulk C** (% (m/m))
FT0	-	1.24
FT1	66.0	12.28
FT2	25.9	2.20
FT3	21.7	3.11
FT4	25.9	1.35
FT5	21.6	0.51
FT6	19.8	0.96

\* Based on all metal ions, oxygen and carbon

\*\* Atomic percent could not be obtained without making further catalyst analysis.

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