THE CONVERSION OF SYNGAS ON Fe/MnO
II. The Role of K in Modified Fe/MnO Catalysts

Guan Naijia

(*Department of Chemistry, Nankai University, Tianjin 300071*)

Abstract   Fe-Mn-K catalysts have been found to exhibit good catalytic activity and high $C_2 \sim C_4$ alkene selectivity in FT-Synthesis. The effects of K, with co-existed Cu, Co, Pd and Rh in the Fe/MnO systems, were investigated. The K acted as a strong promoter, so the effects of Cu, Co, Pd and Rh on the product distribution were inhibited to a great extent. The reactions were performed at $T = 543$ K, $p = 1.1$ MPa and GHSV = 215 h^{-1}. The optimization of the reaction conditions has been studied. The best conditions for 3%K-1%Co-Fe/MnO should be at $T = 573$ K and GHSV = 800 h^{-1}. The catalytic results were related to the surface composition of the catalysts obtained by XPS analysis and coke measurement.

Key words   FT-Synthesis, Fe/MnO catalysts, Potassium, Promoter, XPS

The studies of co-precipitated Fe/Mn oxides for selective production of lower alkenes have been reported[1~5]. The addition of alkali metal to Fe/MnO catalysts, improving alkene/alkane ratio, has also been observed[6]. The modified Fe/Mn oxides have been studied for selective production of short chain olefins and alcoholic products in FT-synthesis. In the earlier work, the addition of 1%K to this system could increase the olefins/paraffins (O/P) ratio in the $C_2 \sim C_4$ effluent, but the CO conversion was a little inhibited. It is assumed that the interaction of Fe and Mn oxide on the surface is altered by the presence of K. In present paper, Cu, Co, Pd and Rh were loaded on K-Fe/MnO catalyst, with the intention of studying the role of K, the catalytic behavior of multi-metal catalysts for CO hydrogenation, and their effects on the production of $C_2^= \sim C_4^=$. The optimization of reaction conditions has also been made. The results are discussed in combination with XPS analysis and determination of coke deposit.

1 Experimental

The Mn-rich 3%K-Fe/Mn oxide ($n_{Fe}/n_{Mn} \doteq 0.25$) was prepared by continuous co-precipitation from K-, Fe-, Mn-nitrates and ammonia solution at 303 K and pH = 9.2, followed by drying at 393 K and calcining at 773 K. The promoter ions were added by impregnating the calcined K-Fe/Mn oxide precursor, followed by drying at 393 K and calcining at 773 K in Ar once more. The composition of the catalysts was determined by AAS and XPS, and the two methods gave the same value.

Table 1   Composition of the catalysts

Catalyst	Composition* (%)					
	(Fe+Mn)**	K	Cu	Co	Pd	Rh
F1A	97	3				
F1B	96	3	1			
F1C	96	3		1		
F1D	96	3			1	
F1E	96	3				1
F1F	96.9	3		0.1		

*   Based on all metal ions

** $n_{Fe}/n_{Mn} \doteq 0.25$

The reactions were carried out in a fixed bed tubular microreactor at $T = 543$ K, $p = 1.1$ MPa and GHSV = 215 h^{-1} for 48 h. 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 cooled by water. After the reaction, the oil phase and water phase were separated and analyzed in a capillary gas chromatograph. The data for evaluating the catalysts were collected at steady state, *i. e.* at constant CO conversion.

2 Results and Discussion

2.1 Reactions

The activity of K-containing catalysts was relatively low at the beginning of the reaction, went through a maximum and then decreased slowly to a lower level (Fig 1). The overall results are listed in Table 2.

Table 2   Product distribution over the catalysts with promoters

Promoter	Conversion (%)	Selectivity (%)				
		$C_1 \sim C_4$	Oxo*	$C_5 \sim C_{22}$	C_{23+}^{**}	CO_2
F1A (3% K)	36.21	17.39	0.30	17.75	24.54	40.02
F1B (3% K-1% Cu)	40.59	17.01	1.94	28.02	13.90	39.13
F1C (3% K-1% Co)	51.47	19.57	1.59	26.06	12.98	39.80
F1D (3% K-1% Pd)	28.10	15.85	0.18	22.07	16.90	45.00
F1E (3% K-1% Rh)	31.14	20.73	0.54	21.23	17.17	40.33
F1F (3% K-0.1% Co)	29.70	15.75	0.47	23.64	24.93	35.21

* Alcoholic compounds, ** Described as carbon deposits

The addition of Cu, Co, Pd and Rh could prolong the duration time of higher activity. The loading of 1% Cu and 1% Co played a positive role in CO hydrogenation to hydrocarbons, while the function of 1% Pd and 1% Rh was strongly depressed by the addition of K in such a system. So a general decrease in CO conversion was observed over these catalysts. The product distribution was also changed. A similar selectivity for olefins was found for all catalysts, which may be attributed to the

Fig 1   Conversion *vs* time on stream
(1) F1A, (2) F1B, (3) F1C,
(4) F1D, (5) F1E, (6) F1F

effect of the K (Fig 2). The O/P ratio of $C_2 \sim C_4$ on multi-metal catalysts is higher than that on K-free samples. The larger the amount of K, the higher was the O/P ratio, which was 4.0 over 1% K and 4.5 over 3% K (Fig 3). Comparing with our earlier work[6], it can be concluded that the K acts as a main promoter in the multi-metal systems. In these series, there was no large difference in the product distribution. If without K, a very clear distinction could be found.

The selectivity for alcoholic compounds seemed not to be affected by the promoters over the catalysts (below 2%). F1B and F1C have the same selectivity as the unmodified Fe/MnO, *i. e.* 1.9% and 1.6% respectively. The others re-
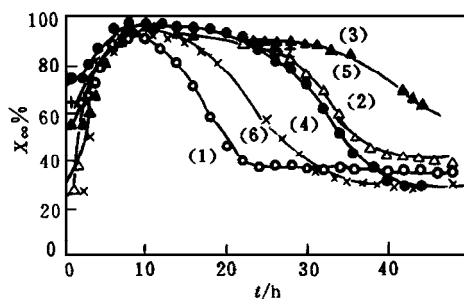
Fig 2   The $C_2^- \sim C_4^-$ selectivity of the catalysts
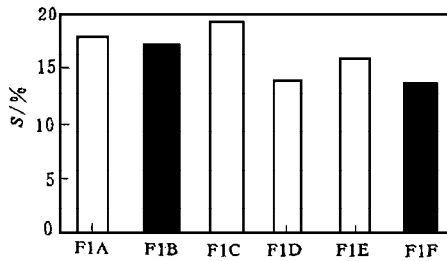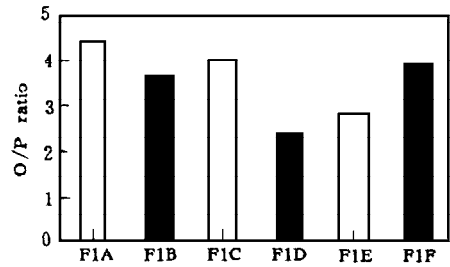

Fig 3   The O/P ratio on the catalysts

mained below 0.6%. Modification with Cu has slightly improved the production of O_2-containing compounds, but not over 2%.

2.2 XPS analysis

In the case of Co-containing catalyst, the XPS analysis was complicated by the fact that the Co lines overlapped with the Auger peaks. The surface composition is listed in Table 3. After reaction, the Fe and Mn amounts at the surface decreased to a great extent. In contrast, the K had enriched greatly. Referring to the earlier work with 1%K-Fe/MnO, the K-content after reaction was only 2 times of the original content. With such a high content of K, it is easy to deduce that the surface structure of the Fe/MnO was altered by the promotion of K strongly. From the coke deposit measurement, it was concluded that K has a very strong influence on the C-deposition. The surface C-content of all K-containing catalysts varied from 66% to 70%, while only about 20% ~ 25% was obtained for other catalysts. This deposited C could cover the active sites of the Fe/MnO. This is why the K-containing catalysts had lower activity for CO hydrogenation.

The bulk C-concentration was determined by measuring the CO_2 amount from C-burning. The K-containing catalysts contained coke deposit of 10% ~ 25%, much higher than the K-free catalysts (lower than 4%).

Table 3   Surface analysis for K-containing system

Catalyst*		Composition (% (n/n))			
		Fe	Mn	K	"Promoter"
F1A	(1)	28.7	68.2	3.1	-
	(2)	12.4	56.9	30.7	-
	(3)	11.6	58.3	30.1	-
	(4)	12.0	61.0	27.0	-
F1B	(1)	25.6	68.4	2.8	3.3
	(4)	10.0	61.0	18.0	11.0
F1C	(1)	25.6	67.4	6.5	0.4
	(4)	10.0	60.0	30.0	-
F1D	(1)	23.3	70.6	3.0	3.1
	(4)	11.0	69.0	19.0	1.0
F1E	(1)	21.4	69.6	4.6	4.4
	(4)	9.0	68.0	23.0	-
F1F	(1)	24.1	71.1	4.8	-
	(4)	8.0	58.0	34.0	-

Excitation: AlKα1 486.6 eV; Vacuum: 1 mPa
* Pretreatment condition: (1) Calcination, (2) Reduction/passivation, (3) *in-situ* reduction, (4) After reaction

Table 4   C-content after the reaction

Catalyst	Surface C* (% (n/n))	Bulk C** (% (m/m))
F1A	60.5	24.72
F1B	67.7	12.58
F1C	60.8	10.83
F1D	65.7	10.69
F1E	59.5	9.86
F1F	70.4	13.95

* Based on all metal ions, oxygen and carbon
** Atomic percent could not be obtained without making further catalyst analysis.

2. 3 Optimization of reaction conditions

Fig 4 has shown that the temperature had a great influence on the product selectivity, and the total amount of $C_1 \sim C_4$ gaseous products grew with the increase of temperature. But high temperature favored only the production of $C_1 \sim C_2$, especially CH_4. Fig 5 and 6 demonstrate the effects of temperature on the selectivity for $C_2^= \sim C_4^=$ and the O/P ratio for F1C as a function of GHSV (described as CO conversion). It has been shown that the influence of GHSV on the selectivity for olefins or the O/P ratio was very limited. An increase in temperature from 543 to 603 K caused a growth of the selectivity, but the O/P ratio decreased slowly with elevated conversion. Additionally, the amount of alcoholic products increased at lower GHSV (Fig 7). The optimal conditions for F1C should be 573 K and GHSV of 800 h^{-1}.
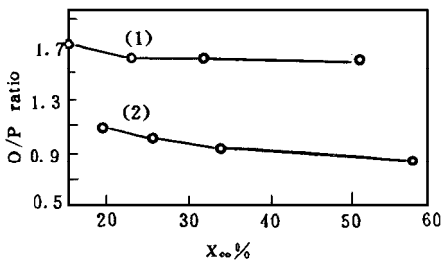

Fig 4 Selectivity *vs* the temperature on F1C catalyst
(1) CH_4, (2) $C_3^=$, (3) $C_2^=$, (4) $C_4^=$, (5) C_2^0, (6) C_3^0, (7) C_4^0

Fig 5 $C_2^= \sim C_4^=$ selectivity *vs* CO conversion on F1C catalyst
(1) 543 K, (2) 573 K, (3) 603 K, (4) 633 K

Fig 6 O/P ratio *vs* CO conversion on F1C catalyst
(1) 543 K, (2) 603 K

Fig 7 Oxo selectivity *vs* GHSV at 603 K on F1C catalyst

References

1 Kölbel H, Tillmetz K D. GP 2 507 647. 1976
2 Schulz H, Goecebay H. In: Kosak J R ed. Chemical Industries, Vol 18: Catalysis of Organic Reactions. New York: Marcel Dekker, 1984. 153
3 Pennline H W, Zarochak M F, Stencel J M *et al. Ind Eng Chem, Res*, 1987, **26**: 595
4 Stencel J M, Diehl J R, Miller S R *et al. Appl Catal*, 1987, **33**: 129
5 Venter J, Kaminsky M, Geoffroy G L *et al. J Catal*, 1987, **105**: 155
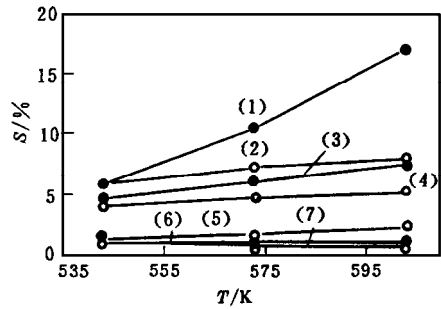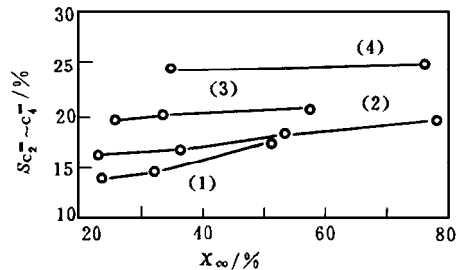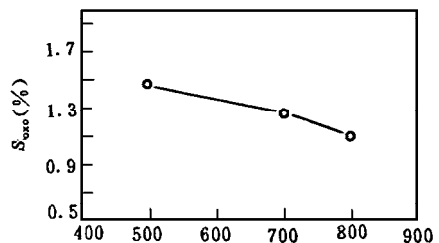6 Guan Naijia. *Chinese J Catal* (*Cuihua Xuebao*), 1996, **17**: 382