

## CATALYTIC BEHAVIOR AND COKE FORMATION OF MODIFIED Fe/MnO CATALYSTS

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**Abstract** A series of Fe/MnO catalysts (Fe/Mn=1/4) modified with K, Cu, Co, Pd and Rh for CO hydrogenation were prepared to obtain a higher selectivity to low molecular weight olefins. The catalytic behavior of these catalysts was studied at temperature of 543 K, under pressure of 1.1 MPa and with GHSV=215 h<sup>-1</sup>. It was found that the activity of CO hydrogenation increased over the modified Fe/MnO catalysts except K-Fe/MnO. An increase in the selectivity to C<sub>2</sub><sup>=</sup>~C<sub>4</sub><sup>=</sup> was also observed over Cu and Co modified catalysts. Influences of coke formation on the catalytic activities of catalysts were investigated. A relationship between the activity of CO hydrogenation and coke deposits was suggested.

**Keywords** F-T synthesis, modified Fe/Mn oxide, coke deposit, olefin selectivity

### Introduction

It has been reported that Fe/MnO is a selective catalyst for the production of low molecular olefins in the F-T synthesis<sup>[1]</sup>. Some researchers have investigated the function of Mn as a promoter. The effect of manganese oxide as a catalytic component has been observed with elements other than Fe, in particular, similar effects have been observed for Co-Mn<sup>[2]</sup> and Ru-Mn<sup>[3]</sup> catalysts. It has been suggested that there is a considerable interaction between iron and manganese oxide, and a solid solution is formed in the catalyst system. Also, it could be supposed that the selectivity to C<sub>2</sub><sup>=</sup>~C<sub>4</sub><sup>=</sup> may be further

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increased by proper modification of Fe/MnO. The "proper metal ions" means that they can modify the catalyst surface property and benefit the reduction of  $\text{Fe}^{3+}$  to  $\text{Fe}^0$ , because  $\text{Fe}^0$  has been thought as an active component for CO hydrogenation<sup>[4]</sup>. In addition, the product distribution can be changed by using Rh- or Pd-catalyst to produce more methanol or alcohols<sup>[5]</sup>. In our work, efforts have been made to increase the  $\text{C}_2^{\sim}\text{C}_4^{\sim}$  selectivity by modifying the Fe/MnO catalysts with different metal promoters. It has been found that there was an activity lost on some catalysts and a certain amount of coke deposits on the surface of catalysts as well as in the bulk. In this paper, we try to correlate both the coke deposition and the catalyst activity with promoter properties.

## Experimental

### *Catalyst preparation and catalytic reaction*

The manganese rich Fe/Mn oxide catalyst (Fe/Mn=1/4) was prepared by continuous co-precipitation of Fe-, Mn-nitrates and ammonia solutions at 70°C and pH=9.2, followed by drying at 120°C and calcination at 500°C for 24 h in Ar in order to forbid the formation of metal carbonates. 1%K, 1%Cu, 1%Co, 1%Pd, 1%Rh and 0.1%Co (in mol%) were loaded respectively by impregnating the calcined Fe/Mn oxide precursor with their nitrates solution followed by treating under the same conditions stated above. The exact compositions of the catalysts were determined by atom adsorption spectrometer. The reactant gas was composed of 30%(vol.)CO, 60%(vol.)H<sub>2</sub> and 10%(vol.)Ar. It was contained in an aluminum cylinder to minimize carbonyl impurity. A tubular stainless-steel reactor (103 mm in length and 12 mm in diameter) was used and charged with 3 g of catalyst. The prepared catalysts were pelleted into cylinder form (3 mm × 3 mm). Before the syngas was charged to the reactor, the catalyst was reduced with hydrogen at 400°C for 12 h. The reactions were mainly performed at 543 K, GHSV=215 h<sup>-1</sup> and P=1.1 MPa. The reaction time was 48 h for most samples. The effluent was directed to an on-line gas chromatograph. The products were analyzed by a Carle AGC 111 with four columns (DC 200/500, Carbowax 1540, Porapak N and molecular sieve 13X). The liquid effluent was condensed in two condensers, which were held at 100°C and cold water respectively. After reaction, the liquid was collected in two condensers and then mixed. The oil phase and water phase were separated and then were weighted. The analysis of products was carried out on a Perkin Elmer Sigma 2B with an OV 101 column.

### *Catalyst characterization*

The catalysts were characterized with X-ray photoelectron spectroscopy in every treatment step, *i.e.* calcination, reduction and passivation, *in situ* reduction as well as

reaction. The XPS studies were performed with a spectrometer of Leybold-Heraeus LHS/10, Al- $K\alpha$ =1486.6 eV in a vacuum system of 0.1 Pa. For XPS studies, the catalysts were calcined in the presence of Ar at 500°C at first. After that, they were reduced with H<sub>2</sub> (65 mL/min) at 400°C for 24 h in another apparatus. Then the catalyst was passivated with a mixed gas composed of 2%(vol.) O<sub>2</sub> and 98%(vol.) N<sub>2</sub> at room temperature for 2 h. The sample to be tested was transferred into the chamber of the XPS spectrometer. Before analysis, it must be *in situ* reduced at 400°C for 1 h.

The bulk coke content was determined by measuring the CO<sub>2</sub> amount which was emitted from the sample burning.

## Results and discussion

### Catalyst activity in CO hydrogenation

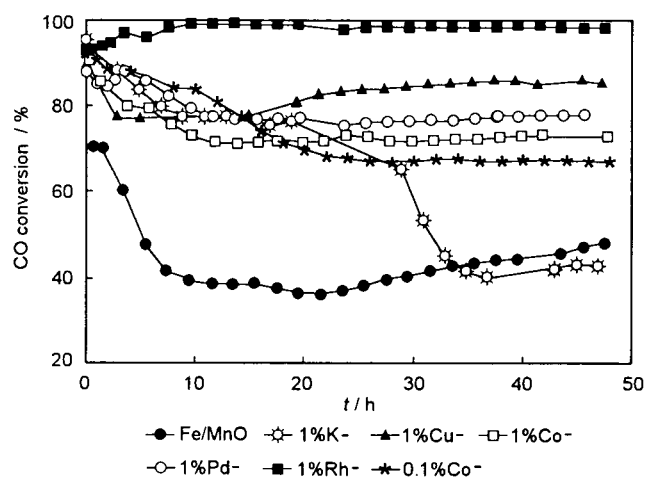
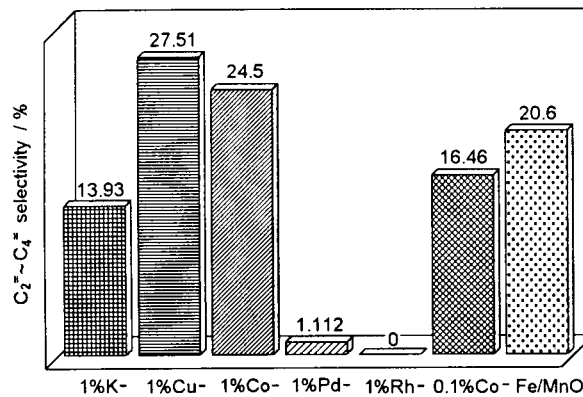


Fig.1 Variation of CO conversion with reaction time

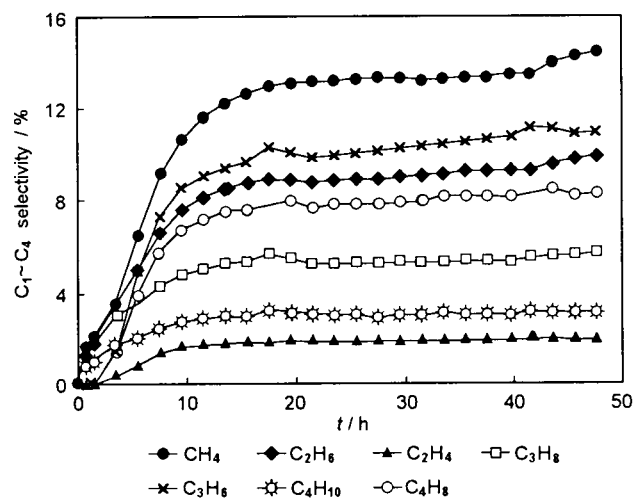
Fig.1 shows the conversion of CO (based on the CO amount in inlet and outlet) as a function of reaction time over different modified catalysts. The results indicated that the conversion of CO was significantly enhanced through the metal modification with Cu, Co, Pd and Rh. A decrease in CO conversion from about 70% at the beginning to 40% after 10 h was observed over the unpromoted Fe/MnO catalyst. A light increase of CO conversion was thereafter observed with reaction time. The K-containing sample also showed a change in activity. There was an obvious conversion fall from about 80% to 40% during the reaction time of 20~35 h, then the conversion tended to be stable. The 1%Rh promoted catalyst had the highest activity with almost 100% of CO conversion,

while other samples had the activity level of 75-85%.

*Effect of metal modification on the selectivity to different products*



**Fig.2** Selectivity to  $C_2=C_4$  olefins at 543 K, GHSV=215  $h^{-1}$  and  $P=1.1$  MPa



**Fig.3** Selectivity to  $C_1-C_4$  hydrocarbons on Fe/MnO at 543 K, GHSV=215  $h^{-1}$  and  $P=1.1$  MPa

Fig.2 shows the selectivity to  $C_2=C_4$  over different catalysts. A significant amount of  $C_2=C_4$  was obtained on the Cu and Co modified catalysts (up to 28% and 25%, respectively,  $CO_2$ -free selectivity). Nevertheless, in contrast to the selectivity to  $C_2=C_4$  over the Cu and Co modified catalysts, the Pd and Rh had a negative effect on the activity of Fe/MnO catalyst to produce  $C_2=C_4$  olefins, only 1% olefins over 1%Pd- was

produced and almost nothing was found over 1%Rh-Fe/MnO. This result is easy to be understood because of their superior hydrogenating function. It can be seen from Figs.3 and 4 that the unmodified Fe/MnO was a good catalyst for the production of short chain olefins (selectivity to  $C_2^=$ ~ $C_4^=$  is 20.6%), nevertheless, compared with 1%Cu-Fe/MnO, on which more olefins were produced, this unmodified catalyst showed lower selectivity. Over 1%Cu-Fe/MnO, the selectivities to  $C_3^=$  and  $C_4^=$  were higher than that of their aliphatic hydrocarbon form (see Figs.3 and 4).

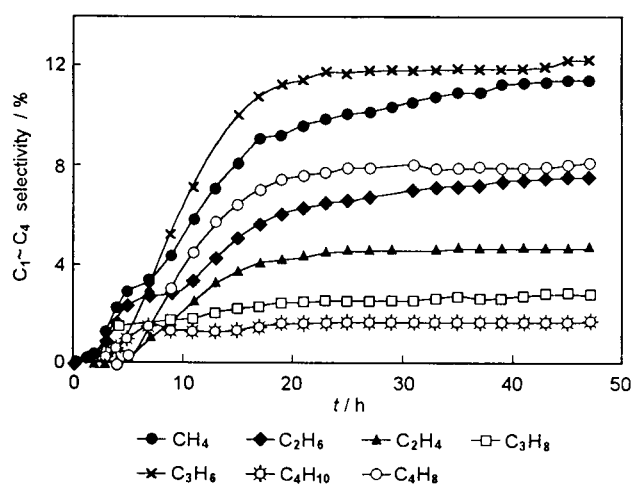


Fig.4 Selectivity to  $C_1$ ~ $C_4$  hydrocarbons on 1%Cu-Fe/MnO at 543 K, GHSV=215  $h^{-1}$  and  $P=1.1$  MPa

#### Effect of different promoters on the coke formation

The coke formation over different modified Fe/MnO catalysts is shown in Table 1. As we can see that a strong enrichment of coke was observed both at the surface and in the bulk of the K-containing catalyst.

The surface content of coke was measured by XPS. It can be also determined if the surface C-species is in the form of graphite or  $C=O/C-C=O$  or  $C-O$ . There were four steps of measurement. The first step was the calcination in Ar (see "calcined"). Then, the calcined catalyst sample was reduced with  $H_2$  and passivated with  $O_2$  to form a thin layer of oxide to inhibit the further oxidation (see "reduced and passivated"). In the third step, the passivated samples were transferred into the chamber of the XPS spectrometer and were *in situ* reduced at 400°C for 1 h before measurement (see "*in situ* reduced"). After reaction, the catalysts were detected by XPS. The total amount of bulk C was measured by the amount of  $CO_2$  from burning of catalyst.

**Table 1** Coke formation over different modified Fe/MnO catalysts

Catalyst	Catalyst treatment	Surface content at%	Bulk content wt%	Attribute of C-species %		
				Graphite	C=O/C-C=O	C-O
Fe/MnO	calcined	8.4*		76	24	--
	reduced and passivated	9.2		81	--	19
	<i>in situ</i> reduced	6.6		100	--	--
	after reaction at 270°C	43.9*	1.24	93	7	--
1%K-Fe/MnO	calcined	39.4*		91	--	9
	reduced and passivated	41.2*		92	--	8
	<i>in situ</i> reduced	26.9*		91	--	9
	after reaction at 270	6.6	12.28	100	--	--
1%Cu-Fe/MnO	calcined	35.8*		92	--	8
	reduced and passivated	6.0		100	--	--
	<i>in situ</i> reduced	3.2		100	--	--
	after reaction at 270°C	25.9	2.20	92	8	--
1%Co-Fe/MnO	calcined	21.0		88	12	--
	reduced and passivated	5.6		78	22	--
	<i>in situ</i> reduced	4.9		100	--	--
	after reaction at 270°C	21.7	3.11	84	16	--
1%Pd-Fe/MnO	calcined	9.2		75	25	--
	reduced and passivated	7.6		85	15	--
	<i>in situ</i> reduced	4.0		100	--	--
	after reaction at 270°C	25.9	1.35	90	10	--
1%Rh-Fe/MnO	calcined	8.1		71	29	--
	reduced and passivated	23.4*		88	--	12
	<i>in situ</i> reduced	--**		--	--	--
	after reaction at 270°C	21.6	0.51	75	--	25
0.1%Co-Fe/MnO	calcined	20.9		89	11	--
	reduced and passivated	7.2		79	21	--
	<i>in situ</i> reduced	7.8		82	--	18
	after reaction at 270°C	19.8	0.96	86	--	14

\* the coke deposited could not be separated from the sample holder for too small amount.

\*\* too small amount

As a result, a strong enrichment of coke was observed both on the surface and in the bulk of the K-containing catalyst after reaction, showing a carbon content of 66% on the surface, while only about 20~25% carbon contents were obtained over the other catalysts. In addition, the bulk of 1%K-Fe/MnO catalyst contained 12 atom% carbon, which is higher than that of the K-free catalysts (carbon content lower than 4%). That is to say, potassium had a very strong influence on the carbon deposition during synthesis. If we

compare 1%K-Fe/MnO with other catalysts (see Fig.1), we can see a declined trend of activity.

After calcination, there was no more than 10% coke found on the surface other than 1%Co- and 0.1%Co-Fe/MnO. When the catalysts were *in situ* reduced in the reactor, the coke deposited mainly exists in graphite C and the amount of deposits on the surface reached a minimum. The relationship between the conversion of CO and the carbon content on different modified catalysts after reaction is shown in Fig.5. It can be seen that there is a parallel relation between the conversion of CO and the coke deposits on the surface (in unit of 1/C-atom% $\times$ 10). It can be deduced that the activity in the quasi-stable period is dependent on the amount of coke deposited on the catalyst surface. Nevertheless, it does not mean that the conversion level at the beginning of the reaction is associated with the coke deposits, it is related to the content of the metallic characters of Fe carbide<sup>[6]</sup>.

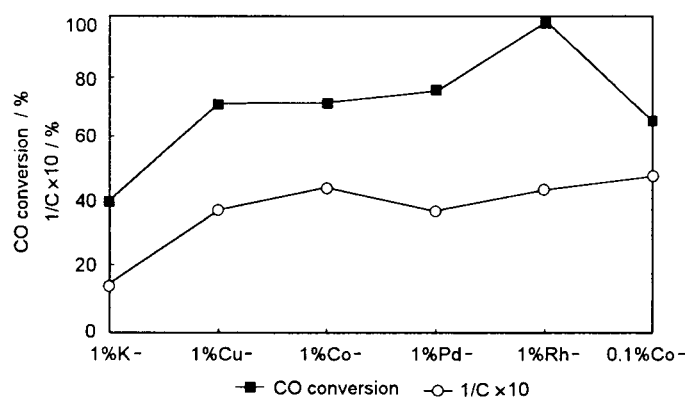


Fig.5 CO conversion and reciprocal( $\times$ 10) of surface coke content over different modified Fe/MnO catalysts

## Conclusions

1. Cu, Co, Pd and Rh modification could enhance the CO conversion over Fe/MnO. The Cu, Co modified Fe/MnO catalysts give higher selectivities to  $C_2^=$ ~ $C_4^=$  than Fe/MnO does.

2.  $C_3^=$  and  $C_4^=$  selectivities were higher than that of their aliphatic hydrocarbon form over Cu-Fe/MnO in comparison with the unpromoted Fe/MnO.

3. The activity in the quasi-stable period is dependent on the amount of coke deposited on the catalyst surface after reaction.

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### Acknowledgment

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## Journal of Natural Gas Chemistry 论文中文摘要

CuCr/CH<sub>3</sub>ONa在浆态相低温甲醇合成中的催化性能(Catalytic Performance of CuCr/CH<sub>3</sub>ONa Used for Low Temperature Methanol Synthesis in Slurry Phase) / 赵玉龙 白亮 胡蕴青 钟炳 彭少逸 (中国科学院山西煤炭化学研究所煤转化国家重点实验室 山西 太原 030001) // *J.Nat.Gas Chem.*, 8(1999)181

**摘要** 在液相介质为二甲苯、甲醇和液体石蜡, 温度100~140°C、压力3.5~4.7 MPa的条件下, 使用H<sub>2</sub>/CO合成气。在1立升搅拌釜内考察了自制的CuCr/甲醇钠催化体系的浆态相低温甲醇合成的反应性能。结果表明, 液相介质以二甲苯为佳, CO转化率随压力而升高, 温度以120°C为宜。44 h的连续运转结果表明, 以CO转化率为代表的该催化体系的反应性能基本稳定。

**关键词** CuCr/CH<sub>3</sub>ONa催化体系 浆态相 低温甲醇合成

改性Fe/MnO催化剂的CO加氢催化性能与表面积碳(Catalytic Behavior and Coke Formation of Modified Fe/MnO Catalysts) / 关乃佳, 云希勤, 单学蕾 (南开大学化学系 天津 300071) // *J.Nat.Gas Chem.*, 8(1999)188

**摘要** 研究了一系列K、Cu、Co、Pd和Rh改性的Fe/MnO催化剂(Fe/Mn=1/4)的CO加氢性能以获得更多的C<sub>2</sub><sup>-</sup>~C<sub>4</sub><sup>-</sup>低碳烯烃。在T=543 K, 压力为1.1 MPa和GHSV=215 h<sup>-1</sup>的反应条件下发现, 除K-Fe/MnO外, 一氧化碳加氢活性在改性催化剂上均有很大提高。其中, 在Cu和Co改性的催化剂上C<sub>2</sub><sup>-</sup>~C<sub>4</sub><sup>-</sup>烯烃有所提高。此外, 还研究了积碳对催化活性的影响, 发现了表面积碳量与催化活性的关系。

**关键词** 费托合成 Fe/Mn氧化物 积碳 烯烃选择性

Cu-Co尖晶石催化CO<sub>2</sub>加氢合成低碳醇(I) (Catalytic Hydrogenation of Carbon Dioxide into C<sub>2</sub>+ Alcohols over Copper-Cobalt Spinels (I)) / 黄伟, 谢克昌, 白英彬, 阴丽华 (太原理工大学煤化工研究所 山西 太原 030024) // *J.Nat.Gas Chem.*, 8(1999)196

**摘要** 制备了几种Cu-Co尖晶石, 并用于催化CO<sub>2</sub>加氢合成低碳醇反应。结果表明, Cu-Co尖晶石是一种极具潜力的催化剂前驱体, 具有出色的C<sub>2</sub>+醇合成能力。但是, 当在该催化剂中加入KOH时, 这种能力下降。XRD表征表明, KOH的加入破坏了Cu-Co合金的生成。一些结果被讨论。

**关键词** Cu-Co催化剂 CO<sub>2</sub>加氢 低碳醇合成

铜基催化剂催化合成甲醇和甲酸甲酯 II. 溶剂及H<sub>2</sub>/CO摩尔比的影响(Concurrent Synthesis of Methanol and Methyl Formate Catalyzed by Copper-Based Catalysts II. Influences of Solvents and H<sub>2</sub>/CO Mole Ratios) / 刘兴泉, 吴玉塘, 罗仕忠, 杨迎春, 贾朝霞, 李顺芬, 陈文凯, 于作龙 (中国科学院成都有机化学研究所 四川 成都 610041) // *J.Nat.Gas Chem.*, 8(1999)203

**摘要** 在低温低压条件下, 采用浆态床反应器和铜基催化剂考察了从合成气一步同时合成甲醇和甲酸甲酯(MF)反应, 并考察了溶剂和H<sub>2</sub>/CO摩尔比对CuCl和Cu-Cr氧化物催化剂的催化活性和MF选择性的影响。结果表明, 溶剂对CuCl和Cu-Cr氧化物催化剂的催化活性和MF选择性都具有较显著的影响。二甲苯和十氢萘是较好的溶剂。Cu-Cr氧化物催化剂的催化活性和MF选择性随着H<sub>2</sub>/CO摩尔比的增加而降低。此外, 用不同沉淀剂制备的Cu-Cr-Mn和Cu-Mn氧化物催化剂的催化活性与其相应的催化剂的比表面积呈正相关。

**关键词** 合成气 甲醇 甲酸甲酯 合成 铜基催化剂 铬 锰

原料气中添加CO对CO<sub>2</sub>在铜基催化剂上加氢反应的促进作用(Hydrogenation of CO<sub>2</sub> over Cu-Based Catalysts Promoted by Additive of CO in the Feed) / 李基涛, 张伟德, 陈明旦 (厦门大学化学系 固体表面物理化学国家重点实验室 物理化学研究所 福建 厦门 361005) 区泽棠 (香港浸会大学化学系 香港 九龙) // *J.Nat.Gas Chem.*, 8(1999)211

**摘要** 研究了CO<sub>2</sub>在Cu-Zn-Al催化剂上的加氢合成甲醇反应。发现在原料气中添加少量的CO可提高甲醇