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Catalysis Today 30 (1996) 207–213



## Development of catalysts for the production of aromatics from syngas

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### Abstract

Different combinations of FT catalysts Fe/MnO and Cu-Fe/MnO with zeolites HZSM-5 and GaZSM-5 have been used for converting syngas directly to aromatics. The manganese rich Fe/MnO FT-catalyst was prepared from nitrates by continuous coprecipitation and the copper as modifier of Fe/MnO was introduced by impregnation. Commercially available HZSM-5 and its Ga substituted form were mechanically mixed with the FT-catalysts and was used in single-bed reaction at 543 and 573 K. Dual-bed reaction has also been tried with Cu-Fe/MnO in the first bed and GaZSM-5 in the second bed. It has been observed that mixing zeolite with FT-catalysts significantly changes the product distribution in alkene/alkane and aromatics. The selectivity to aromatic hydrocarbons over composite catalysts is higher than that in dual-bed. The highest selectivity to aromatics reached 50% over Fe/MnO-GaZSM-5 composite catalyst at 543 K after 5 h on stream, however, a serious deactivation was observed with this catalyst. The conversion of CO with this catalyst reduced from 80 to 9.37% during 22 h. Via XPS measurements, a strong enrichment of Ga was found on the surface, while Mn-content on the surface was reduced. The deactivation of this catalyst might be attributed to the migration of Ga-species.

*Keywords:* FT-synthesis; Aromatics; Fe/Mn oxide; GaZSM-5 zeolite

### 1. Introduction

It has been discovered that aromatic hydrocarbons can be obtained from syngas over a combination of Fischer–Tropsch (FT) catalyst and zeolite. This reaction can be performed in a single-bed system or in a sequentially arranged dual reactor process. In the single-bed reaction the catalyst consists of two components working under the same conditions, a FT-catalyst converting CO and H<sub>2</sub> to hydrocarbons or oxygenates and a zeolite to oligomerize and aromatize these primary products. The two components can be mechanically mixed or isolated by an inert layer. In the dual-bed process, the

syngas was converted in the presence of a FT-catalyst under reaction conditions in favor of the formation of C<sub>2</sub>–C<sub>4</sub> olefins and oxygenates; and in consequence, the products of the first stage are processed in a second reactor with a medium pore zeolite such as ZSM-5 to yield aromatic hydrocarbons [1–5]. The advantages of this system are that the reaction conditions can be optimized for both catalysts and each catalyst can be regenerated separately.

The basic idea to mix FT-catalyst and zeolite was to break the traditional distribution in the FT synthesis controlled by the Schulz–Flory mechanism [6,7]. In this case the intermediate of the FT products at the initial steps of reaction

can be directly converted to aromatics without following hydrogenation. However, in this operation both catalysts must run under the same conditions. For the FT catalysts, the common working temperature is lower than 300°C because of the accelerated production of methane at high temperatures; whilst for the ZSM-5 catalyst, the normally used temperature for aromatization is about 500°C. The first attempt with composite catalyst was made by Chang et al. [1] at the end of the 1970s. They used Fe/Zr, Zn, Cr as the active component for CO conversion and zeolite as the second active center for aromatization in the temperature range from 371–427°C. The mixed catalyst exhibited significant activity and selectivity in converting syngas to aromatics. Since then, there have been many reports on this subject [8–10]. In this paper, the major work is with mixed catalysts. Differing from other works, a Ga-modified form of ZSM-5 as the aromatization component in the composite catalyst has been used. Fe/MnO and Cu-modified Fe/MnO have been selected as FT catalysts because of their good selectivity to C<sub>2</sub>–C<sub>4</sub> olefins [11]. Furthermore, we have also compared the single-bed to the dual-bed system with respect to the CO conversion and selectivity to aromatics. The combination of unmodified Fe/Mn oxide catalyst and HZSM-5 was also tested in this work in order to understand the effects of Ga in ZSM-5. Obviously, the activity of CO hydrogenation and the selectivity to aromatics depend on the composition and structure of each catalyst in such a mixed system. From this point of view, the surface composition of the catalyst at every treatment step has been studied via XPS.

## 2. Experimental

### 2.1. Catalyst preparation and reaction conditions

A manganese rich Fe/MnO oxide catalyst (Fe/Mn = 1/4) was prepared by continuous

coprecipitation from nitrates and ammonia solutions at 70°C and pH = 9.2, followed by drying at 120°C and calcination at 500°C. In the preparation of Cu modified FT catalyst, 1 at% of Cu (based on the metal ions of Fe/MnO) was introduced by impregnation of the Fe/MnO catalyst with copper nitrate. A commercial HZSM-5 zeolite (VAW Bonn, Germany) with a SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio of 27 and a Ga substituted ZSM-5 from the same company with the same SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio and a Ga-content of 2.24 wt% (2.73 at%) were used as the components for mixed catalysts in the single-bed or as the catalyst for aromatization in the second reactor in dual-bed operation. A catalyst referred to as Ga-Fe/MnO in the discussion of XPS was prepared by impregnation the Fe/MnO catalyst with gallium nitrate, with a loading of gallium 1 at% (based on the metal ions).

The composition of the reactant gas was 30 vol% CO, 60 vol% H<sub>2</sub> and 10 vol% Ar. It was premixed in an aluminum cylinder to minimize carbonyl impurities. A tubular stainless steel reactor (103 mm length and 12 mm diameter) was used for the reaction with FT catalyst and composite catalyst with a thermocouple located directly in the middle of the catalyst bed. In the reaction with the FT catalyst, the reactor was charged with 3 g catalyst, which was pelletized into cylindrical pellets (3 × 3 mm). With mixed catalysts, the catalyst bed was kept about 5 cm high as for the case with FT catalysts. The mixed catalysts were made by mechanical mixing of the FT catalyst and zeolite (1:1 by weight) through grinding in a mortar. The material was then pressed into pellets (10 × 2 mm), and afterward, crushed to about 2 mm. A quartz tube (20 × 0.6 cm) was used as the second reactor in the dual-bed operation, and was charged with 0.2 g of zeolite. The effluent from the first reactor was directed either to the on-line GC or to the second reactor.

The products were analyzed by a Carle AGC 111 GC with 4 columns (DC 200/500, Carbowax 1540, Porapak N and 13X molecular sieves) and a Perkin Elmer Sigma 2B GC with

an OV 101 capillary column. Before the syngas was switched to the reactor, both the Fe/MnO based FT catalyst and the composite catalysts were reduced with hydrogen at 400°C for 24 h. The reactions were mainly performed at two temperatures, e.g. 543 and 573 K and at 1.1 MPa in single-bed operations. In the dual-bed process, the first reactor was held at 543 K and 1.1 MPa, the second at 773 K and ambient pressure. The reaction data after running for about 21 to 25 h was taken for comparison in the following discussions.

Regeneration was done by oxidizing the mixed catalyst with an air flow of 45 ml/min at 500°C for 2 h and then reducing them with H<sub>2</sub> under the same conditions as for the fresh catalysts. In the dual-bed system, the zeolite in the second bed was oxidized with air under the same conditions, and the FT-catalyst in the first reactor was not regenerated.

## 2.2. X-ray photoelectron spectroscopy characterization

The composite and the Ga-Fe/MnO catalysts were characterized by XPS at every step of the

treatment, i.e. after calcination, reduction and passivation, in-situ reduction as well as after reaction. The measurements were performed with a Leybold–Heraeus spectrometer LHS/10, Al K<sub>α</sub> = 1486.6 eV in a vacuum system of 0.1 Pa. The reduction of catalysts with H<sub>2</sub> was made in a separate apparatus for XPS at 400°C for 24 h. 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 was transferred into the chamber of the XPS spectrometer. Before the analyzing process, it was in-situ reduced again under the same conditions as that in the reactor. In Table 3 showing the XPS results, the at% is the comparative value of the measured metal ions and the total at% making 100%.

## 3. Results and Discussion

The results obtained in a single-bed with composite catalysts (described as M) and in a dual-bed with separated catalysts (S) as well as pure FT-catalysts in a single-bed are given in Table 1, in which B0 and B1 represent the FT

Table 1  
Effect of zeolites on the product distribution

Ex. No. Catalyst	B0 Fe/MnO	M1 Fe/MnO HZSM-5	M2 Fe/MnO HZSM-5	M3 Fe/MnO GaZSM-5	M4 Fe/MnO GaZSM-5	B1 Cu-Fe/MnO	M5 CuFe/MnO HZSM-5	S1 CuFe/MnO GaZSM-5
Temperature (K)	543	543	573	543	573	543	543	543/773
P (MPa)	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.1/0.1
GHSV (h <sup>-1</sup> )	215	215	900	215	400	215	215	215/1800
Time (h) <sup>a</sup>	25.5	25.3	21.3	21.6	22.6	25.3	23	21
X <sub>CO</sub> (%)	38.17	53.94	52.13	9.37	33.60	68.84	27.54	71.52
Selectivity (%)								
CH <sub>4</sub>	10.59	7.84	12.77	0.97	0.08	7.32	12.39	8.42
C <sub>2</sub> H <sub>6</sub>	7.15	1.54	4.01	0.40		4.23	3.11	8.14
C <sub>3</sub> H <sub>8</sub>	4.25	11.82	12.59	0.30	0.02	1.59	8.06	1.44
C <sub>4</sub> H <sub>10</sub>	2.43	12.39	9.60	0.28		1.11	12.65	
C <sub>2</sub> –C <sub>4</sub> <sup>=</sup>	15.77	0.04	0.14			19.09	0.49	0.30
C <sub>5+</sub> <sup>b</sup>	38.15	38.52	35.15	53.01	93.30	37.15	39.24	68.44
Aromatics		6.96	3.77	40.40	6.34		10.15	3.26
Alcohol	1.61					0.41		
CO <sub>2</sub>	20.05	20.89	21.97	4.64	0.26	29.10	13.92	10.0
<i>i/n</i> -C <sub>4</sub>	0.05	1.97	2.20	only <i>i</i> -C <sub>4</sub>		0.11	1.55	only <i>i</i> -C <sub>4</sub>

<sup>a</sup> Sampling time for the data that follows.

<sup>b</sup> Including coke deposited.

catalysts Fe/MnO and Cu-Fe/MnO without zeolite, respectively.

As illustrated, the product distribution is changed by the presence of both HZSM-5 and GaZSM5 zeolites. In addition to promoting the formation of aromatic hydrocarbons, the mixing of the Ga-ZSM-5 with the FT-catalyst reduced low molecular weight hydrocarbons and shifted the distribution towards  $C_5^+$  hydrocarbons. The  $C_4$ -fraction over composite catalysts contained a major part of isobutane, especially over Fe/MnO-GaZSM-5 and at 543 K, in this case, only isobutane was found. On mixing of HZSM-5 with Fe/MnO, the conversion of CO increased from 38.17% over B0 to 53.94% over M1, while 6.96% of aromatics found in M1. M2 shows the result with this catalyst at elevated temperature (573 K) and a space velocity of  $900\text{ h}^{-1}$  in order to maintain the conversion at a comparable level with M1. The results of M2 showed that the  $C_1$ – $C_3$  fractions increased and the formation of aromatics was not favorable under these conditions. In the case of M3 (Fe/MnO-GaZSM-5) at 543 K, the selectivity to aromatics reached 40.4% and the conversion of CO varied with the reaction time and changed to 9.37% after 22 h. M4 gave the same results the catalyst with M3 but at 573 K and a space velocity of  $400\text{ h}^{-1}$  was used to control the initial conversion to be comparable with M3, after about 22 h, the conversion was still at 33.6%, this is 24% higher than M3. As a result, the production of aromatics was not beneficial under these condition for M4, only 6.34% of aromatics were found in this case, compared with 40.4% for M3. In the case of M5, a decrease of  $CO_2$  selectivity from 29.1% with catalyst B1 (Cu-Fe/MnO without zeolite) to 13.92% was observed, while a selectivity of 10.15% to aromatics was reached under these conditions. In dual-bed operation, the conversion of CO was not affected by the zeolite, and only 3.26% aromatics were obtained.

The dependencies of conversion on reaction time over Fe/MnO and zeolite composite catalysts at two different temperatures are depicted

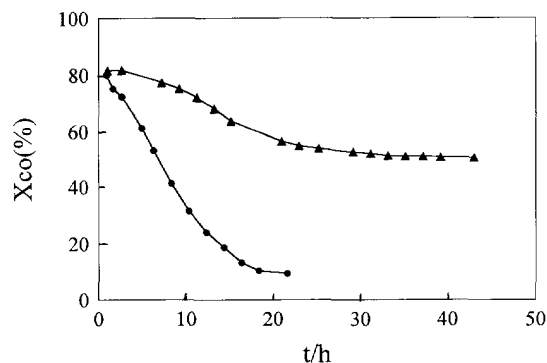


Fig. 1. CO conversion as a function of time on stream at  $P = 1.1$  MPa,  $GHSV = 215\text{ h}^{-1}$ ,  $T = 543\text{ K}$ : ●, Fe/MnO-GaZSM-5; ▲, Fe/MnO-HZSM-5.

in Figs. 1 and 2, respectively. It can be observed that the conversion of CO in the case of Fe/MnO-GaZSM-5 decreased rapidly with time on stream, while the Fe/MnO-HZSM-5 at both 543 K and 573 K did not show such strong deactivation during about 40 h.

Figs. 3 and 4 show the selectivity to aromatics over zeolite-containing Fe/MnO catalysts at two temperatures. The selectivity over Fe/MnO-GaZSM-5 reached 50% after 5 h at 543 K, and reduced to 40.4% after 22 h. At 573 K, the selectivity to aromatics with the same catalyst decreased from 24 to 6.34% after about 22 h. The selectivity obtained over Fe/MnO-HZSM-5 was less than 7% and did not vary much with time on stream.

Fig. 5 shows the results over the catalyst with Cu modified Fe/MnO in combination with

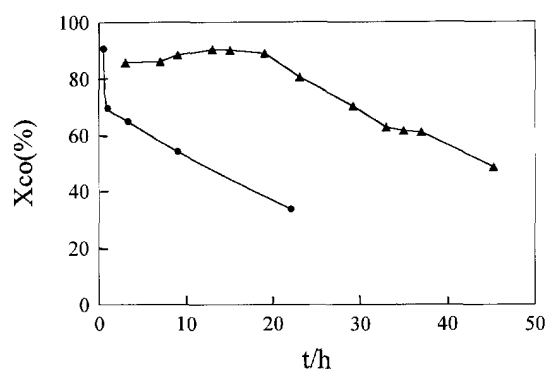


Fig. 2. CO conversion as a function of time on stream at  $P = 1.1$  MPa,  $T = 573\text{ K}$ : ●, Fe/MnO-GaZSM-5; ▲, Fe/MnO-HZSM-5.

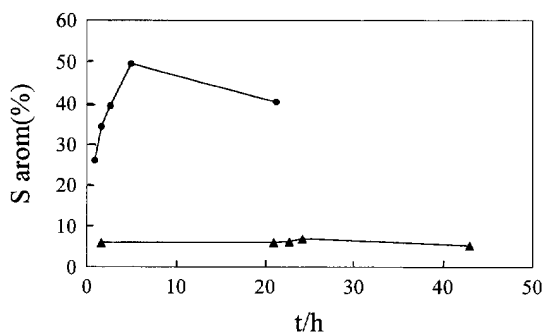


Fig. 3. Selectivity to aromatics as a function of time at  $P = 1.1$  MPa,  $GHSV = 215 \text{ h}^{-1}$ ,  $T = 543 \text{ K}$ : ●, Fe/MnO-GaZSM-5; ▲, Fe/MnO-HZSM-5.

HZSM-5 in a single-bed. It can be seen from the comparison of the data in Table 1 of this catalyst with the unmodified Fe/MnO-HZSM-5 that the introduction of Cu increased the selectivity to aromatics slightly. With the time on stream, the conversion reduced from 68 to 25% after 30 h. Meanwhile, the selectivity increased from 2% to about 11%. It was reported elsewhere [11] that the introduction of copper into Fe/MnO increased the selectivity to  $C_2$ – $C_4$  olefins. The beneficial effect of copper to the production of aromatics may be attributed to the increase of  $C_2$ – $C_4$  olefinic precursors in the system.

One case with CuFe/MnO and GaZSM-5 as FT and aromatization catalyst separately was tried with dual-bed operation. The results in definite sampling time is given in Table 1 as S1. The dependencies of CO conversion and selec-

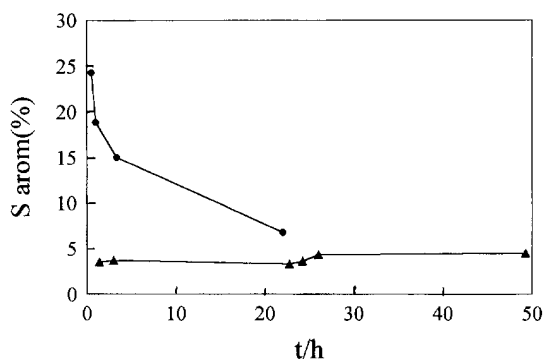


Fig. 4. Selectivity to aromatics as a function of time at  $P = 1.1$  MPa,  $T = 573 \text{ K}$ : ●, Fe/MnO-GaZSM-5; ▲, Fe/MnO-HZSM-5.

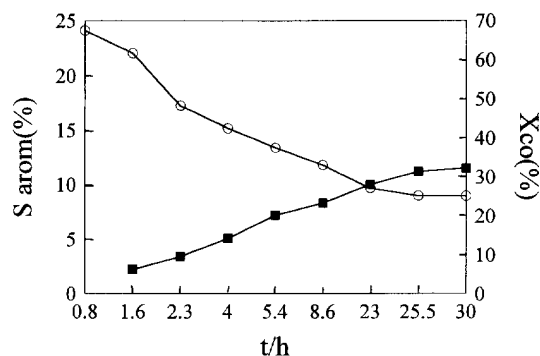


Fig. 5. CO conversion and selectivity to aromatics varied with time over 1%Cu-Fe/MnO-HZSM-5 at  $P = 1.1$  MPa,  $GHSV = 215 \text{ h}^{-1}$ ,  $T = 543 \text{ K}$ : ■,  $S_{\text{aromatics}}$  (%); ○,  $X_{\text{CO}}$  (%).

tivity to aromatics on reaction time are depicted in Fig. 6. As illustrated, the results were different to that in a single-bed. The conversion of CO did not vary to a great extent during 20 h. This process showed a better selectivity at the beginning of reaction (about 10%), then it decreased to 3.26% after 21 h on stream. The purpose of utilizing the dual-bed system was to control the temperature of reactor at the optimal level for the two catalysts. However, as a result, the formation of aromatics was very limited in this operation. Since the products from the first reactor had a wide distribution (from  $C_1$ – $C_{23}$  together with  $\text{CO}_2$  and oxygenates), the aromatization step in the second reactor with such a mixture as the reactant is surely difficult to perform. Efforts to regenerate the catalysts was made in both single-bed (M5) and dual-bed (S1)

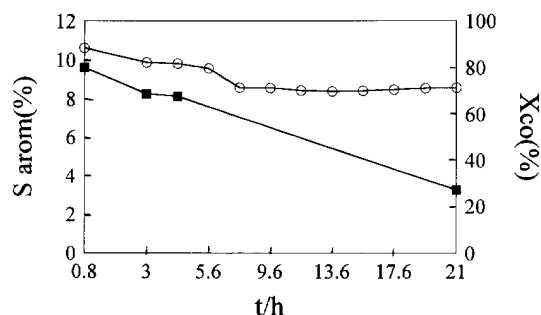


Fig. 6. CO conversion and selectivity to aromatics varied with time in a dual-bed. Bed 1:  $P = 1.1$  MPa,  $GHSV = 215 \text{ h}^{-1}$ ,  $T = 543 \text{ K}$ , 1%Cu-Fe/MnO; Bed 2:  $P = 0.1$  MPa,  $GHSV = 1800 \text{ h}^{-1}$ ,  $T = 773 \text{ K}$ , GAZSM-5. ■,  $S_{\text{aromatics}}$  (%); ○,  $X_{\text{CO}}$  (%).

Table 2  
Distribution of aromatic products

Catalyst	Fe/MnO	Fe/MnO	Fe/MnO	Cu/Fe/MnO
	HZSM-5	GaZSM-5	GaZSM-5	GaZSM-5
	single-bed		single-bed	dual-bed
Temperature (K)	543	543	573	543/773
GHSV (h <sup>-1</sup> )	215	215	400	215/1800
Time on stream (h)	25	21.6	22	21
X <sub>CO</sub> (%)	53.94	9.37	33.60	71.52
S <sub>aromatics</sub> (%)	6.96	40.40	6.34	3.26
Distribution (%)				
Benzene	10.06			
Toluene	43.34			100 <sup>a</sup>
Ethylbenzene	9.44	48.56		
Xylene ( <i>o-m-p</i> )	28.05			
C <sub>9</sub> -aromatics	9.11	51.44	100 <sup>a</sup>	

<sup>a</sup> Other trace components are not included in the total amount.

operations. After regeneration of the zeolite in the dual-bed, the selectivity to aromatics could be recovered to the initial level. In the single-bed with the composite catalyst, after regeneration, followed by reduction the selectivity to aromatics was small and the CO-conversion reduced more rapidly than that of fresh catalyst.

Table 2 shows the distribution of the aromatics obtained over composite catalysts in single-bed and separate catalysts in the dual-bed sys-

tem. The aromatic products are composed of benzene, toluene, xylene and C<sub>9</sub>-aromatics. Over the catalyst with GaZSM-5, the distribution of products tended to be more selective to specific aromatic compounds, which depend on the reaction conditions. In single-bed, over Fe/MnO-GaZSM-5 at 573K, there were only C<sub>9</sub>-aromatics found, while at 543 K there were two compounds formed. In the case of dual-bed operation with Cu-Fe/MnO and GaZSM-5 only toluene was obtained in the effluent.

The surface composition of the mixed catalysts at every step of treatment was determined by XPS. The information about the surface content of Ga, Fe and Mn as well as the carbon deposited are shown in Table 3. It can be seen that the carbon contents over all the samples examined after reaction were more than 10 times those after preparation (calcination). However, these samples showed different activity and selectivity profiles with reaction time and the Ga free catalysts did not deactivate much after a long period. It can be deduced that carbon deposition should not be a major reason for deactivation.

From the results in Table 3, it can be found

Table 3  
Surface composition of the selected catalysts

Catalyst	Catalyst pretreatment	Surface composition in at%			Carbon content (wt%)
		Fe	Mn	Promoter (Cu or Ga)	
Fe/MnO-HZSM5	calcined	22.1	77.9		0.312
	reduced and passivated	16.2	83.8		0.032
	in situ reduced	11.0	89.0		
	after reaction at 270°C	15.5	84.5		1.825
	after reaction at 300°C	20.7	79.3		2.705
Fe/MnO-GaZSM-5	calcined	21.9	75.3	2.7	0.051
	reduced and passivated	11.9	85.9	2.1	0.037
	in situ reduced	14.9	79.8	5.2	
	after reaction at 270°C	15.9	74.1	10.0	0.546
	after reaction at 300°C	14.4	76.5	9.1	0.514
Cu-Fe/MnO-HZSM-5	calcined	22.4	72.8	4.8	0.040
	reduced and passivated	16.2	82.0	1.8	0.020
	in situ reduced	14.4	85.2	0.2	
	after reaction at 270°C	17.1	80.6	0.2	1.668
Ga-Fe/MnO	calcined	18.5	80.5	1.0	0.209
	reduced and passivated	15.6	80.0	4.4	0.073
	in situ reduced	12.5	80.2	7.3	
	after reaction at 270°C	11.5	83.9	4.5	1.960

that the content of Ga in Fe/MnO-GaZSM-5 composite catalysts increased from 2.1 at% after reduction and following passivation treatment to 10 at% after reaction at 543 K. At the same time, the Mn content of this catalyst was reduced from 85.9 to 74.1 at%. For comparison, the data of a Ga doped Fe/MnO catalyst by impregnation are given in the same table. Ga species migration on this catalyst was also observed and the Ga content after reaction was 4.5 times enriched than that after calcination. If we pay attention to the Mn contents of this catalyst, its amount did not decrease, and was even increased slightly (from 80.5% to 83.9%). In contrast, the catalysts without Ga, e.g. Fe/MnO-HZSM-5 and Cu-Fe/MnO-HZSM-5 in Table 3, showed less variation in the surface composition; meanwhile, their stabilities were also better than the Ga doped catalysts, which are shown in Fig. 1, Figs. 2 and 5. These results indicate that the presence of Ga in the catalysts leads to an unstable state in the surface composition. Hutchings et al. suggested [12] that the Fe<sup>0</sup> disperses on the MnO support forming a solid solution in Fe/MnO catalysts, which acts as active sites for CO hydrogenation. Over Fe/MnO-GaZSM-5 composite catalyst, the enriched Ga has strongly suppressed the Mn species at the surface. It seems likely that the enrichment of Ga reduced the Fe/MnO active sites and affected the activity of the catalyst.

#### 4. Conclusions

Aromatic hydrocarbons can be produced from syngas over Fe/MnO and its Cu-modified form in combination with HZSM-5 or GaZSM-5 zeolites. The Ga modified ZSM-5 and Fe/MnO composite catalyst resulted in a catalyst that showed good aromatic selectivity. The highest selectivity to aromatic products reached 50% over this catalyst at 543 K after 5 h of reaction. The catalyst deactivated rapidly from 80% at the beginning to 9.37% after 22 h on stream.

The activity was difficult to recover by an oxidizing process. The aromatics obtained over Ga-free composite catalysts were below 11%. In the dual-bed system with Cu-Fe/MnO in the first reactor and GaZSM-5 in the second, the conversion of CO did not change to a great extent with time on stream, the selectivity to aromatics decreased from about 10 to 3% after 21 h.

A strong enrichment of Ga at the surface of catalyst was found by XPS measurement in all Ga containing catalysts after reaction. The easy deactivation of the Fe/MnO-GaZSM-5 catalysts might be attributed to the migration of Ga, which reduced the Fe/MnO active sites by suppressing the Mn-content at the surface.

#### Acknowledgements

We are grateful to Professor Dr. M. Baerns, Professor Dr. H. Papp and Dr. Lindner (University Bochum, Germany) for valuable discussions and XPS measurements.

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