Conversion of ethane into benzene on Re/ZSM-5

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The reaction of ethane on pure and Re-containing ZSM-5 has been investigated at 773–973 K. Reaction products were analyzed using gas chromatography. ZSM-5 with Si/Al = 30 exhibited relatively high activity towards dehydrogenation, hydrogenolysis and aromatization of ethane above 773 K, whereas ZSM-5 with Si/Al = 280 showed very low activity. Deposition of 2% Re enhanced the conversion of ethane, the selectivity and the yield of benzene production even on the most effective ZSM-5. Further increase in the Re content did not lead to the improvement of the catalyst. The role of the Re is very likely the activation of ethane and the enhanced production of ethylene. ZSM-5 samples were found to be very active in the aromatization of ethylene, which was only slightly influenced by Re.

KEY WORDS: reaction of ethane; aromatization of ethane; effects of the composition of ZSM-5; reaction of ethylene; Re/ZSM-5 catalyst; Re/SiO_2 catalyst.

1. Introduction

A great effort is being made to convert methane into more valuable compounds. Supported Pt metals exhibited a high activity towards the decomposition of methane to produce H_2 and surface carbonaceous species only with minor amounts of C_2 compounds [1–8]. The deposition of carbon, however, causes an early deactivation of the catalysts and hinders the practical application of this reaction for H_2 generation. A more attractive catalytic system is Mo_2C combined with ZSM-5, which transfers methane into benzene with 80% selectivity at 10% conversion at 973 K [9–16]. A great effort was made to explain the role of the two components of the catalyst and to establish the mechanism of this reaction [17–25]. Attempts were also made to find and develop a more active and stable catalyst for the methane – benzene conversion. The most successful test was made by Ichikawa *et al.* [26,27], who found that Re/ZSM-5 exhibits similar catalytic behavior as Mo_2C/ZSM-5 for the aromatization of methane.

As we can expect the formation of ethane in the coupling of the CH_3 radicals, the primary product of the activation of methane, it seemed unavoidable to establish the effects of Re/ZSM-5 on the reactions of ethane. Note that Mo_2C/ZSM-5 was found to be an effective catalyst in the aromatization of ethane [28], ethylene [29], propane [30] and butane [31,32]. We hope that the evaluation of the reaction pathways of ethane over Re/ZSM-5 helps us to understand better the formation of benzene from methane on the same catalyst.

2. Experimental

The gases used were of commercial purity (Linde). NH_4-ZSM-5 was a commercial product (Zeolite Intern.), which was calcined to produce H-ZSM-5 in air at 773 K for 4 h. SiO_2 was the product of Cab-O-Sil. We used two ZSM-5 samples: the surface area of ZSM-5 ($SiO_2/Al_2O_3 = 30$) is 325 m^2/g. The micropore volume is 0.011 cc/g, and the micropore area is 214.7 m^2/g. These values for the other ZSM-5 ($SiO_2/Al_2O_3 = 280$) are as follows: 361.7 m^2/g; 0.05 cc/g, and 99.7 m^2/g, respectively the surface area of SiO_2 (Cabosil) is 200 m^2/g. In the preparation of the catalysts we followed the pattern described by Ichikawa *et al.* [26,27]. Re/HZSM-5 samples with different Re loadings were prepared by impregnation (incipient wetness) of NH_4-ZSM-5 with the aqueous solution of $(NH_4)_2ReO_4 \cdot 4H_2O$. The resulting materials were dried at 393 K and calcined in air at 773 K for 4 h and reduced at 523 for 1 h. Catalytic reactions were carried out at 1 atm of pressure in a fixed-bed, continuous flow reactor consisting of a quartz tube (8 mm i.d.) connected to a capillary tube. The flow rate was 12 mL/min. The carrier gas was Ar. The ethane content was 12.5%. Generally 0.3 g of loosely compressed catalyst sample was used. Reaction products were analyzed gas chromatographically using a Hewlett-Packard 5890 gas chromatograph and a HP-PLOT Al_2O_3 column.

3. Results

3.1. Reactions of ethane on H-ZSM-5

First the catalytic behavior of ZSM-5 of different compositions was tested. The Si/Al ratio dramatically

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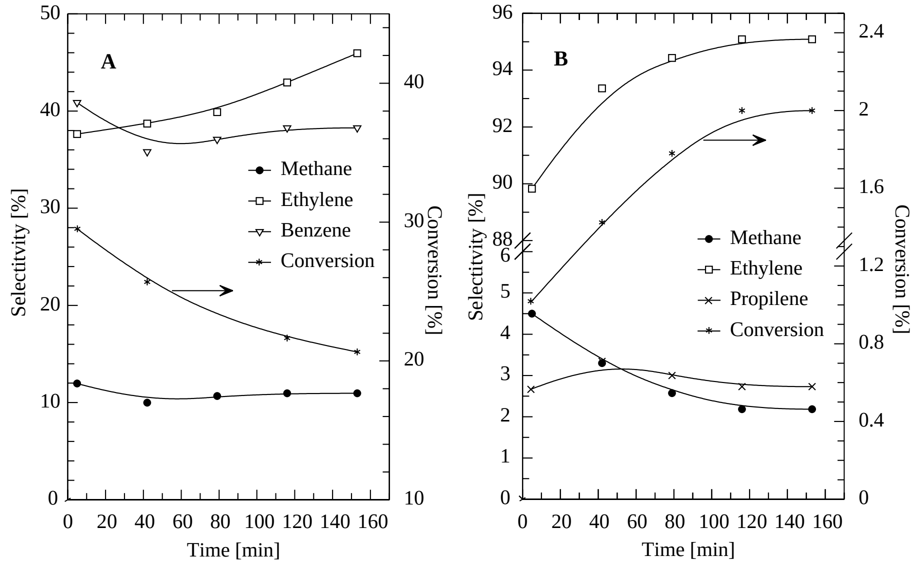

Figure 1. Reactions of ethane on ZSM-5 samples with Si/Al = 30 (A) and with Si/Al = 280 (B) at 873 K.

influenced the catalytic performance of ZSM-5. The highest conversion (30–21%) at 873 K was obtained for the sample (Si/Al = 30) that exhibited relatively high activity towards the dehydrogenation and hydrogenolysis of ethane. There were only moderate changes in the conversion and in the rate of formation of various products in time on stream (5–160 min). The highest selectivity, 38–45%, was measured for ethylene. This was followed by benzene, $S = 41$–38%. Methane was also produced with a selectivity of 12–14% (figure 1A). Minor products were propylene and butane. Traces of propane, pentane and toluene were also detected. Lowering the temperature the conversion of ethane decreased and approached nearly zero value around 773 K. At the same time the selectivity to ethylene increased, whereas that for benzene drastically decreased. No change was observed in the selectivity of methane formation. With the increase of the Si/Al ratio the conversion of ethane gradually decreased. The sample with Si/Al ratio of 280 the conversion was only 1–2% (figure 1B).

3.2. Reactions of ethane on Re/ZSM-5

In the next experimental series Re was deposited on the most effective ZSM-5 support (Si/Al ratio = 30). Results for 2% Re/ZSM-5 are presented in figure 2A. Both the initial and the steady state conversions of ethane have been significantly enhanced as well as the rate of benzene formation. The selectivity of benzene

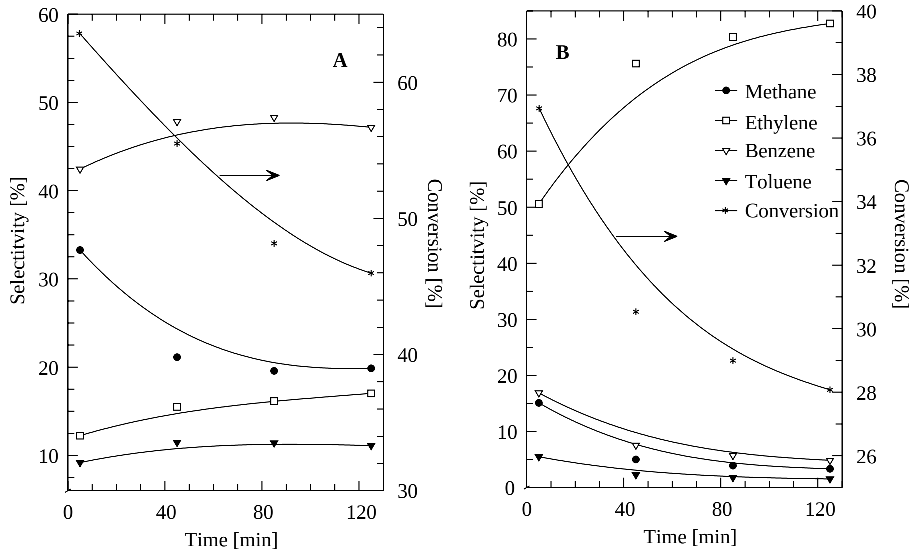

Figure 2. Reactions of ethane on 2% Re/ZSM-5 with Si/Al = 30 (A) and with Si/Al = 280 (B) at 873 K.

Table 1
Characteristic data for the reaction of ethane on ZSM-5 and Re/ZSM-5 catalyst at 873 K

Catalyst	Conversion %	Selectivities				Yields, conversion × selectivity/100		
		CH_4	C_2H_4	C_6H_6	C_7H_8	C_2H_4	C_6H_6	C_7H_8
ZSM-5 (30)	23	10	40	37	–	9.2	8.5	–
ZSM-5 (280)	1.8	2.5	95	–	–	1.7	–	–
2% Re/ZSM-5 (30)	48	20	16	48	11	7.6	23.0	5.2
5% Re/ZSM-5 (30)	35	10	40	30	9	14.0	10.5	3.1
10% Re/ZSM-5 (30)	37	20	30	35	14	11.1	12.9	5.1
2% Re/ZSM-5 (30) + ZSM-5 (30)	46	30	6	50	11	2.7	23.0	5.0
2% Re/ZSM-5 (280) + ZSM-5 (30)	18	17	17	50	12	3.0	9.0	2.1

Data were taken at 80 min.

also increased, while that of ethylene drastically decreased. The favorable effect of the Re is well exhibited in the yield of the production of benzene (table 1). As shown in figure 3 an increase in the loading of Re to 5% and 10% did not lead to the further improvement of the catalyst, although the conversion of ethane as well as the yield of benzene formation were markedly higher than those measured for pure ZSM-5.

The effect of Re has been also tested in the case of the less effective ZSM-5 (Si/Al ratio = 280). Re exerted a more profound influence on its catalytic efficiency: the conversion at 873 K increased from 1–2% to 38–28% (figure 2B). On this catalyst ethylene was produced with high selectivity, 50–85%. The formation of benzene remained at low level with a selectivity of 17–7%. At higher Re content (10%), the conversion of ethane was less than on 2% Re/ZSM-5, but the selectivities of the main products changed only slightly.

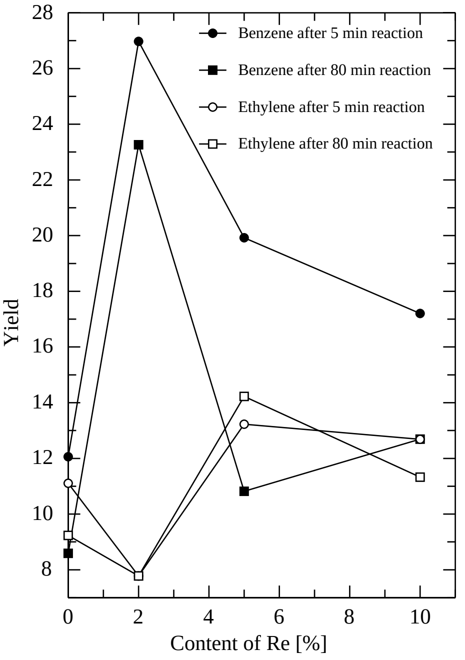

Figure 3. Effects of Re content on the reaction of ethane over ZSM-5 (Si/Al = 30) at 873 K.

The effect of contact time on the reaction of ethane was determined by the variation of space velocity. We obtained that with the increase of contact time, the conversion and the selectivity to methane increased while the selectivity to ethylene decreased. No change occurred in the selectivity to benzene.

Some important data for the conversion of ethane on different catalysts are shown in table 1.

3.3. Examination of the used catalyst

An examination of the Re/ZSM-5 (Si/Al = 30) catalyst after reaction revealed the deposition of carbonaceous species. TPR studies showed that the hydrogenation of this surface carbons on 2%, Re/ZSM-5 starts at 650 K and gave two peaks at 760 and 910 K. The amount of carbon, as determined in the form of methane, was 4.54×10^5 μmol. According to the calculation this amount of carbon means that about 3% of ethane that passed through the catalyst bed decomposed to carbon.

3.4. Reactions of ethylene on ZSM-5 and Re/ZSM-5

In order to explain the significant differences in the catalytic properties of the ZSM-5 samples, the reactions of ethylene have been examined on the most and less effective ZSM-5 samples. The zeolite with Si/Al = 30 was found to be very active towards the aromatization of ethylene. The conversion was more than 90% even at 773 K. Benzene formed with the highest selectivity, 35–25%, followed by propane ($S = 15$–25%) and toluene ($S = 23$–20%). The ZSM-5 with Si/Al = 280 was much less active. The main products were propylene ($S = 53$–57%), butane ($S = 20$%) and pentane ($S = 13$%). The selectivity of benzene remained below 2%. The deposition of Re on these zeolites influenced the product distribution, but did not improve the aromatization ability of zeolites. Some characteristic data are collected in table 2.

3.5. Use of two catalyst beds

As the results in the previous chapter showed ZSM-5 with Si/Al ratio of 30 is an effective catalyst in the

Table 2

Characteristic data for the reaction of ethylene on ZSM-5 and Re/ZSM-5 catalyst at 873 K

Catalyst	Conversion %	Selectivities					Yields			
		CH_4	C_3H_6	C_3H_8	C_6H_6	C_7H_8	C_3H_6	C_3H_8	C_6H_6	C_7H_8
ZSM-5 (30)	94	10	3	26	28	20	2.8	24.4	26.3	18.8
ZSM-5 (280)	42	1	57	2	1	2.2	23.9	0.8	0.4	0.9
2% Re/ZSM-5 (30)	95	8	3	30	23	19	2.8	28.5	21.8	18.0
2% Re/ZSM-5 (280)	68	1	36	6	3	7	24.4	4.0	2.0	4.7

Note: Data were taken at 100 min.

aromatization of ethylene. In the light of this behavior it is remarkable that relatively large amount of ethylene, formed in the dehydrogenation process of ethane on Re/ZSM-5 (Si/Al = 30), remained intact. In order to enhance the yield of benzene a small amount (0.3 g) of pure ZSM-5 (Si/Al = 30) has been placed behind the Re/ZSM-5 (Si/Al = 30) still in the hot zone. Results are given in table 1. As was expected the production of benzene markedly increased at the expense of ethylene formation. In this way the product distribution has been also changed in the case of Re/ZSM-5 (Si/Al = 280), where the aromatization reaction was negligible. With the use of additional ZSM-5 (Si/Al = 30) in the second bed, the selectivity of benzene increased from 9% to 49%, whereas the selectivity of ethylene diminished from 84% to 17%.

4. Discussion

The primary aim of this work was to establish the effect of Re on the reaction pathway of ethane, particularly on the formation of aromatics. The aromatization of ethane over promoted ZSM-5 has been the subject of extensive research [33–41]. At high temperature, above 823 K, this reaction proceeds on undoped ZSM-5 itself: the preparation, the composition of the ZSM-5 and the experimental conditions all influence the conversion and product distribution. On the most effective ZSM-5 (Si/Al = 30) ethylene and benzene formed almost with same selectivities, 38–46%, at a conversion of 30–21% (figure 1). The decrease of the conversion and aromatization of ethane with the increase of SiO_2/AlO_3 ratio of ZSM-5 corresponds to the reduction of Brönstead and Lewis centers of the zeolite [33].

A significant improvement in the catalytic performance of ZSM-5 occurred when Re was deposited on it. Apart from the very initial values, relatively slight changes in the conversion and selectivities to various products were experienced in time on stream. Qualitatively, we observed the formation of the same C-containing compounds as in the case of ZSM-5, which suggests the occurrence of similar reactions. The advantageous properties of Re was particularly revealed at a content of 2%, when the steady-state conversion reached a value of 48% with a 59% selectivity to aromatics (figure 2). Higher Re loading led to less effective catalyst. These results indicate that the highly dispersed Re/ZSM-5 is the best catalyst for the transformation of ethane. Another difference is that on Re/ZSM-5 less ethylene and more methane are formed at the same ethane conversion. In addition, we observed the deposition of carbon. The peak temperatures of its hydrogenation were high, 760 and 910 K. This low reactivity suggests that it is in the form of amorphous carbon. Its formation may occur in the decomposition of ethane

$$C_2H_{6(a)} = CH_{4(g)} + H_{2(g)} + C$$

or more likely in the reaction of ethylene

$$C_2H_{4(a)} = CH_{4(g)} + C$$

The latter process was found to be more rapid on Re/ZSM-5 than the previous one.

The role of the Re is very likely the activation of ethane and the promotion of the formation of ethylene

$$C_2H_{6(a)} = C_2H_{5(a)} + H_{(a)}$$

$$C_2H_{5(a)} = C_2H_{4(a)} + H_{(a)}$$

Further reactions, namely the oligomerization and the aromatization of ethylene proceed on the acidic sites on ZSM-5. In accord with the literature data, we found that the latter reaction is rapid on the ZSM-5. The conversion of ethylene was as high as 94% and the selectivity of benzene formation attained a value of 28% even at 773 K. In the light of these results, it is interesting that a relatively large amount of ethylene is released from the ZSM-5-based catalysts or, in other words, a large fraction of ethylene produced escapes aromatization. This suggests that the Re and/or the carbon formed in the reaction of ethane poisons the acidic sites of ZSM-5 and prevents the aromatization of ethylene. The fact that the use of a second separate bed of ZSM-5 [30] greatly enhanced the extent of aromatization at the expense of ethylene formation supports this explanation.

The reaction pathway of ethane was investigated on the 2% Mo_2C/ZSM-5 [28], so we may compare the results obtained on the two catalysts. The difference is that the conversion of ethane is somewhat higher on Re than on Mo_2C catalyst. Comparing the selectivities at nearly the same conversion, ca. 46%, we obtain that the selectivity of benzene formation is much higher (45%) for Re/ZSM-5 than on Mo_2C/ZSM-5 (~26%). We attribute this to the more extended formation of excess carbon in the later case, which may block some of the acidic sites of ZSM-5.

5. Conclusions

1. The reaction pathways of ethane on ZSM-5 were strongly influenced by the Si/Al ratio in the zeolites. The most effective one was that with Si/Al ratio of 30.
2. Deposition of Re on ZSM-5 greatly improved the catalytic performance of ZSM-5: the conversion of ethane, the selectivity and the yield of benzene formation all increased, which were attributed to the high activity of Re as regards the activation of C–H bond in the ethane.
3. The aromatization of ethylene proceeds with high rate on ZSM-5 samples even at 773 K, which is only slightly influenced by Re.

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