Alkylation of ethylbenzene with methanol over X type zeolites

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The methylation of ethylbenzene over X type zeolites was studied at atmospheric pressure and temperature of 400–500°C. Ring and side-chain alkylation take place, respectively, on the acid and base zeolite, viz. HX and KX. With KX at 500°C, alkylation and dealkylation proceed, respectively, via carbanion and carbonium ion mechanism, whereas dehydrogenation and demethylation occur via free radical mechanism. The ratio of radical to ionic activity increases with increasing contact time, reaction temperature and time-on-stream.

Keywords: Alkylation; ethylbenzene; methanol; X zeolites; acid–base catalysis

1. Introduction

The study of catalytic reaction over base zeolites has drawn increasing attention during the past decade [1]. For the reaction of toluene with methanol and formaldehyde, Yashima et al. [2] reported that xylenes were obtained by alkylation of the benzene ring of toluene on Li exchanged zeolite, while a mixture of styrene and ethylbenzene was produced by the alkylation of the methyl group of toluene on Na, K, Rb and Cs exchanged zeolites. In a series of papers on the side-chain alkylation of alkylbenzene with methanol, Itoh et al. [3–5] proposed that both acid and base sites were necessary in the side-chain alkylation of alkylbenzene with methanol. The IR technique has been used to investigate the adsorbed species on alkali-modified zeolites for the alkylation of toluene with methanol [6,7]. Yang et al. [8] studied the side-chain alkylation of *p*-xylene with methanol on alkali cation zeolite and correlated the catalyst activity and the product selectivity with the acid–base properties of the catalyst.

The purpose of this paper is to investigate the effect of catalyst acidity and basicity on the conversion and the product distribution from the alkylation of ethylbenzene with methanol over KX, NaX and HX zeolites with special attention on the KX zeolite. For the reaction over KX, the influence of contact time, reaction temperature and time-on-stream was studied. Based on the experimental results, the reaction network and associated mechanisms are proposed and discussed.

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2. Experimental

2.1. CATALYST

The powder of NaX zeolite was supplied from Strem Co. HX and KX were prepared, respectively, by ionic exchange of NaX with ammonium chloride and potassium acetate solution. The degrees of cation exchange were 70 and 93%, respectively, for HX and KX as measured by atomic absorption spectroscopy. After drying at 110°C overnight and calcining at 500°C for 4 h, the resulted zeolites were pelleted without a binder, crushed and sized in 50–60 mesh. According to the powder X-ray pattern, NH_4X exhibited a large decrease in peak intensity after calcination.

2.2. APPARATUS AND PROCEDURES

The reaction was performed with a fixed-bed, integral flow reactor at 400–500°C under atmospheric pressure. Before the reaction the catalyst was activated in air at 500°C for 2 h, then flushed with nitrogen gas for 30 min and finally brought to the reaction temperature. The mixture of ethylbenzene and methanol (both 99.8%, Merck) with a molar ratio of 3 was fed via a microfeeder. The reaction products were cooled with an ice trap and collected periodically. The liquid products were analyzed by a Varian GC 3700 gas chromatograph using a flame-ionization detector and a column of GP 5% SP 1200/1.75% Bentone 34 on 100/120 Supelcoport. The gaseous products were analyzed on the same GC with a column of activated alumina. A blank run was also conducted at 500°C with no catalyst in the reactor, showing negligible thermal reaction.

3. Results and discussion

3.1. EFFECT OF CATALYST ACIDITY AND BASICITY

Table 1 lists the typical results of the conversion and the product composition from alkylation of ethylbenzene with methanol over KX, NaX and HX zeolite at 500°C. The conversion and the yield of products were calculated on the basis of the reactant ethylbenzene. The yield of aromatic compounds from methanol alone is negligible as compared to that produced from ethylbenzene. The product distribution varies greatly on these zeolites. For the reaction over NaX, the products include ethyltoluene, toluene, styrene and minor amount of benzene, isopropylbenzene, α-methylstyrene, xylene, trimethylbenzene and diethylbenzene, which were formed via a variety of processes, viz. alkylation, dealkylation, dehydrogenation and disproportionation. In the case of HX, all above products except α-methylstyrene and isopropylbenzene were observed. On the other hand, α-methylstyrene, iso-

Table 1
Alkylation of ethylbenzene (EB) with methanol (M) over zeolites. EB/M = 3; $T = 500°\mathrm{C}$; $W/F = 36.3\ \mathrm{g\,h\,mol^{-1}}$; time-on-stream 20 min

	Catalyst		
	KX	NaX	HX
conversion (mol%)	11.73	9.04	14.00
yield (mol%)			
benzene	0.63	0.09	1.37
toluene	7.61	0.46	0.88
styrene	1.30	0.80	0.31
α-methylstyrene	0.44	0.04	–
isopropylbenzene	1.50	0.09	–
xylene	–	0.04	0.21
ethyltoluene	–	6.45	9.14
trimethylbenzene	–	0.07	0.13
diethylbenzene	–	0.03	0.55
others	0.25	0.97	1.41
R/S	0	49.6	∞

propylbenzene, toluene, styrene and benzene were produced from the reaction over KX zeolite. The conversion (X in mol%) and the activity ratio of ring to side-chain alkylation (R/S) are defined as follows:

$$X\ (\mathrm{mol}) = \frac{(\mathrm{EB})_\mathrm{f} - (\mathrm{EB})_\mathrm{p}}{(\mathrm{EB})_\mathrm{f}} \times 100\%,$$

$$\frac{R}{S} = \frac{(\mathrm{ET})}{(\alpha\text{-MS}) + (\mathrm{IPB})},$$

in which $(\mathrm{EB})_\mathrm{f}$, $(\mathrm{EB})_\mathrm{p}$, (ET), (α-MS) and (IPB) represent, respectively, the moles of ethylbenzene in the feed, ethylbenzene in the product, ethyltoluene, α-methylstyrene and isopropylbenzene. According to the calculated values of R/S, ring and side-chain alkylation took place, respectively, on the acid and base zeolite, viz. HX and KX, whereas both types of alkylation were found on NaX. A similar relationship of alkylating position with the catalyst acidity and basicity was reported for the alkylation of toluene with methanol [2,9].

3.2. EFFECT OF CONTACT TIME

Fig. 1 shows the product yield as a function of contact time for the reaction over KX at 500°C. In the alkylation of toluene with methanol over zeolite, Sidorenko et al. [10] proposed the reaction paths for the formation of styrene and ethylbenzene. Similar reaction pathways suggested in this study are:

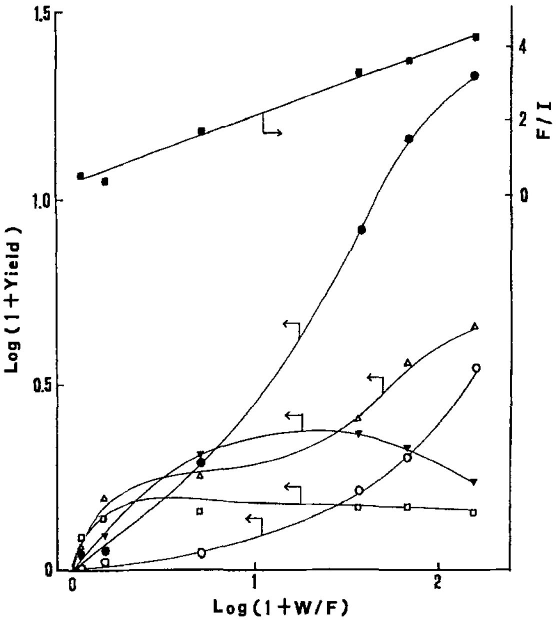

Fig. 1. The yields of products as a function of contact time. Conditions: EB/M = 3; KX; 500°C; time-on-stream 20 min. (○) benzene; (●) toluene; (▼) styrene; (△) isopropylbenzene; (□) α-methylstyrene; (■) F/I.

$$CH_3OH \rightarrow HCHO + H_2,$$

$$C_6H_5CH_2CH_3 + HCHO \rightarrow C_6H_5C(CH_3)CH_2 + H_2O,$$

$$C_6H_5C(CH_3)CH_2 + CH_3OH \rightarrow C_6H_5CH(CH_3)_2 + HCHO,$$

$$C_6H_5C(CH_3)CH_2 + H_2 \rightarrow C_6H_5CH(CH_3)_2.$$

Although KX owns mainly base sites, a certain degree of acidity may also exist due to the partial hydrolysis reactions, e.g. $KX + H_2O \rightleftharpoons HX + KOH$, which may occur during washing following cation exchange, and are known to proceed to the right to a greater extent with Na- than with K-zeolites, in agreement with the relative acidities. Formaldehyde, being produced from methanol on the base site and stabilized on the acid site of KX, is considered as the true alkylating reagent [3,11]. Side-chain alkylation of ethylbenzene with formaldehyde on the base site via carbanion mechanism [7,12] leads to α-methylstyrene, which then combines with methanol and / or H_2 to form isopropylbenzene.

According to fig. 1, both styrene and toluene are primary products. When the contact time was increased, the yield of styrene increased through a maximum and then decreased whereas that of toluene increased steadily and became eventually the major product. There are two possible paths for the formation of styrene: (1)

dehydrogenation of ethylbenzene via acid/base dual site mechanism [13]; (2) formation via free radical mechanism [14]. The former generally takes place on a catalyst with strong basic sites such as mixed metal oxides [13]. In addition, the formation of toluene cannot be interpreted in terms of the ion mechanism. Thus, the latter is supposed to operate for the production of styrene and toluene. Poutsma [14] reported that at reaction temperature higher than 500°C catalytic reaction over zeolites exchanged with alkali or alkaline earth metal proceeded via free radical mechanism. In the reaction of isopropylbenzene over alkali or alkaline earth metal exchanged Y zeolites at 550°C, Richardson [15] deduced that benzene was produced by depropylation of isopropylbenzene via carbonium ion mechanism while α-methylstyrene and ethylbenzene were formed, respectively, by dehydrogenation and demethylation via free radical mechanism. Furthermore, the initial ratio of carbonium ion to free radical activity was 2.03 and increased with increasing contact time. Forni and Carra [16] investigated the reaction of diethylbenzene over NH_4X zeolite exchanged with alkali metal at 500–568°C. The products were ethylbenzene, ethylstyrene and ethyltoluene, which were produced via the mechanism similar to that proposed by Richardson [15]. Under our reaction conditions of KX at 500°C and W/F 67.8 g h mol^{-1}, the main gaseous products are methane, ethane and ethylene with the selectivity, respectively, of 83, 7 and 7 mol% among all gaseous products. Based on these results, we propose a similar free radical mechanism [14] for the formation of toluene, styrene and methane:

$$\begin{aligned}
&\text{initiation :} && C_6H_5CH_2CH_3 \rightarrow C_6H_5\dot{C}H_2 + \cdot CH_3\,,\\
&\text{propagation :} && \cdot CH_3 + C_6H_5CH_2CH_3 \rightarrow CH_4 + C_6H_5\dot{C}HCH_3\,,\\
& && C_6H_5\dot{C}H_2 + C_6H_5CH_2CH_3 \rightarrow C_6H_5CH_3 + C_6H_5\dot{C}HCH_3\,,\\
& && C_6H_5\dot{C}HCH_3 \rightarrow \cdot H + C_6H_5CHCH_2\,,\\
& && \cdot H + C_6H_5CH_2CH_3 \rightarrow H_2 + C_6H_5\dot{C}HCH_3\,,\\
&\text{termination :} && 2C_6H_5\dot{C}HCH_3 \rightarrow C_6H_5CH_2CH_3 + C_6H_5CHCH_2\,.
\end{aligned}$$

Fig. 2 illustrates the proposed reaction network. α-methylstyrene is formed by side-chain alkylation of ethylbenzene via carbanion ion mechanism and its further methylation and/or hydrogenation produces isopropylbenzene (path 1). Benzene is probably formed from dealkylation of ethylbenzene and/or isopropylbenzene via carbonium ion mechanism (path 2). Styrene and toluene are produced, respectively, from dehydrogenation and demethylation of ethylbenzene via free radical mechanism (paths 3 and 4). The ratio of radical to ionic activity (F/I) is thus estimated according to the following formula:

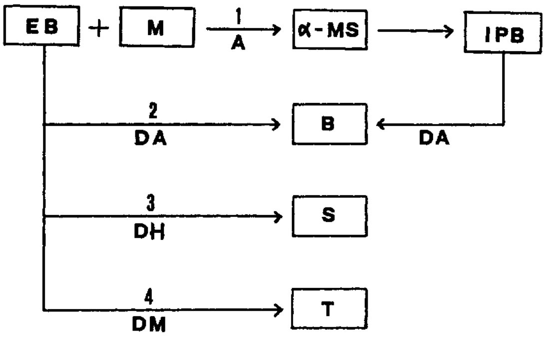

Fig. 2. The reaction network for the methylation of ethylbenzene over KX at 500°C. A, alkylation; DA, dealkylation; DH, dehydrogenation; DM, demethylation.

$$\frac{F}{I}=\frac{(\mathrm{T})+(\mathrm{S})}{(\alpha\text{-MS})+(\mathrm{IPB})+(\mathrm{B})},$$

where (B), (T) and (S) are the moles of benzene, toluene and styrene, respectively. Such value increases with increasing contact time (fig. 1).

3.3. EFFECT OF REACTION TEMPERATURE

Table 2 indicates the influence of reaction temperature on the reaction over KX. As the temperature was increased, the conversion and the yield of products also increased, especially apparent in the yields of toluene and styrene, which resulted in the corresponding increase of the F/I value. These results exhibit the typical trend of favorable radical mechanism at higher temperature [14].

Table 2
The effect of reaction temperature on the reaction over KX. EB/M = 3; $W/F = 36.3$ g h mol^{-1}; time-on-stream 20 min

	Temperature (°C)			
	400	425	450	500
conversion (mol%)	0.72	0.97	2.00	11.73
yield (mol%)				
benzene	0.01	0.03	0.07	0.63
toluene	0.07	0.14	0.68	7.61
styrene	0.01	0.04	0.26	1.30
α-methylstyrene	0.18	0.10	0.17	0.44
isopropylbenzene	0.30	0.48	0.72	1.50
others	0.15	0.18	0.10	0.25
F/I	0.16	0.30	0.98	3.47

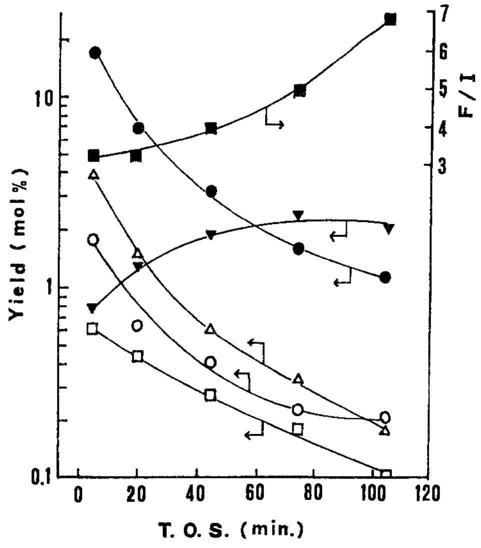

Fig. 3. Effect of time-on-stream on the product yield. Conditions and symbols: the same as in fig. 1 except W/F 36.3 g h mol^{-1}.

3.4. EFFECT OF TIME-ON-STREAM

Fig. 3 shows the effect of time-on-stream on the product yield from the reaction over KX at 500°C. The yields of all products except that of styrene decrease with increased time-on-stream, indicating the promotion of dehydrogenation activity possibly due to coke formation as reported elsewhere [17]. The F/I value increases with increasing time-on-stream as shown in this figure.

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