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The role of acid strength of zeolites in liquid-phase alkylation of benzene with ethylene

Xinde Sun, Qingxia Wang, Longya Xu*, and Shenglin Liu

State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian P.O. Box 110, 116023, PR China

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The role of acid strength of zeolites in liquid-phase alkylation of benzene with ethylene was studied over β, MCM-22, and USY zeolites by means of adsorbing NH_3 at different temperatures. The strong acid sites are active centers, while the weak acid sites are inactive. The selectivity behavior of the strong acid sites varies with the relative acid strength as well as the types of the zeolites.

KEY WORDS: alkylation; ethylbenzene; zeolite β; MCM-22; USY; acid strength.

1. Introduction

The alkylation of benzene with ethylene to produce ethylbenzene (EB) is a well-established process in the petrochemical industry. Over 90% of EB in the world is used for the manufacture of styrene. The alkylation has conventionally been catalyzed by $AlCl_3$-based catalysts, which give rise to many problems concerning the handling, safety, corrosion, and waste disposal of the catalysts [1,2]. In order to avoid these problems, many efforts have been devoted to the search of zeolite-based catalysts instead of the $AlCl_3$-based catalysts. Since 1976 the medium-pore zeolite ZSM-5 has been used in the Mobil-Badger process for the vapor-phase alkylation of benzene with ethylene [3]. In the 1990s, the liquid-phase alkylation process was introduced by Lummus/Unocal/UOP/ using catalysts based on Y or β-type zeolites, and Mobil-Raytheon using catalysts based on MCM-22 zeolites [1].

Perego and co-workers [4,5] investigated the catalytic behaviors of β zeolites with varying SiO_2/Al_2O_3 ratios in the liquid-phase alkylation of benzene with ethylene. The results indicate that by decreasing the framework Al content in the synthesis process or through partial substitution of Al by B, it resulted in a decrease in both the ethylene conversion and selectivity in EB production. Similar conclusion was obtained in the case of MCM-22 catalyst [6].

In the present work, we have investigated the catalytic behaviors of liquid-phase alkylation of benzene with ethylene on β, MCM-22, and USY zeolites by adsorbing NH_3 at different temperatures. In addition, the catalytic performances on β zeolites with different particle size were investigated.

2. Experimental

The β zeolites ($SiO_2/Al_2O_3 = 24.2$, 24.5 and 27.6) and MCM-22 ($SiO_2/Al_2O_3 = 23.2$) were synthesized according to references [7] and [8] respectively. USY ($SiO_2/Al_2O_3 = 5.28$) was provided by the Chinese Wenzhou Huahua Group. The particle size of the β zeolites was determined by transmission electron microscope (instrument model JEM 2000 EX). The zeolites used γ-alumina as the binder in a weight ratio of 70 : 30 (zeolite: γ-alumina), and formed into Φ1.6 mm catalyst extrudates. After burning off the template in a muffle furnace at 813 K for 3 h and ammonium ion exchanging, the catalysts were crushed and sieved into 0.62–1.25 mm particles and calcined in the muffle furnace at 803 K for 2 h to obtain the H-type zeolites.

Alkylation of benzene with ethylene was performed in an up-flow fixed-bed stainless steel tubular microreactor of 15 mm i.d., equipped with a 4 mm o.d. axial thermowell and heated by a two-zone electrical furnace. 1 g of catalyst, diluted with 5 mL SiO_2 of the same size, was loaded into the reactor and activated in a N_2 flow (purity >99.999%, 90 mL min^{-1}) at 823 K for 1 h. Then the sample was cooled to the reaction temperature in a N_2 flow. As the reaction temperature reached 443 K, N_2 was introduced to increase the pressure to about 1 MPa. Subsequently, benzene was fed at 800 mL min^{-1} until the reaction zone was filled up with benzene. As soon as the benzene flow was adjusted to the desired value, and the desired pressure (3.5 MPa) was reached, the ethylene feed was passed through the reactor *via* a gas mass flow controller. The reaction conditions were as follows: pressure, 3.5 MPa; temperature, 443 K; WHSV, 2.0 h^{-1} (referred to ethylene); benzene/ethylene, 1/12 (molar ratio). Under these conditions the reaction took place in the liquid phase.

For NH_3 adsorption of the catalysts, 1 g of the sample, diluted with 5 mL SiO_2 of the same size, was

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* To whom correspondence should be addressed.
E-mail: lyxu@dicp.ac.cn

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activated under a N_2 flowing at 823 K for 1 h in a 15 mm i.d. quartz tube to avoid NH_3 pollution to the reactor. As the catalyst was cooled to the desired temperatures such as 423 or 523 K, 40-mL NH_3 (purity > 99.999%) was slowly injected into the catalyst sample for 5 min. After purged for 0.8 h in a N_2 flow, the sample was quickly transferred into the reactor to perform directly the alkylation reaction as described above.

The gaseous reaction effluents were analyzed by a Model GC-8A Shimadzu GC equipped with a TCD detector and a Poropak QS packed column (2 m long and 3 mm i.d.), while the liquid effluents were analyzed by an Agilent 4890D GC equipped with a FID detector and a CEC-5 capillary column (50 m long and 0.32 mm i.d.). The product selectivities were based on ethylene.

NH_3-temperature-programmed desorption (TPD) was performed on a conventional setup equipped with a TCD detector. 0.14 g of the sample was first flushed with He (30 mL min^{-1}) at 823 K for 1 h, then cooled to the desired temperatures such as 423 or 523 K, and saturated with NH_3 until equilibrium was reached. Subsequently, the sample was cooled to 423 K under a flow of He. When the baseline was stable, NH_3-TPD was conducted from 423 to 873 K at 20 K min^{-1}.

3. Results and discussion

3.1. Influence of particle size on the catalytic behavior of zeolite β for the alkylation of benzene with ethylene

Figure 1 shows the alkylation activities over β zeolite samples by changing the particle size. The ethylene conversion was reduced when the mean particle diameter was changed from 0.15 μm ($SiO_2/Al_2O_3 = 24.2$) to 0.27 μm ($SiO_2/Al_2O_3 = 24.5$), due to the influence of intra-crystal diffusion. This is in accord with the results obtained by other authors for the same reaction in a batch-wise operation [4,5] as well as in the study of mass-transfer [9]. In addition, the stability of catalytic activity decreased with the increase of the particle size, implying that the particle size affects the stability of Hβ catalysts in the liquid-phase alkylation of benzene with ethylene. This can be ascribed to an easier diffusion of the heavy products from the channels of smaller zeolite particles to the liquid bulk phase. And from the point of difference in intra-crystal diffusion resistance, we can explain why less by-products were formed at nearly the same ethylene conversion over the β zeolite with smaller particle size, as shown in table 1. The ethylation selectivities kept the same level (99.79% and 99.73% for 0.15 and 0.27-μm β zeolite respectively) on the same sample with time on stream went on, while high selectivity to C_{10-14} aromatics and low selectivity to diphenylethane and heavy residue were observed at low ethylene conversion.

3.2. Catalytic behavior of β zeolite partially poisoned by adsorbed NH_3

Figure 2 shows the NH_3-TPD profiles of the Hβ catalysts at different NH_3 adsorption temperatures. The profile for NH_3 adsorption at 423 K shows a main desorption peak at about 530 K and a tail peak at about 700 K, corresponding to the situation in which all the acid sites are occupied by NH_3 [10–12]. It is well known that the strength of the acid sites on solid acids, including zeolites, is not uniform. When NH_3 is adsorbed on an acid catalyst at an elevated temperature, it will only be taken up by the stronger acid sites. The NH_3-TPD profiles in figure 2 are consistent with this point of view. The average strength of the active acid sites (strong acid sites) which are accessible to the

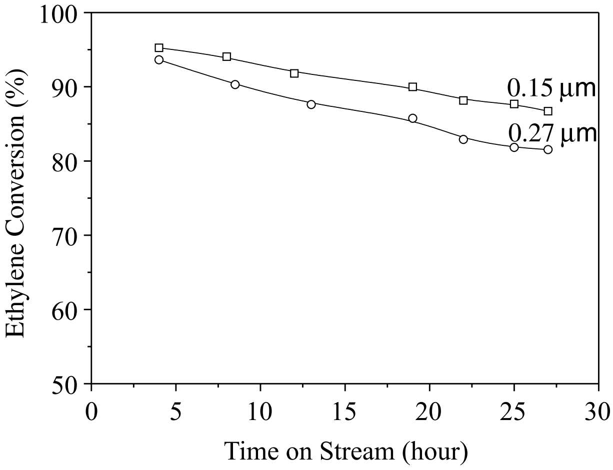

Figure 1. Influence of zeolite Hβ particle size on benzene alkylation with ethylene. $T = 443$ K, $P = 3.5$ MPa, ethylene WHSV = 2.0 h^{-1}, benzene/ethylene = 12 mol ratio.

Table 1
Influence of Hβ particle size on alkylation selectivity of benzene with ethylene

Particle size, μm	0.15	0.27
Time on stream, h	27	19
Ethylene conversion, %	86.72	85.76
Product selectivity, mol%		
Ethylbenzene	92.04	92.04
Diethylbenzene	7.46	7.39
Triethylbenzene	0.29	0.29
Tetraethylbenzene	0.009	0.010
Σ (Ethylation selectivity)	99.81	99.73
C_9 Aromatics	0.006	0.018
C_{10} Aromatics (exclude DEB)	0.094	0.119
C_{11-14} Aromatics (exclude PEB)	0.050	0.083
Diphenylethane	0.019	0.017
Heavy residue	0.017	0.023
Σ (By-product selectivity)	0.19	0.27

$T = 443$ K, $P = 3.5$ MPa, ethylene WHSV = 2.0 h^{-1}, benzene/ethylene = 12 mol ratio, Tos = 2 h

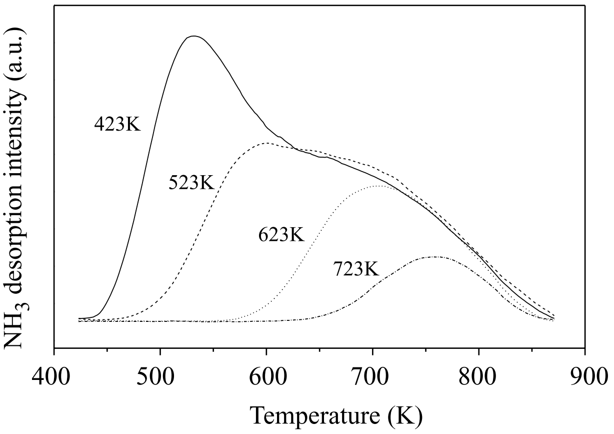

Figure 2. NH_3-TPD profiles of the Hβ zeolite at different NH_3 adsorption temperatures.

reactants, that is, remaining in the H-form, follows a sequence of: Hβ > Hβ with NH_3 adsorbed at 723 K > Hβ with NH_3 adsorbed at 623 K.

In this paper, we refer to the acid sites corresponding the low/high temperature NH_3 desorption peaks as the weak/strong acid sites. When NH_3 was adsorbed by the sample at 523 K, the NH_3 desorption peak in the low temperature range (below 625 K) was much lower than that at 423 K. This shows that the strong acid sites are completely covered with NH_3, while a part of the weak acid sites are free from NH_3 adsorption. When the NH_3 adsorption temperature was increased to 623 K, nearly all the weak acid sites and a part of the strong acid sites were exposed. In the case of NH_3 adsorption at 723 K, only a small fraction of the strong acid sites were occupied by NH_3.

Our results indicated that the NH_4-type zeolites of β, MCM-22, and USY were inactive for the alkylation of benzene with ethylene. Thus, it will allow us to get a better understanding on the different roles of their acid sites with different strength in alkylation by makes a part of the acid sites to be poisoned by NH_3, while the other acid sites are remaining in the H-form.

The catalytic behaviors in benzene alkylation with ethylene over the Hβ and the Hβ adsorbed with NH_3 at different temperatures are shown in table 2. Almost no reaction occurred over the Hβ catalyst with NH_3 adsorbed at 523 K, in which all the strong acid sites were occupied by NH_3, accompanied with quite a number of the weak acid sites remaining in the H-form, as shown in figure 2. This indicates that the weak acid sites are inactive for the alkylation of benzene with ethylene. The ethylene conversion increased rapidly to 44.15% and 70.46%, respectively, when the NH_3 adsorption temperature was raised to 623 and 723 K, which implies that the amount of the exposed strong acid sites was increased. And on Hβ adsorbing no NH_3 whose amount of strong acid sites was the most exhibited the highest ethylene conversion (88.75%). This clearly shows that the strong acid sites are active centers for the alkylation reaction on Hβ, while the contribution of the weak acid sites is negligible.

Table 2
Benzene Alkylation with ethylene on zeolite β adsorbing NH_3 at different temperatures

NH_3 adsorbing temperature, K	523	623	723	/[a]
Ethylene conversion, %	< 1	44.15	70.46	88.75
Product selectivity, mol%				
Ethylbenzene		93.03	90.17	89.23
Diethylbenzene		5.63	8.94	9.88
Triethylbenzene		0.21	0.39	0.51
Tetraethylbenzene		0.013	0.028	0.029
Σ (Ethylation selectivity)		98.88	99.55	99.65
C_9 Aromatics		0.025	0.026	0.026
C_{10} Aromatics (exclude DEB)		0.407	0.261	0.203
C_{11-14} Aromatics (exclude PEB)		0.163	0.047	0.038
Diphenylethane		0.036	0.039	0.039
Heavy residue		0.488	0.046	0.043
Σ (By-product selectivity)		1.12	0.45	0.35

T = 443 K, P = 3.5 MPa, ethylene WHSV = 2.0 h^{-1}, benzene/ethylene = 12 mol ratio, Tos = 2.5 h.
[a] No NH_3 was adsorbed.

With the increase in the average acid strength, the increasing of the EB selectivity and the decreasing of the selectivities towards DEB (diethylbenzene), TEB (triethylbenzene) and TetraEB (tetraethylbenzene) can be ascribed to the decreasing of the ethylene conversion. Moreover, the decreasing of the ethylene conversion will lead to the increasing of the by-products formed by oligomerization, cracking, isomerization, and alkylation of ethylene, owing to increasing of mean ethylene concentration in the reaction mixtures [2,13]. But the total byproducts formation changes very little as discussed in section 3.1. Over the Hβ sample with weaker average acid strength (adsorbing NH_3 at 623 K), much high selectivities to C_{11-14} aromatics and heavy residues was obtained. This indicates that the weaker part of the strong acid sites on the Hβ zeolite produces more C_{11-14} aromatics and heavy residues than the stronger part. No apparent relationship between the hydride transferring activity and the acid strength of the Hβ zeolite could be observed, as the formation of diphenylethane was in the same level. According to the above results, we can conclude that the acid strength of the zeolites affects not only the ethylene conversion, but also the selectivity to target products.

3.3. *Catalytic behaviors of MCM-22 and USY zeolites partially poisoned by adsorbed NH_3*

Table 3 shows the catalytic behaviors of benzene alkylation with ethylene over MCM-22 and USY zeolites, either with adsorbed NH_3 or not. The ethylene conversion of MCM-22 was the lowest among the three zeolites, as shown in tables 2 and 3. It was reported that

Table 3
Comparison of product selectivity for MCM-22 and USY catalysts[a]

	MCM-22		USY		
NH_3 adsorbing temperature, K	723	/[b]	623	723	/[b]
Ethylene conversion, %	17.70	25.46	17.62	38.67	54.86
Product selectivity, mol%					
Ethylbenzene	89.75	95.49	82.38	79.20	74.20
Diethylbenzene	1.75	3.20	5.85	7.77	10.69
Triethylbenzene	0.09	0.12	0.76	1.20	2.40
Tetraethylbenzene	0.025	0.014	0.13	0.20	0.50
Σ (Ethylation selectivity)	91.61	98.82	89.12	88.37	87.80
C_9 Aromatics	0.932	0.081	0.44	0.48	0.58
C_{10} Aromatics (exclude DEB)	3.047	0.496	2.98	3.12	3.10
C_{11-14} Aromatics (exclude PEB)	4.187	0.536	6.94	7.41	7.17
Diphenylethane	0.076	0.018	0.14	0.16	0.32
Heavy residue	0.147	0.047	0.34	0.45	0.62
Σ (By-product selectivity)	8.39	1.18	10.88	11.63	12.20

T = 443 K, P = 3.5 MPa, ethylene WHSV = 2.0 h^{-1}, benzene/ethylene = 12 mol ratio, Tos = 2.5 h.

[a] MCM-22 adsorbing NH_3 at 523, 623 K and USY adsorbing NH_3 at 523 K present ethylene conversion less than 1%.

[b] No NH_3 was adsorbed.

a very large decrease in the alkylation activity of MCM-22 was observed due to the neutralization of the most external acid sites by the bulky 2,6-di-tert-butylpyridine, which implied that only acid sites located in the surface "pockets" of MCM-22 were involved in the reaction [13]. Thus, the activity of the acid sites on MCM-22 which are involved in the alkylation is much higher than that as judged from the ethylene conversions in table 3.

Figure 3 shows the NH_3-TPD profiles of the MCM-22 catalyst at different NH_3 adsorption temperatures. When the MCM-22 zeolite adsorbed NH_3 at 523 or 623 K, nearly all the strong acid sites were occupied by NH_3, except a part of the weak acid sites were still exposed. Almost no activity for the alkylation reaction can be recorded on the samples mentioned above, while the zeolite adsorbing NH_3 at 723 K with a part of the strong acid sites free from NH_3 coverage exhibited 17.7% ethylene conversion, which was lower than that of the catalyst adsorbing no NH_3, i.e., all the strong acid sites were free from NH_3 adsorption, as shown in table 3 and figure 3. This gives us a similar conclusion as that of the Hβ zeolite, and confirms that the strong acid sites are the active centers for the alkylation reaction, while the contribution of the weak acid sites is negligible.

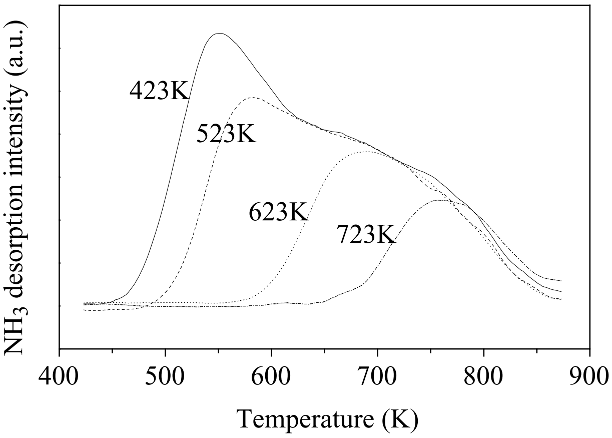

Figure 3. NH_3-TPD profiles of the MCM-22 zeolite at different NH_3 adsorption temperatures.

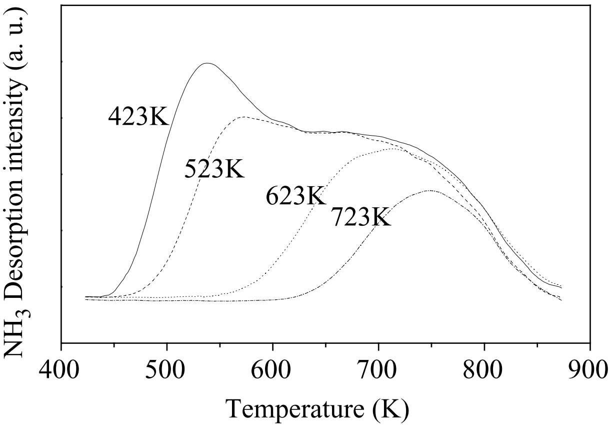

Figure 4. NH_3-TPD profiles of the USY zeolite at different NH_3 adsorption temperatures.

By correlating the catalyst acid strength with the reaction performance, the same conclusion can be drawn concerning the USY zeolite, as shown in figure 4 and table 3. The activity for alkylation of benzene with ethylene over the USY adsorbed with NH_3 at 523 K is negligible. With NH_3 adsorbing temperature rising and amount of H-type strong acid sites increasing, the ethylene conversion increases rapidly to 54.86% over USY adsorbing no NH_3.

Similarly, the acid strength of the MCM-22 zeolite affects not only the ethylene conversion, but also the target products. The average acid strength of the MCM-22 zeolite adsorbing NH_3 at 723 K was weaker than that of the catalyst which did not adsorb NH_3, as shown in figure 3. The data in table 3 shows that among the strong acid sites, the weaker ones present lower selectivity to the target products (EB and polyethylbenzene), and produce much more by-products, including either alkyl benzene via oligomerization, cracking, isomerization, and alkylation of ethylene, or diphenylethane *via* hydride transferring. As for the USY zeolite, no obvious difference in product distribution was observed over the samples with different average acid strengths, and this was different from the β and MCM-22 zeolites.

4. Conclusions

For β, MCM-22, and USY zeolites, the strong acid sites, which correspond to the high temperature peaks of their NH_3-TPD profiles, are active centers for the alkylation of benzene with ethylene, while the weak acid sites which correspond to the low temperature peaks of their NH_3-TPD profiles are inactive sites. The catalytic behaviors of the strong acid sites vary with the relative acid strength as well as with different zeolites. The particle size of the β zeolite affects the catalytic activity, product selectivity, and stability of the liquid-phase alkylation of benzene with ethylene.

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