

# ETHYLATION OF TOLUENE ON HZSM-5 ZEOLITES PREPARED WITHOUT ORGANIC COMPOUNDS

XU QINHUA, Zhu Jianhua

Department of Chemistry, Nanjing University, Nanjing, China

## ABSTRACT

NK-HZSM-5 (Samples obtained from Nankai University, China) used in this paper were prepared without any organic compound. The ethylation of toluene has been compared over NK-HZSM-5 exchanged with HCl (NK-1) or  $\text{NH}_4\text{NO}_3$  (NK-2). The factors of increasing the para-selectivity over the sample NK-2 were investigated, including modification of the samples with steam treatment and selective poisoning by 4-methyl-quinoline, and reaction conditions of different temperatures and WHSV of feeds. High para-selectivity in modified samples has been thus achieved. The treatment of modification is considered to have the effects of poisoning the surface acid sites or reducing the pore dimensions. Both these effects determine the product distribution of ethyltoluene. The suppression of external surface strong acid sites is found to be more important than the reduction of pore dimensions.

## INTRODUCTION

The alkylation of toluene with ethylene is the determining step in the process of producing poly-para-methylstyrene, which is a new kind of improved polymer with properties superior to polystyrene.<sup>(1)</sup> High para-selectivity of ethyltoluene has been obtained by Mobil Company utilizing modified ZSM-5 zeolite catalysts.<sup>(2-6)</sup>

The alkylation of toluene over ZSM-5 catalysts in high para-selectivity has been reported by several papers.<sup>(7-12)</sup> But they have divergent views on the factors of enhancing para-selectivity.

Instead of ZSM-5 synthesized generally with organic compounds, we used NK-ZSM-5 zeolites prepared without any ammonium, alcohols, amines, quaternary ammonium salts or other organic compounds, to study the shape-selective catalysis of ethylation of toluene and to

examine the main factors of enhancing para-selectivity of ethyltoluene.

## EXPERIMENTAL

Samples. Samples NK-HZSM-5 were obtained by the conventional ion exchange method with aqueous solution of HCl (named NK-1) and with solution of  $\text{NH}_4\text{NO}_3$  (NK-2) for six times. The samples obtained were characterized by X-ray diffraction pattern, and found to be consistent with those of literature.<sup>(13)</sup> Their unit cell compositions were listed in Table 1.

Table 1  
The unit cell compositions of NK-HZSM-5 samples

Samples	$\text{SiO}_2/\text{Al}_2\text{O}_3$ mole%	Unit cell composition
NK-1	45.16	$\text{Na}_{0.04}\text{H}_{4.03}\text{Al}_{4.07}\text{Si}_{91.9}^{0192}$
NK-2	43.61	$\text{Na}_{0.04}\text{H}_{4.17}\text{Al}_{4.21}\text{Si}_{91.8}^{0192}$

Methods. The activity of catalysts was measured with a fixed-bed continuous-flow microreactor at the temperature of  $350^\circ\text{C}$  and atmospheric pressure. All the catalysts were tableted without binder.

The adsorption experiments were made by the gravimetric method and the acidities were measured chromatographically.<sup>(14)</sup>

## RESULTS AND DISCUSSION

Evaluation of the catalytic properties. Alkylation of toluene with ethylene to produce ethyltoluene was carried out, in the presence of the catalysts of NK-1 and NK-2 respectively, at temperature of  $350^\circ\text{C}$  and atmospheric pressure. The experiments were made in the presence of hydrogen utilizing a weight hourly space velocity to toluene/ethylene = 1/0.3. The results are listed in Table 2. It is found that the catalytic activity (conversion of toluene, mole%) of NK-1 is greater than that of NK-2, but the selectivity of para-ethyltoluene (mole%) is in reverse order.

The relation between catalytic activity and reaction temperature is shown in Figure 1. From Figure 1 we can see that the sample NK-1 has higher activity above  $300^\circ\text{C}$  than NK-2.

Table 2  
Comparison of the catalytic properties

Samples	Alkylation		Dealkylation	Isomerization
	conversion mole%	p-selectivity mole%	conversion mole%	conversion mole%
NK-1	42.1	43.9	16.9	45.8
NK-2	28.2	54.2	54.0	27.4

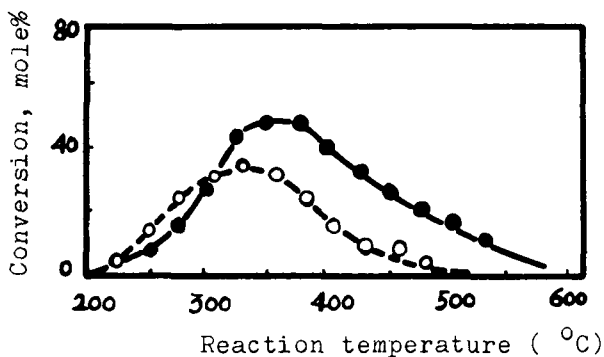


Fig. 1. The relation between activity and reaction temperature for the ethylation of toluene  
 —●—●— NK-1      --o--o-- NK-2

To determine the difference of these two samples in catalytic properties, we investigated the dealkylation of ethyltoluene and isomerization of p-ethyltoluene (the feed containing 88 mole% of p-ethyltoluene and 12 mole% of m-ethyltoluene). The results are also listed in Table 2, which shows that the activity of isomerization over NK-1 is greater than that of NK-2. According to Jacobs<sup>(5)</sup> and Verdrine<sup>(6)</sup>, the isomerization reaction requires stronger acid sites than the alkylation and dealkylation reactions. Therefore, there are more the numbers of strong acid sites on the external surface of NK-1. Our experimental results also support this point of view. The acid strength distribution for these samples was determined. The results show that the numbers of acid sites are almost the same, but the amount of strong acid sites of NK-1 is higher than that of NK-2.

The adsorptive rate of m-xylene on NK-1 and NK-2 samples was determined at the temperature of 120°C, the vapor pressure of adsorbate being maintained at 1mmHg. The amounts of adsorption in 10 mins. on these two samples are 8.2 mg/g and 6.0 mg/g respectively. This

demonstrates that the adsorption rate on NK-2 is smaller, and hence its pore size may be smaller too. Thus, the effect of the shape and size of pore on the primary intracrystalline isomer distribution is considerably important. Therefore, we suggest that the higher para-selectivity of NK-2 may be attributed to its favorable pore size and acid strength distribution on the external surface.

Factors of influence on catalytic properties. We further investigated the factors of enhancing the para-selectivity over the sample NK-2.

1. Steam treatment. The sample NK-2 was subjected to steam treatment for two hours at a flowing rate of  $2 \text{ cm}^3/\text{g}, \text{h}$  under a temperature of  $600^\circ\text{C}$ . The catalytic activity obtained from the sample after steam treatment was slightly decreased while their para-selectivity increased obviously. The data is listed in Table 3.

Table 3

The catalytic activity and selectivity of NK-2 after steam treatment

Samples	Conversion, mole%	Para-selectivity, mole%
before treatment	28.2	54.2
after treatment	26.2	73.0

2. The ratio of WHSV of toluene/ethylene. The influence of WHSV on the activity and selectivity of the ethylation of toluene was studied. The para-selectivity was plotted against the conversion of toluene under different WHSV, giving a good linear relationship between them, over the sample of NK-2 as shown in Figure 2. The results also show that the conversion of toluene was decreased while para-selectivity was increased with the increase of the ratio of WHSV.

3. Reaction temperature. We have measured the activity of dealkylation of toluene at different temperatures.

The relation of dealkylation conversion to reaction temperature is shown in Figure 3, which shows that the extent of dealkylation rose sharply after  $300^\circ\text{C}$ . The reactivity of ethylation of toluene over NK-2 was measured at different temperatures, shown in Figure 4. From Figure 4 it can be seen that there is a maximum in the conversion curve at a temperature of  $325^\circ\text{C}$ . It shows clearly that the decrease of activity above  $325^\circ\text{C}$  is caused by the fact that the reaction of dealkylation of ethyltoluene is now dominating.

In Figure 4, the para-selectivity lowered at first with the

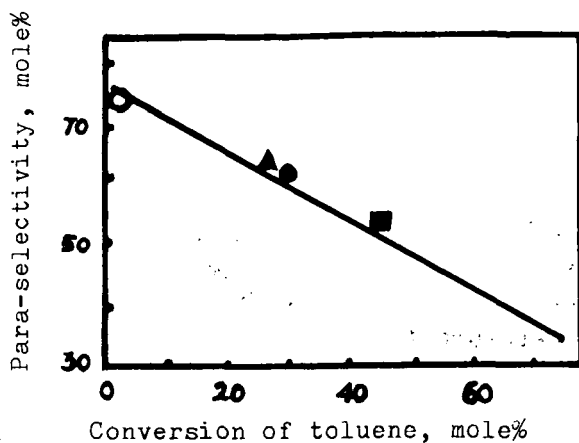


Fig. 2. The influence of ratio of WHSV of toluene/ ethylene, the ratio of WHSV of toluene/ ethylene:

○ 5/0.3, ▲ 5/1, ● 1/0.3, ■ 2/0.7

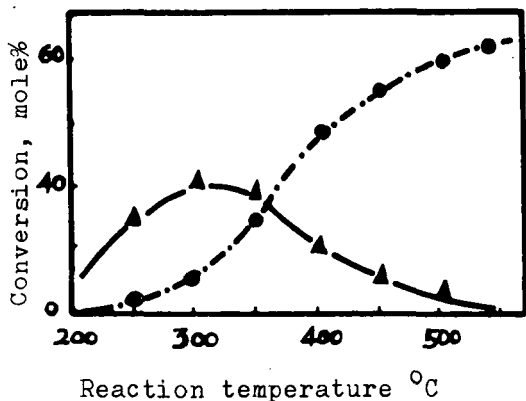


Fig. 3. The relation of activity to reaction temperature

---●--- dealkylation  
 ---▲--- isomerization

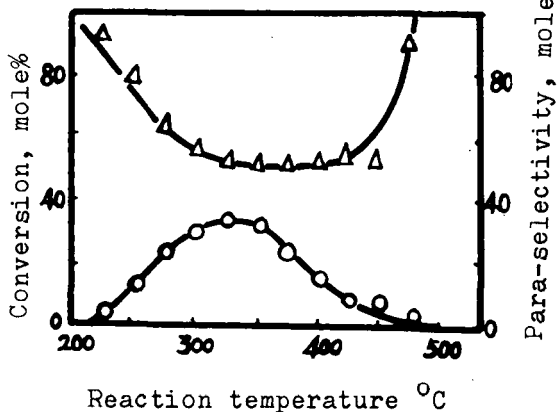


Fig. 4. The relation of reactivity to reaction temperature

increase of the temperature, reaching a lowest level and then going up again. Figures 3 and 4 indicate that the isomerization activity of p-ethyltoluene has the opposite tendency to the para-selectivity of alkylation of toluene with temperature.

4. Modification. To examine the factors controlling the increase of para-selectivity, sample NK-2 was modified with steam treatment as previously described and with selective poisoning by

4-methyl-quinoline respectively.

The adsorption rates were determined on modified samples under the same conditions as described above. The results are shown in Figure 5 and listed in Table 4.

From Table 4 we can see that the adsorption rate of *m*-xylene on the NK-2 modified with steam treatment drops sharply. It implies that a reduction in effective pore size occurred on the pore openings, which could favor outward diffusion of the para-isomer relative to meta and ortho. Therefore the para-selectivity of ethylation of toluene was increased by 10 units. However, the adsorption rate of *m*-xylene on the sample modified with selective poisoning was almost unchanged. It means that no change occurred in the pore size

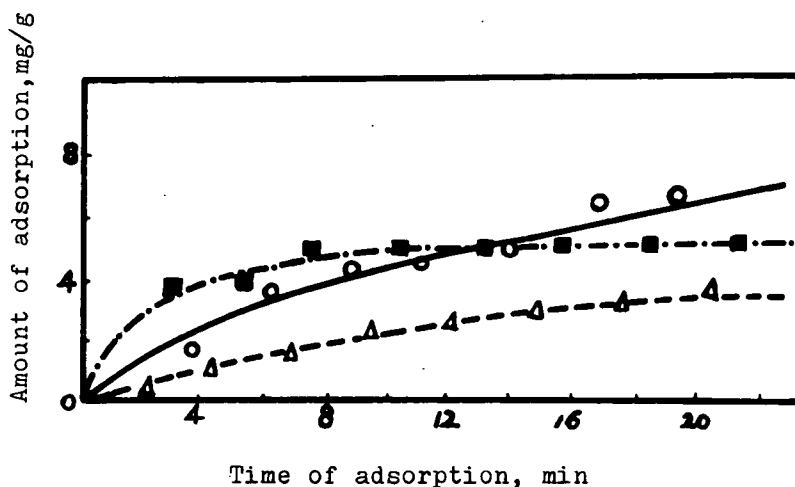


Fig. 5. The adsorption rate on the samples with different treatment

- without treatment
- with selective poisoning
- △---△--- with steam treatment

of the zeolite, but the para-selectivity of this sample was increased by 27 units. It further demonstrates that among the factors of enhancing para-selectivity, the effects of acidity are more important than those of the shape and size of the pore. The strong acid sites on the external surface were reduced by 4-methyl-quinoline, which inhibited the surface isomerization, and consequently the para-selectivity was raised.

The increment of para-selectivity and the decrement of iso-

Table 4

The adsorption rate and para-selectivity of alkylation on the modified samples

Samples	Amount of adsorption of m-xylene in 10 minutes at 120°C, mg/g	Para-selectivity (ratio of WHSV of toluene/ethylene = 7/0.5) at 350°C, mole%
NK-2 without treatment	4.8	71.2
NK-2 modified with steam treatment	2.2	81.0
NK-2 modified with selective poisoning	4.6	98.2

merization activity were almost the same with the amount of 4-methylquinoline, as shown in Figure 6. This experiment gives further evidence that high para-selectivity of ethylation of toluene should be attributed mainly to the acidity on the external surface of the catalysts.

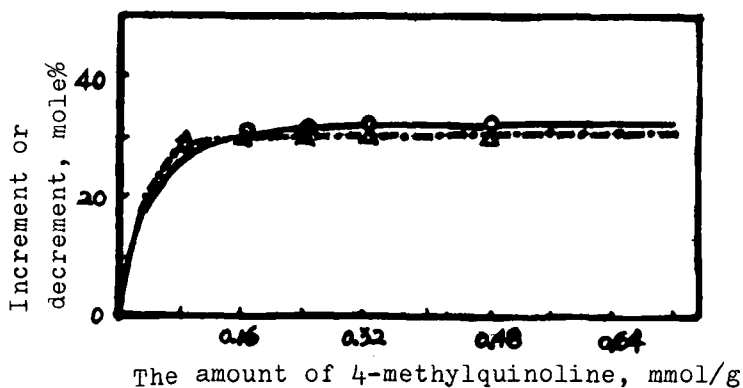


Fig. 6. The increment of para-selectivity ( $\Delta$ ) and the decrement of isomerization activity ( $\circ$ ) with the amount of 4-methylquinoline

## REFERENCES

1. Kaeding, W.W., Young, L.B. and Prapas, A.G., CHEMTECH 556 (1982).
2. Kaeding, W.W., U.S.P. 4, 117, 024 (1978).
3. Kaeding, W.W. and Young, L.B., U.S.P. 4, 094, 921 (1978).
4. Kaeding, W.W. and Young, L.B., U.S.P. 4, 143, 084 (1979).
5. Kaeding, W.W., U.S.P. 4, 128, 592 (1978).
6. Chu, C.C., U.S.P. 4, 420, 418 (1983).
7. Kaeding, W.W., Chu, C.C., Young, L.B., Weinstein, B. and Butter, S.A., Journal of Catalysis, 67, 159 (1981).
8. Young, L.B., Butter, S.A. and Kaeding, W.W., Journal of Catalysis, 76, 418 (1982).
9. Bhat, S.G.T., Journal of Catalysis, 75, 196 (1982).
10. Nunan, J., Cronin, J., and Cunningham, J., Journal of Catalysis, 87, 77 (1984).
11. Yashima, T., Sakaguchi, Y. and Namba, S., in Proc. 7th Inter. Congress Catal., Tykyo (1980).
12. Kaeding, W.W., Young, L.B. and Chu, C.C., Journal of Catalysis, 269 (1984).
13. Argauer, R.J. and Landolt, R.G., U.S.P. 3, 702, 886 (1972).
14. Misono, M., Saito, Y., Yoneda, Y., Third Inter. Cong. Catal., (Amsterdam) 408 (1964).