Russian Journal of Applied Chemistry, Vol. 78, No. 11, 2005, pp. 1854–1858. Translated from Zhurnal Prikladnoi Khimii, Vol. 78, No. 11, 2005, pp. 1886–1890. Original Russian Text Copyright © 2005 by Agaeva, Dadashev, Tagiev, Abasov.

= CATALYSIS =

# Increase in Selectivity of Toluene Disproportionation and in *p*-Xylene Yield by Optimization of Zeolite Microporous Structure

S. B. Agaeva, B. A. Dadashev, D. B. Tagiev, and S. I. Abasov

Mamedaliev Institute of Petrochemical Processes, National Academy of Sciences of Azerbaijan, Baku, Azerbaijan

#### Received September 20, 2004

Abstract—The possibility of increasing the yield of target products and *para*-selectivity of toluene disproportionation on modified zeolites by optimization of their microporous structure was studied.

Benzene and xylenes (especially *p*-xylene) are widely used in industry. The main method of the synthesis of the above compounds is alkene dehydrocyclization. In the process, benzene (BZ) and xylenes (XLs) are formed together with large amounts of toluene (TL). Disproportionation of TL allows an increase in the production of BZ and XLs.

The TL disproportionation (TD) is an acid-type reaction and is catalyzed by H forms of zeolites [1, 2]. A study of TD on Y and M type zeolites and on pentasils showed that TD proceeds with the highest efficiency but with low selectivity on HY and on catalysts based on Y, with rapid deactivation of the catalysts. The catalysts based on mordenite are less active but more selective and stable than Y-based catalysts. The pentasil-based catalysts (ZSM-5) are less active but very selective and stable. They are also characterized by high selectivity for *p*-xylene (*p*-XL).

Thus, development of new zeolite catalysts of TD should involve either Y- and M-based zeolite catalysts or enhancing the activity of ZSM-5. Taking into account that mordenite catalysts are highly active, selective [3–5], have commercial application [6], and are more stable with respect to modification than Y, we believe that the synthesis of more selective and active M-based catalysts for TD is possible.

In this study, we examined the effects of modifying synthetic mordenite on the selectivity of TD and *p*-XL yield.

#### **EXPERIMENTAL**

Na-exchanged zeolites Y (Y), synthetic mordenite M (M), ZSM-5, and natural mordenite (NM) from Chananab deposit (Azerbaijan) were initial materials

for the catalyst synthesis. The samples were synthesized by decationization of the initial zeolites by ion exchange with 2 M NH<sub>4</sub>Cl followed by calcinations at 823 K and dealumination with 2.5 M HCl [7]. After these procedures, the SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio for M was determined by the method suggested in [8]. Then, the zeolites obtained were modified with a rare-earth element (REE) (Gd) by the ion-exchange procedure (0.5 mol % Gd<sub>2</sub>O<sub>3</sub>) and with a transition metal (Co) by ion-exchange impregnation (2.5 wt %). The modified zeolites were molded with a binding agent, alumina gel, taken in the amount of 25 g of Al<sub>2</sub>O<sub>3</sub> per 100 g of dry catalyst.

The catalytic conversion of TL was studied at atmospheric pressure in a flow-type catalytic apparatus equipped with an adiabatic reactor. Experiments were performed within the 673–748 K range at the space velocity of 1  $h^{-1}$  and H<sub>2</sub>/toluene ratio of 3.

The products of TL conversion were analyzed chromatographically on a capillary column ( $50 \times 0.25$  mm) coated with liquid-crystalline phase, methoxyethoxyazobenzene (T = 360 K; carrier gas argon).

Adsorption properties of the catalysts were studied gravimetrically on a vacuum device equipped with a McBain quartz balance. Benzene was used as an adsorbate. Experiments were performed at 293 K within the range of relative pressures  $p/p_0 0-0.3$ . Isotherms of benzene adsorption on zeolites used as catalysts are related to type I isotherms in accordance with Brunauer classification and are well described by the Dubinin–Radushkevich equation [9]

$$\ln a = \ln W_0 \rho - K [RT \ln (p_0/p)]^2,$$

where a is the amount of the adsorbate sorbed

| Catalyst,<br>Co/zeolite | SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> | <i>T</i> , K | Product composition,* wt % |      |      |      |      |     |      |     |  |
|-------------------------|--|--------------|----------------------------|------|------|------|------|-----|------|-----|--|
|                         |  |              | BZ                         | TL   | o-XL | m-XL | p-XL | EBZ | PMBZ | AN  |  |
| Co/HM <sub>10</sub>     | 10   | 673          | 18.2                       | 60.8 | 2.1  | 9.4  | 6.0  | 0.3 | 2.3  | 0.9 |  |
| $Co/HM_{25}^{10}$       | 25   |              | 21.3                       | 54.7 | 2.8  | 11.5 | 6.2  | 0.4 | 2.1  | 1.0 |  |
| $Co/HM_{30}^{20}$       | 30   |              | 22.3                       | 52.5 | 3.2  | 13.2 | 5.4  | 0.3 | 2.2  | 0.9 |  |
| $Co/HM_{10}^{30}$       | 10   | 723          | 20.9                       | 56.2 | 2.2  | 10.6 | 6.6  | 0.4 | 2.5  | 0.6 |  |
| $Co/HM_{25}^{10}$       | 25   |              | 22.4                       | 52.2 | 3.0  | 12.0 | 6.5  | 0.3 | 2.9  | 0.5 |  |
| $Co/HM_{30}^{20}$       | 30   |              | 23.7                       | 51.3 | 3.2  | 12.7 | 5.4  | 0.2 | 3.1  | 0.4 |  |
| Gd/HM <sub>25</sub>     | 25   | 723          | 22.7                       | 52.8 | 2.3  | 13.0 | 4.8  | 0.3 | 3.4  | 0.7 |  |
| GdCo/HM25               | 25   | 723          | 21.5                       | 54.0 | 2.8  | 6.7  | 11.2 | 0.4 | 2.9  | 0.5 |  |
| GdCo/HZŚM-5             | 61   | 748          | 19.5                       | 59.3 | 2.0  | 7.0  | 8.7  | 0.4 | 2.5  | 0.6 |  |
| GdCo/HNM                | 10   | 723          | 17.4                       | 65.0 | 4.0  | 7.6  | 4.3  | 0.2 | 1.0  | 0.5 |  |
| GdCo/HY                 | 5  | 673          | 24.1                       | 49.3 | 4.6  | 9.9  | 4.9  | 0.7 | 5.7  | 0.8 |  |

Table 1. Distribution of products of TL conversion on modified zeolite catalysts

\* (EBZ) Ethylbenzene, (PMBZ) polymethylbenzene, and (AN) alkanes C1-C2.

(mg g<sup>-1</sup>);  $\rho$ , adsorbate density (g cm<sup>-3</sup>); and  $W_0$ , the volume of adsorption area (cm<sup>3</sup> g<sup>-1</sup>), which is found by extrapolation of the isotherms obtained to  $p_0/p = 1$ .

In accordance with the theory of micropore volume filling TMVF [9], the parameter K related to the cross section of zeolite micropore inlets is calculated from the shapes of the Dubinin–Radushkevich isotherms obtained. The results listed in Table 1 show that BZ and XL are the main products of TD.

We also detected among the products ethylbenzene (EBZ), polymethylbenzene (PMBZ), and alkanes  $C_{1-}$ C<sub>2</sub> (AN). Formation and distribution of these products indicate that toluene transforms along different pathways. Large amounts of BZ and XL formed show that TD makes the prevalent contribution to TL transformations; other arenes and AN are formed by side reactions: XL disproportionation, realkylation, hydrodealkylation, etc., which are also acid-catalyzed reactions. As a result, the selectivity is an ambiguous quantity. For instance, when determining the selectivity for TD products found as the weight ratio of BZ + XL to converted TL, the fraction of benzene formed by TD and the conversion of TL are not quite clear because of the occurrence of XL disproportionation and hydrodemethylation, which is confirmed by the presence of the above-mentioned compounds among the conversion products. However, taking into account small amounts of trimethylbenzenes formed, whose participation in BZ and TL transalkylation is insignificant, we can consider the XL mole fraction in the product mixture as the initial value characterizing the TD selectivity.

Thus, the yields of toluene conversion products can be characterized by selectivities for target products, namely, for BZ and XL sum, and for TD. Taking also into account that *p*-XL is of particular significance among XLs [10], the selectivity for *p*-XL should be considered separately. The experimental yields of particular products are listed in Table 1, and quantities reflecting the selectivity for target products (BZ +  $\Sigma$  XL/TL conversion), for TD (molar ratio  $\Sigma$  XL/BZ), and for *p*-XL ( $\gamma = p$ -XL/ $\Sigma$  XL), in Table 2.

As follows from Table 2, the activity of cobalt– mordenite (CoM) catalysts weakly depends on the zeolite dealumination (5-8%). The same conclusion follows from the comparison of the selectivities of these catalysts. Such a behavior of Co-M systems is caused by the diffusion control of the TL conversion. This is confirmed by the independence of the catalyst activity in TD from temperature within the 673-748 K range. Hence, the TL conversion and product yields are, to a first approximation, limited by thermodynamic features of TL transformations and by the probable subsequent transformations of the molecules formed. The process control by diffusion of the reactant to active centers and of the reaction products from the reaction zone can be associated with molecular-sieve properties of zeolites. Such a dependence is known for H forms of the zeolites used [11].

It follows from Table 2 that the mole ratio of XL and BZ formed at 673 K is practically independent of the SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio in mordenite catalysts. As temperature is increased from 673 to 723 K,  $\beta = \Sigma XL/BZ$  corresponding to HM<sub>10</sub> and HM<sub>30</sub> samples decreases, whereas for HM<sub>25</sub> it remains constant. It is interesting that  $\gamma$  characterizing *para*-selectivity for all these samples remains unchanged. Thus, in TL conversion, the distribution of disproportionation products weakly

RUSSIAN JOURNAL OF APPLIED CHEMISTRY Vol. 78 No. 11 2005

| Parameter  | Co/HM <sub>10</sub>       |                           | Co/HM <sub>25</sub>       |                           | Co/HM <sub>30</sub>       |                           | Co/HM <sub>25</sub><br>(I) | Co/HM <sub>25</sub><br>(II) | НҮ                        | HZM                       | HNM                       |
|--|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|----------------------------|-----------------------------|---------------------------|---------------------------|---------------------------|
| $T, K$ $\alpha, * \%$ $S, ** \%$ $\beta = \Sigma XL/BZ, M$ | 673<br>39.2<br>91<br>0.71 | 723<br>43.8<br>92<br>0.68 | 673<br>45.3<br>92<br>0.71 | 723<br>47.8<br>92<br>0.71 | 673<br>47.5<br>93<br>0.72 | 723<br>48.7<br>92<br>0.66 | 723<br>47.2<br>92<br>0.71  | 723<br>46.0<br>92<br>0.82   | 673<br>50.7<br>86<br>0.59 | 748<br>40.7<br>91<br>0.67 | 748<br>35.0<br>95<br>0.67 |
| $\gamma = p - XL / \Sigma XL$                              | 0.34                      | 0.34<br>Ads               | 0.30                      | 0.30                      | 0.25<br>rs of D           | 0.25<br>Lubinin–R         | 0.24<br>adushkevich        | 0.54<br>equation            | 0.25                      | 0.49                      | 0.27                      |

Table 2. Adsorption and catalytic parameters of Co-containing zeolite catalysts of TD

0.0295

 $W_0$ , cm<sup>3</sup> g<sup>-1</sup>
 0.0747
 0.0903
 0.0895
 0.0995
 0.1005
 0.1650
 0.0786

0.0305

0.0250

\* (a) Toluene conversion. \*\* (S) Selectivity to BZ and XL.

0.0255

depends on the temperature. Modifying  $HM_{25}$  with REE [ $M_{25}(I)$ ] does not affect the TD selectivity. The TD selectivity increases by 10–11% only when  $HM_{25}$  is modified with Co and REE. At similar modifications of different zeolites, the TD selectivity depends on their nature (Table 2), similarly to unmodified zeolites [11]. These results demonstrate the influence of molecular-sieve properties of zeolites studied on the selectivity of TL conversion. However, whereas in the series of unmodified zeolites ZSM-5, HM, HY ZSM-5 is the most selective, after modifying with Co and REE the selectivity of this zeolite decreases and that of  $HM_{25}(II)$  increases. Then, the selectivity series becomes as follows:  $HM_{25}(II) > ZSM > HY$ .

The most substantial changes are observed for  $\gamma$ . As seen, the *p*-XL yield decreases with dealumination of the synthetic mordenite with other catalyst parameters remaining practically constant. Modifying of HM<sub>25</sub> with REE also decreases p-XL yield. The modifications performed do not affect the activity of M catalysts, but favor attaining equilibrium distribution of isomeric XLs in TD [12]. Taking into account that enrichment of TD products with the "narrowest" XL isomer (i.e., *p*-XL) is associated with a decrease in size of zeolite micropores [11], the above-mentioned decrease in  $\gamma$  in the series of M catalysts can be attributed to an increase in the cross section of micropore inlets. In this case, modification of HM25 with Co and REE simultaneously gives an opposite effect. Hence, the substantial increase in the selectivity for TD and *p*-XL is associated with a decrease in the inlet cross section in modified HM<sub>25</sub> as compared to the other HMs.

Table 2 allows comparison of the catalytic properties of zeolite samples in TL conversion in relation to the micropore inlet cross sections for various types of zeolites identically modified with Co and REE. It should be noted that, in the series HY,  $HM_{25}(II)$ , HZSM-5, and HNM, the cross sections of the inlets to wide micropores of zeolites decrease. The comparison of the catalytic properties of samples prepared from these zeolites shows that only their activity in TL conversion varies in the same order. The other catalytic parameters listed in Table 2, in contrast to [11], show different trends. Thus, modifying with Co and REE substantially promotes only  $HM_{25}$ .

0.0270

0.0310

0.0260

0.0210

Previously Gnep *et al.* [13] suggested to use the sensitivity of XL transformation to zeolite microporous structure for identification of the nonmodified zeolite type. As mentioned above, the major pathway of TL transformation is disproportionation complicated by the further transformations of XLs formed. Therefore, ambiguous influence of the modification on the selectivity of TL conversion may be due to changes in microporous structure of the zeolites considered.

To estimate the effect of modification on the zeolite microporous structure, we studied the adsorption properties of the TD catalysts synthesized for BZ. The isotherms measured are well described by the Dubinin–Radushkevich two-parameter adsorption equation. The values of parameters are listed in Table 2 and can be interpreted in terms of TMVF [9]. In accordance with these data, only within the range of SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratios from 10 to 25 the volume of adsorption space  $W_0$  noticeable changes, with an increase in the catalyst activity by 4%. The further dealumination of  $HM_{25}$  to  $SiO_2/Al_2O_3$  = 30 and modification with REE or REE + Co affects  $W_0$  insignificantly; however, it should be noted that the catalyst activities and  $W_0$  vary similarly. Such a sensitivity of TL conversion to  $W_0$  is an evidence of reactant interaction with active centers located in micropores. At the same time, whereas the selectivities *S* for the target products remains practically constant, i.e., independent of  $W_0$ , the HM<sub>25</sub>(II) sample, in contrast to the other catalysts of HM series, exhibits higher selectivity for TD. The elevated selectivity for TD of this sample cannot by the result of somewhat elevated  $W_0$ (Table 2).

In contrast to the quantities characterizing the selectivity of TD, the  $\beta$ - $\gamma$  selectivity for p-XL is more sensitive to modification. High sensitivity of  $\gamma$  to modification is attributable to substantial difference between the kinetic diameters of p-XL (0.66 nm) and o-XL and m-XL (0.76 nm) [14]. Taking into account closeness of the kinetic diameters of BZ, TL, and *p*-XL, we can suggest that the diffusion of the reactant to active centers and of products (*p*-XL and BZ) from the reaction zone follows the same relationships, whereas large kinetic diameters of o-XL and m-XL can complicate removal of these products from the reaction zone. Hence, the yield of products of TL transformations on zeolite catalysts depends on the cross section of zeolite micropore inlets. Also, apparently, depending on inlet cross sections, the cases are possible when the internal space of micropores is inaccessible to reactant (HNM), or, vice versa, o-XL and *m*-XL will freely escape from the reaction zone (zeolite of HY type).

Table 2 shows that modification of HMs affects the adsorption parameter *K*. This parameter, related to the diameter of zeolite micropore and channel inlets, increases with dealumination and decreases with introduction of REE. At the same time, introduction of Co into the sample containing REE increases *K*. However, in this case, *K* (0.027) is less than in the absence of REE (0.029). The comparison of the adsorption parameter *K* with the catalytic parameter  $\gamma$  shows that *K* corresponding to maximal  $\gamma$  has an intermediate value in the series of modified HMs studied. This indicates that there is some optimal diameter of micropore inlet, favoring selective TD and elevated yield of *p*-XL.

To comment upon this suggestion, let us consider the results of TL transformation on a series of catalysts prepared from various types of zeolites. In the series HY, HZSM, and HNM, the highest *para*-selectivity  $\gamma$  is shown by HZSM. At the same time, widepore zeolite HY ( $W_0 = 0.165 \text{ cm}^3 \text{ g}^{-1}$ ) and narrowpore HNM ( $W_0 = 0.021 \text{ cm}^3 \text{ g}^{-1}$ ) exhibit approximately equal *para*-selectivity. Obviously, in this case,



*para*-Selectivity of toluene transformation  $\gamma$  as a function of the parameter *K* of Dubinin–Radushkevich adsorption equation.

the above effect of the loss of molecular-sieve properties takes place because of o-XL and m-XL free diffusion from the reaction zone (for HY) or, vice versa, inaccessibility of the inner pore space to TL (for HNM). On the one hand, due to this effect the HY activity is the highest and that of HNM is the lowest. On the other hand, the *para*-selectivity of HNM is close to that of HY, and selectivity for TD, to that of HZSM. The above-mentioned coincidence of HNM an HZSM properties in TD and the difference in the behavior of the HY sample may be due to features of the subsequent XL transformations on these catalysts. As shown in [15–17], TD proceeds on HNM and HZSM in the surface layer and on HY, inside micropores.

In the series of catalysts prepared from various types of zeolites, an  $HM_{25}(II)$  sample stands out by higher selectivity in TD and p-XL formation, and in the activity it is inferior only to HY. In view of the above reasonings, high activity of this sample can be associated with accessibility of the inner volume of mordenite micropores. It is seen from the comparison of  $W_0$  values that these pores are larger than the pores of HZSM and smaller than the pores of HY. Probably, the structure of  $HM_{25}$  pores is such that side transformations of TL are sterically hindered and diffusion of BZ and *p*-XL is easier compared to HZSM. Indeed, the adsorption parameter K of of Dubinin–Radushkevich equation occupies an intermediate position between the values of this parameter for HY and HZSM (Table 2). Thus, the selectivity in *p*-XL formation is governed by the size of inlets to wide pores of zeolites and thus can be characterized by the parameter K of Dubinin-Radushkevich adsorption equation. The dependence of the parameter  $\gamma$  on K is shown in the figure. As seen, the  $\gamma$ -K curve consists of two branches. The left branch corresponds to worsening of molecular-sieve properties due to a decrease in accessibility of zeolite micropores to the reactant, and the right branch corresponds to worsening of molecular-sieve properties because of easier diffusion of large molecules of products (*o*-XL and *m*-XL) from the reaction zone in micropores. Intersection of these branches corresponds to the maximum possible *para*-selectivity and hence to the optimal microstructure of zeolite catalyst for TD.

### CONCLUSIONS

(1) The selectivity of toluene conversion is governed by two cross sections of micropore inlets in zeolite catalysts: the lower limit is dictated by diffusion of the reactant to active centers located in micropores, and the upper limit, by removal of larger products from the reaction zone.

(2) The yield of the target products of toluene conversion and selectivity of TD on modified zeolites can be increased by optimization of their microporous structure.

## REFERENCES

- 1. Jacobs, P.A., *Carboniogenic Activity of Zeolites*, Amsterdam: Elsevier, 1977.
- Isakov, Ya.I., *Neftekhimiya*, 1998, vol. 38, no. 6, pp. 409–412.
- Agaeva, S.B., Dadashev, B.A., Nasirova, F.M., et al., Azerb. Khim. Zh., 2000, no. 3, pp. 19–22.
- Agaeva, S.B., Dadashev, B.A., Nasirova, F.M., et al., Azerb. Khim. Zh., 2000, no. 4, pp. 36–39.

- 5. Agaeva, S.B., Dadashev, B.A., Tagiev, D.B., et al., Neftekhimiya, 2004, vol. 44, no. 1, pp. 42-46.
- 6. ACS Symp. Ser., 1984, no. 248, p. 15.
- Tsybulevskii, A.M., Klyachko, A.L., Brueva, T.R., et al., Izv. Akad. Nauk SSSR, Ser. Khim., 1980, no. 12, pp. 2690–2694.
- Ponomarev, A.I., Metody khimicheskogo analiza silikatnykh i karbonatnykh gornykh porod (Methods of Chemical Analysis of Silicate and Carbonate Rocks), Moscow: Akad. Nauk SSSR, 1961, pp. 18–19.
- Belen'kaya, I.M., Dubinin, M.M., and Kristofori, I.I., *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1971, no. 7, pp. 1391–1397.
- 10. Neft', Gaz Neftekhim. Rubezhom, 1989, no. 11, pp. 100-101.
- Penchev, V., Mavrodinova, V., and Minchev, Khr., *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1982, no. 5, pp. 1168–1171.
- Zhorov, Yu.M., in *Termodinamika khimicheskikh pro*tsessov (Thermodynamics of Chemical Processes), Moscow: Khimiya, 1985, p. 223.
- 13. Gnep, N.S., Tejada, J., and Guisnet, M., Bull. Soc. Chim. Fr., Part 1, nos. 1–2, pp. 5–8.
- 14. Breck, D.W., Zeolite Molecular Sieves, New York: Wiley, 1974.
- 15. Dadashev, B.A., Popova, E.N., Abasov, S.I., et al., Zh. Fiz. Khim., 1988, vol. 62, no. 2, pp. 315-319.
- Agaeva, S.B., Dadashev, B.A., Abasov, S.I., and Tagiev, D.B., *Proc. 13 Int. Zeolite Congr.*, Montpellier (France), 2001, 23-P-15.
- 17. Agaeva, S.B., *Proc. Petrochem. Oil Refining*, 2003, no. 2, pp. 61–65.