

Disproportionation of 1,2,4-Trimethylbenzene over Zeolite NU-87

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Abstract—The catalytic properties of zeolite NU-87 were investigated with respect to the disproportionation of 1,2,4-trimethylbenzene and the results were compared to those obtained over H-beta and H-mordenite with 12-membered ring channel system. In the conversion of 1,2,4-trimethylbenzene, the disproportionation to xylene and tetramethylbenzene is preferred to the isomerization into 1,2,3- and 1,3,5-isomers over all the three zeolites, but this trend is much more pronounced over HNU-87 owing to its peculiar pore structure. Disproportionation reaction is found to proceed within the micropores of HNU-87, whereas isomerization occurs mainly on the external surface. The high selectivity to disproportionation gives more xylenes and tetramethylbenzenes over HNU-87. The detailed descriptions for the product distribution are also reported.

Key words: NU-87, 1,2,4-Trimethylbenzene, Disproportionation, Isomerization

INTRODUCTION

Disproportionation of trimethylbenzene (TMB) to xylene and tetramethylbenzene (TeMB) is an important process for the industry, mainly due to the increasing demand for *p*-xylene to be used for the production of polyester resins. Large pore zeolites such as mordenite, zeolite beta and Y zeolite have been applied for this reaction to reduce the effect of steric hindrance against the bulky reactant and intermediate species, but these catalysts are easily deactivated by coking [Das et al., 1994; Lee et al., 1998; Park et al., 1999]. Although ZSM-5 with medium pore size can also catalyze this reaction, a rather high reaction temperature is needed to overcome its pore size limitation [Röger et al., 1998].

Zeolite NU-87 is a high-silica zeolite which was first synthesized by Casci and Stewart in 1990 [Casci and Stewart, 1990]. The pore system of NU-87 is built from parallel 10-membered ring (MR) channels with a diameter of 4.7 Å×6.0 Å linked together by 12-MR cavities which are accessible only through the 10-MR windows of the channels [Shannon et al., 1991]. This peculiar pore structure renders zeolite NU-87 attractive as a catalyst for reactions in which the desired products are relatively slender and intermediate species are rather bulky. In addition, NU-87 with 10-MR channel system may show higher thermal stability and resistance to coke deposition than 12-MR zeolites such as mordenite and zeolite beta.

In this study, we synthesized zeolite NU-87 and applied this catalyst to the disproportionation of 1,2,4-TMB. The results over NU-87 were compared to those observed over zeolite beta and mordenite with 12-MR channels.

EXPERIMENTAL

1. Catalysts Preparation

H-mordenite (Engelhard, $\text{SiO}_2/\text{Al}_2\text{O}_3=45$) and H-beta (PQ Corp., $\text{SiO}_2/\text{Al}_2\text{O}_3=22$) used in this study were taken from commercial samples. Zeolite NU-87 was synthesized according to the procedure described previously [Shannon et al., 1991]. Colloidal silica sol (Ludox, AS-40) and sodium aluminate were used as the Si and Al sources, respectively. As a template, decamethonium bromide (DecBr_2 , Fluka, >99%) was used.

The as-synthesized zeolite was transformed into the ammonium form by ion exchange with 1 M NH_4NO_3 solution at 80 °C for 12 h, which was repeated three times. It was then calcined in air at 500 °C for 5 h to yield H-form zeolite.

2. Catalysts Characterization

The structure and crystallinity of NU-87 was confirmed by X-ray powder diffraction analysis. The spectra were collected on a Rigaku D/MAX II-A instrument using $\text{Cu K}\alpha$ radiation. The morphology and crystal size was examined by scanning electron microscopy (JEOL, JSM-T200, Scanning Micrograph). Thermal analysis was conducted on a Perkin Elmer TGA instrument.

Infrared spectra were recorded on a Nicolet Impact 410 instrument with a resolution of 4 cm^{-1} . The self-supporting wafers (20 mg) were activated under vacuum in the IR cell at 500 °C for 5 h. After cooling down to 150 °C, the spectrum of the free surface was obtained. The cell was then equilibrated with 5 Torr of pyridine for 1 h and sufficiently evacuated to remove gaseous and physisorbed pyridine. Desorption was continued at elevated temperatures. Infrared spectra of samples were obtained at 150, 200, 300, 350 and 400 °C, respectively.

3. Reaction Experiment

Reaction experiments were conducted in a fixed-bed flow reactor under atmospheric pressure at 200–350 °C. Helium was used as the carrier gas. In a typical experiment, catalyst was activated in a gas flow at 500 °C for 2 h and cooled down to the reaction temperature, then 1,2,4-TMB with the partial pressure of 4.1 kPa

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was passed over catalyst bed. The WHSV was varied from 0.58 to 630.72 hr⁻¹ by changing both the feed flow rate and the catalyst mass. Reaction products were collected and analyzed by an HP 5890 gas chromatograph equipped with FID and the capillary column HP-INNOWAX (60 m, 0.32 mm, ID 0.50 μ m).

RESULTS AND DISCUSSIONS

1. Physicochemical Properties of Catalysts

The XRD patterns of as-synthesized and the calcined NU-87 are shown in Fig. 1. The peak positions and the relative intensities agree well with the published data [Shannon et al., 1991]. Fig. 2 presents the SEM photo of zeolite NU-87. The crystallites have a morphology of rectangular rods similar to those reported in the literature [Gläser et al., 1998]. The crystal size is about 0.2 μ m \times 1.0 μ m.

Thermal analysis of as-synthesized NU-87 showed that the weight loss on heating in an N₂ flow (heating rate 10 °C min⁻¹) occurs in three steps. The first step completed at about 250 °C is assigned to the desorption of water and the two additional steps around 470 °C and 560 °C, respectively, are related to the desorp-

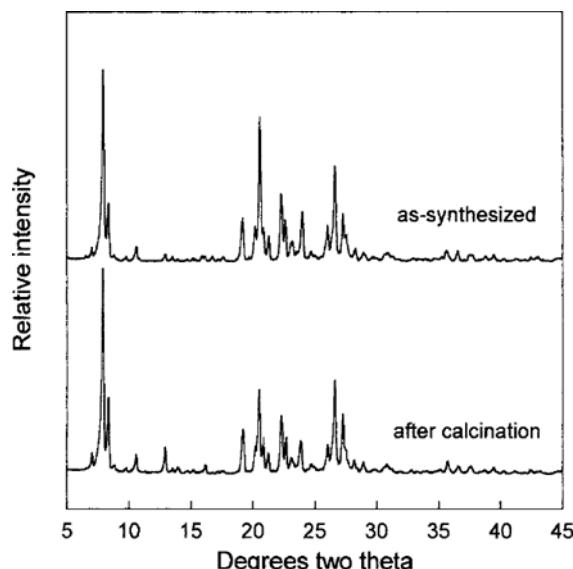


Fig. 1. XRD patterns of zeolite NU-87.

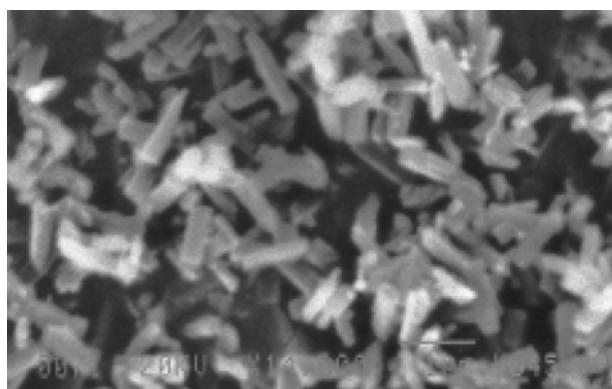


Fig. 2. SEM photograph of the as-synthesized NU-87.

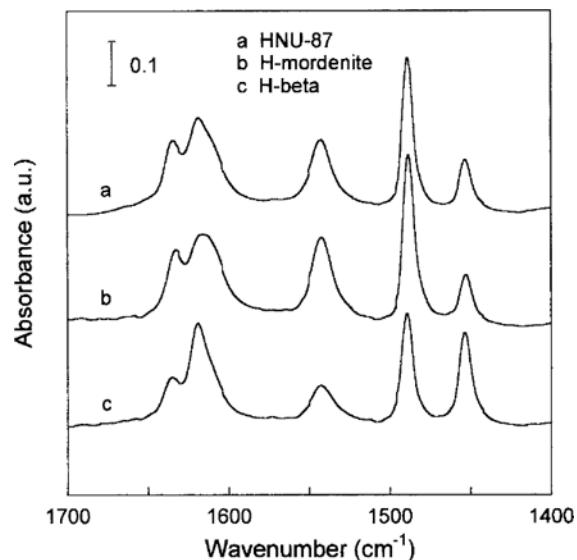


Fig. 3. IR spectra of various zeolites after adsorption and desorption of pyridine at 150 °C.

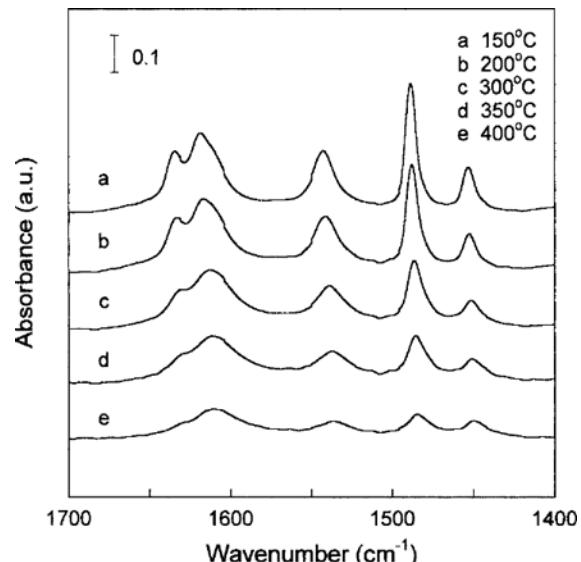


Fig. 4. IR spectra of HNU-87 after adsorption of pyridine at 150 °C and desorption at various temperatures.

tion of organic template. This observation indicates that the organic template is present either in two different configurations or at two different locations (10-MR channels and 12-MR cavities) [Gläser et al., 1998]. From the above results, it is confirmed that zeolite NU-87 was successfully synthesized.

FT-IR spectra of zeolite NU-87 and others in the region of the ring vibrations (1,700-1,400 cm⁻¹) are presented in Figs. 3 and 4. Signals of pyridinium ions formed on Brønsted acid sites (bands at ca. 1,635 and 1,543 cm⁻¹) and those of pyridine coordinated to Lewis acid sites (bands at ca. 1,620 and 1,453 cm⁻¹) are observed. The bands at ca. 1,490 cm⁻¹ are attributed to both types of species [McQueen et al., 1996]. The integrated absorbances of the bands at ca. 1,543 and 1,453 cm⁻¹ (integration regions approximately 1,515-1,565 cm⁻¹ and 1,435-1,470 cm⁻¹, respectively) were determined to measure the amount of pyridine adsorbed on Brønsted

Table 1. Acidity of various zeolites measured in μmol of adsorbed pyridine per g of the zeolite with increasing temperature

Temp. (°C)	Brönsted acidity					Lewis acidity				
	150	200	300	350	400	150	200	300	350	400
HNU-87	156	138	98	65	30	52	41	26	23	16
H-mordenite	188	145	62	24	-	48	44	33	29	24
H-beta	90	59	18	4	-	100	79	48	37	22

and Lewis acid sites, respectively. Extinction coefficients of the pyridine IR bands were taken from the literature [Emeis, 1993]. Quantitative results are given in Table 1.

The distribution of Brönsted and Lewis acidity in HNU-87 is similar to that in H-mordenite. The amount of pyridine adsorbed on Brönsted acid sites at 150 °C is a little bit higher over H-mordenite. However, the Brönsted acidity of H-mordenite decreases rapidly with increasing desorption temperature compared to that of HNU-87. In case of HNU-87, some amount of protonated pyridine is still retained after desorption at 400 °C, indicating the presence of strong acid sites. As is well known, zeolite H-beta has a large number of Lewis acid sites instead of Brönsted acid sites.

The total acidity (Brönsted and Lewis acidity) probed using pyridine increases in the order of H-beta < HNU-87 < H-mordenite as shown in Table 1, but there is little difference in the total acidity among three zeolites.

2. Disproportionation of 1,2,4-Trimethylbenzene

Reaction results of 1,2,4-TMB over HNU-87 taken at different times on stream are presented in Table 2. Here the results are compared with those over H-beta and H-mordenite. Disproportionation of 1,2,4-TMB produces xylenes and TeMBs, whereas isomerization gives 1,3,5- and 1,2,3-isomers. If there are no secondary reactions, the molar ratio of xylene to TeMB should be unity. Benzene, toluene and pentamethylbenzene (PtMB) are formed via secondary reactions such as disproportionation of xylene, transalkylation between xylene and TeMB, dealkylation of alkylbenzenes, etc. [Ko et al., 1994; Röger et al., 1998]. Under the present reaction conditions the portion of these secondary reactions is very small and the xylene to TeMB ratio over all the catalysts turns out to be close to unity as may be noticed in Table 2.

Three zeolites show comparable initial activity for the reaction of 1,2,4-TMB but H-mordenite suffers from a relatively faster deactivation as shown in Fig. 5. Zeolite beta with three dimensional channel system was reported by Wang et al. [Wang et al., 1990]

Table 2. Results of reaction of 1,2,4-trimethylbenzene over HNU-87, H-beta and H-mordenite at 350 °C with WHSV of 2.8 hr⁻¹

Zeolite	HNU-87		H-beta		H-mordenite		Thermodynamic Equilibrium ^c
Time on stream (hr)	1	5	1	5	1	5	
Product Yields (wt%)							
C ₁ -C ₄	0.31	0.26	0.18	0.13	0.21	0.15	
benzene	0.09	0.08	0.09	0.07	0.09	0.08	
toluene	2.64	2.11	2.57	1.35	2.19	0.69	
xylene	21.04	19.8	20.92	18.12	18.17	9.72	
1,3,5-trimethylbenzene	9.46	5.71	13.98	16.61	15.88	20.67	
1,2,4-trimethylbenzene	35.42	41.41	31.75	37.07	35.47	50.08	
1,2,3-trimethylbenzene	4.75	5.56	4.09	4.83	4.64	6.63	
tetramethylbenzene	26.17	25.07	25.08	21.13	22.68	11.82	
pentamethylbenzene	0.13	-	1.33	0.69	0.68	0.15	
Xylene isomers (%)							
p-xylene	24.33	24.34	23.71	22.18	23.56	21.91	(24.1)
m-xylene	53.47	53.69	53.49	51.99	52.83	50.72	(51.4)
o-xylene	22.2	21.97	22.8	25.83	23.61	27.37	(24.5)
TeMB ^a isomers (%)							
1,2,4,5-TeMB	40.47	43.64	39.99	40.08	40.08	40.44	
1,2,3,5-TeMB	49.25	45.27	49.68	49.6	49.52	48.98	
1,2,3,4-TeMB	10.28	11.09	10.33	10.32	10.4	10.58	
Conversion (wt%)	64.58	58.59	68.25	62.93	64.53	49.92	
Selectivity (mol/mol)							
1,3,5-/1,2,3-TMB	1.99	1.03	3.42	3.44	3.42	3.12	(3.45)
p-/o-xylene	1.10	1.11	1.04	0.86	1.00	0.80	(0.98)
1,2,4,5-/1,2,3,5-TeMB	0.82	0.96	0.80	0.81	0.81	0.83	(0.74)
xylene / TeMB	1.02	1.00	1.05	1.08	1.01	1.04	
S _D /S _I ^b	3.30	3.98	2.49	1.77	1.98	0.78	

^a tetramethylbenzene

^b 2(moles of TeMB isomers)/(moles of 1,2,3- and 1,3,5-TMB)

^c referenced from [Earhart, 1982]

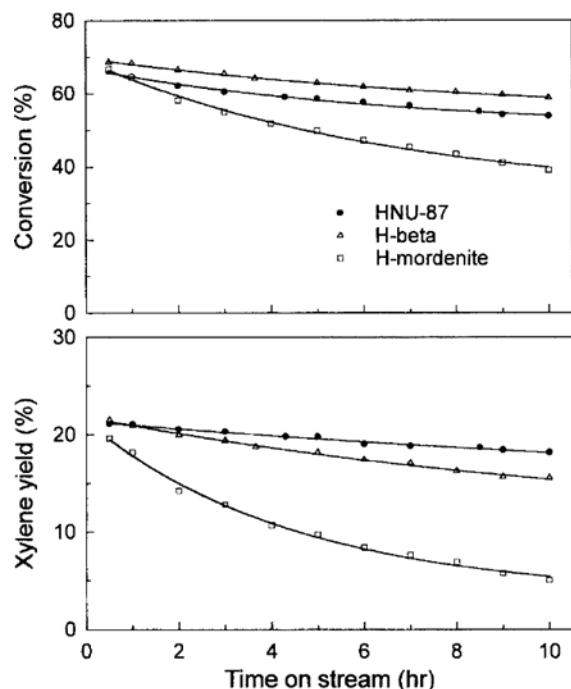


Fig. 5. Conversion and xylene yield versus time on stream over various catalysts at 350 °C.

to be a good catalyst for the disproportionation of 1,2,4-TMB and far more active and stable than both zeolite Y and UST. The conversion and xylene yield over H-beta obtained in the present work are similar to the results obtained by these authors.

HNU-87 exhibits a slightly lower activity than H-beta but the xylene yield is higher over HNU-87. On acid catalysts, disproportionation and isomerization reactions proceed at comparable rates and thus it may be appropriate to define the apparent selectivity ratio (S_p/S_i) between these reactions as given in Table 2. The S_p/S_i ratio over HNU-87 is the highest and increases with the time on stream unlike over H-beta and H-mordenite. Therefore, 1,2,4-TMB undergoes more preferentially disproportionation to isomerization over HNU-87 and this gives rise to the high xylene yield despite its somewhat lower conversion over HNU-87.

As shown in Fig. 5, the rate of deactivation of HNU-87 is similar to that of H-beta, but the xylene yield decreases more slowly over HNU-87. It can be seen from Table 2 that the deactivation of HNU-87 is caused largely by the decrease in the isomerization activity of 1,2,4-TMB, while over H-beta or H-mordenite, disproportionation reaction is more strongly affected by catalytic deactivation than isomerization. Thus, it is evident that HNU-87 has a better catalytic capability in view of xylene yield.

When the minimum Van der Waals diameters are compared, among the three isomers, the molecular size of 1,3,5-TMB is the largest, followed successively by the 1,2,3- and 1,2,4-isomers [Röger et al., 1997]. In view of the shape selectivity, therefore, the formation of 1,2,3-TMB would be preferred to 1,3,5-isomer within the micropore system. However, the 1,3,5-TMB is thermodynamically favored over the 1,2,3-TMB [Earhart, 1982]. As shown in Fig. 6(a), the ratio of 1,3,5- to 1,2,3-TMB over H-beta and H-mordenite is nearly equal to the equilibrium value, whereas that over HNU-87 is far below the equilibrium value. This result

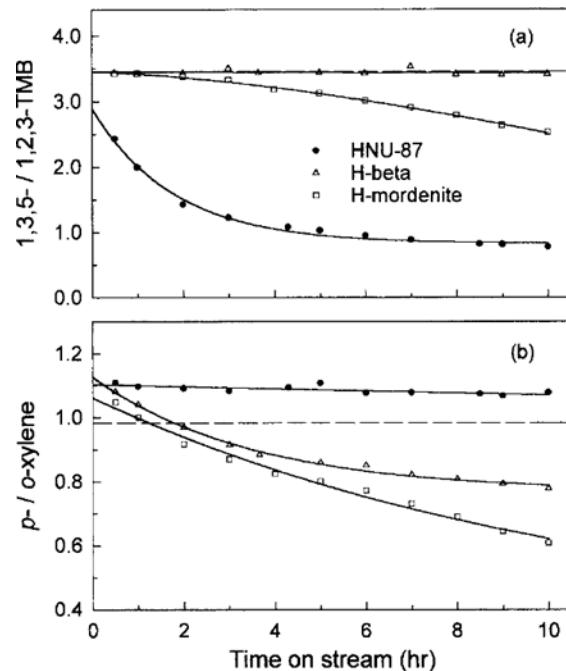


Fig. 6. Product selectivities versus time on stream over various catalysts at 350 °C. Dashed lines: equilibrium values.

indicates that the isomerization of 1,2,4-TMB over HNU-87 is kinetically controlled. The 1,3,5-TMB can be formed in 12-MR cavities of HNU-87 but may be prevented from diffusing out through 10-MR channels. Nevertheless, the ratio of 1,3,5- to 1,2,3-TMB is considerably high in the beginning of reaction. As will be discussed later, this may be the result of isomerization of 1,2,4-TMB taking place on the external surface of HNU-87.

In case of TeMB isomers, the isomer distribution is not thermodynamically equilibrated over all the three catalysts as may be noticed from Table 2. The smallest isomer, 1,2,4,5-TeMB, is formed somewhat preferentially and this trend is much more pronounced over HNU-87 at a large time on stream.

The *p*-xylene/*o*-xylene ratio over HNU-87, as shown in Fig. 6 (b), is a little higher than the equilibrium value and remains nearly constant for a long reaction time, while this ratio over H-beta and H-mordenite decreases with the time on stream. As it was proven before [Hall et al., 1988], when the active sites are partially blocked by coke or poisoned with ammonia, the rates of secondary reactions are more strongly affected than those of primary reactions. Among the xylene isomers, *o*-xylene is preferentially produced by the disproportionation of 1,2,4-TMB in the beginning of reaction and consecutively isomerized into *m*- and *p*-xylene [Wang et al., 1990; Dumitriu et al., 1996]. This will be also shown in the following section. Based on these arguments one can speculate that as coking proceeds, the isomerization of *o*-xylene into *p*- (or *m*-) xylene is suppressed more rapidly than the disproportionation reaction producing *o*-xylene, and thus the *p*-xylene/*o*-xylene ratio over H-beta or H-mordenite decreases with the time on stream. For HNU-87, *o*-xylene formed within the 12-MR cavities could be isomerized into *p*-xylene while passing through the 10-MR channels. This suggests that the ratio of *p*-/*o*-xylene over HNU-87 is less affected by coking than that over H-beta or H-mordenite

Table 3. Results of reaction of 1,2,4-trimethylbenzene over HNU-87 at various residence times with reaction temperature of 350 °C

WHSV (hr ⁻¹)	630.72	29.78	10.50	2.10
Product yields (wt%)				
C ₁ -C ₄	0.03	0.11	0.21	0.31
benzene	0.06	0.08	0.08	0.09
toluene	0.09	0.36	1.11	2.64
xylene	1.07	8.17	13.73	21.04
1,3,5-TMB	0.18	2.10	4.23	9.46
1,2,4-TMB	96.87	75.31	58.57	35.42
1,2,3-TMB	0.45	3.80	5.13	4.75
TeMB	1.25	10.07	17.21	26.17
PtMB	-	-	0.04	0.13
Xylene isomers (%)				
<i>p</i> -xylene	13.08	19.95	22.65	24.33
<i>m</i> -xylene	41.12	49.94	52.00	53.47
<i>o</i> -xylene	45.79	30.11	25.35	22.2
TeMB isomers (%)				
1,2,4,5-TeMB	95.20	60.58	47.76	40.47
1,2,3,5-TeMB	-	25.42	40.67	49.25
1,2,3,4-TeMB	4.80	14.00	11.56	10.28
Conversion (wt%)	3.13	24.69	41.74	64.58
Selectivity (mol/mol)				
xylene/TeMB	1.08	1.03	1.01	1.02
S _D /S _I	3.55	3.06	3.30	3.30

because 10-MR channels are generally more resistant to coke deposition than 12-MR channels.

3. Distribution and Selectivities of Product over HNU-87

Disproportionation of 1,2,4-TMB was conducted over HNU-87 with various values of the residence time. Depending on the flow rate, the time on stream at which the sample was taken varied from 1 min to 2 hr. The typical results are given in Table 3.

All the xylene isomers are detected at a very low conversion of ca. 3%, so all of them may be primary products. However, *o*-xylene is preferentially formed in comparison to *m*- and *p*-xylene with the initial distribution of about 46% of *o*-, 41% *m*- and 13% of *p*-xylene. In addition, the selectivity to 1,2,4,5-TeMB amongst TeMB isomers is far above the thermodynamic equilibrium value. The selective formation of *o*-xylene and 1,2,4,5-TeMB can be explained by the transition state shape selectivity.

A generally accepted disproportionation mechanism of alkylaromatics involves a biphenylic transition state intermediate [Csicsery et al., 1984]. The intermediate, which produces *o*-xylene and 1,2,4,5-TeMB, is the most linear biphenylic one and followed by that forming *m*-xylene and 1,2,4,5-TeMB, so the former is preferentially formed. Similar result was also reported over zeolites beta and Y [Wang et al., 1990; Dumitriu et al., 1996]. This indicates that the disproportionation reaction of 1,2,4-TMB proceeds within the micropores of HNU-87. With the increase in residence time the distributions of xylene and TeMB isomers approach their respective equilibrium compositions by the consecutive reactions of isomerization. At high conversion level, even PtMB which is the largest product is observed. If we consider its molecular size and

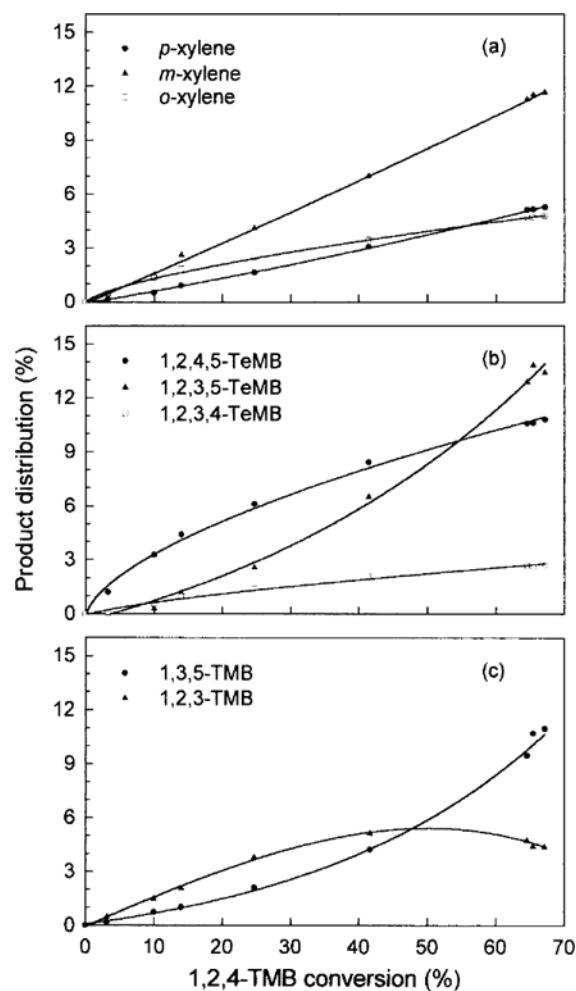


Fig. 7. Product distribution versus conversion of 1,2,4-TMB over HNU-87 at 350 °C.

the above discussion for other products, it is presumable that PtMB is formed on the external surface of HNU-87.

Fig. 7 presents the product distribution at different levels of conversion. In general, there are six types of products in series reactions: primary stable (1S), primary unstable (1U), primary stable plus secondary {(1+2)S}, secondary stable (2S), secondary unstable (2U) and primary unstable plus secondary product {(1+2)U} [Ko et al., 1994]. According to this criterion, xylene isomers are classified as primary products: *m*-xylene (1S), *p*-xylene (1S) and *o*-xylene (1U), as discussed previously. In case of TeMB isomers, 1,2,4,5- and 1,2,3,4-TeMB are observed as primary products (1U) but 1,2,3,5-TeMB must be a secondary product (2S). From these observations, it may be concluded that 1,2,3,4-TeMB formed by decomposition of biphenylic intermediate can diffuse out through 10-MR channels of HNU-87, but 1,2,3,5-TeMB cannot and is formed mainly on the external surface by the isomerization of 1,2,4,5- and 1,2,3,4-TeMB.

1,2,4-TMB competitively isomerizes to 1,3,5- or 1,2,3-TMB. If there are no restrictions, 1,3,5-TMB is favored thermodynamically. As shown in Fig. 7(c), both isomers are produced primarily. On the contrary, however, the rate of formation of 1,2,3-TMB is faster than that of 1,3,5-TMB at relatively low conversion levels. A similar conclusion can be drawn for the case of TeMB isomers;

that is, 1,2,3-TMB can escape from the micropores of HNU-87 but 1,3,5-TMB is prevented from diffusing out through those micropores. In fact, the 1,2,3- and 1,3,5-TMB have the same Van der Waals diameters as 1,2,3,4- (7.9 Å) and 1,2,3,5-TeMB (8.6 Å), respectively [Röger et al., 1997]. The favorable formation of 1,2,3-TMB is maintained to the high conversion of ca. 50%, and as the conversion further increases, the yield of 1,2,3-TMB decreases showing a maximum yield. This indicates that this primary product is consumed in consecutive reactions. However, the yield of 1,3,5-TMB increases rapidly and thus the distribution of TMB isomers approaches the equilibrium composition. Therefore, the formation of 1,3,5-TMB can be considered to occur mainly on the external surface, while the formation of 1,2,3-TMB proceeds to a significant extent within the micropores of HNU-87.

The influence of the reaction temperature on the conversion and product yields after 1 hr of time on stream is shown in Table 4. Similar effect to that of the residence time (*cf.* Table 3) is observed when the reaction temperature is varied. At low reaction temperature of 200 °C, *o*-xylene, 1,2,3-TMB and 1,2,4,5-TeMB are selectively formed amongst their respective isomers, whereas 1,3,5-TMB and 1,2,3,5-TeMB are hardly produced. Upon increasing the reaction temperature, the distribution of isomers approaches the equilibrium composition. These results are in accordance with the previous discussion for the product selectivity. However, if compared at the similar conversion level, e.g., at 24.69% in Table 3 (WHSV=29.78 hr⁻¹) and at 23.07% in Table 4 (220 °C), respectively, there are differences in the product yields. As clearly seen in these tables, this result is mainly caused by the difference

Table 4. Results of reaction of 1,2,4-trimethylbenzene over HNU-87 at various reaction temperatures with WHSV of 2.1 hr⁻¹. The data were taken at 1 hr of time on stream

Reaction temp.	200	220	300	350
Product yields (wt%)				
C ₁ -C ₄	0.02	0.05	0.13	0.31
benzene	-	-	0.05	0.09
toluene	0.12	0.42	1.88	2.64
xylene	2.34	9.13	19.55	21.04
1,3,5-TMB	-	0.44	3.05	9.46
1,2,4-TMB	94.37	76.93	45.80	35.42
1,2,3-TMB	0.20	1.65	4.45	4.75
TeMB	2.95	11.38	25.04	26.17
PtMB	-	-	0.05	0.13
Xylene isomers (%)				
<i>p</i> -xylene	17.52	16.21	23.43	24.33
<i>m</i> -xylene	39.32	44.14	53.76	53.47
<i>o</i> -xylene	43.16	39.65	22.81	22.2
TeMB isomers (%)				
1,2,4,5-TeMB	96.27	71.35	48.12	40.47
1,2,3,5-TeMB	-	17.84	41.97	49.25
1,2,3,4-TeMB	3.73	10.81	9.91	10.28
Conversion (wt%)	5.63	23.07	54.20	64.58
Selectivity (mol/mol)				
xylene/TeMB	1.00	1.01	0.99	1.02
S _D /S _I	26.42	9.75	5.99	3.30

in the selectivity between disproportionation and isomerization reactions. The isomerization of 1,2,4-TMB hardly proceeds at low temperatures, so the S_D/S_I ratio is very high. As the reaction temperature increases, this ratio decreases rapidly. This result may be accounted for by the increased effective channel diameter. Larger amounts of TMB isomers can be produced through micropores as the temperature increases because the channel diameter is gradually extended with increasing temperature.

CONCLUSIONS

Zeolite NU-87 has a good catalytic activity for the reaction of 1,2,4-trimethylbenzene to produce xylene and tetramethylbenzene. Compared to zeolites H-beta and H-mordenite with comparable initial activities, HNU-87 gives a higher and more stable xylene yield. It is found that over HNU-87 the disproportionation to xylene and tetramethylbenzene proceeds more preferentially to isomerization than over the other zeolites. This result is elucidated in terms of the shape selectivity induced by the pore structure. In other words, disproportionation of 1,2,4-TMB takes place within the micropores of HNU-87 while isomerization of 1,2,4-TMB into TMB isomers, especially 1,3,5-TMB, occurs mainly on the external surface of HNU-87. In view of the xylene yield, therefore, HNU-87 is more favorable for the reaction of 1,2,4-TMB than H-beta or H-mordenite.

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