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Shape selective conversion of 1,2,4-trimethylbenzene over zeolite NU-87

Se-Ho Park, Hyun-Ku Rhee*

School of Chemical Engineering and Institute of Chemical Processes, Seoul National University, Kwanak-ku, Seoul 151-742, South Korea

Abstract

The catalytic properties of zeolite NU-87 were investigated in the conversion of 1,2,4-trimethylbenzene in view of the product selectivity. To examine the catalysis by external acid sites, experiments were conducted over NU-87 with external surface poisoned by 1,1,1,3,3,3-hexamethyldisilazane. For comparison, the results obtained over MCM-22, which has a similar pore structure, are also included. Both disproportionation (to xylene and tetramethylbenzene) and isomerization (to 1,2,3- and 1,3,5-isomers) take place over NU-87. Under the present conditions, it is found that the disproportionation proceeds largely within the micropores of NU-87, while the isomerization reaction occurs mainly on the external surface. The distribution of xylene isomers is thermodynamically controlled inside the pores, whereas amongst tetramethylbenzene isomers, the 1,2,4,5-isomer is selectively produced through the channel system. The bulky product, 1,2,3,5-tetramethylbenzene (or 1,3,5-trimethylbenzene), is severely hindered from diffusing through the channel system of NU-87. However, 1,2,3,4-tetramethylbenzene and 1,2,3-trimethylbenzene diffuse out of the micropores to a certain extent. In the case of MCM-22, the conversion of 1,2,4-trimethylbenzene hardly proceeds within the micropores. It is evident that NU-87 has larger pores and thus higher accessibility to 12-MR cavities than MCM-22. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: NU-87; MCM-22; 1,2,4-trimethylbenzene; Disproportionation; Isomerization

1. Introduction

Zeolite NU-87, first synthesized by Casci and Stewart [1], contains both 10-membered ring (MR) and 12-MR pores in the same structure. The pore structure consists of parallel 10-MR channels with a diameter of $4.7 \times 6.0\,\text{Å}^2$ linked together by 12-MR cavities. Interestingly the 12-MR cavities are only accessible through the 10-MR windows of the channels [2]. This peculiar pore structure makes zeolite NU-87 an attractive catalyst for reactions in which the desired products are relatively slender and intermediate species are rather bulky. In addition, NU-87 with its 10-MR channel system may show higher thermal stability and resistance to coke deposition than 12-MR zeolites such as mordenite and beta.

Disproportionation of 1,2,4-trimethylbenzene (TMB) is an old but important industrial process because of the increasing demand for xylenes. Large pore zeolites such as mordenite, beta and Y have been applied for this reaction to reduce steric hindrance effects, but these catalysts are easily deactivated by coking [3–5]. ZSM-5 with medium pore size also catalyzes this reaction at a relatively high temperature, however, mainly by its external surface [6]. The reaction of *m*-xylene has been widely used as a test reaction for probing the effective pore space in zeolites. According to the results obtained with NU-87 [7], this

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* Corresponding author. Tel.: +82-2-880-7405; fax: +82-2-888-7295.
E-mail address: hkrhee@snu.ac.kr (H.-K. Rhee).

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Table 1
Synthesis conditions for zeolites NU-87 and MCM-22

Zeolite	Molar composition	Template	Temperature and duration	Remark
NU-87	$55SiO_2–Al_2O_3–11.5Na_2O–6.8DecBr_2–2800H_2O–2.4NaBr$	Decamethonium bromide	180°C, 10 days	Rotating at 40 rpm
MCM-22	$30SiO_2–Al_2O_3–2.7Na_2O–15HMI–1347H_2O$	Hexamethyleneimine	150°C, 10 days	Rotating at 60 rpm

zeolite has catalytic properties falling between those of medium and large pore zeolites, more likely close to those of large pore zeolite. As expected, NU-87 also deactivates at a rate less than that of zeolite beta in the reaction of *m*-xylene. Therefore, zeolite NU-87 is expected to show a unique catalytic behavior in the conversion of 1,2,4-TMB.

In this study, zeolite NU-87 was applied to the conversion of 1,2,4-TMB. In order to clarify the catalytic properties of NU-87. The results are compared to those observed with MCM-22, which has a similar pore structure, i.e. large void space which are accessible only by 10-MR windows.

2. Experimental

2.1. Catalysts preparation and characterization

Zeolite NU-87 was synthesized according to the procedure described previously [2]. 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. For the synthesis of MCM-22, Cabosil M5, sodium aluminate and hexamethyleneimine (HMI, Aldrich, >99%) were used as reagents. Detailed synthesis procedure was adopted from the literature [8]. Synthesis conditions for NU-87 and MCM-22 are summarized in Table 1.

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 the H-form zeolite.

The structure and crystallinity of NU-87 and MCM-22 were confirmed by X-ray powder diffraction analysis. Both zeolites had 100% crystallinity and no other phases were observed.

To determine the acidities of NU-87 and MCM-22, Fourier transform infrared (FTIR) analysis of chemisorbed pyridine was conducted. FTIR 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 an 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.

2.2. Catalytic experiments

The conversion of 1,2,4-TMB and the cracking of 1,3,5-triisopropylbenzene (TIPB) were carried out in a fixed-bed flow reactor under atmospheric pressure at 350°C. Helium was used as the carrier gas. In a typical experiment, the catalyst was activated in a gas flow at 500°C for 2 h and cooled down to the reaction temperature, then the reactants were passed through the catalyst bed. In the conversion of 1,2,4-TMB, the WHSV was varied from 0.58 to $630.72\,h^{-1}$ 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 μm).

2.3. Poisoning experiments

For the poisoning experiments, excess amounts of 1,1,1,3,3,3,-hexamethyldisilazane (HMDS) were introduced into the catalyst bed at 250°C. In a typical experiment, after pretreatment of the catalyst as described above, the bed temperature was lowered to 250°C and then 0.01 ml of HMDS was evaporated into the catalyst bed several times. The temperature was then elevated to the reaction temperature of 350°C.

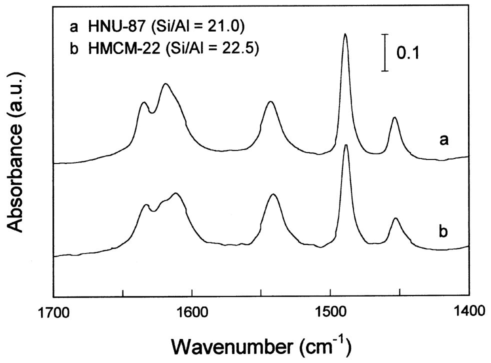

Fig. 1. FTIR spectra of HNU-87 and HMCM-22 after adsorption and desorption of pyridine at 150°C.

3. Results and discussion

3.1. Acidic properties of catalysts

FTIR spectra of HNU-87 and HMCM-22 in the region of the ring vibrations (1700∼1400 cm^{-1}) are presented in Fig. 1. Signals of pyridinium ions formed on Brönsted acid sites (bands at ca. 1635 and 1543 cm^{-1}) and of pyridine coordinated to Lewis acid sites (bands at ca. 1620 and 1453 cm^{-1}) are observed. The band at ca. 1490 cm^{-1} is attributed to both types of species [9]. The integrated absorbances of the bands at ca. 1543 and 1453 cm^{-1} (integration regions approximately 1515∼1565 and 1435∼1470 cm^{-1}, respectively) were determined to measure the amount of pyridine adsorbed on Brönsted and Lewis acid sites, respectively. Extinction coefficients of the pyridine IR bands were taken from the literature [10]. Quantitative results are given in Table 2.

As expected from the similar Si/Al ratio, the density of acid sites is comparable for both zeolites. However, the distribution of their strengths is somewhat different. It can be seen from Table 2 that the Brönsted acid sites in HNU-87 more strongly hold pyridine than those in HMCM-22. HNU-87 possesses a somewhat larger amount of Lewis acid sites, but the distribution of their strengths is similar in two zeolites.

Table 2
Acidity of HNU-87 and HMCM-22 measured in µmol of adsorbed pyridine per g of the zeolite with increasing temperatures (150, 200, 300, 350 and 400)

	Brönsted acidity					Lewis acidity				
Temp. (°C)	150	200	300	350	400	150	200	300	350	400
HNU-87	156	138	98	65	30	52	41	26	23	16
HMCM-22	156	135	83	45	9	44	36	19	16	13

HNU-87 showed a higher strength of Brönsted acid sites as compared to that of H-beta and H-mordenite [11]. Since the strength of acid sites in H-beta lies between those of HZSM-5 and HY [12], zeolite HNU-87 resemble more like HZSM-5 than HY with respect to the acidic properties.

3.2. Conversion of 1,2,4-trimethylbenzene over HNU-87 and HMCM-22

Reaction results of 1,2,4-TMB over HNU-87 at two times on stream are presented in Table 3. Here the results are compared with those over HMCM-22. In the conversion of 1,2,4-TMB, disproportionation and isomerization are the two main reactions. Disproportionation of 1,2,4-TMB produces xylene and tetramethylbenzene (TeMB) whereas isomerization gives 1,3,5- and 1,2,3-isomers. Light gases (C$_1$–C$_4$) mainly come from dealkylation reaction. The other products, benzene, toluene and pentamethylbenzene, are formed via secondary reactions such as disproportionation of xylene, transalkylation between xylene and TeMB, dealkylation of alkylbenzenes, etc. [14,15].

As shown in Table 3, HNU-87 actively disproportionates 1,2,4-TMB to xylene and TeMB at 350°C with a xylene/TeMB molar ratio close to unity. On acid catalysts, disproportionation and isomerization proceed at comparable rates and thus it may be appropriate to define the apparent selectivity ratio (S_D/S_I) between these reactions as given in Table 3. The S_D/S_I ratio over HNU-87 is greater than unity, which indicates that 1,2,4-TMB preferentially undergoes disproportionation. In our previous work [11], HNU-87 showed a better catalytic activity and stability in terms of xylene (or TeMB) yield as compared to those of H-beta and H-mordenite with similar initial activities. The difference in the behavior of these zeolites was the much more pronounced capability of HNU-87 to catalyze disproportionation vis-à-vis isomerization.

The distribution of xylene isomers over HNU-87 is very close to their equilibrium value. In case of TeMB isomers, however, the smallest isomer, 1,2,4,5-TeMB,

Table 3
Results of conversion of 1,2,4-TMB over HNU-87 and HMCM-22 at 350°C with WHSV of 2.1 h^{-1}

Zeolite	HNU-87		HMCM-22		Thermodynamic equilibrium[a]
Time on stream (min)	60	300	60	120	
Product yields (wt. %)					
C_1–C_4	0.31	0.26	0.15	0.13	
Benzene	0.09	0.08	0.09	0.09	
Toluene	2.64	2.11	0.27	0.21	
Xylene	21.04	19.8	2.24	1.53	
1,3,5-TMB	9.46	5.71	24.14	23.97	
1,2,4-TMB	35.42	41.41	62.50	65.03	
1,2,3-TMB	4.75	5.56	8.18	8.39	
TeMB	26.17	25.07	2.43	1.55	
Pentamethylbenzene	0.13	–	–	–	
Xylene isomers (%)					
p-xylene	24.33	24.34	20.77	20.99	(24.1)
m-xylene	53.47	53.69	49.76	48.8	(51.4)
o-xylene	22.2	21.97	29.46	30.20	(24.5)
TeMB isomers (%)[b]					
1,2,4,5-TeMB	40.47	43.64	40.33	39.89	
1,2,3,5-TeMB	49.25	45.27	48.89	49.01	
1,2,3,4-TeMB	10.28	11.09	10.78	11.10	
Conversion (wt.%)	64.58	58.59	37.5	34.97	
Selectivity (mol/mol)					
1,3,5-/1,2,3-TMB	1.99	1.03	2.95	2.86	(3.45)
p-/*o*-xylene	1.10	1.11	0.71	0.70	(0.98)
1,2,4,5-/1,2,3,5-TeMB	0.82	0.96	0.82	0.82	(0.74)
Xylene/TeMB	1.02	1.00	1.16	1.25	
S_D/S_I[c]	3.30	3.98	0.13	0.09	

[a] Referenced from [13].

[b] Tetramethylbenzene.

[c] 2×(moles of TeMB isomers)/(moles of 1,2,3- and 1.3.5-TMB).

is formed somewhat preferentially and this trend is much more pronounced at a large time on stream. The ratio of 1,3,5-/1,2,3-TMB also deviates from the equilibrium. The fraction of the smaller isomer, 1,2,3-TMB, exceeds the equilibrium value. These results indicate that the conversion of 1,2,4-TMB over HNU-87 is a shape selective reaction.

Despite the similar acidity of HNU-87 and HMCM-22, these two zeolites present very different catalytic behavior in the conversion of 1,2,4-TMB. As shown in Table 3, the catalytic activity of HMCM-22 is much lower than that of HNU-87. It is also observed that isomerization reaction proceeds dominantly over HMCM-22 and the ratio of 1,3,5-/1,2,3-TMB is close to the equilibrium value unlike HNU-87. These features may be attributed to the difference in the pore structure between NU-87 and MCM-22, which will be discussed in the latter part.

3.3. Product selectivity in the conversion of 1,2,4-TMB

3.3.1. The effect of contact time

Reaction of 1,2,4-TMB was conducted over HNU-87 with various values of the contact time. Depending on the flow rate, the time on stream at which the sample was taken varied from 1 min to 2 h.

The distribution of xylene, TeMB and TMB fractions is presented in Fig. 2 as a function of the 1,2,4-TMB conversion. Fig. 2a shows, all the xylene isomers to be present at a very low conversion of ca. 3%, so all of them may be primary products.

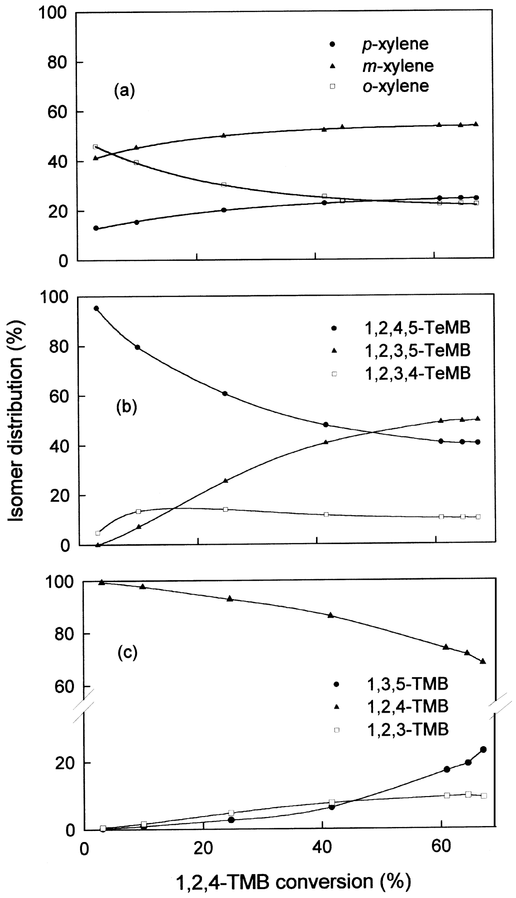

Fig. 2. The isomer distributions versus conversion of 1,2,4-TMB over HNU-87 at 350°C.

However, *o*-xylene is preferentially formed, the initial distribution being about 46% of *o*-, 41% of *m*- and 13% of *p*-xylene. In the case of the TeMB isomers (Fig. 2b), 1,2,4,5-TeMB is dominantly produced at low conversion levels.

The selective formation of *o*-xylene and 1,2,4,5-TeMB can be explained by the transition state shape selectivity. Nine biphenylmethane carbonium ion intermediates can be formed during the disproportionation of 1,2,4-TMB [14]. Among these intermediates, the intermediate producing *o*-xylene and 1,2,4,5-TeMB is the most slender and it is followed by the intermediate forming *m*-xylene and 1,2,4,5-TeMB. Similar results were reported over zeolites beta and Y [16,17].

The isomerization of 1,2,4-TMB competitively yields 1,3,5- and 1,2,3-isomers. Without restrictions, 1,3,5-TMB is favored thermodynamically. However, the fraction of 1,2,3-isomer is higher than that of 1,3,5-isomer up to about 45% of conversion as shown in Fig. 2c. A similar trend is observed in the distribution of TeMB isomers, i.e. the smaller isomer, 1,2,3,4-TeMB, is favorably formed to 1,2,3,5-TeMB at relatively low conversion levels. As the conversion further increases, the distributions of both TMB and TeMB isomers approach their respective equilibrium compositions. These results indicate that 1,2,3-TMB and 1,2,3,4-TeMB are produced in the channel system of HNU-87, while 1,3,5-TMB and 1,2,3,5-TeMB may be formed mainly on the external surface. This will be further clarified in the following section.

3.3.2. Selective poisoning of acid sites on the external surface

1,1,1,3,3,3-HMDS is a selective poison of Brönsted acid sites [18,19], mainly for those sites located at the outer zeolite surface, as it is too large to enter the channel system. This compound remains on the surface and only above 450°C slowly desorbs or decomposes. The conversion of 1,2,4-TMB was carried out after poisoning the catalysts with HMDS to examine the catalysis by external acid sites. The activity of external acid sites was evaluated with the cracking of 1,3,5-TIPB which only occurs on the external surface [20]. The results are given in Table 4.

The 1,3,5-TIPB conversion over HNU-87 dramatically decreases from 62.5 to 1.62% when the parent catalyst is treated with HMDS. This indicates that the

Table 4
Effect of poisoning with HMDS on the conversion of 1,2,4-TMB and the cracking of 1,3,5-TIPB over HNU-87 and HMCM-22

Zeolite HMDS	HNU-87		HMCM-22	
	No	Yes	No	Yes
1,3,5-TIPB conversion (%)	62.52	1.62	74.83	2.21
1,2,4-TMB conversion (%)	64.58	42.13	37.5	2.29
Product yield (%)				
Xylenes	21.04	17.79	2.24	0.08
TeMBs	26.17	21.76	2.43	0.07
1,3,5-TMB yield	9.46	0.20	24.14	1.22
1,2,3-TMB yield	4.75	0.67	8.18	0.43
S_D/S_I ratio	3.30	44.80	0.13	0.08

acid sites on the external surface have been extensively poisoned. However, the 1,2,4-TMB conversion is still considerably high, suggesting that HMDS has no influence on the acid sites within the micropores.

The isomerization activity of HNU-87 is reduced to a low level when the external surface is poisoned by HMDS, but the disproportionation activity is not much influenced. This result implies that the isomerization of 1,2,4-TMB mainly occurs on the external surface of HNU-87, whereas the disproportionation reaction proceeds extensively within the micropores. The intermediates formed during isomerization can be easily accommodated in the large void spaces (12-MR cavities) of HNU-87, so the low selectivity to the isomerization may be attributed to product shape selectivity.

The poisoning by HMDS also influences the product selectivity. The distribution of xylene, TeMB and TMB isomers over poisoned HNU-87 is given in Table 5 at three levels of conversion. As discussed previously, *o*-xylene is preferentially formed by transition state shape selectivity. Because the distribution of xylene isomers over poisoned catalyst is close to the equilibrium value, xylene isomerization appears to be thermodynamically controlled in the channel system of HNU-87.

Table 5
Results of conversion of 1,2,4-TMB over HNU-87 poisoned by HMDS at 350°C for three different values of WHSV

	WHSV (h^{-1})		
	22.3	5.3	2.1
Product yields (wt.%)			
Xylene	4.75	12.89	17.79
TeMB	5.71	14.65	21.76
1,3,5-TMB	0.02	0.08	0.21
1,2,3-TMB	0.08	0.29	0.66
Xylene isomers (%)			
p-xylene	21.3	23.29	24.23
m-xylene	56.81	53.64	53.28
o-xylene	21.89	23.07	22.49
TeMB isomers (%)			
1,2,4,5-TeMB	100	96.69	89.02
1,2,3,5-TeMB	–	1.02	3.95
1,2,3,4-TeMB	–	2.29	7.03
Conversion (wt.%)	10.81	28.91	42.13
Selectivity (mol/mol)			
1,3,5-/1,2,3-TMB	0.25	0.28	0.32
p-/*o*-xylene	0.97	1.01	1.08
1,2,4,5-/1,2,3,5-TeMB	–	94.79	22.54
S_D/S_I	102.28	70.92	44.80

The rate of formation of 1,2,4,5-TeMB increases largely when the catalyst is poisoned by HMDS (see Fig. 2 and Table 5). Additionally, 1,2,4,5-TeMB is selectively produced over both parent and poisoned catalysts at low conversion levels. It is therefore concluded that the 1,2,4,5-TeMB formed within the micropores is consecutively isomerized on the external surface. However, it should be noted that the smaller isomer, 1,2,3,4-TeMB, is favorably produced to 1,2,3,5-TeMB contrary to thermodynamics. This indicates that 1,2,3,4-TeMB is formed to some degree within the pores. Two different reaction paths can give rise to 1,2,3,4-TeMB. One is the decomposition of biphenylic intermediates (primary process) and the other is the consecutive isomerization of 1,2,4,5-TeMB (secondary process). As 1,2,3,4-TeMB is scarcely observed at about 10% of conversion as shown in Table 5, it may be concluded that 1,2,3,4-TeMB is produced from the latter path within the pores. However, it is not clear that 1,2,3,5-TeMB can diffuse out of the 10-MR pores because all the 1,2,3,5-isomer may come from external acid sites, which are not completely poisoned. A similar conclusion can be drawn for the TMB isomers, i.e. 1,2,3-TMB can be produced within the micropores, but it is not obvious that 1,3,5-TMB can diffuse through the 10-MR pores. In fact, 1,2,3- and 1,3,5-TMB have the same minimum Van der Waals diameters as 1,2,3,4- (7.9 Å) and 1,2,3,5-TeMB (8.6 Å), respectively [6].

The reaction results over HMCM-22 poisoned by HMDS are also included in Table 4. Despite the similar pore structure and acidic properties of HNU-87 and HMCM-22, they display different catalytic behaviors. As discussed previously, parent HMCM-22 shows a lower catalytic activity and isomerization reaction proceeds dominantly over this catalyst. As expected, by poisoning the external surface with HMDS, the catalytic activity of HMCM-22 decreases to a very low level. Therefore, it may be concluded that under the present reaction conditions, the diffusion of 1,2,4-TMB is very much limited within the pores of HMCM-22 and thus the conversion of 1,2,4-TMB proceeds mainly on the external surface. A similar result has been reported for the conversion of 2-methylnaphthalene over HNU-87 and

HMCM-22 [21]. In this literature, the rate of isomerization (to 1-methylnaphthalene) was distinctly faster than the rate of disproportionation (to naphthalene and dimethylnaphthalene) over the latter catalyst. HNU-87 appears to have larger entrances pores and thus higher accessibility to the 12-MR cavities than MCM-22.

4. Conclusions

Under the reaction conditions studied zeolite NU-87 selectively catalyzes the conversion of 1,2,4-TMB. Disproportionation to xylene and TeMB proceeds mainly inside the micropores of NU-87, while the isomerization to 1,2,3- and 1,3,5-isomers occurs largely on the external surface. The distribution of xylene isomers is thermodynamically controlled within the micropores, whereas in the case of TeMB isomers, 1,2,4,5-isomer is selectively formed inside the pores and isomerized into the other isomers mainly on the external acid sites. Unexpectedly, some amounts of 1,2,3-TMB and 1,2,3,4-TeMB are observed to diffuse out of the pores of NU-87. It is not clear whether the largest product, 1,3,5-TMB (or 1,2,3,5-TeMB) may diffuse through the 10-MR channels.

Acknowledgements

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