Synthesis Conditions and Catalytic Properties of Highly Acidic Zeolite, UTM-1

Katsutoshi Yamamoto, Motonori Uneme, Jacque Plévert,[†,#] and Takashi Tatsumi[*††]
Department of Applied Chemistry, Graduate School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656
[†]*Department of Chemical Engineering, Graduate School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656*
[††]*Division of Materials Science & Engineering, Graduate School of Engineering, Yokohama National University, 79-5 Tokiwadai, Hodogaya-ku, Yokohama 240-8501*

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Preferable synthesis conditions for zeolite UTM-1 are studied; UTM-1 is crystallized under similar conditions to those of MCM-22, although it prefers high SiO_2/Al_2O_3 ratio in mother gel. UTM-1, composed of the same basic building unit as ZSM-5, shows strong acidity comparable to that of ZSM-5. Although small aperture of UTM-1 actually restricts the catalytic activities, its large outer surface area enables the high catalytic activity in reactions occurring at the outer surface of catalyst.

UTM-1 is one of the synthetic zeolites crystallized in the presence of hexamethyleneimine (HMI) as a structure directing agent,[1–5] and its structure has recently been identified.[6] Structural study indicates that UTM-1 is isostructural to MCM-35[3,7] (MTF topology), although UTM-1 and MCM-35 seem to have some difference in synthesis conditions such as the necessity of agitation and mother gel compositions; for instance, MCM-35 is synthesized from mother gels with the SiO_2/Al_2O_3 ratio of lower than 200,[3] while UTM-1 can be crystallized even from Al-free gel. Regarding its structure, it is of importance to point out that MTF type zeolites have the same basic building unit as ZSM-5, which is well-known as an efficient acid catalyst. Based on the structural similarity, UTM-1 can be expected to show remarkable catalytic activity, even though it has only eight-membered ring aperture. Here we show the preferable synthesis conditions and catalytic activities of UTM-1.

UTM-1 was synthesized by hydrothermally treating the mother gel with the chemical composition of 1.0 SiO_2 : x Al_2O_3 : 0.18 Na^+ : 0.12 OH^- : 45 H_2O : 0.5 HMI under tumbling conditions for 7 days. Proton type UTM-1, H-UTM-1, was obtained through ion-exchange in 1 mol·dm^{-3} NH_4NO_3aq followed by calcination at 813 K. The resultant material was employed as acid catalyst for two reactions without any pretreatment. In the hydrolysis of ethyl acetate, 0.20 g of catalyst was added to the mixture of 0.50 g of ethyl acetate and 10.00 g of water, and this mixture was allowed to react at 333 K for 4 h under vigorous stirring. In the inter-exchange of benzyl benzoate with 1-hexanol, the mixture of 0.05 g catalyst, 0.21 g benzyl benzoate, and 20.44 g 1-hexanol was allowed to react at 423 K for 1 h.

Figure 1 illustrates the relationship between synthesis conditions and the resulting phases. As clearly shown, UTM-1 is crystallized under considerably limited conditions. It can be synthesized at temperatures in the range of 408 to 423 K. Within this temperature region high SiO_2/Al_2O_3 ratio in mother gels is preferred, and at low SiO_2/Al_2O_3 MCM-22 (MWW) is obtained instead. Considering the structural similarity between the MTF and the MFI phases, it is interesting to note that the

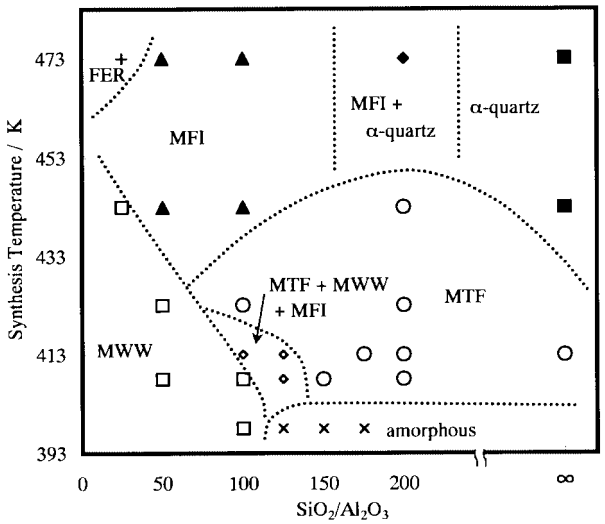

Figure 1. Relationship between synthesis conditions and resulting phases.

MFI phase always appears as an impurity phase when the mixture of the MTF and the MWW phases are obtained. By the use of seed crystals, this limited area of synthesis conditions can be expanded to allow the crystallization of MTF phase at SiO_2/Al_2O_3 ratio of 70. At 413 K, pure silica UTM-1 and Ti-containing material can be crystallized.

Table 1 compares physical properties of H-UTM-1 and H-ZSM-5 synthesized at 413 K under tumbling conditions and having a similar SiO_2/Al_2O_3 ratio. They have almost the same Langmuir surface areas. However, H-UTM-1 has much larger outer surface area than H-ZSM-5. UTM-1 takes very thin plate-like crystal shape (an SEM image is shown in Figure 2), and due to this crystal shape, UTM-1 would be able to have large outer surface area.

Table 1. Physical properties of H-UTM-1 and H-ZSM-5 having similar SiO_2/Al_2O_3 ratio

Zeolites	SiO_2/Al_2O_3	$A_{Langmuir}$[a] $m^2 g^{-1}$	$A_{t\text{-}out}$[b] $m^2 g^{-1}$	acid amount[c] mmol g^{-1}
H-UTM-1	128	452	167	0.22
H-ZSM-5	153	473	88	0.18

[a]Langmuir surface area based on N_2 adsorption at 77 K. [b]Outer surface area estimated from the t-plot of N_2 adsorption at 77 K. [c]The amount of acid sites estimated based on TPD peak area by employing JRC-Z5-25H with 0.99 mmol·g^{-1} of acid site as reference.

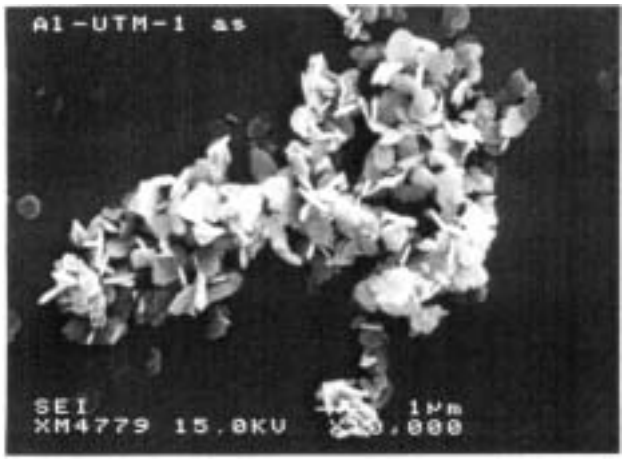

Figure 2. SEM image of UTM-1.

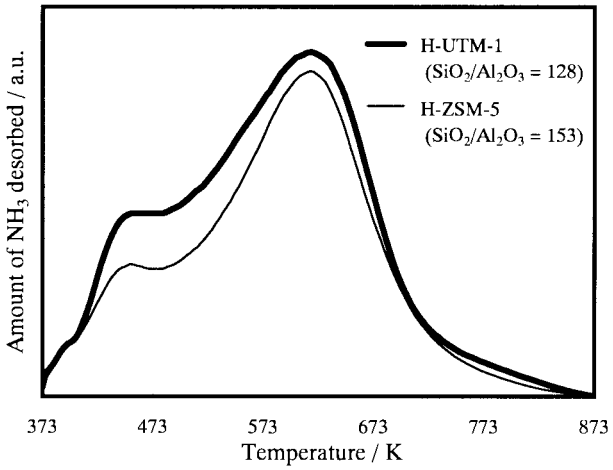

Figure 3. NH_3 TPD profiles of H-UTM-1 and H-ZSM-5.

Figure 3 compares the NH_3 TPD profiles of these two proton type zeolites. Their closely similar desorption profiles indicate that the acidity of H-UTM-1 is almost as strong as that of H-ZSM-5, reflecting their structural similarity.[8] The amount of acid sites, estimated from area of desorption peak centered at 613 K by using JRC-Z5-25H with 0.99 $mmol \cdot g^{-1}$ of acid site as reference, are 0.22 and 0.18 $mmol \cdot g^{-1}$, respectively. For both H-UTM-1 and H-ZSM-5, the acid amount normalized by the Al incorporated is 0.9. Considering that UTM-1 has eight T sites per unit cell that might be inaccessible to NH_3, this accordance might suggest the absence of Al at this site.

Table 2 exhibits their catalytic properties in terms of the conversions in acid catalyzed reactions. In the hydrolysis of ethyl acetate, H-ZSM-5 shows higher conversion than H-UTM-1. As described above, they can be considered to have similar acidity. Therefore, the small 8-membered ring aperture and 1-dimentional pore system of H-UTM-1 would be responsible for the lower activity, limiting the diffusion of reactant molecules into micropores, in contrast to the case of H-ZSM-5 having 10-membered ring aperture and 3-dimentional pore system. On the other hand, UTM-1 shows higher catalytic activity in the inter-exchange of benzyl benzoate. Since this reactant molecule can enter into neither 10- nor 8-membered ring channels, this reaction should occur at the outer surface of catalysts. Thus, in this case larger outer surface area of UTM-1 (Table 1) achieves the higher catalytic conversion. In this way, UTM-1 is expected to show high catalytic activity for bulky reactant molecules owing to its large outer surface area, although its small aperture restricts the diffusivity of reactant molecules into the pore system.

Table 2. Catalytic properties of H-UTM-1 and H-ZSM-5 having similar SiO_2/Al_2O_3 ratio

Catalyst	Pore opening[a]	Conversion / %	
		Hydrolysis of ethyl acetate[b]	Inter-exchange of benzyl benzoate[c]
H-UTM-1(128)	10	2.2	51.5
H-ZSM-5(153)	8	4.8	30.5
no catalyst	–	0.0	0.0

Values in parenthesis indicate the SiO_2/Al_2O_3 ratio. [a]Pore opening in terms of the number of oxygen. [b]Catalyst 0.10 g, ethyl acetate 0.20 g, H_2O 10.00 g, 333 K, 4 h. [c]Catalyst 0.05 g, benzyl benzoate 0.21 g, 1-hexanol 20.44 g, 423 K, 1 h.

References and Notes

Current address: Department of Chemistry and Biochemistry, Arizona State University, Tempe, AZ 85287-1604, U.S.A.

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