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Solid acid porous materials for the catalytic transformation of 1-adamantanol

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Abstract

Catalytic transformation of 1-adamantanol has been carried out over nano-porous materials with pore sizes ranging from 0.55 to 6 nm and acidic sites ranging from 0.07 to 4 mmol/g. Zeolites viz., H-USY, H-beta, H-mordenite, H-L and H-ZSM-5, and sulfonic-acid functionalized mesoporous silica viz., MCM-41, SBA-15 and SBA-16, were employed for the reaction. Shape selectivity in a confined micropore plays a role with the combination of medium strength acid sites toward formation of desirable 2-derivatives, which comprises a maximum amount of 2-adamantanone.

Keywords: Adamantanol; Mesoporous silica; Zeolites; Isomerization; Solid acid; Shape selectivity

1. Introduction

In recent years, production of 2-adamantanone among adamantane derivatives have come spotlighted as important intermediates of a variety of pharmaceuticals and functional materials [1–7]. It is reported by Geluk and Schlatmann [8,9] that 2-derivatives of adamantane can be obtained at a maximum yield by heating 1-adamantanol in concentrated sulfuric acid. The problem of this method is that a large amount of concentrated sulfuric acid is used, thereby necessitating the use of expensive and corrosion-resistant equipment and a material. We have recently reported heterogeneous transformation of 1-adamantanol over solid-acid catalysts such as zeolites [10]; 1-adamantanol is isomerized to 2-adamantanol by a 1,2-hydride shift, followed by an intermolecular disproportionation/dehydration of 2-adamantanol to 2-adamantanone. The overall acidic sites and acidic strength play an important role in the product distribution. In this study, we substantiate the effect of pore size of the catalysts on the formation of 2-derivatives, maintaining similar number acid sites as close as possible. Hence, we have given attention using zeolites viz. USY, beta, mordenite and ZSM-5 for pore size less than 1 nm and in utilizing sulfonic-acid functionalized mesoporous silica (SO_3H-mesoporous silica) viz. SO_3H-SBA-15, SO_3H-SBA-16 and MCM-41 synthesized with surfactant of different chain-length such as SO_3H-MCM-41_C_{16}, SO_3H-MCM-41_C_{12} and SO_3H-MCM-41_C_8 for pore size larger than 1 nm as the development of strongly Brønsted acidic solids with controlled mesostructures is an area of significant interest in catalysis.

2. Experimental procedures

Zeolites beta, mordenite, ZSM-5 and L employed in this study obtained from Tosoh Corporation while USY was supplied by Catalysts & Chemicals Co. Ltd. Sulfonic-acid functionalized mesoporous silica viz., MCM-41, SBA-15 and SBA-16 were prepared in this study. The procedure was similar to that described in the literature for the sulfonic acid functionalization of mesostructured silica [11–16]. The synthesized and calcined materials were characterized by XRD (Bruker-AX; MO3X-HF system with Cu Kα radiation), and the acidity of the materials was determined by temperature-programmed desorption (TPD) of ammonia. Nitrogen-adsorption measurements were carried out using Autosorb-1 Quantachrome instruments.

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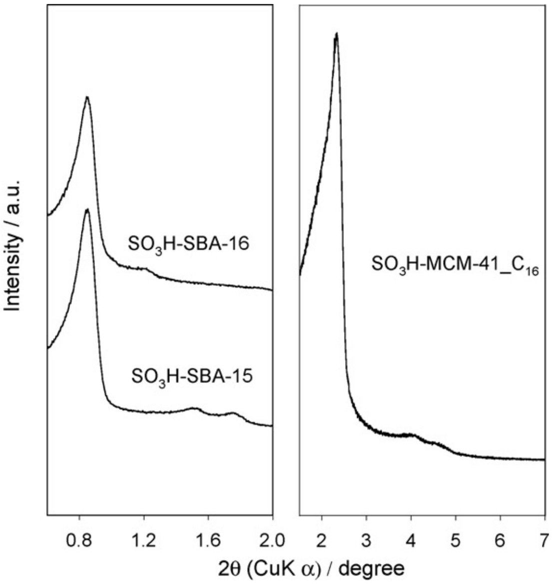

Fig. 1. XRD patterns of SO$_3$H-mesoporous silica used in this study.

Catalytic transformation of 1-adamantanol was carried out in liquid phase where the reaction flask was filled with 0.26 mmol of 1-adamantanol, 40 mg of the catalyst and 4.2 mmol of chloroacetic acid as a solvent. The reaction was carried out at 150 °C typically for 4 h. After the reaction, the product mixture was extracted with toluene and acetone. Then the products were analyzed by a gas-chromatograph (Shimadzu GC-17A) using *n*-nonane as an internal standard.

3. Results and discussion

3.1. Characterization

Powder X-ray diffraction patterns of both the samples synthesized and obtained from the industry exhibited a purity of the desired phase. XRD patterns of the sulfonic-acid functionalized mesoporous silica are shown in Fig. 1. The figure exhibited the presence of mesophase after functionalizing sulfonic acid with each mesoporous silica. Textural properties along with acidity for both zeolites and sulfonic-acid functionalized mesoporous silica are presented in Table 1.

3.2. Adamantanol transformation

1-Adamantanol (1-AdOH) transformation over acid sites results in various products viz. adamantane (AdH), 1-adamantyl acetate (1-AdOAc), 1-adamantyl chloride (1-AdCl), 2-adamantanol (2-AdOH), 2-adamantyl acetate (2-AdOAc), 2-adamantanone (2-AdO) and some of polymerized products [10]. During the catalytic reaction 1-AdOH was first stabilized with chloroacetic acid and formed 1-AdOAc, establishing equilibrium with 1-AdOH. Thereafter, 1-AdOH adsorbs over the acid sites to form 1-adamantyl cation and this might undergo 1,2-hydride shift to form 2-adamantyl cation, which is on further hydroxylation resulting in the formation of 2-AdOH. The rate of 1,2-hydride shift has been proved to be strongly influenced by the acidity of catalysts [7,8,17]. 2-Adamantyl cation also undergoes acetylation in the presence of chloroacetic acid to form 2-AdOAc. AdH was formed from 1-adamantyl cation and 1-AdOH/1-AdOAc by hydride shift, and the hydroxyadamantyl cation undergo ring-opening under acidic conditions resulting in the formation of polymerized products [18]. 1-Adamantyl cation might react with Cl$^-$ to form 1-chloroadamantane, where the acidity of the solvent is not sufficient to form 2-adamantyl cation through 1,2-hydride shift. 2-AdOH/2-AdOAc was formed from 1,2 hydride shift of 1-adamantyl cation and adamantane, which is easily transformed to 2-AdO on the acidic sites (bimolecular transformation followed by dehydration) to form equimolar quantities of 2-AdO and AdH [8–10]. These reaction steps were summarized in Fig. 2.

Table 2 presents the conversion of 1-adamantanol and product yields in mole percent over sulfonic-acid functionalized mesoporous silica and zeolites. The results presented in Table 2 reveal that conversion of 1-adamantanol after 4 h reaction time is almost similar irrespective of the catalysts used. The product distribution was, however, completely different. The desired 2-derivatives were formed in a considerable amount over H-USY followed by H-beta, while the formation of 2-derivatives over sulfonic-acid functionalized mesoporous silica was low. The total yield of 2-derivatives (comprises 2-AdO, 2-AdOAc and 2-AdOH) is ca. 24 mol.% over H-USY followed by H-beta (ca. 15.8 mol.%), and the maximum yield obtained from SO$_3$H-mesoporous silica (SO$_3$H-MCM-41_C$_8$) was only 2.6 mol.%. Mesoporous silica facilitates formation of

Table 1
Textural properties of zeolites and sulfonic-acid functionalized mesoporous silica

Sample (Si/Al ratio)	S_{BET} (m^2/g)	Pore size (nm)	Acid sites (mmol/g)
SO$_3$H-SBA-15	595	5.8	0.34
SO$_3$H-SBA-16	625	3.4	0.29
SO$_3$H-MCM-41_C$_{16}$	780	2.3	0.53
SO$_3$H-MCM-41_C$_{12}$	790	1.5	0.51
SO$_3$H-MCM-41_C$_8$	785	1.4	0.46
H-USY(100, 55, 33, 15, 10, 5.0)	650	0.74	0.16, 0.29, 0.49, 1.5, 2.7
H-L(3.0)	–	0.71	4.0
H-beta (240, 55, 20)	680	0.66	0.07, 0.30, 0.81
H-MOR(5.1)	–	0.65	1.6
H-ZSM-5(12)	–	0.55	1.3

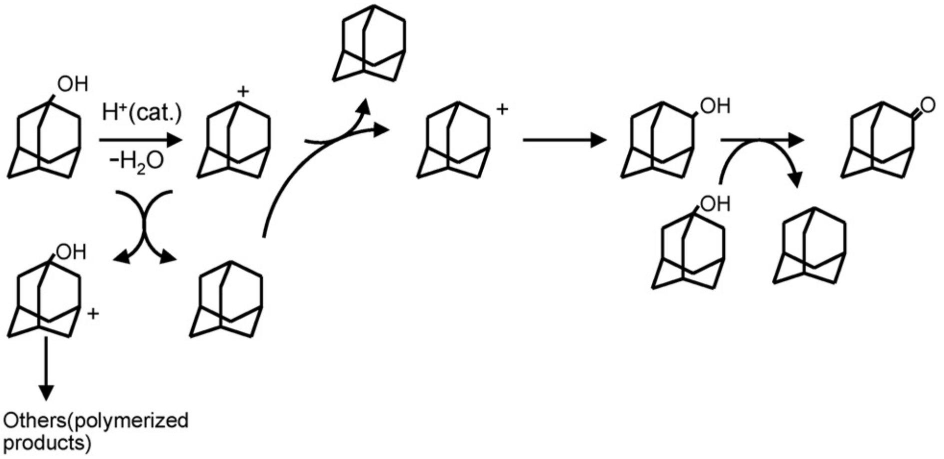

Fig. 2. Proposed reaction scheme of the isomerization of adamantane derivatives.

Table 2
Conversions and product distributions in 1-adamantanol transformation on various porous catalysts

Catalyst	Conversion (mol.%)	Yield (mol.%)							
		1-AdOAc	AdH	1-AdCl	2-AdOAc	2-AdOH	2-AdO	2-Derivatives total	Others
Blank	78	58	1.9	13	0.0	0.0	0.0	0.0	5.0
SO_3H-SBA-15	95	13	26	9.1	0.4	0.8	0.1	1.3	46
SO_3H-SBA-16	97	2.7	25	16	0.3	0.1	0.1	0.5	53
SO_3H-MCM-41_C_{16}	98	2.2	31	7.9	1.0	0.1	0.1	1.2	56
SO_3H-MCM-41_C_{12}	90	6.2	23	7.7	2.0	0.1	0.2	2.3	51
SO_3H-MCM-41_C_8	95	16	14	3.8	0.4	2.1	0.1	2.6	59
H-USY (55)	99	1.5	39	0.6	5.0	0.6	18	24	34
H-L	92	55	0.7	20.0	0.0	0.3	0.0	0.3	16
H-beta (55)	97	7.1	35	7.5	7.6	0.3	7.9	16	32
H-MOR	95	14	19	9.0	1.5	0.1	1.8	3.4	50
H-ZSM-5	96	15	15	36	0.0	0.3	0.2	0.5	29

a considerable amount of polymerized products followed by the formation of AdH.

Fig. 3 presents the yield of 2-derivatives over zeolites and SO_3H-mesoporous silica as a function of pore size. It is interesting to note that among mesoporous silica, although the yield of 2-derivatives was much lower than zeolites, decrease in pore size increased the yield of 2-derivatives. It might be possible that increasing pore size the solid-acid material might behave almost like an acid solvent, leading to less reactivity which was higher in a confined microporous space. Acidity is totally changed when zeolite type used is changed, even though we would like to change only the pore size of zeolite catalyst. The effect of zeolite when changing zeotypes must be carefully compared. On the contrary, sulfonic acid-anchored mesoporous silica can change only the pore size without changing other important parameters such as acidity. It is mainly because acid function is attached after preparation of mesoporous silicas having different pore sizes. Therefore, important results and conclusions could be drawn by adopting such kinds of porous material for this investigation. We substantiate here that confined pore size is essential toward the formation of 2-derivatives [10]. Although the pore size of zeolites used in this study was almost similar, H-L and H-mordenite exhibited a low yield as that of mesoporous silica. 2-AdO was the major composition in the product mixture over all the catalysts. It should be noted that 2-AdO is formed by shape-selective bimolecular transformation and dehydration of 1-AdOHs or 2-AdOHs [10]. Hence, it is also possible that over mordenite and L (Fig. 4), channel size might restrict the transition-state of 1-AdOH/2-AdOH, and hence the formation of a small amount of 2-derivatives.

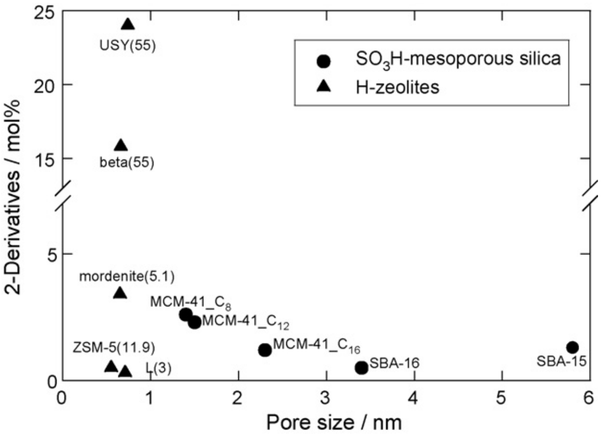

Fig. 3. Dependence of the pore size of catalysts on the yield of 2-derivatives in transformation of 1-adamantanol.

The pore size is effective for the formation of 2-derivatives selectively, at the same time; we have to mention here the

	Pore size (nm)	Yield / mol%	
			2-Derivatives
USY	0.74***	39.3	24.0
Beta	0.66 x 0.67** 0.56 x 0.56*	35.0	15.8
MOR	0.65 x 0.70*	19.0	3.3
L	0.71 x 0.71*	0.7	0.3

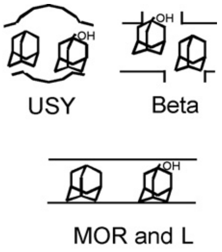

Fig. 4. Influence of micropore size for the bimolecular transformation of adamantanes.

influence of acidity also. Fig. 5 illustrates the difference in acid amount among USY, beta and mesoporous silica. Comparing the same zeolite by varying the acid amount, increase of acid amount increased the 2-derivative sharply and further increase in acidity decreased the 2-derivatives moderately. This is in well agreement with the results reported already [10]. Acidic strength also influences on the catalytic properties; increasing acid strength decreased the formation of 2-derivatives and at the same time polymerized product increased. Fig. 6 shows the influence of acid strength as a measure of heat of adsorption of ammonia [19–21]. Increasing trend of polymerized product at the expense of 2-derivatives is ascribed to the ring-opening of hydroxyadamantyl cation under strong acid sites, which mainly leads to the polymerized product. To decrease the polymerized product, further addition of adamantane along with 1-adamantanol was proven to be necessary. Adamantane suppresses the formations of hydroxyadamantyl cation and adamantane from 1-adamantanol, thereby reduces a larger extent of polymerized product. For instance, in the case of SO_3H-MCM-41_C_{16}, the 2-derivative is only 1.3 mol.% which is increased to 7.4 mol.% by the addition of adamantanol along with the reactants. The yields of others, mainly polymerized products, on MCM-41 and SBA-15 catalysts without attaching SO_3H were 1.8 and 10%, respectively. Therefore, some effect of pore size and volume on the yield of polymerized products might exist when such a large mesoporous material is used, but the results obtained by use of SO_3H-anchored MCM-41 and SBA-15 were derived from the strong acidity of SO_3H, not from the mesostructure.

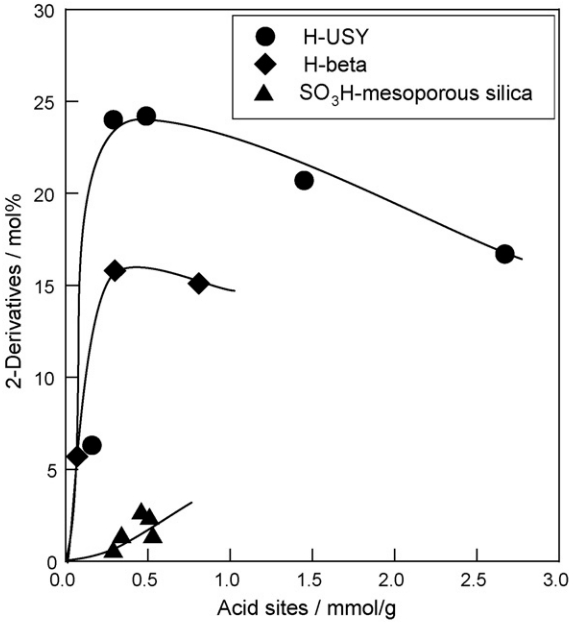

Fig. 5. The yield of 2-derivatives as a function of the amount of acidic sites on H-USY, H-beta zeolites and SO_3H-MCM-41 mesoporous silica.

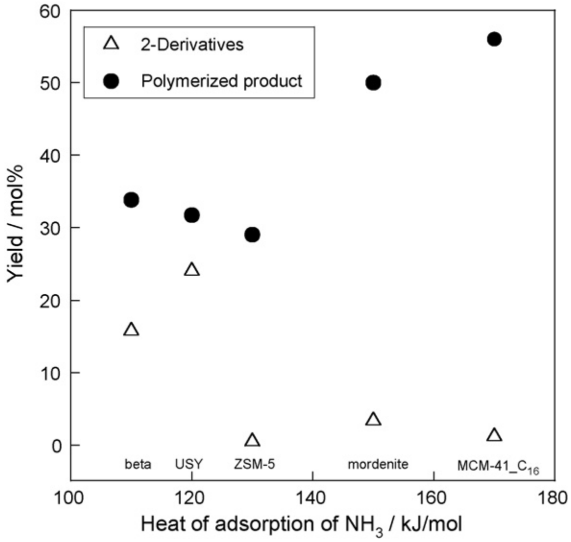

Fig. 6. Effect of acidic strength of the catalysts on the yield of 2-derivatives and polymerized products.

4. Conclusions

A detailed study on the catalytic transformation of 1-adamantanol by varying the pore size and acidity reveals that a confined microporous structure plays a major role in the formation of 2-derivatives of adamantane viz. 2-adamantanol, 2-adamantyl acetate and 2-adamantanone. Hence, the microporous materials particularly USY possessing a large cage exhibit a critical catalytic performance in the shape-selective formation of 2-derivatives compared to sulfonic-acid functionalized mesoporous silica.

References

[1] S. Shinachi, M. Matsushita, K. Yamaguchi, N. Mizuno, J. Catal. 233 (2005) 81.
[2] K. Otsuka, I. Yamanaka, Eur. Pat. Appl., EP 1 408 023 A1, 2002.
[3] R. Neumann, M. Dahan, J. Am. Chem. Soc. 120 (1998) 11969.
[4] D. Farcasiu, A. Ghenciu, J.Q. Li, J. Catal. 158 (1996) 116.
[5] Y. Shiota, N. Kihara, T. Kamachi, K. Yoshizawa, J. Org. Chem. 68 (2003) 3958.
[6] Y. Ishii, T. Iwasawa, S. Sakaguchi, K. Nakayama, Y. Nishiyama, J. Org. Chem. 61 (1996) 4520.
[7] H. Stetter, Angew. Chem. 66 (1954) 217.
[8] H.W. Geluk, J.L.M.A. Schlatmann, Tetrahedron 24 (1968) 5361.
[9] H.W. Geluk, J.L.M.A. Schlatmann, Tetrahedron 24 (1968) 5369.
[10] S.P. Elangovan, K. Inoue, T. Okubo, A. Kojima, M. Ogura, Ind. Eng. Chem. Res. 46 (2007) 1039.
[11] D. Margolese, J.A. Melero, S.C. Christiansen, B.F. Chmelka, G.D. Stucky, Chem. Mater. 12 (2000) 2448.
[12] W.M. Van Rhijn, D.E. De Vos, B.F. Sels, W.D. Bossaert, P.A. Jacobs, Chem. Commun. (1998) 317.

[13] W.M. Van Rhijn, D.E. De Vos, W.D. Bossaert, J. Bullen, B. Wouters, P. Grobet, P.A. Jacobs, Stud. Surf. Sci. Catal. 117 (1998) 183.
[14] I. Diaz, C. Marquez-Alvarez, F. Mohino, J. Perez-Pariente, E. Sastre, J. Catal. 193 (2000) 283.
[15] S. Hamoudi, S. Kaliaguine, Micropor. Mesopor. Mater. 59 (2003) 195.
[16] S. Sreevardhan Reddy, B. David Raju, V. Siva Kumar, A.H. Padmasri, S. Narayanan, K.S. Rama Rao, Catal. Commun. 8 (2007) 261.
[17] N.C. Deno, H.J. Peterson, G.S. Saines, Chem. Rev. 60 (1960) 7.
[18] A.E. Lukach, A.N. Santiago, R.A. Rossi, J. Org. Chem. 62 (1997) 4260.
[19] M. Niwa, N. Katada, M. Sawa, Y. Murakami, J. Phys. Chem. 99 (1995) 8812.
[20] N. Katada, Y. Kageyama, M. Niwa, J. Phys. Chem. B 104 (2000) 7561.
[21] Y. Miyamoto, N. Katada, M. Niwa, Micropor. Mesopor. Mater. 40 (2000) 271.