doi:10.1246/cl.2011.558

Novel Method for Generating Large Mesopores in an Amorphous Silica–Alumina by Controlling the Pore Size with the Gel Skeletal Reinforcement and Its Catalytic Cracking Properties as a Catalyst Matrix

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The pore size of amorphous silica and silica–alumina with large mesopores was controlled for the first time in the range of 5 to 30 nm by gel skeletal reinforcement. The conversion and the ratio of multi-branched to single-branched products increased with increasing the pore diameter of silica–alumina in catalytic cracking of *n*-dodecane with its use as a matrix.

In recent years, the sol–gel method to prepare various inorganic materials has extensively been studied,[1] and among them, much attention has been focused on the preparation of silica and silica–alumina aerogels because they have a large surface area, high porosity, low bulk density, extremely low thermal conductivities, etc.[2–7] In preparation of these materials, supercritical or subcritical conditions[2–6] and alkoxysilylation[4,5] or methylsilylation[7–9] are used to inhibit the extensive shrinkage of large pores during removal of entrapped solvent from the wet gel. In particular alkoxysilylation and methylsilylation are promising methods because they can produce aerogels at ambient pressure by inhibiting rapid hydrolysis and the successive condensation which leads to the shrinkage of pores. Although these methods include the concept of the gel skeletal reinforcement as a major effect, the importance of this concept was not necessarily stressed and has not been described in detail. Further, most of these reports are related to the preparation of bulk materials, and there are very few reports where the extremely large mesopores have been utilized for various catalyses or supports for catalysts.

On the other hand, catalysts in FCC (fluid catalytic cracking) generally include not only zeolite as a major component but also silica–alumina as a matrix.[10] Although zeolite is a very active catalyst,[11] the pore size of zeolite is relatively small. So the pores of zeolite, which mainly consist of micropores, are disadvantageous to carry and diffuse hydrocarbons with large molecular structure such as vacuum gas oil or atmospheric residue.[12,13] Although silica–alumina is used to control activity of zeolite or selectivity of catalytic cracking reactions, academic studies of silica–alumina are fewer than those of zeolite in this field.[14–18] Recently we have reported that silica–aluminas with about 5 nm mesopore prepared using malic acid influence the production of branched hydrocarbons in catalytic cracking of *n*-dodecane.[14]

The purpose of this research is to control the pore size of silica and silica–alumina by the gel skeletal reinforcement and to prepare large mesopore materials which promote the rapid diffusion of molecules and the preferential formation of branched hydrocarbons when used in catalytic cracking as matrices. In the gel skeletal reinforcement, the strength of silica gel skeleton was effectively enhanced by aging with TEOS/2-propanol mixed solution and the shrinkage of the pores was inhibited. Consequently the silicas with large mesopore were prepared, and their pore sizes were controlled by the amount of the TEOS/2-propanol solution. Their catalytic properties were investigated in catalytic cracking of *n*-dodecane.

Silica–alumina was synthesized by the acid–base-catalyzed sol–gel process including the gel skeletal reinforcement, followed by impregnation. A typical method was as follows: Tetraethyl orthosilicate (TEOS) was used as a precursor of silica. To TEOS/2-propanol solution was added 0.1 wt % HCl at 25 °C, and the mixture was stirred for 30 min in a sealed bottle. After pH of the solution was adjusted to 5 by adding aqueous NH_3 solution, the gelation was performed at 50 °C. After gelation, temperature was maintained for 5 h. Then the gel was immersed in deionized water at 50 °C for 24 h. After that, the gel was taken out from water. The gel was cut to a few millimeters of fragments and was washed with 2-propanol for 5 min five times at 50 °C to remove the remaining water in pores thoroughly. After that, the gel was maintained in 80% TEOS/20% 2-propanol solution at 50 °C for 48 h. The weight ratio of TEOS for the gel skeletal reinforcement in this solution was 100, 200, or 362 for 100 of TEOS silica precursor. That is, 100 means that the amount of TEOS in the reinforcement solution was the same as the amount of TEOS silica precursor. 80% TEOS/20% 2-propanol reinforcement solution was removed, and the reinforced gel was washed with 2-propanol for 5 min five times at 50 °C to remove the remaining 80% TEOS/20% 2-propanol solution. After maintaining the obtained gel at 70 °C for 72 h, the silica gel was calcined at 600 °C for 3 h. Aluminium species was introduced into prepared silica using 2-butanol solution of aluminium tri-*sec*-butoxide (ASB) by impregnation to form 5 wt % Al_2O_3 in silica–alumina after successive calcination at 600 °C for 3 h. Synthesized silica–alumina was mixed with alumina sol (as an alumina binder, Cataloid AP-1, Shokubai Kasei), β-zeolite (HSZ-940 HOA, Tosoh), and 2-propanol. It was shaped into a cylindrical pellet (diameter 0.5 mm, length <2 mm) after kneading. The prepared pellets were calcined at 600 °C for 3 h. The amounts of silica–alumina, alumina from the binder, and zeolite in the mixed catalyst were 58, 16, and 26 wt %, respectively.

The structural characteristics of the catalysts were measured by N_2 adsorption (Bel Sorp mini), X-ray diffraction (XRD, Rigaku RAD-C), and NH_3 adsorption and desorption (GC-TCD, Shimadzu GC-8A).

In naming the samples, the weight ratio of 100, 200, or 362 of reinforcing TEOS against 100 of TEOS silica precursor was represented in front of SiO_2. For silica–alumina samples, SA was

Table 1. Surface areas, pore volumes, and pore diameters of silica, silica–alumina, zeolite, and mixed catalysts

Catalyst	BET			BJH		
	Surface area /$m^2 g^{-1}$	Pore volume /$cm^3 g^{-1}$	Pore diameter /nm	Surface area /$m^2 g^{-1}$	Pore volume /$cm^3 g^{-1}$	Pore diameter /nm
$0SiO_2$	837	1.43	6.8	703	1.30	7.1
$100SiO_2$	754	2.57	13.7	721	2.51	18.5
$200SiO_2$	598	2.94	19.7	578	2.90	28.3
$362SiO_2$	588	3.14	21.4	555	3.09	32.6
100SA-5	737	2.49	13.5	719	2.43	18.5
200SA-5	569	3.11	21.8	634	3.08	28.3
362SA-5	621	3.04	19.6	560	2.96	28.3
MAT-100SA-5	567	1.50	10.6	467	1.42	12.1
MAT-200SA-5	530	1.60	12.1	394	1.52	24.5
MAT-362SA-5	512	1.80	14.1	376	1.70	32.6
ref.SA	457	0.87	7.6	537	0.86	6.2
β-Zeolite	613	0.32	2.1	24	0.07	3.3
MAT-(ref.SA)	765	0.64	5.7	340	0.57	6.2

used instead of SiO_2. For the mixed catalyst with zeolite and the binder, MAT- was represented in front of sample name of SA.

Catalytic cracking of *n*-dodecane was carried out using a fixed bed reactor (length 300 mm, i.d. 8 mm, stainless) under the conditions of 500 °C, catalyst 1 g, *n*-dodecane 1.3 mL min^{-1}, 80 s, WHSV 58.5 h^{-1}. After the reaction, N_2 was introduced at 30 mL min^{-1} for 30 min, gas products were recovered in a tedlar bag, and liquid products were collected in a cold trap. The gas and liquid products were determined by GC referring to JIS K 2536-2.

There is no peak in XRD patterns of synthesized silica and silica–alumina, and it was confirmed that they were amorphous. Results from N_2 adsorption are summarized in Table 1. When silica gel was reinforced by TEOS solution, silica with large mesopores was prepared. For example, BJH surface area, pore volume, and pore diameter (PD) for $100SiO_2$ were 721 $m^2 g^{-1}$, 2.51 $cm^3 g^{-1}$, and 18.5 nm, respectively, and were maintained after impregnation of Al species. Without the gel skeletal reinforcement, these three values were 703 $m^2 g^{-1}$, 1.30 $cm^3 g^{-1}$, and 7.1 nm, respectively. The porosity of the material can be increased to a considerable extent by removing water completely before aging in 2-propanol solvent. However, surface areas, pore volumes, and pore diameters of silica and silica–alumina prepared with the gel skeletal reinforcement were considerably large compared with those for conventional silica and silica–alumina. For example, three values of ref.SA (JRC-SAH-1 supplied from Catalysis Society of Japan), which is prepared by a conventional method using water glass and aluminum sulfate, were 537 $m^2 g^{-1}$, 0.86 $cm^3 g^{-1}$, and 6.2 nm(PD), respectively. Although the Ostwald ripening effect to strengthen a gel surface is often described,[2–9] our results suggest that the thorough removal of water in the inside of the gel and the gel skeletal reinforcement are essential for making large mesopores. Figure 1 shows the schematic mechanism of the gel skeletal reinforcement. The thorough removal of water in the inside of the gel in solvent exchange inhibits the hydrolysis of reinforcing TEOS/2-propanol solution. The surface silanol is modified by TEOS to form the new surface covered by triethoxysilyl groups which inhibit the further condensation of the gel skeletal structure in the absence of water. Surface areas and pore volumes by the BET method were almost the same as those by BJH, indicating that most pores of silicas and silica–aluminas prepared by the gel skeletal reinforcement consist of mesopores. Figure 2 shows the BJH pore size distribution. Silica and silica–alumina had larger and broader pore size distribution with increasing the amount of TEOS solution for reinforcement. When 362 wt % TEOS was used for reinforcement, the pore volume and pore diameter measured by BJH reached about 3 $cm^3 g^{-1}$ and 30 nm, respectively. To our knowledge, such high values for materials calcined at 600 °C for 3 h have never been obtained with any other methods. Although some papers reported higher porosity of materials,[6–8] thermal histories for the materials were about 200 °C even at maximum which is much lower than our condition, 600 °C for 3 h. When silica–aluminas were mixed with zeolite and alumina sol (binder), surface areas and pore volumes of mesopores measured by the BJH method decreased; however, almost the same pore diameters and pore distributions were maintained.[19]

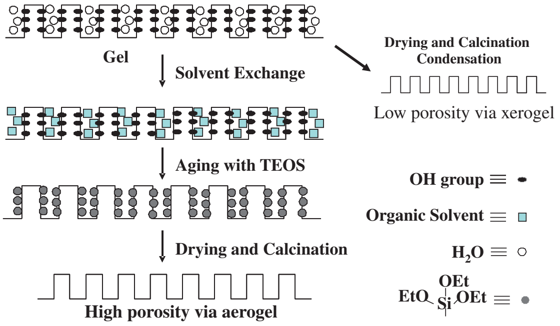

Figure 1. Schematic mechanism of the gel skeletal reinforcement.

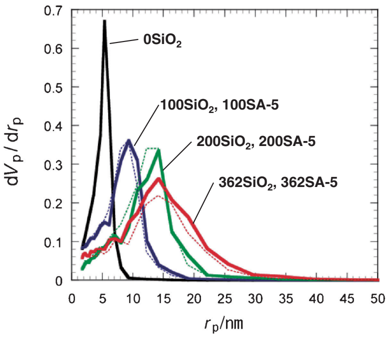

Figure 2. BJH pore-size distribution of silica and silica–alumina: Solid line, silica; dotted line, silica–alumina; r_p, pore radius.

The amounts of NH_3 desorbed from the mixed catalysts were slightly lower than that for zeolite as shown in Table 2. The conversion of *n*-dodecane with single use of zeolite was 84%, and the yield of paraffins was much larger than those of olefins and aromatics as shown in Figure 3.[20] This shows that significant hydrogen transfer to olefins in the formation of aromatics proceeded. When silica–alumina was used in cracking of *n*-dodecane, the conversion was only a few percent and the selectivity for olefin was rather high for each catalyst. The results show that the ability of cracking and hydrogen transfer in the catalytically active sites is limited to extremely low level for single use of silica–alumina. When mixed catalysts were

Table 2. Product distribution and catalytic properties of catalyst[a]

Catalyst	Product distribution /%			Conv. /%	NH_3[b] × 10^4 /mol g^{-1}	Parameters in gasoline fraction			
	C1–C4	Gasoline (C5–C11)	C12–			Olefin/ Paraffin	*iso*• /*n*-	Yield of single branch /%	Yield of multi branch /%
β-Zeolite	58	42	0.5	84	6.2	0.46	2.9	19	1.2
MAT-(ref.SA)	47	53	0.6	78	5.8	0.76	2.7	21	1.8
MAT-100SA-5	38	62	0.2	60	5.1	0.67	2.8	21	2.4
MAT-200SA-5	41	58	0.5	73	5.4	0.55	3.3	23	3.0
MAT-362SA-5	56	44	0.1	83	4.1	0.58	2.6	19	3.0

[a] React. Temp. 500 °C, catalyst 1 g *n*-dodecane 1.3 mL min^{-1}, 80 s, WHSV 58.5 h^{-1}. [b] Measured by NH_3 TPD.

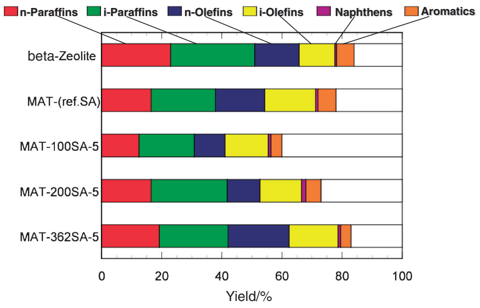

Figure 3. Yields for paraffins, olefins, naphthenes, and aromatics on catalytic cracking: React. Temp. 500 °C, catalyst 1 g, *n*-dodecane 1.3 mL min^{-1}, 80 s, WHSV 58.5 h^{-1}.

prepared with zeolite and silica–alumina with large mesopore, the comparable activities were obtained in cracking of *n*-dodecane although the mixed catalyst included only 26 wt % zeolite. The conversion of dodecane for the mixed catalyst, MAT-362SA-5, was 83% which was almost the same as that for single use of zeolite, indicating that the presence of larger mesopores in the mixed catalyst promoted the diffusion of the reactant molecules effectively. As shown in Figure 3, the difference between the product distributions of the mixed catalysts and the single use zeolite was not so large although the yield of paraffins for the mixed catalysts was slightly less than that of the single use zeolite. To clarify the difference between the mixed catalysts and the single use zeolite or the mixed catalyst using a conventional silica–alumina (refSA), the product distribution of gas (C1–C4) and gasoline (C5–C11) fractions and some parameters in the gasoline fraction were compared, and the results are summarized in Table 2. In the mixed catalysts using the gel skeletal reinforcement, MAT-100SA-5 and MAT-200SA-5, the distribution of gasoline increased although the conversions slightly decreased. The product distribution of the mixed catalyst, MAT-362SA-5, was very similar to that of single use zeolite probably because the conversion was similar to that of single use zeolite. However, the major differences were observed in the yields of multi-branched products and single-branched products (Table 2) and the ratio of those yields (m/s) (Figure 4) for the mixed catalysts, which are important factors to increase the research octane number (RON).[14] In particular, the m/s ratios of the mixed catalysts using the gel skeletal reinforcement were much larger than those for single zeolite and the mixed catalyst with conventional silica–alumina (Figure 4). The approximate linear relationship can be found between the m/s ratios and the values of pore diameters of these catalysts in Figure 4. These results suggest that the presence of larger mesopore in the matrix of the cracking catalysts would promote not only the diffusion of reactant molecules to approach acid sites of zeolite and to produce bulky branched products but also the effective elimination of the branched products to prevent the excess cracking of those products.

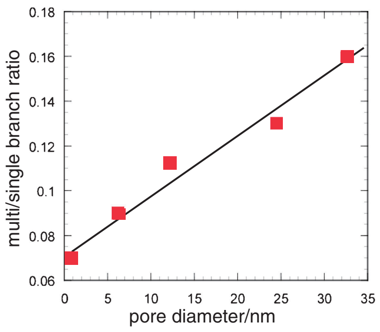

Figure 4. Effect of BJH pore diameter on multi/single branch ratio: Except zeolite, values in the horizontal line represent peaks of BJH pore diameter.

This work was entrusted by the Japan Petroleum Energy Center under a subsidy of the Ministry of Economy, Trade and Industry.

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19 A supplementary material is available: Figure 5 Comparison of BJH pore-size distribution for silica–alumina, mixed catalyst and zeolite.
20 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html. Figure 6 Distribution of carbon numbers on catalytic cracking.