Catalytic Performance of Organically Functionalized Core/Shell Monodispersed Mesoporous Silica Spheres Containing an Adsorption Layer

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A new type of organically functionalized core/shell monodispersed mesoporous silica spheres (MMSS) containing catalytic sites (sulfonic acid groups) in the core portion and adsorption sites (hydrophobic organic functional groups) in the shell portion were successfully prepared by an expansion method. The acid catalytic activity could be enhanced drastically by the introduction of the shell layer.

Mesoporous silicas have attracted much attention because of potential applications in catalysis, adsorption, separation, and sensor design. Among them, sulfonic acid-functionalized mesoporous silicas are of great interest for the use in novel heterogenous catalyst in the field of green chemistry.[1] In addition, it is expected that the incorporation of hydrophobic moieties into mesopores would lead to the enhancement of catalytic performance due to changes in the adsorption and diffusion of reactants, products, and intermediate species. There have been some reports on the synthesis of organically functionalized mesoporous silicas containing sulfonic acid groups and other organic moieties in order to control the hydrophobic character of the surfaces of the mesopores.[2]

We have previously reported that monodispersed mesoporous silica spheres (MMSS) possessing highly ordered hexagonal fine mesopores can be obtained by reacting tetramethoxysilane (TMOS) and *n*-alkyltrimethylammonium halide (C_nTMAX, X = Cl and Br).[3] The catalytic activities of organically functionalized MMSS were higher than other types of mesoporous catalysts, and it is considered that the radially aligned mesopores in MMSS were very advantageous in terms of allowing access of reactants and the release of reaction products.[4] In addition, we have recently successfully synthesized a core/shell MMSS that has a hydrophilic core and a hydrophobic shell by the addition of different silica precursors to the original MMSS particles (expansion method).[5]

One of the challenges in utilizing core/shell structures is to create a novel catalyst consisting of a catalytic core and a functionalized shell that exhibits affinity to the appropriate reactants. We, therefore, attempted to prepare a core/shell MMSS consisting of a catalytic active site (sulfonic acid) in the core portion and an adsorption site (hydrophobic organic groups) in the shell portion by co-condensation/expansion method.[6] Three types of hydrophobic organic functional groups were used for the components of the shell portions: Methyl (M), ethyl (E), and propyl (P) groups. The mercaptopropyl groups in the core portion were then converted into sulfonic acid groups by oxidation, resulting in the production of sulfonic acid-core/hydrophobic-shell MMSS (SO_3H-core/hydrophobic-shell MMSS). Hereinafter in this paper, we abbreviate the synthesized materials as MS-X/Y, where MS denotes the mesoporous silica and X denotes the type of functional group in the core portion: SH (precursor; mercaptopropyl) or SO_3H (sulfonic acid). Y denotes the type of functional group in the shell portion.

For example, MS-SO_3H/M was synthesized by co-condensation/expansion method as follows. 7.04 g of hexadecyltrimethylammonium chloride (C_{16}TMACl) and 6.84 g of 1 M sodium hydroxide solution were dissolved in 1600 g of a methanol/water (50/50 = w/w) solution. Then, 34.7 mmol of a TMOS/3-mercaptopropyltrimethoxysilane (MPTMS) (=90/10 mol/mol) mixture was added to the solution with vigorous stirring at 298 K. After the addition of the TMOS/MPTMS mixture, the clear solution suddenly turned opaque and resulted in a white precipitate. Next, 3.42 g of 1 M sodium hydroxide solution and half the molar amount of TMOS/methyltrimethoxysilane (MTMS) (=90/10 mol/mol, 17.35 mmol) mixture were again added to the solution after a period of 30 min. After 8 h of continuous stirring, the mixture was aged overnight. The resulting white powder was then filtered off, washed three times with distilled water, and dried at 318 K for 72 h. Then, 1 g of the powder was refluxed in 100 mL of ethanol containing 1 mL of hydrochloric acid at 333 K for 3 h to remove the templates. The powder was filtered off, washed several times with ethanol, and finally dried at 318 K. The SH groups were converted into SO_3H groups by mild oxidation with H_2O_2.[4b]

Typical SEM image of the sulfonic acid-core/hydrophobic-shell MMSS sample is shown in Figure 1a. It is obvious that high monodispersity of the samples was retained (standard deviation: 5.9–8.0%), and the average diameters were substantially increased by the addition of the various shell layers (530–570 nm) when compared with the diameter of the MS-SO_3H particles (500 nm),

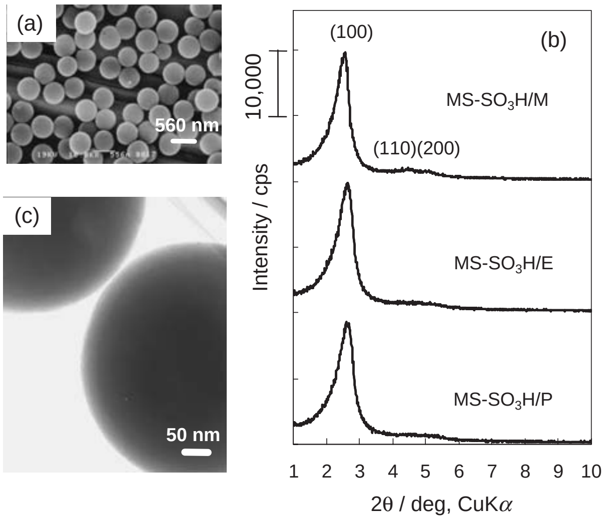

Figure 1. (a) Scanning electron micrograph of MS-SO_3H/P. (b) XRD patterns of the samples. (c) Transmission electron micrograph of gold incorporated MS-SH/P.

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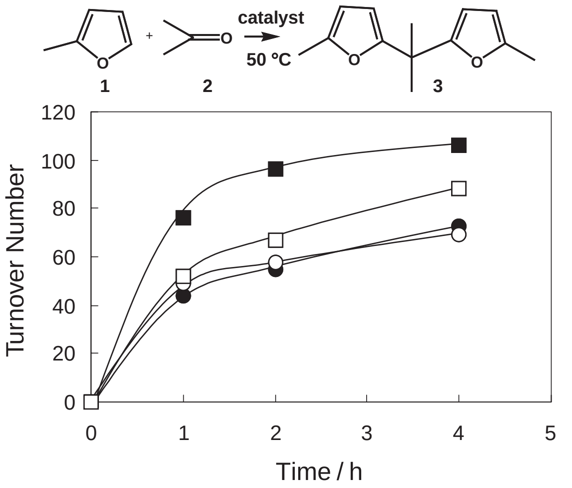

Figure 2. Changes in the activity of MS-SO_3H catalysts in condensation reaction of 2-methylfuran (**1**) and acetone (**2**): (●) MS-SO_3H/TMOS, (○) MS-SO_3H/M, (■) MS-SO_3H/E, (□) MS-SO_3H/P.

which was obtained without the further addition of any silica source. The XRD patterns of the core/shell MMSS samples have three peaks indexed to the d_{100}, d_{110}, and d_{200} diffractions, indicating that the mesopores of all of the samples were highly ordered (Figure 1b). Internal structure of the core/shell MMSS particles was clarified by TEM observation. SH-core/hydrophobic-shell MMSS sample was used as the specimen, taking advantage of the specific adsorption of gold ions to the mercapto group. The sample was immersed in a solution containing gold ions and then reduced chemically using formaldehyde. As shown in Figure 1c, an ovoid structure can be clearly seen because gold (dark part) was selectively adsorbed to the core portion. The thickness of the shells of MS-SH/P was estimated to be 35 nm from Figure 1c, and this value agreed well with the value obtained by calculation, which assumes a proportional distribution based on the average particle diameter derived from the SEM image. We also confirmed their chemical structures by Raman[6] and NMR analyses. The acidities (the number of H^+ per unit) of the core/shell MMSS samples were determined by a titration method. They were in the range between 0.49 and 0.62 mmol $H^+ g^{-1}$, and it was confirmed that sulfonic acid groups were successfully incorporated into MMSS samples. Consequently, we have succeeded for the first time in obtaining an organically separately functionalized core/shell MMSS by a co-condensation/expansion method.

The effect of the shell layer on the acid catalytic activities (Figure 2) was studied by using sulfonic acid-core/hydrophobic-shell MMSS samples. A reaction mixture consisting of 60 mg of the mesoporous silica catalyst and 0.6 g of 2-methylfuran (**1**) in 1.1 g of acetone (**2**) was heated at 323 K with constant stirring. The mixture was filtered and the solids were washed with fresh solvent. The filtrate and the cleaning fluid were combined and then analyzed using a gas chromatograph. Figure 2 shows the catalytic activities of various SO_3H-core/hydrophobic-shell MMSS. When MS-SO_3H was covered by a shell with an inorganic component (MS-SO_3H/TMOS), the TON value at 2 h was 55. However, the incorporation of organic functional groups into the shell layer led to increases in the TON. In particular, it became clear that the TON was drastically increased by incorporation of ethyl groups (MS-SO_3H/E), the TON value at 2 h for this catalyst was about 1.8 times higher than that for MS-SO_3H/TMOS. When a core/shell MMSS is used as a catalyst, it is assumed that adsorption of the reactant happens in the shell portion and that the reactant moves to a reaction site in a core portion, where the catalytic reaction then proceeds. Both methylfuran (reactant) and 2,2-bis(5-methylfuryl)propane (DMP; product) are hydrophobic, and the molecular size of the product is larger than that of the reactant. It is presumed from the above results that the incorporation of ethyl groups in the shell portion was the most effective because these had suitable molecular sizes and hydrophobicity[7] to enable these effects. Moreover, by incorporating hydrophobic groups into the shell layer, the water generated at the reaction is easy to be released out of the particles, and it is considered that the acid catalytic reaction was enhanced.

In conclusion, organically functionalized core/shell MMSS particles containing sulfonic acid groups in the core portion and hydrophobic groups in the shell portion were successfully synthesized for the first time by using a co-condensation/expansion method. These core/shell MMSS had well-ordered hexagonal mesopores, and it was confirmed from TEM observations that the compositions of the organic functional groups were clearly different in the core and the shell portions. It was found that the acid catalytic activities were most enhanced by incorporating ethyl groups into the shell portion. Thus, new types of selective catalyst and multistep reaction catalysts can be expected by incorporating organic functional groups or metals into the core portion and/or the shell portion of a core/shell MMSS.

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