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Synthesis of Mesoporous Molecular Sieves from Fluorosilicon Compound (H₂SiF₆)

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Mesoporous materials have attracted great interest in relation to the utilization as catalysts and separation media for industrial application. Recently, researchers at Mobil oil company[1,2] introduced a new family of silica-based mesoporous molecular sieves. Huo *et al.*[3] showed that synthetic approach can be generalized to non silica-based types such as antimony oxide, tungsten oxide, iron oxide, lead oxide, and zinc oxide. A few researchers[4,5] also introduced mesoporous materials prepared by using metal-alcoxide method. Recently, Daquing *et al.*[6] and Silva *et al.*[7] reported effects of F⁻ ion as the mineralizing agent on the synthesis of mesoporous material and zeolite respectively.

In the synthesis of silica-based MCM-41 materials, previous authors[1,2] make use of silica, sodium silicate, and Si-alcoxide as the silicon source. Especially, if silica is used as starting material, the types of silica to be capable of using are limited because of solubility. Iler[8] reports that the soluble silica, $Si(OH)_4$ is produced by dissolution of silica and ionized to $(HO)_3SiO_2^-$ or $(HO)_2SiO_2^{2-}$ above pH 9. The dissolution of silica accompanied by ionization is a basic step to lead hydrolytic polycondensation with charged micelle template. Therefore, synthetic condition should be forced in dissolution of silica. Strong quaternary ammonium bases as tetramethylammonium hydroxide dissolve silica rapidly, forming silicate salt. Considering this point, many researchers[1,2,9] make use of quaternary ammonium base as silica dissolution media and alkali source. However, silica cannot be dissoloved at atmospheric conditions, and easily soluble silica sources are limited. The problems associated with the use of conventional silica source could be markedly improved by using fluorosilicon compounds such as H_2SiF_6. However, there is no report in the literature on the synthesis of mesoporous materials using fluorosilicon compounds.

We now report a simple method for the synthesis of silica-based mesoporous molecular sieves (MMS) from fluorosilicon compound. The principle is based on the hydrolysis reaction of H_2SiF_6 in the ammonium-based cationic micelle template solution. This method is supposed to be markedly profitable in the industrial aspect because H_2SiF_6 could be industrially obtained from Silex and SiF_4 as well as industrial byproduct. Also, synthetic process could be simplified because products are manufactured for several hours at atmospheric condition.

The synthesis procedures are as follows: H_2SiF_6 solution (10wt% SiO_2) was prepared by gradually dissolving SiO_2 (Aldrich) to the 25wt% hydrofluoric acid (pH of solution: 1.5). Ammonia-surfactant mixed solution (NH_3: 5.1wt%, CTAB: 4wt%) was also prepared by adding ammonia water (Merck, 28 vol%) to the solution containing cetyltrimethylammonium bromide (CTAB) dissolved in distilled water. This solution exhibited pH 11.7. H_2SiF_6 solution (20 g) was added at once to the ammonia-surfactant mixed solution (130 g) stirred vigorously during 2 min at 60 °C. The pH becomes 7.5. White gel was formed abruptly within 10 sec and aged for 5 hours in a dryer at 70 °C. The molar composition of the white gel was 3.33 SiO_2, 1.43 CTAB, 39 NH_3, 22.5 HF, 722 H_2O. The resulting solid product was recovered by filtration, washed five times with distilled water, and dried at 60 °C. Calcining the resulting solid at 600 °C for 4 hours in air afforded a pure silica-based mesoporous material, Si-MMS. The analogous procedures were used to prepare Al-containing mesoporous materials, Al-MMS. Al $(NO_3)_3·9H_2O$ (0.156 g) was added to H_2SiF_6 solution (20 g) and dissolved completely. The solution exhibited pH 1.4. This solution was added at once to the ammonia-surfactant mixed solution (130 g) stirred vigorously during 2 min at 60 °C. The pH of the solution becomes 7.0. The rest of the procedures were the same as the preparation of Si-MMS. A molar composition in the gel was 3.33 SiO_2, 0.0416 $Al(NO_3)_3$ $·9H_2O$, 1.43 CTMB, 39 NH_3, 22.5 HF, 722 H_2O (Si/Al=80). The solid product was filtered, washed, dried, and after calcination afforded Al-containing mesoporous molecular sieve, Al-MMS. Ti-containing mesoporous molecular sieve was prepared by similar procedures. Titanium isopropoxide, Ti $(OC_3H_7)_4$ (0.118 g, Aldrich) was added to H_2SiF_6 (20 g) and dissolved perfectly. This solution was added at once to the ammonia-surfactant mixed solution (130 g) stirred vigorously during 2 min at 60 °C. The pH becomes 7.3. White gel formed abruptly within 10 sec and the gel was aged for 5 hours in a dryer at 70 °C. The molar composition of the gel was 3.33 SiO_2, 0.0416 $Ti(OC_3H_7)_4$, 1.43 CTAB, 39 NH_3, 22.5 HF, 722 H_2O (Si/Ti=80). The solid product after filtration, washing, drying, and calcination afforded Ti-containing mesoporous molecular sieve, Ti-MMS.

X-ray diffraction patterns were obtained from a Rigaku diffractometer equipped with Cu-Kα radiation. Samples for

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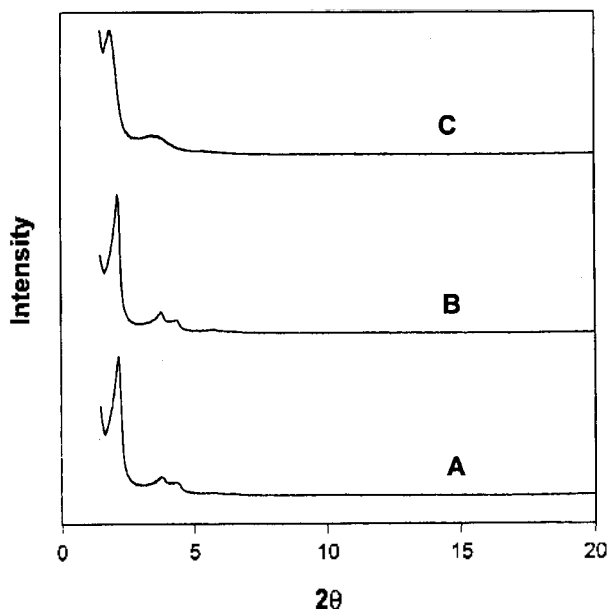
Figure 1. Powder X-ray diffraction patterns of mesoporous molecular sieves : A : Si-MMS, B : Ti-MMS, C : Al-MMS.

Figure 3. Horváth-Kawazoe pore size distributions for Si-MMS, Ti-MMS, and Al- MMS.

nitrogen adsorption/desorption isotherms were degassed at 300 °C under vacuum for 4 hours. Pore size distributions were determined by the Horváth-Kawazoe equation.[10] The powder X-ray diffraction patterns (Figure 1A, B, and C) of the resultant calcined samples correspond to mesoporous molecular sieve MCM41 reported in literature.[1,2] A high intensity first peak (basal spacing) related to pore size was well developed. The basal spacings for (A) Si-MMS, (B) Ti-MMS (C) Al-MMS exhibited 40.7, 42.2, and 43.0 Å, respectively. These values are similar to the values reported in the literature[7]. Despite short aging time in an atmospheric condition, it is interesting to observe that several lower angle peaks that can be indexed to a hexagonal lattice are apparent. This indicates a clear organization of pore structure.
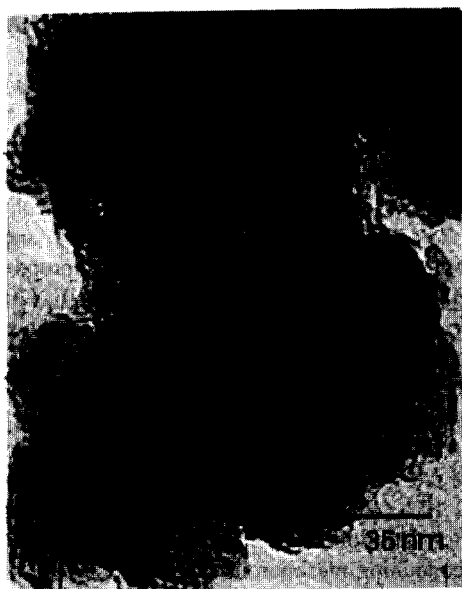

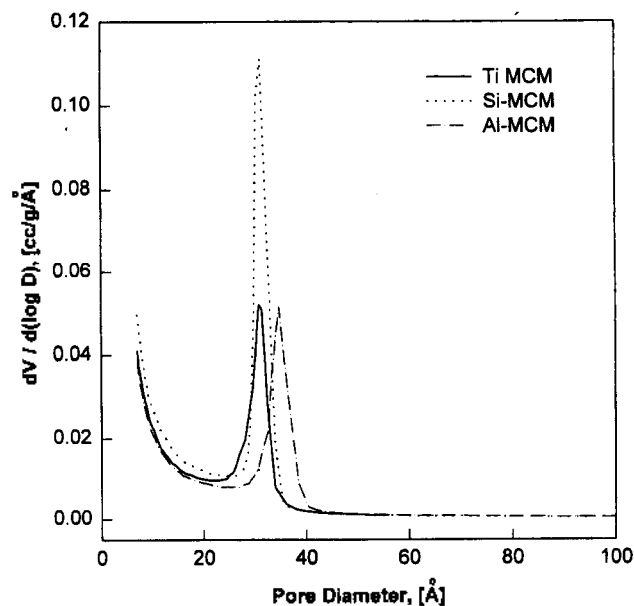
Figure 2. Transmission Electron Micrograph of Si-MMS.

These results imply that fluoride ion has an effect in this synthetic process. Guth *et al.*[11] has shown that the use of fluoride ion as a mineralizing agent, between pH 2-12, acts to diminish the number of defects in the framework. The chemical compositions of Ti-MMS and Al-MMS were determined by Energy Dispersive X-ray Spectrometer (Link system AN 10000-85S). The Si/Al molar ratios of Ti-MMS and Al-MMS are 79 and 75, respectively. The transmission electron micrograph in Figure 2 obtained from Si-MMS shows the regular hexagonal array of uniform channels with a pore size about 30 Å. The BET surface area of the Si-MMS was 1,041 m²/g with exceptionally high sorption capacity. The BET surface areas of Ti-MMS and Al-MMS were 877 and 827 m²/g, respectively. The isotherms for mesoporous molecular sieves exhibited a sharp inflection characteristic of capillary condensation within uniform pores, where the P/P$_0$ position of the inflection point is related to the diameter of the pore.[10,12] Figure 3 shows the Horváth-Kawazoe pore size distributions for Si-MMS, Ti-MMS, and Al-MMS, indicating a narrow pore size distribution similar to those of mesoporous molecular sieves, MCM-41.

In conclusion, the synthesis of silica-based mesoporous molecular sieves based on the hydrolysis reaction of H_2SiF_6 solution with ammonia-surfactant mixed solution afforded well-crystalline mesoporous molecular sieve within several hours at the atmospheric condition. Therefore, we propose that the synthesis of mesoporous materials using the fluorosilicon compound is highly profitable since the fluorosilicon compound such as H_2SiF_6 could be readily obtained from Silex and SiF_4 and from other industrial byproducts.

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Photoaddition Reactions of Duroquinone to Phenyl Substituted Ethylenes

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Quinones are an important class of compounds in organic synthesis, in industry, and in nature. Due to their various spectroscopic properties and reactivities, the photochemistry of *p*-quinones has been a subject of interest in many area.[1-4] Recently, an alkyne has been observed to add to duroquinone **1**, having electron donating methyl groups, to give 1 : 1 and 1 : 2 photoadducts.[5] In connection with our investigation of the scope of these reactions, we examined the photoaddition reaction of duroquinone to phenyl substituted ethylenes, such as *trans*-stilbene **2** and styrene **6**.

We introduce here the formation of 8-membered ring compound **5** from the photoreaction of duroquinone **1** and stilbene **2**. We also introduce competitive pathways in the photoaddition of duroquinone **1** to styrene **6**. Preparative photochemical reactions were conducted in dry nitrogen atmosphere in a photochemical reactor composed of a water-cooled system and a Pyrex reaction vessel with 300 nm UV lamps (Rayonet Photochemical Reactor, Model RPR-208). The photoadducts were isolated by flash column chromatography on silica gel using *n*-hexane and ethyl acetate (10 : 1, v/v) as the eluent. Irradiation (300 nm) of duroquinone **1** (164 mg, 1.0 mmol) and *trans*-stilbene **2** (360 mg, 2.0 mmol) in dichloromethane (100 mL) for 76 h yielded 8-membered ring compound **5** (65%) in one pot, as shown in Scheme 1.[6]

In sharp contrast, competitive pathways were observed in the photoaddition reaction of duroquinone **1** to styrene **6**, as shown in Scheme 2. The photoproducts observed in this photoreaction was 1 : 1 adducts (**8** and **9**) and 1 : 2 adducts (**11** and other two isomers) as cyclobutanes, 1 : 2 adducts (**12** and **13**) as racemic cyclohexanes, and polystyrene-bound duroquinone (**14**). Irradiation (300 nm) of duroquinone **1** (328
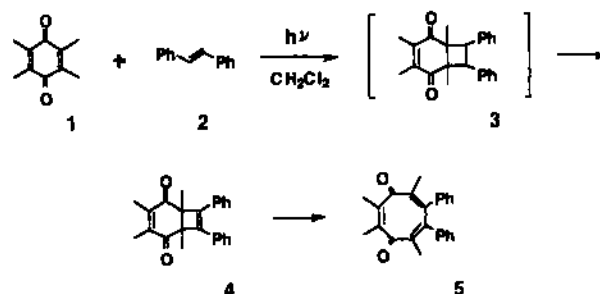
Scheme 1

mg, 2.0 mmol) and styrene **6** (0.05 mL, 0.44 mmol) in benzene (200 mL) for 24 h afforded only 1 : 1 photocycloadducts (**8** and **9**) in 83% yield. ¹H NMR analysis of the photoproducts revealed a 5.1 : 1.0 ratio of **8** to **9**. Proton signals at β and α position of methylene group of **8** were observed at δ 2.45 and 2.58, respectively. A proton signal at β position of methine group was observed at δ 3.59. The formation of 1 : 1 adducts and second intermediate **7** and that of cyclohexanes and polystyrene-bound duroquinone are the results of competition between ring closure and chain enlargement to give the corresponding products.

Increasing the relative amount of styrene decreases the formation of the 1 : 1 adducts. Instead, 1 : 2 adducts (**11** and other two stereoisomers) and another types of 1 : 2 adduct (**12** and **13**) were obtained in moderate yields.

Irradiation of **1** (164 mg, 1 mmol) and **6** (0.6 mL, 5.2 mmol) in benzene (200 mL) for 24 h yielded 1 : 1 adducts (**8** : **9**=1.4 : 1.0) in 22% yield, 1 : 2 adducts (**11** and other two stereoisomers) in 38% yield, and two stereoisomeric mixture of **12** and **13** in 33% yield. ¹H NMR analysis revealed