Pore Size Control of High Surface-Area Silica by Use of Citric Acid

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Pore size and pore volume of an amorphous silica with high specific surface area, ca. 1000 m^2g^{-1}, can be controlled in meso scale by using citric acid as a template in sol-gel reaction of tetraethoxysilane.

Porous silicates with periodic 1-dimensional (1-d) mesopores, families of MCM-41[1] and FSM-16,[2] attract many interests in the field of catalyst. They are prepared from organic-inorganic composites of self-assembled surfactant and silicates by eliminating organic components, and have ordered mesopores with extra high specific surface areas ($\geq$1000 m^2g^{-1}). The narrow pore size distribution and the pore size larger than those of zeolites have been considered to be applied to molecular recognition of large molecules for which zeolites can not be used. Various attempts for application of the 1-d mesoporous silicates as catalyst and catalyst support have been made to develop a reaction system with high selectivity expecting their molecular recognition property.[3-5] On the other hand, conventional amorphous silicates have been also used as catalyst supports, widely.[6,7] Although pore size distribution of them is not so narrow as that of MCM-41, their pores distribute randomly in them, and are considered to link 3-dimensionally. Therefore the use of them as catalyst support has advantages in transportation of reactants and products in pores. In the case of conventional amorphous silicates, however, it is difficult to prepare a material with both large pores and large specific surface areas. MCM-48 with cubic symmetry and 3-d pore system[1] will be applicable in this use. On the other hand, attempts to prepare amorphous silica with high surface area from sol-gel process have also been performed by decomposing organic-inorganic composites.[8-11] However, almost all obtained materials were microporous. In this work, we report a novel method to prepare a mesoporous amorphous silica from tetraethoxysilane (TEOS) and citric acid (CA), which have mesopores with controlled size and high specific surface areas (ca. 1000 m^2g^{-1}, as large as that of MCM-41).

The amorphous mesoporous silica was prepared by adding TEOS into a mixture of 1 mol dm^{-3} nitric acid aqueous solution and ethanol containing a proper amount of CA under stirring. The molar ratio of TEOS:H_2O:EtOH:CA = 1:1:4:r (r=0-1.2). After the mixture had been stirred at room temperature for 15 min, additional ethanol and water were added. Finally, the molar ratio was adjusted to 1:4:6:r. The solution was hold in an open container at 25 °C for 3 days for gelation, and was further dried at 50 °C for 3 days to obtain a Si-CA precursor. It was heated at 500 °C for 2 h in air with heating rate of 100 °C/h to decompose CA. Specific surface areas and pore size distributions of the calcined samples were calculated from adsorption brunch of N_2 isotherm at -196 °C using a BET method and from desorption one by a procedure proposed by Dollimore and Heal,[12] respectively. ^{29}Si MAS-NMR spectra were measured under static magnetic field of 7T (Bruker, DPX300; frequency 59.6 MHz, MAS speed 4000 Hz). Pulse sequences of high-power decoupling were used, and FID signals were accumulated with 30° pulse and recycle time of 100 s for quantitative information.

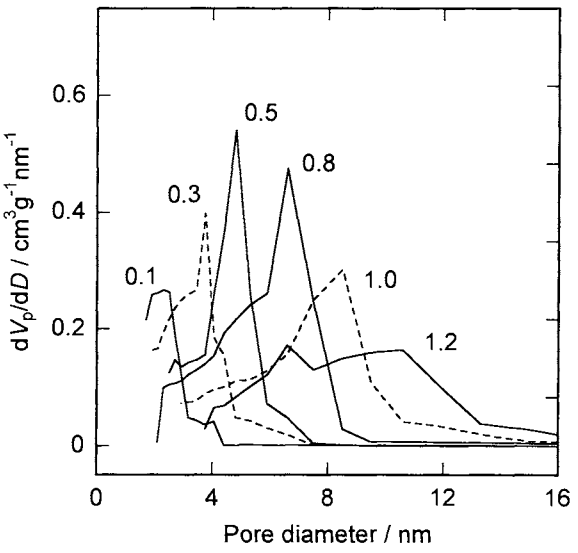

Figure 1. Pore size distributions of silica gels prepared from TEOS using CA. Numbers represent the molar ratios of CA/Si.

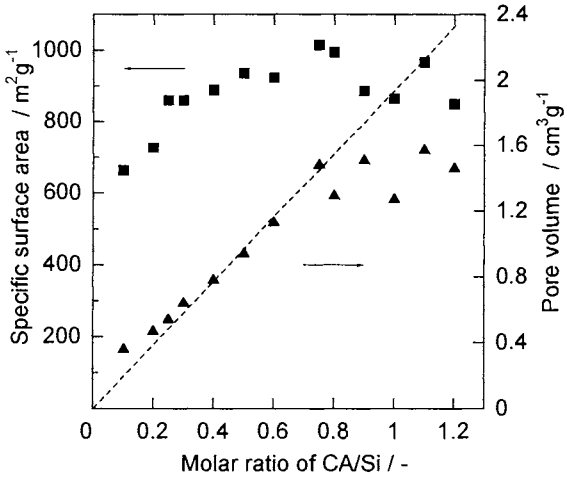

Figure 2. Variations in specific surface area and total pore volume of silica gel with CA content. A dotted line represents the volume occupied with CA in the precursor.

Figure 1 shows pore size distribution curves for selected silica samples with different CA contents. The peak in pore size distribution shifts successively from micropore range to larger size with increasing CA content in the starting composition, while the distribution becomes broader. Figure 2 shows variations in specific surface area and total pore volume of the silica with CA

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content. A sample prepared without CA had no pores and exhibited small specific surface area (<1 m^2g^{-1}). The specific surface area increased steeply with an increase in CA content at r<0.2, and saturated between 900-1000 m^2g^{-1}. The values are as high as that of MCM-41.[1] On the other hand, the total pore volume was linearly proportional to CA content upto r=0.8, and saturated above r=0.8. A dotted line in Figure 2 represents the volume which is occupied with CA in the precursor samples. It agrees well with the total pore volume of calcined samples at r<0.8, suggesting that CA acts as a simple template for the formation of mesopores. The successive increase of pore size with increasing CA content, as shown in Figure 1, also suggests that Si-CA precursor is a organic-inorganic composite mixed in nanometer scale.

In the investigation of structure of the precursors, it was found by XRD measurement that the Si-CA precursors were amorphous without periodic meso phases, such as lamella or hexagonal. Furthermore, no clear interaction between silica gel network and CA was observed by spectroscopic techniques, such as ^{13}C-, ^{29}Si-MAS NMR and IR. TG-DTA results showed that large portion of CA was eliminated endothermically around 250 °C. Because pure CA vaporized at the same temperature, TG-DTA results also suggest that there is no interaction between silica network and CA in the Si-CA precursor. If exists, the interaction must be small.

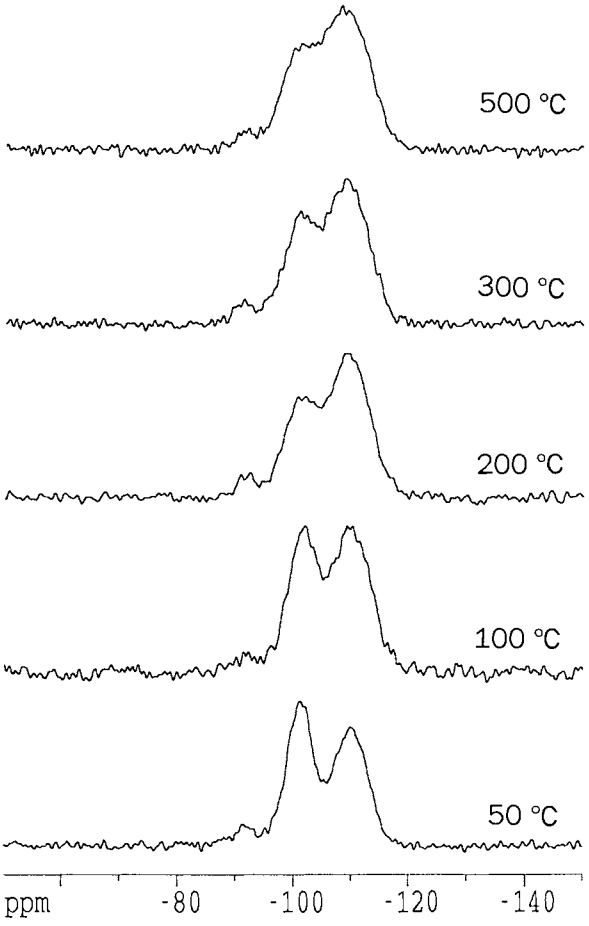

Figure 3. Changes in ^{29}Si NMR spectra of Si-CA precursors with different heating temperatures. The ratio of CA/Si = 1.0.

Although ^{29}Si-MAS NMR measurement did not reveal clear interaction between silica gel network and CA, it elucidated the changes of average condensation degree of SiO_4 units during heating. Figure 3 shows changes of ^{29}Si NMR spectra during calcination for the sample of r=1. In the spectra, peaks around -90, -100 and -110 ppm have been assigned to Q^2, Q^3 and Q^4 species, respectively. Here, Q^n indicates the SiO_4 unit with formula of $Si(OSi)_n(OH)_{4-n}$. With increasing the heating temperature, Q^3 species decreased and Q^4 species increased remarkably up to 200 °C, while small change in the ratio of Q^3 and Q^4 was observed between 200 and 500 °C. Judging from the result of TG-DTA that CA is eliminated over 250 °C, it can be said that bond formation of Si-O-Si in silica network is not inhibited by coexisting CA. Because no or small interaction arises between silica network and CA, the silica gel network can form the additional Si-O-Si bonds in the Si-CA precursors during heating below 200 °C, and the silica gel framework with highly open structure becomes rigid enough for self standing. Therefore, the spaces occupied with CA become pores without collapse after the elimination of CA at r<0.8. At r>0.8, partial collapse of pores will occur, leading to a saturation in pore volume.

In conclusion, amorphous silica gels with high specific surface area as well as controlled mesopores can be prepared from silicon alkoxide and citric acid. The mesopores in the silica is speculated to interlink 3-dimentionally as in the case of conventional amorphous silicates, and therefore the silica is possibly useful for catalyst support. Further studies on the structure of Si-CA precursors and mosoporous silica as well as the pore formation mechanism are now in progress.

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