Direct Crystallization of Amorphous Silicates to Zeolites in Solid State

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(Received February 6, 1996)

A silicate monolithic gel was prepared by the hydrolysis of tetraethyl orthosilicate with tetrapropylammonium hydroxide aqueous solution. The starting powder obtained by drying the gel was converted to zeolite ZSM-5 by heating at 130 °C for 18 h. Silicalite-1 and silicalite-2 were also obtained by the similar conversion. A binderless zeolite disk was obtained by heating a disk shaped with the starting powder.

Zeolites are very advantageous materials to industries dealing with catalysts, separation, sensing and optics. There is an important technical issue that zeolites are difficult to be shaped appropriately. Thus, for example cordierite honeycomb, which is used as a catalyst support for processing exhaust gases, is prepared by direct conversion of the shaped clay to cordierite. If raw materials were converted to the corresponding zeolite after being shaped, the method would be very convenient for the industries. Moreover, in a purely scientific point of view, it would be interesting to study the mechanism of nucleation-crystal growth in solids. It is known that when amorphous sodium aluminosilicates are contacted with vapors of organic materials and water, they crystallize to zeolites in autoclaves. [1-3] Similar methods have also been demonstrated in non-aqueous systems for converting amorphous materials to zeolites in the presence of excess ammonium or diamine compounds. [4, 5] There have been some attempts to exploit the vapor phase transport method to crystallize molded zeolites. [6, 7] The wet gel consisting of a mixture ($Na_2O/Al_2O_3/SiO_2/H_2O$ = 19/10/20/190 in molar ratio) has also been converted to zeolite A by a solid state rearrangement. [8] However, the starting materials and the solid products obtained in these preparation methods are damp and soft. Therefore it is difficult to make membranes or disks using these materials without solid supports. We have found a novel method of crystallizing an amorphous silicate to a zeolite in solid state.

The direct crystallization was performed using powdery silicates and some disks shaped from the powder. The results on the crystallization of some powdery silicates are summarized in Table 1. A monolithic gel was obtained by hydrolyzing a mixture of tetraethyl orthosilicate (TEOS) and aluminum tri-*sec*-butoxide (ATB) with an aqueous solution of TPAOH under heating at 70-80 °C for 3h. The gel was placed over night at room temperature, before being dried under vacuum for about 24h at room temperature. The starting powder was prepared by crushing the xerogel.

From thermogravimetric analysis (TGA) of the starting powder (SiO_2/TPAOH=10/1 in molar ratio), 9% and 21% weight losses were found in the region between 25 and 120 °C, and 120 and 300 °C, assigned mainly to evaporation of adsorbed water and decomposition of TPAOH respectively. 3% weight loss observed between 300 and 1000 °C is assigned to elimination of hydroxyl group. The composition of the starting powder was calculated to be SiO_2/TPAOH/H_2O=100/9/60 in molar ratio.

The starting powder, which was prepared from a mixture (TEOS/ATB/TPAOH=100/2/10 in molar ratio), was enclosed in a glass ampoule. Then, the powder was converted to zeolite ZSM-5 by heating the ampoule at 130 °C for 18 h. The sample was assigned by measuring the powder X-ray diffraction (XRD) and comparing with previous works. [9] Powder prepared from TEOS and TPAOH has also converted to silicalite-1 (pure-silica ZSM-5) by the thermal treatment at 130 °C for 18 h.

Table 1. Crystallization of powdery amorphous silicates containing templates to zeolites in solid

Source		Template	Thermal Treatment		Product
Si	Al		Temp.	Period	
TEOS	-	TPAOH	130 °C	18 h	Silicalite-1
Water Glass	-	TPABr	150 °C	23 h	Silicalite-1
TEOS	ATB[a]	TPAOH	130 °C	18 h	ZSM-5
TEOS	ATB[b]	TPAOH	130 °C	18 h	ZSM-5
TEOS	-	TBAOH	150 °C	20 h	Silicalite-2

TEOS: Tetraethylorthosilicate
ATB: Aluminum tri-*sec*-butoxide
TPAOH: Tetrapropylammonium hydroxide
TBAOH: Tetrabutylammonium hydroxide
TPABr: Tetrapropylammonium bromide
[a] Si/Al =100/1 in molar ratio [b] Si/Al =100/4 in molar ratio

When the starting powder was placed in an open vial, the zeolite was not produced and the powder remained still amorphous. It was considered that some water adsorbed on the starting material played an important role in the crystallization.

In a similar manner, powder obtained from water glass solution and tetrapropylammonium bromide (TPABr) has converted to silicalite-1 after heat treatment.

On the other hand, when powder prepared from TEOS and tetrabutylammonium hydroxide (TBAOH) was heated for 20 h at 150 °C in a sealed ampoule, silicalite-2, which was pure-silica ZSM-11, was obtained. It takes 3 days to obtain silicalite-2 under the hydrothermal synthesis at 170 °C. [9] It was realized that the crystallization took place quickly in solid state under quite mild conditions.

The thermal treatment in the solid state was also applied for amorphous silicate disks. The starting silicate powder prepared from TEOS and TPAOH was molded into a disk by compressing at 74 MPa using an uniaxial molder for infrared spectroscopy. The dimension of the disk was 13 mm in diameter and approximately 1 mm thick. A silicalite-1 disk was produced by heating the starting disk enclosed in a glass ampoule for 19 h in a convection oven at 130 °C. The assignment of the product was carried out by XRD measurement of the ground powder and the

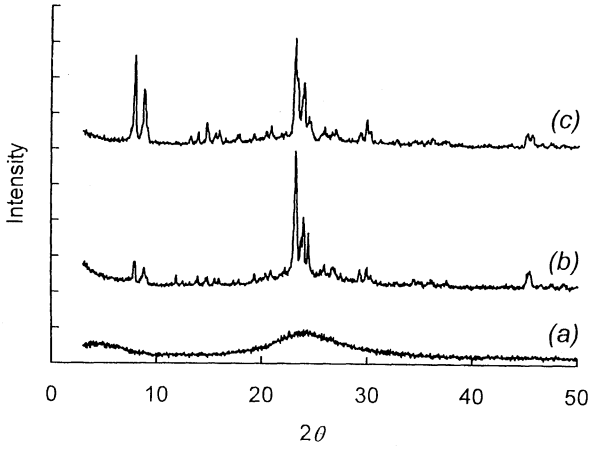

Figure 1. XRD patterns of surface of (a) the starting disk prepared from TEOS and TPAOH, (b) the silicalite-1 disk converted from the starting disk by heating at 130 °C for 19 h and (c) silicalite-1 disk calcined at 500 °C for 20 h.

surface of the disk. The shape survived calcination in air at 500 °C for 20 h. Figure 1 shows the XRD patterns of the surface of the disks before (a) and after (b) the thermal treatment, and (c) after the calcination. Figure 1(a) and (b) show the typical XRD patterns of amorphous silicate gel and silicalite-1 respectively. No dimensional change is detected on the disks after crystallization and calcination. The specific surface area of the calcined disk was 407 $m^2 g^{-1}$ measured by BET method based on nitrogen adsorption at -196 °C. From the powder XRD pattern and the specific surface area data, it is thought that most of the starting material in the disk is converted to silicalite-1. The crystallized disk has enough mechanical strength to keep the shape in usual sample handling.

Figure 2 shows scanning electron micrographs (SEM) of (a) the starting disk (cross-section), (b) silicalite-1 crystals prepared by the solid state crystallization in the disk (cross-section), (c) after the solid state crystallization in powder form and (d) after conventional hydrothermal synthesis at 160 °C for 24 h. The starting disk was observed to consist of very small particles originated from the sol prepared by the hydrolysis of TEOS, as shown in (a). The (b) and (c) crystals are very close in size, and much smaller than (d) crystals prepared by conventional hydrothermal synthesis. In comparison with (c) crystals, which are quite uniform in size, the shape of (b) crystals are not quite uniform. The (b) crystals seem to be affected and distorted by the residual internal stress generated during the molding of starting powder into disk. Although the crystals shown in (d) are typical silicalite-1 crystals in shape, the crystals shown in (b) and (c) indicate a lot of aggregates consisting of intergrowth of small silicalite-1 crystals.

It seems that the mechanism of this conversion is similar to that of the vapor-phase transport method, except that this conversion proceeds with a small amount of water adsorbed in the starting powder. This is useful as a method to produce binderless zeolite shapes. The mechanism would be presumed as follows. Water molecules and hydroxide anions attack the silicate chains at the beginning of the crystallization. The silicate-chain fragments and water molecules are assembled to form certain clusters, which are precursors of the target zeolite, around the templating cations. However, more nucleation sites are generated at the beginning of the solid state crystallization than conventional

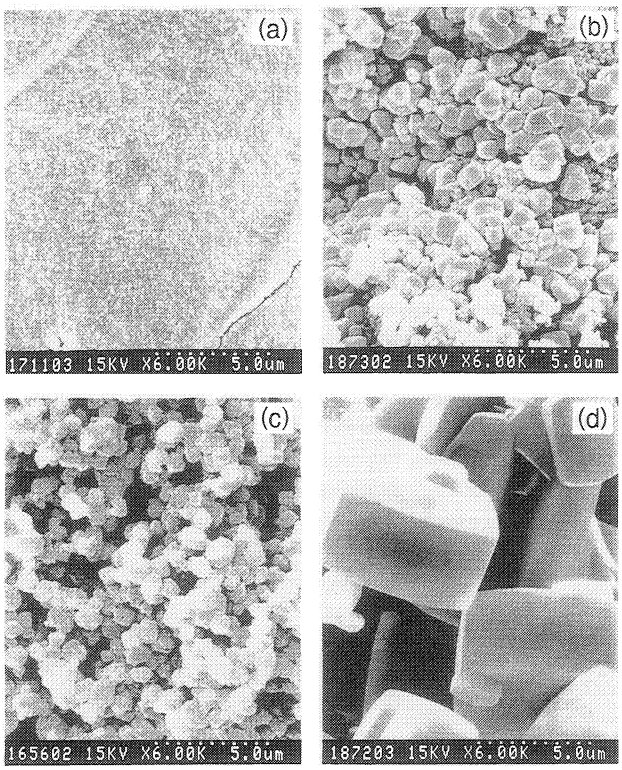

Figure 2. SEM images of cross-section of (a) the starting disk and (b) the silicalite-1 disk, (c) the silicalite-1 powdery crystals prepared by the solid state crystallization and (d) silicalite-1 crystals prepared by hydrothermal synthesis at 160 °C for 24 h.

hydrothermal synthesis, since the solid state crystallization continues with very small amount of water and the material concentration in solid state is higher than in conventional hydrothermal synthesis. It is suggested that most of the crystals intergrow and the rate of crystallization is high in the solid state crystallization, because a lot of crystals are produced by nucleation in such highly concentrated systems. On the other hand, the material transport in solid is so restricted and slow that the growth of the nuclei is much slower. The growths of crystals stop when the reactant concentration is exhausted in the area. These lead to the formation of small crystals by the rapid crystallization.

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