Promoting Effect of Cyclic Ethers in the Layered Silicate Synthesis

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One of the layered silicates RUB-15, having TMA (Tetramethylammonium) ions between the layers, was rapidly synthesized by using cyclic ethers. The reaction with cyclic ethers was 6 times faster than that without cyclic ethers. The other organic solvent did not produce RUB-15 in 5 days. The effect of cyclic ethers is investigated by ^{29}Si NMR.

Layered silicates are very interesting materials because of their remarkable adsorption and ion-exchange properties. They are also interesting precursors for the synthesis of zeolites. We have recently reported the synthesis of novel layered structure, a helical layered silicate (HLS)[1,2] in the presence of SiO_2, TMAOH (tetramethylammonium hydroxide), NaOH, H_2O, and 1,4-dioxane under hydrothermal condition.

We synthesized sodalite, one of the zeolites, from this HLS.[3] These layered compounds are very promising as a precursor of the zeolite. In this point of view, we have tried to synthesize another type of layered silicate via hydrothermal conversion of amorphous silica in TMAOH, H_2O, and 1,4-dioxane without NaOH.

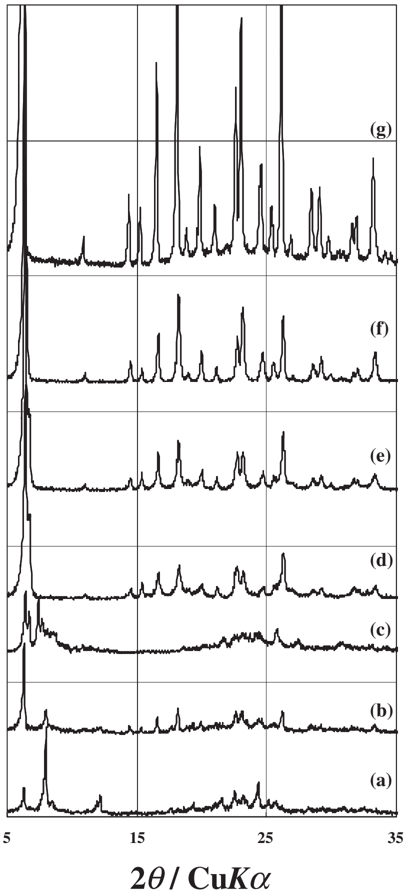

Figure 1. Powder XRD patterns of obtained sample with (a) ethanol, (b) acetone, (c) diethyleneglycoldimethylether, (d) 1,3-dioxane, (e) 1,3,5-trioxane, (f) 12-crown-4 ether, (g) 1,4-dioxane.

On the other hand, many studies using ^{29}Si NMR were reported in the synthesis system of zeolite or layered silicate. However, to the best of our knowledge, most of the papers treated alkoxide, and few did amorphous silica. It is important to in-

(a)

(b)

(c)

Figure 2. Scanning electron micrographs of obtained powders using cyclic ethers as (a) 1,3-dioxane, (b) 1,3,5-trioxane, and (c) 12-crown-4 ether.

vestigate the process of synthesis from amorphous silica to some composition of silica as RUB-15.

In our study, we obtained another type of layered silicate RUB-15[4,5] rapidly. The synthesis of RUB-15, which is composed of silica and TMA and water, was first reported in 1996. In that case without cyclic ethers, the reaction time required four weeks. By our synthetic method, we obtained RUB-15 within 5 days using various cyclic ethers. But it was impossible to obtain RUB-15 using other organic solvents within 5 days. We considered that the cyclic ethers have some reaction-promoting effects. Then, the effect of cyclic ethers was investigated by ^{29}Si NMR.

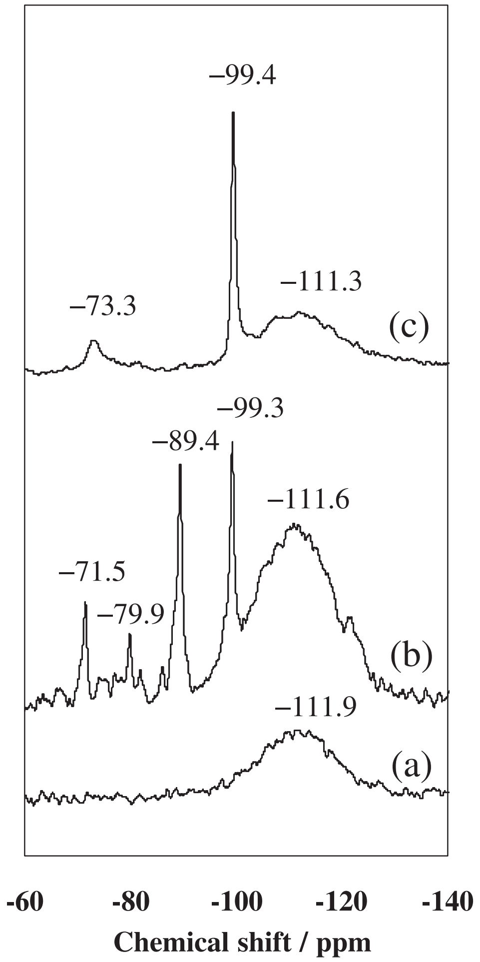

Figure 3. Powder ^{29}Si NMR spectra of various mixture of (a) SiO_2 and 1,4-dioxane, (b) SiO_2 and TMAOH solution, (c) SiO_2, TMAOH solution and 1,4-dioxane.

RUB-15[4,5] was prepared from the reaction mixture of SiO_2, TMAOH and water. We use amorphous silica Cab–O–Sil (M5), which is the product from CABOT CORPORATION, as a silica source and the molar ratio of each agent is 1.7×10^{-2}, 3.6×10^{-3}, and 0.27. We added various organic solvents (5 cc) as reaction-promoting agent and poured them into a Teflon-lined autoclave. The mixture was reacted under static hydrothermal conditions at 140 °C for 5 days. Obtained powder was filtered and washed with acetone and dried in air at 70 °C.

Figure 1 presents the powder XRD patterns of the products after the reaction of SiO_2, TMAOH, H_2O and various organic solvents. RUB-15 was obtained when cyclic ethers were used as solvents, such as 1,4-dioxane, 1,3-dioxane, 1,3,5-trioxane, 12-crown-4-ether, however, the other organic solvents, such as THF, diethyleneglycol–dimethyl ether, ethanol, acetone did not produce RUB-15 in 5 days. In the case of using ethanol and acetone, RUB-15 and unknown phase were formed.

RUB-15 has plate-like structure. Figure 2 shows SEM images of some obtained powders. It seems to prove that RUB-15 was produced because obtained powders are plate-like.

In order to confirm the effect of cyclic ethers to the reaction mixture, ^{29}Si MAS NMR spectra were measured and illustrated in Figure 3. We used the gels from the mixture of SiO_2 and H_2O and/or TMAOH and/or 1,4-dioxane as a representative of cyclic ethers. Although the SiO_2 powder has only one broad peak due to Q^4 species, the mixture of TMAOH, H_2O, SiO_2, and dioxane shows a strong signal at −99.4 ppm due to Q^3 species and a broad signal due to Q^4 species. Without dioxane, the mixture of SiO_2, TMAOH, and H_2O exhibited three strong signals at −99.3, −89.4, and −71.5 ppm, assigned to Q^3, Q^2, and $Q^{1,0}$ species, respectively. The results suggest that alkaline like TMAOH breaks the Si–O–Si bonding of SiO_2, and produces the species from Q^3 to Q^0. The reason why a strong Q^3 signal appears by only adding dioxane to the mixture would be explained as follows. There are some reports that the dioxane molecule can be mixed with water uniformly and break the water structure.[6,7] Then it is considered that in the case without dioxane, Si–O–Si bonding is cut by alkaline, large water molecules enter into the structure of amorphous silica, then they produce Q^0 species. However, by adding dioxane, water molecules form small clusters and they are considered to enter into the amorphous silica gradually with alkaline to produce Q^3 species.

When the other cyclic ethers are put into the reaction mixture, a strong Q^3 signal is considered to appear and the synthesis time to be shortened as same as using 1,4-dioxane.

The cyclic ethers make the silicon form Q^3 species predominantly and promote the synthesis of layered silicate.

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