Synthesis of Nb-Containing Porous Silica Using TEOS and Colloidal K$_2$NbO$_3$F Solution

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K$_2$NbO$_3$F から調製したコロイド溶液と TEOS を用いたメソ多孔体の合成

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Mesoporous materials using a colloidal solution prepared from K$_2$NbO$_3$F and hexadecyltrimethylammonium were synthesized stirring at room temperature for 30 s. It was found that the Nb-containing colloidal solution was reactive to alkyltrimethylammonium. Furthermore, we synthesized porous Si–Nb oxides using the colloidal solution as a Nb source and tetaethoxysilane (TEOS) as a Si source. Microporous material was obtained by stirring at room temperature for 30 s, and mesoporous material was obtained by stirring at 323 K for 3 h. It was discovered that pore size depends on the condensation behavior of the silica network.

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1. Introduction

Mesoporous materials have attracted attention because they have ordered pores with a uniform size of 2–50 nm and a high specific surface area. These materials are expected to have applications as catalyst supports, absorbents and host compounds, and are particularly promising for dealing with nano size molecules. It is reported that mesoporous materials containing transitional metals are useful as catalysts for various reactions. Mesoporous materials containing niobium in the pore wall have been investigated regarding catalytic activity for oxidation and hydrodesulfurization.

Recently, we have synthesized lamellar and 2d-hexagonal-type Nb-containing mesostructured materials from K$_2$NbO$_3$F powder and alkyltrimethylammonium chloride by reaction in water. Furthermore, Nb-containing mesoporous silica with bimodal pores was synthesized using tetaethoxysilane (TEOS) in addition to the starting materials. For application as a catalyst, a higher Nb content is desirable. However, in the case of synthesis from K$_2$NbO$_3$F powder, the Si/Nb molar ratio of the products was 61, although that of the starting composition was 7. Thus, the Nb content in the products is markedly less than that in the starting composition. This may be caused by the low homogeneity of the reacted solution. Toda et al. reported that layered-perovskite K$_2$NbO$_3$F exfoliates in water to form a colloidal solution without addition of an intercalation agent such as tetrabutylammonium, and that thermodynamically metastable cubic perovskite-type KNbO$_3$ was synthesized by centrifugation of the colloidal solution. This colloidal solution was more homogeneous than the reacted solution using K$_2$NbO$_3$F powder. Synthesis using the colloidal solution as a starting material was carried out to increase Nb content. In this study, we successfully synthesized porous Si–Nb oxides that have a Nb content nearly equal to that of the starting composition, and characterized their microstructures and properties.

2. Experimental

2.1 Preparation of colloidal solution

Layered-perovskite K$_2$NbO$_3$F was synthesized by conventional solid-state reaction. KF, K$_2$CO$_3$ and Nb$_2$O$_5$ were used as starting materials. These powders were weighed in the molar ratio KF : K$_2$CO$_3$ : Nb$_2$O$_5$ = 4 : 1 : 1 and mixed in ethanol using a mortar and pestle. The mixture was heated in a platinum crucible at 1083 K for 6 h. After the reaction, excess potassium fluoride was removed by washing the product with distilled water. Five gram of powder K$_2$NbO$_3$F was dispersed into 500 cm$^3$ of distilled water. The suspension was stirred with a magnetic stirrer at room temperature for 24 h and filtered using a membrane filter having a 1 μm pore size. The prepared colloidal solution was dissolved into HF–HNO$_3$ solution, and Nb content was measured using ICP–AES.

2.2 Synthesis of mesostructured materials

The surfactant used as the structure directing agent (SDA) in the synthesis was hexadecyltrimethylammonium chloride (HDTMACI). Thirty cm$^3$ of colloidal solution and 70 cm$^3$ of distilled water were stirred with a magnetic stirrer. The pH adjustment was carried out using 1 mol·dm$^{-3}$ HCl. Then, 12.6 cm$^3$ of 0.1 mol·dm$^{-3}$ HDTMACI aqueous solution was added and vigorously stirred at room temperature for 30 s. The resulting white precipitate was recovered by filtration and drying.

2.3 Synthesis of porous materials

Two cm$^3$ of TEOS was gently added to a previously mixed solution of 28 cm$^3$ of the colloidal solution and 22 cm$^3$ of distilled water. It was found that 1.18 mmol of Nb was included in the 28 cm$^3$ of the colloidal solution. Therefore, it was confirmed that the Si/Nb ratio of the starting composition was 7. Then, 12 cm$^3$ of 0.1 mol·dm$^{-3}$ HDTMACI aqueous solution was immediately added to the solution and stirred with a magnetic stirrer at room temperature for 30 s or 323 K for 3 h; the products of these procedures were denoted 30S and 3H, respectively. The resulting white precipitate was recovered by filtration and drying at 333 K overnight. The dried samples
were calcined in air at 753 K for 3 h to remove SDA.

2.4 Characterization

The structural characteristics of the products were determined by powder XRD method using a diffractometer (Rigaku RAD-PC, Cu Kα radiation). The mesostructure was observed by transmission electron microscopy (TEM, JEOL JEM-1200 120 kV) and K/Nb ratio was determined by energy-dispersive X-ray analysis (EDX, Noran Voyager II). The condensation behavior of Si species was examined in the as-synthesized products by 29Si-CP MAS NMR (JEOL JNM A-400 WB, 1H-29Si contact time, 5 ms) spectroscopy. N2 adsorption–desorption isotherms were recorded using a Japan Bel Belsorp 28SA analyzer at 77 K and the surface area was obtained from a Brunauer–Emmett–Teller (BET) plot.

3. Results and discussion

3.1 Synthesis of mesostructured materials

First, the reactivity of the Nb-containing colloidal solution and HDTMACI was examined. The XRD patterns of synthesized products using the colloidal solution and HDTMACI at room temperature for 30 s are shown in Fig. 1. The product synthesized at pH 10.5 show three peaks in the range 2θ = 1–10°, which were indexed to the lamellar phase. In the case of products synthesized at pH 7, the diffraction peaks were indexed to the 2d-hexagonal phase. Both products obtained by the reaction for 30 s had a mesostructure. These results indicate that the reaction of the Nb-containing colloidal solution and HDTMACI occurred rapidly. On the other hand, it is considered that the change in the mesostructure determined by the pH of the synthetic condition depends on the shape of the liquid crystal of SDA. Such a structural change has been reported in other mesostructured materials.13) The 2d-hexagonal mesostructured material synthesized at pH 7 was calcined at 753 K for 3 h to remove SDA. XRD peaks in the range of 2θ = 1–10° disappeared and peaks ascribed to Nb2O5 were observed. This indicates that the mesostructure collapsed due to calcination.

3.2 Synthesis of porous materials

The XRD patterns of as-synthesized products using TEOS, Nb-containing colloidal solution and HDTMACI are shown in Fig. 2. Only one diffraction peak was observed and the d-spacings were 4.2 nm for 30S and 5.0 nm for 3H, indicating that the products had a mesostructure without a uniform pore arrangement. Rapid formation of mesostructured materials was also observed, in the case of reaction among TEOS, colloidal solution and HDTMACI. When the mixed solutions of 2 cm3 of TEOS and 12 cm3 of 0.1 mol·dm−3 of HDTMACI were stirred for 30 s in water without the colloidal solution, no precipitate was obtained. This result suggests that the colloidal solution is necessary for the formation of a mesostructure under this condition. The wormhole like disordered pore were confirmed by TEM observation. The 29Si-CP MAS NMR spectra of as-synthesized materials are shown Fig. 3. Both spectra were deconvoluted to three peaks at ca. −110 ppm for Q4, ca. −100 ppm for Q3 and ca. −89 ppm for Q2. The Q2/Q3/Q4 ratios were 35/54/11 (30S) and 17/45/37 (3H). These results indicate that 3H has comparatively many Si–O–Si bonds, whereas the polymerization of silica did not progress well for 30S.

The XRD patterns of calcined products are shown in Fig. 4. The diffraction peak of 30S was broad and shifted to a higher angle, and an apparent peak was observed for 3H. These results indicate that the periodicity of the mesostructure remained for both 30S and 3H after removal of SDA. However, periodicity decreased with the removal of SDA for 30S. The nitrogen adsorption–desorption isotherms of the products are shown in Fig. 5. The isotherm of 3H showed a stepwise increase in nitrogen adsorption in the range of 0.2 < P/P0 < 0.4, indicating the presence of mesopores, while type-
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I-like isotherms were observed for 30S. The pore diameter and pore volume were estimated by the t-plot method for 30S or the DH method for 3H. The BET surface area, pore diameter and pore volume are shown in Table 1. TEM images of the calcined products are shown in Fig. 6. Approximately 1 nm diameter pores were observed for 30S and ca. 2.5 nm diameter pores were observed for 3H. These results are consistent with the results of N$_2$ adsorption. The NMR and XRD results of as-synthesized 30S revealed that the mesostructured material formed by reaction for 30 s at room temperature, and the material had an insufficient Si–O–Si network formation. A microporous material was obtained after calcination. This material was formed by shrinkage of inorganic framework. On the other hand, a mesoporous material was obtained by reaction for 3 h at 323 K. It is considered that the Si–O–Si network was sufficiently constituted in the as-synthesized product for 3H, so that mesopores were maintained after the calcination.

The Si/Nb ratios in the porous materials were estimated by EDX to be 6 and 9 for 30S and 3H, respectively. This shows that the Si/Nb ratio was maintained during reaction using the colloidal solution. In the case of synthesis from K$_2$NbO$_3$F powder, the Si/Nb ratio of the products was 61, although that of the starting composition was 7. This result suggests that the composition of products could be strongly influenced by the dispersion condition of Nb in the reaction solution. Thus, it is considered that the homogeneity of the reacted solution improved using the colloidal solution, and products reflecting the Si/Nb ratio of the starting composition were obtained.

4. Conclusions

We found that mesostructured materials rapidly formed from the reactive colloidal solution prepared from K$_2$NbO$_3$F and HDTMACl. Furthermore, Nb-containing porous silica was synthesized from TEOS, the colloidal solution and HDTMACl. Meso- and micro-porous Si–Nb oxides were obtained whose Si/Nb ratio corresponded to the starting composition. Therefore, it was found that the colloidal solution is valuable as a Nb source. NMR study revealed that the preservation of the mesostructure depends on the degree of the condensation of the silica network. An investigation of the role of the colloidal solution in the formation of the mesostructure is in progress.

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References


