

PREPARATION OF Ni-SUPPORTED MESOPOROUS SILICA BY INTERCALATION TREATMENT

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Abstract

A siliceous porous material containing nickel was synthesized by means of an intercalation treatment method using a layered sodium octosilicate ilerite as a starting base material. The sodium ions between the crystalline silicate sheets in the octosilicate were exchanged for hydrogen ions in dilute hydrochloric acid, and then the basal spaces between the silicate sheets were extended by introducing n-octylamine into the silicate sheets. Tetraethylorthosilicate (TEOS) was added to the silicate gel, and the silicate pillars were structured between the silicate sheets by the hydrolysis of TEOS. The intercalation treatments were carried out under various pillaring conditions of the added amount of water or nickel solution which was used as an initiator of the hydrolysis reaction of TEOS. The specific surface area, pore distribution and adsorption-desorption isotherms of the intercalated octosilicates were measured, and the pillar structure in the intercalated octosilicates was characterized. The optimum conditions in the intercalation treatment were determined based on the characteristics of the intercalated octosilicates. The pore characteristics of intercalated octosilicates could be controlled by the added amount and concentration of the nickel solution.

1. Introduction

Porous silica containing metal elements have been widely used in many industries as an adsorbent and a catalyst. Recently, in order to synthesize various types of porous silica and zeolites, intercalation treatments of clay materials are employed. In the intercalation treatments, various clay materials can be used as a base material. Sodium octosilicate ilerite [1–3] is a layered polysilicate and has attracted the attention of many researchers because the octosilicate has a specific regular (rectangular) shape and is composed of silicon, oxygen, hydrogen and sodium, leading to wide applications. In the intercalation treatments of octosilicate for preparing porous silica containing metal elements, the metal oxide pillars are structured between silicate layers by hydrolysis of an expensive metal alkoxide and condensation of hydrated silicates [4]. For industrial production of porous silica using the intercalation treatments, the development of a simple preparation process in a low cost is necessary. In this study, the intercalation treatment of octosilicate has been modified and a method for introducing a metal element (nickel) easily has been proposed. The control of the pore structure of intercalated octosilicates containing nickel is investigated.

2. Experimental

Figure 1 shows the preparation process of pillared octosilicate. A commercially available sodium silicate solution (grade 4 water glass, Nippon Chemical Industrial, SiO₂ 23.3 wt%, Na₂O 6.3 wt%) was used as a starting material in the hydrothermal synthesis of octosilicate [5].

This grade of water glass has a $\text{SiO}_2/\text{Na}_2\text{O}/\text{H}_2\text{O}$ molar ratio ($= 3.8/1/38.7$) similar to the molar ratio suitable for the synthesis of octosilicate [3]. The 50 ml of the water glass was put into a sealed stainless steel bottle of 200 ml capacity. The sealed bottle was placed in a dry bath kept at 383 K for 14 days, and then cooled to room temperature. The solid phase in the bottle was centrifuged and washed with deionized water on a glass filter. The wet sample was dried at 313 K for 3 days in air. The Na-octosilicate crystals (Figure 2) thus obtained were subjected to an acid treatment for 24 hours for exchanging sodium ions between silicate layers with hydrogen ions. The 3.4 ml of n-octylamine was mixed with the H-octosilicate crystals of 1.0 g for 2 hours for expanding the basal spacing of silicate layers, and then the 9.3 ml of tetraethylorthosilicate (TEOS) was added to the mixture. After stirring the solution for 24 hours, the excess octylamine and TEOS were removed by centrifugation. By adding a proper amount m of deionized water or an aqueous solution of nickel acetate with a concentration C of $0.01\text{--}0.5 \text{ kmol}\cdot\text{m}^{-3}$ as an initiator of the hydrolysis reaction of TEOS, the silicate pillars were structured between silicate layers in the octosilicate. The intercalated octosilicates were centrifuged, washed with ethanol, dried at room temperature for 24 hours, and calcined at 811 K for 4 hours. The samples were characterized based on the specific surface area and the adsorption-desorption isotherms of nitrogen at 77 K measured with an automatic surface area analyzer (Model 4200, Beta Scientific) and an automatic vapor adsorption analyzer (BELSORP 18, BEL Japan), respectively.

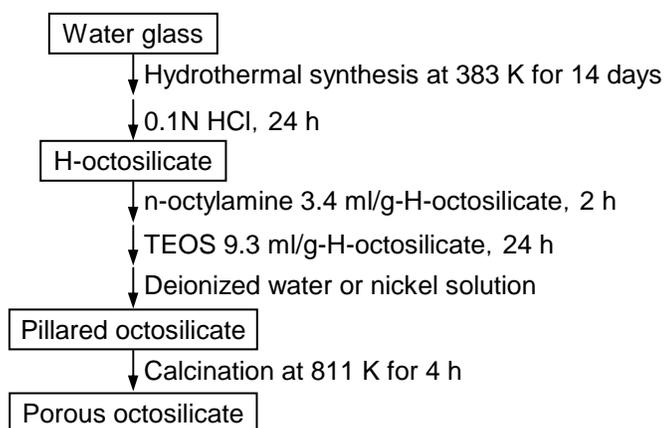


Figure 1. Preparation process of pillared octosilicates containing nickel.

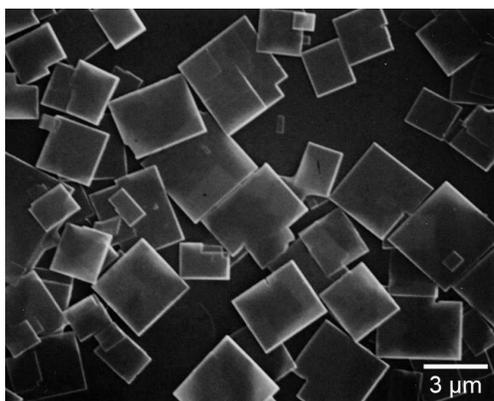


Figure 2. SEM photograph of layered octosilicate ilerite.

3. Results and discussion

Figures 3 and 4 show the influence of added amount m of deionized water (containing no nickel) on the formation of pore structure. The rate of hydrolysis reaction of TEOS increased with m , resulting in an increase in the size of silica particles (pillars) formed between the silicate layers. This led to an increase in the pore size of pillared octosilicates. Figure 5 and 6 show the influence of concentration of nickel acetate on the formation of pore structure at $m = 6.6 \text{ ml}\cdot\text{g}^{-1}$. Except the sample prepared at $C = 0.1 \text{ kmol}\cdot\text{m}^{-3}$, the samples had a microporous structure and a relatively low specific surface area. At a range of low concentration of nickel acetate, acetate ions played a role as a base catalyst and promoted the reaction of hydrolysis of TEOS and condensation of hydrated silica, resulting in a close pillaring between silicate layers. At larger C , a great part of octylamine between silicate layers was exchanged with nickel ions and the interlayer distance decreased, leading to the formation of microporous structure. When $C = 0.1$

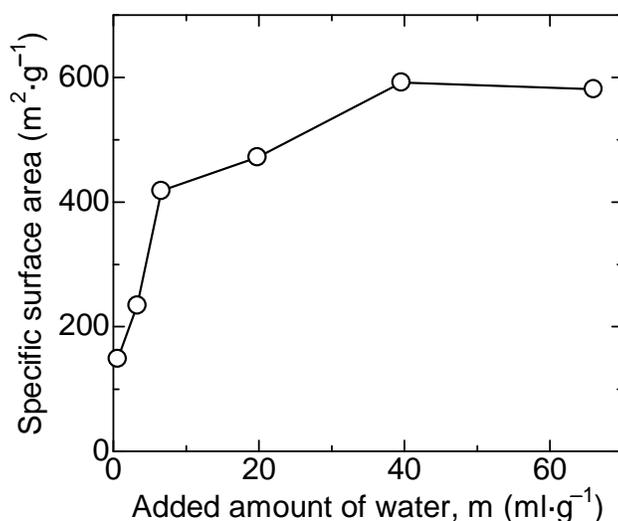


Figure 3. Effect of added amount of water on specific surface area of pillared octosilicate.

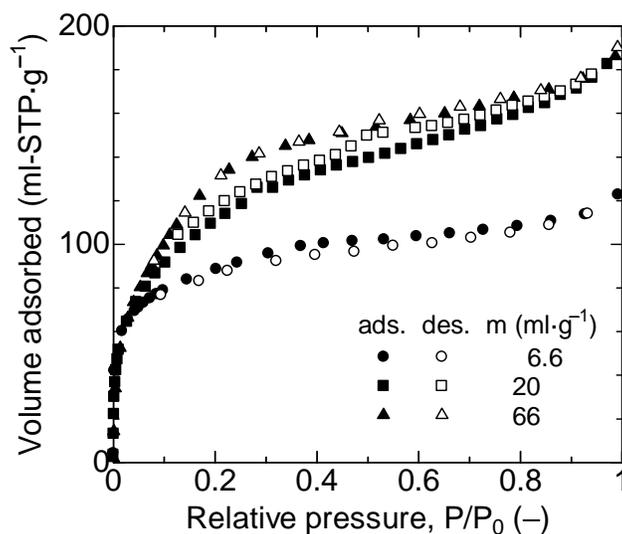


Figure 4. Nitrogen adsorption-desorption isotherms for pillared octosilicates.

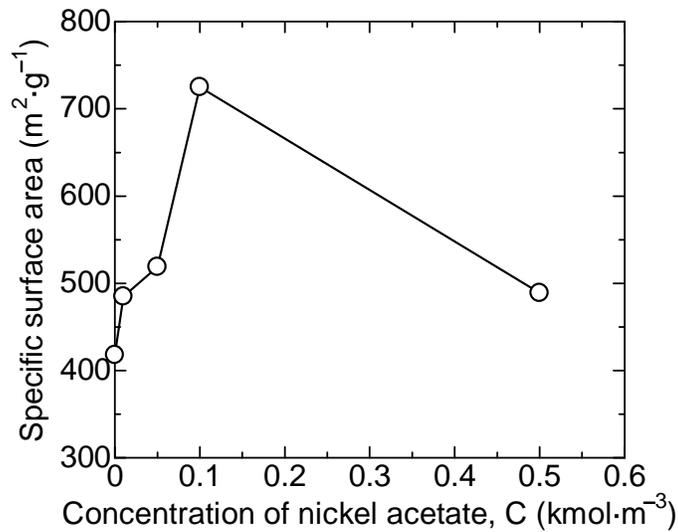


Figure 5. Effect of concentration of nickel acetate on specific surface area of pillared octosilicate containing nickel.

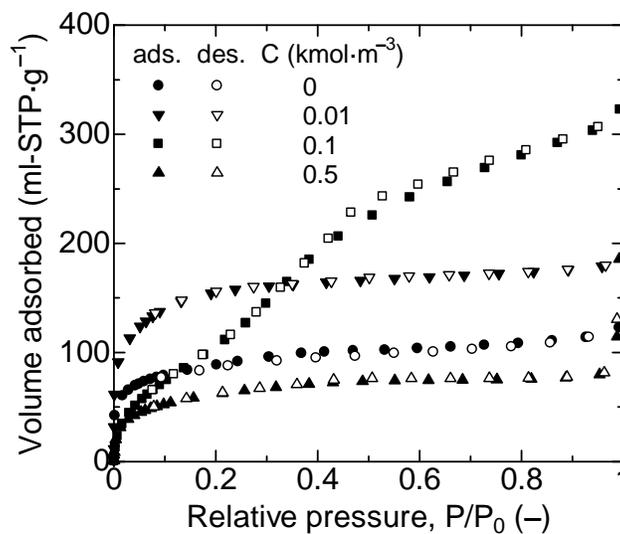


Figure 6. Nitrogen adsorption-desorption isotherms for pillared octosilicates containing nickel.

kmol·m⁻³, the sample having a mesoporous structure was obtained because a proper number of octylamine molecules and nickel ions was in the interlayer and the silica layers were pillared maintaining the initial interlayer distance.

4. Conclusion

A simple process for preparing a porous material as a catalyst containing nickel has been developed using an intercalation treatment of layered octosilicate ilerite. The pore structure formation of pillared octosilicates could be controlled by the pillaring conditions, the

rate of hydrolysis reaction of TEOS (pillaring material). Nickel could be introduced easily into the porous silica by using this process and other catalytic components may be also introduced using this method.

References

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