Preparation of Metal-Oxide-Pillared Clay Using Supercritical Intercalation

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A new method for preparation of metal-oxide-pillared clay by intercalation using supercritical carbon dioxide ($scCO_2$) has been developed. This method is consist of two steps, namely, (1) hydrophobitization of interlayer space by ion exchange of interlayer cations into organic cations in hydrous solution, and (2) intercalation of organic metal compounds followed by hydrolysis with interlayer adsorbed water in $scCO_2$ and calcination. In this work, preparation of silica- and titania-pillared vermiculite was investigated using tetrametoxysilane and titania isopropoxide dissolved in $scCO_{2.}$ Structural changes during intercalation and calcinations were compared with silica- and titania- pillared montmorillonite prepared by similar procedure. Pillared vermiculites showed resistibility to the delamination during intercalation and they have more regulated layered structure than that in pillared montmorillonite.

INTRODUCTION

Pillared clay materials are prepared by intercalating "pillar" compounds into the interlayer space of layered clay minerals. Variety of functional organic molecules and inorganic ions can be intercalated. Metal-oxide-pillared clay has been attracted as a variety of functional materials, such as adsorbents and catalysts, because their function could be designed by choosing the host clay minerals and pillar compounds. Metal-oxide-pillared clay was prepared by ion exchange of metal hydroxide ions or charged colloidal particles. However, their structural control is relatively difficult because of the size distribution of the ions or colloidal particles.

We have developed a new method for fabrication of metal oxide pillared clay, which is consist of (1) hydrophobitization of interlayer space by ion exchange of interlayer cations into organic cations in hydrous solution, and (2) intercalation of organic metal compounds followed by hydrolysis with interlayer adsorbed water in $scCO_2$. The method has a potential to be a useful procedure for designing nanostructures by selecting the size of organic cations. We had reported the preparation of titania-pillared montmorillonite (MNT) with highly dispersed photocatalytic anatase nanoparticles [1]. However, the structural control was insufficient because delamination of clay sheet occurred during supercritical intercalation.

In this work, we investigated the use of vermiculite (VMT) as a clay mineral instead of MNT. VMT has similar crystalline structure to MNT but the layer charging is larger than that of MNT. We expect strong electrostatic force between clay layers and interlayered ions would resist the delamination. Because VMT was not transparent for titania photocatalyst, fabrication of silica pillar in the clay was mainly investigated. Comparison of these two clay systems was investigated.

EXPERIMENTAL

VMT (Australia Vermiculite Co. Ltd) and Na-MNT (Kunimine Industrials Co. Ltd) were previously washed and swelled by soaking in double distilled water. The octadecyltrimethylammonium (C_{18}TMA) ions were selected for control of interlayer space. The excess amount of its chloride salts to cation exchange capacity of clay was used. Interlayer cations of VMT and MNT were ion-exchanged to the C_{18}TMA ions in water. Ion-exchanged samples (C_{18}TMA-VMT and C_{18}TMA-MNT) were washed until chloride was undetectable (using $AgNO_3$) in the washing water using and then dried at 333 K.

Supercritical intercalation was performed using a flow type $scCO_2$ extraction/impregnation system [2]. The apparatus consisted of a high pressure CO_2 pump, a pressurizing vessel (50 cm^3) for the saturation of alkoxide (10 cm^3 of tetramethoxysilane(TMOS) or titania isopropoxide(TP) was introduced under dry conditions) and a pressurizing vessel (1 cm^3) for intercalation (0.2 g of samples were packed) and a back pressure regulator. The temperature of the vessels, pressure in the system and the flow rate of the pump (as a liquid CO_2 at 263 K) was fixed at 353 K, 8 MPa and 2 cm^3/min., respectively, through this work. C_{18}TMA-VMT or C_{18}TMA-MNT was washed with pure $scCO_2$ for five minutes. The saturator was connected to the flow line and the sample exposed to the alkoxide-saturated $scCO_2$ for 5 to 120 minutes. The time is denoted by *t* hearafter.. After that, the saturator was separated from the flow line again and the sample was washed with flesh $scCO_2$ for fifteen minutes. The $scCO_2$ treated sample was exposed to room air. Finarlly the sample was calcinated for six hours in air at 773 K for VMT or at 823 K for MNT. Silica pillared samples before calcination were named as r-Si-C_{18}TMA-VMT and r-Si-C_{18}TMA-MNT, respectively. Calcinated samples were called as Si-C_{18}TMA-VMT and Si-C_{18}TMA-MNT. Microstructure was evaluated using X-ray diffraction analysis (XRD), N_2 adsorption/desorption, and transmittance electron microscopy (TEM).

RESULTS AND DISCUSSION

Fig 1 shows XRD patterns of (100) layered structure of r-Si-C_{18}TMA-VMT and r-Si-C_{18}TMA-MNT. The initial basal spacing of C_{18}TMA-VMT and C_{18}TMA-MNT determined from the XRD peak position was 4.0 and 2.1 nm, respectively. The XRD peak of MNT sample was broadened with increasing the TMOS/$scCO_2$ treatment time, with retention of peak position. It would be caused by the lost of regulated structure caused by intercalation of TMOS. On the other hand, the peak of VMT sample was clear even after the TMOS/$scCO_2$ treatment for 120 min. The peak position was shifted to the smaller angle with the treatment time, indicating expansion of basal spacing of clay layers. VMT layers would resist the delamination by TMOS intercalation and intercalated sample would maintain the regulated layered structure, even though the spacing was expanded. Preparation of titania pillared clay using similar method was also performed for both VMT and MNT, and the similar tendency was observed.

Fig 2 shows XRD patterns of calcinated samples, Si-C_{18}TMA-VMT and Si-C_{18}TMA-MNT. The (100) diffraction peak of the samples without intercalation (*t*=0) was moved to larger angle. The peak was not observed on intercalated samples of *t*=5 to 15. However, the diffraction peak separated from the original was observed on Si-C_{18}TMA-VMT samples after 30 minutes treatment, whereas no significant peak was observed for Si-C_{18}TMA-MNT. With the treatment time, the peak was shifted to smaller angle, like as **Fig 1(a)**. If the peak is assumed to be corresponded to the (100) one, the peak shift would indicate the expansion of basal spacing. The assumed basal spacing was moved from 3.2 nm (*t*=30) to 3.7nm (*t*=120). This result indicates that the nanostructure is controllable by changing treatment time. Similar result was observed on the synthesis of titania pillared VNT and MNT

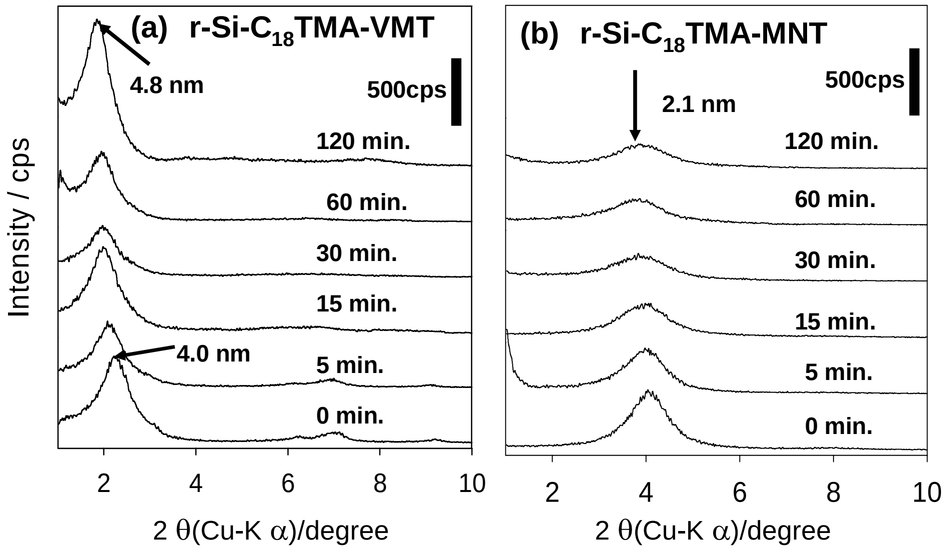

Fig. 1 XRD patterns of (a) r-Si-C_{18}TMA-VMT and (b) r-Si-C_{18}TMA-MNT with different treatment time by TMOS/scCO_2.

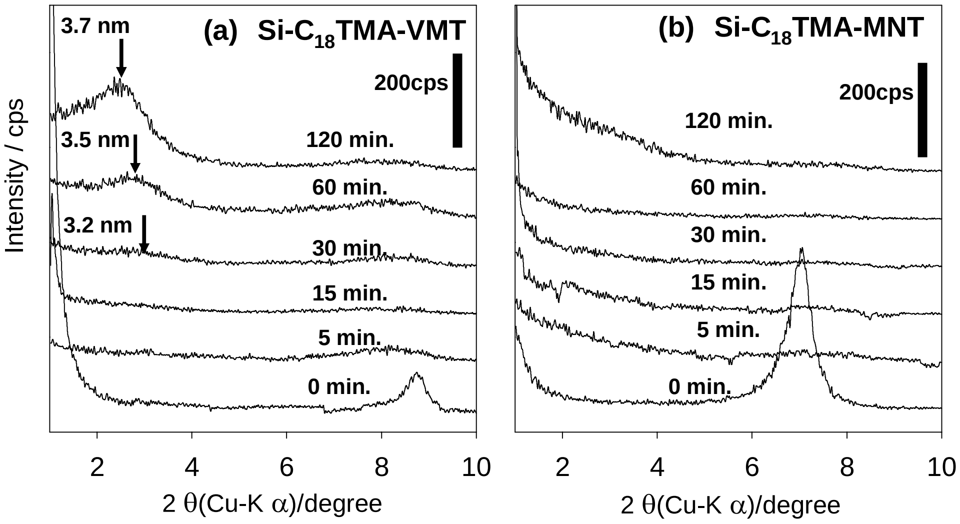

Fig. 2 XRD patterns of (a) Si-C_{18}TMA-VMT and (b) Si-C_{18}TMA-MNT with different treatment time by TMOS /scCO_2.

TEM photographs of Si-C_{18}TMA-VMT (*t*=120) were shown in **Fig. 3** with that of calcinated C_{18}TMA-MNT (i.e. Si-C_{18}TMA-MNT (*t*=0)) for reference. As shown in **Fig. 3(a)** and **(b)**, layered structure of clay was clearly observed. The major spacing was observed as c.a. 3.5 nm and it is obviously larger than that of calcinated C_{18}TMA-Vmt (1.0nm). The 3.5nm spacing is close to the assumed basal spacing from XRD pattern in **Fig. 2**. From these results, we conclude the layered structure of Si-C_{18}TMA-Vmt was based on the expansion of (100) layer.

The long-time-treated VMT sample was revealed to have regulated structure even after calcination. The homogeneity of intercalation would be poor for short time treatment and it is the reason that diffraction peak of (100) layered structure was not detected.

Si-C_{18}TMA-Vmt (t=120) samples have high specific surface area (353 m^2/g). N_2 analysis indicated mesoporosity of the materials. The peak pore size of Si-C_{18}TMA-Vmt (t=120) was calculated by BJH analysis [3] was 2.8 nm. This is close to the interlayer spacing, but BJH method should be applied to cylindrical pores. Further analysis is under investigation.

CONCLUSION

Preparation of silica- and titania-pillared VMT by intercalation of alkoxide dissolved in $scCO_2$ were successfully performed. The pillared VMT showed more regular structure than pillared MNT. Use of VMT having higher charged layer than MNT was revealed to be effective to resist delamination during intercalation.

The basal spacing was controlled by intercalation time on silica pillared VMT. This indicate the potential of seemless control of pore size and pillar size using this method. Application of this method to the other chemicals and clays will be studied.

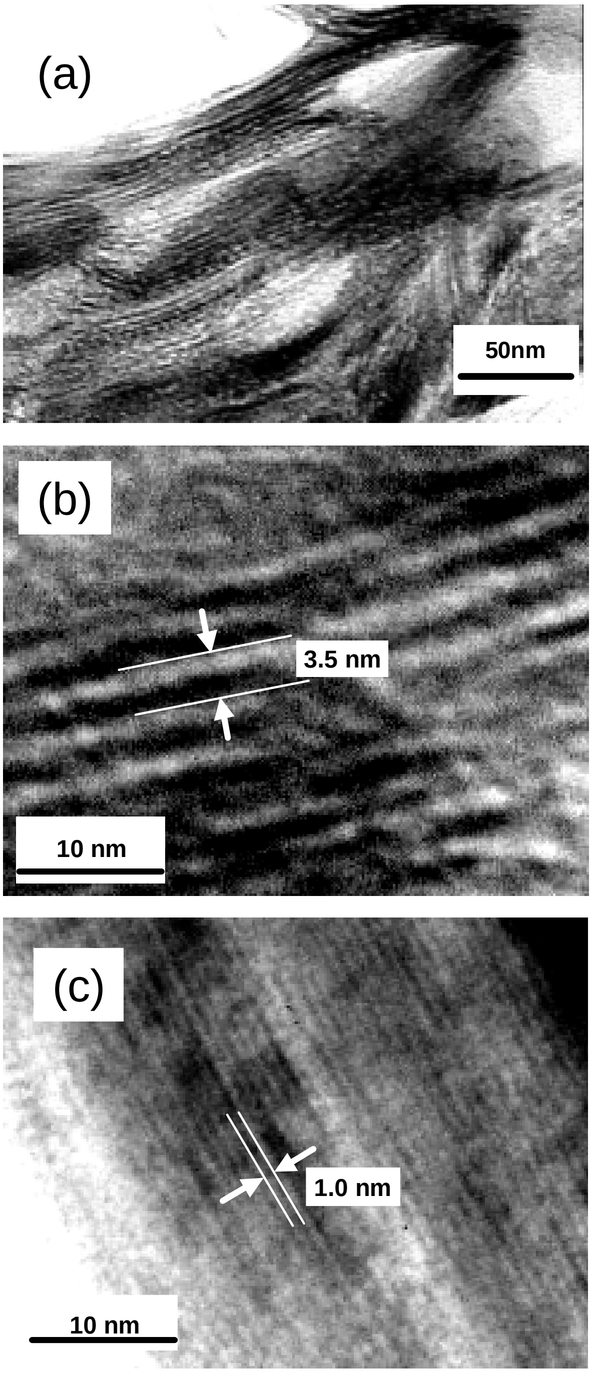

Fig.3 TEM photographs of (a) (b)Si-C_{18}TMA-VMT (t=120 min) and (c) calcinated C_{18}TMA-VMT.

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