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Silica-based mesoporous materials derived from Ti containing layered polysilicate kanemite

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Abstract

Titanium containing layered disodium disilicates that are precursors of kanemite-like layered polysilicates with four-coordinated Ti species (Ti-kanemite) were successfully prepared by using mixed alkoxide solutions of silicon and titanium. According to this synthetic method, colloidal solutions without precipitates can be obtained at Si/Ti molar ratios above 300 under the basic conditions though titanium species are not stable in aqueous solutions under basic conditions. KSW-2-type mesoporous silicas containing TiO_4 units were prepared by using Ti-kanemite with different Ti contents at room temperature through the reaction with hexadecyltrimethylammonium chloride, followed by mild acid treatment. Si/Ti molar ratio of the resultant Ti-KSW-2 without TiO_6 species was as low as ca. 250 in the present system. All of the Ti containing KSW-2 with different Ti contents have high surface areas and pore volumes. Adsorption property of acetaldehyde molecules was investigated by using siliceous and Ti containing KSW-2; acetaldehyde molecules can be adsorbed very fast on the surfaces.

Keywords: Mesoporous; Silica; Titanium; Layered silicate; Kanemite

1. Introduction

Ordered mesoporous silicas can be obtained by using surfactants with self-assembling abilities in aqueous solutions [1–4]. Because of the structural features such as the presence of ordered mesopores, high surface areas and high adsorption capacities, ordered mesoporous silicas are useful as nano-reactors for selective synthesis of fine chemicals that cannot be handled inside micropores of zeolites [5–7]. The ordered mesopores are regurally arraged but the silicate frameworks are amorphous [8]. Therefore, it is considered that silica-based mesoporous materials do not show enough catalytic activities relating to metal species incorporated in the frameworks [6]. Although mesoporous aluminosilicates prepared from solubilized zeolite nanoclusters [9–18] showed a high catalytic performance on cracking, the presence of structural units originated from zeolites has not been confirmed by any experimental data.

It has been reported that an ordered mesoporous silica derived from a layered polysilicate kanemite (FSM-16) are more useful for unique photocatalytic reactions like metathesis, oxidation and decarboxylation than MCM-41 [19–26]. Strained siloxane bridges formed by the condensation of isolated silanol (Si–OH) groups are proposed to be as active sites for those photocatalytic reactions. The isolated Si–OH groups would be effectively condensed on the surfaces of FSM-16 to form strained siloxane bonds because FSM-16 is proposed to be formed through the fragmentation of the silicate sheets due to a crystalline kanemite [27].

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A recent paper on the synthesis from kanemite showed the formation of a novel mesoporous silica (KSW-2) with squared mesopores through two-step reactions with alkyltrimethylammonium surfactants [28]. Structural units originated from kanemite are still remained in the silicate framework of as-synthesized KSW-2. In addition to the formation mechanisms of lamellar, 2-D hexagonal (FSM-16) and 2-D orthorohombic (KSW-2) mesostructures derived from kanemite, structural variations in silicate frameworks have been demonstrated in detail [27–30]. Accordingly, it will be expected that ordered mesoporous silica with precisely controlled framework is synthesized on the basis of the formation mechanisms. On the other hand, there have been few reports on the incorporation of metal species in the silicate framework of kanemite. It is no more than the synthesis of Al, Ga and Sn containing FSM-16 and Al containing KSW-2 [31–34]. Concequently, researches on FSM-16 and KSW-2 applying to catalysts have not been advanced so adequately.

In the present study, incorporation of transition metals into the silicate framework of kanemite was investigated in detail, which would contribute to the development of the derivative mesoporous silicas. We mainly focused on the synthesis of titanium containing kanemite because Ti containing mesoporous silicas are widely investigated as interesting catalysts useful for liquid phase oxidation of alkanes and alkenes [5,6] and unique photocatalytic reactions [35–37]. Thus, the synthesis of KSW-2-type mesoporous silicas was also conducted by using Ti-kanemite and then adsorption property of acetaldehyde molecules on the surfaces of Ti-KSW-2 was investigated.

2. Experimental

2.1. Materials

Tetraethoxysilane (TEOS) and titanium(IV) tetrabutoxide ($Ti(OBu)_4$) were obtained from Wako Chemical Co. and Tokyo Kasei Kogyo Co., respectively. The alkoxides were used without further purification. Aqueous solution of sodium hydroxide (NaOH) and acetic acid (CH_3COOH) were obtained from Wako Chemical Co. Hexadecyltrimethylammonium chloride (C_{16}TMACl) was obtained from Tokyo Kasei Kogyo Co.

2.2. Synthesis of Ti containing kanemite

Ti containing kanemite was synthesized as follows. TEOS and $Ti(OBu)_4$ were mixed in a glove bag filling nitrogen (Si/Ti molar ratio = 100–500). The mixed alkoxide solution was slowly added to an aqueous solution of sodium hydroxide under stirring (Na/(Ti + Si) molar ratio = 1). The stirring was continued for 24 h under the nitrogen atmosphere. The resultant solution was transferred into a porcelain crucible and heated in an electric furnace at temperatures in the range of 650–750 °C (heating rate: 5 °C min^{-1}) for 3 h. The solid product (Ti containing $Na_2Si_2O_5$) was powdered and dispersed in distilled water. After the suspension was stirred for 30 min, the sample was filtered and air-dried. Siliceous kanemite was also prepared by using only TEOS.

2.3. Synthesis of Ti containing KSW-2

According to the previous paper [28], Ti containing KSW-2-type mesoporous silicas were synthesized from Ti containing kanemite (Ti-kanemite). Ti containing $Na_2Si_2O_5$ (possibly forming 1.0 g of Ti-kanemite) was dispersed in 20 mL of distilled water and the suspension was stirred for 30 min. After that, Ti-kanemite was recovered by centrifuging. The wet product was dispersed in 200 mL of 0.1 M C_{16}TMACl aqueous solution (C_{16}TMACl/Si = 2.0) and the reaction was continued for 3 days to obtain a layered C_{16}TMA-kanemite complex. The layered complex was recovered by centrifuging and dispersed in 150 mL of distilled water. To induce the mesostructural transformation of the layered C_{16}TMA-kanemite complex into 2-D orthorhombic phase (space group; C2*mm*), pH value of the suspension was adjusted down to 6.0 by gradual addition of 1.0 M CH_3COOH and the pH value was kept for 1 h. Finally, the product was heated at 550 °C in flowing nitrogen and then calcined at this temperature in flowing oxygen.

2.4. Characterization

Powder X-ray diffraction (XRD) patterns were obtained by using a Rigaku RINT 2100 diffractometer with Cu Kα radiation. Ultraviolet-visible (UV-Vis) spectra were recorded on a Shimadzu UV-2450 spectrophotometer for diffuse reflectance measurement to investigate coordination number of Ti species. $BaSO_4$ was used as a reference. Transmission electron microscopic (TEM) images were taken by a JEOL JEM 2010 (200 kV). Nitrogen adsorption-desorption isotherms were measured by using a Quantachrome Autosorb-1 at 77 K. All the samples were heated at 110 °C for 6 h under vacuum prior to the measurements. Specific surface areas and average pore diameters were calculated by the BET method [38] and the H–K method [39] using adsorption data. Solid-state ^{29}Si magic angle spinning (MAS) nuclear magnetic resonance (NMR) measurements were performed on a JEOL JNM-CMX-400 spectrometer at a spinning rate of 5 kHz and a resonance frequency of 79.42 MHz with a 45° pulse and a recycle time 100 s. The compositions (Si/Ti molar ratio) of the products were measured by ICP (Jarrell Ash ICAP 1000S). FT-IR spectra were obtained by using a Digilab FTS-7000 spectrometer.

3. Results and discussion

3.1. Synthesis of Ti containing kanemite

Ti containing kanemite (Ti-kanemite) can be obtained by using a water glass to which a small amount of titanium