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Mesoporous silica-pillared titanosilicate as catalytic support for partial oxidation of methane

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ABSTRACT

Mesoporous silica-pillared H^+-titanosilicate (SPT) was prepared by hydrolysis of tetraethylorthosilicate using dodecylamine as the template and catalyst in the interlayer space of H^+-titanosilicate ($H_4Ti_2Si_8O_{22}\cdot4H_2O$). SPT exhibited regular gallery height of 3.60 nm, narrow pore distributions of 3.1–3.4 nm, and a large specific surface area of 435–542 m^2/g. The sharpness of the SPT $2d_{001}$ peak was well preserved even after heating for 5 h at 800 °C in air. Ni/STP and Rh/SPT loaded with 5 wt% metal were examined for partial oxidation of methane (POM) at 700 °C. Ni/SPT and Rh/SPT maintained stable activity for almost 100 h on stream. CH_4 conversion (>90%) and H_2 yield (>90%) over Ni/SPT and Rh/SPT were higher than that (>80%) of commercial Rh/Al_2O_3 (loaded with 5 wt% metal). CO yield was very low due to carbon cocking from the formation of carbon nanotubes. Transmission electron microscopy images of the STP catalysts exhibited uniform spacing between the layers even after catalysis and uniform dispersion of metal particles. These observations indicate the unique properties of an SPT catalyst such as the existence of five-coordinated titanium(VI) as an oxidation site, uniform dispersion of metal, ordered pore structure and heat stability, resulting in good performance during POM.

1. Introduction

A number of titanosilicates have been developed for a potential application in catalysis, ion exchange, and separation processes [1]. The layered titanosilicate ($Na_4Ti_2Si_8O_{22}\cdot H_2O$) [2–6] named JDF-L1 contains titanosilicate layers composed of tetrahedral SiO_4 units and a square pyramidal TiO_5 polyhedron [4].

In particular, the interlayer space of JDF-L1 includes five-coordinated titanium(VI); thus, it is less coordinated than octahedrally-coordinated microporous and layered titanosilicates [6]. JDF-L1 is applicable as a potential catalyst for oxidation reactions because the five-coordinated titanium(VI) acts as an oxidation site. Furthermore, JDF-L1 allows intercalation of larger organic and inorganic molecules because of their swelling properties, like clay minerals.

JDF-L1 was synthesized by using Ti-alcoxide [4], $TiCl_4$ [6] and TiO_2 [7,8] as titanium sources. In recent, studies on the practical application on JDF-L1 such as antimicrobial activity test of JDF-L1 ion exchanged with metal ion [9], membrane for H_2/CH_4 separation [10–12] and sorption material for H_2 storage [13] were reported. Various physicochemical approaches such as surface and intercalation chemistry are needed for JDF-L1, similar to clay minerals. However, no study on intercalation chemistry has been conducted except our previous report [14].

We recently reported the pillaring process to introduce metal alkoxides or organic precursors into layered silicates without a preswelling step [14–19]. We also found that this process could be applied to silica pillaring of H^+-titanosilicate (formed by proton exchange of JDF-L1) [14].

In particular, the silica-pillared H^+-titanosilicates (SPTs) prepared by this process are highly applicable as catalytic supports for high temperature reactions because of their high thermal stability. Moreover, SPTs are suitable as potential catalysts for oxidation reactions such as partial oxidation of methane (POM) because of the role of five-coordinated titanium(VI) as an oxidation site. In this study, we report on the preparation of mesoporous SPTs and their applicability as a catalytic support during POM.

2. Experimental section

2.1. Synthesis of JDF-L1 and H^+-titanosilicate

JDF-L1 was prepared as described by Ferdov et al. [6] SiO_2 (29.6 g; particle size 200 μm; Merck, Darmstadt, Germany) and

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NaOH (22.0 g; Junsei, Tokyo, Japan) were added to distilled water (400 ml) and completely dissolved by heating to the boiling point. Subsequently, $TiCl_4$ (6.6 ml; Yakuri Pure Chemical Co., Tokyo, Japan) was hydrolyzed in distilled water (200 ml) and added to the solution. The gel was then transferred to a 1000 ml Teflon-lined autoclave, and crystallization was performed under static conditions at 180 °C for 48 h. The reaction product was filtered, washed with deionized water, and dried at 40 °C.

H^+-titanosilicate was obtained by ion exchange of Na^+ in JDF-L1 by H^+ using 0.1 N HCl solution. A suspension composed of JDF-L1 (20 g) and deionized water (400 ml) was titrated slowly with 0.1 N HCl solution to a final pH of 2.0 and then maintained at this value for an additional 24 h. H^+-titanosilicate was recovered by filtering and washing with deionized water until the solution was Cl^- free, and then dried in air at 40 °C.

2.2. SPT

Mixtures of H^+-titanosilicate, dodecylamine (DDA, Aldrich, Milwaukee, WI, USA) and tetraethylorthosilicate (TEOS, Aldrich) at molar ratios of 1:6–12:16 were reacted for 1 h at room temperature. Unreacted DDA and TEOS were removed from the mixture by vacuum filtration, and the DDA/TEOS intercalated H^+-titanosilicate paste was isolated.

The DDA/TEOS intercalated H^+-titanosilicate paste was dispersed in deionized water at room temperature when the viscous gels became white solids. Bubbles and heat were also produced at ~5 min into this reaction. After soaking for 30 min, the solid products were filtered, washed three times with ethanol, and oven dried at 90 °C. The resulting powder was the SPT. The powdered samples were calcined for 5 h at 600 °C in air to remove the template DDA and organic by-products resulting from TEOS hydrolysis to produce the SPTs. The SPT derivatives were also heated for 5 h at 700 and 800 °C in air to examine thermal stability.

2.3. Preparation of catalysts

Ni/SPT and Rh/SPT catalysts loaded with 5 wt% metal were prepared by the impregnation method. SPT was evaporated after dispersal in an ethanol solution of nickel nitrate (Junsei, special grade) and rhodium nitrate (Junsei, special grade). The use of ethanol instead of water allows for a more uniform dispersion of metal on the gallery surface of SPT because the surface tension of ethanol is lower than that of water.

The SPT-2 (1.0 g) was dispersed for 5 h in 5 mL of nickel nitrate solution (containing 0.26 g of $Ni(NO_3)_2 \cdot 6H_2O$) with stirring. The dispersed solution was evaporated and dried for 24 h at 80 °C and then decomposed for 15 h at 750 °C in air to produce Ni/SPT. Rh/SPT was prepared by the same process. The SPT-2 (1.0 g) was dispersed for 5 h in 5 ml of rhodium nitrate solution (0.168 g of $Rh(NO_3)_2 \cdot 6H_2O$) with stirring. The dispersed solution was evaporated and dried for 24 h at 80 °C and then decomposed for 15 h at 750 °C in air to produce Rh/SPT. Here, commercial Rh/Al_2O_3 (Aldrich, loaded with 5 wt% metal) was also purchased for comparison.

2.4. Catalytic reaction

The catalytic reaction was carried out under atmospheric pressure at 700 °C in a continuous flow quartz microreactor (I.D., 6 mm). The catalyst (30 mg) was placed in the middle of the reactor supported at the bottom with a quartz wool plug. The fresh catalyst was reduced in a flow of H_2 (24 mL/min) for 5 h at 500 °C, and then the temperature was increased to 700 °C at a rate of 20 °C/min before exposure to the reactants. The reactants were passed through the catalyst bed with a molar ratio of $CH_4/O_2 = 2$ and gas hourly space velocity = 7.32×10^4 mL g^{-1} h^{-1} after the hydrogen was turned off at 700 °C.

After purging the reactants with a pressure regulator attached to each gas cylinder, the composition of the reactants was controlled by mass flow meters. The effluent was analyzed with an *in situ* gas chromatograph (Shimadzu Co., Model 14B, Tokyo, Japan) equipped with a thermal conductivity detector using a 5 Å molecular sieve column.

2.5. Catalyst characterization

The powder X-ray diffraction (XRD) measurements of the samples were recorded on a Bruker D8-Advance X-ray powder diffractometer using Cu Kα radiation ($\lambda = 0.1542$ nm) with scattering angles (2θ) of 5–80°, operating at 40 keV, cathode current of 20 mA. N_2 adsorption/desorption isotherms were determined by Micromeritics ASAP 2020 at −196 °C. All samples were outgassed at 300 °C in a vacuum for 4 h. Specific surface area was determined using the BET method [20], and pore size distributions were determined using N_2 adsorption/desorption data and the BJH method [21]. Scanning electron micrographs (SEM) measurements were carried out using a JEOL JSM-840A microscope. Samples were stuck on adhesive tape, sputter coated with gold, and morphological variations were examined. Transmission electron micrographs (TEM) were obtained with a JEOL JEM-200 CX transmission electron microscope operated at 200 kV, using a thin-section technique. The powder samples were embedded in epoxy resin and then sectioned with an ultra microtome.

3. Results and discussion

3.1. Synthesis of JDF-L1 and H^+-titanosilicate

The 48 h hydrothermal reaction at 180 °C produced well-crystallized JDF-L1. The X-ray powder diffraction pattern of air-dried JDF-L1 exhibited several 001 reflections corresponding to a basal spacing of 1.06 nm, as shown in Fig. 1(a). The peak positions of the synthetic sample agreed closely with values reported previously [4,6]. A slow titration of JDF-L1 with 0.1 N HCl produced H^+-titanosilicate by exchanging Na^+ for H^+ in the interlayer region. The X-ray powder diffraction (XRD) pattern of air-dried H^+-titanosilicate exhibited 001 reflections corresponding to a basal spacing of 0.90 nm, as shown in Fig. 1(b). This decrease in basal spacing relative to the Na^+ form indicates a loss of interlayer H_2O upon

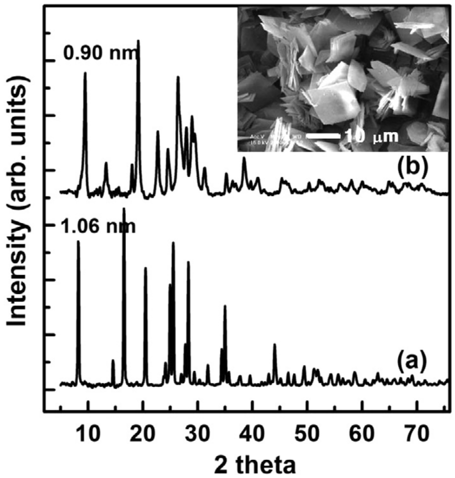

Fig. 1. X-ray diffraction patterns of (a) Na^+-titanosilicate and (b) H^+-titanosilicate (box: scanning electron microscopic morphology of H^+-titanosilicate).