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Zeolite synthesis using mechanochemical reaction

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Abstract

Titanosilicate zeolites are synthesized from bulk titania and silica by a newly developed method using mechanochemical reaction. In this method, an amorphous silica–titania composite is prepared by grinding titania and silica powders with a planetary ball mill and converted into a titanosilicate zeolite through the succeeding hydrothermal treatment. Ti atoms from bulk titania are dispersedly incorporated into the zeolite framework as a tetrahedrally-coordinated species, which is evidenced by several characterization results. By using this new synthesis method, a TS-1 material is obtained highly reproducibly from inexpensive bulk materials without practiced manipulation.

Keywords: Mechanochemical reaction; Titanosilicate; TS-1; Planetary ball mill

1. Introduction

Titanium-containing zeolites [1–7] really stimulate our interests because they exhibit remarkable catalytic activities in various oxidation reactions. It is noticeable that such titanosilicate materials can catalyze oxidation reactions employing hydrogen peroxide as an oxidant. That is, they can act as a catalyst in ‘green’ reaction systems, in which only water is generated as a by-product. TS-1 [1], a member of titanosilicate zeolites having the MFI structure, has been investigated intensively not only because it is the firstly synthesized titanosilicate zeolite but also because it shows particularly high catalytic activity presumably due to its three-dimensional pore structure and high surface hydrophobicity. The attention to this material is further increasing, since it has been industrially applied to the ammoximation of cyclohexanone and will be soon employed as an industrial catalyst to produce propylene oxide.

In conventional synthesis methods for TS-1 [1,8], an expensive titanium alkoxide such as tetrabutyl orthotitanate (TBOT) is usually employed as a Ti source and co-polymerized with a silicon alkoxide to form a precursor hydrogel. Through the succeeding hydrothermal treatment, the Ti species introduced in amorphous silica matrix become tetrahedrally-coordinated Ti atoms isostructurally substituted for Si atoms in the zeolite framework, which are the catalytically active centers of TS-1 [9–11]. However, because of the difference in the hydrolysis rates of titanium and silicon alkoxides, titanium alkoxides are often aggregated separately to become octahedrally-coordinated species. Due to this problem, titanosilicate materials synthesized via conventional methods are sometimes contaminated by extra-framework octahedral Ti species, which are catalytically inactive for oxidation reactions. In this regard, the preparation of a uniformly mixed silica–titania precursor is crucial for the synthesis of highly active titanosilicate catalyst, although it might be difficult without careful manipulation.

In the new synthesis method developed in this study, a uniform silica–titania precursor is prepared not by the polymerization of monomers but by the mechanochemical reaction of bulk titania and silica [12]. Here the mechanochemical reaction would be defined as a chemical reaction promoted by the mechanical energy formed by the collision

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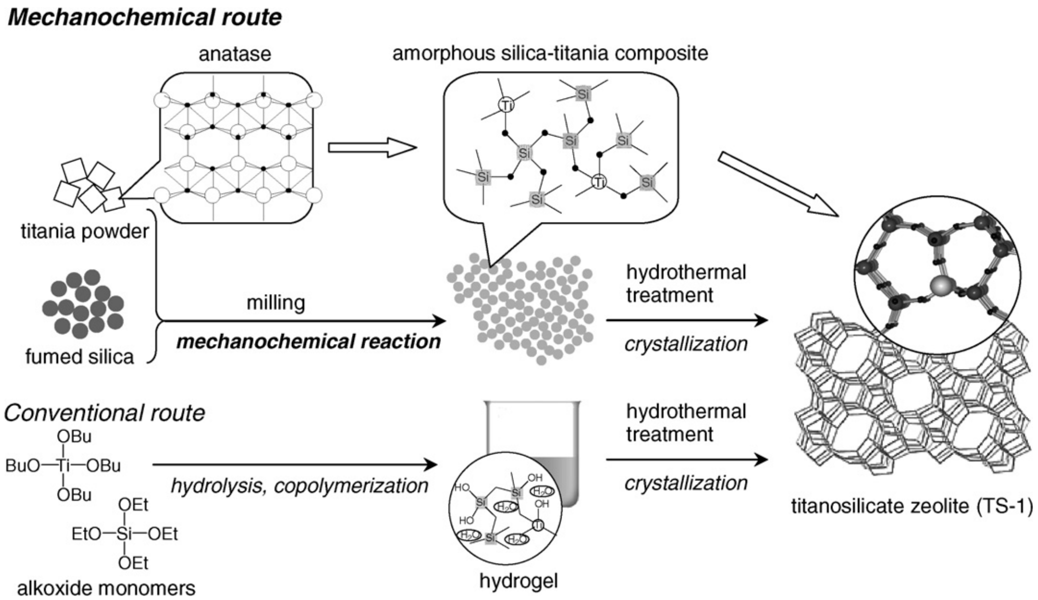

Fig. 1. Schematic illustration of the newly developed mechanochemical synthesis route for TS-1 material.

and/or the friction of milling media. Recently, this reaction has been applied to the detoxification of harmful compounds [13,14] and to the synthesis of nanoparticles [15,16] or composite materials [17] such as Perovskite-type complex oxide materials [18,19]. Considering that the mechanochemical reaction can mix solid materials at the atomic level, it seems reasonable to apply this reaction to the preparation of a titanosilicate precursor.

Fig. 1 illustrates the synthesis scheme of this newly developed method compared with the conventional route. In the mechanochemical route, titania and silica powders are ground with a planetary ball mill. Through the grinding, Ti atoms in bulk titania would be dispersedly mixed into amorphous silica matrix to form a uniform silica–titania composite. Thus prepared precursor composite is crystallized into TS-1 by the succeeding hydrothermal treatment in the presence of tetrapropylammonium hydroxide (TPAOH), a typical structure-directing agent (SDA) for an MFI-type zeolite. This simple method to give titanosilicate materials from a bulk material not only reduces the synthesis cost but also enables the easy and highly reproducible synthesis of titanosilicates.

2. Experimental

2.1. Synthesis

TS-1m, a TS-1 material synthesized via a mechanochemical route, was prepared from anatase-type titania powder (Wako) and fumed silica Aerosil 200V (Nippon Aerosil) as Ti and Si sources, respectively. Their mixture having the Si/Ti molar ratio of 50 was allowed to react mechanochemically through the milling using a planetary ball mill equipped with a silicon nitride pot and balls. The milling was conducted at autogenous temperature for 15 min followed by the pause for 15 min before another 15 min of milling to avoid the overheating of samples. Typically, the material was ground at 700 rpm for the total milling time of 36 h. To the resultant mixture, named g(SiO_2–TiO_2), was added aqueous solution of TPAOH (TCI) as an SDA for an MFI-type zeolite. This mixture having the molar composition of SiO_2:0.02 TiO_2:0.4 TPAOH:20 H_2O was hydrothermally treated in a Teflon-lined stainless autoclave at 170 °C for 3 days under stirring conditions. The product was filtered, washed with distilled water, dried at room temperature, and calcined at 540 °C for 6 h. For a control, TS-1c was synthesized via a conventional method [1,8] using TBOT (Wako) and tetraethyl orthosilicate (TCI) as Ti and Si sources, respectively. The mother gel composition and the hydrothermal synthesis conditions were the same as those of TS-1m.

The mechanochemically reacted silica–titania composite g(SiO_2–TiO_2) was also employed for the synthesis of Ti-containing *BEA-type zeolite [3] and MCM-41-type mesoporous material [20]. In the synthesis of a *BEA-type titanosilicate zeolite, tetraethylammonium hydroxide (Aldrich) was employed as an SDA. The MCM-41-type mesoporous titanosilicate was synthesized by using cetyltrimethylammonium bromide (TCI) as a templating surfactant and tetramethylammonium hydroxide (TCI) as an alkaline source.

2.2. Characterization

The powder X-ray diffraction (XRD) patterns were collected with a PANalytical X'Pert PRO MPD diffractometer. The UV–vis diffuse reflectance spectra were obtained with a Shimadzu UV-2550 spectrometer equipped with an integrating sphere attachment ISR-2200. The diffuse reflectance infrared Fourier transform (DRIFT) was