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Synthesis and catalytic properties of titanium containing extra-large pore zeolite CIT-5

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ABSTRACT

Titanium containing extra-large pore zeolite CIT-5 (IZA code: CFI) was successfully prepared by direct synthesis using Cab-O-Sil M5 and titanium(IV) butoxide in the presence of LiOH. *N*-Methylsparteinium hydroxide was used as a structure directing agent. The product crystallized into thin plate crystals with an approximate size of 20 × 5 × 0.2 μm. The lowest achieved Si/Ti ratio was 23. The necessary duration of hydrothermal synthesis increased with increasing concentration of Ti in the reaction mixture from 11 days (Si/Ti = 63 in product) to 17 days (Si/Ti = 36) at 155 °C. Prepared Ti-CFI samples exhibit BET surface areas in the range of 308–346 m^2/g and micropore volumes of 0.094–0.097 cm^3/g. CFI possesses extra-large pores (14-ring, 7.2 × 7.5 Å) accessible for bulky molecules, therefore, Ti-CFI is a useful catalyst for epoxidation of double bonds in bulky molecules used in perfumery and pharmacy. The Ti-CFI samples proved to be catalytically active in epoxidation of 1-octene, cyclooctene, α-pinene, and norbornene with hydrogen peroxide as oxidation agent.

1. Introduction

Zeolites represent a rich family of porous crystalline aluminosilicates successfully applied as catalysts, adsorbents and ion exchangers [1,2]. The pore size of zeolites is defined by the number of atoms in the pore entrances. The larger pore, the larger molecules can access zeolite inner volume and diffuse to the active sites located mainly inside the pores. Zeolites having more than 12 tetrahedrally coordinated silicon or aluminium atoms in the entrance ring are called extra-large pore zeolites [3,4]. In contrast to aluminosilicate zeolites, a considerable breakthrough was the discovery of zeolite TS-1, having the MFI structure, by Taramasso et al. [5]. The TS-1 is widely used as catalyst in selective oxidations (epoxidations) with hydrogen peroxide providing low waste and being environmentally friendly [6]. Nowadays, the TS-1 is industrially applied by ENI in propylenoxide process [7]. Although the TS-1 is excellent epoxidation catalyst for small linear olefins, the access of larger molecules to the active sites is strongly restricted due to its narrow (10-ring) pores. The increase in accessibility of active sites in titanosilicates with larger pores [8,9] or layered Ti-containing materials was investigated [10] to prepare epoxides from bulky alkenes, cycloalkenes and terpenes. They are requested particularly in pharmacy and perfumery (e.g. α-pinene oxide is a precursor of fragrance ingredients trans-carveol and campholeic aldehyde [11]). Van der Waal reported synthesis of zeolite Ti-BEA and its catalytic behaviour in epoxidation of 1-octene [8] and subsequently of norbornene, camphene, and limonene [12]. Wu et al. reported that Ti-MWW is more active in epoxidation of linear alkenes than TS-1 and Ti-BEA [13]. Corma and co-workers prepared a delaminated MWW zeolite and introduced Ti into the structure to obtain Ti-ITQ-2 material combining the advantages of Ti-MWW structure and easy accessibility of the external surface in delaminated material [14]. However, the Ti-ITQ-2 exhibits high activities only with organic hydroperoxides as oxidants in the absence of water. Tatsumi et al. synthesized Ti-YNU-1 material (interlayer expanded MWW topology) [15], which is active even with aqueous hydrogen peroxide. Another promising material is specially designed TS-1 by Ryoo et al. prepared in the form of nanosheets [10]. This material exhibits activity similar to bulk TS-1 in epoxidation of 1-hexene, however, its activity is an order of magnitude higher in epoxidation of cyclooctene.

While several large-pore titanosilicates (e.g. Ti-BEA, Ti-MOR, Ti-ITQ-7) were synthesized, the only extra-large pore titanosilicate Ti-DON was reported up-to-now [16].

CIT-5 zeolite (IZA code: CFI) is an extra-large pore zeolite with one-dimensional 14-ring channel system. This zeolite shows good thermal stability. Previously it was prepared as pure silica or isomorphously substituted with boron, gallium and aluminium [17]. The CFI zeolite has slightly elliptic pores with diameter 7.2 × 7.5 Å. The synthesis of the CFI is more advantageous in comparison

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with Ti-DON requiring a quaternary ammonium salt as a template instead of a cobalt organometallic complex for DON zeolite [16].

In this contribution, we report the first synthesis of titanosilicate form of the zeolite CIT-5 (Ti-CFI) and a characterization of this material. High thermal stability of the CFI structure as well as easy incorporation of Ti into the framework enables its application as a catalyst for epoxidation of bulky olefins and terpenes. The results of catalytic testing in epoxidation with hydrogen peroxide are also presented as an additional characterization technique with the aim to demonstrate the usefulness of our approach.

2. Experimental

2.1. Synthesis of CFI

Titanium(IV) butoxide (Aldrich, 97%), lithium hydroxide hydrate (Fluka, 99%), Cab-O-Sil M-5 (Havel Composites, Czech Republic), (−)-spartein sulfate pentahydrate (SAFC, 99%), and methyl iodide (Fluka, 99%) were used as purchased.

The *N*(16)-methylsparteinium hydroxide, used as a structure directing agent (SDA), was prepared according to the procedure described in reference [18]. *N*(16)-Methylsparteinium iodide was prepared by a reaction of (−)-spartein and methyl iodide in acetonitrile at room temperature for 72 h. The resulting iodine salt was ion exchanged into hydroxide form using strongly basic anion exchange resin AG1-X8 (Biorad, OH^- form). Properly ion exchanged SDA solution exhibited pH 14.0 and no opacity after acidification with 1 M HNO_3 to pH 1 and addition of 1 volume of 0.06 M $AgNO_3$ solution.

The synthesis of the CFI was based on the procedure described in reference [18]. *N*(16)-Methylsparteinium hydroxide (0.3 M aqueous solution, *N*-MeSpa OH) was mixed with demineralised water and lithium hydroxide hydrate in a Teflon-lined autoclave. A solution of titanium(IV) butoxide in 1-butanol (25%, TBOTi) was added dropwise to the synthesis mixture under vigorous stirring for 2 min. The resulting mixture was homogenized at room temperature for 30 min. Finally, Cab-O-Sil M-5 was added and the mixture was stirred for another 30 min. In some cases the mixture was seeded with earlier prepared "as-synthetized" CFI crystals. The milky homogeneous mixture, with molar composition 0–2.0 TBOTi, 10 *N*-MeSpa OH, 5 LiOH, 50 SiO_2 and 2500 H_2O, was closed in an autoclave and heated under agitation to 155–170 °C for 6–17 days. Lithium hydroxide serves as an accelerator for the crystallization of the CFI phase. On the other hand Li^+ does not compete with *N*-methylsparteinium in templating the structure due to its small ionic radius [18].

The solid product was collected by filtration, washed out with demineralised water and dried overnight at 65 °C. Calcination of the samples was carried out in a stream of air at 570 °C for 8 h.

To remove extra-framework titanium species from the CFI samples, some samples were treated with nitric acid solution prior to the calcination. 30–90 ml (depending on Si/Ti ratio) of 2.0 M HNO_3 solution was used per 1 g of dry as-synthetized material. The mixture was heated at 100 °C for 16 h. After the given time, the solid material was filtered off, washed with water and calcined as described above.

In order to remove Li^+ anions, some samples were ion-exchanged with ammonium nitrate. Calcined samples were treated four-times with 1.0 M NH_4NO_3 solution (Lach-Ner, 99%) for 4 h at room temperature using 100 ml of the solution per 1 g of the sample. The samples were re-calcined at 540 °C for 6 h before use.

2.2. Synthesis of TS-1

Titanosilicate TS-1 was prepared from a gel with initial Si/Ti ratio 40 according to the procedure described in reference [19] using tetraethyl orthotitanate (Aldrich, technical grade), tetraethyl orthosilicate (Aldrich, 98%), and tetrapropylammonium hydroxide (Aldrich, 20% in water) as an SDA.

2.3. Characterization

X-ray powder diffraction patterns (XRD) were collected using a Bruker AXS D8 Advance diffractometer equipped with a graphite monochromator and a position sensitive detector Våntec-1 using CuKα radiation in Bragg–Brentano geometry. Data were collected in continuous mode over the 2θ range of 5–50° with scan speed of 0.0610°/s.

The size and shape of zeolite crystals were examined by scanning electron microscopy (SEM) on a JEOL, JSM-5500LV microscope. The images were collected with acceleration voltage of 20 kV. Energy dispersive X-ray spectroscopy (EDX) analyses were performed using Hitachi S-4800 field emission scanning electron microscope at 25 kV with Noran EDX system. Also some SEM images were collected using the Hitachi system at 5 kV.

Argon sorption isotherms were measured at liquid argon temperature (−186 °C) with Micromeritics ASAP 2020 volumetric instrument. To attain sufficient accuracy in the accumulation of the adsorption data, the ASAP 2020 was equipped with pressure transducers covering the 133 Pa, 1.33 kPa and 133 kPa ranges. Prior to the sorption measurements, individual zeolites were outgassed under turbomolecular pump vacuum at 300 °C for 6 h.

BET area was evaluated using adsorption data in the range of a relative pressure from $p/p_0 = 0.055$ to $p/p_0 = 0.22$. The *t*-plot method [20] was applied to determine the volume of micropores (V_{micro}). The adsorbed amount of argon at $p/p_0 = 0.99$ reflects the total adsorption capacity (V_{total}).

UV–vis absorption spectra were collected for calcined samples using a PerkinElmer Lambda 950 Spectrometer with a 5 mm or 2 mm quartz tube and a large 8 × 16 mm slit. The data were collected in the wavelength range of 190–500 nm.

Chemical composition of the Ti-CFI (60), (40) and (25) was determined also by X-ray fluorescence analysis (XRF) with a spectrometer Philips PW 1404 using an analytical program UniQuant. The samples were mixed with dentacryl as a binder and pressed on the surface of cellulose pellets.

2.4. Catalytic reactions

The catalytic activity of Ti-zeolites was tested in epoxidation of 1-octene (Aldrich, 98%), cyclooctene (Aldrich, 99%), α-pinene (Acros organics, 98%) and norbornene (Aldrich, 99%) with hydrogen peroxide (Aldrich, 35 wt.% aqueous solution) as oxidant in acetonitrile (Fisher chemical, HPLC grade). Mesitylene (Sigma–Aldrich, 99%) or 1,3-diisopropylbenzene (Fluka, 95%) were used as internal standards. The activity was compared with standard TS-1 zeolite. The reactions were carried out at 50 or 60 °C in a following way. The catalyst was activated by heating at 450 °C for 90 min and cooled down in a desiccator. The catalyst (50 mg) was added to 6 ml of acetonitrile followed by 300 mg of the alkene and 150 mg of the internal standard. The mixture was heated in a flask under Dimroth condenser to the reaction temperature and the reaction was started by addition of 0.5 mol equivalent of H_2O_2 (based on alkene). Samples of the reaction mixture were taken in regular intervals, centrifuged and analysed using an Agilent 6850 GC system with 20 m long DB-5 column, an autosampler and a FID or a MS detector. Helium was used as a carrier gas.