



Titanium impregnated borosilicate zeolites for epoxidation catalysis



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ABSTRACT

Titanium containing molecular sieves, known as effective epoxidation catalysts, can be prepared either by direct synthesis or by post-synthesis impregnation. Controlled incorporation of titanium during the post-synthesis modification can be achieved when titanium atoms are inserted into the framework positions previously occupied by heteroatoms such as boron. In this contribution, we report the post-synthesis incorporation of titanium into borosilicates SSZ-24, SSZ-33, SSZ-42 and CIT-5. Parent borosilicates were deboronated using an HCl solution and subsequently impregnated with titanium (IV) butoxide or titanium (IV) chloride. The character of the titanium active sites was investigated using DR-UV/Vis spectroscopy showing that the titanium was incorporated into the framework positions with tetrahedral coordination. In some samples, other titanium species were present as well. The prepared Ti-SSZ-33 provides high yield of cyclooctene oxide 28.3% (after 240 min at 60 °C in acetonitrile, substrate/catalyst ratio = 10, H₂O₂ used as oxidant) in comparison with commonly used TS-1 (2.9%). On the other hand, impregnated zeolites SSZ-24, SSZ-42 and CIT-5 provided lower yields of cyclooctene oxide than the TS-1. The materials were found to catalyse the epoxidation of norbornene and linalool as well. The order of catalysts performance was similar for both substrates: Ti-SSZ-33 (norbornene oxide yield 15.4% after 240 min) > Ti-CIT-5 (yield 3.3%) > TS-1 (yield 1.8%) > Ti-SSZ-42 (yield 0.8%); Ti-SSZ-33 (linalool oxide yield 13.3% after 320 min) > Ti-CIT-5 (yield 3.6%) > TS-1 (yield 3.5%) > Ti-SSZ-42 (yield 1.3%) > Ti-SSZ-24 (yield 0.5%).

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1. Introduction

Titanium containing zeolites have become well established catalysts for C=C double bond epoxidation in past 30 years [1]. They are also able to catalyse other oxidation reactions, e.i., oxidation of alkanes to alcohols and ketones [2], oxidation of aromatic hydrocarbons to phenols [3], ammoxidation of cyclohexanone [4], oxidation of amines to hydroxylamines [5] and thioethers to sulfoxides [6]. Among the catalysts applied, TS-1 zeolite is one of the most studied and also industrially applied catalysts [7,8]. On the other hand, a disadvantage of the TS-1 is the limited access to the active sites for bulkier molecules via its 10-ring pores. Therefore, titanosilicates with larger pores are also subject of interest [9,10].

Titanium containing molecular sieves can be generally prepared either by direct synthesis or by post-synthesis modification [11]. A drawback of the post-synthesis impregnation is that titanium atoms are usually not in well-defined positions and optimum

coordination state [12]. This might be overcome by two step procedure where titanium atoms are inserted into the framework vacancies previously occupied by heteroatoms such as boron or aluminium [13,14].

Wu et al. demonstrated a preparation of Ti-mordenite using dealumination, followed by treatment with TiCl₄ vapour at elevated temperature. ¹⁸O exchange of the samples and subsequent IR analysis showed that the resulting material contained titanium atoms bound in the aluminium vacancies via 4 or 3 oxygen bridges [15]. Ti-mordenite proved to be active catalyst in ketone ammoxidation [16] and hydroxylation of aromatics with hydrogen peroxide [17]. Dartt and Davis reported titanium incorporation into borosilicate SSZ-33 in the same way. Diffuse reflectance ultraviolet (DR-UV/Vis) spectra showed that prepared Ti-SSZ-33 contained mainly titanium atoms incorporated to the zeolite framework and the catalyst was active and selective in cyclooctene epoxidation with hydrogen peroxide (conversion up to 25%, with 99% selectivity at 70 °C after 2 h). On the other hand, the selectivity in 1-hexene epoxidation (12–44% at 5% conversion) and cyclohexene epoxidation (0–2% at 25% conversion) was poor in comparison with the conventional TS-1 [18] due to the epoxide ring-opening reactions.

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Kubota et al. published similar preparation of Ti-MCM-68 from a dealuminated material and its good performance in epoxidation of 1-hexene [19]. Recently, Jin et al. reported post-synthesis titanium introduction into MCM-36 (a layered material with MWW topology) via pillaring of the layers with a mixture of silicon (IV) ethoxide and titanium (IV) butoxide. The resulting material was active catalyst in cyclohexene epoxidation with *tert*-butyl hydroperoxide at 80 °C (conversion 44%, selectivity 87% after 6 h) [20]. Our group reported similar procedure for pillaring of TS-1 nanosheets. The resulting Ti-pillared TS-1 was active in cyclooctene, norbornene, and α -pinene epoxidation with hydrogen peroxide at 60 °C. The yield of cyclooctene oxide over Ti-pillared TS-1 catalyst (16.9% after 4 h) was higher than over TS-1 nanosheets (2.8%) and over pillared TS-1 without titanium addition (3.5%) [21].

In this contribution, we report an impregnation of large-pore borosilicates SSZ-24 (1-dimensional 12-ring channels), SSZ-33 (3D 12-ring x 12-ring x 10-ring channels), SSZ-42 (1D 12-ring channels) and CIT-5 (1D 14-ring channels) with titanium (IV) butoxide in 1-butanol and titanium chloride in toluene. Titanium incorporation into SSZ-24 and SSZ-42 according to the method described in Ref. [18] is also reported. All prepared materials were characterized by X-ray powder diffraction (XRD), nitrogen adsorption, X-ray fluorescence (XRF), and DR-UV/Vis spectroscopy. The prepared catalysts were tested in epoxidation of 1-octene, cyclooctene, norbornene, and linalool with hydrogen peroxide as the oxidant.

2. Experimental

2.1. Synthesis of parent borosilicates and deboronation

Sodium tetraborate decahydrate (Penta, Czech Republic, 99.5%), boric acid (Fluka, 99%), lithium hydroxide hydrate (Fluka, 99%), sodium hydroxide (Penta, Czech Republic, 98%), Cab-O-Sil M-5 (Havel Composites, Czech Republic), (–)-spartein sulfate pentahydrate (SAFC, 99%), and methyl iodide (Fluka, 99%) were used as purchased.

Parent B-SSZ-24 was prepared using a modified procedure described by Lobo and Davis [22]. The *N*(16)-methylsparteinium hydroxide (N-MeSpa-OH), used as a structure directing agent (SDA), was prepared according to the procedure described in Ref. [22]. *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 anion exchange resin AG1-X8 (Biorad, OH[–] form). Properly ion-exchanged SDA solution exhibited pH = 14.0 and no opacity, when 1 ml of the solution was acidified with 1 M HNO₃ to pH = 1 and mixed with 1 ml of 0.06 M AgNO₃ solution. N-MeSpa-OH (0.3 M aqueous solution) was mixed with demineralised water, lithium hydroxide and sodium hydroxide in a Teflon-lined autoclave. After dissolution, sodium tetraborate decahydrate was introduced to the synthesis mixture. Finally, Cab-O-Sil M5 and seeds of earlier prepared SSZ-24 (30 mg) were added and the mixture was homogenized for 30 min. The milky homogeneous mixture, with molar composition 0.625 Na₂B₄O₇ · 10 N-MeSpa-OH: 2.5 NaOH: 2.5 LiOH: 50 SiO₂: 2500H₂O, was closed in a 90 ml Teflon-lined autoclave and heated at 160 °C for 7 days under agitation. The solid product was recovered by filtration, washed out with demineralised water and dried overnight at 65 °C. Calcination of the sample was carried out in a stream of air at 570 °C for 8 h.

Parent B-CIT-5 was prepared according to Yoshikawa et al. [23] and our experience with direct synthesis of Ti-CIT-5 [24] using the same SDA as for SSZ-24. Synthesis gel with molar composition 1H₃BO₃: 10 N-MeSpa-OH: 5 LiOH: 50 SiO₂: 2500H₂O, was closed in a 90 ml Teflon-lined autoclave and heated at 160 °C for 10 days

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

B-SSZ-33 zeolite was synthesized according to the patent [25] using 8-trimethylammoniotricyclo[5.2.1.0^{2,6}]decane hydroxide as the organic template. Structure of the template as well as detailed characterization of B-SSZ-33 zeolite is presented in Ref. [26]. The starting gel had the following composition: 24.5 SDA-OH: 22 NaOH: 1 Na₂B₄O₇ · 10H₂O: 161.5 SiO₂: 7000 H₂O. The reaction was seeded at the 2 wt.% level. The hydrothermal synthesis was carried out in a 90 ml Teflon-lined autoclave heated at 160 °C for 4 days under agitation. The solid product was collected by filtration, washed out with demineralised water, dried overnight at 65 °C and calcined in an oven under a stream of nitrogen. Samples were heated in stages with a rate of 1 °C/min to 120 °C, maintained at 120 °C for 2 h, then heated to 540 °C, kept there for 4 h, and finally heated to 600 °C and hold for an additional 6 h.

The procedure for synthesizing B-SSZ-42 was based on the method proposed by Zones [27]. The zeolite was synthesized using 1-benzyl-1-azonia-4-azabicyclo[2.2.2]octane cation as the template molecule. The reaction mixture has the composition 22 SDA-OH: 1 Na₂B₄O₇ · 10H₂O: 107 SiO₂: 6550 H₂O. The reaction mixture was heated in a 90 ml Teflon-lined autoclave at 150 °C for 17 days without agitation. The solid product was filtered, washed out with demineralised water, dried overnight at 65 °C and calcined in an oven under a stream of nitrogen. Samples were heated in stages with a rate of 1 °C/min to 125 °C, maintained 2 h, then heated to 540 °C, kept for 4 h, and finally heated to 600 °C and hold for an additional 4 h.

The initial Si/B molar ratio for all the materials ranged from 20 to 50. All the samples were deboronated in a 0.01 M solution of HCl. Typically, 1 g of zeolite was suspended in 60 ml of the solution and stirred for 24 h at room temperature. After the given time, the zeolite was filtered off, washed out with distilled water and dried at 65 °C. Successful deboronation was indicated by a strong decrease in the intensity or total disappearance of a characteristic IR band at 1380 cm^{–1}.

2.2. Impregnation procedures

Impregnations with Titanium (IV) ethoxide (TEOTi, Aldrich, 98%) and Titanium (IV) butoxide (TBOTi, Aldrich, 97%) in liquid phase were performed using following procedure. TEOTi or TBOTi was dissolved in absolute ethanol or 1-butanol, respectively. The deboronated zeolite was activated at 450 °C for 60 min, cooled in a desiccator and added to the mixture of titanium alkoxide and alcohol. The mixture was stirred and heated to 45 °C for 16 h in a glass round bottom flask under Dimroth condenser. In particular, 158 mg of TBOTi (0.465 mmol) and 33 ml of 1-butanol were used per 1.0 g of the zeolite. After the given time, the mixture was centrifuged, washed out two times with fresh alcohol and the impregnated zeolite was dried at 65 °C. At the end, the material was calcined at 240 °C for 2 h and then at 560 °C for 6 h with the temperature ramp of 2 °C/min.

Impregnation with TiCl₄ was performed similarly to the above procedure by a solution of TiCl₄ in dry toluene. 0.47 ml of 1 M solution of TiCl₄ (0.47 mmol) was added to a suspension of 1 g of the activated zeolite in 33 ml of dry toluene. The mixture was stirred at 45 °C for 16 h under nitrogen atmosphere. After the given time, the mixture was centrifuged, washed out two times with pure dry toluene, dried at 65 °C and calcined at 240 °C for 2 h and then at 560 °C for 6 h with the temperature ramp of 2 °C/min.

Selected samples were treated with vapour of TiCl₄ according to a procedure described by Dartt and Davis [18]. 500 mg of the activated deboronated zeolite (activation at 450 °C, 60 min) were

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