Synthesis and characterization of titanium-substituted large pore SSZ-42 zeolite

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Titanium-substituted large pore SSZ-42 zeolite was synthesized for the first time using the corresponding borosilicate as starting material. Substitution of boron by titanium took place *via* either high temperature treatment with $TiCl_4$ vapor or by treatment with $Ti(OiPr)_4$ in dry toluene at 120 °C. Both deboronated and boron-containing samples were found to be suitable for post-synthesis incorporation of titanium in the zeolite framework. The obtained materials were characterized by FTIR, UV-visible and XPS. Titanium-modified SSZ-42 was found to be active for phenol hydroxylation and cyclohexene epoxidation.

KEY WORDS: SSZ-42; boron-containing SSZ-42; titanium-substituted SSZ-42; postsynthesis framework modification; large pore zeolite

1. Introduction

Since the advent of titanium-substituted silicalite-1 (TS-1) in the mid eighties [1,2], the synthesis of transition-metals-substituted zeolites has attracted considerable attention. The driving force behind this growth was the remarkable ability of such materials to catalyze the selective oxidation of organic molecules in the presence of environmentally benign dilute hydrogen peroxide. The role of the zeolite framework in stabilizing isolated titanium species (*i.e.*, active sites) in T-atom positions is essential for maintaining the catalytic activity in aqueous media. Moreover, the thermal and hydrothermal stability of the zeolite matrix, and the enhanced hydrophobicity of high silica zeolites are added advantages in favor of selective heterogeneous oxidation in the presence of H_2O_2 as opposed to the often practiced homogeneous stoichiometric oxidation. There are two major routes for incorporating titanium in the framework of zeolites. The first is through direct synthesis by introducing an appropriate precursor of titanium in the synthesis gel. The second approach consists of incorporating titanium *via* post-synthesis treatment of the zeolite in the presence of either $TiCl_4$ vapor at high temperature [3] or titanium isopropoxide in a dry organic solvent [4]. In both cases, either aluminum-, or preferably boron-containing zeolites are used as starting materials. During the post-synthesis treatment, titanium is inserted in the silanol nests formed after the simultaneous removal of Al or B, or after a separate dealumination or deboronation step.

The major drawback of TS-1 which is a medium pore zeolite (MFI structure) is that it cannot accommodate large size organic molecules. This poses an acute problem, particularly regarding the production of pharmaceuticals and fine chemicals involving one or more selective oxidation steps that could benefit from heterogeneization in the presence of such innovative catalysts. It was hoped that the more recent discovery of titanium silicates with periodic mesoporous structure such as Ti-MCM-41 [5,6] and Ti-HMS [7] can solve any problem related to the accessibility of active sites and the diffusion of substrate molecules inside the pore system. Unfortunately, though very useful, mesoporous titanium silicates were found to exhibit much lower *intrinsic* activity than TS-1, *i.e.*, the activity per Ti site for the oxidation of small molecules in the absence of diffusion limitations. For example, Reddy and Sayari [8] found that TS-1 outperformed Ti-MCM-41 and Ti-HMS in the oxidation of propylamine with hydrogen peroxide, in terms of conversion and selectivity to propylamine oxime. Moreover, Sayari *et al.* [6] stated that the only Ti-modified molecular sieve with significant activity in selective oxidation of phenol and alkanes are TS-1 and TS-2 (MEL structure). This was also confirmed by Kulawik *et al.* [9] in a comparative investigation of phenol hydroxylation over TS-1 and Ti-MCM-41.

In addition to active site accessibility, the activity of titanium-modified zeolites and molecular sieves was found to depend, sometimes very strongly, on the structure of the host matrix. The reasons for such variations are not well understood, but they are likely to involve such properties as hydrophobicity, redox potential, and the ease of titanium hydrolysis during reaction [10]. Therefore, the quest for larger pore titanium-containing high silica zeolites remains an important issue in this field [11]. Among the so-called large pore zeolites with 12 member (12 MR) aperture which can be prepared in very high silica form, only ZSM-12 [12], beta [13,14], SSZ-33 [15], and ITQ-7 [16] were successfully substituted by titanium. To our knowledge, large pore zeolites such as SSZ-24 and the newly discovered SSZ-42 [17]

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have not been the subject of isomorphous titanium substitution.

The aim of the present investigation was to prepare titanium-containing SSZ-42 *via* a post-synthesis procedure and test it as a catalyst for selective oxidation of cyclohexene and phenol in the presence of hydrogen peroxide. SSZ-42 (IFR topology) exhibits an undulating, one-dimensional 12 MR channel system of 6.7 Å diameter [17,18].

2. Experimental

2.1. Synthesis

Boron-containing SSZ-42 zeolite was synthesized according to Zones [19]. The molar composition of the synthesis gel was: $SiO_2 : 0.3\ MOH : 0.0375\ NaOH : 0.074\ H_3BO_3 : 30.7\ H_2O$, where MOH indicates the structure-directing agent, N-benzyl-diazabicyclo(2.2.2)octane hydroxide. The latter was prepared *via* reaction of benzyl bromide with diazabicyclo(2.2.2)octane (DABCO) in ethyl acetate at 0 °C followed by ion exchange to the hydroxide form as reported elsewhere [18,19]. In a typical synthesis of B-SSZ-42 (Si/B $=$ 13.5), 0.025 g of NaOH was added to 7.14 g (0.7 mol/l) of an aqueous solution of MOH under vigorous stirring followed by addition of a solution of 0.076 g H_3BO_3 in 2 g of distilled deionized water. Then, 1 g of fumed silica (Cab-O-Sil) was added to the mixture and the resulting gel was stirred at room temperature for 1 h. The mixture was transferred to a Teflon-lined autoclave, heated at 150 °C under slow rotation (60 rpm) for 10 days. The crystallized product was filtered, washed thoroughly with deionized water and allowed to dry under ambient air. To remove the occluded template molecules, the as-synthesized material was calcined in flowing air at 540 °C for 5 h.

Titanium substitution of framework boron was achieved as reported by Rigutto *et al.* [20] *via* post-synthesis treatment of B-SSZ-42 in the presence of $TiCl_4$ vapor at 400 °C. Typically, 0.5 g of borosilicate was loaded into a flow-through quartz reactor and purged with flowing dry nitrogen (30 ml/min) at 600 °C for 4 h. Subsequently, the reactor was cooled down to 400 °C, then nitrogen was allowed to flow through a saturator containing $TiCl_4$ at room temperature. This treatment was performed for 4 h. Finally the sample was purged with nitrogen for another 2 h, then cooled down to room temperature. This was followed by calcination in air at 300 °C for 2 h. The treatment in the presence of $TiCl_4$ was carried out using either boron-containing zeolite or deboronated samples. In the latter case, deboronation took place by contacting the zeolite with dilute aqueous hydrochloric acid solution (pH $=$ 3) as previously described by De Ruiter *et al.* [21]. In the case of titanium incorporation without prior deboronation, removal of the remaining framework boron was performed in the gas phase by methanolysis, as described by Rigutto *et al.* [20].

Alternatively, incorporation of titanium into deboronated samples was performed using a procedure described first by Fraille *et al.* [4] and reported by Tuel [22]. A sample (0.5 g) of deboronated zeolite was first treated under vacuum at 350 °C for 3 h, then dispersed in 20 ml of dry toluene containing titanium isopropoxide. The mixture was refluxed for 3 h under vigorous stirring. The suspension was filtered and the solid sample was washed with toluene, then dried in air at room temperature. It was subsequently calcined at 540 °C in air for 5 h.

2.2. Characterization

X-ray diffraction (XRD) patterns were obtained on a Siemens D5000 diffractometer using Cu Kα radiation ($\lambda =$ 0.15418 nm). Adsorption measurements were performed using a Coulter Ominorp 100 gas analyzer. Pore size distributions were calculated using the Horvath–Kawazoe method [23]. Scanning electron microscopy (SEM) images were recorded on a Jeol 840A microscope operated at an accelerating voltage of 10–20 kV. Infrared spectra were recorded on a Nicolet 550 spectrometer using the KBr pellet technique. Diffuse reflectance UV-visible spectra were obtained on a Perkin–Elmer spectrometer using magnesium oxide for background correction. The elemental analysis was performed by ICP-AES on a Jarell-Ash 975 spectrometer after solubilization of the samples in HF/HCl solutions. High resolution XPS spectra were recorded on a V.G. Scientific Escalab Mark II system using a non-monochromatized Mg Kα X-ray source ($h\nu =$ 1253.6 eV). The spectrometer is equipped with a hemispherical analyzer operated in the constant pass energy mode. A binding energy of 103.3 eV for Si 2p was used as an internal reference.

2.3. Test reactions

Cyclohexene epoxidation and phenol hydroxylation in the presence of dilute aqueous hydrogen peroxide were used as catalytic tests [2,24–27]. These reactions were carried out as described earlier [28,29] in a 250 ml magnetically stirred three-necked round bottom flask. A typical epoxidation reaction was carried out as follows. 0.1 g catalyst, methanol (11.8 g) and cyclohexene (1.35 g, 16.5 mmol) were introduced into the reactor. The mixture was heated and kept at 50 °C. The reaction was then started by injecting 4.1 mmol (0.5 g) H_2O_2 (30%). In the case of phenol hydroxylation, 0.2 g catalyst, acetone (15 g) and phenol (2.0 g, 21.3 mmol) were loaded into the reactor. The mixture was heated and kept at 62 °C. The reaction was initiated by injecting 7.0 mmol (0.8 g) H_2O_2. After 2 h of reaction, aliquots were sampled and analyzed by GC-MS using a non-polar HP-1 or a polar HP-5 capillary column for cyclohexene and phenol reactions, respectively.

3. Results and discussion

The XRD spectrum of boron-containing SSZ-42 is shown in figure 1. As seen, the current material exhibited a well resolved XRD pattern identical to that obtained by Chen

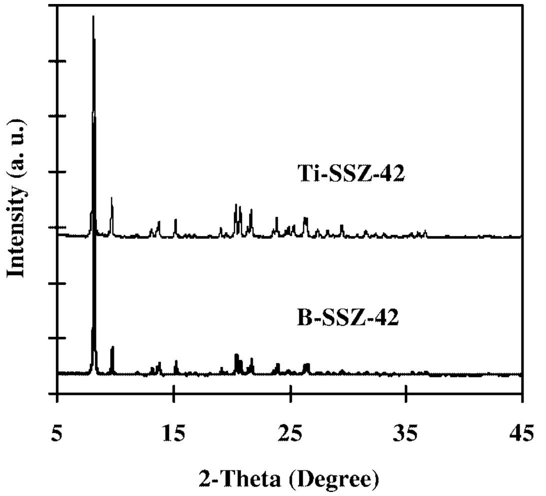


Figure 1. X-ray diffractograms for boron- and titanium-containing SSZ-42 zeolite.

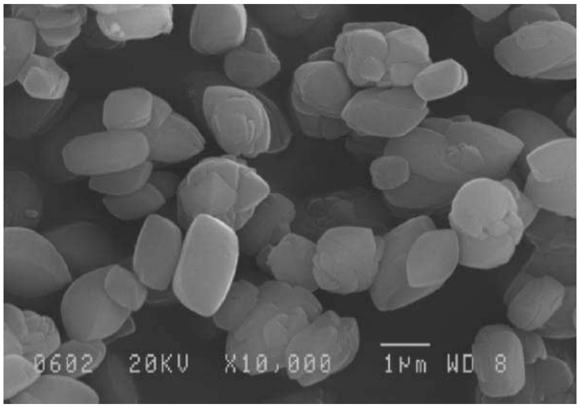
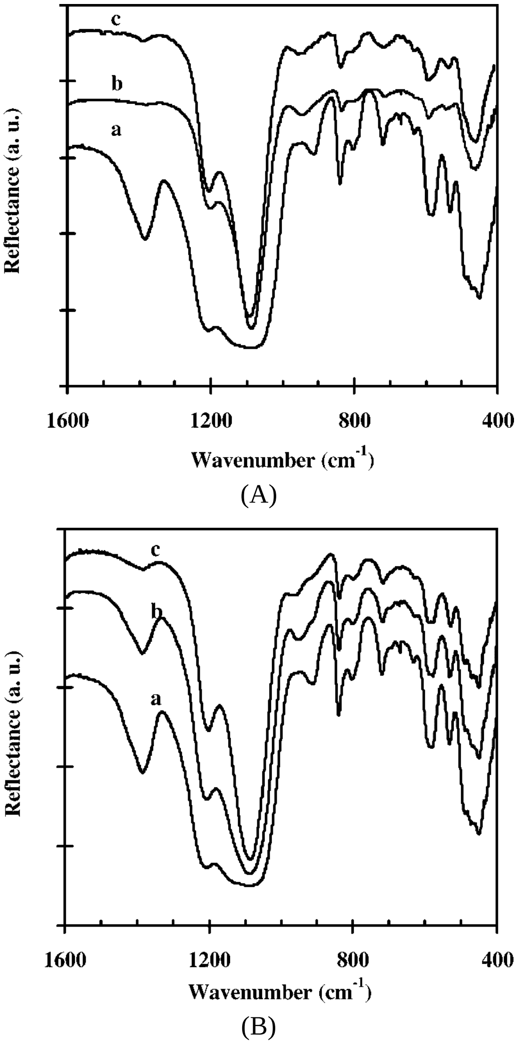


Figure 2. SEM image for B-SSZ-42.

et al. [18]. Furthermore, reproducible syntheses of boron-containing materials were achieved at 150 °C for 10 days and large batches (10 g) were successfully synthesized. Figure 1 also shows the XRD pattern for Ti-containing SSZ-42. Interestingly, incorporation of titanium did not alter the XRD pattern indicating that no structural changes and no significant decrease in crystallinity took place. Furthermore, consistent with the fact that the titanium ion is larger than the silicon, the framework substitution of Ti was accompanied by a small, but significant increase in the *d* values. For instance, the *d* value corresponding to the most intense diffraction peak (110) increased from 10.79 to 10.84 Å. In their work on boron-containing beta zeolite, Rigutto *et al.* [20] observed 20–30% decrease in crystallinity upon treatment upon exposure with $TiCl_4$ vapor at 300 °C, indicating that beta zeolite is more sensitive to the aggressive nature of the post-synthesis treatment.

The surface area determined using the nitrogen adsorption data was 450 m^2/g. The corresponding pore volume was 0.19 ml/g. Both values compare well with those previously reported by Zones [19]. The pore size distribution determined using the Horvath–Kawazoe model indicated that B-SSZ-42 exhibits pore sizes with an average of *ca.* 0.62 nm.



(A)

(B)

Figure 3. (A) FTIR spectra for (a) B-SSZ-42, (b) Ti-SSZ-42 (treatment with $TiCl_4$ without prior deboronation), and (c) Ti-SSZ-42 after methanolysis; (B) FTIR spectra for (a) B-SSZ-42, (b) Ti-SSZ-42 (treatment with $TiCl_4$ after deboronation), and (c) Ti-SSZ-42 (treatment with $Ti(OiPr)_4$ after deboronation).

This value is close also to that reported by Chen *et al.* [18], *i.e.*, 0.67 nm. Figure 2 shows a representative scanning electron micrograph. The zeolite morphology was comprised of very uniform slightly elongated particles about 5 μm in length akin to those reported in the literature [18] which were however only 1–2 μm long.

Figure 3 (A) and (B) depicts the FTIR spectra of B-SSZ-42 and Ti-SSZ-42. The band at 1400 cm^{-1} indicative of the presence of tricoordinated boron [30] was used to monitor the deboronation process. The characteristic IR band at 960 cm^{-1} assigned to the stretching mode of SiO_4 units bonded to Ti(IV) [31] was used as fingerprint for the incorporation of titanium in the silica framework [8,32]. As seen in figure 3 (A) and (B), upon reaction with $TiCl_4$ with (figure 3(A,b)) or without (figure 3(B,b)) prior deboronation, or upon treatment in the presence of $Ti(OiPr)_4$ in dry toluene (figure 3(A,c)), a band developed at 960 cm^{-1}. Simultaneously, the original band located at 930 cm^{-1} disappeared suggesting that it may be associated with the Si–OH groups adjacent to trivalent boron. This indicates that irrespective of the procedure used, Ti is effectively incorporated into the zeolite framework. It can also be seen in figure 3 (A) and (B) that Ti-containing SSZ-42 prepared in the presence of $TiCl_4$ vapor using non-deboronated samples exhibited a more intense 960 cm^{-1} band compared to samples prepared by the same technique after deboronation. Removal of the remaining framework boron by methanolysis (figure 3(B,c)) was confirmed by the drastic decrease in the intensity of the band at 1400 cm^{-1} [32]. Figure 3(A,b) also shows that the acid treatment is very effective for the removal of boron as the 1400 cm^{-1} band almost vanished.

Diffuse reflectance UV-visible spectroscopy is a very sensitive technique for detecting isolated Ti species in tetrahedral environment. UV-visible spectra of calcined boron-containing zeolite as well as the corresponding titanium-modified material are shown in figure 4. The boron-containing precursor did not exhibit any absorption in the range 200–900 nm. Conversely, the titanium-modified sample exhibited strong absorption peaks at *ca*. 220 nm indicating the occurrence of atomically dispersed titanium in tetrahedral coordination [29]. Moreover, the Si/Ti ratio determined by elemental analysis was 37, which means that only 36% of the available boron sites have been substituted by titanium.

Figure 5 displays the Ti 2p photoelectron spectrum for the calcined Ti-SSZ-42 sample. Ti $2p_{3/2}$ exhibited two different binding energies at 459.8 and 458.3 eV corresponding to Ti^{4+} in tetrahedral and octahedral coordinations, respectively [33]. Based on the intensity of the two Ti 2p doublets, the relative amount of tetrahedral titanium was calculated to be 81%. Furthermore, the surface Si/Ti ratio determined by XPS was equal to 38, which is almost identical to the bulk composition as determined by elemental analysis.

Catalytic tests

The catalytic performances of the current Ti-containing zeolite for phenol hydroxylation and cyclohexene epoxidation with hydrogen peroxide are summarized in table 1. For phenol hydroxylation, the activity and selectivity of Ti-SSZ-42 approached those typical of the well-known TS-1 zeolite. The oxidation of cyclohexene with hydrogen peroxide afforded cyclohexene oxide selectively. For this reaction also, high conversions and selectivities were obtained with Ti-SSZ-42 zeolite. However, it is important to point out that only a limited number of heterogeneous catalysts provide

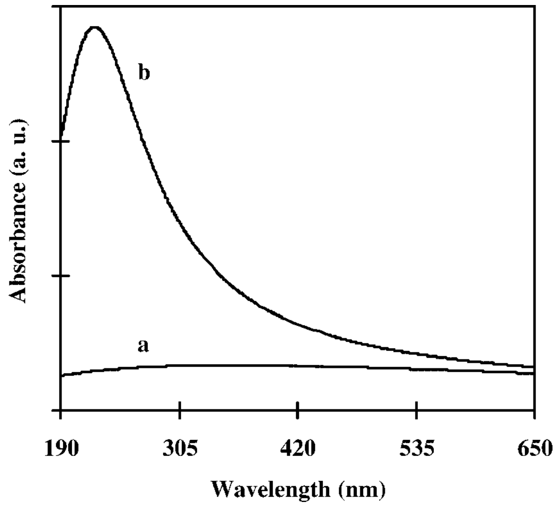


Figure 4. UV-visible spectra for B-SSZ-42 (a) and Ti-SSZ-42 (b).

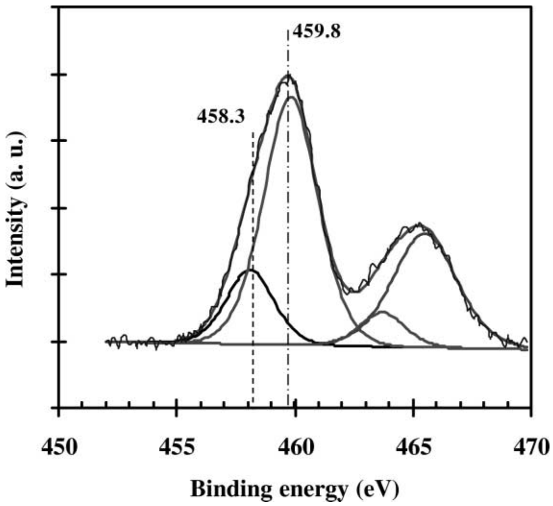


Figure 5. Ti 2p XPS lines for Ti-SSZ-42.

Table 1
Catalytic performances of Ti-SSZ-42 for phenol hydroxylation and cyclohexene epoxidation.

Catalyst	Reactant	Temperature (°C)	Time (h)	Solvent	React./H_2O_2	Conversion (%)	Selectivity (%)
Ti-SSZ-42	Phenol	62	2	CH_3CN	3	22	45[d]
TS-1[a]	Phenol	100	1	$(CH_3)_2CO/H_2O$	3.8	27	50[d]
Ti-SSZ-42	Cyclohexene	50	2	CH_3OH	4	12	58[e]
Ti-beta[b]	Cyclohexene	50	2	CH_3OH	4	18	0[e]
TS-1[c]	Cyclohexene	70	3	$(CH_3)_2CO$	5	5	98[e]

[a] From [34].
[b] From [35].
[c] From [36].
[d] Selectivity to quinone.
[e] Selectivity to epoxide.

selective epoxidation of cycloolefins with hydrogen peroxide [36]. As shown in table 1, Ti-beta zeolite did not exhibit any selectivity toward the epoxide because of fast secondary solvolysis reaction. In addition, TS-1 exhibited quite poor activity in this reaction due to the non-accessibility of the active sites to the relatively bulky reactant molecule.

4. Conclusion

B-SSZ-42 zeolite has been prepared and for the first time successfully modified by incorporating titanium into the framework *via* post-synthesis treatment in the presence of $TiCl_4$ vapor. This procedure proved to be an attractive alternative to the direct hydrothermal synthesis of Ti-containing SSZ-42 zeolite which was very difficult to achieve. The effective incorporation of titanium into the zeolites framework was evidenced by a number of spectroscopic techniques including FTIR, UV-visible and XPS. Catalytic tests encompassing hydroxylation and epoxidation reactions using hydrogen peroxide showed that the Ti-modified zeolite was active for cyclohexene epoxidation.

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