Epoxidation of cyclohexene on Ti/SiO$_2$ catalysts prepared by chemical grafting TiCl$_4$ on deboronated silica xerogel

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Abstract

Ti/SiO$_2$ (or Ti/de[B]SiO$_2$) catalysts were prepared by grafting deboronated silica xerogel with gaseous TiCl$_4$. Using TBHP as oxidant, the Ti/de[B]SiO$_2$ catalyst shows both catalytic activity and selectivity in epoxidation of cyclohexene better than 80%, and the activity can be comparable with that of Ti-β. The catalytic activity of Ti/de[B]SiO$_2$ strongly depends on the content of B of support precursor, and the pretreatment temperature of the support. IR studies show that the sites in the deboronated silica xerogel to react with TiCl$_4$ are not only the silanol nests, but also the defect sites produced during the deboronation. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Ti/de[B]SiO$_2$; Chemical grafting; Deboronation; Cyclohexene; Epoxidation

1. Introduction

The redox zeolites in which some Si atoms are replaced by transition metal cations have demonstrated to be the potential catalysts for selective oxidation, such as epoxidation, in liquid phase [1]. However, these materials are often expensive and relatively difficult to synthesize, as their preparation requires specific conditions to prevent the formation of aggregated metal oxide during the crystallization process [2]. Thus, many studies have been carried out to synthesize zeolites through indirect methods. Kraushaar and van Hooff using dealuminated ZSM-5 for the preparation of TS-1 [3] reported an example of such indirect synthesis or postsynthesis modification. The indirect synthesis of a titanium zeolite often consists of a dealumination or a deboronation step. In the dealumination or deboronation step, vacant sites, i.e. silanol nests, are created in the zeolite framework. Titanium precursors can react with these vacancies in the subsequent titanation procedure to produce the tetrahedral titanium sites in the zeolite framework, which are similar in catalytic property to those sites obtained via a direct synthesis route [3].

Moreover, many attempts have been made to replace these zeolite-based catalysts by matrix-like materials containing highly isolated transition metal cations, for example, transition metal ions on various organic or inorganic supports with high surface area [2]. There has been an important breakthrough with the recent discovery of metal-containing mesoporous silicas that were shown to possess interesting properties in the

selective oxidation of bulky substrates [4–6]. It was also reported that SiO_2–TiO_2 mixed oxides prepared by sol–gel method contain some isolated Ti–O–Si species which could catalyze the epoxidation of olefins with TBHP or other alkyl hydroperoxides [7–12].

In a previous work [13], we have reported the synthesis of Ti/SiO_2 catalysts by chemical grafting of $TiCl_4$ on SiO_2, and also Si/Ti/SiO_2 by chemical grafting silica precursor on Ti/SiO_2. These catalysts show good activity and selectivity in epoxidation of styrene. In the present study, a new method to prepare Ti/SiO_2 catalysts via chemical grafting $TiCl_4$ on de-boronated silica xerogel is reported. The B-containing silica xerogel was prepared by sol–gel method. The xerogel was deboronated with 2 M HCl. And using these deboronated silica xerogels as the support, a series of catalysts were prepared by chemical grafting. These catalysts are active in epoxidation of cyclohexene using TBHP as the oxidant. When the support (deboronated SiO_2–B_2O_5) is calcined at 673 K and the chemical grafting temperature is 773 K, both the conversion of cyclohexene and the selectivity to epoxide exceed 80%. These catalysts have been characterized by FT-IR, Raman and UV-Raman spectroscopies.

2. Experimetal

2.1. Preparation

2.1.1. Synthesis of B-containing silica xerogel

Typically, x ($x = 17.84$, 4.46, 1.78) mmol H_3BO_3 was slowly dissolved in 40 ml ethanol under stirring, then 89.2 mmol tetraethylorthosilicate (TEOS) was added. After the solution becomes homogeneous, 12 ml 4 M HCl was added dropwise in 30 min. The solution was then heated at 353 K for 1 h, and a transparent gel was obtained. The gel was kept in ambient for 48 h, and then it was dried in air at 398 K for 12 h. The xerogel is denoted as SiO_2–B_2O_5 (n) (n is the ratio of SiO_2/B_2O_5, $n = 10$, 40, 100). The synthesis of silica xerogel follows the above procedure, except for the addition of H_3BO_3.

The content of B atom in the B-containing silica xerogel cannot be very large because the mixed SiO_2–B_2O_5 xerogel cannot be formed when the n is beyond a certain limitation. For example, when $n = 5$, some flock material appeared on the surface of

the transparent B-containing silica gel, and the flock material was boric acid.

2.1.2. Deboronation and chemical grafting

Before being used as support, the SiO_2–B_2O_5 was treated with 2 M HCl (20 ml/g) at 353 K for two times, each time for 2 h. The boron atoms in the SiO_2–B_2O_5 can be removed by this treatment and the as-treated sample is denoted as de[B]SiO_2. The de[B]SiO_2 support was calcined in O_2 flow at a given temperature for 4 h, and then was heated to (or cooled down to) 773 K in N_2 flow for 0.5 h. The sample was treated at 773 K with a flow of N_2 that was saturated with $TiCl_4$ at room temperature. The sample was flushed for 2 h with dry N_2 to remove excessive $TiCl_4$, and then the catalyst was cooled down to room temperature in N_2 flow. The as-prepared catalyst was denoted as Ti/de[B]SiO_2 (T) (T is the pretreatment temperature of the support). The grafting temperature of $TiCl_4$ was 773 K for all samples.

2.2. Characterization

UV-Raman spectra were recorded on a homemade Raman spectrometer. The 244 nm line from an Innova 300 FRED laser was used as the excitation source. Visible Raman spectra were obtained on a Jobin Yvon double monochromator (U-1000) coupled to a photomultiplier tube for detection. The 488 nm line of an Argon laser was used to excite the sample.

Infrared spectra were collected on a Nicolet Impact 410 FT-IR spectrometer. The sample was pressed into a self-supported wafer, and the wafer was set in quartz IR cell that was sealed with CaF_2 windows. After calcined at a given temperature for 4 h in flowing O_2, it was cooled to room temperature and then evacuated at 423 K for 1.5 h. After the sample was cooled down to room temperature, a spectrum was measured in the absorbance mode. The absorbance values of the OH groups were normalized with the band at 1800 cm^{-1}.

2.3. Catalytic reactions

The epoxidation of cyclohexene was performed in a 50 ml round-bottom flask, 18 mmol of cyclohexene, 5 ml of solvent, and 200 mg of catalyst were mixed in the flask and heated to a given temperature. Then 3.3 mmol of TBHP was added to the flask. Products

were analyzed by a gas chromatography equipped with a capillary column (SE-30) and a flame ionization detector (FID).

The conversion of cyclohexene is calculated based on the amount of converted cyclohexene and the amount of TBHP used. The TBHP added into the reaction system is usually less than the amount of cyclohexene, and the oxidation reaction between TBHP and cyclohexene gives mainly epoxide, cyclohexenol and cyclohexenone. The stoichiometric ratio of cyclohexene/TBHP is a unit, so a total conversion of cyclohexene is defined when the amount of converted cyclohexene is equal to the amount of TBHP added, and the conversion of cyclohexene is calculated as, conversion (%) = (converted cyclohexene/TBHP) × 100.

3. Results and discussion

3.1. Deboronation

Fig. 1 shows the IR spectra of SiO_2–B_2O_5 (10) and deboronated SiO_2–B_2O_5 (10) samples. Generally, the presence of B gives the IR bands at 1450 and $663 \, cm^{-1}$. The $1450 \, cm^{-1}$ band is assigned to the B atom in trigonal coordination, while the $663 \, cm^{-1}$ band is attributed to the out-of-plane bending mode of B–O–Si species [14,15]. The two bands are not observed for the deboronated sample (Fig. 1a), indicating that the B atoms in the SiO_2–B_2O_5 samples are removed by the deboronation treatment.

IR spectra of the SiO_2–B_2O_5 (10) xerogel before and after deboronation in the hydroxyl region are shown in Fig. 2. Fig. 2a is the spectrum of SiO_2–B_2O_5 (10) sample, which was calcined at 473 K. Fig. 2b–d are the deboronated SiO_2–B_2O_5 (10) samples that were calcined at 473, 673 and 773 K, respectively. For untreated sample SiO_2–B_2O_5 (10), a broad band at 3700–$3400 \, cm^{-1}$ and an intense band at $3740 \, cm^{-1}$ are observed. The broad band possibly arises from the B (OH) Si sites. And the intense band at $3740 \, cm^{-1}$ can be assigned to isolated silanol species [16,17]. For deboronated samples, the $3740 \, cm^{-1}$ band remains unchanged, but the broad band at 3700–$3400 \, cm^{-1}$ shifts to lower frequencies. This is because those silanol groups are derived after the boron atoms were removed, and the silanol groups may be interacted
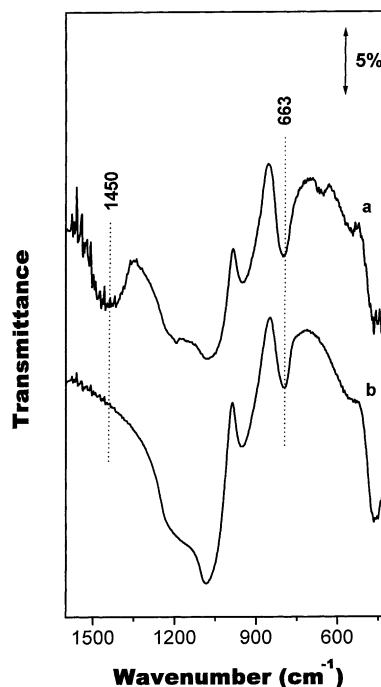

Fig. 1. IR spectra of silica xerogel SiO_2–B_2O_5 (10): (a) before; (b) after treatment with 2 M HCl.

with each other via the hydrogen bonding [18]. But we did not observe the increase in the band intensity of silanol groups after the deboronation, unlike the case for beta zeolite that shows more silanol groups after the deboronation [19]. The intensity of the broad band at 3700–$3400 \, cm^{-1}$ is decreased with the increased pretreatment temperatures due to the dehydroxylation of the silanol groups [18], and some defects could be produced after the deboronation and the subsequent calcination.

3.2. Titanation

The deboronated SiO_2–B_2O_5 (10), SiO_2–B_2O_5 (40), SiO_2–B_2O_5 (100) samples were subsequently titanated using gaseous $TiCl_4$. The as-synthesized catalysts were investigated using visible Raman spectroscopy, UV-resonance Raman spectroscopy and XRD techniques.

UV-resonance Raman spectroscopy is proved to be a powerful technique to identify the framework titanium atoms of TS-1 [20]. Fig. 3 shows the
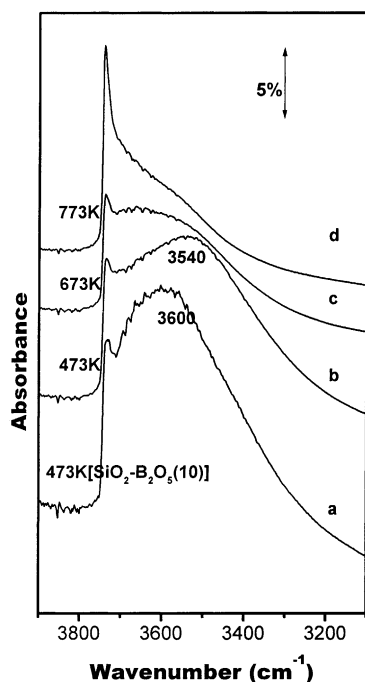
Fig. 2. IR spectra of silica xerogel SiO_2–B_2O_5 (10) before and after deboronation: (a) SiO_2–B_2O_5 (10) treated at 473 K; (b) deboronated SiO_2–B_2O_5 (10) treated at 473 K; (c) deboronated SiO_2–B_2O_5 (10) treated at 673 K; (d) deboronated SiO_2–B_2O_5 (10) treated at 773 K.

Fig. 3. UV-Raman spectra of Ti/de[B]SiO_2: the supports were calcined at different temperatures prior to the reaction with $TiCl_4$ at 773 K: (a) 573 K; (b) 673 K; (c) 773 K; (d) 1073 K.

UV-resonance Raman spectra of Ti/de[B]SiO_2 (T) samples excited by the 244 nm line since the 244 nm line is in the electronic absorption band of isolated titanium ions in tetrahedral coordination. Raman band at 1085 cm^{-1} is observed for the Ti/de[B]SiO_2 (T) samples. This band can be assigned to the asymmetric stretching vibration of the Ti–O–Si species [13]. The UV-Raman band at 1085 cm^{-1} due to Ti–O–Si species is very weak, indicating that the concentration of surface Ti–O–Si species is not very high.

The Raman bands of anatase can be easily detected by visible Raman spectroscopy. Visible Raman spectra of the Ti/de[B]SiO_2 (T) samples excited with 488 nm are shown in Fig. 4. Four characteristic Raman bands of TiO_2 (anatase) at 144, 390, 516, and 630 cm^{-1} are observed [19]. Although, the intensity of the anatase Raman bands is strong, no evident XRD patterns are detected for TiO_2, indicating that TiO_2 was highly dispersed, no matter the TiO_2 particles are amorphous or anatase.

3.3. Catalytic property
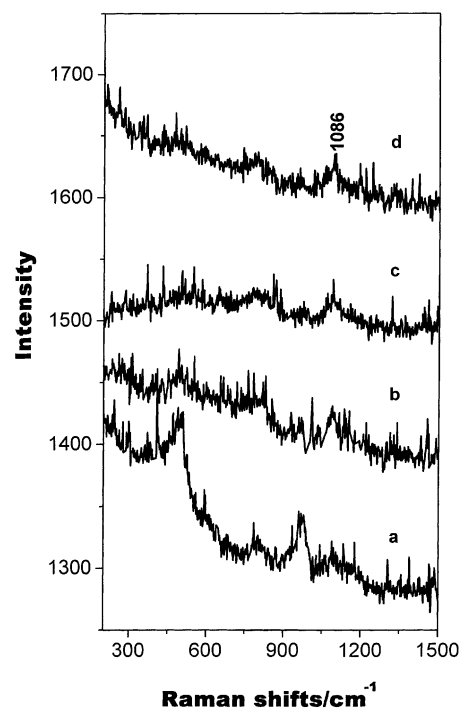
The catalytic properties of the prepared Ti/SiO_2 catalysts were tested by epoxidation of cyclohexene. The epoxidation of cyclohexene yields epoxide and corresponding glycol, cyclohex-2-en-1-ol and ketone.

The catalytic results for the epoxidation of cyclohexene on the Ti/SiO_2 catalysts with SiO_2 treated differently are reported in Table 1. All the SiO_2 supports were calcined at 773 K and their grafting temperature was 773 K. Comparing with Ti/SiO_2, the activity of Ti/[B]SiO_2 is about the same level and its selectivity even decreases in the presence of boron. The catalytic properties of the catalyst (Ti/[B]SiO_2) prepared by direct reaction between SiO_2–B_2O_5 (10) and $TiCl_4$ are almost the same as those of the catalyst (Ti/SiO_2) prepared using silica xerogel as support. This indicates that the direct gas–solid isomorphous substitution less likely takes place. While the catalysts prepared on deboronated silica show much higher conversion and selectivity, particularly the selectivity
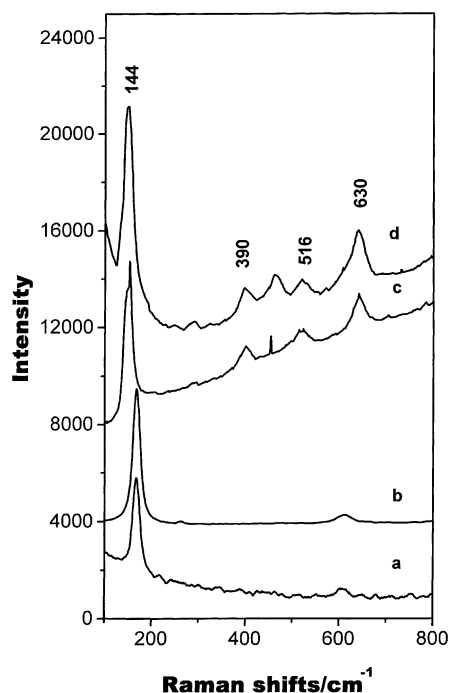
Fig. 4. Visible Raman spectra of Ti/de[B]SiO$_2$: the supports were calcined at different temperatures prior to the reaction with TiCl$_4$ at 773 K: (a) 573 K; (b) 673 K; (c) 773 K; (d) 1073 K.
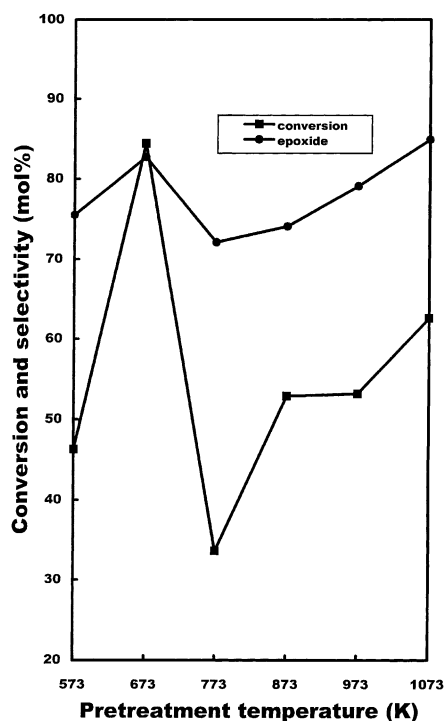

Fig. 5. Epoxidation of cyclohexene on Ti/de[B]SiO$_2$ using TBHP as oxidant. The supports were calcined at different temperatures prior to the chemical grafting with TiCl$_4$ at 773 K. Reaction conditions: cyclohexene, 18 mmol; CH$_3$CN, 5 ml; TBHP, 3.3 mmol; catalyst, 200 mg; temperature, 343 K; reaction time, 3 h.

is increased significantly. This is attributed to that the lattice B atoms are removed during the treatment using HCl, and the defect sites left behind is favorable for TiCl$_4$ to react with.

The catalytic results for epoxidation of cyclohexene on Ti/de[B]SiO$_2$ catalysts prepared at different pretreatment temperatures of supports are reported in Fig. 5 . The grafting temperature for all the samples

was set at 773 K. It appears that the catalytic property varies with the pretreatment temperature of the supports. The activity and selectivity increase slightly when the support of catalyst was calcined at temperatures from 773 to 1073 K. This trend is similar to that of Ti/SiO$_2$ catalyst prepared with commercial silica

Table 1
Epoxidation of cyclohexene on catalysts with different supports[a]

Catalyst	Conversion cyclohexene (mol%)[b]	Selectivity (mol%)		
		Epoxide	Cyclohexenol	Cyclohexenone
Ti/SiO$_2$[c]	24.2	40.9	25.9	33.2
Ti/[B]SiO$_2$[d]	25.2	36.0	20.5	43.5
Ti/de[B]SiO$_2$[e]	33.6	72.1	14.1	13.8

[a] Reaction conditions: cyclohexene, 18 mmol; CH$_3$CN, 5 ml; TBHP, 3.3 mmol; catalyst, 200 mg; temperature, 343 K; reaction time, 3 h.
[b] Conversion (%) = (converted cyclohexene/TBHP) × 100.
[c] SiO$_2$ xerogel as the support.
[d] SiO$_2$–B$_2$O$_5$ (10) as the support.
[e] Deboronated SiO$_2$–B$_2$O$_5$ (10) as the support.

Table 2
Epoxidation of cyclohexene on Ti/de[B]SiO$_2$ catalyst with different SiO$_2$–B$_2$O$_5$ precursors[a]

SiO$_2$:B$_2$O$_5$	Conversion cyclohexene (mol%)[b]	Selectivity (mol%)		
		Epoxide	Cyclohexenol	Cyclohexenone
10:1	84.0	82.7	17.3	0
40:1	60.6	73.8	15.7	10.5
100:1	41.9	67.7	17.3	15.0

[a] Reaction conditions are the same as Table 1.
[b] Conversion (%) = (converted cyclohexene/TBHP) × 100.

by chemical grafting [13]. The catalyst with the support pretreated at 673 K gives the highest activity, i.e. 84% conversion, which is comparable to that of Ti-β.

Under the same reaction conditions, the conversion of cyclohexene on Ti/de[B]SiO$_2$ (673 K) is 17.5%, much higher than 8.5% for Ti-β [21]. But the selectivity to epoxide on Ti/de[B]SiO$_2$ (673 K) is lower than that of Ti-β, which maybe due to the lower content of the isolated titanium species in Ti/de[B]SiO$_2$ catalyst. This indicates that TiCl$_4$ can react with different types of surface sites, surface OH groups and surface defect sites, generated on the deboronated SiO$_2$–B$_2$O$_5$ support. The surface OH groups and the defects generated during the deboronation procedure. TiCl$_4$ reacts with the defect sites, resulting in isolated Ti species Ti–O–Si or highly dispersed TiO$_2$ species. The support needs to be calcined at a proper temperature in order to create the defect sites. Too high temperatures will lead to the collapse of the defects, while too low temperatures are not enough to initiate the dehydroxylation. The presence of too much OH groups is favorable for the formation of amorphous TiO$_2$, which is not active and selective for the epoxidation.

Our results show that 673 K is the optimal temperature for the pretreatment of the support. But according to the IR spectra in Fig. 2, some of the silanol nests have been eliminated at this temperature. Thus, the mechanism of reaction between TiCl$_4$ and deboronated silica may be different from that of deboronated or dealuminated zeolites, where TiCl$_4$ reacts mainly with the silanol nest. While for de[B]SiO$_2$, TiCl$_4$ reacts not only with silanol nest, but also with the defect sites produced during the deboronation.

Table 2 lists the catalytic performance of the Ti/de[B]SiO$_2$ catalysts using deboronated SiO$_2$–B$_2$O$_5$ (10), SiO$_2$–B$_2$O$_5$ (40), and SiO$_2$–B$_2$O$_5$ (100) as supports. With the increasing of B concentration in the support precursors from 1/51 to 1/6, the conversion of cyclohexene increases from 41.9 to 84.0%, and selectivity also increases from 66.7 to 82.7%. This can be explained as that the higher the B concentration, the more defect sites are produced during the deboronation process, consequently more active sites are produced after the titanation.

According to the characterization, the main titanium species on the catalysts is highly dispersed anatase, while the concentration of the highly isolated titanium species is very small. However, the activity and selectivity are still quite high. It turns out that the highly dispersed anatase may also contribute to the epoxidation.

4. Conclusions

Postsynthesis modification of B-containing silica xerogel, consisting of a deboronation and titanation treatment, results in active heterogeneous epoxidation catalysts Ti/de[B]SiO$_2$. The catalyst prepared with the ratio of SiO$_2$:B$_2$O$_5$ ratio of 10, pretreated at 673 K shows the best catalytic performance: the conversion of cyclohexene can be as high as 84% and the selectivity to epoxide is up to 83%. It is found that TiCl$_4$ reacts with both silanol nests and defect sites of the deboronated [B]SiO$_2$.

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