A New and Simple Method for the Preparation of Active Ti-β Zeolite Catalysts

Jale Sudhakar Reddy and Abdelhamid Sayari*

Department of Chemical Engineering and CERPIC, Université Laval, Ste-Foy, Qc, Canada G1K 7P4

Incorporation of titanium into the framework of zeolite beta was achieved by simply treating Al-β zeolite with an ammonium titanyl oxalate solution followed by air calcination; the material obtained is a very active catalyst for the epoxidation of olefins.

Incorporation of titanium into the framework of zeolites is attracting increasing attention because of the potential of such materials as catalysts for various oxidation reactions.[1] The zeolite structures where Ti incorporation via hydrothermal synthesis has been claimed to take place are ZSM-5 (TS-1), ZSM-11 (TS-2), ZSM-48 (TS-48) and beta (Ti-β). More recently, mesoporous titanium silicalites have also been reported.[2] Incorporation of Ti in a zeolite framework can be achieved either by hydrothermal synthesis[1-4] or by post-synthesis modifications.[5,6] Post-synthesis modifications were carried out by the treatment of alumino- or boro-silicates by TiCl₄[5a,6] in the vapour phase, or by ammonium fluorotitanate in solution.[5b] The first method seems to be efficient for Ti incorporation. However, it has some disadvantages like the deposition of titanium oxide over long exposures and the complicated handling of the reactor system. As for the second method, no sufficient evidence was provided for Ti incorporation.

We report here a simple and fast method to prepare titanium-substituted zeolite beta. It consists of treating the corresponding aluminosilicate with a solution of ammonium titanyl oxalate at room temp. and calcining the obtained material at 823 K for 6 h. The titanium containing samples prepared by this method will be designated as Ox-Ti-β.

Aluminum containing zeolite-β was synthesized using a known procedure.[7] Ox-Ti-β samples were prepared by treating the Na or K-form of beta with an ammonium titanyl oxalate solution at room temp. for 24 h. 75 ml of 3 × 10⁻³ mol dm⁻³ ammonium titanyl oxalate solution was used for 1 g of β zeolite. Ti-β was also synthesized under hydrothermal conditions using a literature procedure.[8] All samples were calcined in flowing air at 823 K for 6 h.

Chemical analysis data (Table 1) indicate that during the treatment with ammonium titanyl oxalate, the Al content decreased while complete removal of Na or K took place. XRD pattern of Ox-Ti-β samples showed that its crystallinity was not altered by the treatment and that no other phases such as TiO_2 were present. Moreover, it can be seen in Table 1 that the interplanar d-spacing of Ox-Ti-β samples has increased as compared to the parent aluminosilicate β. Although the unit-cell expansion of zeolite-β is not a solid proof,[9] it may be regarded as an indication of Ti incorporation into the zeolite framework.[7,8]

IR spectra of T-β, Ox-Ti-β and aluminosilicate-β samples are shown in Fig. 1. The Ti-free sample exhibits a weak band at

960 cm⁻¹ attributable to Si-OH defective sites. Introduction of Ti by either direct hydrothermal synthesis or ammonium titanyl oxalate treatment brings about significant increase of the 960 cm⁻¹ band. Since this band was also assigned to the stretching mode of SiO_4 units bonded to a titanium ion,[10] it is inferred that both zeolite modification methods lead to the insertion of Ti in framework positions. The lower intensity of the 960 cm⁻¹ band in the Ox-Ti-β [Fig. 1(b)] as compared to Ti-β [Fig. 1(a)] may be due to the lower Ti content.

UV–VIS spectra of Ti-β and Ox-Ti-β samples are shown in Fig. 2. Ti-β and Ox-Ti-β samples exhibit only one absorption band at ca. 216 and 220 nm, respectively. This is a strong evidence that in both samples, Ti^{IV} is atomically dispersed and has a tetrahedral environment.[10] Hence, Ti^{IV} cations are most likely located in framework positions. Again, Ti-β shows a stronger UV–VIS band than Ox-Ti-β because of higher Ti content.

X-ray photoelectron spectroscopy also lends a strong support to our conclusion. Indeed, using a binding energy (BE) for $Si(2p) = 103.3$ eV as a reference, the BE of Ti ($2p_{3/2}$) in Ox-Ti-β and Ti-β were found to be 459.9 and 460.0 eV, respectively. This high BE is another strong indication that in both samples Ti^{IV} has a tetrahedral environment.[11]

Catalytic testing included the epoxidation of hex-1-ene by H_2O_2. In a typical reaction 200 mg catalyst, 34 mmol hex-1-ene, 2.2 mmol hydrogen peroxide and 750 mmol methanol were

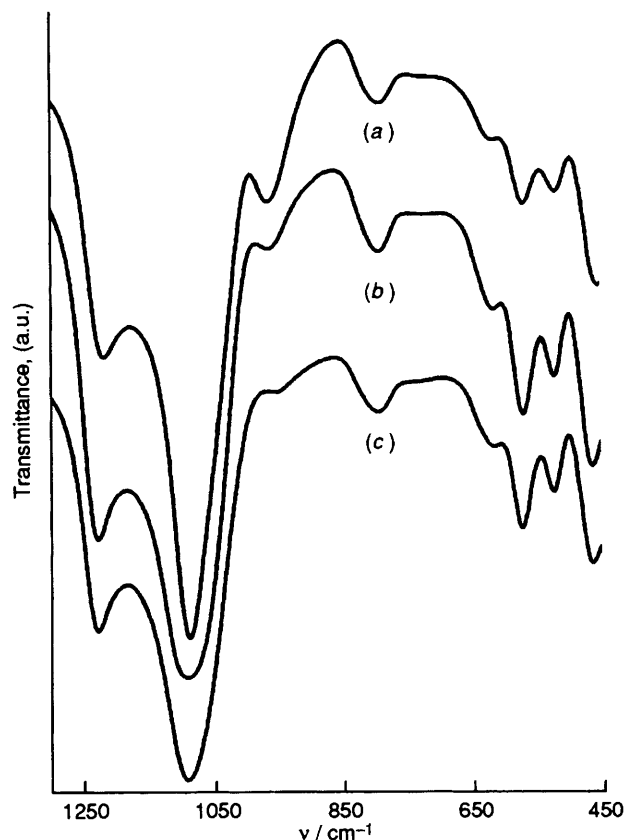**Table 1** Chemical analysis of β samples before and after exchange treatment and their interplanar d-spacings

Sample no.	Parent sample	Before treatment Si/Al	Before treatment Si/Na, K	After treatment Si/Al	After treatment Si/Ti	Interplanar d spacing/Å
1	Ti-β[a]	—	—	46	23	3.960
2	Na, K-β	17	108	—	—	3.933
3	Na, K-β	17	108	20	190	3.948
4	Na, K-β	27	126	—	—	3.935
5	Na, K-β	27	126	32	76	3.952
6	Na, K-β	27	126	32	82	3.949

[a] Prepared according to ref. 8.

Fig. 1 IR spectra of various β samples; Curves (a), (b) and (c) refer to samples 1, 5 and 2, respectively

stirred at 333 K for 5 h. The results obtained are reported in Table 2. It is seen that both Ti-β and Ox-Ti-β samples are active in the epoxidation of hex-1-ene. The major products were ethers obtained from secondary reaction of epoxide with methanol. The low selectivity toward epoxide is attributed to the presence of acid sites associated with aluminum in these zeolites.[12] In the presence of Ox-Ti-β, the reaction proceeded slowly with a high hydrogen peroxide utilization efficiency. Over Ti-β, the reaction was much faster; it was finished in less than 2 h. Titanium oxide and amorphous titanium silicate were almost inactive in this reaction, while the parent aluminosilicate was completely inactive. Since framework Ti has been identified as the active site for epoxidation, and since only framework Ti was found to be active in the presence of aqueous H_2O_2,[13] we concur that Ti in our Ox-Ti-β samples is sited as isolated species in framework positions.

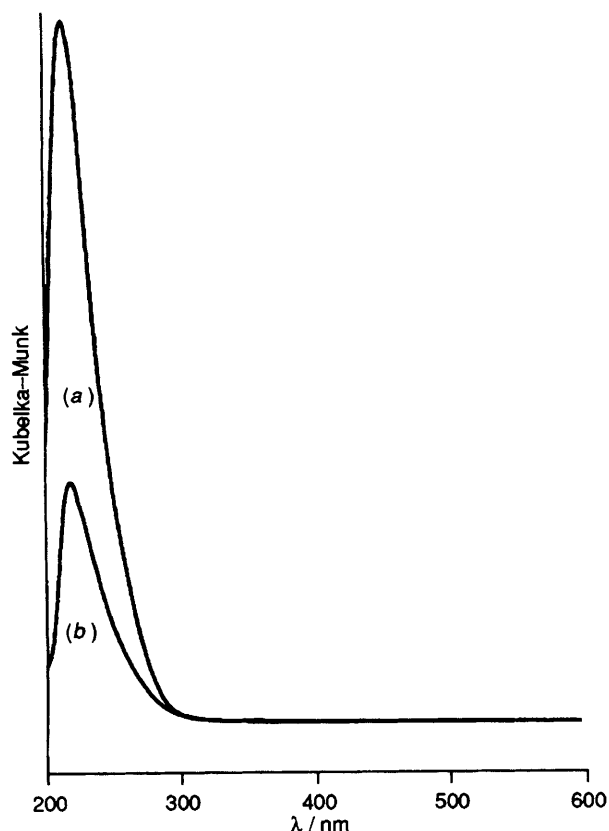**Fig. 2** UV–VIS spectra of (a) Ti-β (sample 1) and (b) Ox-Ti-β(sample 6)

Table 2 Oxidation of hex-1-ene over different catalysts

Catalyst[a]	Conversion (%)	H_2O_2 selectivity (%)[b]	Product selectivity (%) Epoxide	Ethers
TiO_2–SiO_2	0.1	1	100	0
Silicalite	0.2	3	100	0
β(2)	0.4	5	30	0
Ti-β(1)	6.5	95	1	96
Ox-Ti-β(5)	6.4	94	1	85
Ox-Ti-β(6)	5.4	79	19	75

[a] Figures in parentheses indicate the sample number given in Table 1.[b] H_2O_2 selectivity = (mole of epoxide and ethers formed/mol of H_2O_2 consumed) × 100.

Ox-Ti-β samples were also found to be efficient catalysts for epoxidation of bulky organic substrates. For example, the oxidation of norbornylene was carried out in the presence of Ox-Ti-β under the following conditions: 100 mg catalyst; 1 mmol norbornylene; 12 mmol H_2O_2; 250 mmol acetonitrile; 333 K; 5 h. A conversion of 55% was obtained with 72% selectivity towards epoxide and 20% selectivity to alcohols. As in earlier reports on Ti-β,[14,15] all our titanium modified samples had very limited activity in the oxidation of n-hexane.

As mentioned earlier, the insertion of Ti was accompanied by a significant decrease in Al content (Table 1). Moreover, it was found that the treatment of 1 g of an aluminum containing beta zeolite with a 75 ml of 3×10^{-3} mol dm^{-3} oxalic acid solution decreased the Si : Al ratio from its original value of 30 to 85 : 1 due to Al extraction. It is inferred that the presence, in the parent zeolite, of framework cations that can be extracted by oxalate species or the presence of defect sites is a requisite for the subsequent incorporation of titanium.

In conclusion, we have demonstrated the feasibility of incorporation of titanium into the framework of beta zeolite by simple treatment with ammonium titanyl oxalate solution. The catalytic properties of Ox-Ti-β are very similar to those of hydrothermally prepared Ti-β. This method may prove useful for the preparation of other Ti modified silicates, particularly those for which hydrothermal Ti incorporation has been difficult to achieve because of the necessity of using alkali hydroxides.

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