

A new synthesis procedure for titanium-containing zeolites under strong alkaline conditions and the catalytic activity for partial oxidation and photocatalytic decomposition

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Received 31 August 1995; accepted 20 November 1995

A new synthesis procedure for titanium-containing aluminosilicate zeolites has been obtained using a clear colloidal dispersion (sol) which was prepared with titanium isopropoxide, water, hydrochloric acid and colloidal silica, Ludox. When NaY, KL, offretite, mordenite and ZSM-5 zeolites were crystallized from the sol following conventional hydrothermal crystallization procedures, all the aluminosilicate zeolites showed the same X-ray absorption fine structure at the Ti K edge indicating framework Ti. The zeolites showed remarkable catalytic activity for the partial oxidation of cyclohexene using H₂O₂ as an oxidant and the photocatalytic decomposition of trichloroethene using water.

Keywords: zeolite synthesis; Ti incorporation; XANES; EXAFS; partial oxidation of cyclohexene; photocatalytic decomposition of trichloroethene

1. Introduction

Partial oxidation of organic compounds with aqueous solution of H₂O₂ using titanium-containing molecular sieve as catalyst was first reported by Taramasso et al. in 1983 [1]. The catalyst was a MFI-type zeolite designated as TS-1, containing less than 2.5% Ti within the framework. The TS-1 is currently used by Enichem for the conversion of phenol to catechol and hydroquinone [2]. Subsequent studies on titanium incorporation within zeolite frameworks led to the discovery of some other Ti-zeolites such as TS-2 [3], Ti-β [4], Ti-MCM-41 [5], Ti-ZSM-12 [6], etc. The Ti-zeolites were found to exhibit good catalytic activity for selective partial oxidation of alkene, alcohol and aromatic compounds using H₂O₂ [2].

The majority of so far reported molecular sieves are aluminosilicate zeolites containing aluminum in the framework. If titanium can be isomorphically substituted in the framework of aluminosilicate zeolites, catalytic activity and selectivity of the Ti-zeolites are expected to be controlled to a great extent using shape selectivity of the zeolite channels. However, previous investigations aiming at the incorporation of Ti in frameworks of various aluminosilicate zeolites to obtain new partial oxidation catalysts with shape selectivity were severely limited by the synthesis conditions excluding high levels of alkali concentration. X-ray absorption fine structure (XAFS) studies of the Ti-zeolites obtained at the Ti K edge [4,7,8] indicated that an isolated titanium oxide

unit within the framework was a catalytically active site for the partial oxidation. When Ti-containing zeolites were synthesized under strong alkaline conditions in previous works, the zeolites did not show the catalytic activity. The loss of the catalytic activity was found to be due to the formation of a catalytically inactive TiO₂ domain, which made it difficult to incorporate Ti within the frameworks of many other zeolites such as FAU, MOR, LTL, etc. synthesized under strong alkaline conditions. One exception to the loss of catalytic activity has been found very recently by Khouw and Davis [9]. They have reported that the catalytic activity of TS-1 can be recovered upon washing with hydrochloric acid after synthesis under a certain level of alkali cations, opening a possibility to obtain catalytically active Ti-zeolites under strong alkaline conditions, although the tolerable alkali concentrations were still very low compared with the synthesis condition for NaY zeolite.

In the present work, we have investigated how to incorporate Ti in the framework of aluminosilicate zeolites during synthesis under strong alkaline conditions. We have found that if a titanium source is added homogeneously into colloidal silica, before mixing with an alumina source and NaOH for zeolite synthesis, subsequent crystallization to zeolites leads to incorporation of Ti within frameworks. We report here on the preparation of NaY, KL, offretite, mordenite and ZSM-5 zeolites using the new Ti-incorporation procedure, as well as the characterization using XAFS, and the catalytic activity for partial oxidation of cyclohexene using H₂O₂ and photocatalytic decomposition of trichloroethene.

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2. Experimental

2.1. Synthesis of titanium aluminosilicate zeolite

The synthesis of titanium-containing aluminosilicate zeolites has been performed using a clear colloidal dispersion (sol) containing titania and silica sources in water. In order to obtain the sol, titanium isopropoxide (Aldrich, 99%) was first hydrolyzed with doubly distilled water. The resulting gel was quickly filtered and peptized with 35 wt% hydrochloric acid. Then, the resulting solution was added to a colloidal silica, Ludox HS-40 (40 wt% SiO₂ and 60 wt% H₂O, Du Pont) and stirred until a clear sol was obtained. The sol containing titania and silica sources (Ti/Si = 0.01–0.03) was substituted for Ludox to crystallize zeolites following conventional hydrothermal procedures [10–12].

For example, molar composition of the gel used for the synthesis of NaY zeolite [10] containing titanium (Ti-NaY) was 8NaOH : Al₂O₃ : 10SiO₂ : 0.1TiO₂ : 160

H₂O. The gel was aged for 1 day at room temperature. Subsequently, crystallization was performed over 3 days in a polypropylene bottle at 373 K. The zeolites were then washed with doubly distilled water and evacuated at 323 K. Titanium-containing KL [11] (Ti-KL), offretite [10] (Ti-OFF), mordenite [12] (Ti-MOR) and ZSM-5 [10] (Ti-ZSM-5) zeolites were also prepared by known procedures in the literature. Crystallization of the Ti-zeolites took 1.5–5 times longer than crystallization of the zeolite without titanium. X-ray diffraction patterns of the zeolite samples were obtained using a Rigaku D/MAX-III instrument (Cu K_α radiation). The scanning electron micrograph was obtained using a Philips SEM-535M microscope.

2.2. XAFS

Ti-ZSM-5 and Ti-OFF samples were calcined for 12 h at 823 K to remove organic templates used for the synthesis. The other Ti-zeolites were evacuated for 2 h at

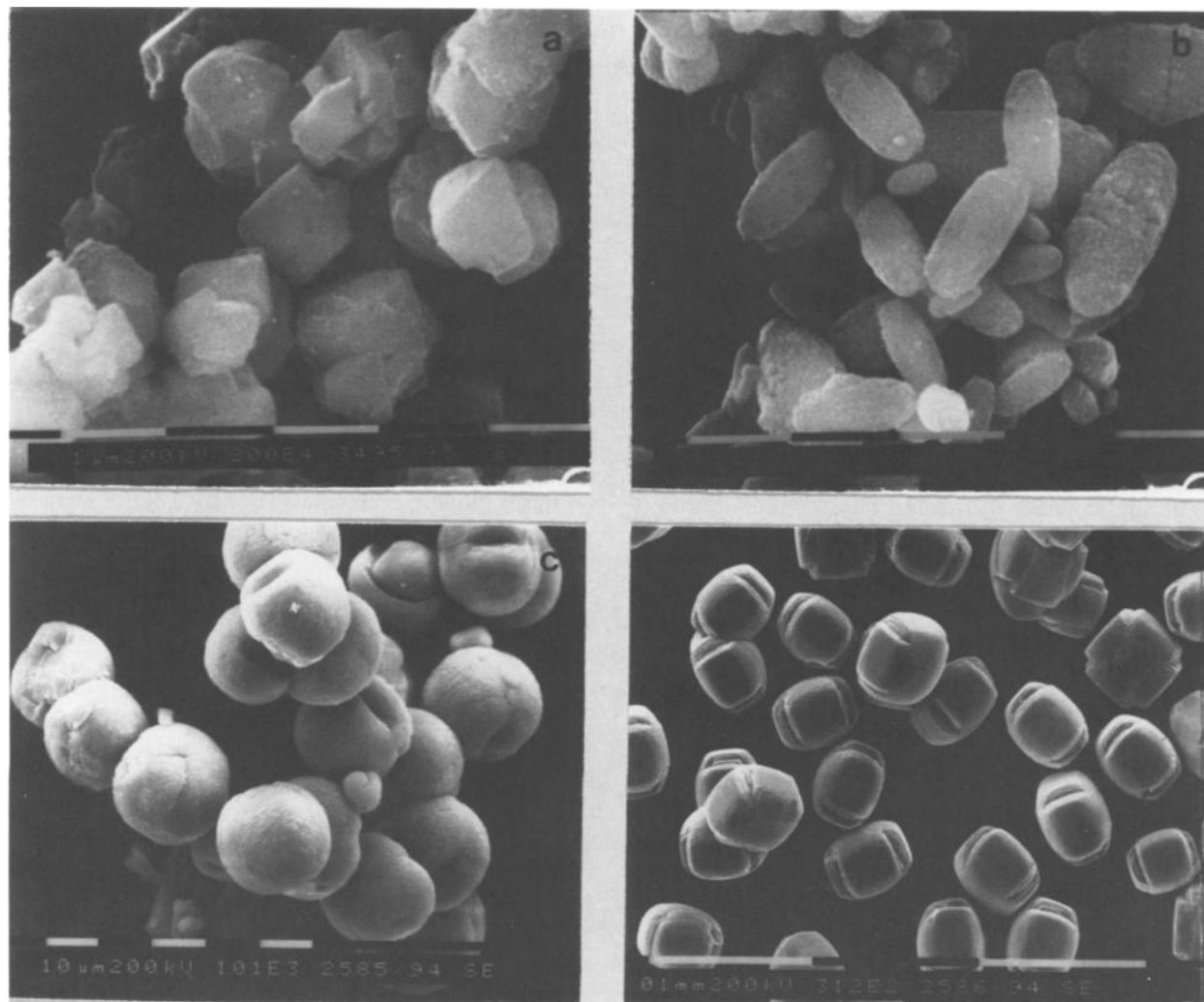


Fig. 1. Scanning electron micrographs of Ti-zeolites: (a) Ti-NaY, (b) Ti-OFF, (c) Ti-MOR and (d) Ti-silicalite.

Table 1
Cyclohexene conversion over Ti-zeolites^a

| Sample | Ti/Si × 100 | Total conversion (%) | Selectivity (%) | | |
|-----------------------|-------------|----------------------|-----------------|--------|---------|
| | | | epoxide | ketone | alcohol |
| Ti-NaY | 1.9 | 4.1 | 5.9 | 25.4 | 68.7 |
| Ti-OFF | 3.6 | 6.3 | 5.8 | 23.0 | 71.2 |
| Ti-MOR | 1.0 | 1.1 | 10.4 | 31.4 | 58.2 |
| Ti-KL | 3.6 | 0.5 | 22.5 | 28.1 | 49.4 |
| Ti-ZSM-5 (Si/Al = 40) | 1.6 | 2.0 | 8.4 | 24.9 | 66.7 |
| Ti-silicalite | 1.3 | 2.8 | 14.1 | 25.3 | 60.6 |
| TS-1 ^b | 3.0 | 2.7 | 35.4 | 18.7 | 45.9 |
| blank | — | 0.0 | — | — | — |

^a Reaction conditions: 10 g cyclohexene, 10 g H₂O₂ and 10 g acetone mixed with 0.1 g catalysts at 333 K for 3 h.

^b Prepared by the procedures given in ref. [1].

673 K. The zeolite samples were stored in capped vials to prevent moisture absorption. The samples were then pasted on a 3 M tape in ambient air. Moisture absorption to some extent was inevitable following the powder handling. The X-ray absorption measurement was carried out above the Ti K edge (4966 eV) at room temperature using synchrotron radiation of Beam Line 7C at the Photon Factory in Tsukuba.

2.3. Catalytic activity test

The catalytic activity for partial oxidation of cyclohexene has been measured with a mixture of 10 g of cyclohexene (BDH, 99%), 10 g H₂O₂ (Aldrich, 30 wt% in H₂O) and 10 g acetone in a glass flask. 0.1 g of the dehydrated zeolite powder was added to the flask containing the reactants. Then, the flask was vigorously stirred for 3 h at 333 K. Products during the period were analyzed with a gas chromatograph (HP 5890 series II) equipped with a Carbowax 20M column using a flame ionization detector.

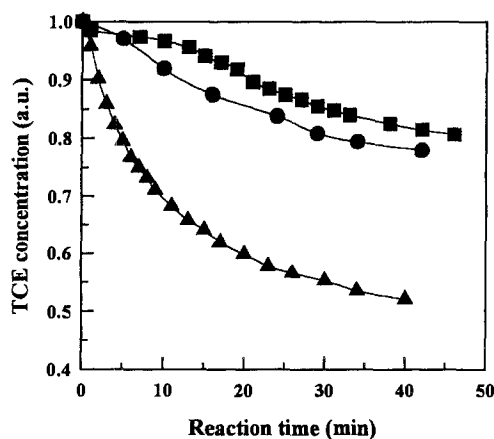


Fig. 2. Trichloroethene concentration plotted against the photocatalytic reaction time: (▲) TiO₂ (Degussa, ~30 nm), (●) Ti-NaY (Ti/Si = 0.019), and (■) Ti-NaY (Ti/Si = 0.056). The reaction was carried out using a 350 nm UV lamp with 0.2 g of catalysts dispersed in 500 ml H₂O containing 400 ppm trichloroethene.

Photocatalytic decomposition of trichloroethene (TCE) [13] over Ti-NaY has been carried out using a 350 nm UV lamp with 0.2 g of catalysts dispersed in 500 ml water containing 400 ppm TCE. Change in the TCE concentration with time was followed using the Cl⁻ concentration which was detected by a Cl⁻ electrode.

3. Results and discussion

X-ray powder diffraction patterns of the Ti-zeolites synthesized in the present work were identical to those of the zeolites without titanium, except that the peaks were slightly broad compared with the zeolite analogs. The scanning electron micrographs of various Ti-zeolites are shown in fig. 1. The shape of the Ti-zeolite crys-

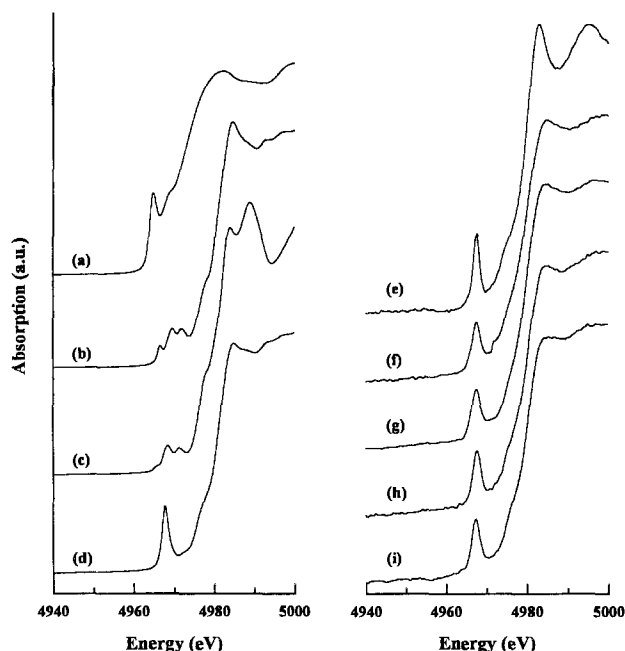


Fig. 3. XANES at the Ti K edge after normalization: (a) Ti foil, (b) rutile, (c) anatase, (d) TS-1, (e) Ti-KL, (f) Ti-NaY, (g) Ti-OFF, (h) Ti-MOR and (i) Ti-ZSM-5.

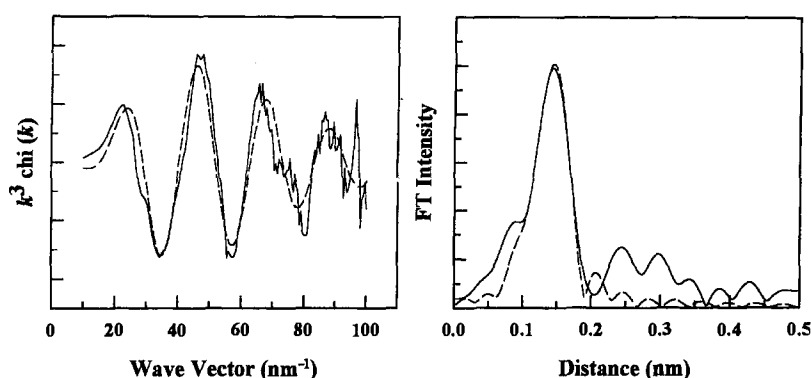


Fig. 4. k^3 -weighted EXAFS and Fourier transform for Ti-NaY (Ti/Si = 0.019): (—) experimental and (---) curve fit.

tallites follows the typical morphology of the zeolite analogs. No amorphous phase is shown at the outer surface of the crystallites.

The conversion of cyclohexene with various Ti-zeolites is listed in table 1. All the Ti-zeolites obtained in the present work showed a remarkable catalytic activity for the partial oxidation reaction, while the Ti-zeolites contained almost the same amount of aluminum and alkali metal cations as the zeolite analogs. Various products such as cyclohexanol, cyclohexanone, epoxide, etc. were obtained during the reaction for 3 h. The product distribution depended on the zeolites as shown in table 1. The catalytic activity indicates that Ti was incorporated within the framework.

Fig. 2 displays decreases in TCE concentration with time due to photocatalytic decomposition over Ti-NaY. The concentration change shows that the catalytic activity of the Ti-zeolite is 10–50 times greater than that of titania (Degussa, particle size ≈ 30 nm), if the activity is based on the total amount of Ti. It is believed that titanium in the Ti-NaY was highly exposed to the reactant inside the zeolite pores, and consequently the Ti-NaY exhibited high catalytic activity.

X-ray absorption near edge structure (XANES) of titanium obtained at the Ti K edge is shown for Ti-zeo-

lites in fig. 3. The XANES spectra for Ti foil, rutile and anatase, used as standards, are consistent with those reported in the literature [7,8]. While rutile and anatase show multiple pre-edge features around 4970 eV characteristic of an octahedral symmetry, all the Ti-zeolites synthesized here show a single pre-edge peak around 4968 eV, similar to TS-1. As suggested in previous works, the single pre-edge peak at 4968 eV is the fingerprint of a tetra- or penta-coordinated symmetry around titanium located within the framework [7,8]. Fig. 4 shows the extended X-ray absorption fine structure (EXAFS) obtained above the Ti K edge for Ti-NaY for example, and our curve fit for the EXAFS obtained using UWXAFS2.0 and FEFF5. Details of the curve-fitting procedure were the same as described in our other EXAFS works [14]. The structural parameters obtained from EXAFS curve fitting are listed in table 2. The average Ti–O coordination number for the Ti-zeolites synthesized in the present work is 4.5 ± 0.4 , similar to the coordination numbers obtained in other works on Ti-zeolites [4,7,8]. Thus, the XAFS data indicate that the local atomic environment of titanium in the present Ti-zeolites is very similar to that of TS-1 which incorporates Ti within the framework.

To summarize, we have found a new procedure for the preparation of Ti-zeolites of catalytic significance for partial oxidation and photocatalytic reaction of organic compounds. XAFS obtained at the Ti K edge indicates that Ti was incorporated within frameworks of the Ti-zeolites thus obtained. The present procedure for Ti incorporation within zeolite frameworks may be used to obtain other Ti-zeolites for shape-selective catalytic applications.

Acknowledgement

The authors thank Professor W.S. Ahn and Professor S.B. Park for their help with the catalytic activity measurements. Ryoo et al. thank the Photon Factory (Proposal No. 92G193) for their supports for XAFS measurements.

Table 2

Structural parameters obtained from EXAFS curve fitting at the Ti K edge for Ti-zeolites

| Sample | N^a | R^b (nm) | σ^2^c (pm ²) |
|---------------------------|-------|------------|---------------------------------|
| Ti-NaY | 3.7 | 0.192 | 82 |
| Ti-OFF | 5.0 | 0.187 | 108 |
| Ti-MOR | 4.0 | 0.186 | 70 |
| Ti-KL | 4.8 | 0.195 | 81 |
| Ti-ZSM-5 (Si/Al = 40) | 4.9 | 0.191 | 84 |
| Ti-silicalite | 5.2 | 0.184 | 94 |
| TS-1 ^d | 6.0 | 0.187 | 99 |
| TiO ₂ (rutile) | 5.8 | 0.195 | 53 |

^a Ti–O coordination number.

^b Ti–O distance.

^c Debye–Waller factor.

^d Prepared by the procedure given in ref. [1]. The TS-1 sample gave a Ti–O coordination number near 6 because it was fully hydrated.

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