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Synthesis of FER titanosilicates from a non-aqueous alkali-free seeded system

Ranjeet Kaur Ahedi and A. N. Kotasthane*

Catalysis Division, National Chemical Laboratory, Pune 411 008, India

We have demonstrated the preparation of a new family of TS-FER products using organothermal synthesis.

The discovery of TS-MFI by the Enichem group[1] gave a major boost to heterogeneous catalysis including epoxidation and hydroxylation of olefins with H_2O_2.[2,3] As the trend continues with more emphasis on new titanosilicates, different structural analogs have been reported.[4–7] Generally, the hydrothermal synthesis of Ti-bearing molecular sieves is difficult since titanium often tends to form a white insoluble phase in alkaline aqueous medium.[8,9] Therefore, we have focused our research efforts on a non-aqueous alkali-free synthesis system. We report a first example showing the efficient synthesis of the ferrierite (IUPAC code FER) topology in terms of Ti^{IV} framework insertion utilizing a non-aqueous alkali-free seeded system.

Synthetic ferrierite (FER) is a high silica, medium pore zeolite containing linked [5^4] polyhedral units having intersecting channels outlined by 10 membered ring (MR) (4.3 × 5.5 Å) and 8 MR (3.4 × 4.8 Å) pores. Although a pure silica derivative of FER topology is known,[10,11] there are no reports on the Ti analog of the FER system.

The synthesis method for the pure silica derivative of FER described by Kuperman *et al.*,[11] using HF/pyridine as the mineralizing agent has been successfully applied to the synthesis of TS-FER. The purpose of this work was to examine the potential of the organothermal system to mobilize titanium species in alkali-free media. Depending upon the synthesis procedure, it can be prepared within a large composition range.[12]

A typical synthesis of TS-FER was as follows. Initially 75.5 g (0.955 mol) pyridine (SQ, Qualigens) plus 31.5 g (0.533 mol) propylamine (E. Merck) plus 3.6 g (0.018 mol) HF/pyridine (Aldrich) were mixed in a polypropylene jar under stirring. The resulting clear solution was divided into two equal parts (*ca.* 62 ml each); into one portion 0.5 g (1.47×10^{-3} mol) of tetrabutylorthotitanate (TBOT, Aldrich) dispersed in 5 ml of isopropanol (S. D. Fine Chemicals Ltd.) was mixed and into the other portion 6.0 g (0.1 mol) Cab-o-Sil (Fluka AG) were allowed to dissolve. The samples were then mixed together forming a silicotitanate clear solution under stirring. Finally, 0.5 g of silica-FER seed precursors synthesized according to a procedure described elsewhere[11] were added to the entire mixture under continuous stirring to yield a uniform dispersion. The resulting solution had a pH of 11.0 ± 0.2. This liquid was transferred to a PTFE lined autoclave for crystallizing at 170 °C for 5 to 7 days under static condition. The crystalline TS-FER was filtered, washed with acetone and dried at 110 °C. The X-ray (Rigaku D Max III VC) powder diffraction pattern confirmed the phase purity of the TS-FER product. The TS-FER product was subsequently calcined at 550 °C (12 h) and then continued till 700 °C for another 4 h to decompose organic compounds occluded during the synthesis step.

Various samples of TS-FER system were prepared with different Si and Ti contents. Table 1 lists the chemical composition of the initial mixture and the corresponding products. For all the samples Ti : Si ratios were higher in the product than in the initial mixture, indicating that not all the silica was involved in the crystallization process. TS-FER was expected to crystallize more readily along with titanium butoxide to form Si—O—Ti oligomers, however, the reaction mixture in which both SiO_2 and titanium butoxide were co-hydrolyzed did not form any FER crystals even after 15–30 days heating, but instead transformed to the ZSM-39 phase in contrast to the pure Si derivative synthesis in which highest crystallinity for the FER phase was attained in 5–6 days under identical conditions. These findings indicate that the presence of Ti^{4+} ions tend to impede and lower the nucleation rates in the organothermal TS-FER system. It was, however, found that adding seed crystals of the Si-FER derivative in small quantities (0.8–1.0 wt.% of gel mixture) accelerates both nucleation and crystallization. It can be seen in Table 1 that in no case was framework titanium in excess of 1.8% found. These results indicate that there exists an upper limit of framework titanium (Ti^{IV}) incorporation (maximum 2.0 wt.%), and extraframework Ti^{IV} appears in the form of TiO_2 when the Ti concentration is increased to 50 mol% relative to the number of moles of Si used (sample no. 4).

Incorporation of Ti^{4+} ions into the framework would generally cause a unit cell volume variation. Based on this, the unit cell volumes of a series of samples as calculated from XRD data are presented in Table 1. The unit cell volume of sample no. 1 showed a marked increase (1977.78 Å^3) in comparison with that of the pure silica FER derivative (1947.96 Å^3).

Thermoanalytical studies on TS-FER samples revealed that the decomposition of occluded organic is complete at 750 °C and structural integrity is maintained until about 1000 °C.

Diffuse reflectance UV–VIS spectroscopy is an efficient technique for qualitative evaluation of the presence of framework Ti in all types of Ti molecular sieves. As shown in Fig. 1A

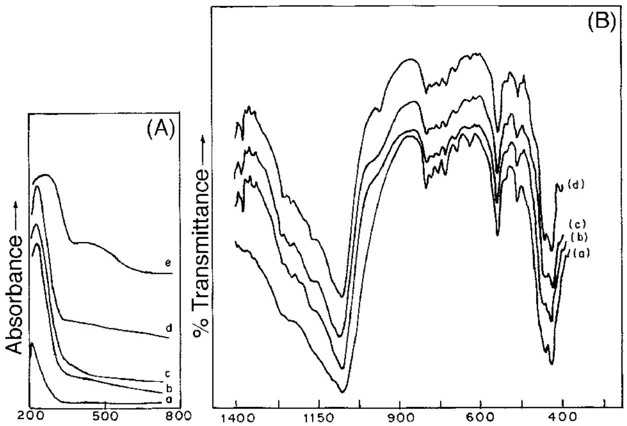

Fig. 1 (A) Diffuse reflectance spectra of sample nos. (a) 5, (b) 1, (c) 2, (d) 3 and (e) 4. (B) Framework region FTIR spectra of sample nos. (a) 5, (b) 3, (c) 2 and (d) 1 (sample numbers from Table 1).

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†E-mail: ank·@dalton.ncl.res.in

Table 1 Physico-chemical properties of TS-FER

sample no.	gel		product Ti/Si	unit cell parameters/Å			U/Å^3	Ti/wt.%
	Si/mol	Ti/mol		a_0	b_0	c_0		
1	0.1	1.2×10^{-3}	1.6×10^{-2}	18.945	14.062	7.424	1977.78	1.8
2	0.1	8.3×10^{-4}	9.0×10^{-3}	18.900	14.061	7.422	1972.41	1.5
3	0.1	5.5×10^{-4}	6.0×10^{-3}	18.829	14.061	7.419	1964.20	1.2
4	0.1	0.05	FER + major anatase	ND	ND	ND	ND	ND
5	0.1	no Al/Ti	—	18.687	14.062	7.413	1947.96	no Al/Ti

ND = not determined.

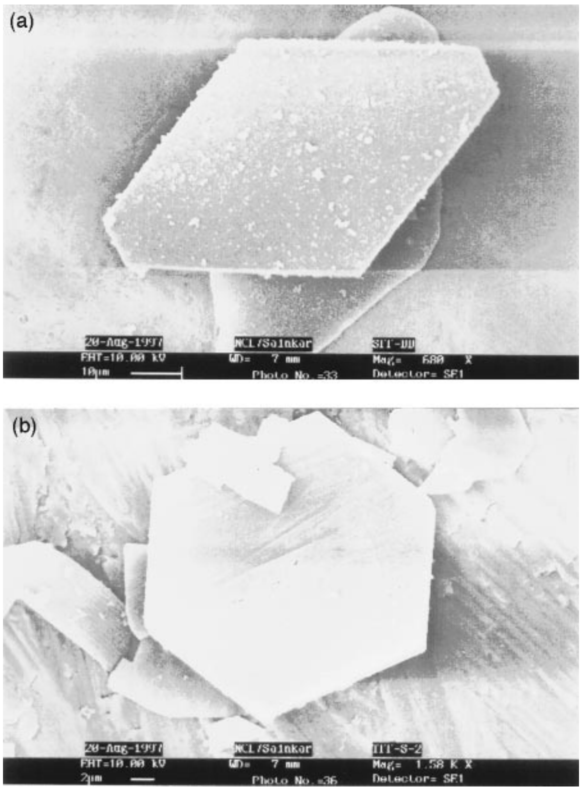

Fig. 2 Scanning electron micrographs of (a) silica FER (sample no. 5), and (b) TS-FER (sample no. 1).

[(b)–(e), sample nos. 1, 2 and 3] showed a single UV absorption band at around 212 nm, corresponding to isolated framework Ti in tetrahedral coordination.[13] The presence of this band could be considered as further proof of Ti incorporation into the FER framework; however, sample no. 4 (Fig. 1A), which has a high Ti content, showed in addition to the 212 nm band another broad band between 300 and 350 nm that was not detected in samples 1, 2 and 3. The broad band has been assigned to the anatase phase.[14] This clearly suggests that any excess of Ti in the non-aqueous reaction mixture would yield a Ti-bearing extraframework phase.

Fig. 1B [(b)–(d); samples 1, 2 and 3] shows the IR spectra of the TS-FER products. The products showed a relatively well resolved IR band at 960 cm^{-1} which otherwise is not detected in the presence of the organothermal pure Si-FER system (sample 5). This band at 960 cm^{-1} is a good indicator (fingerprint) of the existence of framework metallic ions in a series of Ti analogs, *e.g.* TS-1,[15] Ti-MCM-41[13] and TS-NU-1.[7]

Scanning electron micrographs [Fig. 2(a) and 2(b)] revealed that the seed (Si-FER) precursor [Fig. 2(a)] aggregates are made up of very thin plates of 8 × 5 μm size and this morphology changes during the growth of TS-FER producing [Fig. 2(b)] regular hexagonal plates of a 28 × 28 μm (corner to corner) large crystal. This suggest that the presence of Ti in the non-aqueous alkali free seeded system influences the distribution of silicon species during the growth of TS-FER.

TS-FER has been synthesized from an organic hydrothermal system in the presence of seeds. TS-FER was found to be thermally stable up to 1000 °C. Ti incorporation was confirmed by unit cell expansion data and further supported by IR and UV–VIS spectroscopies. Scanning electron micrographs also revealed changes in crystal morphology on incorporation of titanium.

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