

VIBRATIONAL SPECTROSCOPIC EVIDENCE FOR THE PRESENCE OF TiO_6 STRUCTURAL UNITS IN TITANOSILICATE MOLECULAR SIEVE ETS-10

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Abstract – A comparison of infrared and Raman spectra of a titanosilicate molecular sieve ETS-10 with literature data on titanium-containing ZSM-5 (TS-1) and perovskite SrTiO_3 provides conclusive evidence for the presence of intraframework TiO_6 octahedral units in ETS-10. The appearance of a very strong band at 723 cm^{-1} in the Raman spectrum of ETS-10 suggests that the technique can be useful for the characterization of molecular sieves containing TiO_6 structural units.

Key words: ETS-10, TiO_6 Structural Units, Vibrational Spectra

INTRODUCTION

Titanium-substituted molecular sieves are of current interest since they exhibit exceptional catalytic activity and selectivity for mild oxidation reactions [Venuto, 1994]. For example, the titanium-containing derivative of pure-silica ZSM-5 (TS-1) is known to be an active catalyst for numerous oxidation reactions including aromatic hydroxylations, alkane oxidations and alkene epoxidations using aqueous H_2O_2 as an oxidant.

ETS-10 is a new member of titanosilicate molecular sieves first synthesized by the Engelhard Corporation [Kuznicki, 1989; Kuznicki et al., 1992]. Recently, Anderson et al. [1994] have determined the structure of ETS-10 using a combination of high resolution electron microscopy, X-ray diffraction, solid-state NMR and molecular modeling. They have shown that ETS-10 has a three-dimensional 12-membered ring channel system consisting of corner-sharing SiO_4 tetrahedra and TiO_6 octahedra. Here we examine the infrared, Raman and ultraviolet-visible (UV-VIS) reflectance spectra of ETS-10, in order to obtain spectroscopic evidence for the presence of TiO_6 octahedral framework units. The vibrational data analysis is done with the help of literature data on TS-1 and perovskite SrTiO_3 .

EXPERIMENTAL

A Na,K-form of ETS-10 (Si/Ti=4.7) was obtained from Engelhard Corporation. The X-ray powder diffraction pattern of ETS-10 used in this study was very similar to that reported in the literature [Kuznicki et al., 1992].

The Infrared and Raman spectra were recorded on a Perkin-Elmer System 16F PC FT-IR spectrometer using a CsI pellet technique and a Perkin-Elmer system 2000 FT-Raman spectrometer, respectively. The Raman excitation source was the 1064-nm line of Nd:YAG laser at an intensity of about 0.7 W at the sample. Approximately 100 scans were accumulated in

both infrared and Raman experiments. The UV-VIS reflectance spectra were obtained using a Varian Cary 2200 spectrophotometer.

RESULTS AND DISCUSSION

Fig. 1 shows the infrared and Raman spectra of ETS-10 in the region $200\text{--}1400\text{ cm}^{-1}$. The most prominent band appearing at 1030 cm^{-1} in the infrared spectrum (Fig. 1a) can be assigned to the T-O stretching mode [Flanigen et al., 1971], where T is Si or Ti. The position of this band is lower than that of the most prominent infrared band observed for TS-1 or pure-silica ZSM-5. This is not unexpected since ETS-10 used in this study contains a considerable amount (17.5 Ti mol%) of Ti which is heavier than Si. The positions of the major bands and shoulders in Fig. 1a are quite similar to those reported by Das et al. [1995], who have recently reported the infrared spectra in the region $450\text{--}1300\text{ cm}^{-1}$ for ETS-10 samples prepared using different amounts of ETS-4 as seeds. Unlike TS-1, however, ETS-10 gives no distinct infrared band around 960 cm^{-1} , which is usually taken as evidence of the isomorphous substitution of Si by Ti in TS-1 [Bellusi and Fattore, 1991]. This suggests that the vibrational modes of the discrete structural units involving Ti-O bonds in ETS-10 are different from those in TS-1.

The basic building block for ETS-10 is described as a $[\text{Si}_4\text{Ti}_3\text{O}_{33}]^{16-}$ unit [Anderson et al., 1994]. Since the framework of ETS-10 can be explained in terms of different stacking sequences of the eight possible sheets, it displays a considerable degree of disorder. Two specific end members of ordered polymorphs are as follows: (1) polymorph B corresponds to ABCD... stacking sequence. This polymorph has monoclinic lattice with space group C2/c; (2) polymorph A corresponds to ABAB... stacking sequence and this has a tetragonal lattice with either $P4_1$ or $P4_2$ symmetry. Because these two polymorphs contain a large number of atoms per unit cell, there must be numerous vibrational modes which can be predicted by the factor group analysis. In many cases, however, fewer bands are observed in

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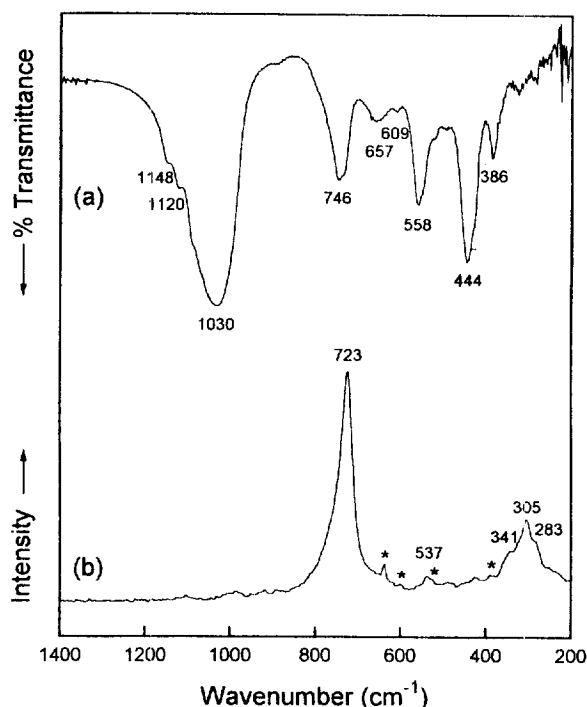


Fig. 1. Infrared (a) and Raman (b) spectra of the structural region for ETS-10. Peaks indicated by an asterisk are due to anatase or rutile.

the vibrational spectrum than were predicted by the factor group analysis. Furthermore, the assignment of the infrared bands in Fig. 1a must be more complicated due to the considerable degree of disorder of ETS-10.

The alternative way to find the vibrational modes involving octahedral Ti atoms in ETS-10 might be to compare the infrared spectrum of ETS-10 with that obtained from titanates which have Ti environment similar to ETS-10. Alkaline-earth titanates with the perovskite structure include CaTiO_3 , SrTiO_3 , and BaTiO_3 , where all Ti atoms occupy the octahedral holes formed exclusively by oxide ions. These materials have been the subject of many investigations because of their unique ferroelectric and ferromagnetic behaviors [Last, 1957; Perry and Hall, 1965; Diaz-Guemes et al., 1989]. Among them, SrTiO_3 is in the most symmetric form and has an ideal cubic symmetry with the space group $\text{Pm}\bar{3}\text{m}(\text{O}_h^1)$ [Nilsen and Skinner, 1968; Balachandran and Eror, 1982]. Therefore, we compare the vibrational spectra of ETS-10 to those of perovskite SrTiO_3 reported in the literature. Last [1957] found that cubic SrTiO_3 shows two strong infrared bands around 395 and 610 cm^{-1} . He considered the vibrations of this material in terms of the TiO_6 octahedra and suggested that these two bands could be assigned to the O-Ti-O bending and Ti-O stretching modes, respectively. Further support for this assignment has been reported by Diaz-Guemes et al. [1989]. As seen in Fig. 1a, ETS-10 exhibits two infrared bands at 386 and 609 cm^{-1} ; their positions are quite similar to those of bands observed in the infrared spectrum of SrTiO_3 [Diaz-Guemes et al., 1989]. Therefore, the two bands at 386 and 609 cm^{-1} in Fig. 1a can be tentatively assigned to the O-Ti-O bending and Ti-O stretching vibration modes of TiO_6 units in ETS-10, respectively. It is neces-

sary to examine whether the intensities of these bands are dependent on the TiO_2 content of ETS-10, since structural bands of zeolites and related materials frequently occur in these regions.

Fig. 1b illustrates the Raman spectrum of the structural region for ETS-10. To assign the vibrations arising from the intraframework Ti atoms in ETS-10, it is first necessary to discriminate the vibrations associated with extraframework Ti species from those of the molecular sieve framework. Previous studies involving TS-1 reveal that Raman spectroscopy is useful for probing the existence of extraframework Ti species such as anatase or rutile [Zecchina et al., 1991; Deo et al., 1993]. Anatase exhibits three strong Raman bands at 403, 516 and 639 cm^{-1} , while rutile gives two bands near 445 and 608 cm^{-1} . Fig. 1b shows that ETS-10 sample used here contains trace amounts of anatase and rutile. An important observation obtained from Fig. 1b is that ETS-10 exhibits a very strong band at 723 cm^{-1} . The asymmetric nature of this band implies the overlapping of more than one vibrational mode. Nilsen and Skinner [1968] reported that cubic single-crystal SrTiO_3 at room temperature exhibits three Raman bands at 629, 684 and 727 cm^{-1} , which are due to the Ti-O stretching modes. Zeolites normally give no noticeable structural Raman bands in the region of 550-750 cm^{-1} [Dutta et al., 1991]. Therefore, we speculate that the Raman band at 723 cm^{-1} in Fig. 1b must be related to the Ti-O stretching vibration of TiO_6 units in ETS-10. This suggests that the very strong Raman band at 723 cm^{-1} can be regarded as a useful probe in the characterization of molecular sieves containing TiO_6 structural units. A small band at 537 cm^{-1} also appears to be from vibrational modes involving octahedral Ti atoms in ETS-10. However, the origin of this band remains unknown at this time.

It is well-established that the strongest structural Raman band of zeolites appears in the region 380-520 cm^{-1} , which can be assigned to the ν_1 (T-O-T) mode [Dutta et al., 1991]. As seen in Fig. 1b, ETS-10 exhibits a strong Raman band at 305 cm^{-1} as well as two shoulders at 341 and 283 cm^{-1} . The strong Raman band at 305 cm^{-1} for ETS-10 is considerably lower in wavenumber than that from any other molecular sieve reported so far. The Raman spectrum of SrTiO_3 at room temperature shows three bands at 251, 308 and 369 cm^{-1} , which are assigned to O-Ti-O bending vibration modes [Nilsen and Skinner, 1968]. This suggests that the band at 305 cm^{-1} in Fig. 1b can be assigned to the O-Ti-O bending vibration of TiO_6 framework units rather than to the lattice vibration of ETS-10.

Fig. 2 shows the UV-VIS reflectance spectra of ETS-10 in both dehydrated and hydrated states. Fig. 2a was obtained after ETS-10 was dehydrated at 423 K under a vacuum of 10^{-4} Torr for 6 h. This spectrum shows a strong absorption band at 280 nm. According to Jorgensen [1970] and Zecchina and co-workers [1992], the electronic transition with ligand to metal charge-transfer (CT) character involving isolated Ti(IV) in tetrahedral coordination is expected at 210 nm, whereas that involving isolated Ti(IV) in octahedral coordination is expected at approximately 240 nm. However, non-isolated octahedrally coordinated Ti(IV) in anatase is known to give the absorption edge approximately at 330 nm [Zecchina et al., 1991]. Obviously, each TiO_6 unit in ETS-10 is not isolated since it is con-

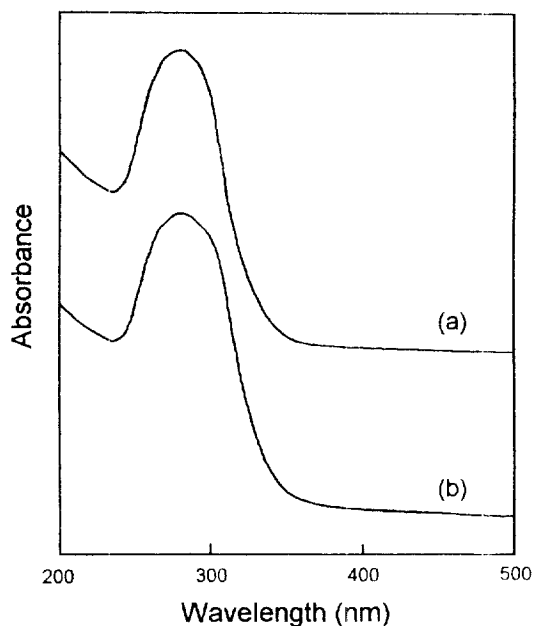


Fig. 2. UV-VIS reflectance spectra of ETS-10: dehydrated (a) and fully hydrated (b).

nected with two neighboring TiO_6 octahedra in addition to four SiO_4 tetrahedra by sharing all the oxygen atoms. This must result in the occurrence of the Ti(IV) CT band at a lower energy region. Therefore, it is most likely that the absorption band at 280 nm in Fig. 2a can be assigned to the CT transition involving Ti atoms in octahedral coordination. The absorption band at 280 nm in Fig. 2a is much narrower than that reported by Das et al. [1995]. The discrepancy with our result can be attributed to differences in the ETS-10 sample used. The position and intensity of the band at 280 nm are not significantly changed even after ETS-10 was fully hydrated over saturated NH_4Cl solution at room temperature for 4 days (Fig. 2b). This suggests that the coordination environment of Ti atoms in ETS-10 remains unchanged during the rehydration step.

In conclusion, results from this study demonstrate that infrared and Raman spectroscopies give complementary information on the existence of intraframework TiO_6 octahedral units in ETS-10. In particular, the Raman technique is found to be an excellent tool for the characterization of molecular sieves containing TiO_6 framework units.

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