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Reassessment of Zeolite and Molecular Sieve Framework Infrared Vibrations

Crystalline aluminosilicates or zeolites have structures consisting of open three-dimensional frameworks of oxygen atoms. Situated in the tetrahedral sites formed by the arrangement of these oxygen atoms within the structure are the silicon or aluminum atoms. In addition to silicon and aluminum, other elements, specifically gallium and iron have been recently reported to occupy these positions resulting in zeolite-like molecular sieves (*1–8*). It is critical in the characterization of these materials that the incorporation of the metal into the framework sites be confirmed. Infrared spectroscopy, a quick, convenient and readily available technique has been examined as a method of confirming the incorporation of these elements into framework positions.

To develop this technique for molecular sieve characterization, we have utilized the known substitution of gallium for aluminum into the tetrahedral sites of the faujasite structure to identify and assign the infrared active framework vibrations (*6–8*). All materials described in this study were confirmed to be highly crystalline and free of extraneous matter. The framework vibration modes examined appear between 600 and 1200 cm^{-1} in the infrared spectrum and have been attributed to the symmetric (600–900 cm^{-1}) and asymmetric (900–122 cm^{-1}) stretching vibrations of the T—O bonds (*9, 10*).

The previously assigned vibrational contribution to these bands for the faujasite materials was of the stretching vibrations O—T—O within the framework structure (*9, 10*). The T atom indicates the inability of IR to discriminate between the two similar mass elements, aluminum and silicon. Since the T atom occupies the central position within this harmonic oscillator, the substitution of a heavier element such as gallium for the aluminum would be expected to shift the asymmetric but not the symmetric vibrations. However, if the oscillator contributing to these bands is due to the Si—O—T symmetric and asymmetric stretches (with T now denoting the elements aluminum, silicon or gallium) then both vibrations would shift when the heavier element, gallium, is substituted for aluminum. This has been previously suggested in studies of layered and clay materials (*11*). By examining the infrared symmetric stretching vibration region for the gallosilicate analogs of the zeolites type X and Y, the two possible vibrational group contributions would be distinguishable.

RESULTS

A significant shift in the two symmetric stretching vibrations of the aluminosilicate type X to lower wavenumber occurs when gallium replaced aluminum in the tetrahedral sites (A and B in Fig. 1). This is consistent with the expected shift based on the change in the reduced mass of the Si—O—T harmonic oscillator. With increasing SiO_2/Ga_2O_3 (formation of the type Y analog), the band near 768 cm^{-1} (C in Fig. 1b) visually increases in intensity with to the increasing SiO_2 content and is attributed to the contribution by the Si—O—Si symmetric stretching vibration. This band is not observable in the aluminosilicate as T is the similar mass atom, aluminum. It is reasonable to expect, when the concentration of silicon is increased changing from type X to type Y, the broad Si—O—T (T = Al, Si) band would shift in position to the higher wavenumber approaching the pure

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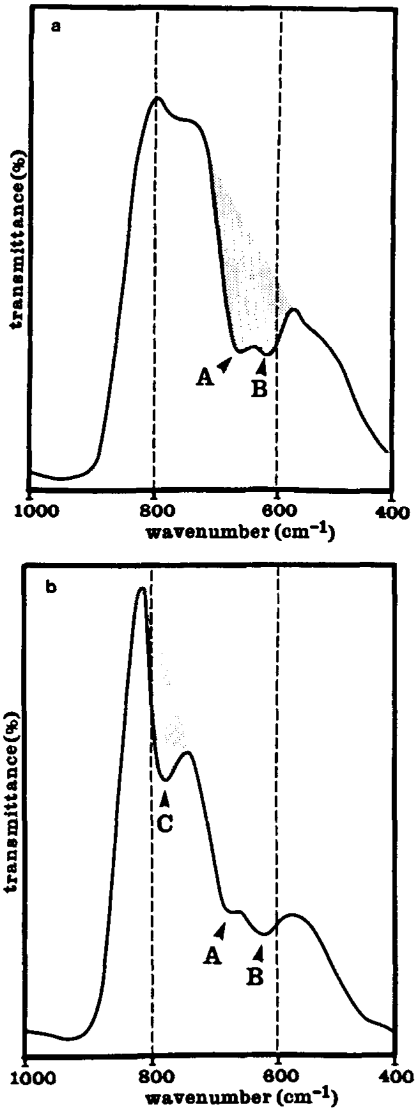

FIG. 1. Infrared spectrum symmetric stretching vibration region, (a) gallosilicate analog of type X with $SiO_2/Ga_2O_3 = 2.5$, (b) gallosilicate analog of Type Y with $SiO_2/Ga_2O_3 = 6$. C indicates the Si-O-Si vibration appearing at 768 cm which increases in intensity with increasing silica content in the molecular sieve.

Si—O—Si vibrations. The shift has been previously noted (*9, 10*). Since the gallosilicate Si—O—Si and Si—O—Ga groups are significantly different in mass, the symmetric stretching vibrations appear at two separate frequencies. A change in band position for each group upon changing SiO_2/Ga_2O_3 is not expected and is not observed. A number of gallosilicates with the faujasite structure containing different amounts of gallium have been examined as a function of the change in their infrared band position. The position of these bands is insensitive to changing gallium concentration. For these materials only the visual increase in the intensity of C (see Fig. 1b) is evident as the concentration of Si—O—Si linkages within the framework increases.

To further verify the proposed assignment, another molecular sieve, an aluminogerminate with the faujasite type X structure has been prepared and its infrared framework vibration spectrum examined (*12*). The harmonic oscillator, Ge—O—Al, is similar in reduced mass to that of the gallosilicate with the heavier element, germanium, occupying the corresponding tetrahedral silicon sites in the structure. If the major contribution to these bands is due to the symmetric stretch of the T—O—T′ unit where T is Si—O—Ga and T′ is Ga or Al, then the Si—O—Ga and Ge—O—Al vibrations should appear at a similar frequency. They do. The two vibrations of the symmetric stretch from the Ge—O—Al fragment, shifts to lower wavenumber to the same extent as the Si—O—Ga vibrations in the gallosilicate analog. No band near 800 cm^{-1} is observed in the aluminogerminate since formation of Al—O—Al units in the structure is prohibited (Lowensteins' Rule).

As the molecular sieve structure consists of an extended array of Si—O—T units, other contributions to these vibrations cannot be neglected. To determine the extent to which the Si—O—T symmetric stretching mode contributes to the vibration in this region of the spectrum and to determine the utility of using the presence of this vibration in characterizing metal incorporation into molecular sieve structures, other molecular sieve analogs of the zeolites were examined.

The band positions for these materials (shown in Table 1) all have the characteristic symmetric stretching vibration associated with the present of the Si—O—Si and Si—O—T (T = Ga or Fe) units. It is significant to note that only single bands are ob-

TABLE 1

Infrared Band Positions between 900 and 600 cm^{-1} Observed for Gallo- and Ferrisilicate Molecular Sieves

Structure	T	ν_s (Si—O—Si) (cm^{-1})	ν_s (Si—O—T) (cm^{-1})
Type X	Ga	—	660,611
Type Y	Ga	768	660,611
Sodalite	Ga	768	611
Sodalite	Fe	768	679
ZSM-5	Fe	798	656

served in these systems. The presence of two bands for the faujasites in the symmetric stretching vibrations region may arise from a secondary or structural lattice contribution to this vibration (*9, 10*). In the faujasites both bands are sensitive to T atom substitution. In the gallosilicate sodalite examined, the two vibrations observed are attributed to the Si—O—Si and Si—O—Ga symmetric stretch. Vibrations attributed to the Si—O—Fe unit for both sodalite and ZSM-5 structures appear within the range predicted based on changing the reduced mass of the Si—O—T harmonic oscillator providing further evidence for the vibrational contribution of the Si—O—T stretch to this band. Slight shifts in band position are observed for both Si—O—Si and Si—O—T vibrations in all these structures.

We conclude based on a study of the gallo- and ferrisilicate analogs of the zeolite molecular sieve, that the symmetric and asymmetric vibrations appearing between 600 and 1200 cm^{-1} in these materials may be more correctly interpreted as using from the Si—O—T vibration than the presently accepted O—T—O vibrational assignment. Other factors such as structure, changing the charge on the T atom or changing the electronegativity and the force constant of the oscillator would also effect the number or position of these bands. However, for applications such as incorporation of the similar elements, gallium and iron, examination of this region of the infrared spectrum appears to be a sensitive method for determining framework incorporation into analogous molecular sieve materials.

EXPERIMENTAL PROCEDURE

The gallosilicate and ferrisilicate analogous of types X, Y, sodalite, and ZSM-5 that were used in this study were prepared in pure highly crystalline form with no detectable extraneous material present. The methods of preparation are reported elsewhere (*1–3, 6–8*).

Perkin–Elmer Infrared Spectrometer, Model-598, computer assisted, was used with KBr-pressed wafers. All faujasite materials were in the Na^+ form. The sodalite and ZSM-5 molecular sieves were in the as-synthesized TMA^+/Na^+ form. This vibrational region is known to be of limited sensitivity to the type of counterion present (*9, 10*). A minimum of two different T atom concentrations were examined for each structure.

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