

Infrared Examination of the Reversible Oxidation of Ferrous Ions in Y Zeolite

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Infrared absorption bands from 400 to 1200 cm^{-1} , exhibited by Fe-Y zeolites oxidized with ^{16}O or ^{18}O are assigned to an iron-oxygen-iron bridge similar to that proposed earlier from Mössbauer spectra. Thus structural information on catalyst supports such as zeolites can be obtained by infrared absorption spectroscopy below 1200 cm^{-1} .

INTRODUCTION

Examination of zeolites by infrared spectroscopy is usually confined to the region 1200-4000 cm^{-1} which is most transparent to infrared radiation. The region below 1200 cm^{-1} is obscured by the fundamental vibrations of the (Si/Al)- O_4 tetrahedra of the zeolite. Above 1200 cm^{-1} , observations are restricted to infrared bands due to adsorbates and hydroxyl groups of the zeolite framework.

The region below 1200 cm^{-1} can give information concerning the zeolite structure, interaction of the cations with the zeolite framework, and the effect of adsorbed materials on the zeolite. Recently Flanigen *et al* (1) reported an extensive infrared study of a large number of zeolites over the range 200-1300 cm^{-1} . These authors were able to establish an association between major structural groups of the zeolite and a number of the infrared bands. The effects of cation exchange and dehydration on some of the more common zeolites were also examined. These data are

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useful in the interpretation of spectra obtained in this region.

The present work was initiated to check a conclusion reached by Garten *et al.* (2) using Mössbauer spectroscopy. It was suggested that, in a dehydrated Y zeolite, ferrous ions which occupy predominantly the hexagonal prism sites, are pulled into the sodalite cages upon oxidation to form an iron-oxygen-iron bridge. The changes observed for a ferrous exchanged Y zeolite upon dehydration and oxidation should be readily accessible by infrared in the region below 1200 cm^{-1} , as suggested by the data of Flanigen *et al.* (1) who reported changes in bands in this region following cation exchange and dehydration.

The same Fe^{2+} -Y zeolite used by Garten *et al.* (2) is examined in this work over the spectral region of 400-1200 cm^{-1} , and an absorption band is observed which is assigned to the Fe-O-Fe bridge as proposed in the earlier study using Mössbauer spectroscopy.

EXPERIMENTAL

Apparatus

A Beckman IR-9 spectrophotometer was used with a spectral resolution of

approximately 4 cm^{-1} in the $400\text{--}1000\text{ cm}^{-1}$ region and 6 cm^{-1} in the 3600 cm^{-1} region.

The infrared cell was similar to that described by Hughes and White (3) but was constructed entirely of stainless steel. The sample, contained in a heated stainless steel tube, was positioned in the infrared beam where it could be heated and cooled while spectra were recorded without moving the sample. The sample wafer was 2.85 cm in diameter and was formed by pressing the zeolite powder in a metallurgical die under a force of $6 \times 10^4\text{ N}$. The sample was uniform and self-supporting. For spectra in the $400\text{--}1000\text{ cm}^{-1}$ region the sample "thickness" was 4 mg cm^{-2} and in the $1200\text{--}4000\text{ cm}^{-1}$ region, 20 mg cm^{-2} .

The infrared cell was connected to a conventional Pyrex high vacuum system by using greased stopcocks. The system was pumped by an 80-liter per sec oil diffusion pump backed by a rotary mechanical pump. The pumps were isolated from the system by a liquid nitrogen cooled trap.

Materials

Hydrogen was generated electrolytically then diffused through a palladium-silver alloy. Deuterium, Matheson 99.5% minimum purity, was passed through an Engelhard Deoxo catalytic purifier and then over dehydrated 5A molecular sieve at 78 K . Oxygen, 99.5% from the Liquid Carbonic Corporation, was dried over dehydrated 5A molecular sieve at 193 K . Isotopic oxygen, $^{18}\text{O}_2$, obtained from Yeda R and D Co., Ltd., Rehovoth, Israel, was 93.07 atom% ^{18}O and 0.599 atom% ^{17}O . Water used to rehydrate the catalyst samples was boiled to remove CO_2 , placed in an ampoule with a stopcock and the fixed gases removed by several freeze-pump-thaw cycles.

The $\text{Fe}^{2+}\text{-Y}$ zeolite was that used in Ref. (2) and listed there as 65% exchanged. The composition of the NaY starting material and the preparation of the

$\text{Fe}^{2+}\text{-Y}$ have been described in detail (2,4). Sodium Y zeolite from the Linde division of Union Carbide Corporation ($\text{Si}/\text{Al} = 2.4$) was exchanged with FeSO_4 under a nitrogen atmosphere. Crystallinity of the $\text{Fe}^{2+}\text{-Y}$ material was checked by X-ray diffraction and nitrogen adsorption at liquid nitrogen temperature.

RESULTS

Infrared spectra from 400 to 1100 cm^{-1} are presented in Fig. 1. The cell with the sample in position was evacuated at room temperature for 2 hr and the infrared spectrum A recorded. The major peaks are at 588 and 797 cm^{-1} with shoulders at 730 and 930 cm^{-1} . There is also a very broad band from 950 to 1200 cm^{-1} . Flowing hydrogen over the sample at room temperature produced no observable change in the infrared spectrum. The sample was then heated in flowing hydrogen at 100 cc min^{-1} to 423 K for 2 hr and then cooled to room temperature to record spectrum B. In a

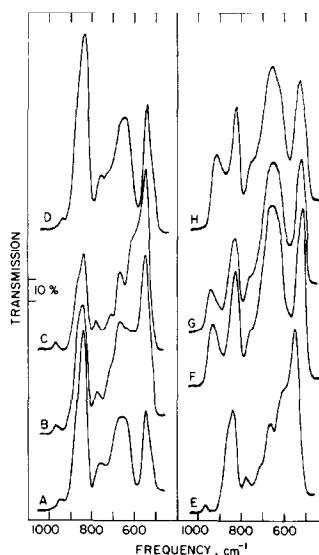


FIG. 1. Fe^{2+} exchanged Y zeolite: (A) Evacuation at room temperature; (B) treatment in flowing H_2 at 423 K ; (C) treatment in flowing H_2 at 673 K ; (D) addition of water vapor at room temperature; (E) evacuation at 673 K ; (F) treatment at 673 K in flowing O_2 ; (G) evacuation at 673 K ; (H) addition of water vapor. All spectra recorded at room temperature.

similar manner the sample was treated in hydrogen at 673 K (spectrum C). The intensity of the 588-cm^{-1} band decreased appreciably at 423 K, to become negligible after treatment at 673 K. A peak appeared at 650 cm^{-1} but it should be noted that this peak may have been obscured in previous spectra by the large peaks on either side. Addition of less than $30\text{ }\mu\text{mol}$ of water at room temperature caused the reappearance of the 588-cm^{-1} peak with the resulting spectrum D almost identical to the initial spectrum A of the evacuated sample. Similarly upon evacuation of the hydrated sample, for 2 hr at 673 K, the spectrum characteristic of the dehydrated material reappeared (Fig. 1E).

Addition of deuterium oxide to the dehydrated and reduced sample gave spectra identical to that produced by water. No shift in the peak at 588 cm^{-1} was observed.

In contrast, treatment of the sample in O_2 flowing at 100 cc min^{-1} for 2 hr at 673 K caused considerable alteration of the spectrum (Fig. 1F). Evacuation at 400°C to remove any water possibly present on the sample did not appreciably change the spectrum (Fig. 1G). The spectral changes upon oxidation include an infrared peak at 580 cm^{-1} similar to that caused by water addition and a band at 895 cm^{-1} not observed previously. Addition of $30\text{ }\mu\text{mol}$ of water had little effect on the spectrum, the band at 580 cm^{-1} neither increasing in intensity or breadth (Fig. 1H). The changes were found to be reversible, treatment in hydrogen or oxygen at 673 K giving spectrum C or F, respectively.

Oxidation of the sample in 120 Torr of $^{18}\text{O}_2$ at 673 K produced a spectrum similar to Fig. 1F with no change in the 580-cm^{-1} band but a shift of the 895-cm^{-1} band to 885 cm^{-1} .

A sample of greater thickness, 20 mg cm^{-1} , was observed in the O-H stretching region after similar pretreatment. After heating the sample at 673 K in flowing H_2

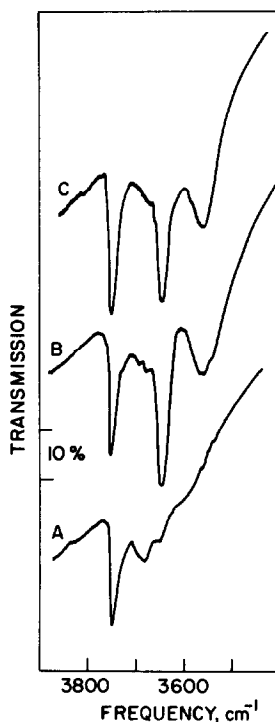


FIG. 2. Fe^{2+} exchanged zeolite: (A) Treatment in flowing H_2 at 673 K; (B) treatment in flowing O_2 at 673 K; (C) evacuation at 673 K. All spectra recorded at room temperature.

for 2 hr, the room temperature spectrum from 3400 to 3900 cm^{-1} , presented in Fig. 2A, was recorded. Hydroxyl groups are observed at 3750 cm^{-1} with a weak broad band near 3650 cm^{-1} . Oxidation of the sample in O_2 at 673 K produced strong bands at 3550 and 3650 cm^{-1} (Fig. 2B). Evacuation of the sample at 673 K caused no change in the spectrum. The effect was reversible since treatment in hydrogen at 673 K gave a spectrum identical to that of Fig. 2A.

DISCUSSION

Before discussing the spectral changes observed here, the assignment of the infrared bands should be made. The region of the infrared spectrum from 1200 to 400 cm^{-1} contains the fundamental vibrations of the $(\text{Si}/\text{Al})\text{-O}_4$ tetrahedra and for that reason should reflect the framework struc-

tures of the zeolite. This region has been studied extensively by Flanigen *et al.* (1) for a series of synthetic zeolites under various conditions of dehydration and cation exchange. From these data several of the infrared bands of interest in this work can be assigned. The band in the region of 580 cm^{-1} is associated with the six-membered double rings of the hexagonal prism. The wave number observed by Flanigen *et al.* for a hydrated NaY sample was 580 cm^{-1} . Upon dehydration at 673 K this value increased slightly. A hydrated calcium exchanged sample gave an infrared spectrum similar to that of a hydrated NaY material including a strong band at 570 cm^{-1} . Upon dehydration at 673 K, the 570 cm^{-1} band is markedly reduced and a weak band appears at 635 cm^{-1} . The 570 cm^{-1} infrared absorption is assigned to a vibration of the 6-ring of the hexagonal prism. The cation position could be either in the plane of the 6-ring (6-coordinate) or outside of the 6-ring in 4-coordinate position S_1' (5). Complete dehydration removes the water and the cation would move to position S_1 in the center of the hexagonal prism. The movement of cations from S_1 to S_1' by interaction with small molecules such as water has been observed by Bennett and Smith (6) using X-ray diffraction.

The other band of interest is that at 895 cm^{-1} which appears on treatment of the $\text{Fe}^{2+}\text{-Y}$ in oxygen at 673 K. No similar band was reported by Flanigen *et al.* for NaY or CaY samples although the bands to either side, at 800 and 950 cm^{-1} , reported by Flanigen *et al.* were observed in all of the spectra reported here.

The results obtained on the Fe^{2+} exchanged Y zeolite will now be discussed. The presence of the infrared band at 590 cm^{-1} for partially hydrated Fe^{2+} zeolite indicates that the major portion of the divalent ions is interacting with the 6-ring of the hexagonal prism. Dehydration at 673 K results in disappearance of this band

corresponding to movement of the iron into the hexagonal prism, site S_1 , where the iron would be 6-coordinate. This interpretation is in general agreement with the conclusions of Delgass *et al.* (4). Mössbauer spectra of dehydrated $\text{Fe}^{2+}\text{-Y}$ indicate ferrous ions in sixfold coordination as in site S_1 . However, the hydrated material obtained after room temperature evacuation also exhibits similar Mössbauer spectra, again indicative of sixfold coordination. This result is compatible with the present data if one assumes the iron ion to be in the plane of the 6-ring hexagonal prism or in position S_1' and coordinated to several water molecules. In fact Delgass *et al.* (4) reported the room temperature evacuated material contained four water molecules per iron atom compared to the dehydrated material. The reversibility of this process is seen by the disappearance of the band upon dehydration 673 K and subsequent reappearance upon rehydration. This reversibility was also obtained by Delgass *et al.*

Since the infrared band at 590 cm^{-1} is due to the cation-hexagonal 6-ring group, it is reasonable that deuterium oxide gave a band identical to that for water.

Oxidation of the $\text{Fe}^{2+}\text{-Y}$ to $\text{Fe}^{3+}\text{-Y}$ produces a similar band at 580 cm^{-1} that cannot be removed by dehydration at 673 K. Also, the 590-cm^{-1} band observed for partially hydrated $\text{Fe}^{2+}\text{-Y}$ could not be produced by addition of water to the $\text{Fe}^{3+}\text{-Y}$ material. The iron ions must, therefore, move into the S_1' position upon oxidation. This interpretation is consistent with that proposed from Mössbauer spectra by Garten *et al.* (2). The Mössbauer spectra indicate a four coordinate Fe^{3+} ion and the measured oxygen uptake during oxidation of $\text{Fe}^{2+}\text{-Y}$ to $\text{Fe}^{3+}\text{-Y}$ corresponds to one oxygen to two iron ions. The results suggest the formation of an iron-oxygen-iron bridge structure in the sodalite cage with the Fe^{3+} ions occupying sites S_1' of two adjacent hexagonal prisms.

The Fe-O-Fe bridge would not be affected by 673 K dehydration nor would addition of water cause any change since the iron ions are already held in the S_1' site by the oxygen bridge.

The presence of an Fe-O-Fe bridge structure in the oxidized material is supported by the infrared band observed at 895 cm^{-1} in the spectrum of the Fe^{3+} sample. The asymmetric stretching mode of the Fe-O-Fe bridge is reported to occur in the region $800\text{--}900\text{ cm}^{-1}$ for several organometallic compounds (7-9). Shift of the band to lower frequency when oxidized by $^{18}\text{O}_2$ is expected but the magnitude of the shift is difficult to calculate. A free structure, analogous to gas phase Al_2O would have a shift of approximately 25 cm^{-1} upon substitution of ^{18}O for ^{16}O assuming an included bond angle of 120° (10). The isotopic shift drops to 10 cm^{-1} for an Fe-O-Fe angle of 150° . Also, the bonding of the iron ions to the 6-ring hexagonal prism is not considered in this calculation. Thus, the observed isotopic shift for oxidation in ^{16}O and ^{18}O , 10 cm^{-1} , is not unreasonable for a bridged Fe-O-Fe structure.

The changes in the O-H stretching region upon oxidation should also be considered. The 3750-cm^{-1} band, characteristic of hydroxyl groups on silica impurities, is constant and independent of H_2 or O_2 treatment (11). The bands at 3640 and 3550 cm^{-1} are most likely associated with framework oxygen O_1 and O_3 , respectively. Oxygen O_1 is the bridging oxygen of the hexagonal prism and O_3 is the oxygen in the 6-ring of the hexagonal prism (12). Movement of the iron ions out of the hexagonal prism upon oxidation would greatly increase the distance between the cation and the oxygens of the 6-ring on the opposite side of the hexagonal prism (O_3). The need for charge compensation in the dehydrated zeolite may lead to creation of hydroxyl groups at the most distant AlO_4 tetrahedra. Also, isolated iron ions, upon

oxidation may form oxide or hydroxide species necessitating structural hydroxyl groups for charge compensation.

CONCLUSION

Although the infrared region below 1200 cm^{-1} is considered unusable in transmission for supported catalysts due to the intense absorption bands of the support, this region contains information on the structure of crystalline supports such as zeolites. If a sufficiently thin sample is used, this region can be readily studied. Not only can changes in the zeolite such as cation movement be followed, but bands resulting from adsorbed species or catalytically active components can also be observed. The latter is especially applicable to zeolites because of the large available surface area.

In the case of Y-type zeolites, the band at 580 cm^{-1} is useful in establishing the position of the cation. When the cation is located in the S_1' position, that is outside the hexagonal prism and coordinated with three oxygens of the hexagonal six-ring, the 580-cm^{-1} absorption band is quite strong. For the Fe^{2+} -Y zeolite, the cation can be held in this position by interaction with water molecules or by formation of an iron-oxygen-iron bridge structure. The observation of the Fe-O-Fe stretching frequency and the reasonable isotopic shift for ^{18}O compared to ^{16}O confirms the presence of the bridged structure within the sodalite cage.

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REFERENCES

1. Flanigen, E. M., Khatami, H., and Szymanski, H. A., in "Molecular Sieve Zeolites," (R. F. Gould, Ed.) Vol. 101, pp. 201-229. American Chemical Society, Washington, D.C., 1971.

2. Garten, R. L., Delgass, W. N., and Boudart, M., *J. Catal.* **18**, 90 (1970).
3. Hughes, T. R., and White, H. M., *J. Phys. Chem.* **71**, 2193 (1967).
4. Delgass, W. N., Garten, R. L., and Boudart, M., *J. Phys. Chem.* **73**, 2970 (1969).
5. Smith, J. V., Bennett, J. M., and Flanigen, E. M., *Nature (London)* **215**, 241 (1967).
6. Bennett, J. M., and Smith, J. V., *Mater. Res. Bull.* **3**, 633 (1968).
7. Khedeker, A. V., Lewis, J. Mabbs, F. E., and Weigold, H., *J. Chem. Soc. Ser. A*, 1561 (1967).
8. Lewis, J., Mabbs, F. E., and Richards, A., *J. Chem. Soc. Ser. A*, 1041 (1967).
9. Reiff, W. M., Baker, W. A., and Erickson, N. E., *J. Amer. Chem. Soc.* **90**, 4794 (1968).
10. Linevsky, M. J., White, D., and Mann, D. E., *J. Chem. Phys.* **41**, 542 (1961).
11. Ward, J. W., *J. Phys. Chem.* **73**, 2086 (1969).
12. Eulenberger, G. R., Shoemaker, D. P., and Kiel, J. G., *J. Phys. Chem.* **71**, 1812 (1967).