

## The Adsorption of Cyclopropane on Zeolite HY

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Infrared and mass spectral evidence indicates that when cyclopropane is passed over zeolite HY at room temperature isobutane is formed as a major product. A mechanism for this transformation involving the formation of a nonclassical protonated cyclopropane ion intermediate is proposed. At 200°C and above cyclopropane isomerizes to propylene and also forms aromatic species.

### INTRODUCTION

Kinetic studies on the isomerization of cyclopropane to propylene in the presence of zeolites X and Y have been carried out at temperatures of 200°C and above. Bassett and Habgood (1) and Habgood and George (2) have studied the isomerization on various zeolites X and Y and have found an increasing catalytic activity for the zeolites as follows:  $KX < NaX < NaY < LiX < HY$ . Bartley *et al.* (3) and George and Habgood (4) in their studies using a deuterated zeolite catalyst have concluded that both exchange and isomerization of cyclopropane proceed via a nonclassical protonated cyclic carbonium ion intermediate. Hall and co-workers (6, 7) and Larson *et al.* (5) in studies of the isomerization over silica-alumina catalysts have raised some questions as to whether the carbonium ion intermediate was formed by addition of a proton from a Bronsted site or by abstraction of a hydride ion by a Lewis acid site. Gerberich *et al.* (8) and Hightower and Hall (9) studied the reac-

tions of alkylcyclopropanes over silica-alumina catalysts and their results support the Bronsted acid mechanism. Flockhart *et al.* (10) have shown that in addition to the Bronsted acid mechanism, a second mechanism, possibly involving a Lewis acid site, may be operative depending on the activation temperature of the zeolite catalyst.

The object of the present work was to examine the behavior of cyclopropane adsorbed on zeolite HY at both room temperature and at elevated temperatures and to examine the products formed in order to obtain an understanding of the transformations taking place.

### EXPERIMENTAL METHODS

Cyclopropane gas of 99.8% purity was used without further purification. The HY zeolite was prepared from a  $NH_4Y$  zeolite obtained by exchanging the sodium ion in NaY zeolite (designated as Linde SK40, lot No. 3606468 without binder) by ammonium ion, using five successive treatments with 1 M  $NH_4Cl$  at room temperature, drying at 120°C overnight and storing over saturated ammonium chloride solution.

The chemical composition of the dehydrated zeolite NaY was as follows:

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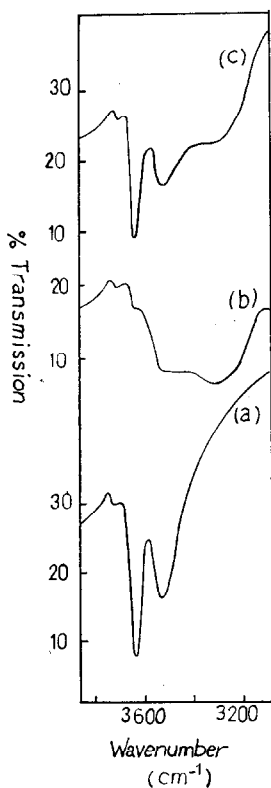


FIG. 1. The infrared spectra of OH groups of zeolite HY: (a) Background; (b) on exposure to ca. 16 cm Hg of cyclopropane gas at room temperature; (c) after partial removal of the cyclopropane gas phase.

$(\text{Na}_2\text{O})_{0.97}(\text{Al}_2\text{O}_3)(\text{SiO}_2)_{4.8}$ , and the ammonium ion exchanged zeolite Y contains 72% ammonium ions. The  $\text{NH}_4\text{Y}$  zeolite was compressed at ca.  $6400 \text{ kg cm}^{-2}$  to form a tablet of  $0.010 \text{ g cm}^{-2}$ . The tablet was mounted in an infrared absorption cell, which has been described previously (11), connected to a conventional gas handling system, outgassed at room temperature until the pressure fell to  $10^{-4}$  Torr, and then heated *in vacuo* at  $150^\circ\text{C}$  for 2 hr. The temperature was raised to  $350^\circ\text{C}$  and held until the pressure again fell to  $10^{-4}$  Torr. The temperature was then raised to  $500^\circ\text{C}$  for 0.5 hr when a pressure of  $10^{-6}$  Torr was obtained. By this procedure the  $\text{NH}_4\text{Y}$  zeolite had been converted to the HY zeolite. The tablet was then exposed to

cyclopropane gas at a pressure of 16 cm Hg and the infrared spectrum of the adsorbed gas was taken. Adsorption was carried out at room temperature and also at  $200^\circ\text{C}$  and all spectra were recorded at room temperature on a Jasco IRA-1 infrared spectrometer at slowest scan speed and maximum wavenumber expansion. The wavenumber accuracy was  $\pm 3 \text{ cm}^{-1}$  in the region  $4000\text{--}2000 \text{ cm}^{-1}$  and  $\pm 2 \text{ cm}^{-1}$  in the region  $200\text{--}610 \text{ cm}^{-1}$ .

## RESULTS

### *Adsorption at Room Temperature*

The infrared spectrum of the zeolite HY in the OH stretching region is shown in Fig. 1a. Three distinct hydroxyl stretching bands were observed at 3740, 3647 and  $3547 \text{ cm}^{-1}$ . The  $3647 \text{ cm}^{-1}$  band was very sharp and the most intense, the  $3547 \text{ cm}^{-1}$  band was broad and weaker and the  $3740 \text{ cm}^{-1}$  band was very weak. Following adsorption of cyclopropane the band at  $3647 \text{ cm}^{-1}$  was shifted to a very intense broad band in the  $3400\text{--}3200 \text{ cm}^{-1}$  region. The bands at 3740 and  $3547 \text{ cm}^{-1}$  appeared to be unaltered though it was difficult to measure the latter band position, being very weak and affected by overlapping of the intense broad band following adsorption (see Fig. 1b).

In the OH stretching region of the zeolite sample incorporating the adsorbed species, on partial removal of the gas phase cyclopropane, the broad hydrogen-bonded OH band in the region  $3400\text{--}3200 \text{ cm}^{-1}$  gradually disappeared leaving some residual intensity at  $3280 \text{ cm}^{-1}$ ; at the same time, the original background band at  $3647 \text{ cm}^{-1}$  was partly regenerated (Fig. 1c). On further evacuation at room temperature all the original OH bands reappeared. This indicates that some physical adsorbed cyclopropane species was hydrogen-bonded to the  $3647 \text{ cm}^{-1}$  OH groups and was easily desorbed.

The spectrum of the adsorbed samples

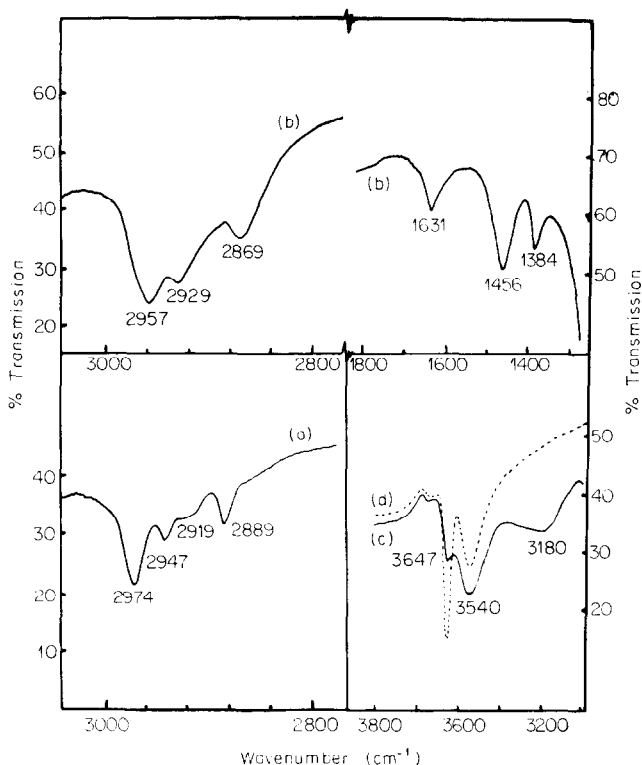


FIG. 2. The infrared spectra of the adsorbed species: (a) After evacuation of the excess gas phase at room temperature for 2 min; (b) after heating the product whose spectrum is shown in (a) at 200°C in a closed cell for 1 hr; (c) the infrared spectrum of the OH groups of the zeolite HY after heating the product as described in (b); (d) the OH groups before heating at 200°C.

following evacuation of the cell for 2 min at room temperature to remove excess cyclopropane is shown in Fig. 2a. Several C-H stretching bands were observed in the region below 3000  $\text{cm}^{-1}$ . The sharp intense band at 2974  $\text{cm}^{-1}$  was assigned to an asymmetrical  $-\text{CH}_3$  stretching mode, the 2889  $\text{cm}^{-1}$  band to the tertiary  $\equiv\text{C}-\text{H}$  group (12, 13) and the bands at 2947 and 2919  $\text{cm}^{-1}$  were assigned to asymmetric and symmetric stretchings, respectively, of  $-\text{CH}_3$  groups. No bands were observed near 3090 and 3030  $\text{cm}^{-1}$  corresponding to olefinic groups such as  $=\text{CH}_2$ ,  $=\text{C}-\text{H}$ , respectively, nor was any band observed in the 1630  $\text{cm}^{-1}$  region corresponding to the C=C stretch.

The cell was evacuated at 150°C for 2 hr and the desorbed species were trapped in a tube cooled in liquid nitrogen. The desorbed

species was fed into a mass spectrometer and the 30 eV mass spectrum showed the presence of a major product having an  $m/e$  value of 58, which, for a hydrocarbon could refer only to *n*-butane or isobutane. The presence of isobutane was confirmed by the fact that in the spectrum of the adsorbed material there was a band at 2889  $\text{cm}^{-1}$  assigned to the tertiary  $\equiv\text{C}-\text{H}$  group and this was supported by the absence of strong bands at 2936–16  $\text{cm}^{-1}$  assigned to the asymmetric stretch (14) of  $-\text{CH}_2$  groups which are present in *n*-butane.

In another experiment cyclopropane was adsorbed on a tablet at room temperature as described previously and instead of desorbing the saturated hydrocarbon product the tablet was heated at 200°C for 1 hr. The color of the tablet changed from

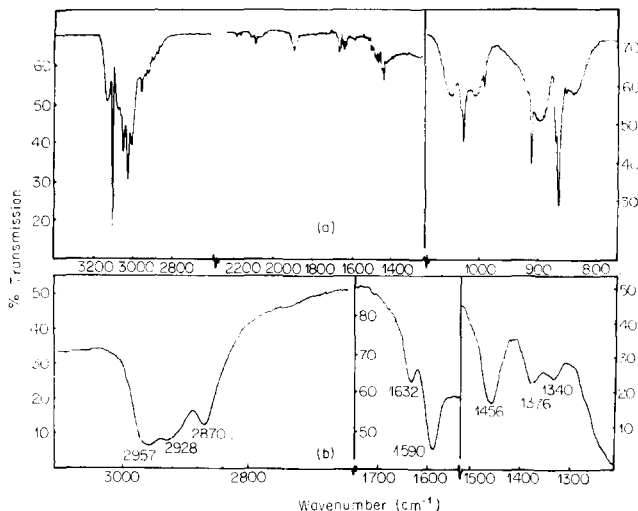


FIG. 3a. The infrared spectrum of the gas phase (the sample not in the path of the infrared beam) following adsorption of cyclopropane on zeolite HY at 200°C; (b) the infrared spectrum of the adsorbed materials after evacuation of the excess gas phase for 10 sec.

white to pale yellow. On cooling to room temperature the infrared spectrum was recorded. As shown in Fig. 2c and d, the  $3647\text{ cm}^{-1}$  band has become weaker than that before heating, and the decrease in intensity was accompanied by the development of a very broad band near  $3180\text{ cm}^{-1}$ . The shift of the  $-\text{OH}$  stretch at  $3180\text{ cm}^{-1}$  due to hydrogen bonding interaction is larger by  $100\text{ cm}^{-1}$  than that observed when the adsorption of cyclopropane was carried out at room temperature, indicating a much stronger interaction. Changes in the spectra in the  $\text{C}-\text{H}$  stretching region are shown in Fig. 2b. Bands were observed at  $2957$ ,  $2929$  and  $2869\text{ cm}^{-1}$  and were assigned to asymmetric  $-\text{CH}_3$ , asymmetric  $-\text{CH}_2$  and symmetric  $\text{CH}_3$  stretching modes, respectively. In the region  $1700\text{--}1300\text{ cm}^{-1}$  in addition to two bands at  $1456$  and  $1384\text{ cm}^{-1}$  due to asymmetric and symmetric  $-\text{CH}_3$  deformation modes a band attributed to the  $\text{C}=\text{C}$  stretching mode was observed at  $1631\text{ cm}^{-1}$  suggesting the formation of olefinic species (see Fig. 2b).

#### Adsorption at 200°C

In a third experiment a tablet was heated for 1 hr at  $200^\circ\text{C}$  and cyclopropane was

admitted at a pressure of  $15\text{ cm Hg}$ . The color of the tablet immediately changed from white to dark yellow. The spectrum of the gas phase (the zeolite sample not in the path of the infrared beam) is shown in Fig. 3a and the presence of propylene is evidenced by bands at  $2955$ ,  $1653$ ,  $1441$ ,  $991$  and  $913\text{ cm}^{-1}$  which were assigned to  $\text{CH}_3$  stretching,  $\text{C}=\text{C}$  stretching,  $\text{CH}_3$  bending,  $\text{CH}$  bending and  $\text{CH}_2$  bending vibrations by comparison with the reported infrared spectrum (15) of gaseous propylene. Excess gas was evacuated from the cell for 10 sec and the spectrum of the adsorbed species was recorded (see Fig. 3b). Strong, distinct bands were observed at  $2957$ ,  $2928$  and  $2870\text{ cm}^{-1}$  and were assigned to saturated  $-\text{CH}_3$  and  $-\text{CH}_2$  stretching modes. Bands due to  $\text{CH}$  deformation modes were also observed at  $1456$ ,  $1376$  and  $1340\text{ cm}^{-1}$ . A band assigned to a  $\text{C}=\text{C}$  stretch was observed at  $1632\text{ cm}^{-1}$ . The appearance of a band near  $1590\text{ cm}^{-1}$  indicated the presence of aromatic species (16).

In the  $\text{OH}$  stretching region the strong sharp band at  $3647\text{ cm}^{-1}$  completely disappeared and only a broad band was observed at  $3540\text{ cm}^{-1}$ . The adsorbed species were strongly held since on pro-

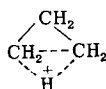
longed evacuation at 200°C there was only a slight decrease in the intensity of the above bands.

#### DISCUSSION

Zeolite HY contains distinct types of structural hydroxyl groups which have different infrared absorption frequencies. The 3740  $\text{cm}^{-1}$  band is assigned to silanol groups at locations terminating the giant lattice (17, 18). The location of the 3647 and 3547  $\text{cm}^{-1}$  bands has been the subject of much discussion (17, 18). Eberly (16) has assigned the former band to OH groups located inside the adsorption cages near 6-membered oxygen rings and the latter band to OH groups in inaccessible bridge positions between two sodalite units. Hughes and White (19) considered that these bands are due to OH groups located on O(1) and O(4) oxygen atoms whereas Olson and Dempsey (28) have assigned the 3647  $\text{cm}^{-1}$  band to OH groups located at the O(1) oxygen pointing into the large cavity and the 3547  $\text{cm}^{-1}$  band to OH groups located at the O(3) oxygen pointing into the double 6-rings.

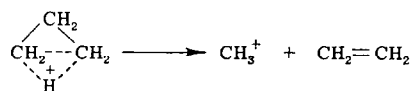
In the present study the 3647  $\text{cm}^{-1}$  OH groups reacted preferentially with adsorbed cyclopropane, whereas the 3547  $\text{cm}^{-1}$  OH groups were hardly affected suggesting that the former OH groups are more accessible and located in the supercages while the latter OH groups are in more inaccessible sites, possibly in the hexagonal prisms.

At temperatures of 200°C and above cyclopropane isomerizes to propylene. Bartley *et al.* (3) and George and Habgood (4) postulated that the isomerization may proceed via a nonclassical protonated cyclopropane ion, in which the proton exists in the ring plane in a bridging position between two carbon atoms, formed



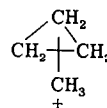
by reaction between the Bronsted site on the catalyst and an adsorbed cyclopropane molecule, and the mechanism of this reaction has been discussed by a number of authors (8, 9). This nonclassical protonated cyclopropane ion was initially proposed by Baird and Aboderin (20) and later supported by many theoretical calculations and experimental observations of other workers (21-25).

Though further studies need to be undertaken to elucidate the mechanism of the conversion of cyclopropane to isobutane at room temperature a possible explanation is as follows: the initial step is the formation of the nonclassical protonated cyclopropane ion described above, which then rearranges forming a methyl ion and ethylene:

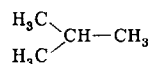


The rearrangement above has been postulated by Rylander and Meyerson (26) to resolve the problems associated with the origin of methyl ions observed in the mass spectra of labeled propanes and butanes.

The methyl ion attacks another cyclopropane molecule forming a methyl cyclopropane ion:



which rearranges to form isobutane:

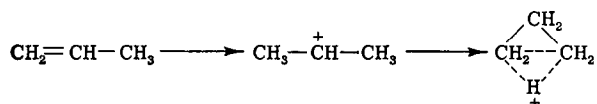


On the basis of the above mechanism it would have been expected that the olefinic  $=\text{C}-\text{H}$  stretching frequency would have been observed but the ethylene formed may well have been removed during the evacuation of the excess cyclopropane in the gas phase. Liengme and Hall (27) have shown that ethylene physically adsorbed on zeolite HY is completely desorbed by evacuation

at room temperature, in support of the above hypothesis.

It should be noted that propylene is converted to isobutane on zeolite HY at room temperature (27) and since cyclopropane and propylene are isomers it is quite

possible that their acid-catalyzed reactions would proceed along similar paths. Thus the secondary carbonium ion which arises from the addition of a proton to propylene could undergo rearrangement to a protonated cyclopropane ion:



which reacts as postulated above forming isobutane.

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