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NOTES

Infrared Spectral Characteristics of the Interaction of Olefins with H-ZSM-5 Zeolite

Aluminosilicate materials of the so-called "pentasil" type have recently acquired great importance in heterogeneous catalysis. Above all there has been much work with the ZSM-5 pentasil, which has especially come into prominence because of its ability to dehydrate methanol to hydrocarbons and its extremely high coke stability in cracking reactions (*1*).

The mechanism of this reaction is an object of much discussion. Omitting the question about the first C–C bond formation, Védrine *et al.*, studying the ir (*2*) and uv spectra (*3*) of adsorbed ethene, propene, butene, methanol, and dimethyl ether, suggested a carbenium ion formation. The aim of our work was to reduce the amount of parallel reactions and to try to detect the carbenium ions just preceding the aromatic ring closure. For this reason we have used higher olefins, namely 1-hexene, 1-heptene, and cyclohexene, as adsorbates. For comparison we have also investigated the ir spectrum of adsorbed benzene.

Zeolite ZSM 5 has been synthesized under conditions similar to those used for the samples described in Ref. (*4*) from batches of the composition $SiO_2:1$, $NaAlO_2:0.02$, TPA-Br : 0.25, NaOH : 0.25, $H_2O:11$ at 373°K. After it was heated at 873°K under an air flow the zeolite was treated at ambient temperature with 0.6 *M* HCl for 24 h and dried at 500°K.

For the ir spectroscopic measurements self-supported wafers (7–10 mg/cm^2) were evacuated at 673°K. The zeolite samples were allowed to equilibrate with the hydrocarbon vapor pressure at ambient temperature after a freeze–pump–thaw purification and drying of the adsorbates with Zeolite 5A. All the spectra were recorded at the temperature of the ir beam using a UR-10 spectrophotometer. The 1-hexene and 1-heptene were Fluka products. Cyclohexene was prepared from cyclohexanol and carefully purified.

The results of 1-hexene adsorption are presented in Fig. 1. After the initial spectrum of the evacuated zeolite wafer (spectrum 1) and overnight contact with the hydrocarbon vapor at room temperature the sample was heated for 15 min in the presence of some gas phase at 373°K (spectrum 2) and at 473°K (spectrum 3).

Spectra 4–7 were recorded after desorptions at different temperatures as noted on the figure. The spectrum of adsorbed 1-hexene after overnight contact with the zeolite at ambient temperature was the same as after heating at 373°K with the gas phase. Similar results have been obtained in the case of 1-heptene and cyclohexene adsorption.

It has been demonstrated that the protons of the pentasil OH groups absorbing at 3610 cm^{-1} interact with the double bonds of the chemisorbed olefins. This causes the disappearance of the OH bands and the appearance at 473°K of a new band at 1515 cm^{-1}. After desorption of the olefin at higher temperatures (573°K) the band disappears and the OH band is restored. The new band disappears also after the introduction of air into the cell. In the case of benzene adsorption the band at 1515 cm^{-1} could not be observed. These effects were also not found on the adsorption of olefins on pentasil which had been first poisoned by pyridine vapors. Taking into account the assumption of Huang (*5*) that the band at 1535 cm^{-1} observed after ethylene adsorption on Cu(I)Y is due to occluded carbonate

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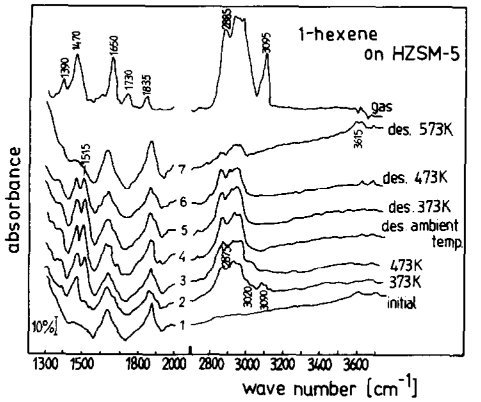


FIG. 1. Infrared spectra of 1-hexene sorbed on H-ZSM-5.

species, we treated the pentasil with CO_2 at 473°K, but no band in this region was registered. The band at 1515 cm^{-1} was present on ethylene adsorption on H-ZSM-5 at 673°K (*2*) and interpreted as due to benzene ring breathing, which was in contradiction with our observations.

Two of us have recently reviewed the data on the ir spectra of hydrocarbons adsorbed on zeolites (*6*). Our conclusion was that in many cases shifts of the double bond C=C stretching vibration at 1620–1650 cm^{-1} toward lower frequencies were observed depending on the strength of the interactions between the olefins and the cations in the zeolite structure. In some cases the shifts were interpreted as due to carbenium ions acting as a coke precursor of the observed formation of coke in the wider channel system of the faujasite (*7*).

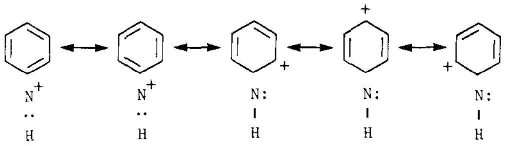
The special characteristics of pentasil must be kept in mind. One of them is the high Si/Al ratio. This produces a relatively large distance between the active centers of sorption and catalytic action, given by protons or other cations, so that a localized interaction may be possible without a too high probability of mutual reaction. Furthermore, the surface of the channels becomes hydrophobic, which drastically increases the time of residence of nonpolar molecules in the cavities compared with that of polar molecules. On the other hand, the 10-membered ring channels cause very special molecular sieving effects, as can be seen for example from the fact that benzene molecules can rotate about an axis parallel to the channel axis, but not around the sixfold axis perpendicular to the channel direction (*8*).

A third aspect which should be mentioned is that the OH groups of the hydrogen form of ZSM-5 seem to have an increased acidity compared with HY and H-mordenite. Finally, the spatial properties of the channel system do not allow the formation of fused hydrocarbon rings, so that the velocity of coke formation is drastically reduced in comparison with the zeolites of the larger cavity systems.

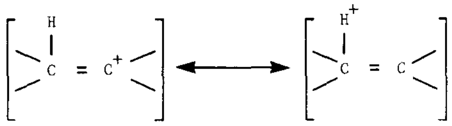
In seeking an interpretation of the band at 1515 cm^{-1} two assumptions might be made; the band might be regarded as belonging to newly formed species or it might represent a shifted C=C double-bond stretching as a result of relatively strong interaction with the zeolite active sites. Because these species are easily desorbed with restoration of the OH band we suppose that the band characterizes a shifted band of a double bond. The shift is quite a large one if only a π complex were formed. In this case the question arises as to the nature of the double-bond perturbation. One might suppose that the band represents an electron-deficient double bond. Such an interaction might be realized by olefin adsorption on the Lewis sites of the zeolite.

For instance, a band at 1512 cm^{-1} characterizes the complex $(C_2H_4)_3Ni$ and its intensity grows markedly after warmup from 15 to 35°K (*9*).

We suggest that such an electron-deficient double bond might occur as well as by interaction with protons. One of the arguments in support of this assumption is the fact that the widely accepted characteristic of Brønsted acidity in aluminosilicates, namely the band at 1545 cm^{-1} of the pyridinium ion (*10*), is also due to the stretching vibration of electron-deficient double bonds C=C. The band at 1545 cm^{-1} appears as a result of the protonation of the pyridine molecule which causes a further decrease of the electron density in the ring



If one accepts that the band at 1515 cm^{-1} is due to an electron deficient C=C double-bond stretching after protonation, one might also suppose that the same band would be characteristic of carbenium ion species, because they also might be described as electron-deficient species, namely



A question obviously arises again as to the stability of such species at high temperature. We suggest that the specific zeolitic channel system might stabilize the intermediate carbenium ions through adsorption and this might also be one of the reasons for the shape selectivity shown by the pentasils.

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H. LECHERT

Institute of Physical Chemistry
University of Hamburg
Laufgraben 24, 2000 Hamburg 13, West Germany

C. DIMITROV
C. BEZUHANOVA
V. NENOVA

Faculty of Chemistry
University of Sofia
1, A. Ivanov, Sofia 1126, Bulgaria

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