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NOTES

The Nature of Active Sites on Zeolites

V. *In Situ* Spectroscopic Observations of Hydrogen Y Zeolite During Cumene Cracking

Synthetic X and Y zeolites have been shown to be very active catalysts when they contain multivalent cations (*1*, *2*). The catalytic activity has been attributed to Brönsted acidity, Lewis acidity, and the electrostatic field (*3–6*). The catalytically active forms of Y zeolite have been shown to contain hydroxyl groups of different acid strengths (*4*, *7*, *8*). Thus, in the hydrogen Y zeolite, the hydroxyl groups giving rise to the 3640-cm^{-1} absorption band in the infrared spectrum form carbonium ions with pyridine, while those giving rise to the 3540-cm^{-1} band only form carbonium ions with the stronger base, piperidine (*7*). The acidic hydroxyl groups are believed to be the Brönsted acid centers. The only study of these surfaces during reaction appears to be the quinoline poisoning studies of Turkevich and Topchieva (*5*, *9*).

In order to study the active centers further, the spectra of hydrogen Y zeolite have been observed during the catalytic dealkylation of cumene. An infrared cell, which could function as a flow reactor, was used. A sample of ammonium Y zeolite, in the form of a pressed disc (*4*), was calcined at 500°C overnight in dry helium flowing at the rate of 50 ml min^{-1}. After recording the spectrum of the zeolite, it was cooled to 250°C. The helium stream was diverted through a saturator containing purified cumene at 25°C so that the cumene-saturated helium passed over the catalyst in the infrared cell. The effluent was monitored by gas chromatography. At a given temperature, the catalyst activity decreased with time until after 16 hr on stream, a steady conversion was obtained.

The spectra were recorded as a function of time of cumene flow and are presented in Fig. 1. A Cary-White 90 Infrared Spectrometer was used. It is seen that at 250°C, the 3540-cm^{-1} band is unaffected by the passage of cumene, indicating that at this temperature, the cumene is neither physically nor chemically adsorbed on this type of hydroxyl group. On the other hand, the intensity of the 3640-cm^{-1} band is decreased. The 3640-cm^{-1} band intensity de-

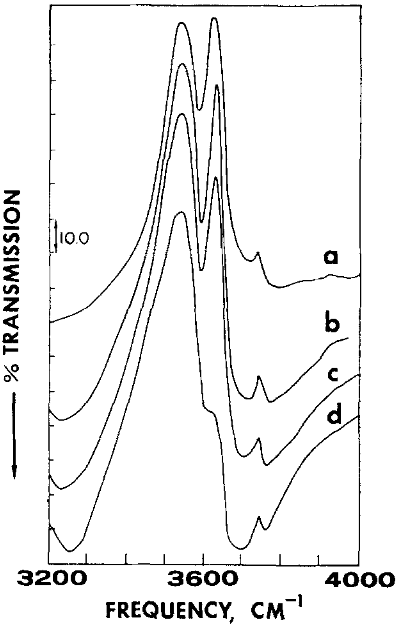

FIG. 1. Infrared spectra of hydrogen Y zeolite during cumene cracking at 250°C: a, after calcination; b, 1½-hr cumene flow; c, 3-hr cumene flow; d, overnight cumene flow.

creases continuously with time until after the cumene has flowed over the catalyst overnight, the band intensity reached a constant value. On increasing the temperature of the zeolite catalyst, the 3640-cm^{-1} band intensity was unaffected. When the temperature was raised to 365°C, a 5% decrease in the intensity of the 3540-cm^{-1} band was observed. Further decreases in intensity of the 3540-cm^{-1} band occurred, as shown in Fig. 2, as the temperature was raised.

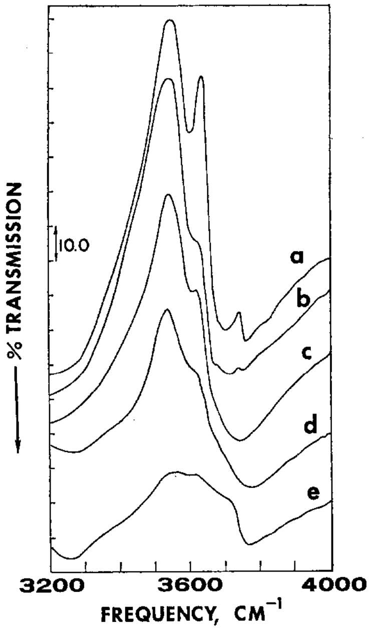

FIG. 2. Infrared spectra of hydrogen Y zeolite during cumene cracking as a function of temperature—3 hr at each temperature: a, 325°; b, 365°; c, 395°; d, 450°; e, 450°C overnight.

These preliminary observations suggest that at temperatures of and below 325°C, no detectable adsorption occurs involving the 3540-cm^{-1} type of hydroxyl groups and therefore these are unlikely to be active centers. The interaction with the 3640-cm^{-1} band suggests that these types of hydroxyl groups are potentially catalytically active sites. As the temperature is raised, the extent of interaction of cumene with the hydroxyl groups increases just as the catalytic activity increases. It is probable that the hydroxyl groups interact with the cumene by proton transfer and thus as the temperature of the catalyst is raised, a larger number of suitably activated hydroxyl groups become available. This is feasible since it has been shown elsewhere that the hydroxyl groups represented by the 3640-cm^{-1} band are not all of the same acid strength (*4*). It also appears likely that, at higher temperatures (>365°C), the hydroxyl groups represented by the 3540-cm^{-1} band become sufficiently acidic or activated to interact with cumene and thus serve as active centers. It is also possible that changes in hydroxyl group intensities could be due to the formation of coke or some other surface species.

It appears that by studying a catalytic reaction by *in situ* infrared spectroscopy, new evidence concerning the centers of adsorption and catalytically active sites can be obtained. Further details of this work and a more extensive study of the surface of zeolites during catalysis will be reported shortly.

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JOHN W. WARD

From the Union Oil Company of California
Union Research Center
Brea, California 92621

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