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NOTES

The Adsorption of Formic Acid on Y Zeolites: An Infrared Absorbance Study

A recent multiple-pulse nuclear magnetic resonance (NMR) study concluded that formic acid is adsorbed on two Y zeolites as unidentate and bidentate groups (*1*). An ammonium–Y (NH_4–Y) zeolite contained approximately equal amounts of each species, whereas an ultrastable hydrogen–Y (H–Y) zeolite contained predominately (83%) bidentate surface groups (*1*). The ultrastable H–Y zeolite is also more active catalytically, with respect to acid-catalyzed reactions (*2*).

The vibrational spectra of the unidentate and bidentate formate compounds can be distinguished by the separation between the frequencies of the C═O and C—O stretches of the formate. The infrared spectrum of the monomer of formic acid, which has a unidentate structure, has a C═O stretch at 1770 cm^{-1} and a C—O stretch at 1105 cm^{-1}, a difference of 665 cm^{-1} (*3*). The two bands in methyl formate and ethyl formate, also unidentate-like, are separated by about 550 cm^{-1} (*4*). The distinction between the two C–O bands vanishes for bidentate formates. Accordingly, the separation between the two bands, more correctly labeled asymmetric and symmetric OCO stretches, decreases to about 230 cm^{-1}, as observed in formate salts (*5*).

This note presents a transmission-infrared study of the adsorption of formic acid on NH_4–Y and ultrastable H–Y zeolites. The assignment of the bands is aided by comparison with the isotopically shifted spectrum of ^{13}C-enriched formic acid.

EXPERIMENTAL PROCEDURES

The preparation and characterization of the two zeolites have been given previously (*1*). The zeolites were outgassed and exposed to formic acid in an infrared sample cell described elsewhere (*6*) with procedures used previously (*1*). A thin layer of the zeolite (typically about 4 mg/cm^2) was deposited onto a horizontal CaF_2 window by sifting the zeolite through a 100-mesh sieve (0.15-mm openings). After outgassing, the zeolite layer adheres to the window and the cell may be rotated to a vertical position to be placed in an infrared beam.

The infrared spectra were measured at several submonolayer coverages of formic acid on the zeolites. No new features developed in the spectra as the coverage approached a monolayer, though there were slight changes in relative peak intensities. The spectra reported here are for a coverage of 0.3 monolayers, approximately the coverage used in the NMR study (*1*).

The transmission-infrared spectra were measured with a Perkin–Elmer Model 180 spectrometer, operated in the double-beam mode, with 2.1-cm^{-1} resolution in the range 2000 to 1000 cm^{-1}. Above 2000 cm^{-1} there were prohibitively large losses in transmittance due to scattering. Below 1000 cm^{-1} the spectrum was blacked out by the strong absorbance of the zeolite substrate.

RESULTS AND DISCUSSION

The infrared spectra for formic acid adsorbed on the NH_4–Y and ultrastable H–Y zeolites, shown in Figs. 1 and 2, respectively, were obtained by subtracting the appropriate background spectrum. In both figures, (a) is the unlabeled and (b) is the 91% ^{13}C-enriched formic acid. Substitution of ^{13}C for ^{12}C in neat formic acid shifts the C═O and C—O stretches by 41 and 9 cm^{-1}, respectively. The C–H bending mode at 1362 cm^{-1} decreases by 11 cm^{-1}. In both

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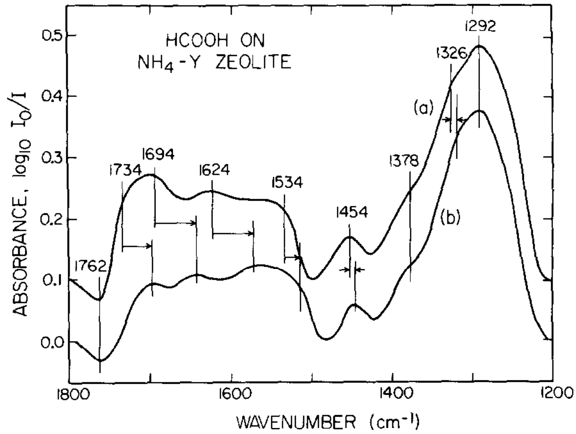

FIG. 1. Background-corrected infrared spectra of formic acid adsorbed on an NH_4-Y zeolite at 295 K; (a) $H^{12}COOH$ and (b) $H^{13}COOH$.

figures, most features in (a) have an isotopically shifted counterpart in (b). Moreover, these counterparts are shifted approximately 40 cm^{-1} in the range 1800 to 1600 cm^{-1} and approximately 10 cm^{-1} in the range 1450 to 1200 cm^{-1}. The proposed shiftings are indicated by arrows in each figure. The wavenumber markers are included only as references and are not to be taken literally as exact assignments.

The infrared spectrum of formic acid on the ultrastable zeolite (Fig. 2) contains distinct features which may be analyzed with respect to previous adsorption studies. The peaks at 1610 and 1385 cm^{-1} are within 10 cm^{-1} of a pair of peaks assigned to the C=O and C—O stretches of a formate species on Al_2O_3 (*7*). Also, the asymmetric and symmetric OCO stretches of aluminum formate are at 1613 and 1387 cm^{-1}, respectively (*5*). Thus, these peaks are assigned to a surface bidentate formate, probably adsorbed at an Al site. The sideband at 1718 cm^{-1} in Fig. 2 is assigned to a C=O stretch of a unidentate formate group. This is in agreement with peaks at 1714 and 1720

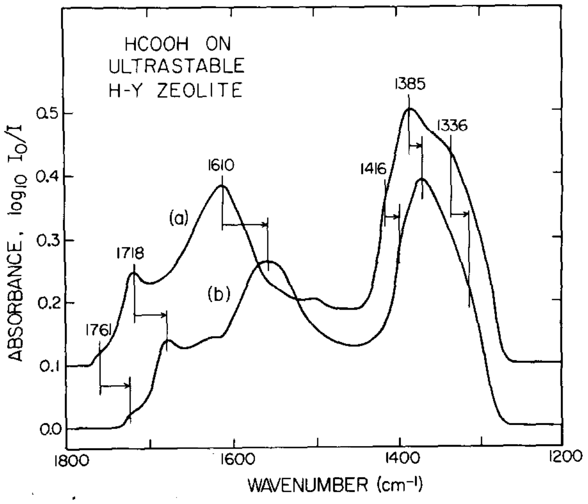

FIG. 2. Background-corrected infrared spectra of formic acid adsorbed on an ultrastable H–Y zeolite at 295 K; (a) $H^{12}COOH$ and (b) $H^{13}COOH$.

cm^{-1} for formic acid on SiO_2 (*8*) and a Na–Y zeolite (*9*). The C—O stretch of the unidentate is probably the sideband at 1336 cm^{-1}, which is the lowest feature observed above 1000 cm^{-1}. Previous studies have found this stretch as low as 960 cm^{-1} (*8*), or it was not observed at all (*9*). The broad sideband at 1416 cm^{-1} is assigned to the C–H bending mode of the bidentate group.

The infrared spectrum of the formic acid adsorbed on the NH_4–Y zeolite contains broad, overlapping features and it is impractical to make precise assignments to each. Qualitatively, the intensity in the region of the C═O stretch (1800 to 1500 cm^{-1})[1] has shifted to higher wavenumbers, relative to Fig. 2. The intensity in the region of the C—O stretch (1400 to 1200 cm^{-1}) has shifted to lower wavenumbers. This suggests that, compared to the ultrastable H–Y sample, the NH_4–Y contains an increased proportion of unidentate formate groups.

Thus, the infrared spectra indicate that the formic acid is adsorbed on the zeolites as unidentate and bidentate formate species. If one assumes that the infrared absorption coefficients for the C═O stretches of each species are equal, the approximate ratios of unidentate to bidentate species are 1 : 1 on the NH_4–Y and 1 : 4 on the ultrastable H–Y. These estimates agree with the quantitative results of the NMR study which found ratios of 1:1 for the NH_4–Y and 1:5 for the ultrastable H–Y (*1*).

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[1] The asymmetric OCO stretch in multivalent formate salts such as Sr, Bi, and Sb are in the range 1553–1541 cm^{-1} (*5*), which suggests that the feature at 1534 $cm^{-1}$is also an OCO stretch. The interpretation of the feature at 1454 cm^{-1} is not clear. A similar peak at 1468 cm^{-1} was observed by inelastic electron tunneling spectroscopy of formic acid Al_2O_3 (*10*).

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