

IR Extinction Coefficients as a Measure of Chemical Activation of Hydrocarbons via Polarization

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Introduction

When characterizing catalysts via probe molecule adsorption and IR spectroscopy, usually frequency shifts of vibrations of surface functional groups (e.g. OH) or of the probe molecule relative to its gaseous state are analyzed. In a series of papers [1–3], we have presented evidence that the intensity distribution of adsorbate vibrations can be used as an additional criterion to identify activated bonds. Intensities of IR bands are proportional to the change of the dipole moment during vibration and thus reflect the polarization and activation of a bond. Here, we move from considering relative intensities to the experimentally more demanding measurement of extinction coefficients of adsorbed species. Zeolites were selected as samples because they provide a high number of comparatively homogeneous sites.

Experimental

Zeolites with different framework structures (MOR, FAU) and various cations (H, Na, Mg and Ca) were investigated. IR spectra were recorded in diffuse reflectance or in transmission using Nicolet spectrometers. Small hydrocarbons were dosed into vacuum at 298–308 K onto pretreated samples. The transmission cell featured a calibrated volume allowing simultaneous measurement of spectra and the adsorbed amount.

Results and Discussion

The DRIFT spectra in Fig. 1 show the range of CH stretching vibrations for ethane adsorbed on a series of mordenite samples. The intensity pattern varies widely for the different cationic forms. These results indicate that, depending on the polarizing power of the cation in the zeolite, certain vibrations become more or less prominent in the spectra; implying that, vice versa, intensities can be exploited to reveal the polarizing power of a catalyst surface.

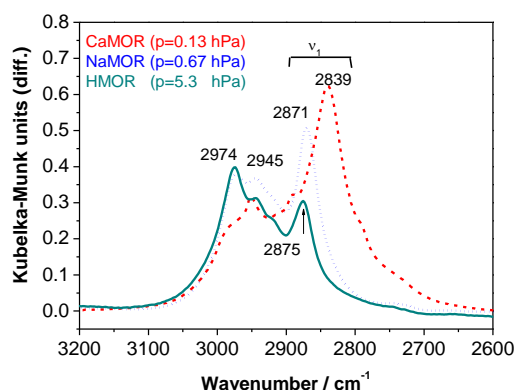


Fig. 1: Adsorption of ethane on different forms of mordenite.

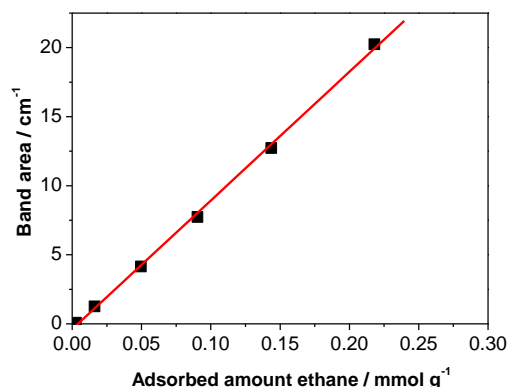


Fig. 2: Integrated intensity vs. adsorbed amount, ethane adsorbed on CaY.

For quantitative measurements, transmission IR spectroscopy was employed. Because concerns about the correctness of extinction coefficients obtained using self-supporting wafers of fine powders have been raised [4], a series of experiments was conducted to ensure the accuracy of the result. For low adsorbate coverages (< 0.2 mmol/g) integrated intensities were always perfectly proportional to the adsorbed amount (Fig. 2). However, as a general trend, the apparent integral molar extinction coefficients increased with the scattering power of the specimen. Scattering increased with increasing wafer thickness and was stronger for the mordenite samples used than for the faujasite-type materials. Hence, absolute intensities were evaluated for thin specimens of zeolite Y samples. The absolute intensities of CH-stretching vibrations of ethane adsorbed on zeolite Y increased in the following sequence for different cations: Na < Mg < Ca.

Conclusions

Absolute intensities of CH stretching vibrations are sensitive to the chemical activation arising from the polarization of the adsorbed molecules by the active sites and may be used as a new quantitative criterion for the perturbation upon adsorption.

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2. V.B. Kazansky, I.R. Subbotina, F.C. Jentoft, J. Catal. 240 (2006) 77.
3. V.B. Kazansky, I.R. Subbotina, F.C. Jentoft, R. Schlögl, J. Phys. Chem. B 110 (2006) 17468.
4. C. Morterra, G. Magnacca, V. Bolis, Catal. Today 70 (2001) 43.