



IR extinction coefficients of hydrocarbons adsorbed on zeolites as a measure of their chemical activation via polarization



I.R. Subbotina,¹ V.B. Kazansky,¹ J. Kröhnert,² F.C. Jentoft,² R. Schlögl²

¹ N.D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences,
Moscow, 117913, Russia

² Dept. of Inorg. Chem., Fritz Haber Institute, Max Planck Society, 14195 Berlin, Germany

Probing the properties of sites by adsorption is one of the most widely applied principles in the investigation of solid catalysts. Many techniques are employed to follow adsorption and desorption or to analyze the adsorbed state. The information gathered from IR spectra is almost exclusively based on band positions, i.e. shifts of vibrations of adsorbed molecules with respect to the free probe molecules in the gas phase, or the shifts of vibrations of surface functional groups (e.g. OH-groups) upon adsorption of the probe [1]. However, the intensity of IR bands is proportional to the change of the dipole moment during the vibration and may thus also reflect the polarization of a molecule through adsorption. Polarization is the beginning of a catalytic transformation and through identification of the affected vibrational modes, mechanistic detail is potentially accessible. In a novel approach we are trying to identify whether intensities of IR bands can be taken as a measure of the polarization and activation of adsorbed molecules. Zeolites have been selected as substrates because of the uniformity of their sites; *n*-butane and ethane were chosen as probe molecules.

Two types of experiments were conducted. Diffuse reflectance Fourier transform IR spectroscopy (DRIFTS) was applied for measurement of the *relative* intensities of bands of adsorbed species in order to distinguish the polarization of different vibrational modes. A Nicolet Impact 410 FTIR spectrometer with a self-made diffuse reflectance attachment and a quartz cell with CaF₂ window were used. Transmission IR experiments in combination with a calibrated volumetric system allowed simultaneous measurement of spectra and the adsorbed amount, so that *absolute* intensities could be analyzed and extinction coefficients could be determined. The experiments were performed with a Nicole Protégé 466 FTIR spectrometer and an all-metal vacuum system with KBr windows. Samples were activated by vacuum treatments at 773 K.

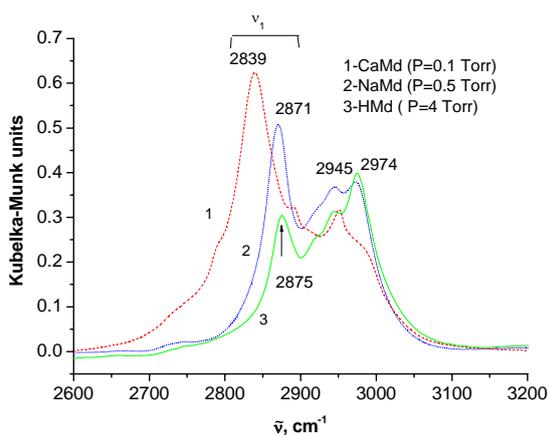


Figure 1: DRIFT spectra of ethane adsorbed on different forms of mordenite at 300 K.

intensity of the symmetric stretching band decreases in the order: bivalent metal cation > monovalent metal cation > proton.

The gas phase integrated Napierian extinction coefficients of ethane and butane in the CH-stretching region (ca. 3050–2750 cm^{-1}) were determined to be 162 and 302 km/mol ; these values are within 10% of those in the literature [2]. Adsorption of ethane on the Na- or H-forms of mordenite resulted in an increase of the extinction coefficient (determination, see Fig. 2) of the CH-stretching vibrations, as did the adsorption of butane on H-mordenite. An increase of up to a factor of 3.3 relative to the gas phase was observed, e.g. for the combination *n*-butane/H-mordenite. Preliminary results on a number of samples suggest that both the type of cation and the type of framework have an influence on the extinction coefficients of the adsorbed species.

Our results demonstrate the validity of this novel approach, i.e. intensities in IR spectra reflect, in a very sensitive way, the changes to a molecule upon its adsorption on a catalyst, and they can be used to discriminate the polarizing power of different surfaces.

REFERENCES

1. H. Knözinger in Handbook of Heterogeneous Catalysis, Eds. G. Ertl, H. Knözinger, J. Weitkamp, VCH 1997, Vol. 2, pp. 707-732.
2. M. Gussoni, C. Castiglioni, J. Molecular Structure, 521 (2000) 1-18.

DRIFT spectra of ethane adsorbed on H-mordenite and various cationic forms of mordenite show that the low frequency band from the ν_1 symmetric C-H stretching vibration is more sensitive to the nature of the cations than the bands from asymmetric stretching (Fig. 1). The high relative intensity of this band in comparison with the other C-H bands indicates a higher polarizability for the corresponding vibrational mode. The relative

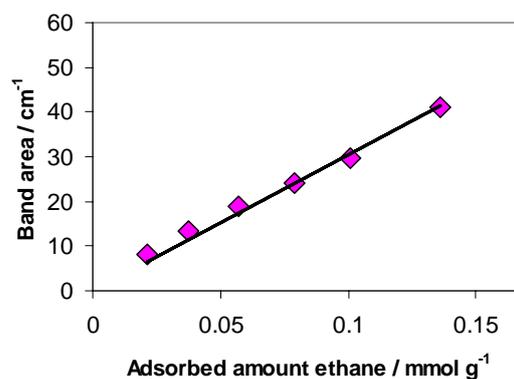


Figure 2: Band area in CH-stretching region vs. adsorbed amount. Adsorption of ethane on H-Mordenite at 313 K. Slope divided by wafer area weight gives extinction coefficient.