

## A Novel Method to Assess Activation on Surfaces

Friederike C. Jentoft,<sup>1,2\*</sup> Jutta Kröhnert,<sup>1</sup> Irina R. Subbotina,<sup>3</sup> and Vladimir B. Kazansky<sup>3</sup>

<sup>1</sup>Department of Inorganic Chemistry, Fritz Haber Institute, Max Planck Society,  
Faradayweg 4-6, 14195 Berlin, Germany

<sup>2</sup>School of Chemical, Biological and Materials Engineering, University of Oklahoma,  
100 East Boyd Street, Norman, OK, 73019, USA

<sup>3</sup>N.D. Zelinsky Institute, Russ. Academy of Sciences, Moscow, 117913, Russia  
\*fcjentoft@ou.edu

### Introduction

The activation of reactants through interaction with a catalyst surface can be monitored by spectroscopic methods. Usually energy shifts of spectroscopic transitions of either the catalyst or the adsorbate are considered to assess the strength of the interaction. Infrared spectroscopy is used extensively for this purpose, and the frequency shifts of vibrations, either of surface functional groups (e.g. OH) or of an adsorbed molecule relative to its gaseous state, are interpreted. Recently, we have presented evidence that additional information can be extracted from the intensity distribution of the C–H vibrations of hydrocarbons adsorbed on zeolites and other oxides [1–3]. Intensities of IR bands depend on the change of the dipole moment during vibration, and hence absorption coefficients reflect the polarization and activation of chemical bonds.

To exploit the information inherent to the vibrational intensities, it is necessary to develop the methodology to reliably determine absorption coefficients of adsorbate vibrations. An important question is the universal applicability of the concept of absorption coefficients as a measure of the chemical activation of bonds; thus the intensities of C–H and of C=C vibrations of adsorbates are investigated.

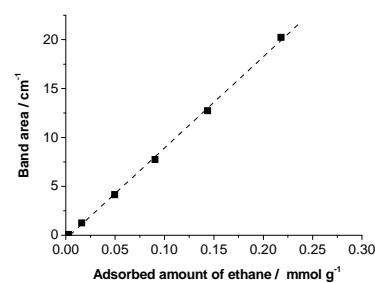
### Materials and Methods

Zeolites with different framework structures (MOR, FAU) and various cations (H, Na, Mg, Ca, Zn) were investigated. IR spectra were recorded in transmission with a Nicolet Protégé 460 or a PerkinElmer Spectrum 100 instrument. Small hydrocarbons were dosed into vacuum at 298–308 K onto pretreated samples. A new transmission cell featured a calibrated volume allowing simultaneous recording of spectra and the adsorbed amount, thus an improvement in comparison to separate collection of these data.

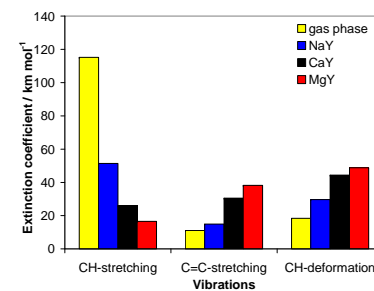
### Results and Discussion

To validate apparatus and measurement procedures, small alkanes and alkenes were adsorbed on a variety of zeolitic and zirconia materials. In general, wafers that scattered strongly because of their thickness or the particle size distribution of the powder were not suitable for the determination of absorption coefficients – falsely enhanced values were obtained. Consistent with the scattering theories, this problem concerned particularly the high wavenumber regions (O–H, C–H vibrations). The simplest solution proved to be the selection of samples with suitable particle morphology.

Ethane was adsorbed on Na<sup>+</sup>, Ca<sup>2+</sup> or Mg<sup>2+</sup> cations in Y zeolite; specific interaction was achieved through working at low pressures. More pronounced shifts of C–H bands towards lower frequencies indicated that the perturbation of the corresponding bonds in ethane upon adsorption by the bivalent Ca<sup>2+</sup> or Mg<sup>2+</sup> ions was much stronger than by the monovalent Na<sup>+</sup> ions. The intensity in the C–H stretching regime increased linearly with coverage (Fig. 1) and absorption coefficients could be calculated. The integral absorption coefficient of the C–H stretching bands of ethane adsorbed by Na<sup>+</sup> ions was only about 53 % of that of gas phase ethane. For adsorption on the bivalent Ca<sup>2+</sup> or Mg<sup>2+</sup> ions the coefficients exceeded those of the free ethane molecule, indicating strong polarization of the C–H bonds during the vibration. Bands representing the fully symmetric C–H stretching vibrations, which are IR inactive for free ethane, were perturbed most strongly upon adsorption.



**Figure 1.** Band area of C–H vibrations (3100–2500 cm<sup>-1</sup>) of ethane adsorbed on CaY at 308 K.



**Figure 2.** Adsorption-induced changes of absorption coefficients for individual vibrations of propene.

When propene was adsorbed on the same series of zeolites, the C=C stretching band shifted towards lower wavenumbers with increasing polarizing power of the cation (Na<sup>+</sup> < Ca<sup>2+</sup> < Mg<sup>2+</sup>). This shift however amounted to only a few wavenumbers. The frequency shift is a small effect in comparison to the variations in intensity that are observed for the C–H stretching and deformation bands and the C=C stretching bands upon interaction of propene with different cations (Fig. 2). The absorption coefficient of the C=C stretching band of propene interacting with Mg<sup>2+</sup> ions was 38 km mol<sup>-1</sup>, much higher than for the free molecule (11 km mol<sup>-1</sup>). The coefficients suggest a lower polarizing power of monovalent in comparison to bivalent cations.

### Significance

Intensities in infrared spectra of adsorbates indicate the chemical activation of bonds through surface sites; e.g. bivalent cations in zeolites strongly activate the C=C double bond in propene.

### References

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