

Intensities of IR Bands as a Criterion for the Activation of Adsorbed Hydrocarbons

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Analysis of adsorbate-surface complexes by IR spectroscopy is widely applied for characterization of heterogeneous catalysts. The choice of probe molecule is usually motivated by a supposition on the nature of the active sites. The information gathered from the spectrum consists of frequency shifts of vibrational bands of the probe itself and of surface functionalities upon formation of the adsorbate complex. This approach is not always successful, e.g. the results of adsorption of basic probes do not explain the excellent low-temperature skeletal isomerization capabilities of sulfated zirconia (SZ) materials [1]. Here, we follow a novel strategy. First, reactants of the target catalytic process are used to ensure that relevant sites are probed. Second, we establish relative and absolute intensities as an additional criterion for the identification of activated bonds.

For a systematic approach, zeolites with different frameworks (MOR, FAU) and various cations were investigated in addition to SZ samples. IR spectra were recorded in diffuse reflectance or in transmission using Nicolet spectrometers. Small hydrocarbons were dosed at 298–308 K onto pretreated samples in vacuum. The transmission cell featured a calibrated volume allowing simultaneous measurement of spectra and the adsorbed amount.

Adsorption of neopentane on SZ and H-MOR produced small shifts with respect to the gas phase vibrations. A band at 2820 cm^{-1} was detectable only for SZ materials, not for H-MOR. Integral molar extinction coefficients for the CH stretching vibrations were seemingly much higher for neopentane adsorbed on SZ than on H-MOR samples, but variation of particle size and wafer thickness showed that increasing extinction coefficients were correlated to increasing scattering by the wafer. A first conclusion is that extinction coefficients derived from transmission spectra of wafers may be incorrect in case of strong scattering.

Adsorption of propene was thus studied on a series of zeolite-Y samples, which scatter only weakly in the range of $< 2000\text{ cm}^{-1}$, and similar extinction coefficients were obtained for different wafers. A number of trends were observed in the relative and absolute intensities. With increasing polarizing power of the cation ($\text{Na} < \text{Mg} < \text{Ca} < \text{Zn}$) the C=C stretching band shifted towards lower wavenumbers. Furthermore, the intensity of the =CH stretching bands decreased relative to that of the C=C band. According to our hypothesis [2], these data indicate activation of the C=C bond, with zinc ions exerting the strongest polarization. Indeed, polymerization of propene was observed on ZnY at room temperature, evidencing that IR intensities provide a sensitive criterion for the identification of activated bonds.

[1] V. Adeeva, J.W. de Haan, J. Jänchen, G.D. Lei, V. Schünemann, L.J.M. van de Ven, W.M.H. Sachtler, R.A. van Santen, *J. Catal.* 151 (1995) 364.

[2] V.B. Kazansky, I.R. Subbotina, F.C. Jentoft, *J. Catal.* 240 (2006) 77.