

Low temperature FTIR spectroscopy in the studies of surface phenomena

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The paper deals with the advances in the application of IR spectroscopy for the studies of adsorption, mechanism of lateral interaction between the adsorbed molecules and linkage isomerism in the adsorbed state.

Spectroscopy at low and variable temperatures enable us to broaden the number of test molecules for surface sites and instead of ammonia, pyridine and nitriles, to use simple molecules that do not adsorb at 300 K, such as CO, NO, H₂ to characterize acidic (electron-accepting) sites, while for basic (electron-donating) centers low-temperature adsorption of weak CH proton-donors like CHF₃ can be used. Quantitative measurements reveal a correlation between the frequency shifts and absorption coefficients of adsorbed molecules.

The strength of surface sites is affected by lateral interactions between the adsorbed species, which can be repulsive or attractive. Static interaction changes the energies of adsorption and shifts the bands of test molecules. Dynamic interaction accounts for the changes in the bandshape and half-width and for splitting of the bands. It manifests itself even in the spectra of symmetric molecules weakly adsorbed on zeolites or amorphous adsorbents.

Some molecules, such as CO, reveal linkage isomerism and form with the cations in Y or ZSM-5 zeolites, besides the usual C-bonded species, the energetically unfavorable O-bonded complexes. Besides the frequencies, different geometry of isomeric species leads to dissimilarity in the isotopic shifts on ¹³C or ¹⁸O substitution. The linkage isomerism can be explained by electrostatic model, which also accounts for the absence of this phenomenon for oxides or X-zeolites, where formation of side-on complexes with surface anions or interaction with dual cationic sites is preferable. According to the model, isomerism is possible for halogenides or layered aluminosilicates where negative charge of anions is lower or is delocalized over the polyanionic layers, that was recently confirmed by variable temperature FTIR measurements. Surface isomeric states were established for some other adsorbed species, such as cyanide ion CN⁻ produced by HCN dissociation.