Adsorption de l'isobutanol dans les zeolithes : apport des analyses multivariées

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Abstract

Classical quantitative analytical methods for the characterization of adsorbents such as gravimetric analysis or calorimetry yield enthalpy values averaged over the various adsorption sites. In this study, in situ IR spectroscopy combined with multivariate analysis has been used to identify and quantitatively characterize alcohol adsorption on zeolites. The method of multivariate curve resolution by alternating least squares – (MCR-ALS), used for the first time in the field of adsorption, enabled us to recover pure response profiles: spectral profiles, allowing the identification of distinct species, and their corresponding adsorption isotherms, allowing the evaluation of adsorption parameters by curve fitting a local isotherm such as the Langmuir isotherm or implementing the isotherm as a hard constraint. Isobutanol adsorption on acid zeolites (MFI and FER), silica and silicalite was studied by infrared spectroscopy, coupled or not to gravimetric measurements, then analyzed by multivariate analysis methods to distinguish adsorption on the different zeolite sites, and obtain their thermodynamic parameters. We began with a quantitative study to determine the molar absorption coefficients of pyridine, isobutanol and hydroxyls on an MFI zeolite, in order to quantify the quantities adsorbed on this zeolite, and to demonstrate the usefulness of multivariate analysis in refining this type of study. The MCR-ALS methodology was then developed and applied to the adsorption of isobutanol on a calcined MFI zeolite, with the aim of determining the adsorption enthalpies and entropies specific to each adsorbed species. Three adsorption modes were distinguished for this system: adsorption of isobutanol on the external surface (Silanols), on the extra-lattice aluminums known as EF-AlOH, and on the micropores (bridged hydroxyls) of the zeolite. The study was extended to the previous MFI steam-treated at moderate temperature (773 K) and two ferrierites with different crystal sizes. For the steamed MFI, the methodology revealed the presence of a fourth species corresponding to a different type of Silanols (referred to as strong Silanols in this study), appearing with steaming. It was also found that steam treatment increased the enthalpy values the acid sites of the MFI. The application of FTIR-MCRALS methodology to iBuOH/FER systems shows that adsorption takes place mainly on the external surface and has identified the contribution of two types of silanols