DFT approach for the calculation of NMR and IR spectral parameters of olefins on Zn-modified zeolites

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Zn-modified zeolites have demonstrated their promising properties for converting light C_2–C_4 olefins to methyl-substituted benzenes [1-4]. For further advances in developing effective catalysts based on Zn-zeolites, reliable information is needed concerning the mechanisms of olefin transformations. Such research can be performed with the aid of solid-state NMR and FTIR spectroscopy. However, the interpretation of the spectra is a very challenging task since the detected chemical shifts (^{13}C) and wavenumbers for detected intermediates and the products are affected by the interaction of hydrocarbon molecules and zeolite active sites. The application of DFT, which could provide the spectral parameters and stabilization energies, can be helpful to solve the problem of ^{13}C NMR signal and IR band assignment. The keystone is the methodology for this type of calculations concerning its application to the adsorbed hydrocarbon species.

Here, we report an approach for calculating ^{13}C chemical shift and wavenumber values examined for a variety of olefinic species adsorbed on Zn-modified BEA and ZSM-5 zeolites. It has been inferred that the reliable result is achieved by using the following steps: zeolite framework optimization with periodic DFT (pPBE), cluster geometry optimization with hybrid GGA (PBE0), and calculation of NMR and IR parameters. TPSS/cc-pVTZ method has been found to provide the best computational cost/accuracy ratio. The advantage of the linear regression method for converting the calculated chemical shielding constant to the chemical shift has been demonstrated.

Additionally, the linear correlation between the adsorption energy of C_2–C_4 olefins on Zn^{2+} sites of the zeolites and the spectral parameters has been revealed. The higher the adsorption energy the larger the red-shift of the $\nu_{C=C}$ band and the lower the downfield shift of the ^{13}C NMR signal for a C-2 atom. This finding provides the basis for a new method of measuring hydrocarbon adsorption energy using spectroscopic techniques.

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