Selective Adsorptive Desulfurization of Liquid Fuels over Cu(I)Y, Ni(II)Y, and Ce(IV)Y Zeolites

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Increasing concerns on air pollution have led many countries to adopt more stringent regulations which impose an ultra-low concentration of sulfur in liquid fuels. In this study, deep-desulfurization (sulfur levels of <1 µg/g) tests were performed by ion exchanging faujasite type zeolites with Cu\textsuperscript{+}, Ni\textsuperscript{2+} or Ce\textsuperscript{3+} cations using liquid phase ion exchange (LPIE) method. The selective adsorption capacities of sulfur-containing compounds on the ion-exchanged Y zeolites with different cations and the possible effect of olefins and aromatics on the adsorption of the organosulfur compounds are investigated by using fixed-bed adsorption, FT-IR, UV-DRS and the Density functional theory (DFT) molecular simulation techniques. The fuels tested for desulfurization include commerical and model fuels. In addition, the treated and untreated fuels comprising the major refractory sulfur compounds were fully characterized by using the latest generation of SCD detectors in our laboratory, which are capable of distinguishing different sulfides.

The desulfurization performance of the sorbents studied decreases as follows: Cu(I)Y > Ni(II)Y > Ce(IV)Y. The adsorption capacities of each sulfur compounds on the zeolites are different but present a similar trend that benzo thiophenes possess higher sulfur adsorption capacities than thiophene and that the refractory sulfur compounds with substituents have higher sulfur adsorption capacities than those without substituents except 4,6-dimethyl dibenzothiophene (4,6-DMDBT), which agrees well with the DFT calculation results. It has been found that the effect of olefins on desulfurization of the sorbents decreases in the order of diolefins > cyclenes > linear-monenes for all the sorbents. The studies of FT-IR and UV-DRS spectra, as well as the DFT calculations, show that the interactions between the sorbate compounds and the sorbents increase in the order of aromatics < sulfur compounds < olefins. The influence of aromatics and olefins on the desulfurization is, however, different for different sorbents. For the Cu(I)Y zeolite, the effect of aromatics on desulfurization overweighs that of olefins, while for the Ce(IV)Y zeolite, opposed results were found, implying that the competitive adsorption mechanisms of the sorbate compounds are different on the zeolites containing different metal cations. These findings can be ascribed to the interplay of both adsorption and diffusion processes occurring in the systems.

References