Multinuclear solid-state NMR studies of the interactions involved in the $CHClF_2$ adsorption over basic faujasite-type zeolites

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A valid approach to characterize zeolite basicity is the use of weakly-acid probe molecules as adsorbates,[1] which form hydrogen bonds with the framework oxygen atoms. The position of the infrared frequencies and ^{1}H NMR chemical shift correlate with the mean zeolite basicity. However, the existence of additional interactions, even for the molecules of most extended use such as pyrrole and chloroform[2], limits their application as probes of basic sites. We have investigated chlorodiflouromethane ($CHClF_2$) as a probe of zeolites basicity by using infrared and multinuclear NMR spectroscopies, and a series of alkali-exchanged FAU-type with different Si/Al ratio (X and Y) and alkaline cations.

The results obtained show that the CH stretching frequency of adsorbed $CHClF_2$ poorly correlates with the zeolite basicity, what is attributed to the simultaneous electrostatic interaction of the fluorine atom with the alkaline cation. This extra interaction, which has been made clear in other halocarbon-zeolite systems by alkali (^{7}Li, ^{23}Na, ^{133}Cs) NMR,[2] is evidenced by ^{19}F NMR chemical shift (Figure 1A), and by spin-spin coupling constants, a parameter sensitive to the magnitude of the fluorine-cation interactions. Meanwhile, ^{1}H NMR chemical shift of adsorbed $CHClF_2$ appears to be a valid estimation of the mean zeolite basicity (Figure 1B), and therefore both interactions, can be independently estimated by NMR.

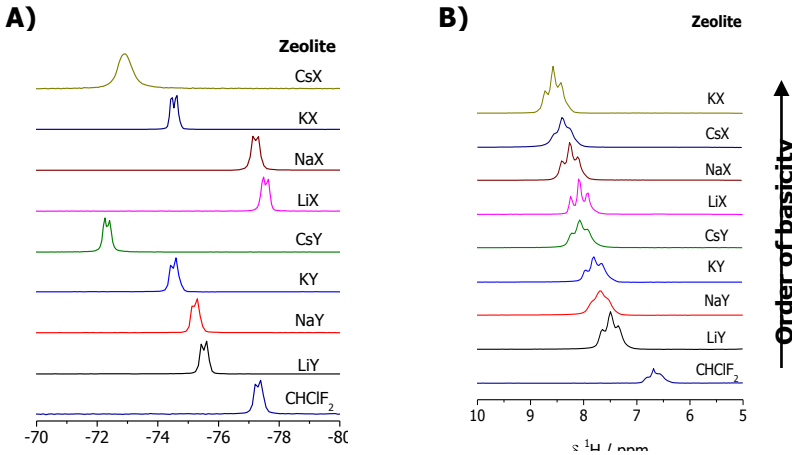

Figure 1. A) ^{19}F and B) ^{1}H chemical shift of $CHClF_2$ adsorbed over the indicated zeolites.

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