$^{19}F/^{23}Na$ Cross polarization NMR study of hydrofluorocarbon–zeolite binding on zeolite NaY

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$^{19}F/^{23}Na$ Cross polarization (CP) MAS NMR experiments of various asymmetric hydrofluorocarbons (HFCs) such as CF_3CFH_2 (HFC-134a) and CF_2HCFH_2 (HFC-143) adsorbed on zeolite NaY, demonstrate that the hydrogen-containing groups are bound more strongly to the zeolite framework, in the order $CF_3 << CF_2H < CFH_2$; the results help explain the preferential binding of CF_2HCF_2H (HFC-134) over HFC-134a, and hence the effectiveness of basic zeolites in the separation of HFC-134/134a gas mixtures.

The complete phase-out of chlorofluorocarbon (CFC) production in developed countries by the year 2000 has resulted in the development and production of a variety of environmentally-friendly alternatives (the HFCs) for different applications.[1] The syntheses of the HFCs are more complex than the syntheses of the CFCs and unwanted HFC and hydrochlorofluorocarbon isomers are often produced. For example, HFC-134 is a common byproduct in the synthesis of HFC-134a, the replacement for the refrigerant CFC-12 (CF_2Cl_2).[1] Basic molecular sieves have been proposed as a method for separating some of these isomer mixtures.[2] We have, therefore, been applying a variety of NMR and X-ray powder diffraction methods to determine the importance of different interactions in controlling the sorption properties of these gases on faujasite zeolites, and to rationalize trends in separations behavior and HFC reactivity.[3,4] Our previous work on the binding of HFC-134 on zeolite NaY demonstrated that Na–F interactions are very important in these systems, and are strong enough to cause migration of cations from the sodalite cages into the supercage where they can bind to both ends of the HFC molecule.[4]

The efficiency of ^{19}F magnetization transfer in a $^{19}F–^{23}Na$ CP experiment, from the different ends of the HFC molecule to the sodium cations present in the supercages of the zeolite, has been explored in research described here. The CP efficiency is very sensitive to the offset-frequency of the ^{19}F radio frequency (rf) field: as the offset frequency (Δv) of the rf field (v_1) is increased, the polarization transfer rate is decreased by a factor $v_1^2/(v_1^2 + \Delta v^2)$.[5] Thus, if the CP experiment is performed with low rf power, the effect of offset-frequency on the transfer rate will be significant. Since the ^{19}F NMR spectra of the asymmetric HFCs show well separated resonances for the different $CF_{3-n}H_n$ groups (for example, the chemical shifts for the CF_3 and CFH_2 groups of HFC-134a are -81 and -246 ppm, respectively), it is possible to study the CP dynamics of the end-groups separately.

Methods used to prepare the samples are identical to those described elsewhere[4] and the samples are labeled xHFC/NaY, where x indicates the number of HFC molecules per unit cell. The ^{23}Na MAS NMR spectrum of the fully loaded HFC134a/NaY sample ($x \approx 44$–48) at -150 °C is shown in Fig. 1(a). The narrow resonance at -7 ppm is assigned to the site I cations of the faujasite structure (in the double six-rings), and the broader resonance centered at -40 ppm contains overlapping resonances from sodium nuclei originally in the site II and I′ positions, in the super and sodalite cages respectively.[4] The narrowing of this resonance, in comparison to that of bare NaY, suggests that some cation migration from site I′ to sites in the supercages may also be occurring on adsorption of HFC-134a.

Variable-temperature ^{19}F MAS NMR was initially performed to confirm that the isotropic motion of the HFCs was frozen out at -150 °C. Rf field strengths of 10–20 and 20–40 kHz were used for ^{23}Na and ^{19}F, respectively, in order to match the Hartmann–Hahn condition for quadrupolar nuclei with non-zero quadrupole coupling constants[5,6] and low rf field strengths and fast spinning speeds were used to help ensure effective ^{23}Na spin-locking.[7]

Fig. 1(b) and (c) show the $^{19}F \rightarrow ^{23}Na$ CP MAS spectra of the fully-loaded HFC134a/NaY at -150 °C, where the ^{19}F irradiation frequency is placed on the ^{19}F CFH_2 and CF_3 group resonances, respectively. Only one broad ^{23}Na resonance at approximately -40 ppm is observed and the site I resonance is absent, indicating that polarization is only transferred to cations in close proximity to the HFCs. Surprisingly, the CP intensity from the CFH_2 group is much higher than that from the CF_3 group which contains more fluorine spins. In order to investigate this behavior more fully, CP experiments were performed as a function of fluorine irradiation offset: A dramatic decrease in ^{23}Na CP intensity for 32HFC-134a/NaY was observed, as the fluorine irradiation offset Δv_1 is changed from on-resonance for the CFH_2 group (-58 kHz) to on-
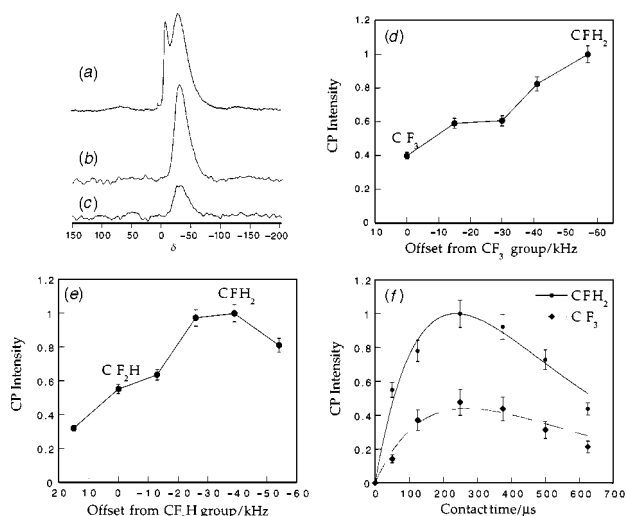

Fig. 1 (a) The ^{23}Na MAS NMR spectra of fully-loaded HFC-134a/NaY at -150 °C. Spinning speeds of 10 kHz were used; (b) and (c): The $^{19}F \rightarrow ^{23}Na$ CP MAS spectra of fully-loaded HFC-134a/NaY at -150 °C. The ^{19}F frequency was placed on resonance for the CFH_2 resonance and CF_3 resonance in (b) and (c), respectively. Spinning speeds of 9.5 kHz, a 400 μs CP contact time (ct) and an ^{19}F rf field strength, v_1, of 40 kHz were used, and 1640 FIDs were recorded for each spectrum. $^{19}F \rightarrow ^{23}Na$ CP intensity as a function of fluorine irradiation offset of (d) 32HFC-134a/NaY at -150 °C (spinning speed = 9 kHz; ct = 333 μs; v_1, = 40 kHz) and (e) 32HFC-143/NaY at -150 °C (spinning speed = 8 kHz; ct = 250 μs; v_1 = 20 kHz). (f) 32HFC-134a/NaY at -150 °C, as a function of contact time (v_1 = 20 kHz). The two curves drawn in (f) were obtained with equations for CP intensity given in refs. 11 and 13 (see text). Spectra were acquired with a double-tuned Chemagnetics probe, on a CMX-360 spectrometer with resonance frequencies for ^{19}F and ^{23}Na of 338.7 MHz and 95.2 MHz, respectively. The ^{23}Na chemical shifts reported were referenced to solid NaCl at 0.0 ppm.

resonance for the CF$_3$ group (0 kHz) [Fig. 1(*d*)]. The same experiment was performed for 32HFC-143/NaY and the CP intensity for on-resonance irradiation of the CFH$_2$ group was higher than that for the CF$_2$H group [Fig. (*e*)].

The ^{19}F→^{23}Na CP intensity was studied as a function of the contact time for both samples and the CP curve for HFC-134a is shown in Fig 1(*f*). In order to fit these curves, $T_{1\rho}$ values for the ^{23}Na spins and the ^{19}F in the different groups were all independently measured. The ^{19}F $T_{1\rho}$s (150–300 μs) were much shorter than those for ^{23}Na (*ca.* 600 μs) and are responsible for the relatively rapid decrease in CP intensity for contact times of greater than *ca.* 250 μs. Fits to these curves using the measured $T_{1\rho}$s, using modified versions of expressions given in refs. 5 and 6, demonstrate that the polarization transfer rates ($1/T_{IS}$) are considerably larger for the more hydrogenated groups. For example, using the $T_{1\rho}$ values of 230 ± 5 and 205 ± 5 μs obtained for the CFH$_2$ and CF$_3$ and groups of HFC-134a, values of T_{IS} of 480 ± 20 and 1000 ± 50 μs were obtained assuming that each end group is close to only one sodium cation.

Partial charges for the hydrofluorocarbons, calculated with Hartree–Fock methods, are slightly higher for the CFH$_2$ fluorine in comparison to those found on the CF$_3$ fluorine atoms of HFC-134a,[8] which should result in an increased Na–F electrostatic interaction. Inelastic neutron scattering and Raman spectroscopy studies of HFC-134 and HFC-134a molecules adsorbed on zeolite NaX have shown that hydrogen bonding to the framework oxygen may also be important.[9] Our ^{1}H MAS NMR studies of HFC-143 (CFH$_2$CF$_2$H) and HFC-134a (CF$_3$CFH$_2$) adsorbed on NaY are consistent with this: the ^{1}H NMR resonance is shifted to higher frequency by 2 ppm on lowering the temperature to −150 °C, suggesting that the hydrogen-containing groups are hydrogen-bonded to the framework oxygens of the zeolite. These results imply that the hydrogen-bonding plays an important role in the binding of the asymmetric HFC molecules. Thus we propose that it is the combination of this hydrogen bonding, and the strong Na–F interaction, that tethers the CFH$_2$ group tightly to the framework at −150 °C, resulting in efficient fluorine-to-sodium magnetization transfer. The CFH$_2$ group is more strongly bound than the CF$_2$H group of HFC-143: again this may be a consequence of the higher partial charge for the CFH$_2$ group and the potential for more hydrogen bonding.

In conclusion, the double resonance experiments clearly show very different binding for the different end groups of asymmetric HFCs, and demonstrate that the hydrogen-containing groups are bound more strongly to the zeolite framework. The results are consistent with the higher heat of adsorption of CF$_2$HCF$_2$H (HFC-134) over HFC-134a,[2] the former containing two hydrogen-containing groups. These findings help provide a fundamental understanding of the role of basic zeolites in the separation of HFC-134/134a gas mixtures. Finally, the NMR results suggest new methods for probing interactions and gas binding in systems involving larger molecules with multiple gas–surface interactions. In these systems, while methods such as calorimetry and adsorption isotherm measurements will provide measures of the average heat of adsorption of the molecule, experiments sensitive to local structure and interactions will be extremely useful in helping to deconvolute the relative importance of the different, sometimes competing, interactions. The CP technique will be particularly applicable when one or more NMR nucleus has a large chemical shift range.

Notes and References

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