LETTER TO THE EDITOR

Reply to the Comments of Dan Fărcaşiu in "Solid Acids and Acids in Solution: The Reversible Transfer of Hydrons to Carbonyl Groups"

The recent note by Dan Fărcaşiu (1) on protonation of ketones and aldehydes in solid acids and acid solutions, in which the interpretation of our ^{13}C NMR and microcalorimetry results in zeolites is questioned, prompts us to respond. Three issues require clarification.

(1) The NMR spectra of adsorbed aldehydes and ketones, at coverages below one/site and room temperature, correspond to the hydrogen-bonded complex.

Fărcaşiu's statement regarding our "novel interpretation rejecting reversible hydrogen transfer" and his quotation from our work "that 'there is no equilibrium between ... species in H–ZSM-5'" seem to suggest that we question the principle of microscopic reversibility and well-established reaction schemes which include ionic species along the reaction coordinate. Fărcaşiu's statements take our work out of context and fail to point out that our statements referred to descriptions of spectroscopically observable, 1:1, stoichiometric adsorption complexes (2–4). Characterization of these complexes requires working with surface coverages corresponding to less than one molecule per Brønsted site, at room temperature and below. Under these conditions, the proton-decoupled, ^{13}C NMR spectrum of 2-^{13}C-2-propanone gives the chemical shielding tensor of a *single localized species*, similar to that of the pure solid, with a spin count that agrees within experimental error to the known coverage (2). It is not possible to observe an equilibrium between a protonated and a nonprotonated species under these conditions within the sensitivity, resolution, and timescale of the NMR experiment. The adsorption complex is obviously in equilibrium with its environment, but that equilibrium strongly favors the hydrogen bonded species with regard to proton transfer.

Interpretations which describe NMR spectra of the 1:1 adsorption complex for acetone and other carbonyl-containing molecules in H–ZSM-5 as being the result of some chemical equilibrium process cannot explain our results. If indeed two observable species undergoing rapid isotropic proton exchange (equilibrium) were present, then one would observe Lorentzian line shapes whose maxima correspond to the weighted average of their isotropic shifts (5). Both the line shape and the position of the maxima would be temperature dependent. If two species were present but the transition frequency between them were slow on the NMR timescale (the rigid lattice regime), one would observe two overlapping chemical shielding tensors characteristic of each species. The integrated intensities of each tensor would correspond to the concentrations of a "frozen-in" equilibrium. Finally, if the NMR line shape resulted from anisotropic molecular reorientations, due to a restricted rotation on proton exchange, there would be measurable changes in the powder line shape as a function of temperature. The experimental line shape corresponds to none of these three cases (2–4). As stated earlier, the principal elements and trace for the ^{13}C chemical shielding tensor correspond to a single species, best described as hydrogen bonded.

The relationship between the hydrogen-bonded ($>$C=O$\cdots$H–A, species 3 of Fărcaşiu) and the protonated complex ($>$C$^+$–O–H$\cdots$$^-$A, species 4) can be understood with the help of theoretical, *ab initio* calculations for acetone and other weak bases (6–8). With acetone, for example, calculation of the potential energy surface as a function of the acid proton coordinates (i.e., the distance of separation between the acid proton and the oxygen atom of the acetone) shows that there are, indeed, at least two energy minima, as shown in Fig. 1. However, the energy difference between the hydrogen-bonded species (Fig. 1, left) and the protonated addition compound (Fig. 1, right) is simply too large to observe its presence in equilibrium at room temperature or below, regardless of the nature of the dynamics associated with the exchange. The energy difference to an *uncoordinated*, protonated species, such as indicated by species 4 or 2 in Eq. [1] of Ref. (1), would be much higher.

To summarize, the choice of experimental conditions in our NMR studies (low coverages and relatively low temperatures) leads to a nearly rigid, highly localized species at the Brønsted sites. The dynamics about which Fărcaşiu (1) speculates are not observable in our measurements.
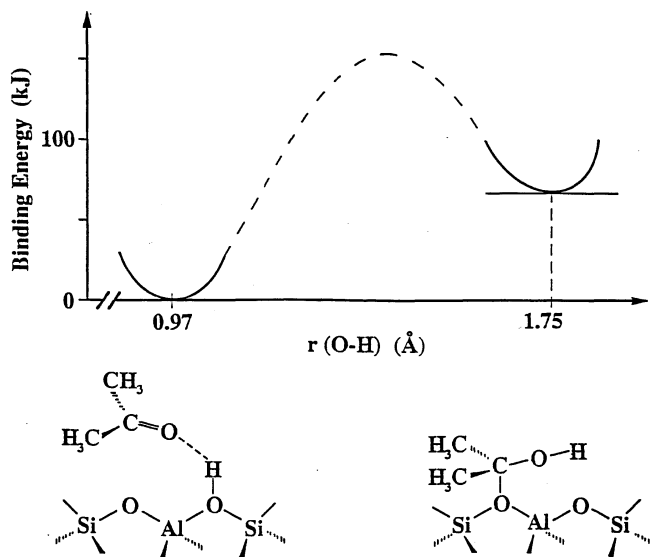
FIG. 1. Schematic of ground state potential energy as a function of proton coordinate.

(2) Inferring acid strengths in zeolites based on solution reference conditions is untenable.

The statement by Fǎrcaşiu that we indicate "hydronated [*sic*] species do not intervene even in ion pairs, as unstable intermediates of enolization" is a distortion of what we have written. As stated above, we did not include charged species in our reaction diagrams because we have found that they are not spectroscopically observable at room temperature or below. We do not question the existence of charged species along the reaction coordinate or that long-established, carbocation mechanisms are involved in organic reactions on zeolites, as our earlier publications clearly show (10, 11). In the same way, we do not question the fact that Fǎrcaşiu believes hydrogen-bonded complexes are sometimes important intermediates, even though he often does not include them in his reaction schemes (9). However, the energetics of protonation and the relative stability of carbocations are *very* different in the zeolite compared to acid solutions (11–13). One cannot use solution-phase acidity scales and the ability of the zeolite to protonate a particular base, including corrugated ketones like methyl oxide to infer anything about the ability of the zeolite to protonate another base (13).

Activation barriers in the zeolite will also differ from that in solution phase. For example, the barrier that separates the hydrogen-bonded complex ($>C=O \cdots H-A$) and the protonated complex ($>C^+-O-H \cdots {}^-A$) in the zeolite will not be the same as that in solution phase. One should even expect that a reaction which can proceed along two parallel reaction pathways could have very different selectivities in solution phase and in the zeolite because of these differences in energies. We believe that these differences

represent severe limitations to the use of acidity scales referenced to pK_a or H_0 for predicting the reaction chemistry of solid acids.

(3) The stability and structure of adsorption complexes result from both proton transfer and local bonding interactions.

Finally, Fǎrcaşiu states that there is an inconsistency between the idea that binding energies of bases in H–ZSM-5 correlate with gas-phase proton affinities and the suggestion that some bases may be bound as neutral complexes while others may be bound as ion pairs. In particular, he points out that water and ammonia exist as ion pairs, while acetone, which has a proton affinity intermediate between water and ammonia, exists as a neutral hydrogen-bound complex. There are two problems with his argument: (1) Unless one works with high water loadings (14), it appears that water is hydrogen bonded to the site and does not exist as an ion pair at a coverage of one/site (15–18); therefore, there is probably no inconsistency. (2) More important, one should only expect correlations with gas-phase acidity to be true within a structurally similar series of bases, as has been observed in solution (19). The specific interactions with the zeolite framework for different classes of bases will complicate the comparison of molecules with different functional groups, as we have discussed in detail elsewhere (13).

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