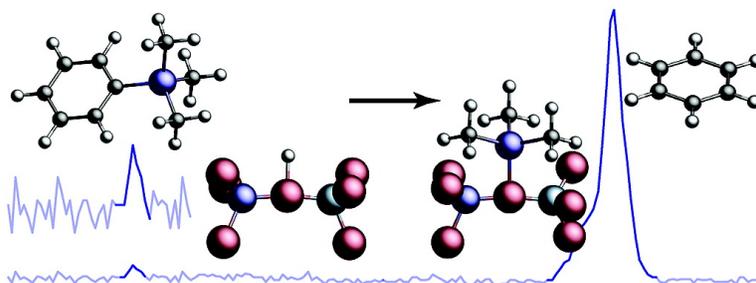Communication

Trimethylsilylation of Framework Brønsted Acid Sites in Microporous Zeolites and Silico-Aluminophosphates

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Trimethylsilylation of Framework Brønsted Acid Sites in Microporous Zeolites and Silico-Aluminophosphates

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The framework Brønsted acid site in many solid acid catalysts consists of hydrogen covalently bonded to an oxygen-bridging aluminum and silicon in the microporous framework, as shown in **1**.[1] This local structure is found in both aluminosilicate zeolites such as H-Beta (*BEA topology) or HZSM-5 (MFI) and silico-aluminophosphates such as HSAPO-5 (AFI).[2] Some of the more frequently studied intermediates in zeolite chemistry are framework-bound alkoxy (alkoxonium) species in which the proton in **1** is replaced by a hydrocarbenium group. For example, in 1989 one of us reported ^{13}C NMR evidence that the framework-bound isopropoxy species **2** formed on acidic zeolites during the low-temperature (i.e., $\leq$298 K) oligomerization of propene.[3] Theoretical modeling has shown that **2** forms through a concerted reaction in which the proton transfers from one oxygen on the zeolite to C_1 of propene as C_2 bonds to an adjacent oxygen.[4,5]
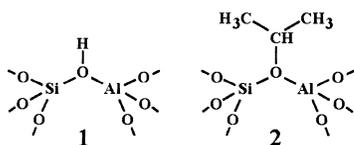
But framework alkoxy intermediates have not been detected in other catalytic reactions for which their formation seems reasonable. For example, the high-temperature reaction of cumene (isopropylbenzene) on zeolite H-Beta produces propene and benzene,[6,7] but no evidence of **2**, and the analogous reaction of *tert*-butylbenzene on that zeolite at 648 K yields stoichiometric amounts of olefins, primarily isobutene, and benzene (Figure 1a). Of course, these reactions take place at much higher temperatures than that used to observe **2**, and it may simply be that while alkoxy species do form in the de-alkylation of cumene or *tert*-butylbenzene, they rapidly desorb as olefins.

One of the more striking differences between Si and C is the difference in the strengths of their bonds to oxygen. Thus, a standard C−O bond has a dissociation energy of only 358 kJ/mol, but breaking a Si−O bond requires 452 kJ/mol.[8] Yet, a Si−C bond is weaker than a C−C bond by 28 kJ/mol. We exploited these differences in bond energies to realize the reaction in Scheme 1 and form a zeolite framework-bound siloxy species[9] on both zeolite H-Beta and HSAPO-5.[10] When we pulsed phenyltrimethylsilane onto catalyst beds of either material at 648 K, **3** formed stoichiometrically, and benzene was the only volatile product until repeated pulses of phenyltrimethylsilane exactly titrated the expected number of acid sites, at which point starting material also appeared in the product stream (Figure 1b−d). Co-injection of phenyltrimethylsilane and either water or methanol instead yielded benzene and trimethylsilanol as volatile products. Furthermore, when benzyltrimethylsilane was pulsed onto HSAPO-5 at 648 K, the volatile product
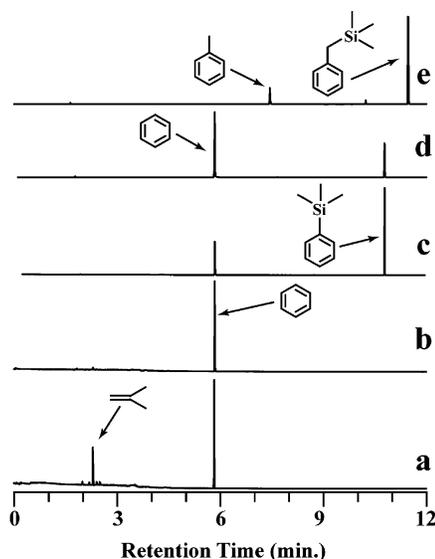

Figure 1. GC−MS total ion chromatograms characterizing the volatile products exiting catalytic reactors (300 mg fresh catalyst in every case) operated at 648 K 3.6 s after pulsing 0.03 mmol of reagent. (a) *tert*-Butylbenzene on H-Beta showing that both benzene and isobutene exit the catalyst. (b) Following the first shot of phenyltrimethylsilane only benzene exits H-Beta, suggesting the formation of stable **3**. (c) Following the fourth shot of phenyltrimethylsilane onto the same bed of H-Beta, showing the approach of the endpoint in the titration of acid sites. (d) A first shot of phenyltrimethylsilane onto HSAPO-5 confirms the lower acid site density for this catalyst sample. (e) A first shot of benzyltrimethylsilane onto HSAPO-5 shows the expected volatile product, toluene, but lower reactivity than seen with the phenyl derivative.

Scheme 1
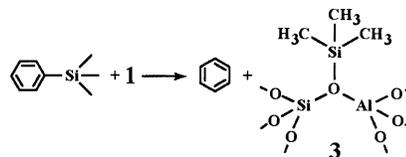
was toluene (Figure 1e), although in this case the reaction did not go as far to completion as with the phenyl derivative (cf. Figure 1d).

The magic-angle spinning solid-state NMR spectra[11] in Figure 2 support the identification of species **3**. Zeolite H-Beta samples were pulsed with phenyltrimethylsilane at 648 K, and then 4 s later the reactor temperature was very rapidly reduced (pulse−quench experiment).[12] The entire contents of catalytic reactors were then transferred in a glovebox to MAS NMR sample rotors, and both [29]Si and ^{13}C spectra were acquired at room temperature. The [29]Si MAS spectrum in Figure 2a shows the expected signals near −110 ppm for framework silicons in a sample without exposure to phenyltrimethylsilane (control experiment). As shown in Figure 2b,
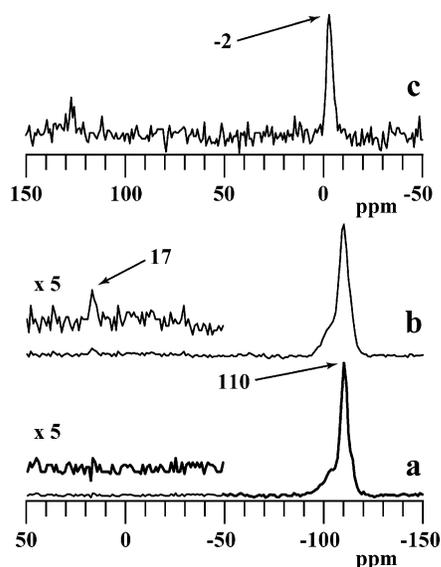
Figure 2. Solid-state NMR spectra of some of the catalyst beds studied in this investigation. (a) ²⁹Si MAS spectrum of unmodified H-Beta (control experiment) showing signals only due to the zeolite framework. (b) ²⁹Si MAS spectrum of H-Beta quenched to room temperature 4 s after pulsed introduction of phenyltrimethylsilane at 648 K. The signal at 17 ppm has the intensity expected based on the Si/Al ratio of the catalyst, suggesting stoichiometric formation of **3**. (c) ¹³C CP/MAS spectrum (natural abundance) showing the methyl group signals of **3** at −2 ppm.

a catalyst bed quenched after exposure to phenyltrimethylsilane at 648 K has a new ²⁹Si signal at 17 ppm. This chemical shift is in excellent agreement with that expected for trimethylsilyl ethers in solution.[13] Finally, the ¹³C MAS spectrum in Figure 2c shows the expected carbon resonance for **3** (zeolite H-Beta) at −2 ppm.

We believe that *tert*-butylbenzene and phenyltrimethylsilane react on the microporous solid acid catalysts by very similar mechanisms, but the greater strength of the Si−O bond relative to the C−O bond places **3** in a much deeper potential energy well than the analogous *tert*-butoxy intermediate. Hence, the siloxy intermediate is stable to dissociation for at least a few seconds at 648 K while the corresponding alkoxy is readily eliminated as isobutene, a pathway that is not so readily available for **3**, given the difficulty of forming 2-silaisobutene. The results here are reminiscent of other results and concepts in silicon solution chemistry. The reaction in Scheme 1 is an example of the well-known tendency of phenylsilanes to undergo ipso substitution by electrophiles.[14] The results here can also be appreciated in the context of the β effect of silicon (related to σ conjugation),[15] especially in the ease of displacing benzene compared to other leaving groups.

The reaction in Scheme 1 seems to be potentially useful for counting acid sites.[16,17] We found good agreement between the total moles of phenyltrimethylsilane converted to benzene in a multiple-

shot experiment and the acid site densities determined otherwise for several H-Beta samples of diverse composition. While we have not yet sought to demonstrate any useful catalytic reactivity for materials modified in part or whole by Scheme 1, we note that this reaction might be useful for introducing a controlled amount of silicon into a catalyst prior to pyrolysis or some other treatment step.

Theoretical studies have suggested that the difficulty in forming teritiary alkoxy species (most simply *tert*-butoxy) in some zeolites is a result of steric clashes between the methyl hydrogens and the curving surface of the zeolite.[18] Here, we used large-pore (12-ring) materials with less curvature than some of the materials studied previously. Furthermore, a typical Si−O bond length is 163 pm vs 143 pm for a C−O bond; therefore, we expect **3** to be more readily accommodated on the curved surfaces of zeolites. The possibility of counting or, better yet, selectively deactivating acid sites based on subtle variations in local topology is one of the many implications of the present work that we are actively pursuing.

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