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NOTE

^{13}C NMR Studies of Acetone in Dealuminated Faujasites: A Probe for Nonframework Alumina

Dealumination is an important process in the preparation of stable zeolite-based hydrocarbon cracking catalysts. Depending on the method used for dealumination (i.e., chemical versus steam dealumination), one may or may not leave substantial amounts of nonframework alumina in the structure. These extraframework species appear to be very important since the hydrocarbon cracking activity is increased dramatically on materials which contain these species (1). Significant effort has gone into trying to understand the sites responsible for activity enhancement (1–4), but the question remains unresolved. There are three general reasons that have been suggested for the enhanced activity in steamed materials. (i) The Brønsted acid sites are strengthened by interaction with the nonframework Al (2). (ii) The extraframework species, themselves, are catalytically active (3). (iii) The reaction is assisted by cooperative effects between neighboring Brønsted and Lewis acid sites (4).

We recently investigated the adsorption of C-2–^{13}C-labeled 2-propanone using ^{13}C NMR on a series of simple (i.e., no nonframework Al) zeolites at low coverages (below one per acid site), where reaction and exchange processes are minimal, and demonstrated that the ^{13}C chemical shift is a measure of the tendency toward hydrogen bonding between the carbonyl group and the Brønsted acid sites (5, 6). Because measurable proton transfer does not occur for acetone except in very strong acids, much stronger than that of molecular sieves examined in our study, the chemical shift provides a sensitive probe of the acid-site environment. For simple zeolites, the downfield chemical shift of adsorbed acetone was found to be in the range 13–18 ppm in pure acetone (6), compared to shifts of 14.1 and 9.1 ppm, respectively, in trifluoroacetic acid and formic acid solutions (7). In this note we explore the acidic environment in H–Y to determine the existence of sites that can be associated with the enhanced activity of steamed zeolites.

The zeolite samples used in this study have been characterized extensively elsewhere, with a summary of some important properties given in Table 1 (5, 6, 8). PQ(7) is a typical US–Y catalyst obtained from the PQ Corporation and was steamed prior to ammonium ion exchange. It contains significant amounts of nonframework Al. PQ(20) was steamed, acid leached, and steamed again to further decrease the Al content. CD(12) was dealuminated chemically and contained very little nonframework Al. The activated γ-Al_2O_3 was obtained from Aldrich (standard grade, acidic) and had a surface area of 155 m^2/g.

Acetone-doped samples for NMR measurements were prepared as described previously (5, 6). Carefully measured doses of acetone (99% C-2–^{13}C, Cambridge Isotope Labs) were added to each sample, with the amount corresponding to less than one molecule per Brønsted acid site in all cases. The conditions for the ^{13}C NMR spectra are also described in Refs. (5) and (6). Spectra were obtained by observation of proton-decoupled Hahn echoes (HE) under MAS conditions. The echo sequence consisted of a series of 90°-τ-180° pulses in quadrature, with a delay time, τ, of 30 μs. When necessary, signal enhancement was achieved by ^{1}H–^{13}C cross polarization (CP).

In Fig. 1, the proton-decoupled, 3.1 kHz MAS spectrum of the carbonyl carbon of acetone is shown for adsorption on each zeolite at 295 K. With the exception of Fig. 1f, a ^{1}H–^{13}C CP spectrum, each spectrum represents Fourier transforms of Hahn echoes of the fully relaxed systems. The integrated intensities, to a first approximation, are thus a reasonable measure of abundances.

Figure 1a shows the spectrum of acetone in the chemically dealuminated H–Y sample, CD(12), at a coverage of 0.7 molecules per Brønsted acid site, while a similar result for H–ZSM-5 is shown in Fig. 1b for comparison. In both cases, the predominant peaks at 219 ppm (CD(12)) and 222 ppm (H–ZSM-5) correspond to chemically shifted, unreacted acetone (The chemical shift of pure acetone is 205 ppm relative to TMS). The small difference in chemical shift (219 vs 222 ppm) can be associated with a difference in the strength of the hydrogen bond with the Brønsted site (6). More important, however, is the presence of the additional feature at 233 ppm and the absence of spinning sidebands for the unreacted acetone in CD(12). The absence of spinning sidebands is clearly consistent with motional averaging in the large supercage

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TABLE I

Physical Characteristics of the Samples Used in this Study

Sample	Bulk Al (Al/u.c.)[a]	u.c. size (nm)	Al_F (Al/u.c.)[b]	Pore volume (cm^3/g)[c]	[H^+] (μmol/g)[d]	Activity (× 10^6 mol/g · s)[e]
CD(12)	29	2.4488	27	0.296	860	2.2
PQ(7)	43	2.4478	26	0.321	850	12
PQ(20)	18	2.4292	6	0.293	220	1.5

[a] Obtained from atomic absorption spectroscopy.

[b] Determined from ^{29}Si NMR and lattice parameter correlations (8).

[c] Measured by O_2 uptakes at P/P_0 = 0.4 and 77 K.

[d] *Measured using TPD–TGA of isopropylamine (8).*

[e] *n*-Hexane cracking rates at 798 K and 47 Torr (8).

of H–Y (6). The feature at 233 ppm might be attributable to a reaction product; however, given that it is absent in zeolites which have not undergone dealumination and that it is enhanced by increasing amounts of nonframework alumina in the zeolite, it is probably associated with residual nonframework Al.

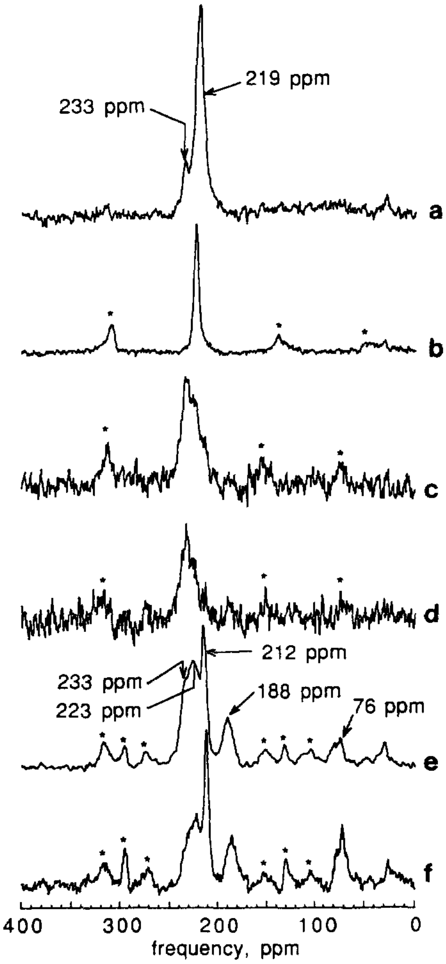

FIG. 1. 3.1 kHz ^{13}C MAS acetone HE spectra (except (f)); 5 s rep. time. (a) CD(12), 0.7 molecules per Brønsted acid site. (b) H–ZSM-5, 0.85 molecules/site. (c) PQ(7), 0.3 molecules/site. (d) PQ(20), 0.7 molecules/site. (e) PQ(7), 0.7 molecules/site. (f) CP spectrum of acetone in PQ(7), 0.7 molecules/site.

Materials containing nonframework alumina were very reactive and it was necessary to work at low coverages (or reduce the amount of nonframework species), as well as short times for adsorption and data acquisition, in order to observe the initial species. Under these conditions, we observe a feature at 233 ppm in Figs. 1c and 1d which we assign to unreacted acetone on nonframework alumina sites in PQ(7) and PQ(20). With time (at 300 K), the spectra evolve to show the formation of mesityl oxide (9). The results suggest that the sites associated with the 233-ppm peak catalyze the bimolecular processes much more readily than the Brønsted acid sites in unsteamed zeolites, CD(12) and H–ZSM-5. For higher acetone coverages on PQ(7) (a coverage of 0.7 molecules/site is shown in Fig. 1e), the relative intensity of the 233-ppm feature relative to other peaks decreases significantly and reaction products dominate the spectrum. Three new features at 211, 188, and 76 ppm are due to bimolecular products resulting from the enhanced reactivity of PQ(7), and their relative intensity increases with cross polarization (Fig. 1f). Finally, it should be noted that, unlike the 223-ppm feature which is probably associated with Brønsted sites based on a comparison with CD(12), both the 233-ppm feature and the most intense reaction product bands exhibit sidebands characteristic of a rigid lattice or partially averaged anisotropic shielding tensor.

An examination of the behavior of adsorbed acetone on the activated alumina catalyst, shown in Fig. 2, provides the basis for an explanation of the results for the steamed H–Y samples. Figure 2a shows the ^{13}C NMR

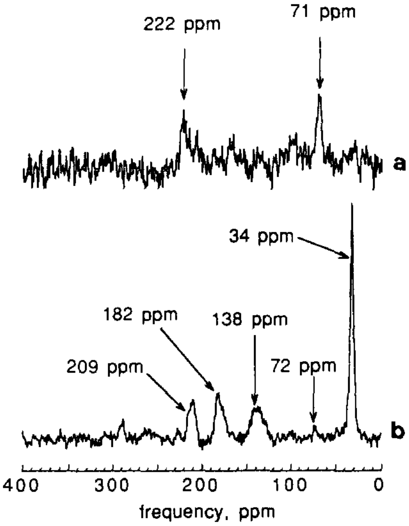

FIG. 2. 3.1 kHz ^{13}C MAS HE spectra of acetone on γ-Al_2O_3; 5 s rep. time. (a) Immediately after exposure, 512 scans. (b) 12 h after initial exposure, 8192 scans.

spectrum of acetone on alumina (5×10^{17} molecules/m^2) obtained immediately after exposure, while Fig. 2b shows the spectrum taken 12 h later. These results are entirely consistent with the earlier and more comprehensive studies of Bell *et al.* (10, 11) and Reichle (12), who identified the aldol condensation products for acetone on activated alumina at much higher surface coverages. The features at 222 and 71 ppm obtained initially are probably due to the formation of diacetone alcohol from the 2–^{13}C-labeled acetone (Reaction 1 in Fig. 3). The chemical shift of the carbonyl carbon from liquid diacetone alcohol (208 ppm) suggests a large deshielding when adsorbed on alumina. Longer reaction times result in the disappearance of the alcohol and the formation of mesityl oxide, with peaks in the vicinity of 209 ppm (C-1) and 182 ppm (C-3), as shown in Reaction 2 in Fig. 3. It is interesting to note the large deshielding of the C-3 carbon in mesityl oxide (182 vs 153 ppm), which is characteristic of the hydroxyallylic carbocation that one expects in acidic media (13). Finally, additional bimolecular processes lead to the fingerprint peaks of isophorone and mesitylene, with bands at 138 and 34 ppm. This is illustrated in Reaction 3 in Fig. 3, which shows, in the absence of any ^{13}C scrambling, the identities all of the observable ^{13}C atoms in the products.

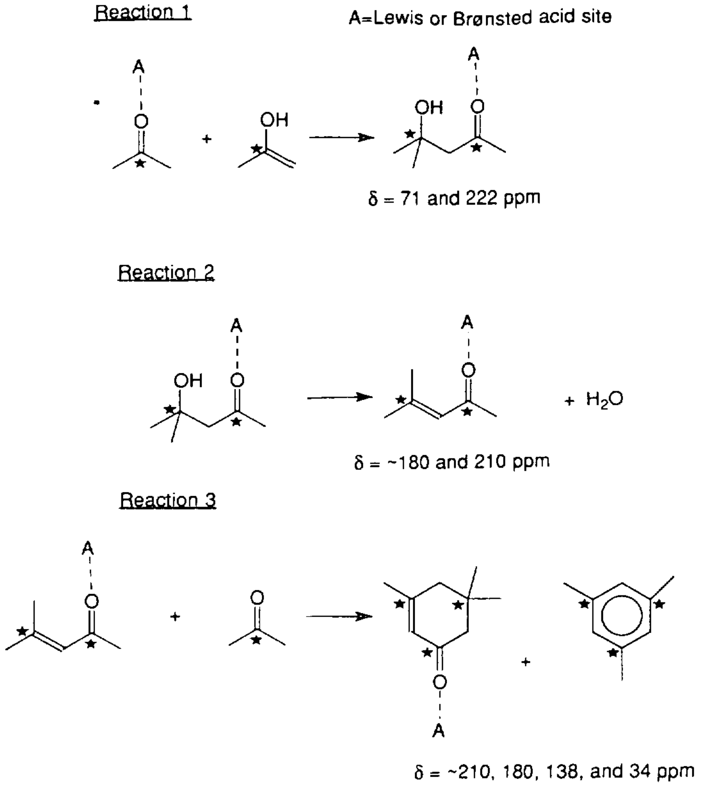

FIG. 3. Schematic diagram of the reactions of acetone on H–Y and activated alumina.

By recognizing the constraints imposed by the cavity in the zeolites, one can interpret the reaction products in PQ(7) as resulting from the same aldol condensation reactions observed on alumina. Bimolecular processes lead initially to diacetone alcohol (76 and 212 ppm) but proceed no further than the formation of mesityl oxide (~212 and 182 ppm), at least at room temperature.

While our results are certainly important for understanding reactions involving aldehydes and ketones in zeolites (9, 14), it is also interesting to consider what they tell us about general aspects of acidity in steamed zeolites. Based on our assignments, acetone at the Brønsted acid sites in steamed H–Y, corresponding to a peak near 223 ppm which is motionally averaged at room temperature, does not appear to be significantly different from acetone in chemically dealuminated H–Y. The question remains, however, regarding the exact nature of the site responsible for the 233-ppm feature. This carbonyl carbon is significantly deshielded with respect to that observed on any of the unsteamed, high-silica materials examined by us. It is clearly caused by extraframework species and is responsible for the reactions observed in this study. However, we cannot determine whether the site responsible is Brønsted or Lewis. Since the observed reactions are similar to those in activated alumina, the sites may simply be nonframework Al.

Finally, we note that hydrocarbon cracking reactions are very complex. The enhanced rates in steamed zeolites may well be caused by factors other than increased acidity (8).

Based on our studies, we conclude the following: (i) The high reactivity of adsorbed acetone on steamed H–Y at room temperature, relative to unsteamed zeolite, is due to nonframework alumina, with a ^{13}C chemical shift that differs from that of the framework sites. (ii) The surface-catalyzed, bimolecular reactions associated with the nonframework alumina are very similar, and perhaps even identical, to those which occur on activated alumina. (iii) Although we cannot unambiguously locate the position of the nonframework Al, the presence of spinning sidebands for all features associated with molecules at these sites suggests that the mobility of these molecules is considerably reduced over that of molecules adsorbed at framework, Brønsted sites within the supercages.

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