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Acidity Studies of Fluid Catalytic Cracking Catalysts by Microcalorimetry and Infrared Spectroscopy

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The acidic properties of a USY-based fluid catalytic cracking catalyst steamed at various severities and amorphous silica–alumina were investigated by microcalorimetry and infrared spectroscopy using pyridine adsorption at 473 K. Microcalorimetric measurements of the differential heat of pyridine adsorption versus adsorbate coverage revealed a heterogeneous acid site distribution for the catalysts. Besides showing the expected progressive decrease in the number of acid sites for pyridine adsorption, our measurements showed that the strength of Brønsted acid sites decreased with increasing severity of steam treatment. Infrared spectra of adsorbed pyridine revealed a significant decrease in the ratio of Brønsted to Lewis acid sites upon steaming. Amorphous silica–alumina had a relatively large number of acid sites of which a large proportion were Brønsted acid sites. However, the strength of these Brønsted sites was lower than that of the mildly steamed USY catalysts. This lower Brønsted acid strength, we believe, is related to lower activity for gas–oil cracking over silica–alumina. © 1992 Academic Press, Inc.

INTRODUCTION

Characterization and measurement of Y zeolite acidity is important for understanding and controlling the catalytic centers where hydrocarbon cracking and related reactions take place. For such studies, complementary techniques such as heat flow microcalorimetry and infrared spectroscopy are important. Microcalorimetry involves the measurement of differential heats evolved upon adsorption of small quantities (e.g., μmol) of basic probe molecules onto the catalyst. Such measurements over a range of surface coverage yield information about the acid strength distribution, i.e., the number of sites having a particular heat of adsorption for the basic probe molecule. However, microcalorimetry cannot generally distinguish between Lewis and Brønsted acid sites. Infrared spectroscopy of adsorbed basic probe molecules such as pyridine and ammonia allows the type of acid site to be identified but gives only a qualitative measure of acid site strength. The combination of these two techniques provides a valuable means of characterizing acid properties of solid catalysts.

Infrared spectroscopy of adsorbed base molecules on Y zeolites is an established technique dating to the work of Ward (*1*, *2*), Uytterhoeven (*3*), Hall (*4*), Hughes and White (*5*), Eberly (*6*), and others. Heat flow microcalorimetry has also been used by a number of workers in the study of solid acid catalysts, as discussed in a recent review (*7* and references therein). Several studies of the effect of dealumination on HY zeolite acidity have employed this technique. Auroux and Ben Taarit (*8*), studied steam-dealuminated HY zeolite with Si/Al ranging from 2.4 to 49, whereas Macedo *et al.* (*9*)

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conducted similar measurements on steam-dealuminated HY zeolites from Si/Al ratios between 8 and 100. Shi *et al.* (*10*) measured the acid strength of HY zeolites dealuminated by $SiCl_4$, instead of by steaming, for Si/Al ratios ranging from 4.2 to 37.1. Mitani *et al.* (*11*) studied HY zeolites dealuminated by ethylenediaminetetraacetic acid (H_4EDTA) over Si/Al ratios from 2.5 to 5.1.

In this paper, we examine acid properties of USY zeolite catalysts, similar to those used commercially in fluid catalytic cracking (FCC), via heat flow microcalorimetry, IR spectroscopy, and microactivity tests of gas–oil cracking. These materials were dealuminated via steaming to obtain samples whose unit cell (uc) sizes and hence framework aluminum (Al_F) contents closely mimic working FCC catalysts. Our objectives were to probe the acidity and in particular the acid strengths of the various steam-treated Y-based catalysts, focusing on the catalytically important Brønsted acid sites, and to compare the acid characteristics of these Y zeolite catalysts with a commercial amorphous silica–alumina catalyst. These studies highlight the necessity of using multiple techniques for acid catalyst characterization.

EXPERIMENTAL

Catalysts

The USY based FCC catalysts were made via *in situ* zeolite crystallization (*12, 13*). Kaolin microspheres were first calcined at 1255 K, then aged in sodium hydroxide for 6 h at 310 K, followed by zeolite crystallization at 355 K. The microspheres containing zeolites were subsequently exchanged with ammonium nitrate, dried, and calcined at 810 K. The final untreated material contained 12 wt% Y zeolite and 2.5 wt% Na_2O on zeolite basis, the rest being amorphous clay left over from the crystallization procedure. One batch, HYC, was further calcined for 2 h at 823 K. Four other batches were prepared by fluidizing each batch in 100% steam at atmospheric pressure and 1060 K for 0.25, 2, 15, and 60 h. For comparison with these *in-situ* crystallized zeolite samples, we also studied (i) a pure HY zeolite sample with an Si/Al ratio equal to 2.4 (corresponding to 56 framework aluminum cations per unit cell) and 3 wt% Na_2O, containing no amorphous matrix material, and (ii) an amorphous silica–alumina (Davison) containing 13 wt% alumina calcined for 2 h at 823 K.

The properties of the calcined and steamed zeolites and amorphous silica–alumina (SAC) are shown in Table 1. For the zeolite-containing samples, an N_2 BET of the entire sample minus the surface area of pores larger than 2 nm diameter, obtained by replotting the adsorption data as a "*t*" plot, gave the microporous surface area. This latter area is mainly the area of the zeolite component. Unit cell size measurements via X-ray diffraction were performed using a Si standard, and Al_F/uc values were obtained via the correlation given by Sohn *et al.* (*14*). A comparison between HYC and the most severely steamed sample shows that the zeolite content decreased by about a factor of 2, whereas Al_F/uc decreased by a factor of 14.

Procedures

Heat-flow microcalorimetry was performed using a Setaram C80 Calvet type calorimeter attached to a volumetric system equipped with a Baratron capacitance manometer. Catalysts were first evacuated at 673 K for 0.5 h, then treated in oxygen at 723 K for 4 h, followed by further evacuation at 723 K for 1.5 h. Calorimetric measurements of pyridine adsorption were made at 473 K, a temperature at which pyridine does not decompose and at which it retains sufficient surface mobility to equilibrate with the acid sites (*15*).

The differential heat of adsorption of pyridine as a function of coverage was obtained by the following procedure. Each dose of pyridine, typically 1 μmol, was allowed to equilibrate in the dosing volume before being admitted into the calorimeter. The heat

TABLE 1

Sample Properties

Sample[a]	Unit cell size (nm)	Framework Al (atoms/u.c.)	Si/Al$_F$	Total BET surface area (m^2/g)	Surface area of pores $d < 2$ nm[b] (m^2/g)	MAT activity (arbitrary units)
HYC	2.455	33.4	4.8	195	82	6.94
HY0.25	2.436	13.1	13.7	175	66	4.13
HY2	2.432	8.8	20.8	162	58	2.85
HY15	2.427	3.4	55	139	44	1.23
HY60	2.426	2.4	80	119	36	0.81
SAC	—	—	—	422	—	2.5

[a] Numbers correspond to steaming times in hours.

[b] Corresponds to primarily zeolite surface area.

of adsorption evolved for that dose was calculated from the resulting thermogram. The amount of gas adsorbed was calculated from the initial and final dosing temperature and pressure. Sequential dosing, without evacuation of the sample chamber, gave the differential heat as a function of coverage; the adsorption isotherms consisted of 30 to 70 doses. Details regarding the experiments and calculations are given elsewhere (*15*, *16*).

Infrared spectra were collected at 313 K in the diffuse reflectance mode using a Spectra Tech controlled-environment chamber in a Perkin–Elmer 1750 spectrometer. The diffuse reflectance mode has been used extensively in our laboratories to eliminate the need to prepare thin wafers for transmission IR studies. The samples were dried for 1 h at 723 K under flowing N_2, and the dehydration process was monitored by observing the disappearance of the water band at 1645 cm^{-1}. Pyridine vapor was then introduced to the sample in flowing N_2 at room temperature; after 1 min the flow was shut off and the sample allowed to equilibrate with the pyridine for 1 h. Spectra collected after each of three successive 1-h purges in N_2 at 313, 473, and 673 K indicated three distinct desorption stages. The lowest temperature purge removed predominantly physisorbed pyridine (1583 cm^{-1}), the second eliminated hydrogen-bonded pyridine (1600 cm^{-1}), and the highest temperature purge removed all but pyridine on the strongest sites. Pyridine was not measurably decomposed at the highest desorption temperature. Infrared band areas (Kubelka–Munk units) at 1450 and 1550 cm^{-1} were used to estimate the amounts of pyridine adsorbed on Lewis and Brønsted acid sites respectively (*17*). These areas were reproducible to within only about 10% due to variations in sample grinding and packing in the reflectance chamber sample cup (*18*).

Unlike conventional quantitative transmission infrared spectroscopy, where extinction coefficients are obtained from a linear plot of band intensity versus sample concentration, there is no clearly defined equivalent "beam scatter" parameter for the diffuse reflectance technique. This makes defining an extinction coefficient in diffuse reflectance subjective; it includes contributions from the experimental setup and the sample density which are difficult to quantify. In this study, extinction coefficients have been estimated by correcting errors due to sample density differences by using both ammonia desorption and thermogravimetric pyridine adsorption techniques (*19*) to obtain total acidity estimates for our samples. Therefore the extinction coefficients used in this paper to quantify our data are termed effective extinction coefficients, and these values may not be directly trans-

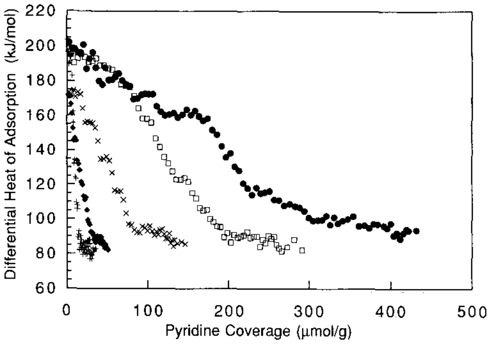

FIG. 1. Differential heats of pyridine adsorption on USY-based FCC catalysts steamed to varying extents. HYC (●), HY0.25 (□), HY2 (×), HY15 (◆), HY60 (+).

ferable to a different experimental setup. Their relative values, however, will be constant, allowing quantitative comparison between the various samples of this study.

Catalytic activity studies were carried out in a microactivity test (MAT) unit using mid-continent gas oil having a molecular weight of 264 and a final boiling point of 812 K. The reaction procedure was similar to that described by ASTM method 3907. A catalyst charge of 6 g was loaded in the reactor and pretreated at 760 K in flowing nitrogen for at least 0.5 h. Catalytic activity studies were carried out at 760 K, for a catalyst/oil weight ratio of 5 and an oil delivery time of 48 s. Conversion was defined as the sum of the yields of gas, coke, and gasoline. Gasoline yields were obtained via simulation distillation chromatography (ASTM method D2887) with a cut-off for gasoline at 489 K. We have chosen to conduct microactivity tests in the present study, rather than a simpler hydrocarbon model reaction, to assess the effects of steaming on a commercial feed and to compare steamed Y-based FCC catalysts to amorphous silica–alumina.

RESULTS

Microcalorimetry

Figure 1 shows the differential heat versus coverage for five USY FCC catalysts. Some difficulty was encountered in obtaining accurate measurements of total acidity because of slow desorption of pyridine from the walls of the dosing volume and sample cell. Hence we used values of total acidity for the samples obtained from temperature programmed desorption of NH_3 and thermogravimetric measurements of pyridine adsorption (*19*) to scale the total acidity obtained from microcalorimetry. The scaling values for the various samples ranged from 0.75 to 2.0

Each microcalorimetric curve shows regions of nearly constant heat with respect to coverage and other regions in which the heat decreases with increasing coverage. A region of constant heat is characteristic of a set of acid sites of homogeneous strength. It is clear that these commercial catalysts, calcined as well as steamed, display a complex acid strength distribution. Results for HY zeolite, Fig. 2, indicate a somewhat less complicated acid strength distribution, but regions of different acid strength still exist.

The curves are generally distinguished by three features: (a) an initial region of high heat of adsorption representing adsorption on the strongest sites, (b) one or more regions of intermediate strength sites, and (c) a heat of adsorption for all the samples at high coverages approaching a constant value between 90 and 100 kJ/mol. This latter value is characteristic of hydrogen-bonding between pyridine and the sample (*15*). (The

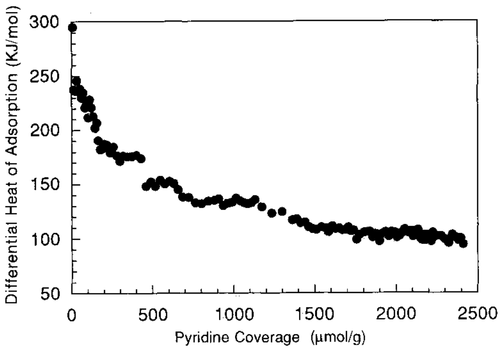

FIG. 2. Differential heat of pyridine adsorption on HY Zeolite.

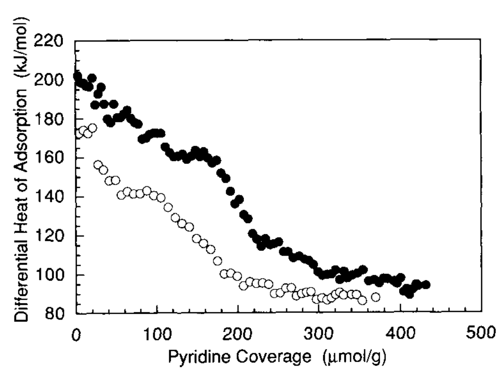

FIG. 3. Differential heats of pyridine adsorption on silica–alumina (○) and HYC (●).

heat of pyridine condensation is approximately equal to 40 kJ/mol). For this set sample set, the maximum heat of adsorption is less than 220 kJ/mol; following the work of Cardona-Martínez and Dumesic (*15*), pyridine should adsorb on these sites selectively at 473 K, filling the stronger sites first via surface mobility of adsorbed pyridine. Weaker sites are progressively filled at higher pyridine coverages. Our infrared spectroscopic studies also suggest that surface diffusion of pyridine takes place at 473 K, since the IR band intensities for pyridine adsorbed on Lewis and Brønsted acid sites vary with time after initial exposure of a sample to a small dose of pyridine, whereas the total IR band intensity remains essentially constant.

The effect of steaming on the number and strength of acid sites is apparent from comparison of the differential heat curves for the dealuminated zeolites. There is a sharp decrease in total acidity after just 15 min of steaming at 1060 K. The initial heats of pyridine adsorption, corresponding to the strength of the strongest acid sites, decrease with increasing time of steaming from about 200 kJ/mol for HYC to about 170 for HY15. However, the most highly steamed sample, HY60, shows an initial heat similar to HYC. The microcalorimetric curves also show that the strength of sites comprising the intermediate plateau region progressively decrease with steaming severity. We discuss this effect of steaming on intermediate strength sites as well as the recovery of the high initial heat for HY60 in the Discussion section.

Calcined amorphous silica–alumina, as shown in Fig. 3, in comparison with HYC, has a lower initial heat of adsorption as well as a lower heat for the intermediate region of constant heat.

Infrared Spectroscopy

Infrared bands at 1550 and 1450 cm^{-1} attributable to pyridinium ion and adsorbed pyridine were used to measure the populations of Brønsted and Lewis acid sites respectively (*17*). As discussed earlier, the total acidity was assessed using both temperature programmed desorption of ammonia and thermogravimetric measurements of pyridine adsorption (*19*), and effective extinction coefficients representative for our setup and catalysts were obtained. The ratio of effective extinction coefficients for Lewis/Brønsted acid sites for the zeolite samples was 1.4.

The number of Brønsted acid sites (Table 2) decreases rapidly with steam treatment. Treatment for only 15 min at 1060 K results in a reduction by a factor of about 3 in the number of Brønsted acid sites. For the most severely steamed sample, HY60, the number of Brønsted acid sites is drastically reduced. This result concurs with IR investi-

TABLE 2

Site populations from IR and 2-propylamine TPD

Sample	Site population (μmol/g)			Brønsted population by 2-propylamine TPD (μmol/g) Ref. (26)
	Lewis	Brønsted	Total	
HYC	128	180	308	190
HY0.25	115	61	176	79
HY2	57	23	80	53
HY15	25	7	32	17
HY60	13	2	15	11
SAC	114	90	204	100[a]

[a] Unpublished data from R. J. Gorte.

gations by Mauge *et al.* (*20*) of severely steamed H–Y zeolites. Furthermore, the ratio of Lewis to Brønsted acid sites increases by about one order of magnitude with increased steaming severity. It is interesting to note that for amorphous silica–alumina the Brønsted and Lewis acid site populations are nearly equivalent, showing a much higher relative Brønsted acid site population than that for the steamed zeolites.

The IR experiments on the various steamed samples reveal qualitative changes in the populations of strong and weak sites. The ratio of strong Lewis acid sites (i.e., sites from which pyridine was not removed by heating in flowing N_2 to 673) to total Lewis sites remains relatively constant with increasing steam treatment. In contrast, a similar ratio of strong Brønsted acid sites to total Brønsted acid sites decreases dramatically with increasing steam treatment. This behavior supports the view that the strongest acid sites are Lewis acid sites.

Microactivity Tests

Microactivity tests were carried out for the purpose of noting gas oil cracking activities with changes in catalyst acidity. Product yields will not be discussed here but in a separate publication. MAT activity is defined for a second order reaction as (% conversion)/(100-% conversion), and these values are summarized in Table 1. As expected there is a monotonic decrease in activity with increased steaming severity. We note that the silica–alumina sample shows relatively low activity in comparison with the steamed HY0.25 zeolite sample with lower number of acid sites.

DISCUSSION

Acid Site Type and Strength

The combined use of microcalorimetry and infrared spectroscopy allows one to relate different acid site types to different acid strengths. Such a connection between site strength and site type would result in a more thorough depiction of the effects of steam dealumination. Due to the complex nature of the acid strength distribution seen in Fig. 1, it is not possible to make a detailed correlation between sites of various strengths and their type. It is possible, however, to discuss the ranges of site strength and relate these ranges to Brønsted or Lewis acid sites.

Sites of high strength, 180 kJ/mol or more for pyridine adsorption, have been previously associated with Lewis acidity on silica-supported metal oxides (*16, 21*). Previous microcalorimetric studies of dealuminated Y zeolites by Shi *et al.* (*10*) and Auroux and Ben Taarit (*8*) have attributed the initial strong sites to Lewis acidity generated by alumina phases or nonframework aluminum. In agreement, our IR studies after pyridine desorption at 673 K also indicate qualitatively that Lewis acid sites exist which are stronger than Brønsted acid sites. This result agrees with the early IR work of Eberly (*6*), who also noted that Lewis acid sites are stronger than Brønsted acid sites for pure Y zeolites. We therefore ascribe sites with heats of adsorption greater than 180 kJ/mol to be predominantly Lewis acid sites.

Brønsted acid sites in zeolites are generally associated with heats for pyridine adsorption ranging from about 130 to 180 kJ/mol (*15, 16, 22, 23*). Indeed, we note from Fig. 3 a region of constant heat at 160 kJ/mol for HYC and a corresponding region at 140 kJ/mol for the amorphous silica–alumina. On pure HY (Fig. 2) we similarly note that the predominant values for the heat of adsorption of pyridine are in this strength range, and infrared spectra of adsorbed pyridine at low coverages on this sample indicate that these are Brønsted acid sites. We thus concur with Mitani *et al.* (*23*) who proposed that such intermediate heats for pyridine adsorption on Y zeolites are due to Brønsted acid sites. Such sites of intermediate strength are also associated with Brønsted acidity on silica supported metal oxides (*15, 16*) and for H-mordenite (*24*). Using cluster approximation and quantum-chemical calculations, Paukshtis *et al.* (*25*) studied the formation of pyridinium ions on

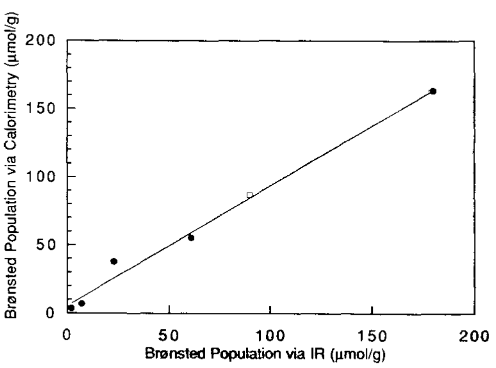

FIG. 4. Brønsted acid site population as measured by microcalorimetry and IR spectroscopy for USY FCC catalysts (●) and silica–alumina (□).

the surface of alumino-silicates. They determined a range of 134 to 153 kJ/mol for the heat of adsorption of pyridine on Brønsted acid sites.

Most previous work suggests that intermediate strength acid sites are predominantly Brønsted acid sites. Since in our work for both IR and microcalorimetry only total acidity was calculated as discussed in the Results section, we should be able to extract Brønsted acidity quantitatively via IR and microcalorimetry. Figure 4 compares Brønsted acid sites obtained from the pyridinium ion intensity via IR and from the intermediate strength sites via microcalorimetry. The good agreement substantiates the premise that intermediate strength sites in microcalorimetry are Brønsted acid sites, and lends support to the methods used in scaling coverages from microcalorimetry. These values also agree with Brønsted acidity measurements on these same samples using temperature programmed decomposition of isopropylamine by Biaglow *et al.* (*26*) and summarized in Table 2. The results of this study and those in the literature thus suggest that sites with intermediate heats of adsorption are predominantly Brønsted acid sites.

Earlier we noted that as pyridine is desorbed at temperatures above 473 K, the IR intensity for pyridine adsorbed on Lewis acid sites decreases until at 673 K about 60% of the original intensity remains for all the samples studied. Adsorbed pyridine remaining after treatment in flowing carrier gas at 673 K is associated with strong Lewis acid sites. The sites from which pyridine desorbed at lower temperatures are weak Lewis sites. We tentatively assign these weak sites to have heats of adsorption lower than about 130 kJ/mol. There is evidence in the literature for weak Lewis acidity with heats lower than 135 kJ/mol on a variety of silica-supported oxides (*15*). As mentioned earlier, the lowest heats of adsorption in the range of 90–100 kJ/mol are due to hydrogen-bonded pyridine (*15, 16, 22*).

It is important to note that for the FCC catalysts studied here, the catalyst matrix is the clay component left after zeolite crystallization. This component is only mildly acidic (*27*), and the acid sites may be represented by a portion of the weak Lewis acid sites. However, the formation of nonframework Al and amorphous material made via dealumination and zeolite destruction due to severe steaming may have important implications for the overall acidity of the sample. This is discussed in the next section.

Effects of Steam Dealumination

Steam dealumination of our FCC catalysts results in a decrease of about a factor of 2 in the zeolite surface area but a much larger factor of 14 decrease in Al_F/uc. This latter effect is accompanied by a significant decrease (see Table 2) in the number of Brønsted acid sites. For example, steam treatment for 15 min decreases Al_F/uc by a factor of 2.5 resulting in a 60% decrease in Brønsted acid sites, whereas Lewis acid sites decrease by only 10%. Figure 5 shows the number of Lewis and Brønsted acid sites plotted against framework aluminum content. There is a good relationship between framework aluminum content and population of Brønsted acid sites; however, a similar simple relationship does not exist between aluminum content and the Lewis acid site population. We also note that for the

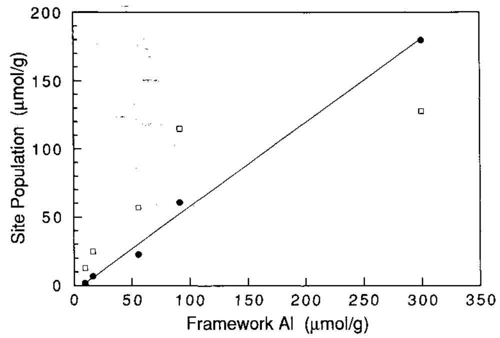

FIG. 5. Brønsted (●) and Lewis (☐) acid site populations versus framework Al content.

pure HY sample the ratio of number of Brønsted acid sites (as titrated by pyridine) to framework aluminum is 0.5, close to the value of 0.6 obtained from Fig. 5. Some framework aluminums may have no acidic protons associated with them and some acid sites may be inaccessible to pyridine and hence to most hydrocarbons during reaction. For example, pyridine may not titrate acid sites that face into the sodalite cages.

The scatter in the plot of the number of Lewis acid sites versus the number of framework aluminums may be due to the fact that nonframework aluminum gives rise to Lewis acid sites. It may be for this reason that the total acidity measured by pyridine adsorption is larger than the number of framework aluminum cations for several steamed samples. It has been suggested that nonframework aluminum cations can form amorphous phases of alumina or silica–alumina (*8, 20, 28–31*) or can remain in cationic form within the zeolite micropore structure (*9, 32, 33*). These forms of Al in steamed samples affect catalyst acidity. The initial heats of adsorption, which were due primarily to strong Lewis acid sites, decreased continuously for the set of steamed samples from 200 kJ/mol for HYC to 170 kJ/mol for HY15. The latter value is close to that of the initial heat of adsorption, 175 kJ/mol, for calcined silica–alumina. However, for the severely steamed HY60, the initial heat of adsorption increased to 200 kJ/mol. One explanation for this behavior is that severe steaming may lead to the formation of an alumino–silicate with Lewis acidity stronger than conventional silica–alumina. Earlier we had stated that the initial clay matrix had only weak, if any, Lewis acidity. Interactions between the matrix, the nonframework aluminum and parts of the destroyed zeolite during steaming may give rise to an alumino–silicate phase with strong Lewis acidity.

Identification of the sites of intermediate strength as Brønsted acid sites allows us to comment on possible changes in Brønsted acidity with increased steaming. In addition to a decrease in the number of these sites with steaming, microcalorimetric results also indicate a decrease in the strength of the Brønsted acid sites as steaming severity increases. Figure 6 shows this decrease in the average strength of the intermediate sites with increased steaming time. The corresponding value for the pure HY sample was 160 kJ/mol, and for SAC it was 136 kJ/mol.

In general, the influence of dealumination on the FCC catalysts of this study is similar to that for pure HY zeolites. Increasing severity of steam treatment has been associated with decreases in total acidity for all reported studies. In agreement with the results depicted in Fig. 1, Auroux and Ben Taarit (*8*) found that increasing steam dealumination resulted in a decrease in the

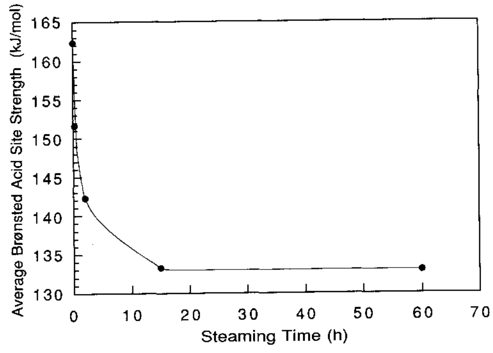

FIG. 6. Brønsted acid site strength as a function of steaming.

number of intermediate strength sites of constant heat, i.e., the plateau regions in the differential heat curve. They also found that the initial differential heat of ammonia adsorption first increased with Si/Al ratio and then decreased for further dealumination beyond Si/Al ratios of 10. The strength of intermediate sites, corresponding to Brønsted acid sites, also passed through a maximum at an Si/Al ratio equal to 10. These authors proposed that a guest alumina-like component is formed which shows a broad strength distribution at high acid strength; the remaining structural sites are decreased in strength due to extreme dilution, i.e., an optimum site density is required for strong acidity. Macedo *et al.*, also studying HY zeolites dealuminated by steaming, found that the strength of intermediate sites decreased with increased dealumination for Si/Al ratios from 8 to greater than 100 (*9*). Shi *et al.* measured the strength of HY zeolites dealuminated by treatment with $SiCl_4$ for Si/Al ranging from 4.2 to 37.1, and they also found a decrease in the number of intermediate strength sites with increasing dealumination (*10*). As the Si/Al ratio was increased the initial heat of adsorption first increased and then passed through a maximum at a Si/Al ratio equal to 37. The heats of adsorption on Brønsted acid sites passed through a maximum at a Si/Al ratio equal to 9.5. Mitani *et al.,* studied HY zeolites dealuminated by ethylenediaminetetraacetic acid (H_4EDTA) for Si/Al ratios from 2.5 to 5.1. In this range, they found a moderate increase in the initial heat (up to 170 kJ/mol for pyridine adsorption) and the heat characteristic of the intermediate strength sites with increasing dealumination (*11*). The heat of pyridine adsorption on intermediate strength Brønsted sites ranged from 145 to 160 kJ/mol in good agreement with the values found in the present study.

The decrease in Brønsted acid strength with steam treatment is intriguing in light of the work of Beaumont and Barthomeuf (*34*) which suggests that Y zeolites containing 35 or fewer Al_F/uc have a single strong acidity; i.e., the Brønsted acid strength should remain constant. Such constant strong acidity would be expected when a framework Al has no next nearest Al neighbors (*35*). Wachter (*36*) using statistical calculations and Barthomeuf (*37*) using topological density theory obtain Si/Al_F values of 7 and 6.8 respectively at which point Al_F would have 0 next nearest neighbors. Y zeolites with higher Si/Al_F values would, therefore, be expected to have constant Brønsted acid strength. Our results, however, indicate that as we dealuminate via steaming and progress from an Si/Al_F value of 5 for HYC to 80 for HY60, the average strength of the Brønsted acid sites decreases from about 160 kJ/mol to about 133 kJ/mol. We therefore suggest that the origin of this decrease in Brønsted acid strength may be related to the presence of nonframework aluminum.

The above suggestion may be rather controversial. For example, Macedo *et al.* (*9, 28*) suggested that Brønsted acid sites are poisoned by cationic nonframework Al species. These authors showed that selective acid leaching of steamed catalysts significantly increased cyclohexene conversions (hydride ion transfer and isomerization) suggesting that such a treatment eliminated the poisoning Al species allowing the strong Brønsted sites to be available for reaction. In contrast, however, Sohn *et al.*, suggested that cationic Al in dealuminated Y zeolite enhanced acidity and hexane cracking rates (*33*), and Beyerlein *et al.* noted the same for isobutane reactions (*38*). At this time we can only speculate about the reason for the decrease in Brønsted acid strength with severe steam treatment. Brønsted acid strength should decrease if the charge on framework oxygen increases. Barthomeuf and de Mallman (*39*) suggest that since a framework oxygen is not mobile the charge on each oxygen is localized and is sensitive to structural effects such as lattice distortion and location of cations. Accordingly, we spectulate that in our case the presence of nonframework Al species has an effect of increasing the framework oxygen charge.

The extent to which localized framework distortions caused by steaming affect acid strength needs to be investigated.

It may be argued that steam treatment may create weak Brønsted acid sites on the amorphous part of the catalyst obtained from the destroyed Y zeolite, and the low average Brønsted acidity we measure may be due to the presence of a large number of these weak sites and a few strong framework sites associated with isolated Al_F. However, microcalorimetry shows few, if any strong Brønsted acid sites near 160 kJ/mol for HY15 or HY60. Furthermore, the linear relationship between Al_F and the number of Brønsted acid sites provides evidence against the generation of new Brønsted acid sites by nonframework aluminum.

The fact that steaming decreases the strength of Brønsted acid sites has important implications since it cannot be assumed, as in Ref. (*40*), that steam dealuminated Y-based FCC catalysts with 0 next nearest Al_F neighbors necessarily possess strong Brønsted acidity. In general, we expect that changes in selectivity during FCC should take into account the effect of decreasing Brønsted acid strength via steam treatment as proposed in Ref. (*41*).

Comparison of FCC Catalysts and Amorphous Silica–Alumina

Silica–alumina has a relatively large number of acid sites per gram (Table 2) in comparison to the steamed zeolite samples. Furthermore the number of Brønsted acid sites for SAC represents nearly half of the total number of sites, a proportion higher than all but the nonsteamed Y zeolite sample. However, the average strength of the Brønsted acid site for SAC is lower than for HY, HYC, HY0.25 and HY2, and it is only slightly higher than for the most severely steamed Y samples. Silica–alumina which has 30% more Brønsted acid sites and the same number of Lewis acid sites as HY0.25 has a 40% lower MAT activity than the Y catalyst. On comparing SAC and HY2, we note that SAC has significantly more Brønsted and Lewis acid sites, yet these two catalysts have similar MAT activities. Importantly, while these two samples have the same initial heats of pyridine adsorption, i.e., Lewis acid strengths, HY2 has stronger Brønsted acidity. The importance of Brønsted acid sites for catalytic cracking is well documented in the literature. The consistent picture which emerges from the present study is that amorphous silica–alumina has a large number of Brønsted acid sites but that stronger Brønsted acid sites of Y zeolites are responsible for higher catalytic activity in gas–oil cracking.

CONCLUSIONS

Commercial steamed FCC catalysts show complex acidity features. We have identified heats of pyridine adsorption in the range of 130–180 kJ/mol, in agreement with the literature, to be associated with Brønsted acid sites. Steaming rapidly decreases the number of Brønsted acid sites; steaming at 1060 K for 0.25 h results in the loss of over 60% of the Brønsted acidity but only 10% of the Lewis acidity. More importantly, we find that with increased steaming there is a measurable decrease in the strength of Brønsted acid sites. Silica–alumina has a relatively large proportion of Brønsted acid sites but with strength lower than all but the most severely steamed samples. The low gas oil cracking activity for silica–alumina indicates the importance of Brønsted acid strength in catalytic cracking and is consistent with acidity measurements. We also note that the adsorption and decomposition of 2-propylamine, as demonstrated by Gorte and co-workers (*26, 42–44*), yields results consistent with the Brønsted acid site populations measured in this study.

This study has demonstrated that microcalorimetry, infrared spectroscopy, and pyridine adsorption may be used together effectively to probe acid site strengths and obtain relative populations of Brønsted and Lewis acid sites. In general, a combination of measurement techniques is essential to describe the acidity characteristics of complex commercially important FCC catalysts.

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