JOURNAL OF CATALYSIS **138**, 714–720 (1992)

Isopropylamine Adsorption for the Characterization of Acid Sites in Silica–Alumina Catalysts

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Received May 4, 1992; revised June 29, 1992

The adsorption and reaction of isopropylamine has been studied using temperature-programmed desorption (TPD) and thermogravimetric analysis (TGA) on a series of silica–alumina catalysts as a function of alumina content, and the results have been correlated with cracking activities for *n*-hexane. The TPD–TGA curves on the amorphous silica–aluminas exhibit similar features to that observed on high-silica zeolites in that a well-defined feature is observed which desorbs as propene and ammonia between 575 and 650 K. This desorption feature appears to be due to strong Brønsted sites which are not present on either pure silica or alumina. The concentration of these sites increases in a regular manner with Al content and correlates well with the *n*-hexane cracking activity. This suggests that the TPD–TGA measurement of isopropylamine is a useful probe of the catalytically active sites on amorphous silica–aluminas. © 1992 Academic Press, Inc.

INTRODUCTION

Amorphous silica–aluminas have been used as acid catalysts for many years for important industrial reactions such as catalytic cracking, isomerization, and alkylation of hydrocarbons (*1–3*). Although zeolites have replaced amorphous catalysts for many processes, amorphous silica–aluminas are still widely used as the major matrix component in zeolite-containing, fluid-catalytic-cracking (FCC) catalysts; and the surface acidity and activity of these materials are still of great importance (*2*). However, characterization of acidity in amorphous catalysts is difficult. While infrared spectroscopy of adsorbed pyridine has demonstrated the presence of Brønsted and Lewis sites in these materials (*3–5*), quantification of site concentrations is nontrivial, particularly since water exposure is reported to cause the conversion of Lewis to Brønsted sites (*3*). Temperature-programmed desorption of ammonia is also widely used for determining site concentrations, but the complexities of the desorption process (*6, 7*) and of silica–alumina surfaces themselves make it difficult to identify the desorption features which are responsible for catalytic activity. Other techniques, including NMR (*8*) and microcalorimetric measurements of base adsorption (*9–11*), have been used successfully to examine the acidity of silica–aluminas; but these techniques are too difficult and expensive for routine analysis.

A promising approach to determining the concentrations of catalytically active sites is TPD of reactive probe molecules like simple amines. On high-silica zeolites, it has been demonstrated that well-defined adsorption complexes, corresponding to one molecule per framework Al, can be easily identified in TPD (*12–15*). In the case of isopropylamine, the adsorption complex associated with Al sites decomposes to propene and ammonia between 575 and 650 K and is easily separated from physisorbed amines which desorb unreacted. Other amines, such as *t*-butylamine and *n*-propylamine, also react to olefin and ammonia products at a coverage of one molecule/Al (*14*); however, the temperature at which decomposition occurs varies depending on the alkyl group, and isopropylamine amine was found to be the

0021-9517/92 $5.00

most convenient. The decomposition of simple amines appears to occur via a reaction similar to the Hofmann elimination reaction, which implies that the reacting species is an alkylammonium ion and that the site being probed is a Brønsted site. Since the number of molecules which decompose on high-silica zeolites is identical to the number of framework Al atoms, the reaction is probing only the Brønsted sites associated with tetrahedral, framework Al (*15*). Furthermore, the technique is capable of distinguishing the strong Brønsted sites even on complex, FCC catalysts (*16*). Since Brønsted sites are believed to be the most important for catalytic cracking (*1*, *2*), this is an added benefit.

In this paper, we demonstrate the TPD–TGA of isopropylamine is useful for characterizing amorphous silica–alumina catalysts. We show that the concentration of sites which decompose isopropylamine in TPD–TGA measurements correlates well with the cracking activities of the catalysts.

EXPERIMENTAL

The TPD–TGA experiments were carried out simultaneously in a vacuum chamber with a base pressure of $\sim 1 \times 10^{-7}$ Torr. Between 15 and 30 mg of sample were placed in the pan of a Cahn microbalance, heated in vacuum to 750 K, cooled to room temperature, and exposed to 10 Torr of isopropylamine until no further weight changes were observed. The samples were then evacuated for 2 hr, after which the temperature was ramped at 10 K/min while a mass spectrometer monitored the partial pressures of desorbing species. The only products observed in desorption were isopropylamine (m/e = 44, 41, and 17), propene (m/e = 41), and ammonia (m/e = 17). For each sample, all of the isopropylamine was completely removed after heating to 750 K, and the weight of each sample returned to its initial value. The amounts of propene and ammonia leaving the sample were obtained by integrating the peak at m/e = 41 between 575 and 650 K, using the microbalance to calibrate the peak areas. Further details on the equipment and adsorption procedures have been discussed elsewhere (*12–15*).

Catalytic activity measurements were made in a differential, tubular reactor at atmospheric pressure. Approximately 150 mg of the waferized catalyst was centered in a stainless-steel tube, with the remaining volume having been filled with quartz chips to reduce the residence time. The feed was introduced into the reactor using a nitrogen carrier flowing through a saturator containing *n*-hexane (99%, Baker Instra-Analyzed) maintained at 273 K in an ice bath. Before introducing the hydrocarbon feed and between reaction measurements, dry nitrogen was passed through the reactor. All measurements were made at 650 K and the time that the catalyst was exposed to reactant was short enough so that deactivation was found to be negligible. The product stream was analyzed, on-line with a gas chromatograph and conversions were always less than 2%. For these conditions, the conversions increased linearly with residence time, so that the rates could be obtained from the slope of a plot of conversion versus space time.

Two types of silica–alumina samples were examined. The first set of samples were prepared by precipitation of alumina onto commercially available, TriSyl® silica to concentrations of 3.07, 5.01, and 9.76 wt% alumina. For example, the 3.07 wt% sample was prepared by dissolving 5.23 g of $Al_2(SO_4)_3 \cdot 18H_2O$ in 400 cc H_2O, followed by addition of 57.1 g (hydrous basis) of TriSyl (TV = 65%). Alumina was precipitated by the addition of 30 wt% aqueous ammonia to the stirred mixture until the pH of the solution was approximately 8. The solids were isolated by filtration and washed thoroughly. The products were then calcined in air at 1030 K for 2.5 hr. Elemental analysis showed that some alumina was lost in the preparation and indicated that there were virtually no sulfate ions present on these samples (<0.1 wt% sulfates). The cogel samples with nominal alumina contents of

TABLE 1

Physical Characteristics of the Samples Used in this Study

Sample	Alumina content (wt%, solids basis)	Sulfates (wt%)	Pore volume (cm^3/g)	BET surface area (m^2/g)
Alumina				180
3.07% alumina	3.07	<0.1	1.37	366
5.01% alumina	5.01	<0.1	1.30	356
9.76% alumina	9.76	<0.1	1.31	342
13% cogel	12.42	0.26	0.88	340
25% cogel	26.43	0.54	0.76	325

13 and 25% were commercial Davison silica–alumina catalysts. These samples were prepared by gelling sodium silicate in the presence of an alumina source, followed by washing and calcination in air at 810 K for 2.5 hr. The alumina was an Engelhard, reforming-grade, γ-Al_2O_3, with a BET surface area of approximately 180 m^2/g. Besides alumina, it contained 150 ppm Fe and 470 ppm TiO_2. The properties of each of the samples which were studied are given in Table 1.

RESULTS AND DISCUSSION

Figures 1 and 2 show the TPD–TGA results for isopropylamine on silica and alumina. For silica, only a small amount remains on the sample after evacuation and most of this desorbs as unreacted isopropylamine below 450 K. On alumina, the coverage of amine remaining after evacuation is substantial, ~26 mg/g. Using the BET surface area, one can show that this coverage corresponds to ~1.5 × 10^{18} molecules/m^2, a coverage which approaches that expected for a monolayer of the amine. This is also close to the site density for alumina reported by Pines and Haag (*17*). Upon heating, most of the isopropylamine desorbs unreacted in a broad band between 350 and 600 K. (The apparent peaks at 450 and 475 K are due to fluctuations in the heating rate.) A small fraction of the amine also decomposes between 575 and 650 K.

We suggest that the majority of the isopropylamine on the alumina interacts with Lewis-acid sites and that this accounts for the broad, unreacted, desorption feature. In a previous TPD study of 2-propanol on this same alumina, the coverage after evacuation was again ~2 × 10^{18} molecules/m^2 (*18*). In the case of 2-propanol, most of these molecules decomposed to propene and water prior to desorption. Therefore, it appears

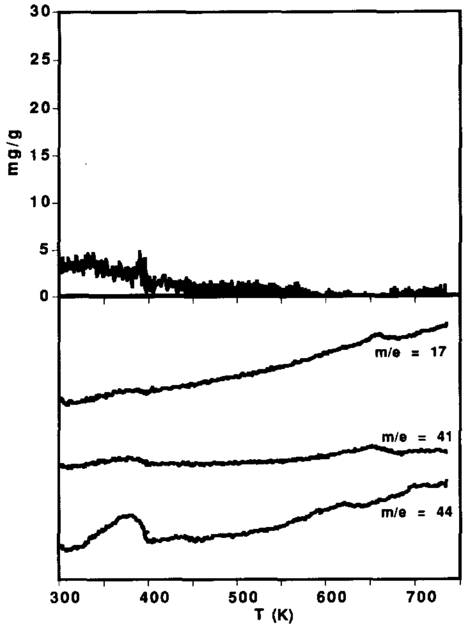

FIG. 1. TPD–TGA for isopropylamine from silica. The features in the TPD correspond to isopropylamine (*m*/*e* = 44, 41, and 17), propene (*m*/*e* × 41), and ammonia (*m*/*e* × 17). Baselines for each of the peaks have been shifted in order to separate the features.

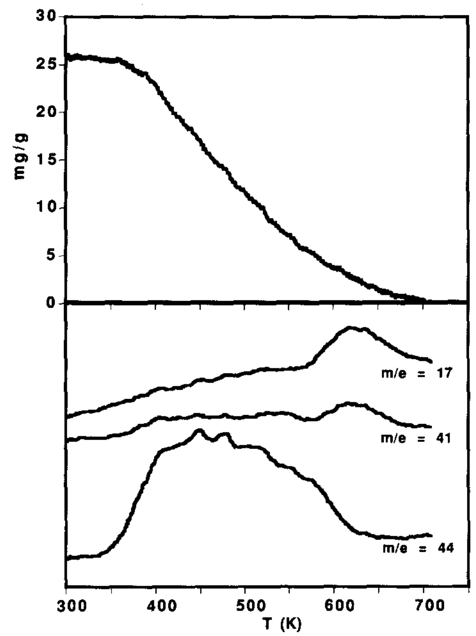

FIG. 2. TPD–TGA for isopropylamine from alumina.

that isopropylamine and 2-propanol interact with the same sites, but that these sites are not capable of catalyzing the decomposition of isopropylamine. The small amount of isopropylamine which decomposes in TPD–TGA may arise from Brønsted sites associated with impurities like Fe or Ti in the alumina sample (*5*). The concentration of these sites is only 29 μmol/g. While the decomposition temperature for isopropylamine on the alumina is the same as that observed on high-silica zeolites (*12–15*), it has been shown previously that the reaction is limited by the decomposition rate of the isopropylammonium ion in a reaction similar to the Hofmann elimination (*19*), which implies that the decomposition temperature is not affected by the substrate so long as the acidity is strong enough to maintain the ion up to that reaction temperature. Therefore, the strength of the sites responsible for the feature between 575 and 650 K on alumina are likely to be much different from those sites responsible for the same feature on zeolites.

TPD–TGA curves for the silica–alumina samples are similar to that for alumina, except that the amounts of reacting isopropylamine are much higher. This is demonstrated by the curves for the 13% cogel sample in Fig. 3. TPD–TGA curves for the other silica–aluminas were qualitatively similar, differing only in the quantities which desorbed unreacted below 600 K and which decompose between 575 and 650 K. The results are summarized in Table 2. From Table 2, it can be seen that the amount of isopropylamine desorbing as propene and ammonia varies considerably with the alumina content and sample preparation procedure, with the site concentration going from 42 μmol/g for the 3.07% alumina sample to 108 μmol/g for the 25% alumina cogel. The amount of isopropylamine which desorbed unreacted increased monotonically with the alumina content but, except for the 25% cogel sample, was less than the amount which desorbed from the alumina sample.

It is interesting to consider the 3.07% alu-

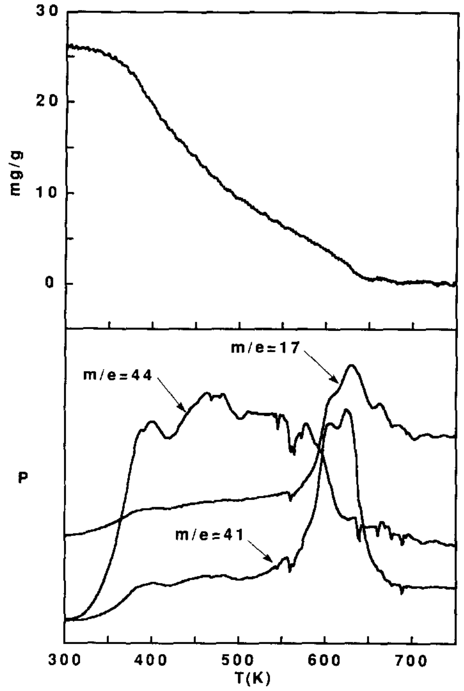

FIG. 3. TPD–TGA for isopropylamine from the Davison 13% cogel.

TABLE 2

Summary of TPD–TGA Results

Sample	Alumina content (μmol/g)	Isopropylamine (unreacted from TPD) (μmol/g)	Isopropylamine (unreacted from TPD) (sites/m^2)	Propene (reacted from TPD) (μmol/g)	Propene (reacted from TPD) (sites/m^2)
Silica		20		~5	
Alumina		440	1.5×10^{18}	29	0.97×10^{17}
3.07% alumina	602	170	0.28×10^{18}	42	0.69×10^{17}
5.01% alumina	982	250	0.42×10^{18}	63	1.1×10^{17}
9.76% alumina	1910	270	0.48×10^{18}	56	0.99×10^{17}
13% cogel	2440	340	0.60×10^{18}	97	1.7×10^{17}
25% cogel	5180	460	0.85×10^{18}	108	2.0×10^{17}

mina sample in order to understand the nature of the different adsorption sites which are present on these materials. Since very little adsorption occurred on the pure silica, alumina must be responsible for the sites on this sample. The Al content is approximately 602 μmol/g, which implies that the sites which are responsible for isopropylamine decomposition in TPD–TGA are created by a relatively small percentage of the Al atoms. For reasons stated earlier, isopropylamine decomposition appears to occur at strong Brønsted sites; therefore, it is probable that decomposition of the amine occurs at sites generated by tetrahedral Al in a silica environment, probably similar to those created by framework Al in a zeolite.

The isopropylamine which desorbs unreacted at lower temperatures may be interacting with sites similar to those present on pure alumina and might include weak Brønsted sites and Lewis sites. On a surface-area basis, the 3.07% alumina sample has a strong Brønsted-site concentration of ~0.07 × 10^{18} sites/m^2, with weaker adsorption sites present at a concentration of ~0.28 × 10^{18} sites/m^2. Similar numbers for each of the silica–aluminas have been tabulated in Table 2. Among the silica–aluminas, the 25% cogel sample exhibits the highest coverage of unreacted isopropylamine, with a specific coverage corresponding to slightly less than 60% of that for alumina. Therefore, the amount of isopropylamine that desorbs unreacted under these conditions is plausibly proportional to the fraction of the surface that is chemically similar to bulk alumina.

The decomposition of amines on silica-aluminas during TPD has been observed by others (*20, 21*). One group reported that the activity of the catalysts increased linearly with the number of sites which were able to cause amine decomposition (*21*). In order to determine the relationship between catalytic activity and our TPD results, *n*-hexane cracking measurements were performed on all of the samples. For the conditions used in this experiment, the conversions on each sample were found to increase linearly with space time, with the line going through the origin. Rates determined from the slope of these lines are reported in Table 3. It can

TABLE 3

Summary of Cracking Results for *n*-Hexane

Sample	Reaction rate (mol/sec g)
Silica	0.67×10^{-10}
Alumina	0.92×10^{-10}
3.07% alumina	3.59×10^{-10}
5.01% alumina	7.56×10^{-10}
9.76% alumina	6.33×10^{-10}
13% cogel	7.88×10^{-10}
25% cogel	7.97×10^{-10}

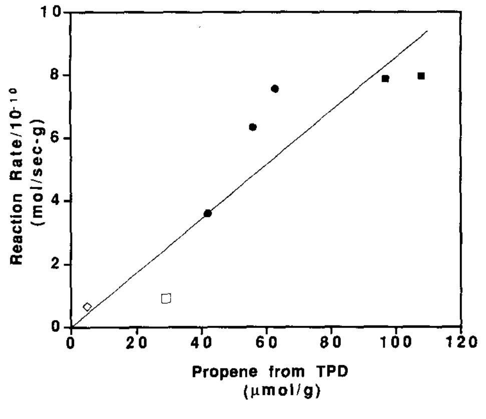

FIG. 4. Plot of the *n*-hexane cracking activity as a function of the site concentration as determined from TPD–TGA measurements. Silica (◇), alumina (□), impregnated silicas (●), and cogels (■) are designated separately.

be seen that the activities for each of the silica–alumina catalysts were considerably higher than that for either silica or alumina. Furthermore, the rates increased monotonically with the concentration of sites which decompose isopropylamine in TPD–TGA. This is shown in Fig. 4, which is a plot of *n*-hexane cracking activity as a function of site concentration. Because it is known from zeolite work that the lattice structure can affect the rates observed for *n*-hexane cracking and because the microscopic structure near each site on the silica–aluminas will be slightly different, it is probably not possible to obtain a constant turnover frequency for the sites in amorphous silica–aluminas. In particular, the points in Fig. 4 seem to indicate that the average rate/site on the supported-alumina and the cogel samples are different, probably due to differences in the structure of the two sets of materials. However, data from the various samples do follow similar trends so that an average turnover frequency can be determined from the slope of the best-fit line through all the points. This line gives an average rate for *n*-hexane cracking per site of ~9.3×10^{-6}/sec at 650 K for a partial pressure of 41 Torr.

It is interesting to compare this rate to those measured in zeolites. On H-ZSM-5 at 623 K, the turnover frequency is reported to be 2.2×10^{-4}/sec (*22*), which is more than 20 times the rate observed on the silica–aluminas at 650 K. Since *n*-hexane cracking can be autocatalytic and we performed our reaction measurements on the silica–aluminas at very low conversions in order to avoid the autocatalytic behavior (*23*), this comparison may underestimate the true activity of the silica–aluminas; however, it is clear that the concentrations of Brønsted-acid sites, determined by the amount of amine which decomposes in TPD–TGA measurements, are sufficient to explain the cracking activity that we observe in the silica–aluminas, even if it is acknowledged that the specific activity per site is considerably higher on zeolites. This strengthens the argument that it is Brønsted acidity that is primarily involved in alkane cracking on silica–aluminas. TPD–TGA of isopropylamine appears to be a good method for measuring the concentrations of these sites.

CONCLUSIONS

TPD–TGA of isopropylamine is a useful method for characterizing the acid-site concentrations in amorphous silica–alumina catalysts. Isopropylamine decomposes to propene and ammonia between 575 and 650 K at strong, Brønsted-acid sites. The concentration of Brønsted-acid sites determined from this technique correlates well with *n*-hexane cracking activities.

ACKNOWLEDGMENTS

JGT and RJG acknowledge the support of the DOE, Basic Energy Sciences, Grant DOE DE-FG02-85 13350. We also thank Andy Biaglow for his assistance in this work.

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