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2-Propanamine Adsorption on a Fluid Catalytic Cracking Catalyst[1]

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We have examined temperature-programmed desorption (TPD) and thermogravimetric analysis (TGA) of 2-propanamine on a fluid catalytic cracking catalyst as a function of steam deactivation time and compared the results to the activity for gas-oil cracking. The TPD–TGA results for the FCC catalyst are similar to results obtained on high-silica zeolites and show ammonia and propene desorbing in a well-defined feature between 575 and 650 K. The sites responsible for this desorption feature appear to be acid sites associated with framework Al in the zeolite phase. The concentration of these sites decreases steadily with steam deactivation and correlates very well with the activities for gas-oil cracking. © 1991 Academic Press, Inc.

INTRODUCTION

Commercial fluid catalytic cracking (FCC) catalysts are complex materials composed of a crystalline zeolite Y and usually a clay or amorphous silica–alumina matrix. Since these materials are used for acid-catalyzed reactions, it is important to characterize the acid sites which are present, so that the effect of synthesis and pretreatment conditions can be determined. Typical methods which are used in characterizing these materials include infrared (IR) spectra of adsorbed pyridine for distinguishing Lewis and Brønsted acid sites (*1*, *2*), temperature-programmed desorption (TPD) of ammonia for determining site densities and strengths, and reactivity measurements such as the micro-activity test (MAT) for determining catalytic activity (*3*).

In this paper, we discuss the use of base adsorption for measuring acid-site densities and strengths. While TPD of ammonia is widely used for this, the interpretation is not trivial. Diffusion and readsorption can shift desorption features significantly (*4*, *5*), and overlapping desorption peaks are often difficult to deconvolute. Even in high-silica zeolites like H-ZSM-5, desorption features corresponding to ammonia which is in excess of the number of Al atoms in the zeolite frequently overlap those features which are associated with the Al sites (*6*), suggesting that TPD may overcount the number of acid sites present (*7–9*).

Recently, studies of 2-propanamine adsorption in H-ZSM-5 and other high-silica molecular sieves have demonstrated that well-defined adsorption states, corresponding to one 2-propanamine per framework Al, can be easily identified with a combination of TPD and thermogravimetric analysis (TGA) measurements (*10–12*). Since the number of acid sites is directly related to the Al concentration in H-ZSM-5 (*13*), desorption of 2-propanamine may be useful for measuring acid-site concentrations in unknown materials. Furthermore, the amine molecules associated with the 1 : 1 complex undergo an acid-catalyzed decomposition to propene and ammonia in TPD, verifying that catalytic sites are being examined. The decomposition of the 2-propanamine molecules associated with the 1 : 1 state appears to occur through a 2-propylammonium ion intermediate (*14*), which implies that the de-

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sorption feature should be sensitive only to Brønsted acid sites. Since Brønsted acid sites are believed to be most important for catalytic cracking (*15, 16*), this is an added benefit. Finally, the technique has advantages over determination by lattice parameters in that materials with different structures can be compared.

In this paper, we demonstrate that TPD–TGA of 2-propanamine appears to be very useful for determining acid-site densities for a commercial FCC catalyst. We show that the TPD–TGA results correlate very well with the cracking activity of the catalyst.

EXPERIMENTAL TECHNIQUES

The FCC catalyst used in this study was made by Engelhard's *in situ* crystallization technique (*17*). The catalyst was synthesized by carrying out a partial crystallization of calcined kaolin, so that the resulting material consisted of approximately 11% faujasite in a clay matrix. The material was calcined and then ion exchanged with NH_4^+ prior to further pretreatment to reduce the Na_2O content to 0.3 wt% of total material. Samples were then deactivated in 760-Torr steam at 1060 K for various lengths of time. One sample, HY-C, was not steamed and was used after calcination for 2 h at 823 K. A nitrogen BET surface area of the whole sample minus the surface area of pores >2-nm diameter obtained by replotting the adsorption data as a "*t*" plot gave the surface area of pores <2-nm diameter. This latter area is mainly the surface area of the zeolite component. Unit cell size measurements via X-ray diffraction were performed using an Si standard and a procedure similar to ASTM D3942-85. Catalytic performance was obtained from MAT activities, which are a measure of a catalyst's activity for cracking a standard mid-continent gas oil. The gas oil had a molecular weight of 264 and a final boiling point of 812 K. The experimental conditions differed from the ASTM Method 3907. Gas oil, 1.2 g, was delivered in 48 s over 6 g of catalyst at 761 K. Conversion of gas oil was defined as the sum of the yields of gas, coke, and gasoline, the latter being obtained via simulation distillation chromatography with a cut-off for gasoline being 489 K. MAT activity is conversion/(100 − conversion). Table 1 lists the steaming times which were used, along with the resulting BET surface areas, zeolite surface areas, unit cell volumes obtained from X-ray diffraction for the faujasite component, and the number of Al atoms/unit cell in the faujasite crystals (Al_F). Table 2 lists the MAT activities obtained for these samples.

The TPD and TGA experiments were carried out simultaneously using a microbalance mounted within a high-vacuum chamber. The system could be evacuated with a turbomolecular pump to a base pressure below 1×10^{-7} Torr, and the desorbing gases could be monitored using a quadrupole mass spectrometer interfaced to a microcomputer. Approximately 20 mg of catalyst was spread over a flat sample pan to avoid bed effects in desorption (*4, 5*). Catalyst samples were first heated to 750 K in vacuum, cooled to 295 K, and then exposed to 2-propanamine by admitting ~10 Torr of the vapor until no further weight changes were observed in the catalyst. The samples were then evacuated for ~2 h to remove some of the weakly adsorbed amine before beginning a TPD–TGA experiment. The only products observed in desorption were 2-propanamine (m/e = 44, with additional peaks at m/e = 41, and 17), propene (m/e = 41), and ammonia (m/e = 17). All of the 2-propanamine was completely removed in the TPD–TGA measurement, and the sample weight returned to its initial value before 2-propanamine exposure. The heating rate during desorption was maintained at 10 K/min by a feedback controller. The amounts of propene and ammonia leaving the sample were obtained by integrating the TPD peaks between 575 and 650 K, using the TGA to calibrate the peak areas. Further details on

TABLE 1

Physical Characteristics of the Samples Used in the TPD–TGA and Reaction Studies

Sample	Steaming time (h)	BET area (m^2/g)	Area ($d < 2$ nm) (m^2/g)	Unit cell size (nm)	Al_F/uc[a]
HY-C	–	195	82	2.455	33.4
HY-0.25	0.25	175	66	2.436	13.1
HY-1.5	1.5	167	60	2.432	8.8
HY-2.0	2.0	162	58	2.432	8.8
HY-4.0	4.0	159	53	2.428	4.5
HY-15.	15.0	139	44	2.427	3.4
HY-60.	60.0	119	36	2.426	2.4

[a] Calculated from the unit cell size and correlation in J. R. Sohn, S. J. DeCanio, J. H. Lunsford, and D. J. O'Donnell, *Zeolites* **6,** 225 (1986).

the equipment and adsorption procedures have been discussed previously (*10–12*).

RESULTS AND DISCUSSION

The TPD–TGA results for 2-propanamine on all of the samples showed several common features. This is demonstrated in Fig. 1(a) and 1(b), which show TPD–TGA curves for the HY-C sample and a sample which had been steamed for 15 h. Below approximately 575 K, only unreacted 2-propanamine is observed in a very broad desorption feature. Between 575 and 650 K, propene and ammonia evolve simultaneously. The results for samples which had been steamed for other lengths of time differed only in the amounts desorbing in each feature, as shown in Table 2. The amount of unreacted 2-propanamine desorbing below 575 K depended on the evacuation time but, for equivalent evacuation times, roughly follows the BET surface area, suggesting that this is due to sites which are rather nonspecific. However, the amount of propene and ammonia desorbing from the sample is a very strong function of the deactivation time. More than 15 times as much 2-propanamine reacted on the HY-C sample as reacted on the sample which had been steamed for 60 h. HY-60.

It is interesting to compare the desorption curves in Fig. 1 to previous results on high-silica H-ZSM-5, H-ZSM-12, and H-mordenite zeolites (*11*). On these high-silica zeolites, all unreacting 2-propanamine desorbed between 350 and 450 K. It has been suggested that this low-temperature feature may be due to interaction between the amine

TABLE 2

Summary of MAT Activities and TPD Results for FCC Catalysts after Various Steaming Times

Sample	MAT activity	2-Propanamine in TPD (mmol/g)	Propene in TPD (mmol/g)
HY-C	6.94	0.317	0.190
HY-0.25	4.13	0.236	0.079
HY-1.5	3.35	0.138	0.050
HY-2.0	2.85	0.110	0.053
HY-4.0	1.91	0.057	0.036
HY-15	1.23	0.097	0.017
HY-60	0.81	0.069	0.011

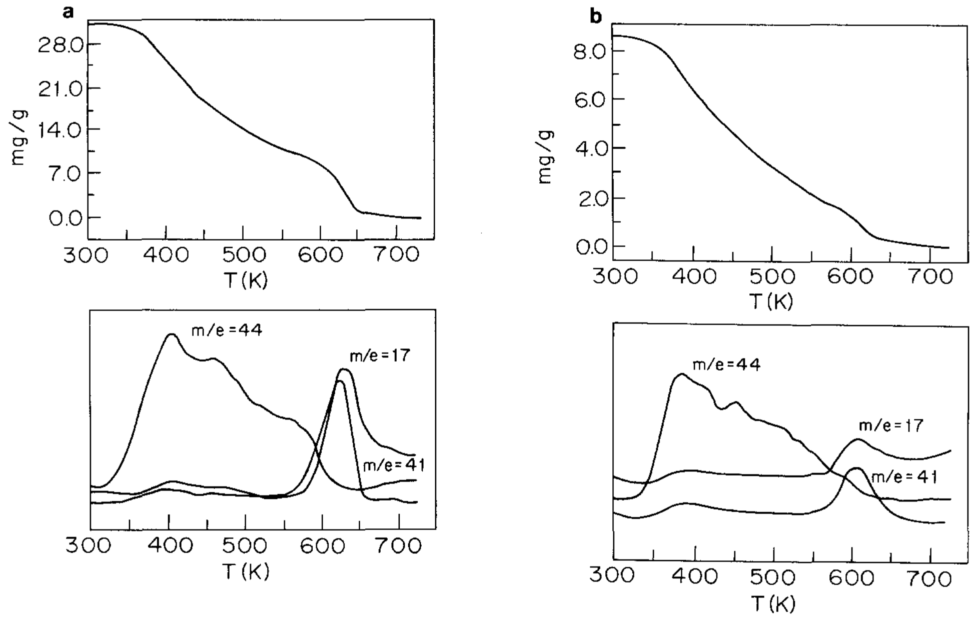

FIG. 1. TPD–TGA results for 2-propanamine adsorption on the (a) HY-C and (b) HY-15 samples. The intensities of the mass spectrum signals are arbitrary and correspond to 2-propanamine (*m/e* = 44), propene (*m/e* = 41), and ammonia (*m/e* = 17).

and internal silanols since it was observed even for materials with very low Al contents and seemed to vary with the apparent crystallinity of the sample (*12*). Above 450 K on the high-silica samples, only propene and ammonia were seen desorbing between 575 and 650 K, the same temperature range observed in this present study of an FCC catalyst. The temperature at which the 2-propanamine decomposes to propene and ammonia is probably not directly related to the strength of the sites. This temperature was found to be the same in both H-[Fe]-ZSM-5^{6} and H-[Ga]-ZSM-5^{12} as on Al zeolites, even though the strengths of the sites in these materials is not the same. The reaction appears to require formation of the 2-propylammonium ion; however, the main role of the Brønsted acid site in the decomposition, besides protonation of the amine, is to simply maintain the 2-propylammonium ion up to the temperature at which reaction occurs (*14*). This implies that the 2-propanamine molecules corresponding to the decomposition feature are associated with acid sites capable of maintaining the 2-propylammonium ion up to the decomposition temperature. On H-ZSM-5, H-ZSM-12, and H-mordenite, the concentration of these Brønsted acid sites is identical to the framework Al concentration (*10, 11*).

Application of previous papers on high-silica zeolites to the present study is apparent. The decomposition feature between 575 and 650 K on the FCC catalysts appears to be due to Brønsted acid sites associated with tetrahedral Al. The concentration of these sites varies significantly with steaming time and correlates well with the activity of the catalysts. This is shown in Fig. 2(a), where the MAT activity has been plotted against the relative amounts of 2-propanamine in the decomposition feature. Clearly, there is a strong correlation between the activity and the concentration of sites which decompose 2-propanamine. While the number of sites counted in TPD–TGA of 2-propanamine may not include all or only those sites which

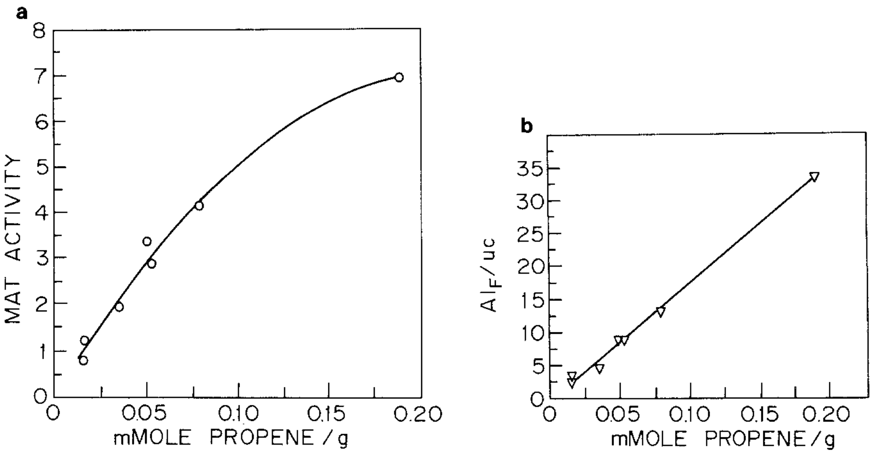

FIG. 2. (a) Plot of the MAT activities of the samples as a function of the amount of 2-propanamine reacting to propene and ammonia in TPD. (b) Plot of the framework Al content (Al_F/uc) as a function of the amount of 2-propanamine reacting to propene and ammonia in TPD.

are active, the number must be related. Since the MAT activity is not a simple reaction rate, one should not expect the relation between activity and the number of active sites to be linear.

It is also interesting to plot the Al concentration in the crystalline phase, as determined by X-ray diffraction, as a function of the concentration of sites capable of decomposing 2-propanamine. This is shown in Fig. 2(b). While the relationship appears to be linear, it is important to note that steam deactivation reduced the fraction of the crystalline phase as well as the framework Al content in the crystalline phase, Al_F/uc. Zeolite surface area measurements in Table 1 imply that the crystallinity or zeolite index has been reduced by a factor of ~2, from 11% initially to ~5% after 60 h steaming, whereas dealumination as seen by Al_F/uc changes by a factor of approximately 14. However, the concentration of active sites in catalytic cracking is almost certainly related to the framework Al concentration (*18–20*). (Figure 2(b) implies that the sites counted in the TPD–TGA measurements are also related to Al_F/uc. Comparison of the absolute concentrations of sites and Al_F/uc are in rough agreement. For the HY-C sample, the results indicate that the concentration of sites which react to 2-propanamine is approximately half of Al_F/uc. Since the number of Brønsted acid sites could be less than the number of Al_F for a number of reasons, including inactivity of Al's with Al next-nearest neighbors (*21*), Al_F associated with Lewis acid sites, the presence of other cations besides protons for charge balance, etc., we suggest that all of the sites probed in our TPD–TGA measurements are, in fact, associated with active framework Al atoms.

It should be noted that the peak for unreacted 2-propanamine in our measurements is broader and extends to considerably higher temperatures on the FCC catalyst compared to results on high-silica zeolites. Since peak temperatures in TPD are strongly influenced by mass transfer effects, this may be due to morphological effects as well as additional weak acid sites on the FCC catalyst. In either case, the sites responsible for desorption of unreacted 2-propanamine do not appear to be important for catalytic activity under the conditions of our experiments.

To check if the choice of probe molecule strongly influenced the results, we also performed TPD–TGA measurements with pyridine on the HY-C and HY-60 samples. On H-ZSM-5, it has been shown that pyridine in excess of one molecule/Al desorbs below 450 K, leaving a 1 : 1 species which is bound to a Brønsted acid site (*14, 22*). The 1 : 1 species desorbs above 700 K. On the FCC catalysts, we were unable to observe any well-defined desorption features, only a steady weight change over the whole temperature range. However, at an arbitrary temperature of 550 K, the moles of pyridine remaining on the catalyst matched the moles of 2-propanamine which decomposed on both samples, suggesting that both probe molecules were examining the same sites. The results in this paper strongly suggest that these sites are responsible for the catalytic activity of the FCC catalysts and further work is underway in our laboratories to characterize the nature of these sites.

CONCLUSIONS

Combined temperature-programmed desorption/thermogravimetric analysis measurements of 2-propanamine appear to be a very useful method for characterizing the acid site concentration of complex FCC catalysts. The amount of 2-propanamine decomposing to propene and ammonia is strongly affected by steam deactivation and correlates well with both the MAT activity of the catalyst and the framework Al concentration of the faujasite component of the catalyst.

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