

CHARACTERIZATION OF ACIDIC PROPERTIES OF MICROPOROUS AND MESOPOROUS ZEOLITE CATALYSTS USING TGA AND DSC

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ABSTRACT

Thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) were applied for characterizing the acidic properties of microporous and mesoporous zeolite catalysts through temperature-programmed desorption (TPD) of *n*-butylamine (*n*-BA) as a base probe molecule. A flow system was designed with heating and evacuation capability for preparing the *n*-BA adsorbed sample. In the TGA, *n*-BA desorption at different temperatures represents the interaction with surface acidic sites of different strength. The acid sites corresponding to base desorption at 100-240°C, 240-340°C, and 340-500°C, were classified as weak, intermediate, and strong acid sites, respectively. DSC indicates the endothermic nature of the differential thermogravimetric peaks (observed from TGA) in the above temperature regimes, confirming the TPD data. The microporous zeolites examined include three proton-form mordenites, three proton-form and metal-ion exchanged Y-zeolites, and four noble metal catalysts supported on mordenite and Y-zeolite. Four mesoporous zeolites were synthesized and examined by the same TPD method. Both the total acidity (mmol/g) and acid strength distribution depend on the zeolite type, Si/Al ratio, and metal loading. Ni and La ion-exchange decreased the strong acid sites. Pt and Pd loading on an HY decreased the strong acid sites but their loading on an H-mordenite had little effect on its strong acid sites. Mesoporous zeolites showed lower acidity and lower fraction of strong acid sites compared to HY and H-mordenites. However, the acidity of mesoporous zeolites strongly depends on the aluminum source compounds used in the hydrothermal synthesis of the zeolites.

INTRODUCTION

Recently, we have initiated a major effort in exploring microporous and mesoporous zeolite catalysts for conversion of polycyclic hydrocarbons related to fuel processing and shape-selective catalysis [Song and Kirby, 1994; Song and Moffatt, 1994; Schmitz and Song, 1994, 1995; Lai and Song, 1995; Reddy and Song, 1995a,b,c; Lai et al., 1995; Schmitz et al., 1995]. For a wide range of fuel processing reactions and shape-selective reactions, zeolite acidity is a key factor affecting activity and selectivity. In the present work, we attempt to characterize the acidic properties of mesoporous and microporous zeolites using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC).

Base molecules adsorb on Bronsted and Lewis acidic sites of solid surface, and can be removed by thermal desorption at elevated temperatures. The desorption temperature depends on the strength of the interaction between the base and the surface acidic sites. A widely used technique for characterizing the acidity of solid surface is temperature-programmed desorption of a base (e.g., ammonia) using thermal conductivity detector [Fernandes et al., 1994; Hunger and Szombathely, 1994]. However, acidity characterization can also be carried out using several other techniques, including infrared spectroscopy [Cannings, 1968; Lefrancois and Malbois, 1971; Ward, 1976; Makarova et al., 1994], nuclear magnetic resonance [Brunner et al., 1994], TGA [Ghosh and Curthoys, 1984], and calorimetry [Chen et al., 1992; Cardona-Martinez and Dumesic, 1992; Parrillo et al., 1994].

In this paper, we report acidity characterization of zeolites by temperature-programmed desorption of *n*-butylamine (*n*-BA) using TGA and DSC as detector. There are two advantages of using *n*-BA with TGA detection. The first one is that, compared to NH₃, *n*-BA is closer in size and length to hydrocarbon molecules, and the acid sites detected by *n*-BA desorption may be practically more useful. The second is that using a higher-molecular-weight base (relative to NH₃) can enhance the sensitivity of the TPD conducted on TGA, since TGA is not as sensitive as TCD. However, these advantages do not come without problems. Possible problems are *n*-BA decomposition at high temperatures [Ghosh and Curthoys, 1984] and likely slower diffusion compared to that of ammonia. Nonetheless, *n*-BA has been found to be a useful probe molecule for acidity characterization of zeolites.

EXPERIMENTAL

Microporous Zeolites

The microporous zeolites examined in this work include three hydrogen mordenites (HML8, HM20A, and HM30A), two noble metal loaded mordenites (Pt/HM30A and Pd/HM30A), and two sets of Y zeolite-based catalysts: the first set includes a hydrogen Y zeolite (HY-1 with SiO₂/Al₂O₃ molar ratio of 4.8) and two metal ion-exchanged Y zeolites (LaHY and NiHY); the second set includes another hydrogen Y-zeolite (HY-2 with SiO₂/Al₂O₃ molar ratio of 5.0) and two noble metal-loaded Y-zeolites (Pt/HY and Pd/HY). The three H-mordenites (HML8, HM20A, and HM30A) with different SiO₂/Al₂O₃ molar ratios (17, 21, and 38, respectively) were prepared by heat treatment of three commercial ammonium mordenite samples [Lai and Song, 1995; Schmitz et al., 1995]. The noble metal-loaded zeolites (Pt/HM30A, Pd/HM30A, Pt/HY, Pd/HY) were prepared by incipient wetness impregnation from aqueous solution of platinum and palladium salts: aqueous H₂PtCl₆ solution and aqueous PdCl₂ dissolved in hydrochloric acid (H₂PdCl₄). The noble metal loading on the support was nominally 6 wt%. The metal-loaded catalysts were calcined in air at 450 °C for 2 h after being dried in a vacuum oven. The three Y zeolites (HY, LaHY, and NiHY) were prepared according to the procedures described elsewhere [Song and Moffatt, 1994]. More details on the preparation and properties of the catalysts are described elsewhere [Song et al., 1991; Schmitz and Song, 1995].

Mesoporous Zeolites

The mesoporous materials were synthesized according to the procedure described elsewhere [Reddy and Song, 1995b]. Briefly, the mesoporous zeolites were synthesized from a mixture of reactants with the following composition: 50SiO₂·xAl₂O₃·4.32Na₂O·2.19(TMA)₂O·15.62(CTMA)Br·3165H₂O; where x=1.0 and 2.0. The organic template from the as-synthesized solids was removed by calcining the samples in a tubular furnace at 550 °C for one hour in

nitrogen and 6 hours in air flow. The calcined samples were ion-exchanged with ammonium nitrate (0.5M) at 90°C. The protonated form was then obtained by calcining these ammonium ion-exchanged samples at 480 °C for 3 hours. More details for synthesis and spectroscopic characterization may be found elsewhere [Reddy and Song, 1995b].

TGA and DSC of Base-Saturated Samples

The acidity of catalysts were characterized by the temperature-programmed desorption of a base using thermogravimetric analysis (TGA) in combination with differential scanning calorimetry (DSC). *n*-Butylamine (*n*-BA) was chosen as the base for adsorption-desorption study; it was obtained from Aldrich Chemical Company and was used as received with a purity of 99+%.

For the preparation of *n*-BA adsorbed samples, we have designed a flow system with heating and evacuation capability, where a given zeolite was degassed in vacuo at 400°C, cooled to room temperature, and then exposed to *n*-BA vapor in flowing ultra-high purity nitrogen for 1 hour; N₂ with a flow rate of about 100 cm³/min was used as a carrier gas. The base-saturated catalyst was then transferred to TGA or DSC for analysis.

The desorption experiments were carried out with base-saturated catalyst contained in an uncovered alumina crucible using Mettler TG50 thermogravimetric balance. Samples of about 10 mg were used in each measurement and a purge gas (N₂) flow of 200 cm³/min at room temperature was used. Before the thermal analysis was started, the base-saturated sample was kept at 30 °C for 30 minutes with purge flow to remove physisorbed *n*-BA. The desorption temperature was programmed from 30 to 600 °C at a heating rate of 10 °C/min, and the decrease in weight with increasing temperature was monitored. TGA and DTG (differential thermogravimetry) data were then obtained.

The desorption was also carried out in a differential scanning calorimeter using Mettler model DSC 27HP. About 7.5 mg of each of the catalysts was placed in an uncovered standard aluminum crucible (40 mL), and was heated from 30 to 600 °C at a rate of 10 °C/min with an initial isothermal time of 30 min. The system was continuously purged with 100 cm³/min of N₂.

RESULTS AND DISCUSSION

Figure 1 shows the TGA and DSC profiles of temperature-programmed desorption of *n*-BA from HY (HY-1). DSC curve shows only endothermic peaks: a low-temperature peak near 100 °C, a shallow peak near 200 °C, a large peak at 405 °C, and a shoulder near 440 °C. DTG shows similar results except that the peak near 100 °C is not as clear as that in DSC. It can be seen that for HY the results from DTG compared fairly well with that from DSC. The peak near 100 °C may be due to the desorption of physisorbed *n*-BA, and *n*-BA adsorbed on weak acid sites. As another possible contributing factor, trace amount of water might have re-adsorbed on the base-covered catalyst. However, prior to *n*-BA adsorption, the previously calcined catalysts were further thermally pretreated in situ under vacuum to remove moisture, then covered and saturated with base in situ, and transferred to TGA in a closed vial. Thus only the base-saturated sample is exposed to air during sample unloading from the adsorption apparatus and loading into the TGA cell. On the other hand, the high-temperature peaks above ca. 300 °C are attributed to *n*-BA desorption from acid sites. Stronger acid sites desorb the base (*n*-BA) at higher temperatures. Therefore, the *n*-BA desorption at different temperatures corresponds to the surface acidic sites with different acid strength.

The surface acidic sites corresponding to TGA-derived weight loss due to base desorption at 100-240°C, 240-340°C, and 340-500°C, were classified as weak, intermediate, and strong acid sites, respectively. DSC indicates the endothermic nature of the differential thermogravimetric (DTG) peaks, confirming the TPD data obtained using TGA. It was assumed that the weight loss below 100 °C (about 1-1.5 weight % of the saturated catalysts) was due to the desorption of physisorbed base, and thus only the amount of *n*-BA desorbed above 100 °C was considered in the calculation of acidity. The low temperature range of 100-240°C was chosen to represent weak acid sites based on the report of Ghosh and Curthoys [1984]. The temperature limit was set at 500 °C because it was suggested that the weight loss above 500 °C may also be due to the dehydroxylation of the catalysts [Ghosh and Curthoys, 1984].

Acidic Characteristics of Microporous Zeolites

The DSC and TGA curves of *n*-BA desorption are presented in Figure 2 for HY (HY-1) and metal-ion exchanged Y zeolites (and HM20A), and in Figure 3 for mordenites and noble metal-loaded mordenite catalysts. On the basis of Figures 2 and 3, the weight losses (due to *n*-BA desorption) from Y-zeolite catalysts are greater than those for the mordenites at all temperatures, indicating that the Y-zeolites have both more acid sites and higher acid strength than the mordenites.

Among the three Y-zeolites (HY, LaHY, NiHY), LaHY has slightly more weak sites than the other two, but it has fewer strong sites than HY. HY has more strong acid sites judged from the enormous endothermic heat flow (Figure 2, right) and sharp weight loss (Figure 2, left) in the 340-500 °C range. NiHY has similar amount of weaker sites but much fewer strong sites than HY and LaHY (Figure 2, left). Among the mordenite based catalysts, HML8 only possesses a small number of weak sites, in fact the least among the eight catalysts; however, it has similar amount of strong sites as HM30A has, although they have different SiO₂/Al₂O₃ ratio.

We also compared two sets of metal-loaded Y-zeolites prepared by impregnation. Their *n*-BA TPD profiles are presented in Figure 4. The metal loaded Y zeolites (Pt/HY, Pd/HY) give almost linear weight loss curves, devoid of the rapid weight loss at 340-500°C which is apparent with HY (HY-2, Figure 4, left). One explanation for this behavior is that the metal particles preferentially attach to the support at strong acid centers. Metal-support interactions of this nature may explain why Group VIII metals on acidic zeolites, especially on HY, are known to be electron-deficient [Stanislaus and Cooper, 1994]. A second possibility is that metal particles prevent *n*-BA from diffusing onto strong acid sites by blocking the channel.

Pd/HM38 (identical to Pd/HM30A in Figure 3) and Pt/HM38 (identical to Pt/HM30A in Figure 3) give TPD profiles that are similar to each other. In this case, the presence of metal does not significantly impede diffusion of *n*-BA. It is possible that a significant portion of the metals reside in the mordenite side-pocket channels (dimension 2.9 x 5.7 Å) that run perpendicular to the main channels. The two noble metal loaded mordenites have quite similar acidity, and they possess fewer strong sites than HM30A.

Tables 1-3 summarize the acidity of the microporous zeolite catalysts determined from the amount of *n*-BA desorbed (from the TGA measurements) at three temperature ranges (100-240, 240-340, and 340-500 °C). From Tables 1 and 2, the total acidity of the catalysts decrease in the following order: HY > LaHY > NiHY > Pt/HY = Pd/HY > HM20A >

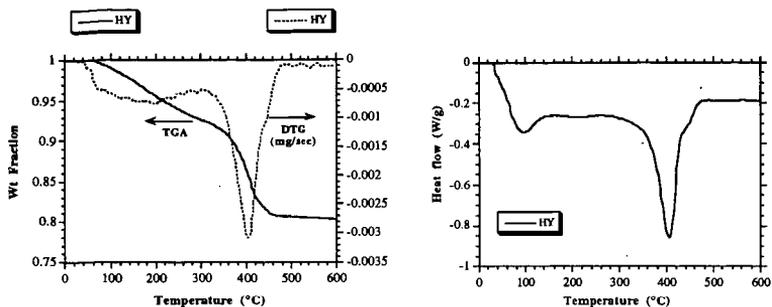


Figure 1. Temperature-programmed desorption of n-BA from HY zeolite (HY-1) conducted on TGA (left) and DSC (right).

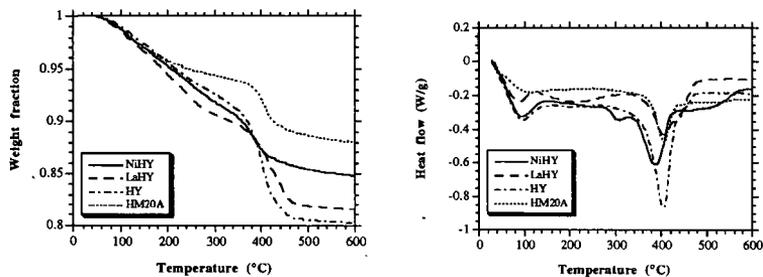


Figure 2. Temperature-programmed desorption of n-BA from proton-form zeolite catalysts conducted on TGA (left) and DSC (right).

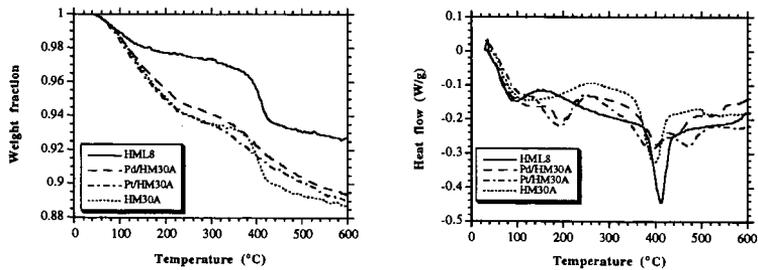


Figure 3. Temperature-programmed desorption of n-BA from mordenite-based catalysts conducted on TGA (left) and DSC (right).

HM30A > Pd/HM30A ≈ Pt/HM30A > HML8. Table 3 shows that the reproducibility of the TPD data is reasonably good.

Table 1. Acidity of Y-Zeolites from n-BA TPD (Acidity Unit: mmol/g)

Cat ID	HY (1)	LaHY	NiHY	HY (2)	Pt/HY	Pd/HY
Alt No.	HY-1	LaHY-1	NiHY-1	HY-2	Pt/HY-2	Pd/HY-2
T range, °C						
100 - 240	0.79	0.97	0.76	0.88	0.63	0.60
240 - 340	0.49	0.48	0.51	0.52	0.49	0.44
340 - 500	1.85	1.32	0.84	1.50	0.63	0.66
Total, mmol/g	3.12	2.77	2.11	2.90	1.75	1.71

Table 2. Acidity of Mordenites from n-BA TPD (Acidity Unit: mmol/g).

Cat ID	HML8	HM20A	HM30A	Pt/HM30A	Pd/HM30A
Alt No.	HM17 AS+WL	HM21 AS+WL	HM38 AS+WL	Pt/HM38	Pd/HM38
T range, °C					
100 - 240	0.19	0.56	0.75	0.68	0.62
240 - 340	0.10	0.17	0.15	0.18	0.17
340 - 500	0.57	0.80	0.61	0.44	0.51
Total, mmol/g	0.86	1.53	1.51	1.30	1.29

Table 3. Reproducibility of the Acidity Data (mmol/g) from n-BA TPD on TGA

Cat ID	HML8	HML8	HM20A	HM20A	HM30A	HM30A
Alt No.	HM17 WL	HM17 AS	HM21 WL	HM21 AS	HM38 WL	HM38 AS
T range, °C						
100 - 240	0.20	0.19	0.56	0.56	0.69	0.81
240 - 340	0.09	0.10	0.16	0.18	0.13	0.16
340 - 500	0.56	0.57	0.82	0.78	0.63	0.59
Total, mmol/g	0.86	0.86	1.54	1.52	1.45	1.56

Acid Characteristics of Mesoporous Zeolites

Mesoporous molecular sieves of MCM-41 type represent a new family of crystalline materials, and their synthesis has been made possible recently by Mobil researchers [Kresge et al., 1992; Beck et al., 1992]. The mesoporous zeolites (aluminosilicates) of MCM-41 type are of particular interest, because their uniform pores can be tuned in the range of 15 to 100 Å. Several research groups have reported the synthesis of mesoporous zeolites [Chen et al., 1993a,b; Corma et al., 1994; Borade and Clearfield, 1995; Reddy and Song, 1995a,b,c].

We have synthesized mesoporous zeolites, and found that the catalytic properties of the MCM-41 zeolites depend on the type of Al source compounds used for their synthesis [Reddy and Song, 1995b]. Here we compare the acidic properties of MCM-41 type mesoporous zeolites synthesized using alumina (pseudo boehmite), Al sulfate, Al isopropoxide, and sodium aluminate.

Figure 5 and Table 4 show the TGA results for TPD of n-BA from the mesoporous zeolites synthesized with feed SiO₂/Al₂O₃ molar ratio of 50 using four different Al source compounds. From the weight losses due to n-butylamine desorption, it is clear that MCM-41 samples prepared with aluminum isopropoxide and aluminum sulfate adsorbed more n-BA (about 18 wt%), whereas the sample prepared with pseudo boehmite adsorbed less n-butylamine (about 10 wt%). These results indicate that first two samples adsorbed more base, hence they are more acidic than the last one, which confirms that aluminum incorporation is better for the first two samples. The better Al incorporation was also verified by solid-state NMR and XRD, as reported elsewhere [Song and Reddy, 1995b]. The highest amount of n-BA was desorbed from the mesoporous zeolite prepared from sodium aluminate, in both the 100-240°C and the 340-500°C ranges. It seems that this mesoporous zeolite has the highest acidity among the four samples (synthesized with SiO₂/Al₂O₃ molar ratio of 50) examined.

Table 4. Acidity of Mesoporous Zeolites Determined from Desorption of n-Butylamine

n-Butylamine Desorption Temperature (°C)	Acid Strength	Acidity (mmol/g) of MCM-41			
		PB2(44) ^a	AS2(87) ^a	Al2(47) ^a	SA2(49) ^a
100-240	Weak ^b	0.81 ^b	1.27 ^b	0.84 ^b	1.84 ^b
240-340	Intermediate	0.06	0.17	0.25	0.16
340-500	Strong	0.10	0.29	0.32	0.42
Total acidity		0.97	1.73	1.41	2.42

^a Values in the parentheses indicate SiO₂/Al₂O₃ molar ratios of the samples synthesized using PB (pseudo boehmite), AS (Al sulfate), AI (Al isopropoxide) and SA (sodium aluminate).

^b A portion of the n-BA desorbed at 100-240°C may be due to physical adsorption.

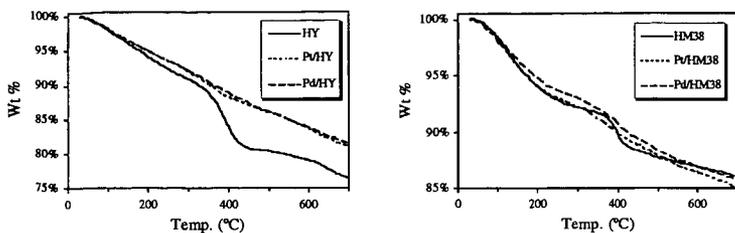


Figure 4. TGA-derived n-BA TPD from Pt- and Pd-loaded Y-zeolite (left, HY-2) and Pt- and Pd-loaded mordenite catalysts (right).

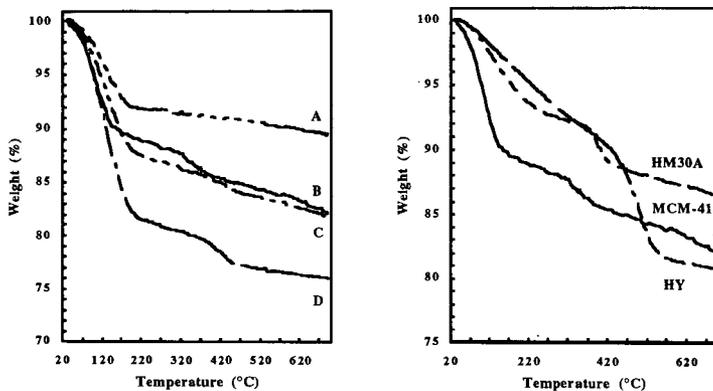


Figure 5 (Left). n-BA TPD from MCM-41 prepared using (A) pseudo boemite, (B) Al isopropoxide, (C) Al sulfate, and (D) sodium aluminate.

Figure 6 (Right). Comparison of n-BA TPD from MCM-41 prepared from Al isopropoxide and H-Y (HY) and H-mordenite (HM30A).

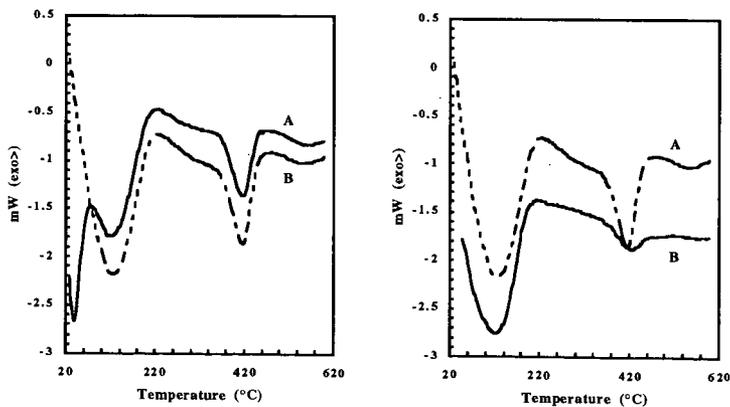


Figure 7 (Left). DSC for n-BA desorption from MCM-41 prepared from sodium aluminate (SiO₂/Al₂O₃ = 25) without (A) and with (B) initial N₂ flushing at room temperature for 30 min (DSC run started after the N₂ flushing).

Figure 8 (Right). DSC profiles of n-BA desorption from MCM-41 prepared from sodium aluminate with SiO₂/Al₂O₃ ratio of 25 (A) and 50 (B).

Figure 6 compares the n-BA TPD profile of a proton-form mesoporous zeolite (synthesized using Al isopropoxide with feed $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio of 50) with those of a H-Y zeolite (HY) and a H-mordenite (HM30A). Our preliminary TPD results indicate that compared to a hydrogen Y-zeolite ($\text{SiO}_2/\text{Al}_2\text{O}_3$: 5) and a hydrogen mordenite ($\text{SiO}_2/\text{Al}_2\text{O}_3$: 38), there are less number of strong acid sites in the MCM-41 samples. In terms of the relative amount of n-butylamine desorption in the temperature range of 340-500°C, the qualitative order of acidity is HY > HM > protonated MCM-41. From Figure 6, it appears that the amount of the n-BA desorbed from MCM-41 below 200 °C is much higher than that from either HY or HM. The higher amount of low temperature desorption compared to mordenite could be due to several factors: 1) larger number of acid sites with low acid strength, 2) larger pore volume and larger sorption capacity which lead to more n-BA physical adsorption, and 3) the easier out-of-pore diffusion of n-BA from mesopores which are not readily available in microporous zeolites.

On the basis of the above discussion, a question that arises is whether all the n-BA desorption at 100-240°C is really due to weak acid sites in the case of mesoporous zeolites. Figure 7 shows DSC profiles of a mesoporous zeolite (synthesized using sodium aluminate with feed $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio of 25) with and without initial N_2 flushing (purge flow). The initial N_2 flushing affects the n-BA desorption at low temperatures (<220°C), but does not affect the n-BA desorption at high temperatures. Figure 8 shows DSC profiles of two mesoporous zeolites (synthesized using sodium aluminate with feed $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratios of 25 and 50). Since the acidity of zeolites is associated with Al in tetrahedral coordination, the zeolite with higher Si/Al ratio should have lower acidity. As shown in Figure 8, increasing Si/Al ratio decreased the high-temperature DSC peak, as expected. However, the effect of Si/Al ratio on the low-temperature peak appears to be significantly less compared to that on the high-temperature DSC peak. These results suggest that the low-temperature DSC peak with the mesoporous zeolites is partly due to physical sorption.

Summary

TGA and DSC are useful techniques for characterizing acidic properties of microporous and mesoporous zeolites by temperature-programmed desorption of n-BA. The desorption of n-BA at different temperatures represents its interaction with surface acidic sites of different acid strength. Base desorption at 100-240°C, 240-340°C, and 340-500°C, was classified as weak, intermediate, and strong acid sites, respectively. DSC indicates the endothermic nature of the DTG peaks (observed from TGA) in the above temperature regimes, confirming the TPD data. However, desorption of physisorbed n-BA may also contribute to the peak in the 100-240°C range.

For the microporous zeolites (Y and mordenites) examined, both the total acidity (mmol/g) and acid strength distribution depend on the zeolite type, Si/Al ratio, and metal loading. Among the three proton-form mordenites, no linear correlation between their acidity and their Si/Al ratio was observed. Ni and La ion-exchange of HY decreased the strong acid sites. Pt and Pd loading by impregnation on HY decreased the strong acid sites but their loading on an H-mordenite had little effect on its strong acid sites.

Mesoporous zeolite samples of MCM-41 type prepared using different aluminum sources do show acidity in their proton-form. Mesoporous zeolites show lower acidity and lower fraction of strong acid sites compared to HY and H-mordenites. However, the acidity of mesoporous zeolites strongly depends on the aluminum source compounds used in the hydrothermal synthesis of the zeolites. The acidity measured by n-BA desorption at 240-500°C decreases with respect to the Al source in the following order: sodium aluminate > Al isopropoxide > Al sulfate > pseudo boemite.

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