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Microcalorimetric studies of ammonia adsorption on γ-Al_2O_3, HNa-Y zeolite, and H-mordenite

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The acidities of γ-Al_2O_3, HNa-Y zeolite, and H-mordenite have been examined by microcalorimetric measurements of ammonia adsorption at 423 K. The differential heat of adsorption on γ-Al_2O_3 decreases continuously with ammonia coverage from an initial value of 165 kJ/mol at low coverages to a value of 70 kJ/mol at higher coverages. The differential heat of adsorption on HNa-Y zeolite shows similar behavior, with a plateau of nearly constant heat at 115 kJ/mol. H-mordenite exhibits a nearly constant heat of adsorption equal to 155 kJ/mol. The results from these microcalorimetric measurements are in agreement with thermogravimetric and temperature-programmed desorption results collected at higher temperatures. Adsorbed ammonia has sufficient mobility at 423 K to equilibrate with the catalyst surface on the time scale of microcalorimetric measurements, and these measurements provide an effective method for quantifying acid site distributions of solid-acid catalysts.

Keywords: Acidity; heat of adsorption; microcalorimetry; ammonia; zeolite; γ-Al_2O_3; HNa-Y; H-mordenite

1. Introduction

Solid-acid catalysts have found applications for important reactions including hydrocarbon cracking, isomerization, alkylation, and alcohol dehydration [1]. Quantitative characterization of catalyst acidity requires knowledge of the type of acid site, the number of acid sites, and the acid site strength. Infrared spectroscopy has been used extensively with probe molecules to identify types of acid sites [1–6]. Microcalorimetry has been suggested to be an effective tool for the measurements of the number and strength of acid sites [7–16]. In particular, microcalorimetry is typically used to measure the differential heat of adsorption of basic molecules on acid catalysts.

Achieving thermodynamic equilibrium between the adsorbed probe molecule

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and the acid sites on the time scale of microcalorimetric measurements (e.g., 30 min) is a prerequisite for application of adsorption microcalorimetry to the study of solid-acid catalysts. Accordingly, the temperature at which the adsorption is conducted should be sufficiently high to facilitate equilibration of the base molecule with the acid sites. The choice of adsorption temperature, however, is constrained and involves a compromise between using high temperatures to reduce equilibration times, and using lower temperatures to achieve high coverage of the acid sites at reasonable pressures. Lower temperatures are also used to ensure that the basic molecule does not decompose on the surface. In general, bases that adsorb more strongly must be studied at higher temperatures.

Ammonia has been used by various authors at temperatures near 450 K to probe the acid strengths of zeolites and oxide catalysts [8,11–16]. At these temperatures, equilibrium between gaseous and adsorbed ammonia may not necessarily be achieved [17], and equilibration of the ammonia between the various acid sites has been suggested to involve surface diffusion [8,11,16]. We will test this hypothesis in the present note by microcalorimetrically measuring the differential heat of ammonia adsorption at 423 K on acid catalysts that have been studied by other investigators using thermogravimetric techniques at elevated temperatures with long equilibration times [17,18] and temperature-programmed desorption (TPD) [11]. Specifically, we have used heat-flux microcalorimetry to study the acidic properties of γ-Al_2O_3, HNa-Y zeolite (Si/Al = 2.4) and H-mordenite (Si/Al = 13). The heats of ammonia adsorption determined calorimetrically on these materials agree with the results obtained by thermogravimetric and temperature-programmed desorption methods, providing evidence that microcalorimetric studies of ammonia adsorption at 423 K can be used to probe the acid-strength distribution of heterogeneous catalysts. Additionally, we have measured the differential heat of pyridine adsorption on γ-Al_2O_3 for comparison with equilibrated thermogravimetric data published by Deeba and Hall [17].

2. Experimental

Microcalorimetric studies were performed using a Tian–Calvet type heat-flux calorimeter, the design of which has been described elsewhere [19]. The microcalorimeter was attached to a gas-handling system and a volumetric system, equipped with a Baratron capacitance manometer for precision pressure measurements. Doses (25–45) of the probe molecule, ranging in size from 2 to 10 μmol, were admitted sequentially to the sample cell at 423 K. The sample cell typically contained 0.1 g of catalyst. The differential heat was detected by heat-flux transducers arranged in series around a reference cell and a sample cell. Measurements of the differential heat were determined by integrating the heat response versus time.

The γ-Al_2O_3 sample studied in this work was supplied by the Davison Company. The HNa-Y zeolite sample (Si/Al = 2.4), having 82% of the Na exchange cations replaced by protons, was provided by W.S. Millman at the University of Wisconsin – Milwaukee. A sample of H-mordenite (Si/Al = 13) was provided by the Conteka Corporation. Prior to microcalorimetric measurements, these catalysts were pelletized, dried under vacuum at 573 K for 1 h, calcined for 5–6 h in 500 Torr of oxygen at 723 K, and evacuated for 1–2 h at 723 K. Research grade oxygen, purified by passage through activated molecular sieves at 195 K, was used for calcination treatments. Ammonia and pyridine were purified before use by successive freeze/pump/thaw cycles with liquid nitrogen.

3. Results and discussion

The microcalorimetric results of ammonia adsorption on γ-Al_2O_3 at 423 K are shown in fig. 1. Ammonia has an initial heat of adsorption of 165 kJ/mol, and the differential heat of adsorption decreases with increasing ammonia coverage. This behavior indicates that the surface contains a distribution of acid strengths or that lateral, repulsive interactions between adsorbed ammonia molecules progressively weaken the gas–solid interaction at higher ammonia coverages. For example, Knözinger [20] has reviewed surface models for γ-Al_2O_3 and suggests that various acid sites having different strengths are formed on the surface during dehydration. The random nature of catalyst dehydration creates acid sites in different chemical environments.

The thermogravimetric results of Deeba and Hall [17] for pyridine adsorption on γ-Al_2O_3 are also shown in fig. 1. These authors suggest that similar results are expected for ammonia adsorption on γ-Al_2O_3. The excellent agreement between our microcalorimetric results and the thermogravimetric data provides evidence

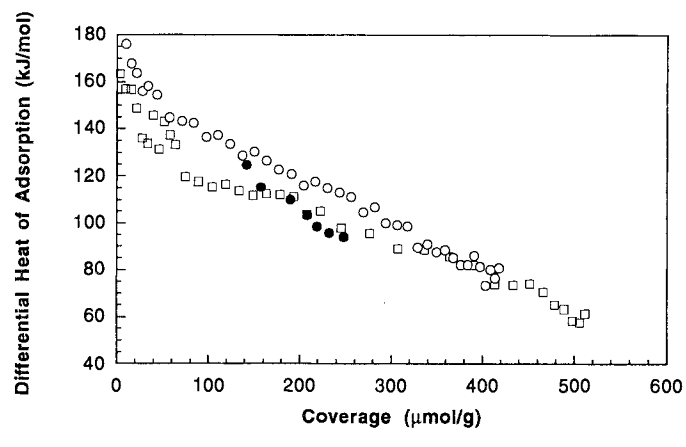

Fig. 1. Microcalorimetric measurements of differential heat of ammonia (□) and pyridine (○) adsorption versus coverage on γ-Al_2O_3 at 423 K. Thermogravimetric results of pyridine adsorption (●) on γ-Al_2O_3 [17].

that adsorbed ammonia at 423 K has sufficient mobility to equilibrate with the acid sites on the surface of γ-Al_2O_3 at the adsorption temperature.

The differential heat of pyridine adsorption on γ-Al_2O_3 at 423 K is also plotted in fig. 1 for comparison with the differential heat values obtained from the equilibrated thermogravimetric data of Deeba and Hall [17]. The results of pyridine adsorption are qualitatively similar to those of ammonia adsorption, and show a decline in the heat of adsorption with increasing coverage. The initial heat of pyridine adsorption is 10 kJ/mol higher than that for ammonia adsorption. The higher heat of adsorption observed with pyridine agrees with similar microcalorimetric measurements of ammonia and pyridine adsorption on silica/alumina [8] and zeolites [10–12]. This behavior is also consistent with the higher gas phase basicity of pyridine [21]. The subtle difference between the differential heat plots of pyridine adsorption obtained in the present study and measured by Deeba and Hall may reflect differences in preparation and treatment conditions of the γ-Al_2O_3 samples. These results support the notion that surface equilibration is achieved for pyridine adsorption at 423 K, as well.

Fig. 2 shows the results for ammonia adsorption on HNa-Y zeolite at 423 K. An initial heat of adsorption of 130 kJ/mol is observed. The heat decreases to a plateau at 115 kJ/mol, indicating that ca. 750 μmol/g of the sites are relatively homogeneous in strength. After ca. 1000 μmol/g of ammonia has adsorbed on the surface, the heat gradually decreases to a value of 70 kJ/mol, which corresponds to hydrogen bonding of ammonia to non-acidic hydroxyl groups [8].

The thermogravimetric results obtained by Benson et al. [18] are also shown in fig. 2 for ammonia adsorption on a sample of HNa-Y zeolite having similar Si/Al ratio (Si/Al = 2.25) and exchange level (70% of the Na cations exchanged by protons). The excellent agreement between our microcalorimetric results and the ther-

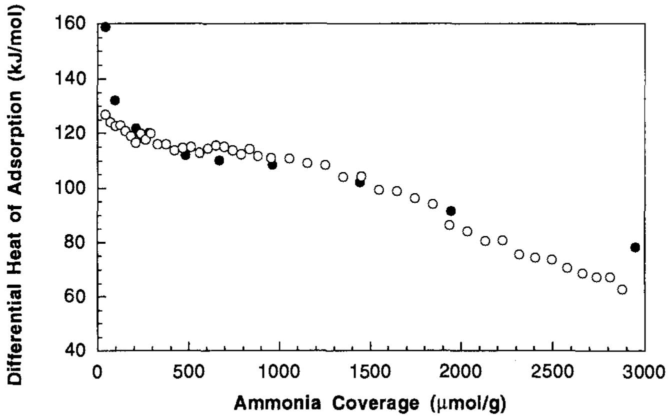

Fig. 2. Microcalorimetric measurements of differential heat of ammonia adsorption versus coverage on HNa-Y zeolite (○) at 423 K. Thermogravimetric results of ammonia adsorption (●) on HNa-Y zeolite [18].

mogravimetric data provides further evidence that ammonia adsorbed at 423 K in HNa-Y zeolite has sufficient mobility to equilibrate with the acid sites.

Ward [1] has shown that decationated H-Y zeolites calcined between 573 and 773 K exhibit primarily Brønsted acid sites. The small plateaus observed in the differential heat plot of fig. 2 indicate that several classes of sites are present having distinct strengths. We may suggest that these Brønsted acid sites with various strengths may be Si–OH–Al species having different numbers of next-nearest-neighbor Al species [22–25]. These effects would not be observed for zeolites like H-mordenite having higher Si/Al ratios where the Si–OH–Al species are widely separated and can be considered to be isolated.

The microcalorimetric results of ammonia adsorption at 423 K on H-mordenite are shown in fig. 3. The plot of the differential heat of adsorption versus coverage shows a nearly constant value of 155 kJ/mol, indicating a homogeneous site distribution. At coverages higher than ~ 800 μmol/g, the heat decreases to a value of 70 kJ/mol, which corresponds to hydrogen bonding on non-acidic hydroxyl groups [8]. Similar plateaus of nearly constant heat are observed in previous work by Chen et al. [10], Sharma et al. [11], and Parrillo and Gorte [16] for ammonia and pyridine adsorption on H-mordenite. The important feature of fig. 3 is that H-mordenite has a uniform acid strength distribution, as expected for this zeolite containing a higher Si/Al ratio than the HNa-Y zeolite. Moreover, the value of 155 kJ/mol for the heat of ammonia adsorption agrees well with the value of 153 kJ/mol determined by Sharma et al. [11] using temperature-programmed desorption methods and the value of 160 kJ/mol determined microcalorimetrically by Parrillo and Gorte [16].

We note that Chen et al. [10] showed evidence for a small number of strong Lewis acid sites with the adsorption of pyridine at 473 K on an identical sample of H-mordenite. These sites would have been saturated by the relatively large initial

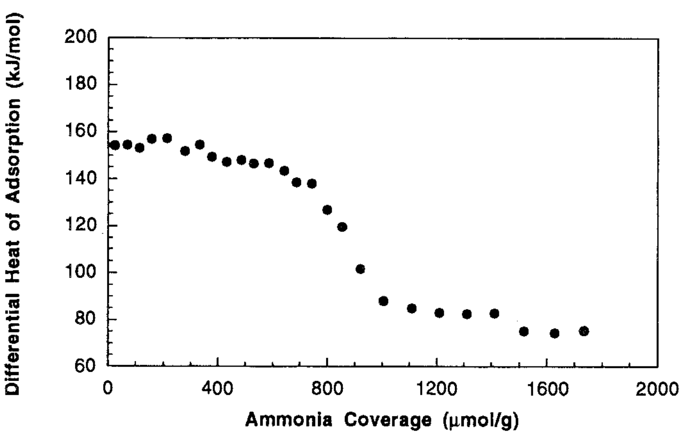

Fig. 3. Microcalorimetric measurements of differential heat of ammonia adsorption versus coverage on H-mordenite at 423 K.

doses of ammonia used in the present study; therefore, these sites do not give rise to a distinct feature in fig. 3.

As mentioned earlier, equilibrium between gaseous and strongly adsorbed ammonia is not achieved at 423 K. There is agreement, however, between the microcalorimetric measurements on γ-Al_2O_3, HNa-Y zeolite, and H-mordenite with results from thermogravimetric measurements [17,18] and temperature-programmed desorption studies [11] of similar materials. These observations suggest that surface mobility of adsorbed ammonia plays an important role in allowing stronger acid sites to be titrated selectively. We conclude that microcalorimetric measurements of ammonia adsorption at 423 K can be used as an effective tool for the measurement of solid acidity.

4. Conclusion

Microcalorimetric measurements have been used to determine the heats of ammonia adsorption at 423 K on γ-Al_2O_3, HNa-Y zeolite, and H-mordenite. Whereas the heat of adsorption decreases with ammonia coverage on γ-Al_2O_3 and HNa-Y zeolite, H-mordenite possesses acid sites of nearly constant strength. Importantly, these microcalorimetric results are in agreement with thermogravimetric and temperature-programmed desorption results obtained on similar samples at higher temperatures. The combination of results from these measurements suggests that the surface mobility of ammonia on solid acid catalysts at 423 K is sufficient to allow reliable microcalorimetric measurements of differential heats of ammonia adsorption.

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