Microcalorimetric studies of ammonia adsorption on \( \gamma-\text{Al}_2\text{O}_3 \), HNa-Y zeolite, and H-mordenite

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Received 20 July 1993; accepted 5 October 1993

The acidities of \( \gamma-\text{Al}_2\text{O}_3 \), HNa-Y zeolite, and H-mordenite have been examined by microcalorimetric measurements of ammonia adsorption at 423 K. The differential heat of adsorption on \( \gamma-\text{Al}_2\text{O}_3 \) 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; \( \gamma-\text{Al}_2\text{O}_3 \); 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
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-Al₂O₃, 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-Al₂O₃ 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-Al₂O₃ 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