Quantification of acid site densities on zeolites in the presence of solvents via determination of extinction coefficients of adsorbed pyridine

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A B S T R A C T

Fourier transform infrared (FTIR) spectroscopy is frequently used to characterize properties of catalytic sites, identify reaction intermediates, and probe interactions between adsorbates and surfaces, making it a versatile tool for elucidating reaction mechanisms in heterogeneous catalysis. While this technique is typically regarded as qualitative or semiquantitative in nature, quantitative results can be obtained by determining integrated molar extinction coefficients (IMECs), or the amount of signal per mole of adsorbed or bulk species. IMECs for vibrational modes corresponding to pyridine adsorbed onto Brønsted and Lewis acid sites have been determined in the vapor phase; however, the effect of solvents on catalytic sites cannot be captured. Liquid-phase IMECs enable quantification of adsorbates in the presence of solvents, allowing quantitative evaluations of the effect of solvents on catalysts. A method is outlined for determining IMECs of pyridine adsorbed on zeolites in the liquid phase in an attenuated total reflection (ATR) configuration. The method can also be applied to substrates other than pyridine. The IMECs for pyridine adsorbed onto Brønsted and Lewis acid sites in water, acetonitrile, and ethanol are determined. The IMEC values are shown to be dependent on solvent choice, but independent of zeolite framework.

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1. Introduction

Understanding the effect of solvents on the nature and density of catalytic sites is a key to establishing structure–activity relationships in liquid-phase heterogeneous reactions [1–3]. Reactions occurring at solid–liquid interfaces are ubiquitous in biomass upgrade processes, where a solvent is typically required due to the highly oxygenated feedstock [4–6]. However, solvent effects are poorly understood, because most catalyst characterizations are conducted either under vacuum or in vapor phase, e.g., temperature-programmed desorption of NH_3, and CO chemisorption. Spectroscopic investigations of liquid–solid interfaces are challenging because solvents are typically present at higher concentrations than adsorbates, which overwhelms the spectral features originating from the interfacial region. Thus, it is desirable to develop spectroscopic tools capable of characterizing and quantifying catalytic sites under conditions identical or similar to those used in liquid-phase reactions, i.e., in the presence of a solvent and at elevated temperatures and pressures.

Although Fourier transform infrared (FTIR) spectroscopy is typically regarded as a qualitative tool for probing surface-adsorbed species, a quantitative method for determining acid site densities on solid acids, e.g., zeolites, has been developed in vacuum (or inert gas atmosphere) [7]. Signature vibrational bands of pyridine adsorbed onto zeolites and other solid acids can reliably detect and differentiate the presence of Brønsted and/or Lewis acid sites [8,9]. Quantification of the density of pyridine adsorbed onto Brønsted and Lewis sites requires knowledge of integrated molar extinction coefficients (IMECs) of characteristic modes. An FTIR method for estimating vapor-phase IMECs for both Brønsted and Lewis sites (1.67 and 2.22 cm/μmol, respectively) has been reported in the transmission configuration, with ~15% uncertainty [7]. However, IMEC values have yet to be determined for pyridine adsorbed onto solid acids in the presence of solvents. These values would allow quantitative characterizations of Brønsted and Lewis acid sites in zeolites under conditions relevant to biomass conversion reactions. Furthermore, application of these values can lead to a fundamental understanding of how solvent choice affects catalyst acidity and accessibility.

Here, we report a method for measuring adsorbed pyridine IMECs in the liquid phase with an FTIR flow cell in an attenuated

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total reflection (ATR) configuration. The IMECs are independent of zeolite framework, but dependent on solvent choice. These values are used to compare the amount of protonated pyridine on zeolites quantitatively at equilibrium in three common solvents: water, ethanol, and acetonitrile. Protonated pyridine in the solvent is compared with the gas-phase Brønsted acid site (BAS) density measured via an *n*-propylamine decomposition reaction. The results indicate that accessible BAS are saturated in liquid acetonitrile at room temperature across all zeolite frameworks except H/MOR. However, quantification of protonated pyridine suggests oversaturation in liquid water in both H/ZSM-5 and H/MOR zeolites and undersaturation in ethanol in the case of H/ZSM-5. The values obtained via the IMEC method confirm that solvent choice has an impact on zeolite Brønsted acidity, and catalyst characterization under vacuum or inert gas atmosphere may not be fully representative of properties of acid sites on zeolites in the presence of solvents.

2. Experimental technique description

2.1. Materials preparation

The following zeolites were purchased from Zeolyst International: $NH_4/ZSM-5$ (Si/Al = 11.5 and 40), H/Y (Si/Al = 2.5, 15, and 30), NH_4/Y (Si/Al = 6), NH_4/MOR (Si/Al = 10), H/Beta (Si/Al = 150), and $NH_4/Beta$ (Si/Al = 12). H/ZSM-5 with a Si/Al of 14 was purchased from Albemarle Corporation. All zeolite samples were calcined in air at 500 °C for 10 h with a heating ramp of 1 °C/min prior to use. Pyridine, acetonitrile, and ethanol were obtained from Sigma Aldrich and used without further purification.

2.2. Materials characterization

Micropore volumes of the samples were determined using N_2 adsorption at −196 °C and the *t*-plot method and are recorded in the Supporting Information (Table S1). Isotherms were collected on a Micromeritics ASAP 2020 instrument. Prior to the adsorption measurements, all samples were degassed for 24 h at 300 °C. ^{29}Si and ^{27}Al magic-angle spinning nuclear magnetic resonance (MAS-NMR) spectra of the zeolite samples were recorded on a Bruker DSX-200 spectrometer with a Bruker 7 mm MAS probe. A 90° pulse of 4 μs was used and a strong ^1H decoupling pulse was applied during signal application. Sample spinning rate was 4 kHz and the recycle delay was 30 s. The ^{29}Si and ^{27}Al NMR spectra are included in the supporting information (Figs. S1 and S2) and are labeled with Si/Al ratios estimated from the ^{29}Si NMR results. Powder X-ray diffraction (XRD) patterns were collected on a Bruker D8 Discover powder diffractometer with a CuKα source over the range 5–50° with a step size of 0.025° and 2 s per step. XRD patterns of all zeolite samples are presented in the Supporting Information (Fig. S3). Zeolite particle sizes were estimated using a scanning electron microscope (SEM, JSM 7400-F operating at 5 kV) and the Scherrer equation and are reported in Table S1. The results from these two techniques are in general agreement. Selected SEM images are included in the Supporting Information (Fig. S4).

### 2.3. Characterization of Brønsted acid site densities

Brønsted acid site densities were measured via *n*-propylamine decomposition into propylene and ammonia using a flow reactor with an online Agilent 7890A gas chromatograph (GC) equipped with an HP-PLOT Q column. This was accomplished using a microreactor system similar to that described by Kresnawahjuesa et al. [10]. All gas lines between the location of *n*-propylamine

introduction and the GC were heat-traced with temperature maintained at or above 75 °C. Approximately 15 mg of a zeolite sample was loaded into a quartz tube in the reactor. The sample was heated to 500 °C at a rate of 10 °C/min in flowing He (100 mL/min) and held at 500 °C for 45 min. Then the sample was cooled to 100 °C and exposed to flowing He saturated with *n*-propylamine for 15 min via a bubbler. The sample was subsequently heated to 200 °C and held for 90 min to desorb excess *n*-propylamine and ensure a 1:1 ratio of adsorbed *n*-propylamine to BAS. Finally, the temperature was increased to 500 °C at a rate of 30 °C/min. The GC sampling loop was immersed in liquid nitrogen to collect the desorbed reaction products, which were subsequently quantified via a thermal conductivity detector (TCD).

2.4. In situ attenuated total reflection FTIR spectroscopy

Liquid-phase in situ FTIR spectroscopic studies with a 4 cm^{-1} spectral resolution and a 0.5 cm^{-1} aperture were conducted in a homemade multiple reflection ATR flow cell (Scheme 1) [11]. A trapezoidal ZnSe (45° cut) ATR crystal provides six total internal reflections. Before catalyst was deposited on the ZnSe crystal, the mirror between the ATR cell and the detector was adjusted to maintain a constant interferogram intensity of 5.0 a.u. (arbitrary units on an Agilent CARY 660 FTIR spectrometer). The catalyst layer is deposited directly on the top side of the ATR crystal by evaporation of the solvent from a catalyst slurry. The seal between the ZnSe crystal and the top plate is achieved by pressing an o-ring into a groove on the bottom surface of the top plate. The internal dimensions of the cell are 1.75″ length × 0.5″ width × 20 μm thickness for a total volume of 1.1×10^{-2} cm^3. A piece of quartz microfiber filter paper (pore size 2.7 m, Whatman Inc.) is placed between the catalyst layer and the top plate to prevent catalyst powder from being washed out by flowing solvent. No loss of catalyst with up to 24 h of continuous flow of solvent was observed in any experiments reported in this work. In addition, no probe molecule adsorption was detected on the filter paper in control experiments devoid of catalyst. Solvents with or without dissolved probe molecules, e.g., pyridine, are introduced onto the catalyst layer via an HPLC pump (Waters 515) at a rate ranging from 0.5 to 2 mL/min.

The ATR-FTIR spectroscopy samples both the bulk liquid phase and the liquid–solid interface within the penetration depth of the evanescent wave from the top of the ZnSe crystal [12]. Thus, spectra contain signals from both bulk and adsorbed species.
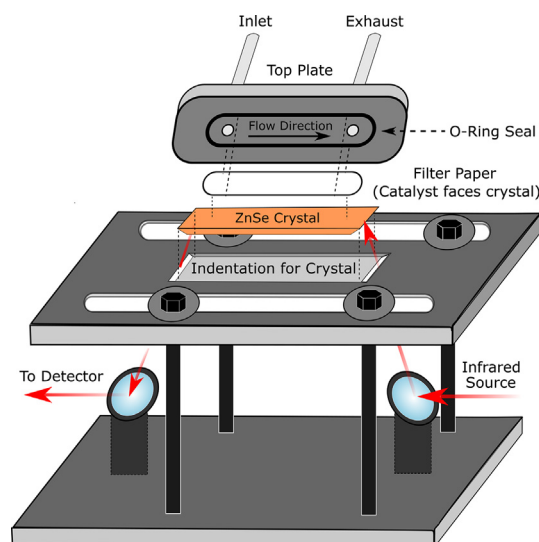
Scheme 1. Schematic of the ATR-FTIR flow cell used in this study.