

Investigation of Solid/Liquid Interfaces by Sum Frequency Spectroscopy: Acetonitrile Adsorption and Hydrogenation on Pt/Al₂O₃

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Introduction

Heterogeneous liquid phase nitrile hydrogenation is an important industrial reaction for producing primary, secondary and tertiary amines [1] that are important for the production of certain textiles, surfactants and nylons [2], among others. Many kinetic studies are available in the literature, which reveal the general features of this catalytic system. However, there are very few studies of nitrile/H₂/amine surface chemistry on supported metal catalysts, especially in situ under typical liquid-phase reaction conditions. Thus, there is an opportunity to apply novel in situ vibrational approaches to directly identify adsorbed species on the catalyst surface. One of the main obstacles in studying solid catalyst-liquid interfaces is the significant bulk-phase interference that is encountered when using linear spectroscopic techniques (e.g., infrared spectroscopy). Sum frequency generation spectroscopy (SFG) is a relatively new nonlinear optical technique that is increasingly being utilized to investigate so-called “buried interfaces” [3]. This is due to its ability to selectively probe interfacial molecular vibrational properties even in the presence of significant bulk phase species with similar (or identical) vibrational signatures.

In this study, SFS has been used to probe the interface between a model Pt/Al₂O₃ catalyst and liquids ranging from pure acetonitrile to various concentrations of acetonitrile in ethanol and water. The effect of liquid-phase acetonitrile concentration on adsorption mode and surface coverage has been investigated. Nitrile/H₂ co-adsorption experiments have been performed under both steady state and transient conditions in order to study the reactivity of adsorbed nitrile species.

Materials and Methods

SFS experiments were performed using a 20 picosecond pulsed laser that pumps an optical parametric generator/amplifier (OPG/OPA) to create both a constant frequency visible beam (532 nm, 20-30 μJ/pulse) and a tunable infrared beam (0.4-14 μm, 20-250 μJ/pulse). The spectrometer setup has been described in considerable detail elsewhere [4] and all experiments were conducted using the same preparation procedures. Chemicals used were of reagent grade quality and gases were ultrahigh purity grade. The catalyst consisted of a ca. 7 nm platinum film deposited by sputter deposition on 100 nm Al₂O₃/CaF₂.

Results and Discussion

In the case of the neat acetonitrile, vibrational features associated with C≡N stretching (2238 and 2281 cm⁻¹) and C-H stretching (2939 and 2984 cm⁻¹) were observed. These peak positions were compared with those observed in the absence of Pt [4] and the peaks are shifted further from bulk values when Pt is present, indicating a stronger bond on Pt than on the support. In the case of ethanol and water, a series of spectra were taken for different

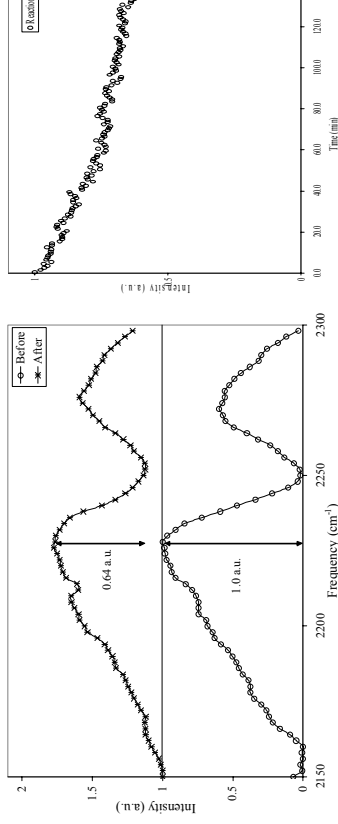


Figure 1. a) SF spectrum of 15 mM AN/ethanol solution over Pt/Al₂O₃ before reaction and one after 130 minutes on stream with hydrogen b) Transient SFS data tracking the disappearance of the C≡N stretch of adsorbed acetonitrile during exposure to H₂.

concentrations of acetonitrile in each solvent. For acetonitrile adsorption in ethanol, significant shifting of both the C≡N and C-H stretches were observed with changing concentration of acetonitrile (2238 cm⁻¹ at 100 vol. % to 2220 cm⁻¹ at 20 vol. % for the C≡N and 2939 cm⁻¹ at 100 vol. % to 2932 cm⁻¹ at 20 vol. % for the C-H). For acetonitrile adsorption in water, significantly less shifting was observed for both the C≡N and the C-H stretches (2238 cm⁻¹ at 100 vol. % to 2234 cm⁻¹ at 20 vol. % for the C≡N and 2939 cm⁻¹ at 100 vol. % to 2936 cm⁻¹ at 20 vol. % for the C-H) indicating the ability of water to solvate the adsorbed acetonitrile molecules. During hydrogenation, SFS was used to not only probe the surface before and after reaction, but to also track the reaction environment on the Pt surface in real time. For example, Figure 1 shows typical SFS data for the response of adsorbed acetonitrile in ethanol to the introduction of H₂ to the liquid phase. The data show that the surface concentration of acetonitrile decreases as a function of time, beginning to reach steady state after around 2 hrs of exposure. Spectra obtained throughout the NH stretching region (3200-3400 cm⁻¹) confirm the formation of surface amine species. This suggests that the observed decrease in acetonitrile coverage under reaction conditions results from competitive adsorption between the reactant and product.

Significance

To our knowledge this is the first surface spectroscopic study of nitrile adsorption and hydrogenation on platinum at elevated concentrations in the liquid phase. The results suggest that the SFS approach will be effective for exploring surface chemistry for a range of other solid-liquid catalyzed liquid-phase reactions using model supported catalyst systems.

References

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