In situ ATR study of adsorbed species and photogenerated electrons during G-S and L-S photocatalytic reactions

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Introduction

Fundamental research in photocatalysis can significantly benefit from methods that can probe the catalytic liquid-solid interface. Correlating the properties of the catalyst with the photo-generated electrons, the oxidation state, and the nature of adsorbates and their reactivity can provide information on the reaction mechanism. The liquid phase reaction, however, presents a challenge for identifying reaction intermediates and reaction pathways. Isopropyl alcohol (2-propanol) hydrogenation has been used as a model compound because it provides a simple and standard way to measure the photocatalyst activity in liquid phase reactions.

The objective of this study is to investigate the mechanism of photocatalytic alcohol dehydrogenation on Au/TiO_2, Pd/TiO_2, and Pd/Al_2O_3 under UV-irradiation using Attenuated Total Reflection Infrared Spectroscopy (ATR-IR) during liquid-solid (L-S) reaction and Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) during gas-solid (G-S) reaction. These in situ infrared techniques allow monitoring of photo-generated electrons along with changes in the concentration of adsorbed species under UV-irradiation (1, 2). The dehydrogenation reaction is carried out in the presence and absence of UV-irradiation. Au/TiO_2 is used for its activity and selectivity for partial oxidation which may facilitate oxidative dehydrogenation; Pd/TiO_2 and Pd/Al_2O_3 were used for their activities in alcohol dehydrogenation.

Materials and Methods

The 1 wt % Pd/TiO_2 and Pd/Al_2O_3 catalysts were prepared by incipient wetness impregnation of Pd onto Degussa P25 TiO_2 and γ-Al_2O_3 (STREM). The 1 wt % Au/TiO_2 was prepared by the homogeneous deposition precipitation of Au onto TiO_2. A thin-film was prepared from 10 mg catalyst in 5 ml 2-propanol. The catalyst slurry was sonicated for 30 min. and allowed to sit stagnant over night. The DRIFTS reactor was loaded with 150 mg catalyst for the G-S reaction study. Prior to the L-S reaction studies, a 0.1 ml of the catalyst slurry was added onto a ZnSe trough plate internal reflection element (0056-100 Thermo Nicolet). Dynamic behaviors of adsorbed species on all three catalysts were studied during UV-irradiation in the presence and absence of H_2 and O_2 using ATR-IR and DRIFTS spectroscopy.

Results and Discussion

Irradiating the catalyst thin-film with UV-radiation under flowing Argon caused the excitation of trapped electrons, producing absorption in the mid-IR region (1000 – 3000 cm^{-1}) on Au/TiO_2, shown in Figure 1(a). The thin-film was subsequently exposed to 2-propanol in the presence of hydrogen. Figure 1(b) shows the development of changes in the absorbance IR intensity of observable adsorbates during the UV-irradiation at 298 K. A drop in the IR intensity of 2-propanol bands and emergence of acetone bands, in Fig. 1(b), revealed the occurrence of dehydrogenation of 2-propanol to acetone. Turing-off the UV-light caused acetone to be hydrogenated back to 2-propanol as evidenced by the disappearance/reappearance of their characteristic bands. The Pd/TiO_2 and Pd/Al_2O_3 catalysts, giving lower IR intensity of featureless infrared absorbance in 1000 – 3000 cm^{-1} range (i.e., lower quantity of photogenerated electrons) were less active for dehydrogenation than Au/TiO_2. The higher activity of Au/TiO_2 could be due to its ability to produce high quantity of photogenerated electrons. This paper will (i) present the relationship between the IR intensity related to photogenerated electrons, adsorbed species, and rate of their formation, (ii) discuss the reaction mechanism of G-S and L-S photocatalytic reactions over the Pd and Au catalysts, and (iii) provide a coherent picture of G-S and L-S photocatalytic reaction mechanisms.

Significance

- The activity of Au/TiO_2 is attributed to its unique capability for producing photogenerated electrons, which is evidenced by the featureless IR absorption during UV-irradiation.
- Infrared results of G-S and L-S photocatalytic reactions allow elucidation of a coherent picture of photocatalytic reaction mechanisms, assisting in catalyst design.

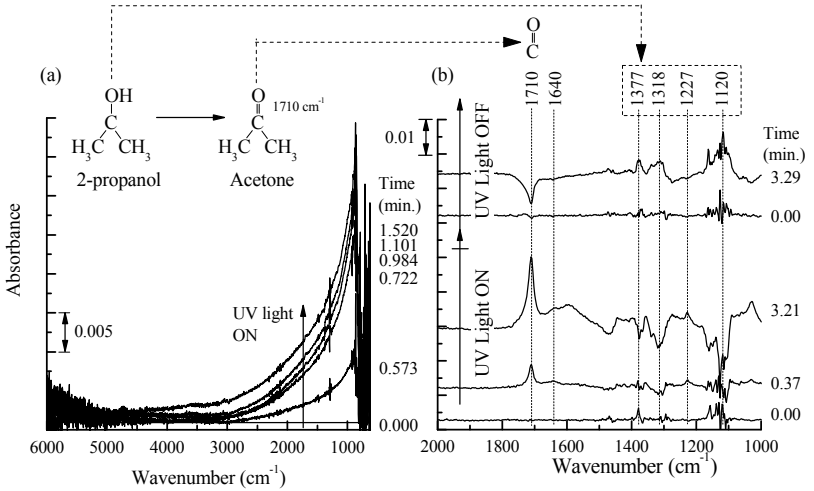

Figure 1 ATR absorbance spectrum of Au/TiO_2 thin-film on ZnSe crystal upon UV-irradiation at 298 K (a) under argon and (b) with 2-propanol and hydrogen.

References

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