

In situ IR study of adsorbed species and photogenerated electrons produced during photocatalytic degradation of ethanol on TiO₂

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Introduction

Photocatalytic reactions on semiconductor TiO₂ powders have attracted research interest due to their potential environmental applications for the destruction of organic compounds on polluted air and wastewaters. These reactions are characterized by the transfer of light-induced charge carriers (i.e., photogenerated electron and hole pairs) to the electron donors and acceptors adsorbed on the semiconductor catalyst surface [1]. Development of catalysts with high photocatalytic degradation rate, limited production of harmful intermediate species, and enhanced resistance to deactivation requires a better understanding of the mechanisms of photocatalytic reactions.

Elucidation of photocatalytic reaction mechanisms involves not only the knowledge of the dynamic behavior of adsorbates but also an understanding of the transient nature of photogenerated electrons and holes. Infrared (IR) spectroscopy is a useful technique for determining the dynamic behavior of adsorbed species and photogenerated electrons [2]. The objective of this study is to investigate the dynamic behavior of IR-observable species and their relation to photogenerated electrons during photocatalytic reactions of ethanol on the TiO₂ surface. The reaction pathways are elucidated from the evolution of IR intensities of reaction intermediates, final products and photogenerated electrons.

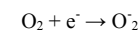
Materials and Methods

The photocatalytic degradation of ethanol was studied using a in situ IR apparatus composed of: (i) a Diffuse Reflectance Infrared Fourier Transform (DRIFT) cell (Harrick scientific HVC-DRP), (ii) a Xe 350 W mercury lamp (Oriel 6286) with a light condenser (Oriel 77800), and (iii) a gas manifold for admission of inert gases and ethanol vapor into the DRIFT cell. During each experiment, a thin 8-mg layer of TiO₂ catalyst (Degussa, P25) was placed on top of 80 mg of inert CaF₂ powder (Alfa Aesar, 325 mesh) in the DRIFT sample holder. The sample holder was enclosed by a dome with two IR transparent windows (ZnSe) and a third transparent (CaF₂) window for UV illumination with an intensity of 25 mW/cm². The photocatalytic degradation reactions were carried on the TiO₂ surface at 30 °C and 1 atm under inert He atmosphere.

Results and Discussion

Figure 1(a) presents the IR absorbance spectra during 60 min of photocatalytic degradation of 758 μmol (high coverage) of adsorbed ethanol (CH₃CH₂OH_{ad}) per gram of TiO₂ catalyst. This coverage of ethanol was resulted from exposure of the TiO₂ catalyst layer to flowing He/ethanol for 10 min followed by He purging for 20 min. During the first 10 min, this reaction consumed CH₃CH₂OH_{ad}, indicated by the decrease in the IR intensity of the C-H stretching vibrations of CH₃CH₂OH_{ad} at 2971, 2931, and 2870 cm⁻¹, and generated an

increasing IR background shift around 2000 cm⁻¹, associated with the accumulation of photogenerated electrons on the TiO₂ surface [2]. Injection of 100 μl O₂ into the DRIFT reactor at 10 min resulted in the rapid decrease of the background shift and the formation of adsorbed intermediate species, providing experimental evidence that supports the reaction of oxygen with photogenerated electrons producing O₂⁻ oxidizing species according to the equation:



Due to the overlap of the bands of CH₃CH₂OH_{ad} with the bands of the intermediate species produced during the reaction, the intensity variations of those IR absorbance bands in the 1300-1750 cm⁻¹ region must be revealed by subtracting the IR spectrum of the catalyst at 0 min (i.e., before the reaction) from subsequent IR spectra, as shown in the IR difference spectra from figure 1(b). Figure 1(b) reveals formation of acetic acid (CH₃COOH_{ad}) at 1680 cm⁻¹ and acetate CH₃COO⁻_{ad} at 1542 and 1446 cm⁻¹ occurred after 10 min of reaction, with the simultaneous decrease in the IR intensity at 2000 cm⁻¹, suggesting the photogenerated electrons begin extensive participation on the reaction. This paper will present the dynamic behavior of adsorbed species and photogenerated electrons and discuss the ethanol reaction pathways leading to the formation of CO₂, H₂O, and organics.

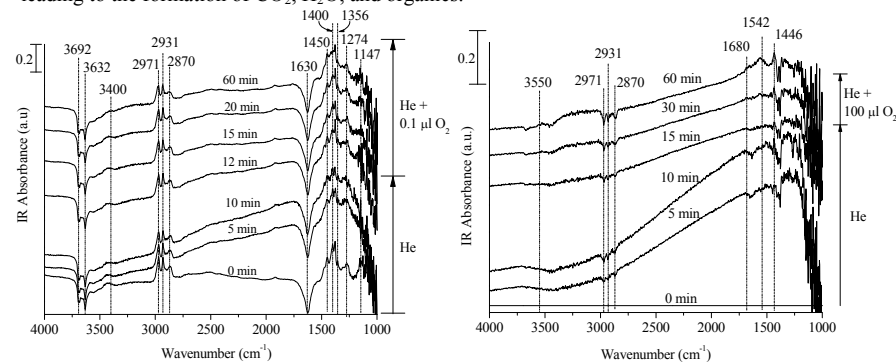


Figure 1. (a) IR absorbance spectra and (b) difference spectra during 20 min of photocatalytic degradation of ethanol on the TiO₂ surface.

Significance

A fundamental understanding of the ethanol photocatalytic reaction pathways could assist in the design of highly efficient photocatalysts.

References

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2. Panayotov, D.A., and Yates, J.T. Jr. *Chem. Phys. Lett.* 410, 11 (2005).