Photocatalytic reaction pathways of ethanol on TiO_2

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Introduction

The photocatalytic reactions of ethanol absorbed on the surface of semiconductor catalysts such as TiO_2 can result in a variety of products including H_2, CO and CO_2, depending on reaction conditions, as shown in the following scheme.

$$CH_3CH_2OH \xrightarrow{h\nu,\ H_2O} H_2 + CO + CO_2$$
$$CH_3CH_2OH \xrightarrow{h\nu,\ O_2} H_2O + CO_2$$
$$CH_3CH_2OH \xrightarrow{h\nu} CO + H_2O + CO_2$$

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]. 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 TiO_2 surface. The reaction pathways are elucidated from the evolution of IR intensities of reaction intermediates, final products and photogenerated electrons.

Materials and Methods

Photocatalytic reactions of ethanol were studied using an in situ IR apparatus consisting of: (i) a DRIFTS cell residing in a FTIR bench, (ii) a Xe lamp 350 W mercury lamp with a light condenser, and (iii) a flow manifold for introducing oxygen and ethanol vapor into the DRIFTS cell. During each experiment 15 mg of TiO_2 catalyst (Degussa P25) were placed on top of 80 mg inert CaF_2 powder in a DRIFT sample holder enclosed by a dome with two IR transparent windows (ZnSe) and a third window (CaF_2) for UV illumination with an intensity of 25 mW/cm^2. Photocatalytic reactions were carried on the TiO_2 surface at 30 °C and 1 atm for 120 min.

Results and Discussion

Figure 1 shows the difference spectra during 120 min of photocatalytic reaction of 713 μmol (high coverage) of adsorbed ethanol per gram of TiO_2 catalyst. This high coverage of adsorbed ethanol resulted from exposure of TiO_2 to flowing O_2/ethanol for 10 min followed by O_2 purging for 20 min. During the first 2 minutes, this reaction generated a conspicuous $CH_3COO^-_{ad}$ band at 1542 and 1446 cm^{-1} with the concurrent decreases in IR intensities of the C-H stretching of $CH_3CH_2OH_{ad}$/$CH_3CH_2O_{ad}$ at 2971, 2931, and 2872 cm^{-1}. As the ethanol reaction proceeded beyond 2 min, the marked decline in the C-H stretching intensities was accompanied by the rising bands of CH_3CHO_{ad} at 1718 cm^{-1}, CO_2 at 2362 cm^{-1}, isolated OH group at 3692 cm^{-1} and H_2O_{ad} at 3550 cm^{-1}. The variation in the intensity of adsorbed ethanol, CH_3CHO_{ad}, $CH_3COO^-_{ad}$, and CO_2 suggests that the ethanol reaction proceeds via CH_3CHO_{ad} and $CH_3COO^-_{ad}$ intermediates to produce CO_2.

Figure 2 shows significant CO_2 formation occurred after 60 min of the reaction while the IR background at 2000 cm^{-1} (i.e., a measure of photogenerated electrons [2]) showed a substantial decrease, suggesting that the photogenerated electrons begin extensive participation in the oxidation of intermediate species to CO_2 and H_2O_{ad}. This paper will present dynamic behavior of adsorbed species and photogenerated electrons and discuss the ethanol reaction pathways leading to the formation of CO_2, H_2O, and H_2.

Significance

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

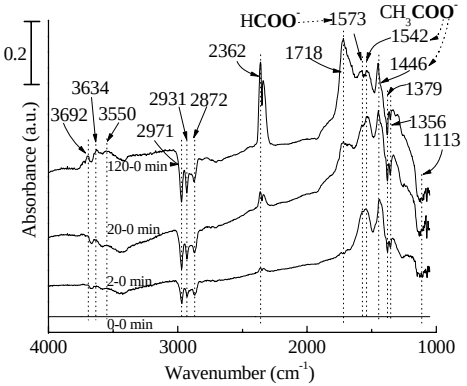

Figure 1: Difference spectra during 120 min of photocatalytic oxidation of high coverage ethanol. Difference spectra are obtained by subtracting the spectrum prior to the reaction from the spectra taken during the reaction.

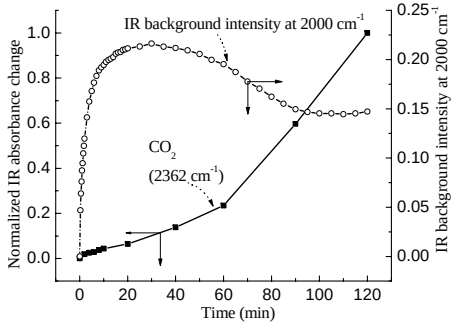

Figure 2: Variation of the normalized IR intensity of CO_2 and IR background intensity at 2000 cm^{-1} during 120 min of photocatalytic oxidation of high coverage ethanol.

References

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