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Active sites and effects of H_2O and temperature on the photocatalytic oxidation of ^{13}C-acetic acid on TiO_2

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Abstract

Acetic acid adsorbs both molecularly and dissociatively as acetate on titanium dioxide. Photocatalytic oxidation (PCO) oxidizes the α-carbon in acetic acid to CO_2 without forming any long-lived intermediates, while the β-carbon forms CO_2 through methoxy, formaldehyde, and formate. Elevated temperatures desorb molecularly adsorbed acetic acid and also increase the inherent activity of sites. At least two types of active sites exist for acetic acid PCO on TiO_2. Water, which is produced during PCO, redistributes molecularly adsorbed acetic acid on the surface by displacement. Water displaces at least one-third of an acetic acid monolayer and converts some molecularly adsorbed acetic acid into acetate. Acetate is the active species for PCO and molecularly adsorbed acetic acid oxidizes during PCO by first forming acetate.

Keywords: Acetic acid; Acetate; Water; Photocatalytic oxidation; TiO_2; Transient reaction; DRIFTS

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1. Introduction

Heterogeneous photocatalytic oxidation (PCO) removes low concentrations of both gas- and liquid phase organics at room temperature by oxidizing them to environmentally benign compounds, such as CO_2 and H_2O [2–13]. Photocatalytic oxidation employs UV or near-UV irradiation to oxidize organics adsorbed on a semiconductor catalyst, such as titanium dioxide (TiO_2). Ultraviolet light excites electrons from the valence band to the conduction band of the catalyst, leaving holes behind. These electron–hole pairs migrate to the surface and initiate redox reactions with adsorbed species. Previous studies have demonstrated that PCO successfully oxidizes many gas phase organics, but reaction pathways are not fully understood and intermediates are often not identified [2,3,6,7,14–16].

In order to develop improved photocatalysts, a more fundamental understanding of reaction pathways must be acquired. This, in turn, necessitates identifying surface species and active sites on the most promising photocatalyst, TiO_2. Understanding the reaction mechanism and identifying surface species during acetic acid PCO are important because many organic pollutants that consist of two or more carbons react through an acetic acid intermediate [2–4,17,18].

Previous studies reported that acetic acid adsorbs both molecularly and dissociatively on acid–base pairs of several catalysts [19–21]. In addition to molecular adsorption, Peng and Barteau [20] concluded that acetic acid dissociated on MgO with acetate adsorbing on the Mg cation and the proton adsorbing on an oxygen anion at low temperatures. Similarly, Xu and Koel [19] used Fourier transform infrared (FTIR) spectroscopy to show that acetic acid dissociated upon adsorption on MgO(1 0 0) and formed acetate at temperatures as low as 120 K. The authors concluded that acetate adsorbed in a monodentate configuration, whereas Hasan et al. [21] reported that acetic acid adsorbed dissociatively on TiO_2 as bidentate acetate. In addition, Hasan et al. [21] concluded that dissociative adsorption required Lewis acid–base pairs and suggested $OH^{\delta+}$ sites as the primary molecular adsorption sites for H-bonded acetic

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acid. Liao et al. [22] also reported that acetic acid adsorbed molecularly and dissociatively as acetate on TiO_2 at 308 K. Heating to 443 K removed acetic acid that was molecularly adsorbed via H-bonding or Lewis acid–base interaction, yet left acetate on the surface [22].

Pei and Ponec [23] used FTIR spectroscopy to study the intermediates that formed during acetic acid oxidation. They identified molecularly adsorbed acetic acid, unidentate acetate, and symmetrical bidentate acetate following acetic acid adsorption on TiO_2 at ambient temperatures. Heating the catalyst to 673 K decreased the intensities of bands attributed to molecularly adsorbed acetic acid and weakly bound unidentate acetate, yet bidentate acetate absorptions increased. The authors proposed that elevated temperatures converted some weakly bound species into the bidentate form and hence increased bidentate acetate coverage.

Using FTIR spectroscopy, Sato et al. [24] examined the surface species during acetic acid decomposition over Au/TiO_2 and Au/Pt/TiO_2 films. The authors identified surface species following both liquid- and gas phase acetic acid adsorption. They concluded that molecularly adsorbed acetic acid coverage was greater than that of acetate following gas phase acetic acid adsorption due to the absence of H_2O, which promoted ionization of CH_3COOH to CH_3COO^- in the liquid phase. The authors proposed that increased coverage of carbonate intermediates and photo-adsorbed H_2O led to competition for acetic acid and acetate adsorption sites because the addition of H_2O decreased both acetic acid and acetate coverage.

Previous studies have shown that elevated temperatures both increased [10,15,25] and decreased [26] the PCO activity of TiO_2. Kennedy and Datye [10] studied the photothermal oxidation of ethanol on TiO_2 (Degussa P25, 75% anatase, 25% rutile) under steady-state conditions. The authors reported that the optimum activity for PCO on TiO_2 occurred near 373 K, in agreement with Blake and griffin [15], and concluded that a thermally activated process increased PCO rates at 373 K. Similarly, previous studies [25,27] found that PCO carried out at 373 K on TiO_2 oxidized formic acid and methyl formate approximately twice as fast as at room temperature. In contrast, Falconer and Magrini-Bair [26] reported that acetaldehyde underwent a thermal catalytic reaction in parallel with PCO on TiO_2, and that the decomposition products deactivated the catalyst above 333 K.

In this study, transient reaction techniques and temperature-programmed oxidation (TPO) were combined with FTIR spectroscopy to investigate acetic acid adsorption and PCO on TiO_2. In addition to identifying adsorbed species and linking them to PCO activity, this study explores the effects of H_2O and heating on acetic acid adsorption and photocatalytic oxidation. Because this work utilized *transient* PCO instead of steady-state techniques, subsequent results facilitated a richer understanding of the effect of temperature during PCO.

This study also shows that multiple active sites exist for PCO on TiO_2. The identification of two active sites for carboxylic acid PCO explains the differences between steady-state and transient PCO results. Previous steady-state studies [18,28] of formic and acetic acids PCO proposed that accumulation of these species on the surface poisoned sites, yet transient PCO [4,11,29,30] found that both acids oxidized quickly to CO_2. However, carboxylic acids adsorbed on less-active sites are expected to remain on the surface after steady-state PCO regardless as to whether or not they poison the catalyst because these species react slowly. Species adsorbed on more-active sites form CO_2 quickly and the initial rates during transient PCO measure primarily the activity of the sites that are more active during PCO, while both more- and less-active sites determine steady-state reaction rates. This study further explores the complex effect of H_2O during transient PCO and determines that this effect merits significant consideration in interpreting transient reaction data, especially when fitting models to reaction rate data.

2. Experimental methods

2.1. Transient photocatalytic oxidation with mass spectrometry

The experimental apparatus used in this study has been described previously [11]. An annular pyrex reactor identical to those used in previous studies [11,31] allowed for high gas flow rates and uniform UV irradiation of the catalyst. Using the same experimental apparatus and procedure as this study, previous work investigated and eliminated several other possible experimental artifacts [25,27,32]. Approximately 30 mg of Degussa P-25 TiO_2 coated the inner surfaces of the photoreactor (with a 1-mm annular gap). A furnace, which consisted of Ni–Cr wire wrapped around a quartz cylinder, encased the reactor and six 8-W UV lamps (Johnlite) surrounded the furnace for PCO experiments. These lamps generate light in the 300–500 nm range with a maximum intensity near 360 nm [33]. A 0.5-mm chromel–alumel shielded thermocouple contacted the catalyst film to provide feedback to the temperature programmer. A Balzers QMS 200 quadrupole mass spectrometer sampled the effluent directly downstream of the reactor and monitored multiple gas phase species simultaneously. The mass spectrometer signals were calibrated by injecting known volumes of each product into the gas flow downstream of the reactor and were corrected for cracking in the mass spectrometer. Integration of the areas under the calibration curves provided a means to convert mass spectrometer signals to reaction rates.

Before each isothermal PCO, the catalyst was heated at a constant rate of 1 K/s to 723 K in 100 sccm flow of 20% O_2 in He (Praxair, UHP) and held at this temperature for 20 min before subsequent cooling to create a reproducible surface. Three pulses of 1-^{13}C-acetic acid (550 μmol/g catalyst) injected upstream of the reactor saturated the catalyst and the carrier gas flushed excess species from the gas phase.