

# Effect of Gas Phase Water on Formic and Acetic Acid Adsorption on Anatase TiO<sub>2</sub>

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## Introduction

Titania can photocatalytically oxidize low concentrations of organics, and the anatase form of TiO<sub>2</sub> has higher activity than the rutile form [1]. Gas phase water, which is usually present during photocatalytic oxidation (PCO), can increase or decrease PCO and photocatalytic decomposition (PCD) rates. Thus, the effect of water on species adsorbed on TiO<sub>2</sub> is of interest.

Vittadini et al. used density functional theory to investigate the effect of coadsorbed water on the chemisorbed state of formic acid on anatase (101). They found that formic acid adsorbed molecularly on TiO<sub>2</sub> anatase (101), but water promoted formic acid dissociation to formate [2]. This observation that water changes the adsorbed state of formic acid may be the cause for the increase seen in the photocatalytic rate. We used infrared spectroscopy, temperature programmed desorption (TPD), and density functional theory (DFT) calculations to examine the effect of gas phase water on formic and acetic acid adsorbed on anatase TiO<sub>2</sub>.

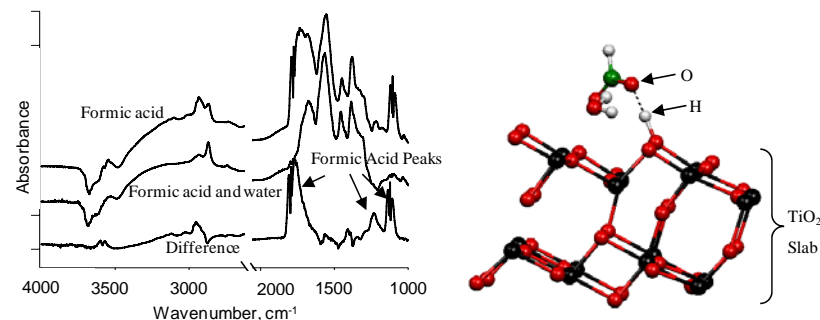
## Materials and Methods

A Nicolet 6700 FT-IR Spectrometer was used to record infrared spectra. Titania samples were prepared by pressing Degussa P25 TiO<sub>2</sub> (80% anatase, 20% rutile) powder into a tungsten grid with a hydraulic press. The sample was placed in a stainless steel vacuum chamber attached to a vacuum pump and formic acid, acetic acid, and water were dosed onto the surface of TiO<sub>2</sub>. Temperature-programmed desorption to 723 K was carried out in a packed-bed tubular reactor with 106 mg of Degussa P25 TiO<sub>2</sub> placed on a quartz frit in the reactor. The Vienna Ab-initio Simulation Package, VASP, was used for DFT calculations, and the TiO<sub>2</sub> surface was modeled using a repeated slab geometry. The slab consisted of a 2 X 2 unit cell, 2 layers thick, and contained 16 TiO<sub>2</sub> units with the anatase (101) surface exposed. The upper half of the slab was relaxed for all calculations. Adsorption energies, equilibrium structures, and vibrational frequencies were calculated for molecularly adsorbed water, formic acid, and acetic acid using VASP.

## Results and Discussion

In agreement with previous studies, DFT calculations indicate that coadsorbed water promotes O-H bond dissociation of formic and acetic acid to form formate or acetate species. Multiple water coverages were examined (one to eight water molecules) and dissociation was seen for all coverages. Vibrational frequency calculations showed the CH stretching peak shift from 3023 cm<sup>-1</sup> (formic acid) to 2921 cm<sup>-1</sup> (formate) with the addition of water, which is consistent with the peaks for formic acid and formate from the IR data described below.

However, though formate and acetate are observed in IR and TPD experiments, water-induced decomposition of the acids to formate or acetate was not seen. Instead, water preferentially displaces molecular formic and acetic acid while leaving formate and acetate on the surface. FTIR experiments revealed that water reduced the intensity of the formic acid ν(CH) peak at 2937 cm<sup>-1</sup>, b(CH) peaks for the monomer and dimer at 1220 and 1105 cm<sup>-1</sup>, and C=O peaks for the monomer and dimer at 1778 and 1684 cm<sup>-1</sup>. Water had no effect on the formate ν(CH) peak at 2868 cm<sup>-1</sup> and COO<sup>-</sup> peaks at 1583 and 1387 cm<sup>-1</sup>. Water also reduced the acetic acid peaks, and had no effect on the acetate peaks. The peaks for formic and acetic acid with gas phase water were independent of water pressure up to saturation (2.6 kPa). TPD experiments also showed that water removed 80% of adsorbed formic acid at room temperature.



**Figure 1. IR spectra indicate removal of formic acid after introduction of gas phase water so that only a formate state remains. DFT calculations on model surfaces indicate that water promotes dissociation of the formic acid O-H bond to produce formate.**

## Significance

The mechanism for promotion of formic and acetic acid PCD by water does not appear to be via promotion of the decomposition to formate and acetate; rather, experimental studies suggest that water competes for sites with formic acid and acetic acid rather than inducing additional decomposition.

## References

1. Linsebigler, A. L., Lu, G. Q., and Yates, J.T. *Chem Rev.* 95, 735 (1995).
2. Vittadini, A., Selloni, A., Rotzinger, F. P., and Gratzel, M. *J. of Phys. Chem. B* 104, 1300 (2000).