

# Effect of water on photocatalytic decomposition of tetrahydrofuran on TiO<sub>2</sub>

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## Introduction

Water can either promote or inhibit photocatalytic reactions. For example, during benzene photocatalytic decomposition (PCD) on TiO<sub>2</sub>, water at low humidity increased the decomposition rate, but the reaction was inhibited at high humidity [1]. Competitive adsorption between benzene and water for active TiO<sub>2</sub> sites appears to cause the rate decrease, but the reasons for rate increase are less clear.

Tetrahydrofuran PCD on TiO<sub>2</sub> was studied to probe the effects and mechanisms by which water accelerates PCD of a volatile organic. Water dramatically increased the PCD rate of THF. This effect was studied using mass spectrometry and temperature-programmed desorption (TPD). Density functional theory (DFT) calculations were also employed to elucidate the preferred adsorption structure for THF on a perfect and defective anatase (101) surface.

## Materials and Methods

The TPD and PCD experiments were performed in an annular Pyrex reactor coated with about 30 mg of TiO<sub>2</sub> (Degussa P25). At the beginning of each experiment, the catalyst was saturated with THF. The effect of water on the THF-saturated catalyst was studied with and without UV illumination. To analyze the species on the catalyst, TPD was then performed at a rate of 1 K/s to 723 K. The reactor effluent was analyzed using mass spectrometry.

DFT calculations were performed using the Vienna Ab initio Software Program (VASP). The anatase (101) surface was modeled as a periodically repeated slab. Adsorption of THF over a perfect surface, a surface with an oxygen vacancy (exposing Ti<sub>5c</sub> and Ti<sub>4c</sub> defect sites) and a surface with step defects (exposing only Ti<sub>5c</sub> defect sites) was studied.

## Results and Discussion

During TPD without water or UV exposure, THF initially desorbs molecularly, then decomposes to form butadiene, butene, and water above 573 K (Figure 1). During PCD, in the absence of water, THF reacted but no gas-phase products were detected. The subsequent TPD showed that less THF and butadiene desorbed, while slightly more CO<sub>2</sub> desorbed. No butene was detected. When water was injected over the THF-saturated catalyst, water displaced ~50% of the adsorbed THF. However, when water was injected into the system during PCD, water displaced only ~15% of the originally adsorbed THF. Water also increased the PCD rate by a factor of 5, and caused THF to react to form CO<sub>2</sub>. Interestingly, the subsequent TPD (Figure 2) shows that despite the reduced amount of THF on the catalyst, the amount of butene and CO<sub>2</sub> that desorbed increased. The TPD peaks of butadiene and butene also shifted to lower

temperatures. This peak temperature lowering effect of water suggests that water aids in the decomposition of the intermediate that forms butene and butadiene.

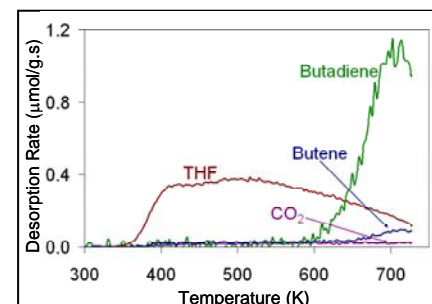


Figure 1. TPD spectra of THF from TiO<sub>2</sub>.

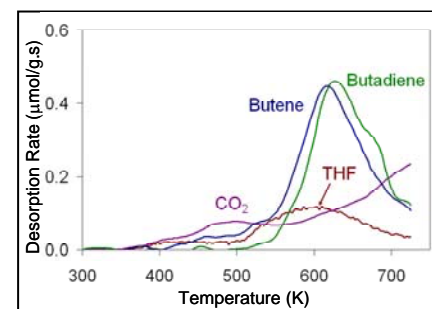


Figure 2. TPD spectra of THF after PCD performed with water injection

The DFT calculations of THF adsorption predicted a TPD peak temperature of 265 K on a perfect anatase (101) surface, 450 K over an oxygen vacancy, and 380 K over step defects. These results suggest that, at and above room temperature, THF adsorbs on defect sites.

## Significance

The addition of water appears to promote the decomposition of THF by increasing the rate of decomposition of reactive intermediates; this mechanism may be important for other reactions in humid or aqueous-phase environments.

## References

1. Wu, J.F., Hung, C.H., Yuan, C.S. Journal of Photochemistry and Photobiology A: Chemistry 170, 299 (2005).