



Photocatalytic C–C bond cleavage in ethylene glycol on TiO₂: A molecular level picture and the effect of metal nanoparticles



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ABSTRACT

Polyol conversion to value-added products is of great interest for the bio-diesel industry. Photocatalytic oxidation processes may offer a green approach for polyol conversion; however the lack of comprehensive mechanistic understanding from an interdisciplinary perspective limits or even misleads the design of highly selective and efficient photocatalysts for such process. Here we have studied the photocatalytic polyol conversion on pristine TiO₂ and metal (Au, Pd, and Pt) nanoparticles (NPs) decorated TiO₂ using ethylene glycol (EG) as the model compound. We have developed a mechanistic picture at molecular level by coupling *in-situ* surface science study on rutile (110) surface with *in-situ* vibrational-mass spectrometry study on TiO₂ nanopowders. The C–C bond cleavage was found to be the only pathway in EG photo-conversion under deaerated conditions, leading to the formation of formaldehyde and hydrogen. We rationalized that the desorption of the surface adsorbed H (H_{ads}) to be the rate determining step (RDS), making pristine TiO₂ a poor photocatalyst that only catalyze the EG conversion at very low surface coverages. The addition of metal NPs on TiO₂ surface promotes the desorption of H_{ads} significantly, thus leading to an enhanced C–C bond cleavage performance at higher surface coverages that is more applicable.

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1. Introduction

Polyols, ranging from diols, triols, sugars, cyclitols to celluloses, are a branch of alcohols that contain multiple hydroxyl groups. Polyols exist in large quantities in the world, either produced by natural processes or synthesized as by-products in chemical industry, making the value of most polyols low in general (e.g., \$ 0.01–0.08 USD/lb of glycerol) [1]. Therefore the conversion of polyols to high-value added chemicals (i.e., polyurethanes, polyesters, polycarbonates) is of potential importance and interest in the chemical industry [2].

Conventional catalytic hydrogenolysis process has been used to crack the polyols to smaller molecules with high values by metal

based catalysts under high pressure H₂ environment [3–5]. Glycerol can be selectively converted into various products (i.e., 1,2-propanediol, EG, 1-propanol, ethanol) by carefully controlling the surface properties of the catalyst. Selective oxidation has also been applied to convert polyols to their corresponding aldehydes or acids under relatively mild conditions [5,6]. The polyols can also undergo reforming process to produce synthesis gas (CO + nH₂) for Fischer-Tropsch or methanol synthesis [7]. However, all the aforementioned processes require significant energy input for heating, as well as nano-sized noble metals catalysts (i.e., Ru, Pt, Au).

Photocatalytic polyol conversion provides an alternative process that can be performed using solar energy under ambient conditions [8–11]. The photo-generated electron-hole (e[−]–h⁺) pairs offer the possibility of either performing selective reduction or oxidation by controlling the reaction conditions [12,13]. The redox potential of the e[−]–h⁺ pairs can also be tuned by manipulating the electronic structure of the photocatalyst to realize selective conversion of polyols [14,15]. However, the quantum efficiency

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and selectivity of photocatalytic polyol conversion still need to be enhanced for applications. Besides, the effect of metal NPs that are frequently applied as promoters remains unclear. Unfortunately, fundamental understanding of such a process is limited and still trapped at the level of global kinetic schemes. This is far behind the development in comparison to other photocatalytic reactions (*i.e.*, H₂ and O₂ evolution, CO₂ reduction), where reasonable theories have been developed by various surface science techniques or *in-situ* spectroscopy methods to guide the design of efficient photocatalysts [16–18]. However, cautions should be paid upon these unilateral conclusions that obtained by monotonous analytic methods, as they may limit or even mislead the material design. The heterogeneous catalytic conversion of polyols has been extensively investigated and molecular level mechanistic understandings have been obtained by surface science approaches [19–24], however, the photocatalytic process is completely different compared to the thermal dissociation of polyols that normally operated above 400 K. Thus it is urgently required to establish a clear picture of the photocatalytic polyol conversion process at molecular level.

Here we have used the simplest polyol, ethylene glycol (EG), to understand the photocatalytic polyol conversion. We aim at establishing a clear mechanistic understanding of bond cleavage and the rate determining step (RDS) in the EG photo-conversion process by employing interdisciplinary analytic methods. The effect of EG surface coverage and noble metal NPs as promoters on EG photo-conversion have been studied by coupling *in-situ* surface science analysis on TiO₂ single crystal and *in-situ* vibrational spectroscopy combined with mass spectrometry on TiO₂ nanopowders.

2. Experimental section

2.1. Surface science analysis procedures

Scanning tunneling microscopic (STM) analyses were performed using a low temperature STM (Matrix, Omicron) at an ultra-high vacuum condition (UHV, base pressure <4e⁻¹¹ mbar). The rutile TiO₂ (1 1 0) (Princeton Scientific, 10 × 5 × 1 mm³) sample was cleaned by repeated cycles of Ar⁺ sputtering (1 keV, 1.5 μA, 10 min) and UHV annealing (850 K, 20 min). The clean, reduced TiO₂ (1 1 0)-(1 × 1) was obtained and verified by STM. An electrochemically etched tungsten tip was used for all scanning during the experiment. All STM images were scanned in constant current mode (100 pA) at a bias voltage of +1.25 V at 80 K. EG (Sigma-Aldrich, 98%) was cleaned *via* several freeze-pump-thaw cycles. The experiments were performed at 80 K, and the gas lines were heated to increase the vapor pressure of EG. The tip was retracted back ~20 μm during the EG exposure [25].

The temperature programmed desorption (TPD) experiments were performed using an UHV apparatus (base pressure <3e⁻¹¹ mbar) [17]. A QMS (Extrel) was used as the detector and the UHV condition (<2e⁻¹² mbar) could be maintained in the electron-impact ionisation during experiments. The rutile TiO₂(1 1 0) crystal was cleaned by standard cycles of Ar⁺ sputtering and UHV annealing, and the cleanness was confirmed by Auger electron spectroscopy (AES) and a sharp (1 × 1) low energy electron diffraction (LEED) pattern. The population of the surface bridging oxygen vacancy (BBOv) measured by H₂O TPD was 4–5%. The purified EG was then dosed to the sample at 110 K through a home-built calibrated molecular beam doser. TPD spectra were collected with a heating rate of 2 K/s after irradiation with the sample facing to the QMS detector.

A 355 nm nanosecond laser (HIPPO, Spectra-Physics) was used as the light source for all STM and TPD experiments with power intensity varied from 25 to 75 mW in different experiments. The laser was operated with a pulse time of 12 ns and a frequency of

50 kHz. The spot size of the beam was 6 mm in diameter, and a grazing angle of 30° was used for the irradiation. During the laser irradiation, the STM tip was also retracted about 20 μm to avoid the shadow effect. We have also estimated the local transient temperature raise [ΔT(t)] caused by the laser irradiation using the equation provided by E. Weitz and co-authors [26,27]:

$$\Delta T(t) = (F/K)(\kappa t/\pi)^{1/2} \quad (1)$$

where F is the absorbed energy density (~0.003 mJ cm⁻²) calculated from the average laser fluence (83 mW cm⁻²/50 kHz = 0.00165 mJ cm⁻²) and the reflectivity of TiO₂ (12% at 355 nm irradiation), and K and κ are the thermal conductivity (0.2 W cm⁻¹ K⁻¹ at 100 K) and the thermal diffusivity of TiO₂ (0.2 cm² s⁻¹ at 100 K), respectively [27]. The maximum surface temperature, 80 K+ ΔT(t), at the cessation of a 12 ns pulse is then calculated to be 80.5 K. Therefore the heating effect of the laser is negligible in our experiments.

2.2. Synthesis and characterization of photocatalysts

Degussa Aeroxide® P25 (P25) powders were used for spectroscopy analysis. Metal (Au, Pt, and Pd) NPs were loaded on P25 *via* a photo-deposition method [28]. 200 mg of TiO₂ powders were added into 4 ml of deionized (DI) water, sonicated for 1 h, and then transferred to a beaker that contains 96 ml of 1:1 (v/v) water-ethanol solution. Then the aqueous metal salt solution (HAuCl₄ 4H₂O, H₂PtCl₆ 6H₂O, or PdCl₂) that contains the equivalent amount of 2 mg metal (1 wt% metal loading) was added into the beaker. The mixed suspension was continuously stirred and deaerated by N₂ to fully remove dissolved O₂. The UV irradiation was then commenced for 0.5 h after the suspension was purged for 0.5 h under dark to deposit the metal on the TiO₂. After irradiation the powders were collected by centrifugation and washed by DI water for three times, and eventually dried at 80 °C for 12 h. X-ray photoelectron spectroscopy (XPS) was performed to analyze the chemical composition and oxidation states of all samples. Transmission electron microscopy (TEM) was taken to characterize the metal NPs.

2.3. Photocatalytic process analysis

The EG photo-dissociation on pristine and metal NPs loaded TiO₂ powders was studied using an *in-situ* FTIR (Vertex 70, Bruker) combined with an *in-situ* QMS (HPR-20, Hiden). The setup allows us to precisely control the reaction condition and to probe the evolution of the reactant, the intermediates, and the products both in the surface and gas phase. The FTIR and QMS were connected *via* a multi reflection attenuated total reflection (ATR) flow cell (Harrick). Prior to each experiment, the photocatalyst materials (10 mg) were deposited on the Ge window of the ATR cell. The cell was leak tight and all experiments were performed under an O₂ partial pressure of <1e⁻¹² mbar (C(O₂) < 10 ppm). The bypass pump valve (V_D) was closed and the cell was kept in dark for 2 h to check the leakage. The IR spectra were recorded repeatedly every 5 min for all experiments. The schematic drawing of the apparatus, detailed experimental procedures, and data processing protocols (*i.e.*, integration method of the vibrational peaks) can be found in the Supporting Information [25].

3. Results and discussion

3.1. Pristine TiO₂

We first studied the photo-oxidation process of EG on rutile TiO₂ single crystal by *in-situ* surface science techniques. Fig. 1(a) shows a scanning tunneling microscope (STM) image of a typical

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