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In-situ probing photocatalytic C—C bond cleavage in ethylene glycol under ambient conditions and the effect of metal cocatalyst

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ABSTRACT

Photocatalytic polyol conversion provides a green approach for the synthesis of value-added products. However, efficient and selective photocatalysts that can prevent unwanted full oxidation are still missing, mostly due to a lack of mechanistic understanding. Here we use ethylene glycol (EG) as model compound to study the reaction pathways in photocatalytic polyol dissociation under aerated conditions using *in-situ* vibrational spectroscopy coupled with mass spectrometry. On pristine TiO_2, the presence of oxygen leads to the formation of formaldehyde *via* photocatalytic C—C bond cleavage, where the removal of photo-generated surface adsorbed proton (H^+_{ads}) in the form of water is the rate determining step (RDS). The photo-generated formaldehyde molecules subsequently convert into CO_2 *via* complete oxidation by oxygen, or into paraformaldehyde by polymerization with water. A promotion effect is observed when noble metal (Au, Pt, Ag) nanoparticles (NPs) are used as cocatalysts. While Ag and Au selectively promote the formation of paraformaldehyde, the addition of Pt facilitates the complete oxidation of EG into CO_2. By performing the reaction under a low oxygen partial pressure, we rationalize that Ag and Au NPs accelerate the polymerization of formaldehyde by providing water rapidly through direct oxidation of H_{ads} oxidation, whereas Pt NPs supply water indirectly, in a pathway *via* H_2 or formaldehyde oxidation.

1. Introduction

Polyols are alcohols with multiple hydroxyl groups. They appear in large quantities as by-products in the bio-diesel industry [1]. The upgrading of bio-derived polyols (*i.e.*, glycerol, erythritol, sorbitol) to value-added products including fuels, precursors for electronics and medicines by means of catalysis has attracted significant attentions for many years [2–4]. Hydrogenolysis, selective oxidation, and reforming are the most frequently applied approaches to convert polyols into fuels, aldehydes, acids, and syngas [5–9]. Many investigations have been carried out aiming at the design of efficient catalyst with high selectivity under mild conditions [10–12]. However, the previously addressed processes generally require substantial energy input for heating, along with the use of expensive catalysts and additional oxidants or reductants (*e.g.*, H_2O_2, H_2). Therefore it is desirable to find alternative approaches to reduce the cost of polyol conversion.

Photocatalysis provides an economic and green process for organic synthesis, as it can potentially use solar energy to drive various catalytic reactions [13–15]. By controlling the reaction conditions and the presence of electron donors and acceptors, the photo-generated electron-hole (e^-—h^+) pairs can be used to perform selective hydrogenation/dehydrogenation, hydrogenolysis, N-N and C-C coupling, and Diels-Alder reactions to enable the synthesis of many value-added chemicals [16–20].

Significant progress in the photo-conversion of polyols to value-add products has been also achieved. Chong et al. report the selective conversion of glycerol to hydroxyacetaldehyde (glycolaldehyde) using the Rh loaded on shape-controlled TiO_2 photocatalyst at 80 °C [21]. Meanwhile, the photosynthesis of dihydroxyacetone *via* partial oxidation of glycerol has been realised using a Bi_2WO_6 photocatalyst under visible light [22]. However, the low

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quantum efficiencies and poor control in selectivity in photocatalytic polyol conversion under ambient conditions limit such processes for large-scale applications.

The design of efficient photocatalysts for polyol conversion requires detailed mechanistic understanding of the reactions. Lercher and coworkers have applied global kinetic analysis to investigate the photo-reforming pathways of various polyols (ethylene glycol, glycerol, erythritol, arabitol and sorbitol) on Rh/TiO_2 in the absence of oxygen [23,24]. It has been found that the C—C bond cleavage pathway is the dominant process as compared to the oxidation of primary or secondary carbon and the dehydration process. This mechanistic insight suggests that the selectivity in photocatalytic polyol reforming may be controlled *via* tuning the electronic structure of surface atoms to alter the adsorption of the reactants, which provides guidelines for the design of new photocatalyst materials. By combining *in-situ* scanning tunneling microscopy (STM) with *in-situ* spectroscopy analysis, we have studied the photocatalytic dissociation pathway and the rate determining step (RDS) therein of ethylene glycol (EG) on TiO_2 single crystal and polycrystalline powders [25]. The EG molecule adsorbs on the surface Ti site and solely dissociates into formaldehyde *via* C—C bond cleavage, with desorption of H_{ads} in the form of H_2 as the RDS under conditions free of O_2 and water. Although the formation of formaldehyde can be accelerated by use of noble metal nanoparticles (NPs) to promote the release of H_2, the overall reaction rate still remains relatively slow.

Another challenge in photocatalytic polyol conversion under realistic conditions is to prevent the full oxidation of polyols and intermediates to CO_2. This occurs even under deaerated conditions, as the photogenerated charge carriers are generally considered to be non-selective [23]. Although the full oxidation of polyols seems inevitable, surface engineering of the photocatalyst to promote the desorption or polymerization of the reaction intermediates could be a feasible approach to slow down their consecutive oxidations. The feasibility of such a strategy has been demonstrated in surface science studies on single crystals model catalyst under ultrahigh vacuum conditions [26,27], however it is yet unclear how the electronic and geometrical structure of a photocatalyst surface can be manipulated to tune the suppression of total oxidation under realistic catalytic conditions.

Here we have investigated the reaction mechanism of photocatalytic polyol conversion under aerated conditions by employing EG as a model compound. We have performed *in-situ* vibrational spectroscopy coupled with mass spectrometry to explore the reaction pathways as a function of the EG surface coverage using pristine TiO_2 under ambient conditions. We have further investigated how the identity of metal (Au, Pt, and Ag) NPs loaded on TiO_2 influence the reaction rates and selectivities by careful controlling the reaction conditions.

2. Experimental section

2.1. Synthesis and characterization of photocatalysts

Degussa Aeroxide® P25 (P25) powders were chosen as pristine TiO_2 for *in-situ* spectroscopy analysis without further treatment. A standard photo-deposition method was applied to modify the P25 with 1 wt% of metal (Au, Pt, and Ag) NPs [28]. In practice, TiO_2 powders (200 mg) were added into deionized (DI) water (4 mL) and sonicated for 1 h to form a homogeneous suspension, which was then added dropwise to a 96 mL of 1:1 (v/v) water-ethanol solution under vigorous stirring. Aqueous solutions of $HAuCl_4·4H_2O$, $H_2PtCl_6·6H_2O$, or $AgNO_3$ containing equivalent amounts of metal (2 mg, corresponding to 1 wt% loading on TiO_2) were then added into the suspension under continuously stirring in the dark. The suspension was then deaerated by continuous N_2 purging to remove dissolved O_2. A UV LED (365 nm, Spectroline TRITAN 365) was then switched on for 0.5 h to deposit metal NPs on the TiO_2 after the suspension was purged for 0.5 h under dark. After irradiation, the suspension was centrifuged to collect the powders, which were subsequently washed by DI water for three times and finally dried at 80 °C for 12 h.

The samples were characterized by a transmission electron microscope (TEM, Talos TALOS F200A) with a TWIN lens system, an X-FEG electron source and a Ceta 16M Camera. X-ray photoelectron spectroscopy (XPS, K-Alpha, Thermo-Scientific) was applied to analyze the chemical composition and oxidation state of the elements in all samples. A monochromatic Al Kα source operated at an emission current of 6 mA and an accelerating voltage of 12 kV was used as the X-ray source. Survey scans were collected using a pass energy of 160 eV with a step size of 1 eV and a rate of 0.1 s/step, whereas the high-resolution spectra were acquired in the desired energy regions using pass energy of 40 eV with a step size of 0.1 eV and a rate of 0.5 s/step. The C1s binding energy of 284.6 eV for adventitious carbon was used for calibration. X-ray diffraction (XRD) analysis was performed using a Bruker D8 diffractometer with a step of 0.05° and an integration time of 2 s. The diffuse reflectance spectra (DRS) of the samples were recorded by a spectrophotometer coupled with a spherical integrating detector (UH4150, Hitachi).

2.2. Photocatalytic process analysis

The EG photo-dissociation was investigated using the previously established *in-situ* Fourier transform infrared spectrometer coupled with a quadruple mass spectrometer (FTIR-QMS, Supplementary Fig. S1) [25]. In short, the FTIR (Vertex 70, Bruker) and QMS (HPR-20, Hiden analytics) were connected by a multi reflection attenuated total reflection flow cell (ATR, Harrick) and a leak-valve. The ATR cell has a quartz window on top, which allows UV light (365 nm, Spectroline OPTIMAX™ 365) to irradiate the powder samples (deposited on a Ge window) while recording the vibrational spectra. The FTIR-QMS is a close loop, leak-tight system with a total volume of 55 mL, which allows continuous controlling and monitoring of the gas-phase composition by the QMS. Prior to the photocatalytic reaction, a desired volume of EG was dosed onto the photocatalyst film using a 1 μL syringe. The flow cell was then sealed and the leakage of the system was checked. The photo-dissociation of EG was evaluated by using pristine and metal (Au, Pt, Ag) decorated TiO_2 under ambient O_2 partial pressure [pO_2, $C(O_2) \approx 21 * 10^4$ ppm] and low pO_2 ($C(O_2) = 2100$ ppm), respectively. The control of initial O_2 concentrations was realized using an O_2 gas (>99.999%) cylinder and a bypass pump. While the IR spectra were recorded repeatedly every 5 min, the masses of 28 (N_2), 32 (O_2), 44 (CO_2) and 2 (H_2) were recorded continuously for all experiments. A minimum of two-hour stabilization in open air under dark conditions was applied for each experiment to allow precise calibration of all masses for quantitative analysis of the evolved gases. Prior to irradiation, the pre-adsorbed water on the photocatalyst was fully removed according to the IR spectra (Fig. S9). More details of the apparatus, experimental procedures and data processing protocols can be found in the Supporting Information [29].

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.jcat.2018.07.017.

3. Results and discussion

3.1. Photo-dissociation of ethylene glycol on pristine TiO_2

Our previous study shows that under deaerated conditions, the photo-dissociation of EG on pristine TiO_2 photocatalyst only takes