Photocatalytic organic synthesis: from fundamental to applications

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Abstract: Photocatalytic organic synthesis has attracted huge attention in recent years. The selective conversion of alcohols and nitrobenzenes to value-added products has been realised using various photocatalysts, however the efficiency and selectivity still need to be improved. Moreover, the lack of mechanistic understanding limits the design of high performance photocatalyst materials. Here we have studied the photocatalytic alcohol conversion from molecular to kinetic level by coupling surface science and *in-situ* spectroscopies analyses. We have also presented a scalable strategy for the controllable, efficient photosynthesis of a series of important azo- and azoxy- aromatics from nitro-aromatics under visible light irradiation.

Keywords: Photocatalysis, Organic synthesis, Reaction mechanisms.

1. Introduction

Photocatalysis has attracted huge attention for the last decades as it can drive several important reactions (*i.e.*, water splitting and CO_2 reduction) by directly utilizing solar energy.[1,2] Recently, photocatalytic organic synthesis has been in progress, especially in conversion of cheap chemicals to valuable products. The photo-generated electron-hole (e^--h^+) pairs offer the possibility of performing selective reduction or oxidation by controlling the reaction conditions; however the efficiency and selectivity still need to be enhanced.

Here we have investigated the reaction mechanisms and possible application of photocatalytic ethylene glycol (EG, the simplest polyol) and nitrobenzene conversion using metal/TiO_2 and the graphitic C_3N_4 (g-C_3N_4) photocatalysts, respectively. For the photocatalytic EG conversion, we have probed the bond cleavage and the rate determining step (RDS) by coupling interdisciplinary *in-situ* analytic methods. For the photocatalytic nitrobenzene conversion, we have shown that the valuable azobenzene or azoxybenzene can be efficiently and selectively synthesised using the g-C_3N_4 by controlling the irradiation conditions. The reaction mechanism has been also revealed by a set of *in-situ* analyses with calculations.

2. Experimental

For photocatalytic EG conversion, the Degussa P25 TiO_2 powders were used for spectroscopy study. Metal (Au, Pt, and Pd) nanoparticles (NPs) were loaded on P25 *via* a photo-deposition method. The EG photo-dissociation on pristine and metal/TiO_2 powders was studied using an *in-situ* Fourier transform infrared (FTIR) combined with an *in-situ* QMS. For photocatalytic nitrobenzene conversion, the g-C_3N_4 synthesised *via* pyrolysis of urea was used as photocatalyst. The gas chromatography (GC) was used to determine the products. Post mortem temperature programmed desorption (P-TPD) were performed to analyse the bonding strength of the surface adsorbed hydrogen (H_{ads}) under reaction conditions.

3. Results and discussion

One part of EG converts into two parts of formaldehyde and two parts of H_{ads} on pure TiO_2 according to *in-situ* scanning tunnelling microscopic (STM), TPD, and FTIR upon UV irradiation under deaerated conditions.[3] Figure 1(a) compares the evolution of formaldehyde using pure TiO_2 and Au, Pd, Pt NPs loaded TiO_2 derived from *in-situ* FTIR. The metal NPs significantly enhanced the formation of formaldehyde followed the order of Pt > Au ≈ Pd > pristine TiO_2. Meanwhile, the increase in H_2 evolution rates also followed the same order (Fig. 1b). The zero order kinetics of the H_2 evolution rate for pure TiO_2 suggest that the H_{ads} desorption is the RDS for the photocatalytic EG conversion. The first order kinetics of the H_2 evolution for all metal/TiO_2 samples imply that the metal NPs promotes the H_{ads} desorption thus enhancing the photocatalytic EG dissociation, as schematically presented in Fig. 1(c).

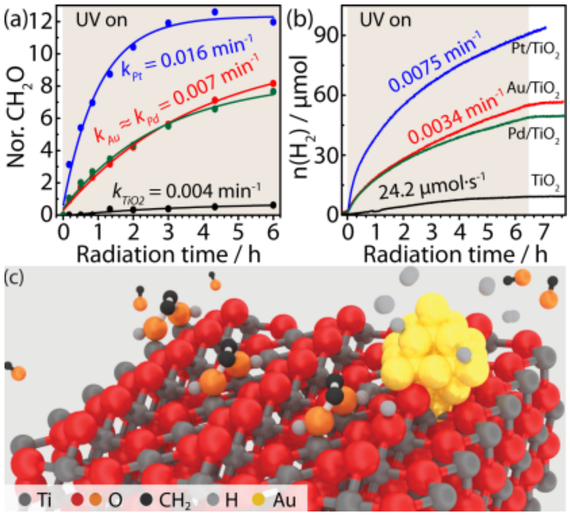

Figure 1. Evolution of formaldehyde (a) and H_2 gas (b) during photocatalytic EG conversion using pristine and metal/TiO_2. (c) Proposed promotion effect of metal NPs on photocatalytic EG conversion.

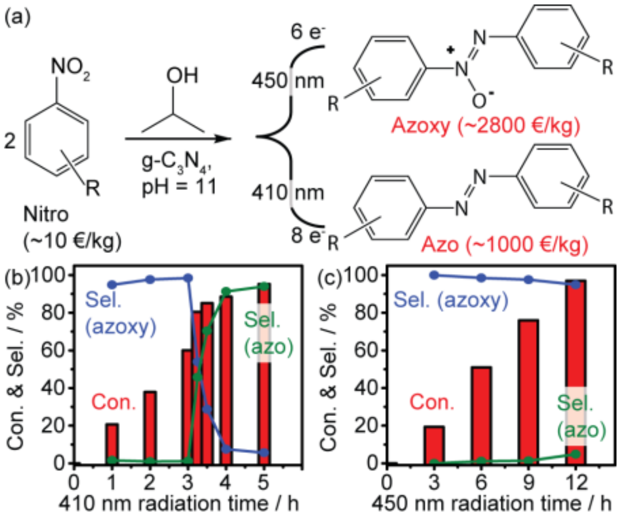

Figure 2. (a) Reaction scheme of nitrobenzene photoconversion. (b) and (c) Conversion (Con.) and selectivity (Sel.) to azobenzene and azoxybenzene using g-C_3N_4 under 410 nm and 450 nm irradiation.

Figure 2(a) shows the reaction scheme of selective photoconversion of nitrobenzene and a series of derivatives to either azoxybenzene or azobenzene using g-C_3N_4 with the presence of isopropanol as electron donor under basic conditions.[4] Whilst azobenzene was gradually formed in a two-step reduction *via* azoxybenzene formation under 410 nm irradiation (Fig. 2b), the azoxybenzene was found to be the main product throughout the 450 nm irradiation course (Fig. 2c). Under both irradiation conditions, the nitrobenzene reached full conversion (> 95%) with high selectivity (> 94%) without the formation of cheap aniline. Our mechanistic study reveals that the g-C_3N_4 facilitates the photocatalytic N-N coupling of the nitro-aromatics, and the weakly adsorbed photogenerated H_{ads} contributes to the excellent performance in the multi-electron transfer process.

4. Conclusions

We have presented two case studies in photocatalytic organic synthesis. For the photocatalytic EG conversion, a molecular level mechanism picture has been proposed based on surface science and *in-situ* spectroscopies analyses. We anticipate that our mechanistic study will promote the understanding of the photo-conversion of more complicated polyols to help the design of novel photocatalyst materials. We also present a scalable photocatalytic strategy for the controllable, efficient synthesis of a series of important azo- and azoxy- aromatics from their corresponding nitro-aromatics under visible light irradiation at RT.

References

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