Selective Hydrogenation via Cascade Catalysis on

Amorphous TiO₂

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1, Experiment section

1.1 Materials

All chemicals involved were of analytical grade and used without further purification.

1.2 Preparation of A-TiO₂

The amorphous TiO₂ (A-TiO₂) was prepared through the photo-induced hydrolyzation of titanium glycolate, which was reported by Zou *et al.* previously.¹ Typically, 50 mL of glycol was added into the flask and heated to 150 °C (oil bath) under reflux. Then, 3 mL of tetrabutyl titanate was added into the flask. The system was heated to 160 °C and maintained for 2 h. The obtained white precipitate was washed with ethanol several times and dried at 60 °C. Subsequently, 1 g of the white precipitate was evacuated by N₂ and sealed, the illumination (300 W Xenon lamp) was turned on for 6 h. The obtained material was washed with water for several times, dried at 60 °C and then ground into powder to be used.

2、Characterization

X-ray diffraction (XRD) patterns were collected by a Rigaku Miniflex II desktop X-ray diffractometer operating at 30 kV and 100 mA, while the wavelength of the monochromatized Cu K α radiation was 0.15418 nm. The FTIR spectra were collected by a Lambda FTIR-7600 spectrometer over 4000-400 cm⁻¹ with a resolution of 4 cm⁻¹. The UV-visible absorption spectra were measured by a Hitachi U-3010 spectrophotometer.

3、Hydrogenation reaction of HMF

All the experiments were carried out in a customized photochemical reactor under N₂ atmosphere. The temperature of the system was maintained at 25 °C. The hydrogenation cascade reaction of HMF was divided to two reactions. Reaction 1 (the storage of H^+/e^- species on the A-TiO₂): 50 mg of the A-TiO₂ was dispersed in 50 mL ethanol then illuminated under 25 W UV light for 1 h; Reaction 2 (hydrogenation of HMF): 15 µmol of HMF was injected and the system was kept in the "dark" for 1 h. The liquid products were analyzed by a Agilent 1260 Infinity high performance liquid chromatography equipped with a C18 column and a UV detector, as well as a Techcomp GC7900 gas chromatographer with a SE-54 column and a flame ionization detector. The gaseous products were analyzed by the gas chromatographer with a TDX-01 column.

4、 Additional date



Figure S1. Time course of HMF and BHMF in the hydrogenation process.



Figure S2. XRD patterns of fresh $A-TiO_2$ and $A-TiO_2$ after cycling test.



Figure S3. a, The selectivity of BHMF varies with illumination time in ethanol and isopropanol, respectively; **b**, UV-visible absorption spectra of BHMF (green line) and possible condensation reaction product (red line) of BHMF and acetone under the irradiation of UV light.

As shown in Figure S3a, the selectivity of BHMF in ethanol remained at high level (~99%). However, the selectivity of BHMF decreased in isopropanol, which implied that BHMF might be consumed with illumination time during the photocatalytic process. Considering isopropanol could be photo-oxidized into acetone, we designed an experiment between BHMF and acetone under UV light irradiation. As demonstrated in Figure S3b, the reaction between BHMF and acetone was detected, which would lead to the decrease of the selectivity of BHMF.



Figure S4. The analysis of oxidative product: **a**, gaseous products analyzed by GC; **b**, liquid products analyzed by HPLC; **c**, the standard samples of several possible products.



Figure S5. Gas chromatography analysis of the solvent after UV irradiation.



Figure S6. FTIR spectra of cinnamaldehyde, A-TiO₂, and A-TiO₂ after cinnamaldehyde adsorption.2

References

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