

Photocatalytic hydrogenation of acetophenone on a titanium dioxide cellulose film

- Supporting Information -

Tabea A. Thiel ^a, Keisuke Obata ^b, Fatwa F. Abdi ^b, Roel van de Krol ^b, R. Schomäcker ^a, Michael Schwarze ^a

^aTechnische Universität Berlin, Department of Chemistry, TC8, Straße des 17. Juni 124, 10623 Berlin

^bInstitute for Solar Fuels, Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Hahn-Meitner-Platz 1, 14109 Berlin, Germany

Modification of cellulose

Cellulose isolated from *Styela Clava* (abbreviated as UnCe, Otto-Van-de-Berg-Company) and sulfuric acid H₂SO₄ (96 %, ≥95 wt%, Roth) were used as chemicals. The synthesis of modified cellulose (ModCe) by sulfuric acid hydrolysis was conducted by a method reported by van der Berg et al. with slight modifications.¹ Concentrated H₂SO₄ (120 mL) was slowly added under vigorous stirring to a mixture of UnCe (4.5 g) in water (120 mL) at a temperature of 4 °C using a double-walled glass reactor (600 mL). The mixture was then stirred at 60 °C for 2 hours and cooled down to 4 °C again. The obtained suspension was filtered and washed over a small-pore glass fritted filter until the pH became neutral. The modified cellulose was freeze-dried for three days (Alpha 1-4, Christ).

Dissolved oxygen concentration

The approximate oxygen concentration dissolved in ethanol c_{O_2} from the air in the gas phase is calculated with the Henry constant K_{H,O_2} using Eqn. S1-S3, where x is the mole fraction, p is the pressure of the gas phase, ρ_{EtOH} the density of ethanol, and M_{EtOH} the molar mass.

$$K_{H,O_2} = \frac{p}{x} \cdot 0,21 \quad (S1)$$

$$c_{O_2} \approx x \frac{\rho_{EtOH}}{M_{EtOH}} = x \cdot 17.13 \frac{mol}{L} \quad (S2)$$

$$c_{O_2} = \frac{p}{K_{H,O_2}} \cdot 0.21 \cdot 17.13 \frac{mol}{L} \quad (S3)$$

With a Henry constant of 1760 atm^2 for 293 K and an atmospheric pressure of 1 atm, an atmospheric oxygen concentration of 2.04 mol/L is obtained. For comparison, the atmospheric oxygen concentration in water is 0.27 mmol/L.³ With the ideal gas equation, the atmospheric oxygen concentration in the headspace is 22,73 mol/L.

HPLC chromatography

Figure S1 shows the HPLC chromatogram for different wavelengths applied in the photocatalytic hydrogenation of ACP.

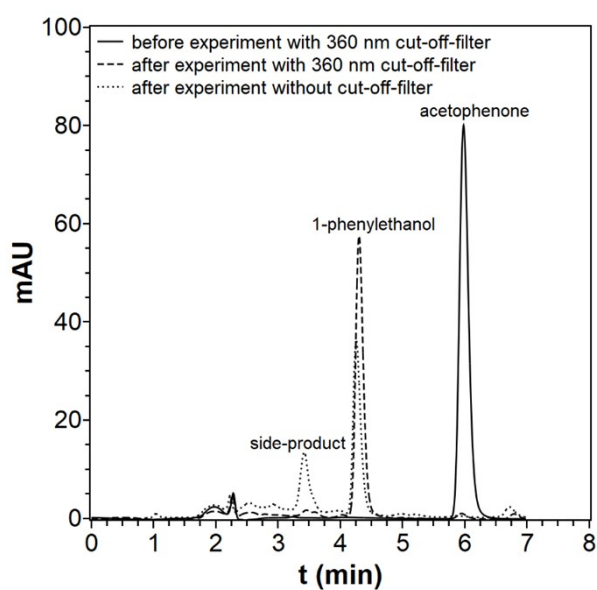


Figure S1: Chromatograms of the reaction solution before an experiment containing ACP only and afterward containing the product 1-phenylethanol. When no filter or filter that blocks wavelengths $\leq 300 \text{ nm}$ is used, another signal appears which is a side-product.

Side-irradiation reactor (SIR)

For kinetic investigations, the SIR (Figure S2) was used. The SIR has a total volume of 35 mL and consists of a planar quartz glass window.

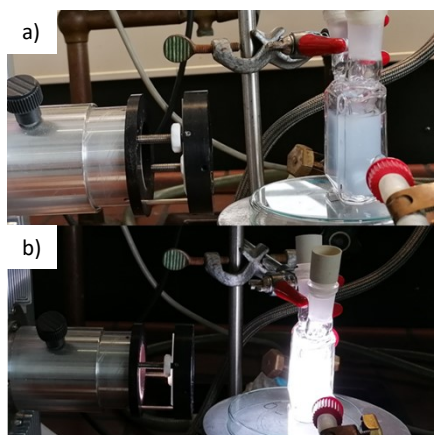


Figure S2: Photocatalytic hydrogenation in SIR after irradiation (a) and during irradiation (b).

Top-irradiation reactor (TIR)

The TIR was used for the experiments with the film (Figure S3). The TIR consists of borosilicate glass with a total volume of 250 mL and has a removable quartz glass window (\varnothing 4 cm) on top. The irradiated circular surface of the PCF fixed on the Teflon substrate holder had a diameter of 3 cm. The substrate holder has a total diameter of 3.8 cm, and the lower part, on which the PCF lies, has a height of 0.5 cm. The height of the liquid phase is 11 cm. The total distance between lamp and PCF is 12 cm. The PCF containing TiO₂ (PC500) turns blue during the reaction and white when oxygen reaches the PCF, which was already reported in the literature^{4,5}

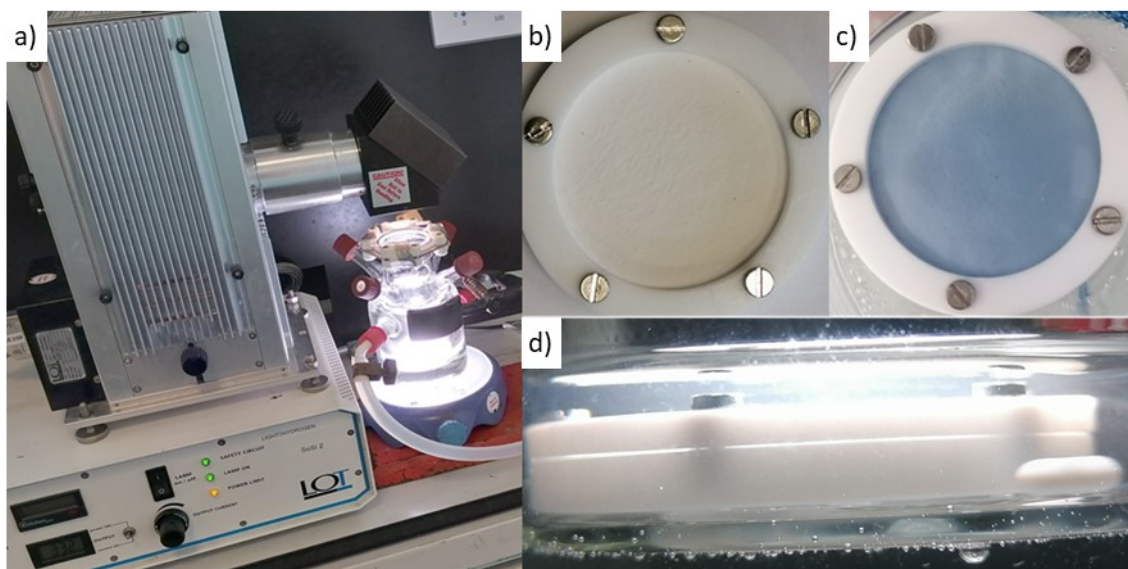


Figure S3: Photocatalytic hydrogenation of acetophenone in the TIR (a), PCF before irradiation (b), PCF after irradiation (c), and the substrate with PCF in the liquid phase (d).

Further results from reaction kinetics

The reaction was performed at different temperatures (Table S1) to determine the activation energy. In addition to the 1st order kinetics, the Langmuir-Hinshelwood equation was used to fit the experimental data.

Table S1: Reaction rate constants k for different reaction temperatures T.

T (K)	278	285	292	303
k (10⁻³·min⁻¹)	8.3	11.8	16.1	21.1

Here k is the rate constant, K_{LH} is the Langmuir-Hinshelwood constant, and c_{ACP} is the concentration of acetophenone:

$$-\frac{d}{dt}c_{ACP} = \frac{k \cdot K_{LH} \cdot c_{ACP}}{1 + K_{LH} \cdot c_{ACP}} \quad (S4)$$

When c_{ACP} is low, the LH equation can be simplified into the pseudo 1st order rate law. The fitting of the concentration-time profiles with the 1st order rate law and the Langmuir-Hinshelwood equation in Figure S4 have minor differences, which are also shown by the rate constants in Table 2.

Table S2: Obtained rate constants of the photocatalytic hydrogenation of acetophenone using the pseudo 1st order and Langmuir-Hinshelwood model.

1st order	Langmuir-Hinshelwood		
k_{1st}	k	K_{LH}	k_{1st} = k·K_{LH}
(10⁻³·min⁻¹)	(L·min⁻¹·mol⁻¹)	(10⁻⁴·L·mol⁻¹)	(10⁻³·min⁻¹)
17.0	23.5	9.6	22.5

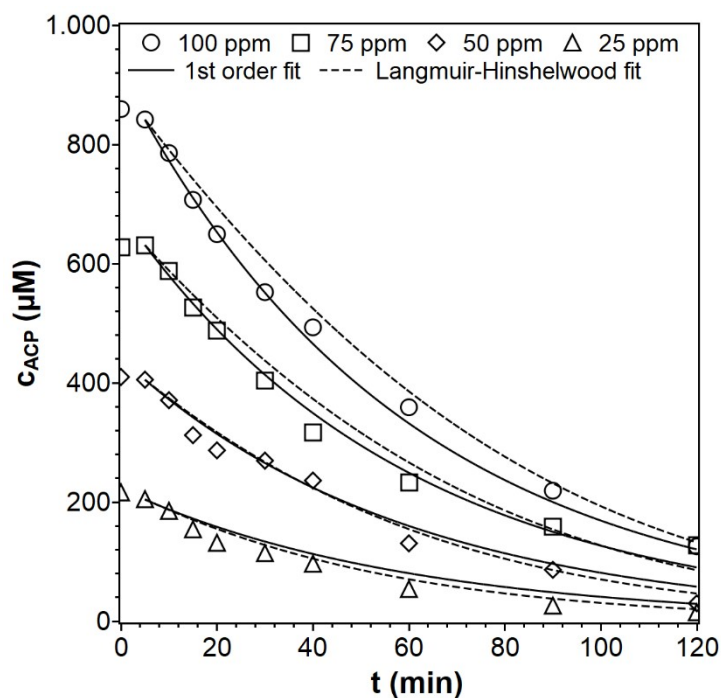


Figure S4: Concentration-time profiles of ACP with pseudo 1st order and Langmuir-Hinshelwood fit.

Energy profiles for different types of hydrogenation

To compare the different types of hydrogenation, their energy profiles were constructed using Eqn. S5-S6. The standard values for the reactants (Table S3) were taken from the literature and the calculated enthalpies are summarized in Table S4.

$$\Delta_R H_{reaction} = \sum_{product} \Delta_f H_{product}^0 - \sum_{educt} \Delta_f H_{educt}^0 \quad (S5)$$

$$\Delta_R G_{reaction} = \sum_{product} \Delta_f G_{product}^0 - \sum_{educt} \Delta_f G_{educt}^0 \quad (S6)$$

Table S3: Standard enthalpies of formation for all educts and products of the photocatalytic, conventional and transfer hydrogenation reaction.

	$\Delta_f H^0$ (kJ/mol)	$\Delta_f G^0$ (kJ/mol)
Acetophenone ⁶	-142.50	-0.03
1-phenyl ethanol	-138.70 ⁷	-10.37 ⁸
Hydrogen	0.00	0.00
Ethanol ⁹	-277.05	-170.86

Isopropanol ¹⁰	-317.00	-164.88
Ethanal ¹¹	-196.4	-133.56
Acetone ¹²	-249.4	-154.54

Table S4: Calculated reaction and free enthalpies of the photocatalytic, conventional, and transfer hydrogenation reaction.

	$\Delta_R H^0$ (kJ/mol)	$\Delta_R G^0$ (kJ/mol)
Classic hydrogenation	3.80	-10.34
Transfer hydrogenation	71.40	0.00
Photocatalytic hydrogenation	-205.02	-233.04

Recycling experiment

The film was recycled several times, and the individual concentration profiles were fitted to the pseudo 1st order rate law. The rate constants are summarized in Table S5. The optical behavior of the films after each recycling is shown in Figure S5.

Table S5: Rate constants k of the reaction performed in the SIR and TIR with suspended TiO_2 , and with TiO_2 immobilized as PCF before (1st run) and after multiple recyclings (2nd – 4th runs).

	k ($10^{-3} \cdot \text{min}^{-1}$)
SIR (TiO_2 powder)	16.2
TIR (TiO_2 powder)	6.2
PCF (1 st run)	3.9
PCF (2 nd run)	3.3
PCF (3 rd run)	4.0
PCF (4 th run)	2.8

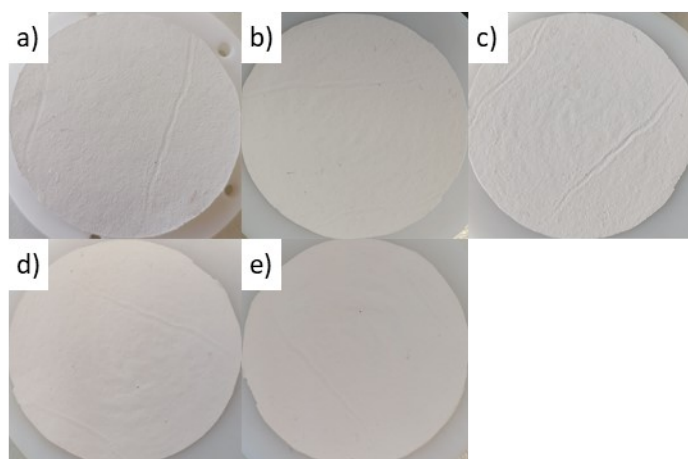


Figure S5: Optical behaviour of the films before the 1st run (a), after the 1st run (b), after the 2nd run (c), after the 3rd run (d), and after the 4th run (e).

Cellulose characterization

The structure of the modified cellulose, from which the film was prepared, is shown in Figure S6.



Figure S6: TEM image cellulose before preparation of the PCF.

Catalyst/Cellulose separation

For the recovery of the TiO₂ photocatalyst, the film can be treated with concentrated sulphuric acid, which will lead to complete the dissolution of cellulose. From this dispersion, TiO₂ can be recovered, e.g., by centrifugation. The individual steps are shown in Figure S7.

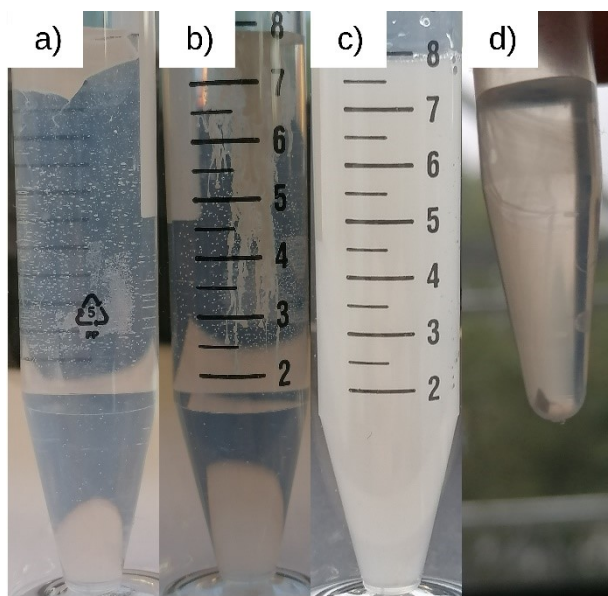


Figure S7: A piece of PCF before (a) and during the dissolution of the cellulose and the associated release of the TiO₂ (b), complete dissolved cellulose and dispersed photocatalyst (c), and settled TiO₂ after centrifugation (d).

References

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