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

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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. 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 𝑐₀₂ from the air in the gas phase is calculated with the Henry constant 𝐾_{Η, 𝒏₂} using Eqn. S1-S3, where 𝑥 is the mole fraction, 𝑝 is the pressure of the gas phase, 𝑝_{ Erot} the density of ethanol, and 𝑀_{ Erot} the molar mass.

\[ 𝐾_{Η, 𝒏₂} = \frac{𝑝}{𝑥} \cdot 0.21 \]  
\[ 𝑐₀₂ ≈ x \cdot \frac{𝑝_{ Erot}}{𝑀_{ Erot}} = x \cdot 17.13 \frac{mol}{L} \]  
\[ 𝑐₀₂ = \left( \frac{𝑝}{𝐾_{Η, 𝒏₂}} \right) \cdot 0.21 \cdot 17.13 \frac{mol}{L} \]  

(S1)

(S2)

(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.

![HPLC Chromatogram](image)

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 ≤ 300 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 (Ø 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.

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 |
|---------|-----|-----|-----|-----|
| $k$ ($10^{-3}\cdot$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:

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

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 |
|-----------|----------------------|
| $k_{1st}$ ($10^{-3} \cdot$min$^{-1}$) | $k$ (L$\cdot$min$^{-1}$$\cdot$mol$^{-1}$) | $K_{LH}$ ($10^{-4} \cdot$L$\cdot$mol$^{-1}$) | $k_{1st} = k \cdot K_{LH}$ ($10^{-3} \cdot$min$^{-1}$) |
| 17.0 | 23.5 | 9.6 | 22.5 |
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.

\[
\Delta_H^{\text{reaction}} = \sum_{\text{product}} \Delta H_0^{\text{product}} - \sum_{\text{educt}} \Delta H_0^{\text{educt}} \tag{S5}
\]

\[
\Delta G^{\text{reaction}} = \sum_{\text{product}} \Delta G_0^{\text{product}} - \sum_{\text{educt}} \Delta G_0^{\text{educt}} \tag{S6}
\]

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

|                      | \(\Delta H_0^0\) (kJ/mol) | \(\Delta G_0^0\) (kJ/mol) |
|----------------------|-----------------------------|-----------------------------|
| Acetophenone         | -142.50                     | -0.03                       |
| 1-phenyl ethanol     | -138.70                     | -10.37                      |
| Hydrogen             | 0.00                        | 0.00                        |
| Ethanol              | -277.05                     | -170.86                     |
| Substance      | $\Delta R H^0$ (kJ/mol) | $\Delta R G^0$ (kJ/mol) |
|---------------|--------------------------|--------------------------|
| Isopropanol   | -317.00                  | -164.88                  |
| Ethanal       | -196.4                   | -133.56                  |
| Acetone       | -249.4                   | -154.54                  |

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

| Reaction Type                | $\Delta R H^0$ (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                  |

Recovering 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).

| Reaction Type      | $k$ ($10^3$-min$^{-1}$) |
|--------------------|--------------------------|
| SIR (TiO$_2$ powder) | 16.2                     |
| TIR (TiO$_2$ powder) | 6.2                      |
| PCF (1st run)      | 3.9                      |
| PCF (2nd run)      | 3.3                      |
| PCF (3rd run)      | 4.0                      |
| PCF (4th 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 TiO$_2$ photocatalyst, the film can be treated with concentrated sulphuric acid, which will lead to complete the dissolution of cellulose. From this dispersion, TiO$_2$ 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 TiO$_2$ (b), complete dissolved cellulose and dispersed photocatalyst (c), and settled TiO$_2$ after centrifugation (d).
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