Titania Supported on Silica as Efficient Catalyst for Deep Oxidative Desulfurization of a Model Fuel with Exceptionally Diluted H₂O₂

Electronic supplementary Materials

C. G. Piscopo, a J. Tochtermann, a M. Schwarzer, a D. Boskovic, a R. Maggi, b G. Maestri b and S. Loebbecke a

a Fraunhofer Institute for Chemical Technology, Energetic Materials, Joseph-von-Fraunhoferstr. 7, 76327 Pfinztal (Germany)

b Clean Synthetic Methodology Group, Department of Chemical and Life Sciences and Environmental Sustainability, University of Parma, Parco Area delle Scienze 17A, 43124 Parma (Italy).

1. Materials and methods

Chemicals and solvents were analytical grade, purchased from various commercial suppliers and used without further purification.

Powder diffraction measurements were performed on a Bragg-Brentano Diffractometer, D8 Advance from Bruker AXS, equipped with copper tube, 2.5° Soller collimators, 0.3 mm divergence slit, anti-scatter screen, flip-stick stage and silicon strip detector (LynxEye) with 3° 2θ detector opening. The diffraction patterns were monitored between 5° and 65° 2θ with 0.06° 2θ step width and 3s counting time per step.

Nitrogen adsorption/desorption isotherms were measured at 77 K using a Quantachrome Autosorb IQ-C surface area analyzer. Samples were degased in vacuum for 18 h at 100°C prior to the analysis. BET pressure range varied between 3∙10⁻³ and 7.2∙10⁻² bar. For the calculation of the BET surface area all the criteria for a correct estimation where taken into account.

SEM snapshots were acquired using a Zeiss Supra 55VP microscope allowing the observation of the different crystal micro and nano morphologies.

HPLC (Instrument: Agilent 1200; column: Zorbax Bonus RP 250 ×4.6, 5 μm; eluent: MeOH/H₂O + 0.03% TFA with gradient–gradient: 0 min. 38% MeOH, 5 min. 38% MeOH, 5.1 min. 82% MeOH, 12 min. 82% MeOH; flow rate: 1 mL min⁻¹; injection volume: 5 μL; detector: DAD at 254 nm; temperature: 25 °C). Dibenzothiophene sulphoxide and sulfone were identified by comparison with pure reference samples.

B.E.T. references:
2. Catalyst preparation and preliminary tests

**Ti-SBA15 synthesis**

10 g of surfactant Pluronic P-123 (MW: ≈5800; 1.7 mmol) were dissolved at 35 °C in 80 ml of a solution 1:1 of H₂O/EtOH inside a 500 ml three neck round bottom flask, equipped with a gas valve, drop funnel and a bubble counter, under argon atmosphere. Then 100 ml of a 2M HCl were added to the solution. Subsequently 18.4 ml of Tetraethyl orthosilicate (d: 0.94 g/mL; MW: 208.32; 83 mmol) and 0.4 ml of TiCl₄ (d: 1.73 g/mL; MW: 189.71; 3.3 mmol, equivalent to 3.5 w/w %) were dripped slowly into the flask. The solution was allowed to stir at 35 °C for 1 day, obtaining a gel, which has been transferred into a Teflon vessel and left aging without stirring at 50 °C for 4 days. The obtained solid has been filtered off, washed with plenty of H₂O, dried overnight in an oven at 50 °C and finally calcined at 450 °C for 6 h.

Ref:

**TS-1 synthesis**

0.5 g of surfactant Pluronic P-123 (MW: ≈5800; 0.09 mmol) were dissolved in 1 ml of H₂O and 4 ml of Tetraethyl orthosilicate (d: 0.94 g/mL; MW: 208.32; 18 mmol) and left under stirring for at least 30 minutes in order to obtain a homogeneous solution (Solution A). 0.07 ml of TiCl₄ (d: 1.73 g/mL; MW: 189.71; 0.6 mmol) were dissolved in 3 ml of isopropanol and dripped into the solution A. The resulting solution was allowed to stir at room temperature for 12 h; the temperature has been later raised to 80 °C maintaining the stir for additional 3 h. 10 ml of H₂O were added to the solution, which was transferred in to a glass dish crystallization and allow to dry at room temperature for 4 days. The obtained solid has been washed with plenty of H₂O and calcined at 500 °C for 6 h.

Ref:

**TS-1-B-doped synthesis**

1 ml of TiCl₄ (d: 1.73 g/mL; MW: 189.71; 9.1 mmol) was dissolved in 56 ml of H₂O and 5.1 ml of aqueous H₂O₂ 30% w/w and left under vigorous stirring at room temperature for 2 h (solution A). 5 g of surfactant Pluronic P-123 (MW: ≈5800; 0.86 mmol) were dissolved in a mixture of 50 mL of H₂O and 64.5 ml of Tetraethyl orthosilicate (d: 0.94 g/mL; MW: 208.32; 290 mmol) (Solution B). 3.6 g of Boric acid (MW: 61.83; 56.6 mmol) were dissolved in 120 ml of H₂O and poured slowly into the solution B. The resulting mixture (Solution C) was vigorously stirred for 15 minutes and subsequently kept at 65 °C for 3 h. Once the Solution C has been cooled down to room temperature, the Solution A has been dripped on it. The pH of the resulting mixture was increased to 11 through
the addition of aqueous NH₃ (35% w/w). The mixture was transferred into a Teflon vessel and kept at 175 °C for 5 days, without stirring. The obtained solid has been filtered off, washed with plenty of H₂O and calcined at 550 °C for 4 h.

Ref:

**TiO₂@SiO₂ synthesis**

\[
\text{Si-OH} + \text{TiCl}_4 \xrightarrow{\text{heptane, N}_2, 100^\circ\text{C}} \text{SiOH} \quad \text{then calcined at 500℃}
\]

10 g of SiO₂ were dried in an oven at 120 °C overnight. The solid material was transferred into a 50 ml three neck round bottom flask, equipped with gas valve, dropping funnel and bulb condenser and provided with NaOH scrubber. The flask was flushed with argon and a solution of of TiCl₄ (0.48 mL; 4.38 mmol) in 22 ml of heptane has been added slowly through the dropping funnel. The mixture was heated up to 100 °C and kept under stirring for 2 h, after that the condenser has been removed and the temperature was raised up to 130 °C to allow the evaporation of the solvent. The obtained solid has been calcined at 500 °C for 6 h.

**TiO₂@SiO₂-Sil synthesis**

\[
\text{Si-OH} + \text{OCH}_3 \xrightarrow{\text{toluene, N}_2, 120^\circ\text{C}} \text{Si-O-Si}
\]

10 g of TiO₂ @SiO₂ were suspended in 100 mL of toluene in a 500 ml three neck round bottom flask, equipped with gas valve, dropping funnel and bulb condenser. The flask was flushed with argon and the mixture was heated up to 120 °C under vigorous stirring. 3.19 ml of ethyltrimethoxysilane (d: 0.94 g/mL; MW: 150.25; 20 mmol) were added to the suspension through the dropping funnel and the mixture was allowed to stir under reflux for 4 h. The obtained solid has been filtered off, washed with plenty of toluene and dried at air.

Ref:
**Scheme 1.** Biphasic oxidative desulfurization of a model fuel, using Dibenzothiophene 1 as sulfur source.

**Table 1.** Batch optimization of DBT 1 oxidation with aqueous hydrogen peroxide\(^{[a]}\)

<table>
<thead>
<tr>
<th>Entry</th>
<th>H(_2)O(_2)/1</th>
<th>T °C</th>
<th>Cat. Amount (mg)</th>
<th>Final sulfur (ppm)(^{[b]})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5:1</td>
<td>60</td>
<td>50</td>
<td>810</td>
</tr>
<tr>
<td>2</td>
<td>10:1</td>
<td>60</td>
<td>50</td>
<td>698</td>
</tr>
<tr>
<td>3</td>
<td>20:1</td>
<td>60</td>
<td>50</td>
<td>673</td>
</tr>
<tr>
<td>4</td>
<td>10:1</td>
<td>80</td>
<td>50</td>
<td>650</td>
</tr>
<tr>
<td>5</td>
<td>10:1</td>
<td>60</td>
<td>250</td>
<td>345</td>
</tr>
</tbody>
</table>

\(^{[a]}\) Reaction conditions: 2 ml of DBT 1 solution in dodecane (0.024 mol/L), 2ml of acetonitrile, catalyst: Amberlite IR 120 H, X ml of H\(_2\)O\(_2\) solution at 3%, time: 24 h

\(^{[b]}\) Determined by HPLC analysis


**Table 2.** B.E.T. Surface Area and Total Pore Volume of TiO\(_2\)@SiO\(_2\) and TiO\(_2\)@SiO\(_2\)-Sil catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>B.E.T. Surface Area m(^2)/g</th>
<th>Total Pore Volume cc/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO(_2)@SiO(_2) fresh</td>
<td>436</td>
<td>6.34 (\cdot) 10(^{-1})</td>
</tr>
<tr>
<td>TiO(_2)@SiO(_2) used</td>
<td>437</td>
<td>6.12 (\cdot) 10(^{-1})</td>
</tr>
<tr>
<td>TiO(_2)@SiO(_2)-Sil fresh</td>
<td>377</td>
<td>4.51 (\cdot) 10(^{-1})</td>
</tr>
<tr>
<td>TiO(_2)@SiO(_2)-Sil used</td>
<td>387</td>
<td>4.13 (\cdot) 10(^{-1})</td>
</tr>
</tbody>
</table>
Figure 1. Nitrogen adsorption isotherms of fresh TiO$_2$@SiO$_2$ (a) and TiO$_2$@SiO$_2$-Sil (b)

Figure 2. Nitrogen adsorption and desorption isotherms of used TiO$_2$@SiO$_2$ (a) and TiO$_2$@SiO$_2$-Sil (b)
**Figure 3.** DFT Pore Size distribution of fresh TiO$_2$@SiO$_2$ (a) and TiO$_2$@SiO$_2$-Sil (b)

**Figure 4.** TGA of TiO$_2$@SiO$_2$ (a) and TiO$_2$@SiO$_2$-Sil (b)

**Figure 5.** SEM snapshots of TiO$_2$@SiO$_2$ (a), calcinated TiO$_2$@SiO$_2$ (b) and TiO$_2$@SiO$_2$-Sil (c).
Figure 6. Experimental Setup used for the ODS of a model fuel. The syringe pumps on the left fed the model fuel and the diluted hydrogen peroxide into the tubular glass reactor dipped into a water bath.