

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

Electronic supplementary Materials

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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 degassed 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 were 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:

- T. Düren, F. Millange, G. Férey, K. S. Walton and R. Q. Snurr, *J. Phys. Chem. C*, **2007**, 111, 15350.
- I. Senkovska and S. Kaskel, *Chem. Commun.*, **2014**, 50, 7089.

2. Catalyst preparation and preliminary tests

Ti-SBA15 synthesis

10 g of surfactant Pluronic P-123 (MW: \approx 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:

- W. Zhan, J. Yao, Z. Xiao, Y. Guo, Y. Wang, Y. Guo and G. Lu, *Micropor. Mesopor. Mat.*, **2014**, 183, 150-155
- R. H. Acuña, R. Nava, C. L. Peza-Ledesma, J. Lara-Romero, G. Alonso-Nuñez, B. Pawelec and E. M. Rivera-Muñoz, *Materials*, **2013**, 6, 4139-4167.
- S. Y. Chen, L. Y. Jang and S. Cheng, *Chem. Mater.*, **2004**, 16, 4174-7180

TS-1 synthesis

0.5 g of surfactant Pluronic P-123 (MW: \approx 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:

- C. Shen, Y. J. Wang, J. H. Xu and G. S. Luo, *Chem. Eng. J.*, **2015**, 259, 552-561.
- X. Wang, x. Zhang, Y. Wang, H. Liu, J. Wang, J. Qiu, H. L. Ho, W. Han and K. L. Yeung, *Chem. Eng. J.*, **2011**, 175, 408-416.

TS-1-B-doped synthesis

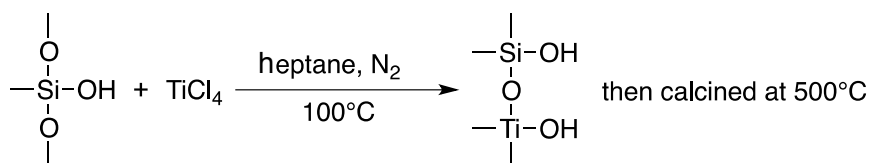
1 ml of TiCl₄ (d: 1.73 g/mL; MW: 189,71; 9.1 mmol) was dissolved in 56 ml of H₂O and 5.1 ml of aqueous H₂O₂ 30% w/w and left under vigorous stirring at room temperature for 2 h (solution A). 5 g of surfactant Pluronic P-123 (MW: \approx 5800; 0.86 mmol) were dissolved in a mixture of 50 mL of H₂O and 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:

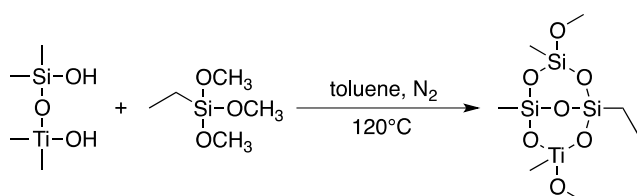
- M. V. Shamzhy, C. Ochoa-Hernández, V. I. Kasneryk, M. V. Opanasenko and M. Mazur, *Catal. Today*, **2016**, 277, 37-47.
- M. G. Vargas, S. Stevenson and D. F. Shantz, *Micropor. Mesopor. Mat.*, **2013**, 170, 131-140.
- D. T. On, S. Kaliaguine and L. Bonneviot, *J. Catal.*, **1995**, 157, 235-243

TiO₂@SiO₂ synthesis



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 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



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:

- R. Castillo, B. Kock, P. Ruiz and B. Delmon, *J. Mat. Chem.*, **1995**, 4, 903-906
- C. J. Karas, Y. Z. Han and D. W. Leyshon, *Patent No.:* US Pat., 20040178122A1, 2004.

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

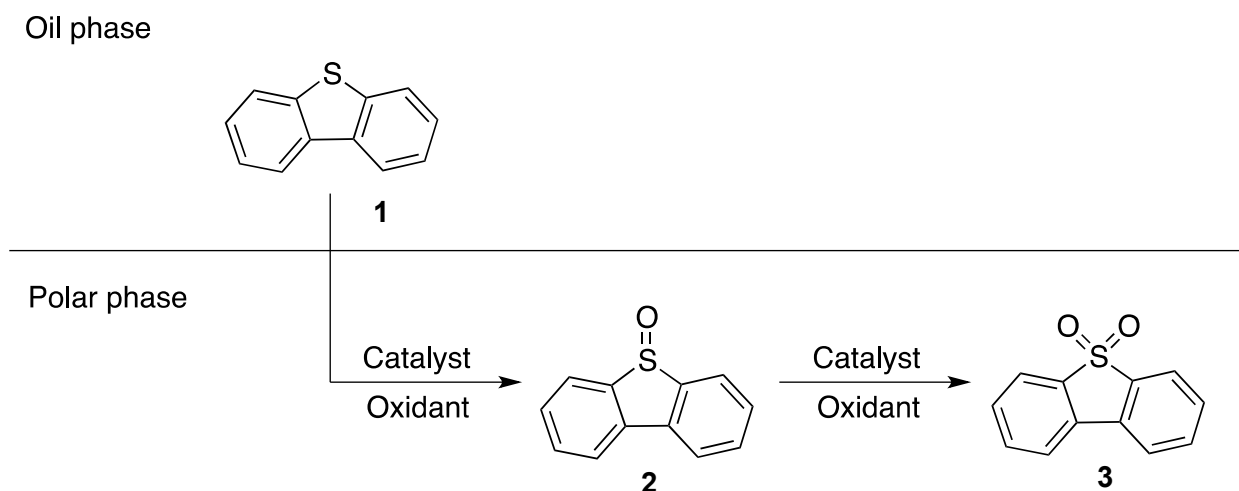


Table 1. Batch optimization of DBT **1** oxidation with aqueous hydrogen peroxide^[a]

Entry	H ₂ O ₂ /1	T °C	Cat. Amount (mg)	Final sulfur (ppm) ^[b]
1	5:1	60	50	810
2	10:1	60	50	698
3	20:1	60	50	673
4	10:1	80	50	650
5	10:1	60	250	345

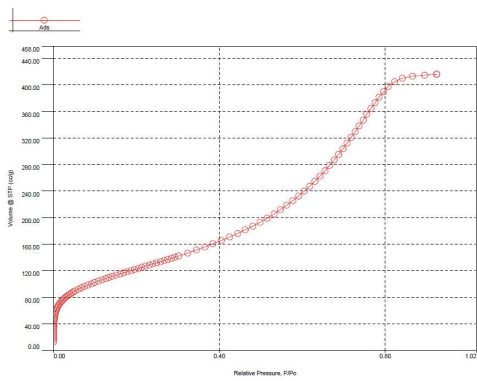
^[a] Reaction conditions: 2 ml of DBT **1** solution in dodecane (0.024 mol/L), 2ml of acetonitrile, catalyst: Amberlite IR 120 H, X ml of H₂O₂ solution at 3%, time: 24 h

^[b] Determined by HPLC analysis

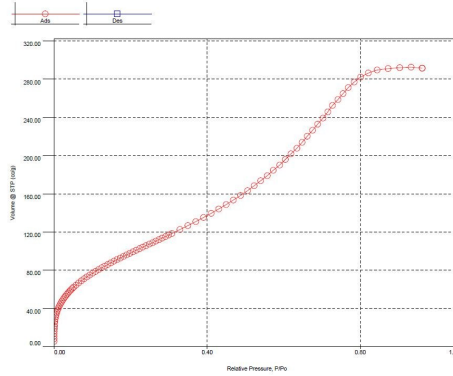
3. TiO₂@SiO₂ and TiO₂@SiO₂-Sil characterization

Table 2. B.E.T. Surface Area and Total Pore Volume of TiO₂@SiO₂ and TiO₂@SiO₂-Sil catalysts

Catalyst	B.E.T. Surface Area m ² /g	Total Pore Volume cc/g
TiO ₂ @SiO ₂ fresh	436	6.34 · 10 ⁻¹
TiO ₂ @SiO ₂ used	437	6.12 · 10 ⁻¹
TiO ₂ @SiO ₂ -Sil fresh	377	4.51 · 10 ⁻¹
TiO ₂ @SiO ₂ -Sil used	387	4.13 · 10 ⁻¹

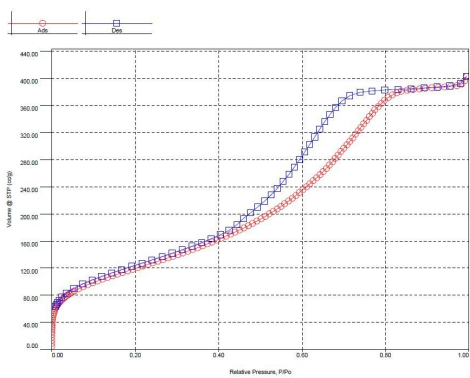


a)

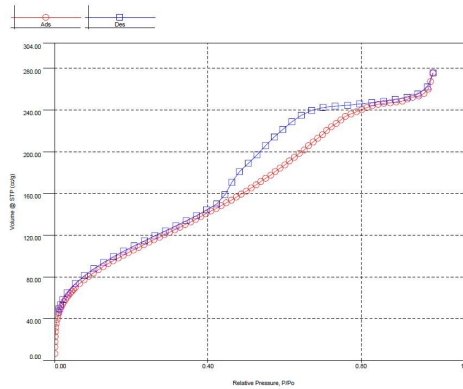


b)

Figure1. Nitrogen adsorption isotherms of fresh $\text{TiO}_2@\text{SiO}_2$ (a) and $\text{TiO}_2@\text{SiO}_2\text{-Sil}$ (b)

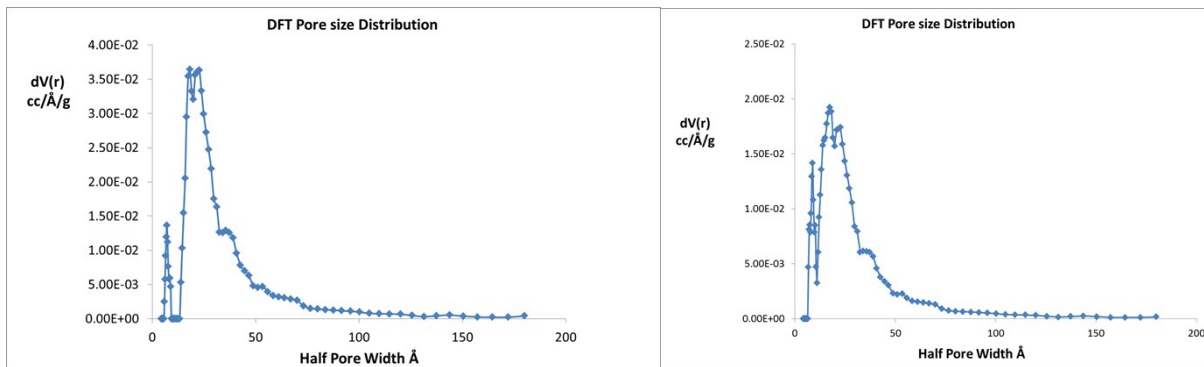


a)

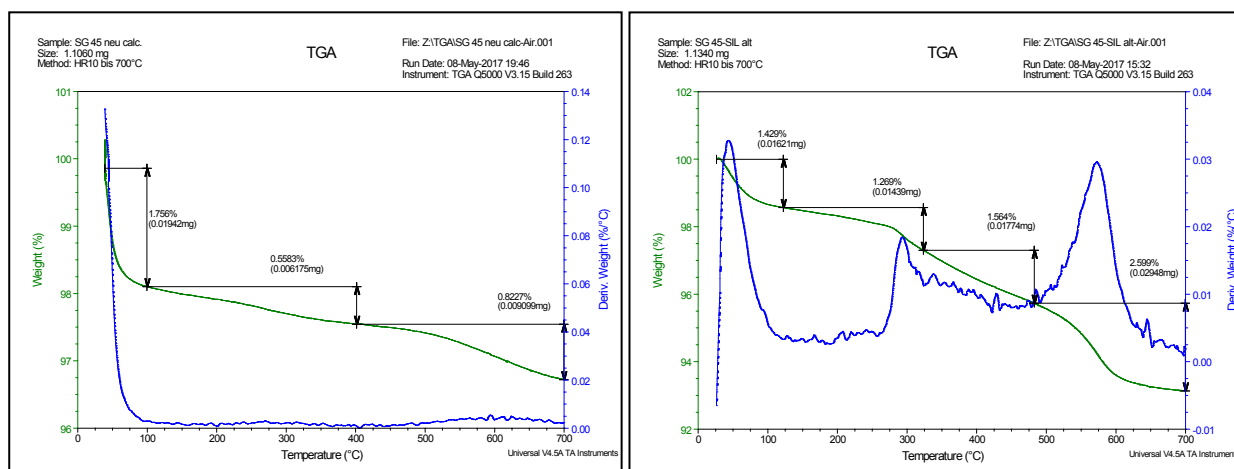


b)

Figure2. Nitrogen adsorption and desorption isotherms of used $\text{TiO}_2@\text{SiO}_2$ (a) and $\text{TiO}_2@\text{SiO}_2\text{-Sil}$ (b)



a) **b)**
Figure 3. DFT Pore Size distribution of fresh $\text{TiO}_2@SiO_2$ (a) and $\text{TiO}_2@SiO_2\text{-Sil}$ (b)



a) **b)**
Figure 4. TGA of $\text{TiO}_2@SiO_2$ (a) and $\text{TiO}_2@SiO_2\text{-Sil}$ (b)

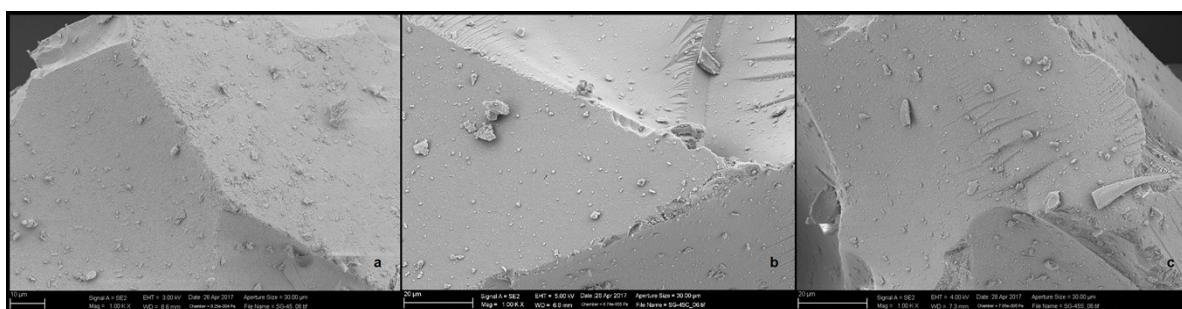


Figure 5. SEM snapshots of $\text{TiO}_2@SiO_2$ (a), calcinated $\text{TiO}_2@SiO_2$ (b) and $\text{TiO}_2@SiO_2\text{-Sil}$ (c).



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.