Nanoparticle catalysed oxidation of sulfides to sulfones by *in situ* generated H_2O_2 in supercritical carbon dioxide / water biphasic medium

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Electronic Supplementary Information

Safety warning: Experiments using large amounts of compressed gases, especially molecular oxygen and supercritical fluids, are potentially hazardous and must be carried out only with suitable high-pressure equipment under appropriate safety precautions.

Materials and instrumentation

Pd/C (10 wt%), $Pd_2(dba)_3$, thioanisole, palladium acetate, acetic anhydrite, *o*-toluenediamine, triethylamine and trifluoroacetic acid (TFA) were purchased from Sigma-Aldrich, TiO_2 P25 from Degussa and used as received. Silica gel 60 (0.04-0.063 mm) was obtained from Merck. All other solvents and chemicals were used of highest purity.

Transmission electron microscopy (TEM) images were taken on a JEOL 2000 FX II instrument at Central Facility for Electron Microscopy (GFE), RWTH Aachen University. Powder XRD spectra were recorded on a Siemens D5000 instrument with Cu Kα radiation. DRIFT spectra of samples were measured with a “Thermo Nicolet 4700 FT-IR” spectrometer with a liquid nitrogen cooled detector with the following parameters: 300 scans, 600-3500 cm^{-1} scan range, 4 cm^{-1} resolution. The palladium content of Pd/SiO_2 was determined by inductively coupled plasma atomic emission spectrometry (ICP-AES) using a Spectro Ciros Vision, ICP-OES. An SDTQ600 instrument from TA Instruments was used for determination of the palladium content of the unsupported particles.

The high pressure reactors and gas dosing unit used for the catalytic tests were built by the mechanical workshop of the Institut für Technische und Makromolekulare Chemie, RWTH Aachen University.

The composition of reaction mixtures was determined using a gas chromatograph (Siemens AG, AUT3 Chromatographie Service, Karlsruhe, Germany) equipped with a Cp-Sil-8-CB column (30m × 0.32 mm i.d.) and FID detector. The carrier gas for the GC analysis was N_2. The following temperature program was used: 80°C (5 min), 80-280°C (12°C/min). The intensity of the signals was referenced to benzophenone as internal standard. Retention times of thioanisole, methyl phenyl sulfoxide, methyl phenyl sulfone and benzophenone were 4.90, 9.79, 10.85, and 13.76 minutes, respectively.

Preparation and characterisation of Pd/SiO_2

2,3-Diacetamidotoluene was prepared by stirring a mixture of *o*-toluenediamine (3.67 g, 30 mmol), excess acetic anhydrite (9.18 g) and excess triethylamine (30.3 g) in dichloromethane for 1 day under argon. A pink precipitate formed in the initially homogeneous mixture, which was collected *via* filtration and washed with diethyl ether. Subsequently, Pd/SiO_2 was prepared by adding silica gel (1000 mg) to a solution of $Pd(OAc)_2$ (275 mg, 1.21 mmol) and 2,3-diacetamidotoluene (500 mg, 2.42 mmol) in trifluoroacetic acid (20 ml). The mixture was refluxed for two weeks under argon. Thereafter, the supernatant was transparent, while silica was completely black. The later was separated, washed with ample water and methanol and dried in air at 60°C.

The palladium content in Pd/SiO_2 was 8.4 wt%, which was close to the expected 10 wt% determined from the loading of the Pd precursor. XRD showed a peak at $2\theta = 39°$, indicating the presence of the [111] crystal face of Pd clusters (Fig. S1). TEM revealed palladium particles of ~12 nm size, which formed agglomerates of 50-70 nm size (Fig. S2 and S3). Also some larger 100-200 nm agglomerates of unsupported palladium were observed. An EDX analysis confirmed the presence of palladium and silicon in Pd/SiO_2 (Fig. S4). Note that the Cu signal is due to the grid used for electron microscopy.

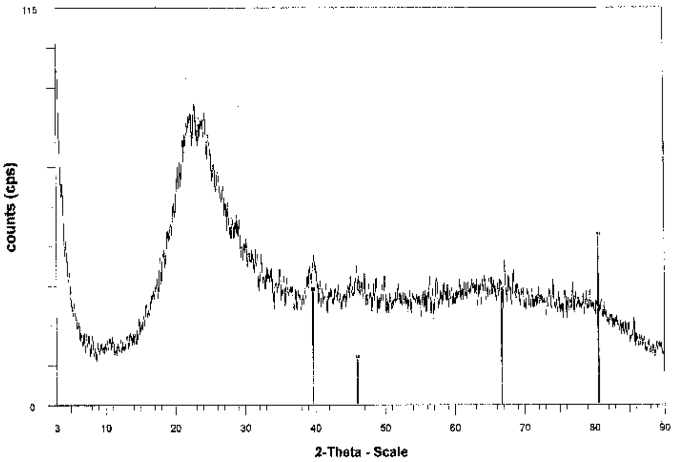

Fig. S1 XRD spectrum of the Pd/SiO_2 catalyst.

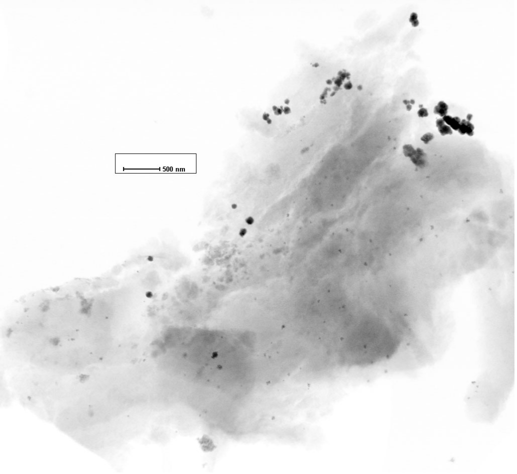

Fig. S2 TEM image of a typical Pd/SiO_2 particle. The scale bar is 500 nm.

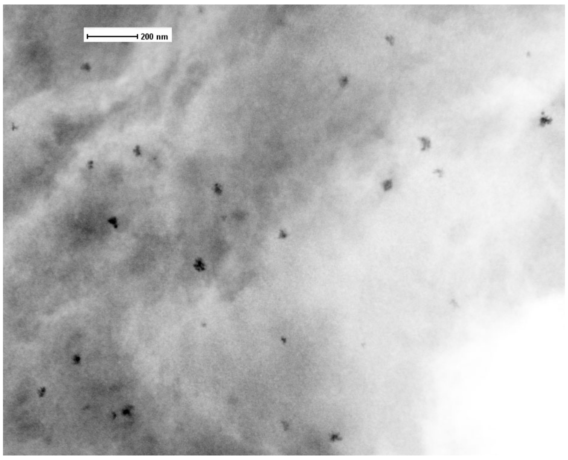

Fig. S3 TEM image of the edge of a typical Pd/SiO_2 particle. The scale bar is 200 nm.

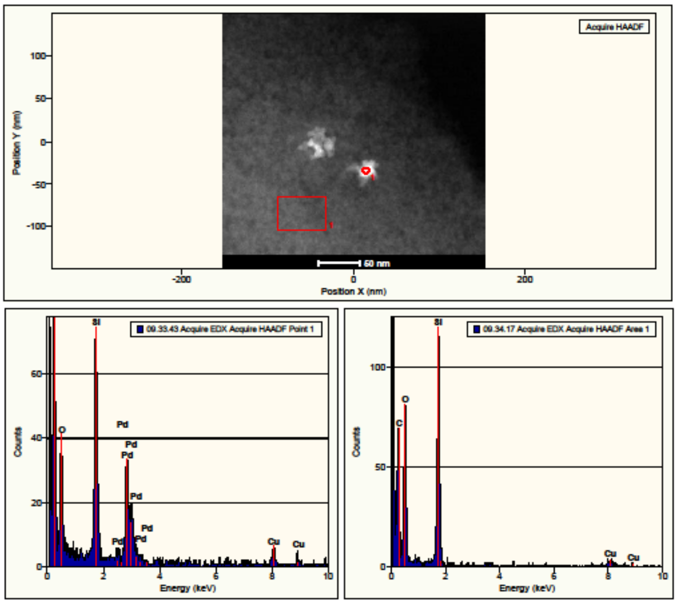

Fig. S4 EDX analysis of Pd/SiO_2. The scale bar in the scanning electron micrograph is 50 nm.

Preparation and characterisation of unsupported Pd nanoparticles

Benzene (294.4 mg, 3.77 mmol) was added to a solution of palladium acetate (855 mg, 3.77 mmol Pd) in 60 ml trifluoroacetic acid at room temperature under Ar and constant stirring. After 3 days the stirring was stopped and a black precipitate was found on the bottom of the flask. The precipitate was collected by filtration and dried in vacuum for 3 hours. The powder (377 mg) was fully redispersible in organic solvents, as, e.g., ethanol.

The palladium content was found to be 40 wt% from TGA heating the sample from 30 to 1000°C under a flow of nitrogen (10 $mL\cdot min^{-1}$). Specimens for TEM were prepared by placing a drop of the colloidal solution onto a copper grid with carbon film subsequently allowing the solvent to evaporate. The average size of Pd nanoparticles determined from TEM was 3-5 nm (Fig. S5 and S6).

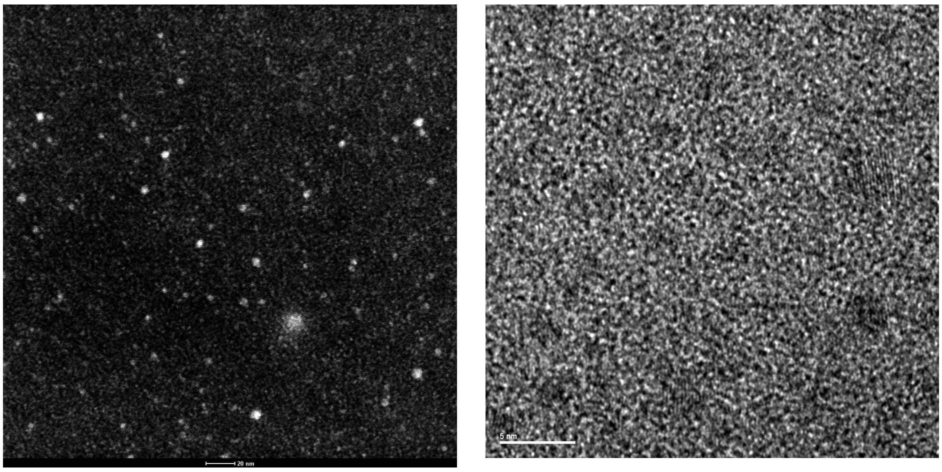

Fig. S5. Low (left) and high resolution TEM image (right) of the unsupported Pd nanoparticles. The scale bars are 20 and 5 nm, respectively.

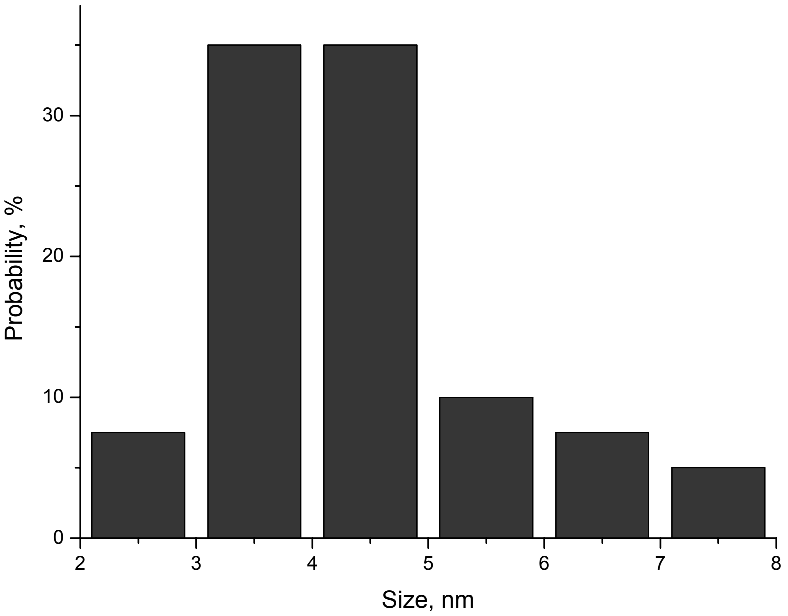

Fig. S6. Size distribution of the unsupported Pd nanoparticles.

XRD showed a broad reflection at 2Θ=37.65°, which is shifted slightly relative to the 39° reflection assigned to the [111] plane of metallic palladium (Fig. S7). Based on the Scherrer equation, the average size of the primary metal particles was estimated to 0.9 nm. This is significantly lower as found by analysis of the TEM images consistent with partial agglomeration of the particles.

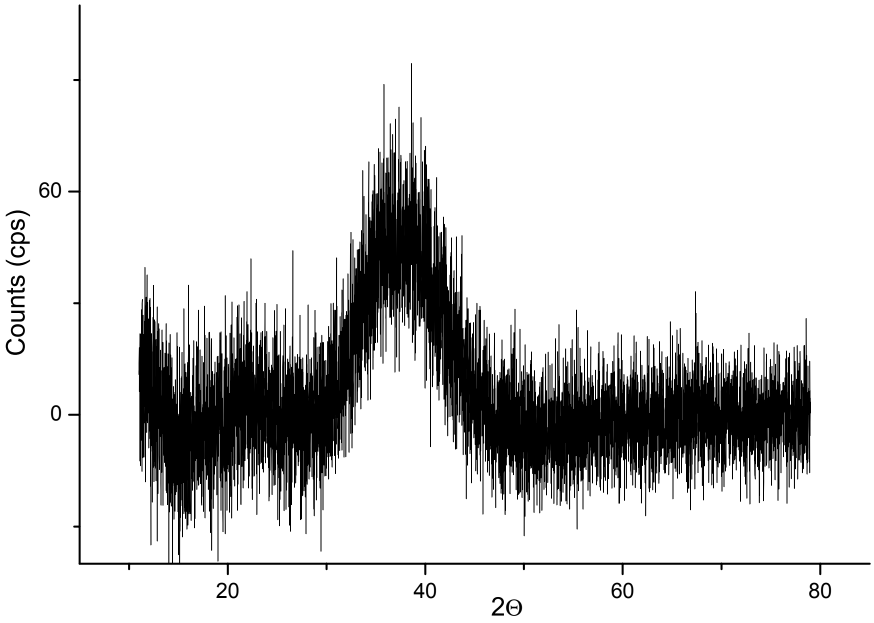

Fig. S7. XRD spectrum of unsupported Pd nanoparticles.

Catalysis

The experiments were performed in accordance with the published procedure.[1] All reactions were carried out using a stainless-steel high pressure reactor (25 mL). For catalyst screening (Table S1), the reactor was charged with thioanisole (62 mg, 0.5 mmol) and distilled H_2O (1 mL) and a palladium catalyst *viz.* Pd/SiO_2 (100 mg, 0.078 mmol Pd), Pd/C (100 mg, 0.094 mmol Pd), or $Pd_2(dba)_3$ as catalyst precursor (100 mg, 0.218 mmol Pd) as well as TiO_2 (100 mg, 2.5 mmol). In case of $Pd_2(dba)_3$, $CHCl_3$ (1.6 mL) was added as solvent. If not stated otherwise, the reactor was pressurised with CO_2 (0.5 MPa), O_2 (0.5 MPa) and H_2 (0.5 MPa) and the overall pressure adjusted with CO_2 to 13 MPa using a gas dosing unit.[1] Reactions were carried out at 80°C for 24 h. After the reaction, the vessel was cooled using an ice bath and depressurized slowly. The remaining water phase was extracted using ethyl acetate and the conversion was determined by GC. In all cases, the overall mass balance was closed with 0.99.

Table S1. Comparison of the performance of Pd catalysts in the oxidation of thioanisole with *in-situ* generated H_2O_2.

Entry	Catalyst (precursor)	Conversion / %	Selectivity[1] / %	Yield / %
1	Pd/SiO_2	89	95	85
2	Pd/C	55	60	33
3	$Pd_2(dba)_3$	74	81	60

[1] Selectivity to methyl phenyl sulfone

Reactions varying in the overall pressure (5, 10, 13, 15, 20, 25 and 30 MPa) and the reaction temperature (40, 60, 80, 100 and 120°C) were carried out for 24 h following the same procedure as stated for catalyst screening. The reactor was charged with thioanisole (62 mg, 0.5 mmol), distilled H_2O (1 mL), Pd/SiO_2 (100 mg, 0.078 mmol Pd) and TiO_2 (100 mg, 2.5 mmol). If not stated otherwise, the reactor was pressurised with CO_2 (0.5 MPa), O_2 (0.5 MPa) and H_2 (0.5 MPa) and the overall pressure adjusted with CO_2 to 13 - 15 MPa using a gas dosing unit.[1] The mixture was then stirred for 24 h. Subsequently, the vessel was cooled using an ice bath and depressurized slowly. The remaining water phase was extracted using ethyl acetate and the conversion was determined by GC (Table S2).

Table S2 Reaction conditions and results for the conversion of thioanisole to methyl phenyl sulfone using *in situ* generated H_2O_2

Entry	Thioanisole / mmol	H_2O / mL	Temp. / °C	pH_2 / MPa	pO_2 / MPa	Conversion [a] / %	Selectivity / %	Yield / %
1	0.25	1	80	0.5	0.5	99	96	95
2	0.50	-	80	0.5	0.5	99	72	71
3	0.50	1	80	0.5	0.5	89	95	85
4	0.50	1	80	0.5	0.5	36 [b]	98	35
5	1.00	1	80	0.5	0.5	81	77	62
6	1.00	1	80	0.6	0.6	88	85	75
7	1.00	1	80	1.2	0.6	35	62	22
8	1.00	1	80	1.8	0.6	22	50	11
1	0.50	1	40	0.5	0.5	33	69	23
2	0.50	1	60	0.5	0.5	66	55	36
3	0.50	1	80	0.5	0.5	89	95	85
4	0.50	1	120	0.5	0.5	11	36	4

[a] Reactions were carried out using Pd/SiO_2 and TiO_2 as catalyst at 13 MPa overall pressure, 24 h; [b] 12 h

References

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1 S. K. Karmee, C. Roosen, C. Kohlmann, S. Lütz, L. Greiner, W. Leitner, *Green Chem.*, 2009, **11**, 1052.