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Supporting information

Manuscript:

Co and Mn polysiloxanes as unique initiator-catalyst-systems for the selective liquid phase oxidation of *o*-xylene

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(SI1) Experimental details

Spherical polysiloxanes were synthesized by applying the sol-gel process [1, 2] using a mixture of tetraethyl orthosilicate, 3-aminopropyltrimethoxysilane, 1-butanol, dibutyl tin dilaurate and a transition metal source, which was injected into a water filled column heated to 333 K. The detailed procedure of the synthesis is described elsewhere. [3] All chemicals were purchased from Sigma Aldrich (purity > 98%). The concentration of the metal in the solid catalysts was determined by atomic absorption spectroscopy using a UNICAM Solaar M5 Spectrometer.

Liquid phase oxidation experiments were carried out in a bubble column reactor consisting of a 10 mm inner diameter glass tube loaded with reactant and catalyst without a solvent. Reactions were carried out at a total pressure of 2.4 bar. The gas was directed through a glass frit to form small bubbles. Hexachlorobenzene was used as internal standard. Analysis of reaction components was performed in a Shimadzu GC-2010 gas chromatograph equipped with a 30 m DB-5 column (0.25 mm inner diameter and 0.25 µm film thickness) and a FID detector was used. For quantification tetradecane was added as internal GC standard. As hydroperoxides decompose at high temperatures in the GC an indirect route was applied to quantify the concentration of 2-methylbenzyl hydroperoxide described by Shul´pin *et al*. [4]

IR spectra of self supporting wafers were recorded in transmission mode with a Bruker IFS88 spectrometer using a resolution of 4 cm^{-1}. After activation in vacuum (10^{-6} mbar) at 723 K (heating rate 10 K min^{-1}) for one hour the samples were cooled to 300 K and CO or water was adsorbed at partial pressure between 10^{-3} mbar and 1 mbar.

(SI2) Material characterization and properties

The Co^{2+} or Mn^{3+} containing polysiloxane materials were synthesized from tetraethyl orthosilicate and 3-aminopropyltrimethoxysilane as precursors in molar ratio of 2 : 1. The chemical composition of the used Co^{2+} and Mn^{3+} containing materials is summarized in Table S1. The particle diameter of the spherical polysiloxane materials was 800 μm for all experiments.

Table S1: Chemical composition of the Co and Mn containing catalysts. Note that the difference to 100% is balanced by oxygen.

Sample name	Metal concentration (wt. %)	C concentration (wt. %)	Si concentration (wt. %)	N concentration (wt. %)	H concentration (wt. %)
Co-0.3	0.3	6.7	33.6	1.1	2.7
Co-0.8	0.8	7.6	34.2	1.8	2.5
Co-1.1	1.1	8.7	33.1	2.0	2.5
Co-1.9	1.9	8.0	25.7	2.2	3.0
Mn-1.1	1.1	12.5	31.9	3.1	3.6
Mn-2.0	2.0	14.3	31.5	3.1	3.7

The CO adsorption for catalysts with varying Co concentrations increased linearly with increasing concentration of the metal cation, while the bare functionalized polysiloxane did not adsorb CO under the conditions used (Figure 4). The adsorption of CO was quantified from the intensity of the CO stretching band adsorbed to Co^{2+} at 2169 cm^{-1}.

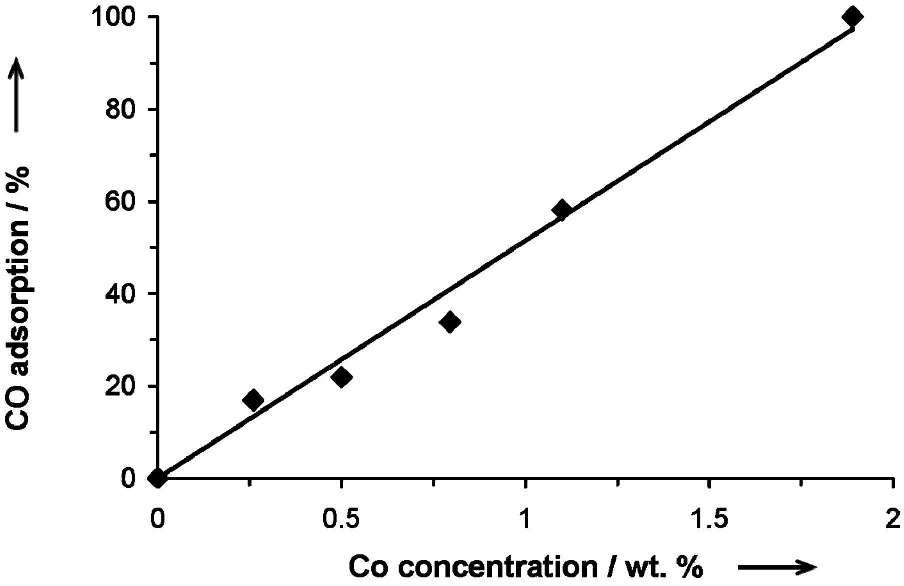

Figure S1: CO coverage as function of the Co concentration of the catalyst.

(SI3) Selectivity towards oxidation products

The total selectivity towards the main products 2-methylbenzyl hydroperoxide, 2-methylbenzyl alcohol, *o*-tolualdehyde and *o*-toluic acid was above 90 mol % in all experiments. The most significantly formed side product formed with a yield of 1 mol % at 20 mol % conversion was phthalide. Only minor concentrations of side products such as *o*-xylene dimers, esters of *o*-toluic acid and 2-methylbenzyl alcohol, formiates of 2-methylbenzyl alcohol, toluene and phthalic anhydride were detected (molar yields below 0.4 mol % each at high conversions of 20 mol %) demonstrating the high selectivity of the new initiator - catalyst materials.

Table S2: Oxygenate selectivity in mol % at 20 mol % conversion of *o*-xylene for applied transition metal catalysts at 445 K.

	Co	Mn
o-tolualdehyde	17	15
2-methylbenzyl alcohol	17	25
2-methylbenzyl hydroperoxide	0	0
o-toluic acid	60	52
Phthalide	4	5
Side products	2	3

The selectivity towards oxygenates was independent of the transition metal concentration in the material. Under the tested reaction conditions conversions of up to 35 mol % of *o*-xylene were observed after reaction durations of 5 h.

(SI4) Leaching experiments and catalyst stability

To verify that the transition metal was not leached from the catalyst during the reaction, the Co^{2+} containing catalyst was used under the typical reaction conditions at 445 K until 2-methylbenzyl hydroperoxide was decomposed, i.e., 8 mol % conversion. At this point, the catalyst was removed from the liquid phase by hot filtration at 353 K and the reaction mixture was allowed to react further at 445 K. In absence of the catalyst the concentration of 2-methylbenzyl hydroperoxide increased again, while the concentration of *o*-tolualdehyde and 2-methylbenzyl alcohol remained constant until the maximum hydroperoxide yield was reached. Here, the decomposition rate of the hydroperoxide in the liquid phase became larger than the formation rate equal to the reaction carried out without catalyst and accordingly the concentrations of the partially oxidized intermediates (alcohol and aldehyde) started to increase further.

To control that Co^{2+} is not leached into the reaction mixture, AAS analysis of the liquid phase after the oxidation reaction (conversion of 20 mol %) was performed, confirming the absence of Co in the solution (concentration < 0.01 mg l^{-1}). Starting the reaction with a composition of reaction products corresponding to 8 mol % conversion without a catalyst the reaction behavior was identical to that of an experiment in which the catalyst was removed at 8 mol % conversion by hot filtration. These experiments show that Co^{2+} is not leached from the catalyst even when the polarity of the organic phase increases by formation of high acid concentrations. As no Co^{2+} is leached to the liquid phase the polysiloxane based materials act as true heterogeneous catalysts.

The stability of the Co particles in the polysiloxane matrix was approved by adsorption of CO to used catalyst. The adsorption capacity was equal to fresh materials showing the unchanged character of the transition metal in the polysiloxane materials. Additionally, spent catalysts showed equal activity when these were reused.

Reference of the supporting information

[1] H. Witossek, E. Bratz, *Chem. Eng. Technol.*, 20 (**1997**) 429-433.

[2] E. Yacoub-George, E. Bratz, H. Tiltscher, *J. Non-Cryst. Solids*, 167 (**1994**) 9-15.

[3] T. Förster, S. Scholz, Y. Zhu, J.A. Lercher, *Microporous and Mesoporous Mater.*, (**2010**) submitted for publication.

[4] G.B. Shulpin, D. Attanasio, L. Suber, *J. Catal.*, 142 (**1993**) 147-152.