



Supporting Information

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Tuning catalytic activity between homogeneous and heterogeneous catalysis: Improved activity and selectivity of free nano-Fe₂O₃ in selective oxidations

Feng Shi,^a Man Kin Tse,^{a,b} Marga-Matina Pohl,^c Angelika Brückner,^c Shengmao Zhang,^d and Matthias Beller^{a,b*}

^aLeibniz-Institut für Katalyse e.V. an der Universität Rostock, Albert-Einstein-Str. 29a, 18059 Rostock, Germany;
^bUniversity of Rostock, Center for Life Science Automation (CELISCA), Friedrich-Barnewitz-Str. 8, D-18119 Rostock-Warnemünde, Germany; ^cLeibniz-Institut für Katalyse e.V. an der Universität Rostock, Außenstelle Berlin, Richard-Willstätter-Str. 3, 12489 Berlin, Germany; ^dSpecial Functional Material Laboratory, Henan University, 475001, Kaifeng, China

Generals:

Chemicals: Bulk α -Fe₂O₃ (product no.: 31005-0) and nano- γ -Fe₂O₃ **1** (product no.: 544884) were purchased from Aldrich. Nano- γ -Fe₂O₃ **2** and bulk γ -Fe₂O₃ were prepared with the reported method.¹ All the other chemicals were directly used without any purification.

TEM: A transmission electron microscope CM20 STWIN (Philips) equipped with an energy dispersive X-ray spectrometer (EDXS) PV9900 (EDAX) was used at 200kV. For TEM investigations the catalysts were dispersed by an ultrasonic bath in ethanol and deposited on carbon coated copper grids. The PV9900 allows qualitative and quantitative measurements of elements above Na.

XRD: For XRD measurements a STADI P automated transmission diffractometer (STOE) was used with an incident beam curved germanium monochromator selecting Cu K α 1 radiation and a 6° position sensitive detector (PSD). It must be mentioned that for iron oxides, Cu K α 1 radiation is not optimal. The XRD patterns were scanned in the 2 θ range of 5-60° (step width: 0.5°, 100 s per step). For the data interpretation the software WinXpov (STOE) and the database of Powder Diffraction File (PDF) of the International Centre of Diffraction Data (ICDD) were used.

XPS: The X-ray photoelectron spectroscopy (XPS) measurements were carried out on a VG ESCALAB220iXL spectrometer with Al K α radiation (E = 1486.6 eV). The samples were fixed by a double-sided adhesive carbon tape on a stainless steel sample holder. The electron binding energy was referenced to the O1s peak of Fe₂O₃ at 529.6 eV. The peaks were fitted by Gaussian-Lorentzian curves after a Shirley background subtraction. For quantitative analysis, the peak area was divided by the element-specific Scofield factor and the transmission function of the analyser. The background pressure in the chamber was better than 10⁻⁷ Pa.

¹ (a) Bourlinos, A. B.; Simopoulos, A.; Petridis, D. *Chem. Mater.* **2002**, *14*, 899-903;
(b) Ozaki, M.; Matijevic, E. *J. Colloid Interf. Sci.* **1985**, *107*, 199-203.

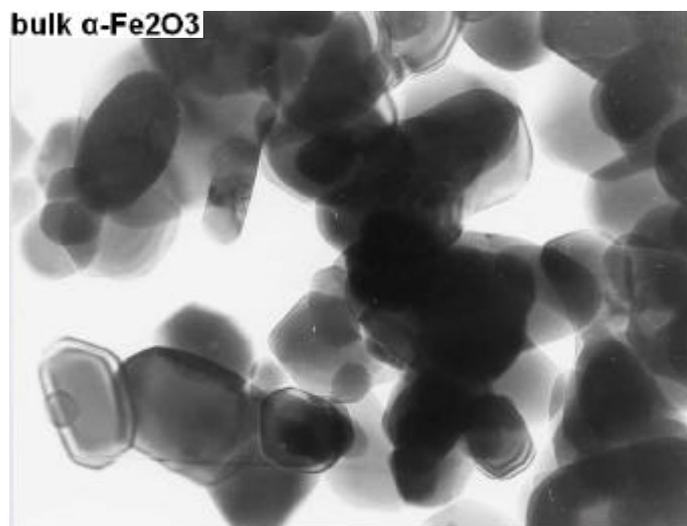
Experimental

Analysis: Qualitative and quantitative analysis were carried with **GC-FID** (HP6890N with FID detector, column HP5 30m×0.250mm×0.25μm) and **GC-MS** (HP6890N with MSD5973, column HP5MS 30m×0.250mm×0.25μm) and compared with the authentic samples.

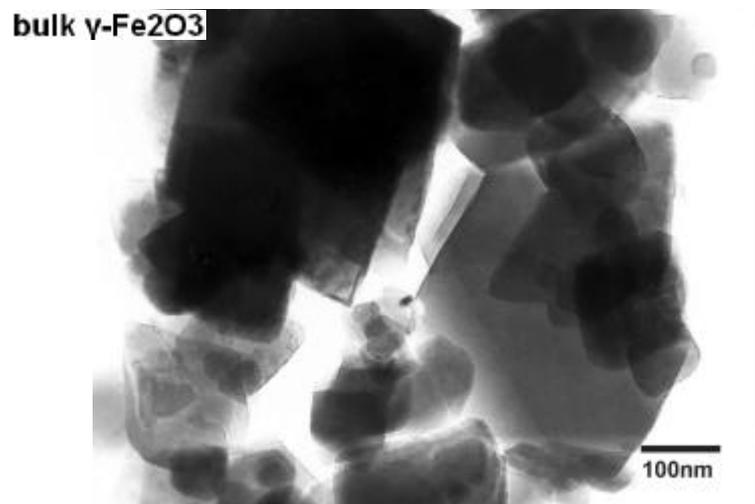
General procedure for the selective oxidation of alcohol to aldehyde: All reactions were carried out with a multi-reactor (Carousel 12 station, RADLEYS). To a glass reactor (~50 mL), benzyl alcohol (1081 mg, 10.0 mmol) and 1 mol% of nano-Fe₂O₃ **1** (16.0 mg) were added respectively. The reaction mixture was vigorously stirred (500-750 rpm) at 75 °C. H₂O₂ (30wt% in water, from VWR, 1.0 mL, 10.0 mmol) were added continuously in 12 h. The mixture was then cooled to room temperature and dioxane (1760 mg, 20 mmol) was added for qualitative analysis by GC-FID.

A demonstration of scaling up for the selective oxidation of benzyl alcohol: The reaction was carried out in an oil bath (75 °C, oil bath temperature). To a round bottom flask (250 mL), benzyl alcohol (31.6 g, 200 mmol) and 1 mol% of nano-Fe₂O₃ **1** (320 mg) were added respectively. The reaction mixture was vigorously stirred (500-750 rpm) at 75 °C. H₂O₂ (30wt% in water, from VWR, 20 ml, 200 mmol) were added continuously in 12 h. The mixture was then cooled to room temperature and dioxane (35.2 g, 400 mmol) was added for qualitative analysis by GC-FID. The reaction was repeated two times, the product was isolated in 7.6 g (conversion 25%, selectivity 96%;).

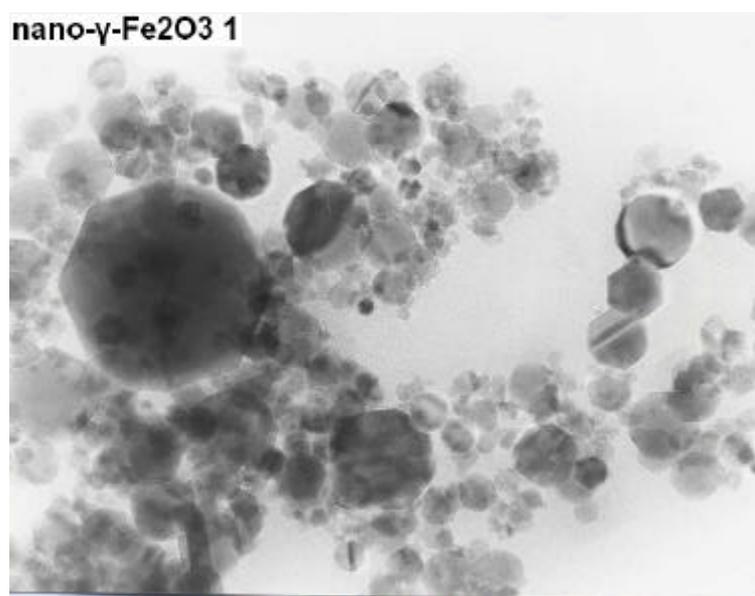
General procedure for the selective oxidation of olefin to aldehyde: All reactions were carried out in an oil bath (75 °C, oil bath temperature). To a glass reactor (~50 mL), olefin (10.0 mmol), H₂O₂ (30wt% in water, from VWR, 2.0 ml, 20.0 mmol) and 1 mol% of nano-Fe₂O₃ **1** (16.0 mg) were added respectively. The reaction was vigorously stirred (500-750 rpm) at 75 °C for 5 h. The mixture was then cooled to room temperature and dioxane (1760 mg, 20 mmol) was added for qualitative analysis by GC-FID.



(a) Bulk α -Fe₂O₃: archive 2745/03/07, magnification 114000, 11.4 mm = 100 nm



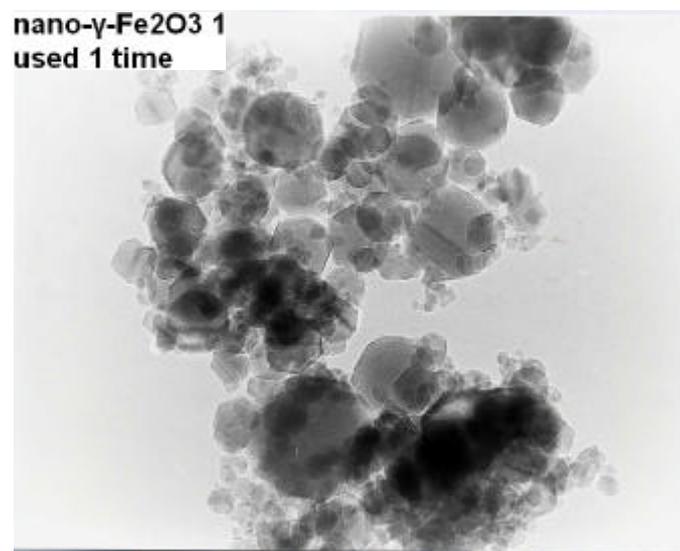
(b) Bulk γ -Fe₂O₃ bulk, archive 2955/05/07



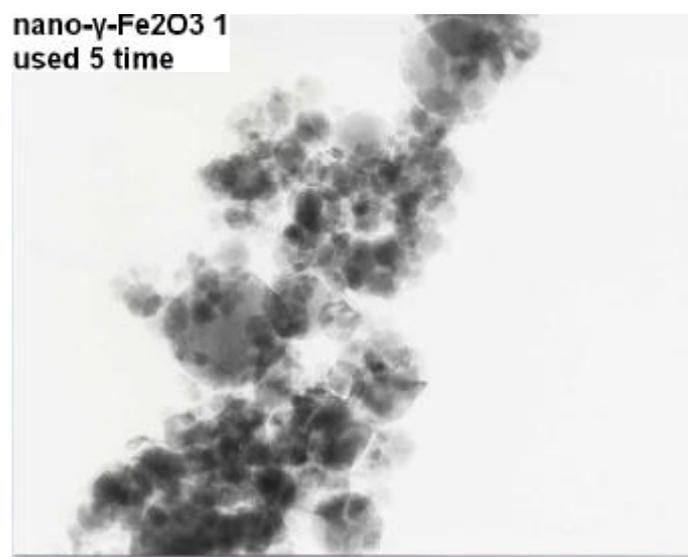
(c) Nano- γ -Fe₂O₃ 1: archive 2740/03/07, magnification 1940000, 19.4 mm = 100 nm



(d) Nano- γ -Fe₂O₃ 2: archive 2794/03/07, magnification 760000, 7.6 mm = 10 nm



(e) Nano- γ -Fe₂O₃ 1 used 1 time: archive 2774/03/07, magnification 270000, 27 mm = 100 nm



(f) Nano- γ -Fe₂O₃ 1 used 5 times: archive 2782/03/07, magnification 194000, 19.4 mm=100 nm

Fig. S1. TEM pictures for different Fe₂O₃ catalysts