Nanoparticle Catalysts

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Tuning Catalytic Activity between Homogeneous and Heterogeneous Catalysis: Improved Activity and Selectivity of Free Nano-Fe_2O_3 in Selective Oxidations**

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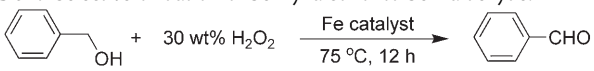
Nanocatalysis is considered to be a bridge between homogeneous and heterogeneous catalysis.[1] Nanostructured compounds may combine the advantages of both disciplines and offer unique activity with high selectivity in catalysis. Unfortunately, unsupported nanoparticles are usually unstable and the coagulation of the nanoparticles during reaction is frequently unavoidable.[2] Thus, till now, the investigation of "free" nanoparticles as catalysts has been rare, although it is an important tool to gain a fundamental understanding of catalysis.[3] Clearly, the development of "free" nanoparticles with tunable catalytic activity is of great significance for both academia and industry.

Iron compounds are abundantly available and play a crucial role in many biological systems.[4] In comparison with other transition metals extensively used, iron-based catalysts are inexpensive, environmentally benign, and relatively nontoxic. In the past decades, various iron salts have been applied as Lewis acids (Fe^{3+}) in homogeneous catalysis and different catalytically active iron complexes were also reported.[5] In heterogeneous catalysis, iron oxides have been frequently used as catalysts and supports in bulk industrial processes, usually at high temperature (> 300 °C) and pressure.[6] As part of our continuous efforts to develop iron-based catalytic processes,[7] herein, we report our use of "free" nano-iron oxide as an oxidation catalyst under mild reaction conditions.

Firstly, the oxidation of benzyl alcohol applying hydrogen peroxide was investigated as a typical benchmark reaction for liquid-phase oxidation (Table 1).[8] As expected, bulk Fe_2O_3 (α or γ, particle size ≥ 100 nm; see Figure S1 a,b in the Supporting Information) displayed only low activity (Table 1, entries 1 and 2). Next, we chose different particle sizes of γ-Fe_2O_3 because of their ferrimagnetic property, hence recovery and recycling of the catalyst can be easily achieved (see below).[4,9] In the presence of nano-γ-Fe_2O_3 **1**, in which the majority of the particles is 20–50 nm in size (Figure 1 a), the conversion reached 33% with an excellent benzaldehyde selectivity of 97% (Table 1, entry 3). The

Table 1: Selective oxidation of benzyl alcohol to benzaldehyde.[a]



Entry	Catalyst	H_2O_2 [equiv]	TON[b]	Selectivity [%][c]
1	bulk α-Fe_2O_3	1	5	99
2	bulk γ-Fe_2O_3	1	4	99
3	nano-γ-Fe_2O_3 **1**	1	32	97
4	nano-γ-Fe_2O_3 **2**	1	30	35
5	$Fe(NO_3)_3 \cdot 9H_2O$	1	25	35
6[d]	nano-γ-Fe_2O_3 **1**	1	18	88
7[e]	nano-γ-Fe_2O_3 **1**	1	10	85
8[f]	nano-γ-Fe_2O_3 **1**	1.5	12	66
9[g]	nano-γ-Fe_2O_3 **1**	1	25	96

[a] 10 mmol benzyl alcohol (1.08 g), 1 equiv H_2O_2 (10 mmol, 1.0 mL, 30 wt% in water), 1 mol% catalyst, 75 °C, 12 h. H_2O_2 was added continuously over 12 h. [b] Number of moles of aldehyde produced per mole of catalyst. [c] Selectivity based on alcohol conversion. [d] 2 mol% catalyst. [e] 4 mol% catalyst. [f] 4 mol% catalyst, 1.5 equiv H_2O_2. [g] 200 mmol benzyl alcohol, 200 mmol H_2O_2 (30 wt%), 1 mol% catalyst, 75 °C, 12 h, repeated two times.

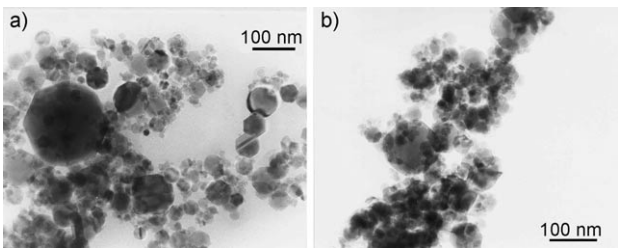


Figure 1. TEM pictures of nano-γ-Fe_2O_3 **1** before use (a) and after reuse five times (b).

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corresponding catalytic activity is higher by a factor of eight relative to the corresponding bulk Fe_2O_3. By applying nano-Fe_2O_3 **1**, the selectivity with respect to hydrogen peroxide (1 equiv) is approximately 30%. Interestingly, nano-γ-Fe_2O_3 **2**, which consists of rather uniform particles of markedly smaller size (3–5 nm; see Figure S1 d in the Supporting Information), showed an even higher activity. Here, the conversion was 85% but the selectivity was only 35% (Table 1, entry 4).

Benzoic acid, benzyl benzoate, and oligomers are observed as side products by GC-MS analysis. Noteworthy, the activity and selectivity of nano-γ-Fe_2O_3 **2**, which has a particle size of 3–5 nm, is already close to that of a homogeneous iron system in which $Fe(NO_3)_3$ served as a Fe^{3+} source (Table 1, entry 5). The use of soluble $FeCl_3$ gave similar results. To exclude the involvement of homogeneous species in the oxidation with bulk and nano-Fe_2O_3, acetone was added after a catalytic run and the reaction mixture was filtered. The filtrate was concentrated under vacuum, and the remaining crude oil was analyzed by atomic absorption spectroscopy (AAS). The measured iron content is below the detection limit of our machine (Perkin Elmer Analyst 300). These results clearly illustrate that by downsizing the particle diameter in solid Fe_2O_3 catalysts, it is possible to approach catalytic activity and selectivity values close to those obtained with homogeneous Fe^{3+} single-site catalysts. The catalytic activity increases while the selectivity decreases with decreasing Fe_2O_3 particle size. Hence, with a suitable particle size, heterogeneous nano-Fe_2O_3 particles can display improved catalytic activity as well as excellent selectivity as compared to bulk Fe_2O_3.

X-ray diffraction (XRD) powder patterns confirm that bulk and nano-Fe_2O_3 have the same crystal structure. From the binding energies derived from X-ray photoelectron spectroscopy (XPS), it is clear that the surface iron ions are trivalent in both samples, although minor reduction to Fe^{2+} cannot be completely excluded for nano-γ-Fe_2O_3 **1** as suggested by the weak shoulder of the main $Fe2p_{3/2}$ peak at lower binding energies. For nano-γ-Fe_2O_3 **2**, the characteristic XRD reflections are not observed. This might be due to the very low particle size of 3–5 nm which is at the detection limit of XRD. However, measurements of ferromagnetic resonance indicate that this sample consists of superparamagnetic particles. This suggests that despite the much smaller particle size, the molecular structures of nano-γ-Fe_2O_3 **1** and **2** should be similar.

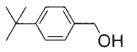
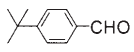
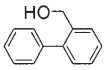
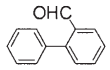
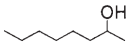
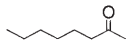
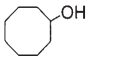
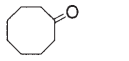
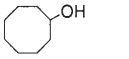
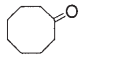
The reason for the improved activity of nano-iron oxide most probably originates from the nanometer size of the bulk iron oxide. In general, nanoscale heterogeneous catalysts should offer higher surface areas, low-coordinated sites, and surface vacancies, which are responsible for the higher catalytic activity.[10] Theoretically, it can be assumed that with a decrease of the particle size down to a "molecular" level, the nanocatalyst behaves as a homogeneous system in which the catalytic activity is not controlled by the surface area of the catalyst but governed by the concentration.[11] The most important significance of these results is that "free" nano-Fe_2O_3, but not immobilized nano-Fe_2O_3, is highly active, selective, and stable by merely controlling the particle size.

Variation of the amount of hydrogen peroxide (1.5 equiv) and catalyst **1** (4 mol%) revealed an increased conversion of benzyl alcohol and a product yield of 48% (Table 1, entry 8), which makes the system already interesting for batch applications. In this regard, it is interesting that the present system can be easily scaled up. With 200 mmol (21.6 g) benzyl alcohol as the starting material, a catalyst turnover number of 25 was obtained with 96% selectivity.

Next, the selective oxidation of various alcohols in the presence of 1 mol% of "free" nano-γ-Fe_2O_3 was studied.[12] In general, the nanocatalyst exhibits good activity with excellent selectivity (Table 2). Importantly, note that the ferrimagnetic property of γ-Fe_2O_3 made the isolation and reuse of this catalyst very easy. In the presence of a magnetic stirrer bar, nano-γ-Fe_2O_3 **1** moved onto the stirrer bar steadily and the reaction mixture turned clear within 10 s. The catalyst can be isolated by simple decantation. After washing with acetone and drying in air, the nano-Fe_2O_3 can be directly reused without any deactivation even after five rounds of selective oxidation of cyclooctanol to cyclooctanone. The characterization of the nano-γ-Fe_2O_3 before and after reuse five times showed the same particle size by transmission electron microscopy (TEM; Figure 1 b) and the same crystal structure by XRD. The only difference is visible from XPS, which showed lower peak intensity after the fifth use. This is due to the increased carbon content of the surface. The C/Fe ratio rose from 0.64 atom% in fresh nano-γ-Fe_2O_3 **1** to 2.82 atom% after the fifth use in cyclooctanol oxidation. We believe that this is also the possible reason for the high stability of the nano-Fe_2O_3 presented herein. A thin layer of carbon is formed during the reaction which prevents significant coagulation of the nano-Fe_2O_3. Obviously, carbon-containing deposits cover the iron oxide particles partly during reaction which, however, seems not to be detrimental to the activity.

Notably, the nano-Fe_2O_3 is not only active for selective alcohol oxidations. Aromatic olefins can also be oxidized to the corresponding aldehydes smoothly in the presence of nano-γ-Fe_2O_3 **1** (Table 3). For 2-chlorostyrene, the catalyst

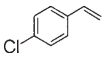
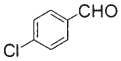
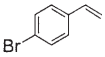
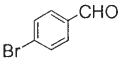
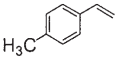
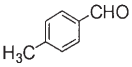
Table 2: Selective oxidation of alcohols to aldehydes and ketones.[a]

Entry	Substrate	Product	TON[b]	Select. [%][c]
1			10	>99
2			6	>99
3			6	>99
4			14	>99
5[d]			70[e]	>99

[a] 10 mmol benzyl alcohol (1.08 g), 1.5 equiv H_2O_2 (10 mmol, 1.0 mL, 30 wt% in water), 1 mol% catalyst, 75 °C, 12 h. H_2O_2 was added continuously over 12 h. [b] Number of moles of aldehyde produced per mole of catalyst. [c] Selectivity based on alcohol conversion. [d] The catalyst was reused five times. [e] Total turnover number of five experiments.

turnover number reached a value of up to 31 with greater than 99% chemoselectivity (Table 3, entry 3), while the highest catalyst activity was exhibited with 4-methylstyrene as reactant (48% conversion, 75% selectivity).

Table 3: Nano-Fe_2O_3-catalyzed reaction of olefins to aldehydes.[a]

Entry	Substrate	Product	TON[b]	Select. [%][c]
1			19	>99
2			31	>99
3			17	>99
4			14	>99
5			36	75

[a] 10 mmol olefin, 1 mol% nano-γ-Fe_2O_3 **1**, 20 mmol (2.0 mL) hydrogen peroxide, 75 °C, 5 h. H_2O_2 was added in one portion. The conversion and yield are based on GC-FID analysis with an external standard of dioxane. [b] Number of moles of aldehyde produced per mole of catalyst. [c] Selectivity based on the olefin conversion.

In conclusion, unsupported "free" nano-γ-Fe_2O_3 has been shown to be an active, stable, and highly selective catalyst for various oxidations applying hydrogen peroxide. Clearly, for general applications in organic synthesis, the activity of the catalyst system should be further improved. Nevertheless, because of its simple recyclability, the catalyst is well-suited for continuous processes. From a scientific point, our results expand the application of "free" nanoparticles. They should be helpful to understand the relationship between homogeneous and heterogeneous catalysis and for the development of new catalytic systems.

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[8] General procedure for the selective oxidation of alcohols to aldehydes: All reactions were carried out with a multireactor (Carousel 12 station, RADLEYS). Benzyl alcohol (1081 mg, 10.0 mmol) and nano-Fe_2O_3 **1** (16.0 mg, 1 mol%) were added to a glass reactor (ca. 50 mL). The reaction mixture was vigorously stirred (500–750 rpm) at 75 °C. H_2O_2 (30 wt% in water, 1.0 mL, 10.0 mmol; VWR) was added continuously over 12 h. The mixture was then cooled to room temperature, and dioxane (1760 mg, 20 mmol) was added for qualitative analysis by GC-FID.

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[12] General procedure for the selective oxidation of olefins to aldehydes: All reactions were carried out in an oil bath (oil bath temperature 75 °C). The olefin (10.0 mmol), H_2O_2 (30 wt% in water, 2.0 mL, 20.0 mmol; VWR), and nano-Fe_2O_3 **1** (16.0 mg, 1 mol%) were added to a glass reactor (ca. 50 mL). The reaction mixture was vigorously stirred (500–750 rpm) at 75 °C for 5 h and cooled to room temperature, and then dioxane (1760 mg, 20 mmol) was added for qualitative analysis by GC-FID.