## Hierarchically Structured MnO<sub>2</sub>-Co/C Nanocomposites: Highly Efficient and Magnetically Recyclable Catalysts for the Aerobic Oxidation of Alcohols

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Dedicated to Manfred Scheer on the occasion of his 60th birthday

Porous  $MnO_2$  microspheres distributed around magnetic carbon-coated cobalt nanoparticles were developed. The performance of these nanoparticles rivals that of Pd-based catalysts for the selective oxidation of alcohols. Excellent recyclability was conveniently achieved by magnetic decantation and is demonstrated in ten consecutive cycles with no apparent material or performance losses.

The oxidation of alcohols to aldehydes or ketones is a widely used transformation in organic synthesis, and especially, catalytic variants exploiting oxygen as the terminal oxidant are of eminent importance to substitute established but environmentally problematic methods that necessitate the (over)stoichiometric use of heavy metals.<sup>[1,2]</sup> Significant advances have been made with the use of ruthenium-, palladium-, and gold-based catalysts, often supported on carbon or TiO<sub>2</sub> carriers to facilitate recovery and recyclability.<sup>[3]</sup> However, these catalysts involve the use of expensive noble metal components. The development of inexpensive heterogeneous catalytic systems is thus highly desirable.<sup>[4]</sup>

It is well recognized that the activity of a catalyst is closely related to its morphology.<sup>[5]</sup> Targeting more efficient catalyst utilization, heterogeneous MnO<sub>x</sub> catalysts with different nanostructures such as plate-like layers,<sup>[6]</sup> hollow spheres,<sup>[7]</sup> octahedral molecular sieves,<sup>[8,9]</sup> and nanoparticles<sup>[10]</sup> have been investigated for the aerobic oxidation of alcohols. Under optimal conditions, the amount of MnO<sub>x</sub> applied can be reduced to 10 mol% (0.1 equiv. with respect to the substrate), which provides high yields of aldehydes and ketones.<sup>[10,11]</sup> However, the recovery and reuse of such catalysts is challenging and generally calls for filtration or centrifugation steps that lead to progressive material loss, which requires replenishment of the catalyst to preserve the performance.<sup>[2,8]</sup>

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The application of magnetic nanoparticles has rapidly gained popularity as a convenient and cost-effective platform to manipulate and recycle catalysts.<sup>[12,13]</sup> Among those, iron oxide nanoparticles have been used most widely; however, their relatively low saturation magnetization ( $M_{S,bulk} \leq 92 \text{ emu g}^{-1}$ ) limits the amount of nonmagnetic active component that can be loaded while still permitting the efficient separation of the resulting core–shell nanocomposites by external magnetic fields.<sup>[14,15]</sup>

Recently, Stark et al. reported ferromagnetic graphenecoated cobalt nanoparticles 1 (Figure 1) that can be synthesized by reducing flame-spray pyrolysis on large scale  $(>30 \text{ gh}^{-1})$ .<sup>[16,17]</sup> The deposition of a thin graphene layer over the intrinsically pyrophoric metal core enables remarkable thermal stability<sup>[18]</sup> without any detriment to the magnetization  $(M_{\rm S bulk} = 158 \text{ emu g}^{-1})$ . Therefore, **1** seems to be a suitable platform for magnetic hybrid materials if they can be successfully integrated into catalytic materials.<sup>[13]</sup> Different strategies, for example, the direct deposition of metals, the noncovalent and covalent attachment of molecular metal complexes, or the growth of dendritic or polymeric metal-ligand assemblies onto the graphene surface, have been successfully explored.<sup>[19]</sup> In each case, the graphene layer on the nanoparticles serves as an anchor point, but otherwise it does not impact the synthesis of the attached catalytic material. Herein, we report the synthesis of unprecedented hierarchically structured microspheres composed of MnO<sub>2</sub> nanoplatelets, in which Co/C nanoparticles are homogeneously distributed. The resulting material (denoted 4, Figure 1) functions as a highly efficient and selective catalyst in the aerobic oxidation of aliphatic and aromatic alcohols at ambient pressure; it outperforms known MnO<sub>2</sub>-based catalysts<sup>[20]</sup> and rivals the activity of those based on palladium.<sup>[21]</sup> More importantly, owing to homogeneous dispersion of Co/C nanoparticles, MnO<sub>2</sub> species are firmly anchored around the magnetic component of the catalyst, which ensures efficient magnetic separation, as established over 10 reaction cycles in the oxidation of benzyl alcohol.

The synthesis of magnetic  $MnO_2$  microspheres **4** commenced with the in situ growth of  $MnO_2$  nanosheets by a microwave-assisted redox reaction, which was performed by utilizing the graphene layer of **1** as the reducing agent to produce  $MnO_2$  [Scheme S1, Eq. (1) in the Supporting Information].<sup>[22]</sup> Scanning electron microscopy (Figure 1a) revealed that resulting material **2** consists of large and intergrown sheetlike structures. The high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) image of the





**Figure 1.** a) Synthesis of hierarchically structured  $MnO_2$ -Co/C catalysts (4). b, c) SEM and HAADF-STEM images of initial  $MnO_2$ -Co/C composite **2**. d) SEM image of the composite **3** obtained after mechanical milling. e, f) SEM and TEM images of **4**. g) HAADF-STEM image and h) correlative chemical map of Mn (blue) and Co (orange) of a thin cross section of **4**. i) Ar isotherms and j) corresponding NLDFT pore-size distributions of sample **4** before (**4**, fresh) and after 5 cycles in the aerobic oxidation of benzyl alcohol (**4**, used).

thin cross-sectional area reveals that **1** is randomly distributed among the MnO<sub>2</sub> nanosheets (Figure 1b). The X-ray diffraction (XRD) pattern of **2** (Figure 2a) evidences the presence of the  $\delta$ phase of MnO<sub>2</sub> (JCPDS 42-1317)<sup>[22]</sup> and of cobalt crystals (reflections at  $2\theta = 44.2$  and  $51.5^{\circ}$ ). Subsequent mechanical milling (10 min) to form **3** [68 wt% MnO<sub>2</sub> determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES); Figure 1c] has two main roles, that is, it compacts the loosely aggregated nanosheets and improves the dispersion of the Co/C nanoparticles within the MnO<sub>2</sub> matrix.

Upon dispersion of **3** in an aqueous solution containing  $KMnO_4$  and  $MnSO_4$ ,  $MnO_2$  nanoplatelets quickly form [Eq. (S2)].<sup>[23]</sup> After continuous stirring at 60 °C for 45 min, 3 D hierarchical microspheres **4** (66 wt %  $MnO_2$  determined by ICP-AES; Figure 1 e, f) are obtained. Both the known instability of  $\delta$ -MnO<sub>2</sub> in acidic solution<sup>[24]</sup> and the high density of defects generated by mechanical milling are thought to facilitate nuclea-

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tion and growth of the MnO<sub>2</sub> nanoplatelets, which successfully leads to morphological transformation into an open intergrown network in which the cobalt/ carbon nanoparticles are embedded. The diffraction peaks at  $2\theta = 38.3$ , 42.2, and 57.2° in the XRD pattern are assigned to orthorhombic γ-MnO<sub>2</sub> (JCPDS 14-644), which confirms the complete phase transition from  $\delta$ -MnO<sub>2</sub>.<sup>[25]</sup> Owing to the protective graphene layer, no diffraction peaks belonging to cobalt oxides are evidenced in 4, which indicates that the Co nanoparticles are not oxidized during the synthesis. Examination of a thin cross section ( $\approx$  30–50 nm thick) of a single particle of 4 by HAADF-STEM (Figure 1g) and corresponding chemical mapping (Figure 1 h) of Mn (blue) and Co (orange) by energy dispersive X-ray (EDX) spectroscopy proves that the redistributed Co/ C nanoparticles are firmly embedded within the matrix of nanoplatelets.<sup>[26]</sup> MnO<sub>2</sub> The metal oxidation states of 4 were analyzed by X-ray photoelectron spectroscopy (XPS). The spectra of the Mn2p region (Figure 2b) displays two distinct peaks at binding energies of 642.3 and 653.7 eV, which originate from the Mn 2p<sub>3/2</sub> and Mn 2p<sub>1/2</sub> spinorbit peaks, respectively, corre-



**Figure 2.** a) XRD patterns of **2**, **3**, and **4**.  $\forall$ :  $\gamma$ -MnO<sub>2</sub>,  $\bullet$ :  $\delta$ -MnO<sub>2</sub>,  $\bullet$ : Co metal. b) XPS spectrum of the Mn2p region and c,d,e) STEM image and corresponding EDX maps of **4**.



sponding to  $Mn^{4+,[27]}$  Owing to the redistribution of Co/C nanoparticles in **4**, Mn (green) and Co (red) are essentially seen to overlap in the EDX maps of the catalyst acquired by STEM (Figure 2 c-e). Such a homogeneous distribution of the magnetic species is beneficial to maintain the magnetization of the whole microsphere.<sup>[28]</sup>

To further characterize the porous structure of the final nanocomposites, 4 was analyzed by argon adsorption at 77 K. The type IV isotherms evidenced (Figure 1 i) display an increasing uptake across the entire range of relative pressures, which is significantly higher than that displayed by the precursor nanosheets in 2; this suggests the development of extensive micro- and/or mesoporosity.<sup>[29]</sup> This is confirmed by the corresponding nonlocal density functional theory (NLDFT) pore-size distribution (Figure 1 j), which indicates a broad pore-size distribution, with two prominent peaks centered at approximately d=1.7 and 3 nm. Correspondingly, a BET surface area of 225  $m^2 g^{-1}$  is evidenced (Table S1), which is the highest value reported so far for nanostructured MnO<sub>2</sub> materials.<sup>[30]</sup> The high porosity originates from the network of interparticle spaces formed between the MnO<sub>2</sub> nanoplatelets (Figure 1 d, e),<sup>[31]</sup> which offers an excellent balance between accessibility and surface area of the active phase.<sup>[32]</sup> As a result, **4** appears to be promising for applications in catalysis.

Thus, **4** (66 wt % MnO<sub>2</sub>) was investigated as a catalyst for the aerobic oxidation of alcohols (Table 1). Under optimized reaction conditions (see the Supporting Information) a catalyst loading of 3.8 mol% was sufficient to achieve the oxidation of benzyl alcohol to its corresponding aldehyde in high yields with excellent chemoselectivity (Table 1, entry 1) within 4 h at 80 °C, which compares favorably to all MnO<sub>2</sub> catalysts reported

<b>Table 1.</b> Aerobic oxidation of various alcohols by employing <b>4</b> as a recyclable catalyst. <sup>(a)</sup> OH $4 \longrightarrow p_1^2$ DMF 80°C $p_1^2$ $p_2^2$								
Entry	R <sup>1</sup>	R <sup>2</sup>	t [h]	Conversion <sup>(b)</sup>	Yield <sup>[b,c]</sup> [%]	TON <sup>[d]</sup>		
1	C <sub>6</sub> H <sub>5</sub>	Н	4	97	96 (95)	25		
2 <sup>[e]</sup>	C <sub>6</sub> H <sub>5</sub>	Н	4	23	20 (18)	5		
3 <sup>[f]</sup>	C <sub>6</sub> H <sub>5</sub>	Н	10	94	93 (91)	93		
4	4-MeOC <sub>6</sub> H <sub>4</sub>	Н	4	90	88 (86)	23		
5	4-CIC <sub>6</sub> H <sub>4</sub>	Н	4	92	90 (88)	23		
6	$4-O_2NC_6H_4$	Н	4	95	92 (91)	24		
7	C <sub>6</sub> H <sub>5</sub>	C₅H₅	4	94	91 (90)	24		
8	C <sub>6</sub> H₅CH=CH−	Н	4	87	83 (80)	22		
9	2,6-(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	Н	4	85	82 (78)	21		
10	$CH_3(CH_2)_2$	CH₃	8	81	79	20		
11	$CH_2 = CHCH_2$	-	8	77	74	19		
12	cyclohexanol	-	8	73	70	18		
13	furfuryl alcohol	-	8	75	72	19		
[a] Reaction conditions: Alcohol (1 mmol), DMF (0.5 mL), and <b>4</b> catalyst (5 mg, 3.8 mol% MnO <sub>2</sub> ), 80 °C, under bubbling of oxygen. [b] Determined by GC analysis by using dodecane as an internal standard. [c] Values in brackets are the yields of the isolated products [d] $TON = (mol product)/(d)$								

by GC analysis by using dodecane as an internal standard. [c] Values in brackets are the yields of the isolated products. [d]  $TON = (mol product)/(mol MnO_2)$ . [e] Commercial  $MnO_2$  powder as catalyst (Sigma–Aldrich). [f] Alcohol (4 mmol), DMF (15 mL), and catalyst **4** (5 mg, 0.95 mol% MnO<sub>2</sub>), 80 °C, under bubbling of oxygen.

so far for such reactions.<sup>[11,20,33]</sup> For comparison, commercial  $MnO_2$  showed very poor catalytic activity under the same conditions (Table 1, entry 2). With a lower catalyst loading of **4** (0.95 mol%), almost complete conversion of benzaldehyde could still be obtained after prolonging the reaction time to 10 h (Table 1, entry 3), and a turnover number (TON) of 93 was achieved. Equally good results were obtained with both electron-rich- and electron-poor-substituted benzyl alcohols, as well as with cinnamyl alcohol (Table 1, entries 4–8). Even in the case of a severely sterically hindered alcohol (Table 1, entry 9) were a high conversion and yield obtained. Aliphatic, allylic, and heteroaromatic alcohols also proved to be suitable substrates; however, the reaction time had to be increased to 8 h (Table 1, entries 10–13).

The room-temperature magnetization of **4** (Figure S1) was found to be 78.4 emu g<sup>-1</sup>, which is significantly lower than that of unfunctionalized **1** (158 emu g<sup>-1</sup>) as a consequence of the deposition of substantial amounts of nonmagnetic  $MnO_2$ . Nonetheless, complete recovery of the catalyst could still be achieved within 10 s upon application of an external neodym magnet (Figure 3 a), without any mass loss of  $MnO_2$  or cobalt



**Figure 3.** a) Photo illustrating the magnetic recovery of 4 dispersed in toluene. b) HAADF-STEM image of 4 after 5 cycles. c) Recyclability test of 4 and 4' [benzyl alcohol (1 mmol), DMF (0.5 mL), 4 or 4' (3.8 mol% MnO<sub>2</sub>), 80 °C under bubbling of oxygen, 4 h; total TON: 250 for 4 and 111 for 4']. d) Kinetic profiles for the aerobic oxidation of benzyl alcohol catalyzed by 4 (1 mmol benzyl alcohol, 0.5 mL DMF, and 3.8 mol% MnO<sub>2</sub> as catalyst, 80 °C under bubbling of oxygen) and commercial Pd/C (10 wt%) [1 mmol benzyl alcohol, 2 mL of 1.25 M aqueous NaOH, 40 mg Pd/C (3.8 mol% Pd), 90 °C under bubbling of oxygen]. Yields were determined by GC analysis by using dodecane as an internal standard.

into the product phase, as determined by ICP-AES after each run (Figure S2). Consistently, the morphology and pore structure of **4** remained unchanged after 5 cycles (Figures 3 b and 1 i,j), whereas the constant high activity was evidenced over 10 consecutives runs (Figure 3 c). The scanning electron microscopy (SEM) micrographs recorded after 10 cycles still showed no evidence of alteration of the  $MnO_2$  hierarchical nanostructures (Figure S3), and XPS analysis (Figure S4) also confirmed the

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preserved structure of the material, as judged by the unchanged Mn 2p signal.

In contrast to the route described, attempts to directly grow  $MnO_2$  nanoplatelets on 1 (resulting in sample 4') yielded an inferior catalyst. Aggregated clusters of Co/C nanoparticles were distributed among the MnO<sub>2</sub> nanoplatelet spheres (Figure S6), which resulted in a low affinity between MnO<sub>2</sub> and the magnetic cores. Thus, significant leaching of manganese was observed upon application (Figure S2), which led to a sharp decrease in activity in consecutive catalytic runs (Figure 3c). Considering Pd<sup>0</sup> as the best catalyst for the title transformation,<sup>[20]</sup> we compared the kinetic profiles for the aerobic oxidation of benzyl alcohol catalyzed by 4 and by Pd<sup>0</sup> supported on activated carbon (Pd/C, 10 wt%). To ensure a fair comparison, the latter reaction was conducted under the optimal conditions reported, that is, at a reaction temperature of 90 °C.<sup>[34]</sup> With the use of the same catalyst amount (3.8 mol%), the activity of 4 was somewhat lower than that of Pd/C, but a comparable yield of the product was obtained within 4 h of reaction (Figure 3 d). Considering the cost, inexpensive 4 appears to be a highly competitive alternative to noble palladium in the oxidation of alcohols, particularly given that considerably lower amounts of material are required to achieve the same TON for a given reaction (4 containing 1 mmol MnO<sub>2</sub>=0.13 g; Pd/C containing 1 mmol  $Pd^0 = 1.2$  g).

In conclusion, hierarchically structured MnO<sub>2</sub>-Co/C nanocomposites were developed as magnetically recoverable catalysts for the aerobic oxidations of alcohols. These hybrid systems offer high catalytic activity, outperform traditional oxidation systems by using MnO<sub>2</sub> as the oxidant, rival the activity of Pdbased catalysts, can be conveniently separated by external magnets, and offer excellent recyclability. Finally, they can be readily prepared from commercially available Co/C nanoparticles and manganese salts.

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