A GENUINELY MULTIDISCIPLINARY JOURNAL

CHEMPLUSCHEM

CENTERING ON CHEMISTRY

Accepted Article

Title: Mesoporous Assembled Mn3O4 Nanoparticle Networks as Efficient Catalysts for Selective Oxidation of Alkenes and Aryl Alkanes

Authors: Euaggelia Skliri; Stelios Papadogiorgakis; Ioannis Lykakis; Gerasimos S. Armatas

This manuscript has been accepted after peer review and the authors have elected to post their Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: ChemPlusChem 10.1002/cplu.201600460

Link to VoR: http://dx.doi.org/10.1002/cplu.201600460



WILEY-VCH

www.chempluschem.org

Mesoporous Assembled Mn₃O₄ Nanoparticle Networks as Efficient Catalysts for Selective Oxidation of Alkenes and Aryl Alkanes

Euaggelia Skliri,^[a] Stelios Papadogiorgakis,^[a] Ioannis N. Lykakis,^[b] and Gerasimos S. Armatas*^[a]

Abstract: Designing materials at the nanoscale has been considered important for enhancing surface properties for catalysis. Metal oxide nanoparticles have a large number of exposed surface active sites, but they suffer from low reactivity and poor stability resulted from the excessive aggregation in less active microscopic structures. Herein, we present the synthesis of mesoporous Mn₃O₄ nanoparticle assemblies by a polymer-assisted self-assembly approach and demonstrate their catalytic activity in oxidation of various saturated and unsaturated hydrocarbons, including aromatic alkenes and aryl alkanes, in the presence of *tert*-butyl hydroperoxide as mild oxidant. We also show, through comparative studies, that the high catalytic activity and stability of these Mn_3O_4 assemblies arise from the unique three-dimensional open-pore structure, high internal surface area (90 m² g⁻¹) and uniform mesopores (ca. 6.6 nm in size).

Introduction

Olefinic hydrocarbons, which are main constituents of oil and natural gas, are excellent feedstocks for chemical industry. Catalytic oxo-functionalization of aromatic and aliphatic alkenes towards the production of more valuable products, such as alcohols, ketones, acids and peroxides, is one of the most important transformations in organic chemistry.^[1] In this regard, significant advancements have been made in the use of solid, recyclable catalysts, in respect of environmental friendly conditions using molecular oxygen or hydrogen peroxides as mild oxidants.^[2] The use of solid catalysts offers several advantages over homogeneous systems, including catalyst recovery and controlled regio- and chemo-selective transformations.^[3] So far, although a diverse range of supported transition-metal oxides, such as CuO, ZnO, CeO₂, Fe₂O₃ and WO₃,^[4] metal nanoparticles (NPs), such as Pd and Ru,^[5] and polvoxometalate clusters. such as $[W_{10}O_{32}]^{4-}$ $[Mn_2ZnW(ZnW_9O_{34})_2]^{10-}$ and $[XW_{12}O_{40}]^{n-}$ (X = P, Si),^[6] have been applied to these reactions, the selective oxidation of olefins with

[a]	E. Skliri, S. Papadogiorgakis, Prof. Dr. G.S. Armatas Department of Materials Science and Technology University of Crete
	Heraklion 71003 (Greece)
	E-mail: garmatas@materials.uoc.gr
[b]	Prof. Dr. I.N. Lykakis
	Department of Chemistry
	Aristotle University of Thessaloniki
	Thessaloniki 54124 (Greece)

Supporting information for this article is given via a link at the end of the document.

high associated product yield still remains a challenge.

Manganese oxides, especially Mn_3O_4 , have attracted particular attention in catalysis because of their intriguing oxidation–reduction (redox) properties and excellent chemical stability. As a result, in recent years, a number of Mn_3O_4 -containing materials have been successfully used in various catalytic applications, including degradation of phenols^[7], reduction of nitrobenzenes^[8], and oxidation of arenes^[9], alcohols^[10] and alkyl-substituted alkenes^[11]. In addition, hausmannite Mn_3O_4 has received a considerable interest as electrode material for lithium-ion batteries and supercapacitors owing to its low cost, good electrochemical performance, and most impotently excellent cycling stability even at high current rates.^[12]

Earlier studies have shown that Mn₃O₄ nanostructures with a large number of exposed catalytically active edge sites, such as nanoparticles, nanorods and nanosheets, are particularly effective for a variety of redox reactions. For example, these materials displayed exemplary activity in oxidation of volatile organic compounds (VOCs)^[13] and electrocatalytic reduction of oxygen^[14]. In principle, small-sized Mn₃O₄ NPs and onedimensional (1D) nanorods might exhibit distinctive functionalities owing to the high reactivity, large exposed surface area and adequate interactions between the active sites and reactants, portending great potentials for use in future catalytic applications.^[7a,15] However, despite these promising advances, thermodynamics favours the excessive agglomeration of such nanomaterials in large close-packed superstructures (e.g. bulklike structures and densely packed NP aggregates) with irregular shape and low porosity, limiting the catalytic activity. Consequently, the integration of these nanoscale building blocks into high surface-to-volume ratio architectures with internal porosity is a promising approach to address these limitations.^[16]

We recently demonstrated the synthesis of ordered mesoporous iron oxide architectures using ligand-stripped y-Fe₂O₃ NPs as primary building blocks.^[17] To construct these materials, we first utilize nitrosonium tetrafluoroborate (NOBF₄) to gently strip the native ligands (oleyl alcohol) from the surface of γ -Fe₂O₃ NPs and charge stabilized them by BF₄⁻ anions. This procedure was necessary to obtain ligand-free NPs that preferentially segregate to the polar domains of the polymer template (through electrostatic or hydrogen-bonding interactions) during synthesis. Thermal annealing is then used to decompose the polymer and fuse the NPs into a rigid mesoporous network. As a result of the accessible pore channels and large surface area, mesoporous γ -Fe₂O₃ NP assemblies have been shown to be highly effective for reduction of nitroarenes into the corresponding aryl amines and oximes, using methylhydrazine or hydrazine as reducing agents.^[17a]

In this study, we report the synthesis of a new mesoporous network consisting of interconnected Mn₃O₄ NPs through a polymer-assisted self-assembly method and demonstrate its high activity for the catalytic oxo-functionalization of aliphatic and aromatic alkenes as well as aryl alkanes using tert-butyl hydroperoxide as a mild oxidant. An advantage of this synthetic route is that it allows the construction of extended threedimensional (3D) porous networks from metal oxide NPs as building blocks in contrast to the preparation of isolated NPs and nanorods and close-packed thin films.^[18] The resulting material possesses a network structure of interconnected 6-7 nm-sized Mn₃O₄ NPs and shows highly accessible surface area and narrow pore-size distribution. We show that, compared to other morphologies of Mn₃O₄ such as bulk microparticles, individual NPs and random NP aggregates, mesoporous assemblies of Mn₃O₄ NPs have the potential to provide more exposed active sites between the NPs, leading to improved catalytic performance. Furthermore, we demonstrate that although these Mn₃O₄-catalyzed reactions proceed under mild conditions, they are particularly selective towards saturated and unsaturated carbonyl compounds.

Results and Discussion

Catalysts synthesis and characterization

A schematic overview of mesoporous Mn₃O₄ NP assemblies (Mn₃O₄ MNAs) synthesis by the polymer-templated aggregating self-assembly (ASA) method is shown in Scheme 1. Briefly, for the synthesis of Mn₃O₄ MNAs, a dimethylformamide (DMF) solution containing BF4-coated Mn3O4 NPs was added to an ethanol solution of poly(ethylene oxide)-b-poly(propylene oxide)b-poly(ethylene oxide) (EO₂₀PO₇₀EO₂₀) block copolymer. The reaction mixture was then placed in an oven to boost the aggregation process. We observed that the initial concentration of Mn₃O₄ NPs and the evaporation time of solvents have a considerable influence on the porosity of the products. We obtained optimal results (on the basis of surface area of the final products) with a slow evaporation of solvents (within ~6-7 days, at 40 °C) and using a copolymer:Mn₃O₄:ethanol:DMF molar ratio of 0.07:1:49.7:12.3. In these conditions, as the reaction progresses, the Mn₃O₄ NPs co-assemble with the liquidcrystalline block copolymer, and eventually formed a hybrid polymer-NP supramolecular mesostructure. This intermediate product was then calcined in air at 350 °C for 4 h to yield a Mn₃O₄ NP-linked mesoporous network with 3D interconnected porosity. The complete elimination of the polymer template was confirmed by thermogravimetric analysis (TGA), where the mesoporous sample did not show any appreciable weight loss up to 600 °C (Figure S1 in the Supporting Information).



Scheme 1. Schematic illustration of the synthesis of Mn_3O_4 MNAs (ASA: Aggregating Self-Assembly, Cal: Calcination, MNAs: Mesoporous Nanoparticle Assemblies).

The porous structure of the as-obtained Mn₃O₄ MNAs material was characterized by small-angle X-ray scattering (SAXS), transmission electron microscopy (TEM), X-ray diffraction (XRD) and N₂ physisorption. The SAXS pattern is shown in Figure 1, where a relative broad but resolved scattering peak at 0.49 nm⁻¹ q (= $4\pi \cdot \sin\theta/\lambda$, where 2 θ is the scattering angle and λ is the wavelength of Cu irradiation) range can be observed. The peak position of this reflection corroborates to the NP aggregates with an average interparticle spacing (from d = $2\pi/q$) of 12.8 nm. Moreover, analysis of the scattering data by the Guinier equation^[19] showed that the constituting NPs have an average particle size of about 6.9 nm (Figure 1a, inset). As we will show below, this particle size is very close to the diameter of the starting materials (ca. 7 nm, as determined from XRD data), which implies minimal grain coarsening of Mn₃O₄ NPs during synthesis.



Figure 1. SAXS pattern of the mesoporous assemblies from Mn₃O₄ NPs. Inset: Guinier plot [In(I(q)) $\propto q^2 \cdot R_g^2/3$, where R_g is the radius of gyration ($qR_g < 1$)] for the Mn₃O₄ MNAs sample derived from the low *q*-region of the scattering curve. The red line is fit to the data.

Typical TEM images of the Mn_3O_4 MNAs are shown in Figures 2a and 2b. The images reveal a disordered porous network that is constructed solely by individual NPs with grain sizes 6.7 ±0.9 nm (see the inset in Figure 2a), in agreement with SAXS results. To probe the crystal structure of the mesoporous

framework, we utilized high-resolution TEM (HRTEM) and selected-area electron diffraction (SAED). The HRTEM image, in Figure 2b (inset), displays a portion of the porous structure and demonstrates the high crystallinity of constituting NPs; it shows distinct lattice fringes with 2.9 and 4.9 Å interplanar spacings, which correspond to the (200) and (101) crystal planes (along the [010] direction) of tetragonal Mn₃O₄, respectively. Besides, the SAED pattern, in Figure 2c, reveals that the Mn₃O₄ NPs embedded in the pore walls are randomly oriented, showing a series of Debye-Scherrer diffraction rings that can be assigned to the hausmannite structure of Mn₃O₄ (JCPDS card no. 24-0734).

Consistent with electron microscopy studies, the wide-angle XRD pattern of the Mn₃O₄ MNAs material revealed its highly crystalline nature as shown in Figure 2d. All of the diffraction peaks can be readily indexed to the hausmannite phase of Mn_3O_4 with a tetragonal lattice structure (space group: $I4_1/amd$). It is worth noting that the XRD pattern of Mn₃O₄ MNAs is identical to that of the precursor NPs, and no other diffraction peaks were detected for impure crystalline phases (e.g., Mn₂O₃ and MnO2 oxides). This is collaborated with Raman spectroscopy results, which indicates only the characteristic shifts of hausmannite structure (647, 362, 304 and 281 cm⁻¹) for the Mn₃O₄ MNAs, see Figure S2 in the Supporting Information. Also, the broadening of the XRD peaks suggests that Mn₃O₄ occurs as very fine grained particles. On the basis of Scherrer analysis^[20] of the (211) reflection, the average domain size of Mn_3O_4 crystallites was estimated to be ~7 nm for both mesoporous Mn₃O₄ assemblies and precursor (BF₄⁻-capped) Mn₃O₄ NPs. Taken together with TEM images, these results verify that the constituting Mn₃O₄ NPs prevent, to a great extent, interparticle sintering and maintain their initial nanostructure during heating treatment.



Figure 2. a, b) Representative TEM images (inset of panel a: particle-size distribution histogram showing an average particle diameter of 6.7 \pm 0.9 nm) and high-resolution TEM image of an individual Mn₃O₄ NP (inset of panel b),

and c) SAED pattern for the Mn_3O_4 MNAs sample. d) XRD patterns of mesoporous Mn_3O_4 assemblies (Mn_3O_4 MNAs) (i) and isolated $BF_4^-capped$ Mn_3O_4 NPs (ii).

The porosity of the template-free material was examined by nitrogen physisorption measurements. Figure 3 shows N₂ adsorption-desorption isotherms and the corresponding pore size distribution plot for mesoporous Mn₃O₄ assemblies (Mn₃O₄ MNAs) along with those of non-templated analogous. The adsorption isotherm of the Mn₃O₄ MNAs sample is of type IV with a combination of H₂ and H₃-type hysteresis loop (according to IUPAC classification), which is ascribed to an interconnected mesoporous structure with slit-like pores.[21] The Brunauer-Emmett-Teller (BET) surface area and total pore volume assessed from the adsorption branch of the isotherms are 90 m² g^{-1} and 0.19 cm³ g^{-1} , respectively. The mesoporous Mn₃O₄ assemblies feature a narrow non-local density functional theory (NLDFT) pore-size distribution with the maximum of the peak centered at ~6.6 nm (Figure 3, inset). This pore size is related to the void space among the assembled NPs. Given an average interparticle distance of 12.8 nm (determined by SAXS), the difference between the repeat distance and the pore size gives an estimate of the wall thickness at 6.2 nm. This value corresponds well with the diameter of the Mn₃O₄ NPs obtained by TEM (ca. 6.7 nm) as well as SAXS analysis (ca. 6.9 nm). Thus, it appears that the layers of interconnected NPs that comprise the walls of Mn₃O₄ MNAs are single.



Figure 3. N₂ adsorption–desorption isotherms at -196 $^{\circ}C$ and the corresponding NLDFT pore-size distribution plots (inset) of the polymer-templated mesoporous assemblies (Mn₃O₄ MNAs) (i) and random aggregates (Mn₃O₄ RNAs) (ii) of Mn₃O₄ NPs (STP: standard temperature and pressure).

Crucially, the polymer-templated ASA process yielded porous network of assembled Mn_3O_4 NPs with mesoscale porosity. For comparison, in the absence of template, the BF₄⁻⁻capped Mn_3O_4 NPs are randomly aggregated into close-packed structures. This is illustrated by the N₂ adsorption-desorption isotherms shown in Figure 3; the shape of which confirms the difference in morphology between the templated and non-templated NP assemblies. The N₂ adsorption-desorption

WILEY-VCH

isotherms of the random aggregates of Mn₃O₄ NPs (Mn₃O₄ RNAs) are of type IV with a H₃-type hysteresis loop, typically found with random porous networks with slit-like pores.^[21] Analysis of the adsorption data reveals that this sample has a BET surface area of 107 m² g⁻¹ and a total pore volume of 0.10 cm³ g⁻¹. In addition, the estimated NLDFT pore-size distribution plot (assuming slit-shaped pores) indicates the formation of NP aggregates with ca. 2.7 nm-sized interstitial voids. In order to estimate the micropore volume in these materials, we performed CO2 physisorption measurements at 0 °C and the obtained isotherms were analyzed by the Dubinin-Radushkevich (DR) method (see Figure S3 in the Supporting Information). The DR plot for the Mn₃O₄ assemblies prepared with polymer template shows a micropore volume of 0.02 cm³ g⁻¹ (corresponding to a microporosity of ~11%), while random aggregates of Mn₃O₄ NPs show a micropore volume of 0.05 cm³ g⁻¹ (corresponding to a microporosity of ~50%). On the basis of the above results, it can thus be concluded that the polymer-templated sample mainly contains mesopores within the assembled structure, while the randomly agglomerated NPs adopt a more densely packed structure with significant fraction of micropores (d < 2 nm).

Catalytic activity

To assess the catalytic activity of the Mn₃O₄ MNAs and to determine the optimum reaction conditions, the oxidations of styrene (1) using different oxidants and solvents was initially study. Following various catalytic experiments, an almost quantitatively conversion of 1 (ca. 93%) was observed in the presence of 10 mol % (based on 1) Mn₃O₄ MNAs catalyst and 3 equiv. of tert-butyl hydroperoxide (TBHP) in 2 mL of CH₃CN, within 3 h (Table 1, entry 3). In all cases, the corresponding benzaldehyde (1a) was observed as the major product accompanying with small amounts of phenyl acetaldehyde (1b), epoxystyrene (1c) and double oxidative product 2-oxo-2phenylacetaldehyde (1d), see Table 1. Noted that addition of equimolar amount of TBHP (with respect to 1) resulted in incomplete oxidation of 1, while in the presence of 2 equiv. of TBHP, a 60 % conversion of 1 was observed in 3 h (Table 1, entries 1 and 2). The increase of the TBHP amount (5 eq.) did not result in a significant enhancement of the transformation of 1, while the selectivity to 1a notably decreased (Table 1, entry 4). Among the solvents studied, the catalytic performance of Mn₃O₄ MNAs can be improved when the reaction is carried out in acetonitrile, affording 61% yield of 1a in 3 h; comparatively, methanol and ethanol resulted in a lower oxidation activity, giving 1a in 49% and 22% product yield, respectively, under similar conditions (Figure S4, Supporting Information). This is probably due to the efficient coordination of 1 to the surface active sites of Mn₃O₄ in polar solvents. Meanwhile, no appreciable oxidation of 1 takes place when molecular oxygen (1 atm) and hydrogen peroxide (H_2O_2) were used as oxidants under the same conditions (Table 1, entries 5 and 6). Besides, in the case of H₂O₂ oxidation (3 equiv.), a large amount of gasbubbles appeared as soon as the oxidant was injected into the reactor, implying a fast catalytic decomposition of H₂O₂ by the Mn₃O₄ NPs. The reaction activity also strongly depends on the catalyst loading and reaction temperature. We found that the

optimum catalyst loading for **1** oxidation was attained at 10 mol % (see Table 1, entries 7 and 8). At 50 °C, the conversion to **1a** was moderate (ca. 46%, Table 1, entry 9), while upon increasing the temperature at 70 °C, **1** was selectivity oxidized to **1a** with 61% yield. Higher reaction temperature (90 °C), however, did not result in significant improvement of **1a** formation (Table 1, entry 10). Control experiments showed that in the absence of catalyst or TBHP oxidant, no oxidation of **1** occurred (even over a 4-hour reaction period), indicating that oxidation reaction is really a catalytic process.

Table 1. Conditions evaluation in the oxidation of styrene (1) using various ${\sf Mn}_3{\sf O}_4{\sf -}{\sf based}$ catalysts and oxidants. $^{[a]}$

5	Mn ₃ O ₄ , oxidant CH ₃ CN, 3 h	~ •	+	+	
1		1a	1b	1c	1d

Entry	Catalyst		Conv.	Yield (%) ^[b]				
		Oxidant	(%) ^[b]	1a	1b	1c	1d	
1 ^[c]	Mn ₃ O ₄ MNAs	TBHP	38%	27%	4%	3%	4%	
2 ^[c]	Mn ₃ O ₄ MNAs	TBHP	60%	38%	7%	9%	6%	
3	Mn₃O₄ MNAs	твнр	88%	61%	7%	12%	8%	
4 ^[c]	Mn ₃ O ₄ MNAs	TBHP	93%	50%	10%	24%	9%	
5	Mn ₃ O ₄ MNAs	O ₂	Nr ^[d]					
6	Mn ₃ O ₄ MNAs	H_2O_2	<1%	<1%				
7 ^[e]	Mn ₃ O ₄ MNAs	TBHP	64%	42%	5%	12%	5%	
8 ^[e]	Mn ₃ O ₄ MNAs	TBHP	74%	49%	6%	14%	5%	
9 ^[f]	Mn ₃ O ₄ MNAs	TBHP	70%	46%	8%	9%	7%	
10 ^[f]	Mn ₃ O ₄ MNAs	TBHP	92%	62%	9%	13%	8%	
11	Mn_3O_4 NPs	TBHP	53%	34%	4%	12%	3%	
12	Mn ₃ O ₄ RNAs	TBHP	65%	40%	6%	9%	9%	
13	Mn ₃ O ₄ bulk	TBHP	45%	31%	3%	6%	5%	

[a] Reaction conditions: **1** (0.4 mmol), catalyst (0.04 mmol, 10 mol% with respect to **1**), TBHP (3 equiv.), CH₃CN (2 mL), for 3 h at 70 °C. [b] Based on the consumption of **1** determined by GC-MS. [c] These experiments were performed with 1.0 equivalent (entry 1), 2.0 equivalent (entry 2) and 5.0 equivalent (entry 4) of TBHP. [d] No reaction. [e] These experiments were performed with 0.02 mmol (entry 7) and 0.06 mmol (entry 8) of catalyst. [f] These reactions were carried out at 50 °C (entry 9) and 90 °C (entry 10).

It is notably that Mn_3O_4 MNAs shows higher catalytic activity than individual Mn_3O_4 NPs and random aggregates of Mn_3O_4 NPs. In particular, when BF_4 -capped Mn_3O_4 NPs were introduced as catalyst, they afforded a **1** conversion of 53% in 3 h (Table 1, entry 11), which is remarkably lower than that of Mn_3O_4 MNAs. This may be attributed to the aggregation of NPs, resulting in a decreased number of active sites available for

10.1002/cplu.201600460

WILEY-VCH

catalysis. Also, random Mn₃O₄ NP aggregates (Mn₃O₄ RNAs), although possess higher surface area, gave a lower conversion of 1 (ca. 65%), under identical conditions (Table 1, entry 12). Overall, these findings suggest that the high activity of the Mn₃O₄ MNAs can be attributed to the small grain size of Mn₃O₄ particles, which provides a large number of surface active sites, and the 3D mesoporous structure, which facilitates reactant contact with the NP surface. In agreement to this, we also found that use of Mn_3O_4 micropowder (BET surface area < 1 m² g⁻¹) resulted in approximately two times lower activity than that found for mesoporous assemblies of Mn₃O₄ NPs (see Table 1, entry 13). Notable, the catalytic activity of Mn₃O₄ MNAs compared higher or even comparable to that of other commonly used metal oxide catalysts (see Table S1, Supporting Information). For example, Mn₃O₄ MNAs catalyst outperforms the catalytic activity of $MoO_3^{[22]}$, $MoO_2^{[23]}$, $Fe_3O_4^{[24]}$, $NiFe_2O_4^{[25]}$ and $Mg_{0.4}Fe_{2.6}O_4^{[25]}$ NPs, NiCoFe spinel-type oxide nanosheets^[26], NiO and CoO microparticles^[27] and mesoporous vanadium silicate-1 zeolites^[28]. while it nearly as effective as the $Co_3O_4^{[29]}$ and $CuO^{[30]}$ NPs and Zr-doped CeO₂ nanorods^[31] studied under similar reaction conditions.



Figure 4. a) Recycling study of Mn_3O_4 MNAs in the oxidation of styrene (1). b) Time profiles of *para*-substituted styrenes and cycloalkenes (2–5) oxidation over Mn_3O_4 MNAs catalyst. Reaction conditions: 0.4 mmol of substrate, 0.04 mmol of catalyst, 3 eq. of TBHP, 2 mL of CH₃CN, 70 °C.

The Mn₃O₄ MNAs also demonstrated exceptionally high stability under the examined conditions. The reusability of the catalyst was assessed by performing repeated catalytic tests, in which 1 was oxidized under the reaction conditions described above. After each test, the catalyst was recovered from the reaction mixture by filtration, washed several times with deionized water and used for the next catalytic run. Catalytic results, shown in Figure 4a, indicated that the conversion level of 1 remains as high as 88-90% (at 3 h reaction time) after five catalytic runs, reflecting excellent reusability. Characterization of the regenerated catalyst by XRD showed that the phase remained Mn₃O₄ and the crystallite size did not change (ca. 7 nm, as determined by Scherrer analysis), Figure S5 of the Supporting Information. However, N_2 physisorption measurements revealed that the retrieved sample has a BET surface area of 68 m² g⁻¹, which is lower than that of the fresh catalyst (ca. 90 m² g⁻¹), and a pore volume of 0.12 cm³ g⁻¹. In addition, pore size analysis points to the formation of a slightly wider pore-size distribution with a peak maximum at 6.3 nm (Figure S6 of the Supporting Information). These preliminary studies indicate a structural deformation (i.e., small shrinkage of the pore structure) of the Mn₃O₄ NP assemblies during catalysis. To check the possibility of leaching Mn from catalyst, ICP-MS analysis was performed on the solution following a 15-h reaction time (after the catalyst was removed by centrifugation). The results indicated that there is no leaching of Mn to the solution phase; the metal content was below the detection limit of 0.3 ng L⁻¹.

To study the general applicability of the above oxidation process, various para-substituted styrenes (2 and 3) and cyclic alkenes (4 and 5) were examined. Figure 4b summarizes the results obtained from these oxidation reactions using Mn₃O₄ MNAs catalyst and TBHP oxidant. As can be seen, both methyl (2) and chloro (3) para-substituted styrenes were selectively oxidized by the Mn₃O₄ MNAs, yielding the corresponding aldehydes (2a and 3a) as the only products. However, oxidation of electron-deficient aromatic styrene 2 (p-Cl-substituted) proceeded faster than electron-rich styrene 3 (p-Me-substituted), giving the respective aldehyde in 98% and 90% yield, respectively, in 3 h. Furthermore, an almost quantitative consumption (ca. 95%) of cyclohexene (4) was observed by GC-MS under the conditions described above, in which the corresponding conjugated cyclohexenone (4a) was obtained at 90% relative yield with a small amount of the allylic cyclohexenol (4b, 5% yield) in 2 h. However, in contrast to cyclohexene, cyclooctene (5) was oxidized to cyclooctene oxide (5a) and cyclooctenone (5b) at 31% and 12% relative yields, respectively. Noted that aliphatic 1-octene does not oxidized under the present conditions (results not shown).

Regarding the mechanism of these organic transformations, we believe that a radical process probably is involved in the oxidation of alkenes to carbonyl compounds; although the formation of a metal dioxirane-type intermediate due the interaction of TBHP with the Mn_3O_4 catalyst cannot be excluded. This hypothesis found support from above oxidation reactions in which electron-rich aryl alkenes (styrenes) were oxidized faster than cyclic and aliphatic alkenes. In addition, further evidence



could be obtained by the oxidation of a series of aromatic saturated hydrocarbons, such as ethyl benzene (6). diphenylmethane (7), fluorene (8) and cumene (9). In general, the oxidation of saturated α -carbon C-H bonds in aromatic alkanes, under mild oxidative conditions, represents one of the most important and synthetically useful reactions.^[32] Such organic transformations usually suffer from very low selectivity and proceed under harsh reaction conditions, like high temperature and pressures or high-energy radiation.^[2] Surprisingly, under the examined conditions, the aromatic hydrocarbons 6-8 were selectively oxidized to the desired carbonyl compounds (6a-8a) in appreciable yields, as shown in Scheme 2. While very small amounts (~1-5% product yields) of the corresponding secondary alcohols 6b-8b were detected among the reaction mixture by GC-MS. This observation indicates that the oxidation reaction proceeds through the initial formation of the corresponding alcohols, which rapidly oxidized to ketones 6a-8a. In order to support this assumption, we examined the oxidation of 1-phenvlethanol (6b) under the same conditions. Indeed, within 3 h, acetophenone (6a) was obtained as the only product in 91% yield (Scheme 2). In the case of cumene (9), acetophenone (9a) was observed by GC-MS and ¹H NMR as the major product, accompanying with a significant amount of the corresponding tertiary alcohol (9b, ~9% product yield). Acetophenone is a C-C bond cleavage product which is formed from the corresponding peroxy- or alcoxy radical intermediate during the oxidation process.[33]



Scheme 2. Oxo-functionalization of aromatic hydrocarbons 6–9 into the corresponding carbonyl compounds catalyzed by Mn_3O_4 MNAs. In parentheses: the corresponding isolated yield and selectivity. Reaction conditions: 0.4 mmol substrate, 0.04 mmol catalyst, 3 equiv. TBHP, 2 mL CH₃CN, 70 °C.

Of particular note, Mn_3O_4 MNAs catalyst also exhibited very good catalytic activity and chemoselectivity in oxidation of aliphatic cycloalkanes, such as cyclooctane (**10**), with TBHP. Catalytic results showed that **10** oxidized to the corresponding

cyclooctanone (**10a**) in 51% yield, accompanied with cyclooctanol (**10b**) in low yield (6%) within a 3-h reaction period. To the best of our knowledge, there is no report that describes cyclooctane oxidation with such a high relative yield (89%) to cyclooctanone using Mn-based catalyst. Overall, these findings suggest that the present Mn_3O_4 MNAs/TBHP catalytic system represents an expeditious approach towards a lab as well as a large-scale production of carbonyl compounds from styrenes or aromatic hydrocarbons in high yields and selectivity.

Conclusions

In summary, we have successfully prepared mesoporous assemblies of Mn₃O₄ NPs (Mn₃O₄ MNAs) with accessible pores through a polymer-assisted aggregating self-assembly method. Structural characterization with SAXS, TEM, XRD and N₂ physisorption indicated that Mn₃O₄ MNAs material consists of an interconnected network of 6-7 nm-sized hausmannite (Mn₃O₄) NPs and exhibits a large surface area of 90 m² g⁻¹ with a narrow range of pore sizes (the peak maximum centered at about 6.6 nm). These mesoporous Mn₃O₄ assemblies demonstrate great application perspectives in catalytic oxidation of various aromatic and cyclic alkenes as well as aryl alkanes with tert-butyl hydroperoxide. As compared to individual Mn₃O₄ NPs, randomly aggregated Mn₃O₄ NPs and bulk Mn₃O₄ solid, the higher reactivity of Mn₃O₄ MNAs is attributed to the 3D open-pore structure and large accessible surface area, which allow facile mass transport throughout the assembled structure. Moreover, product analysis indicated that the reaction between the selected alkenes and the TBHP-Mn₃O₄ catalyst proceeds via an allylic oxygenate intermediate obtained by a radical process; however, further mechanistic studies are needed to fully understand the mechanism of these reactions. These preliminary results open up the possibility of using mesoporous assembled structures of small-sized Mn₃O₄ NPs for selective alkene and aryl alkane oxidations.

Experimental Section

Chemicals

Poly(ethylene glycol)-*block*-poly(propylene glycol)-*block*-poly(ethylene glycol) block copolymer (Pluronic P123, $M_n \sim 5800$ g mol⁻¹), oleic acid (90%), oleylamine (70%), *N*,*N*-dimethylformamide (DMF, 99.9%), xylene (>98%), acetonitrile (99.9%), *n*-hexane (95%), toluene (99.7%), absolute ethanol and *tert*-butyl hydroperoxide solution (TBHP, 70% in water) were obtained from Aldrich Chemical Co. Nitrosonium tetrafluoroborate (NOBF₄, 97%) was purchased from Acros Organics. Manganese (II) acetate (Mn(CH₃CO₂)₂, 98%) was acquired from Sigma-Aldrich. All organic substrates were of high purity and were obtained from Aldrich. All chemicals were used as received without further purification.

Synthesis of Mn₃O₄ NPs

 Mn_3O_4 NPs (6–7 nm in size) stabilized with oleic acid were prepared according to a literature procedure. $^{[34]}$ In detail, 1 mmol of $Mn(CH_3CO_2)_2$

WILEY-VCH

and 2 mmol oleic acid dissolved in 10 mmol of oleylamine were added in 15 mL of xylene in air atmosphere. After slowly heating to 90 °C, 1 mL of deionized water was injected into the solution under vigorous stirring, and the resulting solution was aged at 90 °C for 3 h. A total of 100 mL of ethanol was added to precipitate the NPs, which was followed by centrifugation to retrieve the NPs in powdery form. The NPs synthesized were dispersed in *n*-hexane to form a stable colloidal solution (10 mg mL⁻¹).

Ligand-exchange of Mn₃O₄ NPs

The ligand-exchange process was carried out according to a previously reported method.^[35] In a typical reaction, 5 mL of Mn_3O_4 NP dispersion in hexane was added in 5 mL of a solution of NOBF₄ in DMF (10 mg/mL) and the mixture was kept stirring at room temperature until the NPs were transferred to the DMF phase. The Mn_3O_4 NPs were then collected by precipitation with toluene followed by centrifugation at 13000 rpm for 15 min. The ligand-stripped Mn_3O_4 NPs were dispersed in DMF to give a final concentration of 240 mg mL⁻¹.

Synthesis of mesoporous Mn_3O_4 MNAs

The mesoporous Mn_3O_4 NP assemblies (Mn_3O_4 MNAs) were synthesized as follows: 0.2 g of Pluronic P123 ($EO_{70}PO_{20}EO_{70}$) block copolymer was dissolved in 1.5 mL of anhydrous ethanol at room temperature. Then, 0.5 mL of colloidal Mn_3O_4 NP solution was slowly added dropwise to the surfactant solution with continuous stirring. The resulting mixture was kept at room temperature for 2 h and then stored in an oven at 40 °C for about 6 to 7 days under static condition. Removal of the template between the Mn_3O_4 NPs as well as interparticle connection was achieved by heating the dry product at 350 °C for 4 h in air, using a 0.5 C min⁻¹ heating rate.

For comparison, random aggregates of Mn_3O_4 NPs (Mn_3O_4 RNAs) were also prepared by a similar procedure without the addition of polymer template. Bulk-like Mn_3O_4 solid was also prepared by thermal decomposition of $MnCO_3$ in air at 950 °C for 2 h. Powder XRD confirms the formation of single phase Mn_3O_4 .

Physical characterization

Thermogravimetric analysis (TGA) was performed using a Perkin-Elmer Diamond system. Thermal analysis was conducted from 40 to 600 °C in air atmosphere (under a ~200 mL min⁻¹ flow rate) with a heating rate of 5 °C min⁻¹. Small-angle X-ray scattering (SAXS) measurements were performed on a Rigaku S-MAX 300 high-brilliance system using Cu Ka radiation (80 kV and 40 mA). Measurements were performed by transmission in samples that gently grounded and held in a quartz capillary tube (inner diameter of 1 mm). The sample-to-detector distance and center of the beam were precisely measured using a Ag-behenate standard ($d_{001} = 58.38$ Å). The two-dimensional diffraction images were integrated into a one-dimensional diffraction pattern, as a function of q, with the Fit2D program.^[36] Powder XRD patterns were recorded on a PANanalytical X'pert Pro MPD X-ray diffractometer equipped with a Cu (λ =1.5418 Å) rotating anode (40 mA and 45 kV), in the Bragg-Brentano geometry. TEM studies were completed using a JEOL JEM-2100 electron microscope (LaB₆ filament) operating at 200 kV accelerated voltage. Samples for TEM analysis were prepared by drying a ethanolic dispersion of the particles on a holey carbon-coated Cu grid. Nitrogen adsorption-desorption isotherms were measured at -196 °C with a Quantachrome NOVA 3200e sorption analyzer. All of the samples were degassed under vacuum (<10⁻⁴ mbar) at 150 °C for 12 h prior analysis. The specific surface areas were calculated using the Brunauer-Emmett-Teller (BET) method on the adsorption data in the 0.05-0.24 relative pressure (P/P_o) region. The total pore volumes were estimated from the adsorbed amount at the P/P_o = 0.98 and the pore size distributions were derived from the adsorption branch of the isotherms using the nonlocal density functional theory (NLDFT) model (assuming slit-like pores). The Raman spectra were collected at room temperature on a Nicolet Almega XR micro-Raman spectrometer equipped with a 473 nm blue laser (15 mW) as an excitation source. Inductively coupled plasma-mass spectrometry (ICP-MS) analysis was performed on a Perkin Elmer NexION 300X instrument. For ICP-MS analysis, 1 mL of the sample solution was evaporated to dryness, followed by the addition of 100 mL of 2% HNO₃.

Catalytic reactions

In a typical experiment, a mixture of hydrocarbon (0.4 mmol) and catalyst (0.04 mmol) in 2 mL of acetonitrile was placed in a 4 mL glass reactor closed with a Teflon cap. The reaction was initiated by adding TBHP (3 eq.) and the mixture was vigorous stirred at 70 °C. The reaction conversion and the products characterization were realized by a combination of gas chromatography – mass spectrometry (Shimadzu GCMS-QP2010 Ultra) and ¹H NMR spectroscopy (Bruker AMX 300 MHz) by withdrawing small aliquots from the reaction mixture. The spectroscopic data of the products are in agreement with the corresponding commercially available.

Acknowledgements

This work was supported by the European Union and the Greek Ministry of Education (NSRF) under the ERC Grant Schemes (ERC-09, MIS 374071). We kindly thank Prof. S. Pergantis (University of Crete) and Dr. A. Katsoulidis (University of Liverpool) for collecting the ICP-MS and SAXS data, respectively.

Keywords: manganese • mesoporous materials • nanoparticles • heterogeneous catalysis • alkenes

References

- R. A. Sheldon, J. K. Kochi in *Metal-Catalyzed Oxidations of Organic Compounds*, Academic Press, New York, **1981**.
- a) R. A. Sheldon, I. W. C. E. Arends, A. Dijksman, *Catal. Today* 2000, 57, 157; b) R. Neumann, *Prog. Inorg. Chem.* 1998, 47, 317; c) N. Mizuno, M. Misono, *Chem. Rev.* 1998, 98, 199; d) M. A. Khenkin, J. W. L. Shimon, R. Neumann, *Inorg. Chem.* 2003, 42, 3331.
- [3] D. Ravelli, D. Dondi, M. Fagnoni, A. Albini, Chem. Soc. Rev. 2009, 38, 1999.
- [4] a) P. Spannring, P. C. A. Bruijnincx, B. M. Weckhuysen, R. J. M. Klein Gebbink, *Catal. Sci. Technol.* **2014**, *4*, 2182; b) A. L. Linsebigler, G. Q. Lu, J. T. Yates, *Chem. Rev.* **1995**, *95*, 735; c) A. Kubacka, M. Fernández-García, G. Colón, *Chem. Rev.* **2012**, *112*, 1555; d) A. Maldotti, A. Molinari, *Top. Curr. Chem.* **2011**, *303*, 185; e) M. Fagnoni, D. Dondi, D. Ravelli, A. Albini, *Chem. Rev.* **2007**, *107*, 2725; f) W. Jia, Y. Liu, P. Hu, R. Yu, Y. Wang, L. Ma, D. Wang, Y. Li, *Chem. Commun.* **2015**, *51*, 8817; g) O. A. Kholdeeva, *Catal. Sci. Technol.* **2014**, *4*, 1869.
- [5] a) J. J. Dong, W. R. Browne, B. L. Feringa, Angew. Chem. Int. Ed. 2015, 54, 734; b) G. Maayan, R. Neumann, Chem Commun. 2005, 36, 4595.

WILEY-VCH

- [6] a) E. Skliri, I. N. Lykakis, G. S. Armatas, *RSC Adv.* **2014**, *4*, 8402; b) I.
- Tamiolakis, I. N. Lykakis, A. P. Katsoulidis, C. D. Malliakas, G. S. Armatas, *J. Mater. Chem.* 2012, 22, 6919; c) I. Tamiolakis, I. N. Lykakis, A. P. Katsoulidis, G. S. Armatas, *Chem. Commun.* 2012, 48, 6687; d) I. N. Lykakis M. Orfanopoulos, *Tetrahedron Lett.* 2004, 7645; e) I. N. Lykakis, M. Orfanopoulos, C. Tanielian, *Org. Lett.* 2003, *5*, 2875.
- a) C. Chen, G. Ding, D. Zhang, Z. Jiao, M. Wu, C.-H. Shek, C. M. L.
 Wu, J. K. L. Lai, Z. Chen, *Nanoscale* 2012, *4*, 2590; b) M. Biswal, V. V.
 Dhas, V. R. Mate, A. Banerjee, P. Pachfule, K. L. Agrawal, S. B. Ogale,
 C. V. Rode, *J. Phys. Chem. C* 2011, *115*, 15440.
- [8] a) E. J. Grootendorst, Y. Verbeek, V. Ponce, J. Catal. 1995, 157, 706;
 b) A. Maltha, M. Muhler, V. Ponec, Appl. Catal. A: Gen. 1994, 115, 69.
- [9] J. Mondal, P. Borah, S. Sreejith, K. T. Nguyen, X. Han, X. Ma, Y. Zhao, ChemCatChem 2014, 6, 3518.
- a) M. Yang, Q. Ling, R. Rao, H. Yang, Q. Zhang, H. Liu, A. Zhang, J. Mol. Catal. A: Chem. 2013, 380, 61; b) J. Mao, G. Zhao, D. Wang, Y. A. Li, RSC Adv. 2014, 4, 25384; c) K. Dhanalaxmi, R. Singuru, S. K. Kundu, B. M. Reddy, A. Bhaumik, J. Mondal, RSC Adv. 2016, 6, 36728.
- [11] a) B. Qi, L.-L. Lou, K. Yu, W. Bian, S. Liu, *Catal. Commun.* 2011, *15*, 52. b) S. S. Acharyya, S. Ghosh, S. K. Sharma, R. Bal, *RSC Adv.* 2015, *5*, 89879.
- a) S. L. Brock, N. Duan, Z. R. Tian, O. Giraldo, H. Zhou, S. L. Suib, *Chem. Mater.* **1998**, *10*, 2619; b) L. Wang, Y. Li, Z. Han, L. Chen, B. Qian, X. Jiang, J. Pinto, G. Yang, *J. Mater. Chem. A* **2013**, *1*, 8385.
- [13] H. Huang, Y. Xu, Q. Feng, D. Y. C. Leung, *Catal. Sci. Technol.* 2015, 5, 2649.
- [14] S. Bag, K. Roy, C. S. Gopinath, C. R. Raj, ACS Appl. Mater. Interfaces 2014, 6, 2692.
- [15] S. S. Acharyya, S. Ghosh, S. K. Sharma, R. Bal, New J. Chem. 2016, 40, 3812.
- [16] a) S. K. Das, M. K. Bhunia, A. Bhaumik, *Dalton Trans.* 2010, *39*, 4382;
 b) C. Cannas, A. Ardu, A. Musinu, L. Suber, G. Ciasca, H. Amenitsch, G. Campi, *ACS Nano* 2015, *9*, 7277; c) M. Grzelczak, J. Vermant, E. M. Furst, Luis M. Liz-Marzán, *ACS Nano* 2010, *4*, 3591; d) D. J. Milliron, R. Buonsanti, A. Llordes, B. A. Helms, *Acc. Chem. Res.* 2014, *47*, 236; e)
 Y. Liu, Z. Chen, C.-H. Shek, C. M. L. Wu, J. K. L. Lai, *ACS Appl. Mater. Interfaces* 2014, *6*, 9776.

- [17] a) I. T. Papadas, S. Fountoulaki, I. N. Lykakis, G. S. Armatas, *Chem. Eur. J.* **2016**, 22, 1; b) I. T. Papadas, I. Vamvasakis, I. Tamiolakis, G. S. Armatas, *Chem. Mater.* **2016**, *28*, 2886.
- [18] a) Z. W. Chen, Z. Jiao, M. H. Wu, C. H. Shek, C. M. L. Wu, J. K. L. Lai, *Prog. Mater. Sci.* **2011**, *56*, 901; b) Z. Chen, Z. Jiao, D. Pan, Z. Li, M. Wu, C.-H. Shek, C. M. L. Wu, J. K. L. Lai, *Chem. Rev.* **2012**, *112*, 3833.
- [19] O. Glatter, O.Kratky in Small angle X-ray Scattering, Academic Press, London, 1982.
- [20] A. L. Patterson, *Phys. Rev.* **1939**, *56*, 978.
- [21] F. Rouquerol, J. Rouquerol, K. S. W. Sing in Adsorption by Powders and Porous Solids. Principles Methodology and Applications, Academic Press, London, 1999.
- [22] C. I. Fernandes, S. C. Capelli, P. D. Vaz, C. D. Nunes, Appl. Catal. A: Gen. 2015, 504, 344.
- [23] A. Bento, A. Sanches, E. Medina, C. D. Nunesa, P. D. Vaz, *Appl. Catal.* A: Gen. 2015, 504, 399.
- [24] D. Guin, B. Baruwati, S. V. Manorama, J. Mol. Catal. A: Chem. 2005, 242, 26.
- [25] N. Ma, Y. Yue, W. Hua, Z. Gao, Appl. Catal. A: Gen. 2003, 251, 39.
- [26] G. Meng, Q. Yang, Y. Wang, X. Sun, J. Liu, RSC Adv. 2014, 4, 57804.
- [27] V. R. Choudhary, R. Jha, P. Jana, Catal. Commun. 2008, 10, 205.
- [28] B. Singh, A. K. Sinha, J. Mater. Chem. A 2014, 2, 1930.
- [29] Z. Wang, X. Hou, J. Shen, T. Li, RSC Adv. 2016, 6, 89503.
- [30] D. Ge, J. Wang, H. Geng, S. Lu, D. Wang, X. Li, X. Zhao, X. Cao, H. Gu, ChemPlusChem 2015, 80, 511.
- [31] X. Liu, J. Ding, X. Lin, R. Gao, Z. Li, W.-L. Dai, Appl. Catal. A: Gen. 2015, 503, 117.
- [32] A. Maldotti, A. Molinari, R. Amadelli, Chem. Rev. 2002, 102, 3811.
- [33] a) E. Baciocchi, M. Bietti, M. Salamone, S. Steenken, S. J. Org. Chem.
 2002, 67, 2266; b) D. V. Avila, K. U. Ingold, J. Lusztyk, J. Am. Chem.
 Soc. 1995, 117, 2929; c) D. V. Avila, C. E. Brown, K. U. Ingold, J. Lusztyk, J. Am. Chem. Soc. 1993, 115, 466.
- [34] T. Yu, J. Moon, J. Park, Y. I. Park, H. B. Na, B. H. Kim, I. C. Song, W. K. Moon, T. Hyeon, *Chem. Mater.* 2009, 21, 2272.
- [35] A. Dong, X. Ye, J. Chen, Y. Kang, T. Gordon, J. M. Kikkawa, C. B. Murray, J. Am. Chem. Soc. 2011, 133, 998.
- [36] F. A. P. Hammersley in ESRF98 A01T: FIT2D V9.129 Reference Manual, V3.1, ESRF Internal Report, France, 1998.

This article is protected by copyright. All rights reserved

WILEY-VCH

FULL PAPER

Entry for the Table of Contents

FULL PAPER

Mesoporous networks of cross-linked $6-7 \text{ nm }Mn_3O_4$ nanoparticles (NPs) with large internal surface area and uniform pores have been successfully prepared via a polymer-assisted aggregating self-assembly method. These assembled Mn_3O_4 NP networks demonstrate great application perspectives in catalytic oxidation of various aromatic and cyclic alkenes as well as aryl alkanes with *tert*-butyl hydroperoxide.



E. Skliri, S. Papadogiorgakis, I. N. Lykakis, G. S. Armatas*

Page No. – Page No.

Mesoporous Assembled Mn₃O₄ Nanoparticle Networks as Efficient Catalysts for Selective Oxidation of Alkenes and Aryl Alkanes