

A simple and green procedure to prepare efficient manganese oxide nanopowder for the low temperature removal of formaldehyde

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Abstract: Activated Reactive Synthesis, as a top-down synthesis approach, is proposed for the production of nanocrystalline, high surface area, manganese (IV) oxide starting from commercial micrometric α -MnO₂. The developed approach consists in a two-step process: (1) a High Energy Ball Mill (HEBM) step, to produce nanosized material, (2) a Low Energy Ball Mill (LEBM) step, to improve textural properties. During the first HEBM step, elementary crystals are observed to evolve from several hundred of nanometers elongated cylindrical particles to short length cylinders and pseudo spherical particles. Despite fractioning of elementary crystals, surface area remains low over HEBM derived solid. The second LEBM step, of attrition type, achieves crystal shape modification, given rise to only pseudo-spherical nanometric particles. LEBM step allows to significantly increase material surface area that reaches ~60-80 m² g ¹. Catalytic activity of α -MnO₂ powder is significantly affected by the grinding process. Material activity is observed to remain close to the initial one after HEBM, and increases upon LEBM to rapidly reach a maximum for LEBM time of 1 h. Thereafter, activity remains constant despite the further increase in surface area upon prolonged LEBM time. The presence of an optimal activity after limited LEBM time, with the absence of activity increase at prolonged time despite the increase in surface area, is paralleled with the increase of the iron contamination occurring at prolonged LEBM time that impacts manganese reducibility and results in less reactive surface.

Introduction

Formaldehyde is always a widely used chemical for the production of many goods, despite the consequence of

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formaldehyde on the human health and on the environment. The substitution of formaldehyde in industrial processes, including furniture and wood panel branches, is strongly encouraged.^[1] Unfortunately, its substitution by other molecules while maintaining technical properties acceptable in final products is, even today, not always possible. Formaldehyde stays then an often encountered indoor air pollutant, since widely used for the production of building and decoration materials. To date there is no regulatory limit for occupational exposure to formaldehyde. The Scientific Committee on Occupational Exposure Limits (SCOEL) however recommends a 8 h permissible exposure limit of 0.2 ppm and a 15 min short term exposure limit of 0.4 ppm to formaldehyde.^[2] Such low exposure limit obviously stimulates research of substitute. However, this approach is sometimes not feasible with an acceptable delay, and the consumption of formaldehyde in industrial production process makes necessary the research of innovative solutions to limit user and consumer exposure to formaldehyde, and to limit its impact on the environment.^[3,4] Different approaches are then proposed, among elimination physical process, adsorption, heterogeneous catalysis etc. whole taking into account the necessity to limit energy consumption (the concentration of formaldehyde in air is generally of few ppmv, and often, like in indoor air, below the ppmv).^[5] Among the efficient approaches is the adsorption. Active carbons are shown to be efficient for the formaldehyde removal,^[6-10] with adsorption capacity that can reach 400 mg formaldehyde per g of adsorbent (with initial formaldehyde concentration ranging from 20 to 35 ppm in the feed).^[10] Some zeolitic supports are also presenting interesting properties, [11-13] with capacities such as 585 mg/g over NaY type zeolite (adsorption capacity at 25°C, under 2 hPa of formaldehyde).^[14] However, pore network characteristics and surface properties of zeolites are significantly impacting adsorption capacities.^[14] NH₂ functionalized silica are also promising adsorbents.^[15-17] with adsorption capacities reported to be three times higher than those for carbons. Formaldehyde is removed from air that is efficient from health and security point of views since it efficiently decreases exposure of users and consumers to formaldehyde. However, some drawbacks arise from this technology, such as the necessity to periodically replace adsorbent, and to treat the adsorbent cartridge for final elimination. A second way proposed for the formaldehyde elimination is the low temperature catalytic oxidation process. Advantages of this approach are (i) process durability, (ii) elimination with limited energy consumption, and (iii) direct conversion, even at low temperature, of formaldehyde into harmless carbon dioxide and water.^[18] Supported noble metal based catalysts were initially

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proposed for this reaction, [19-26] with good efficiencies since formaldehyde can be converted at ambient temperature. Titania supported platinum is shown as the most promising system,^[21] with possibility to improve its activity by sodium doping:[22] 600 ppm of formaldehyde can be selectively converted into CO₂ and H₂O at 15°C, at a GHSV of 120000 h⁻¹, over 2%Na-1%Pt/TiO₂. Platinum is more active than palladium, rhodium and gold.^[21] However, the support properties play a key role on the activity of the supported phase. As an example, when gold is supported over 3D ordered macroporous ceria,[27] removal of formaldehyde at room temperature can be achieved, with selective conversion of formaldehyde into CO2. Due to extensive use of noble metal for applications other than chemistry and their limited resources, some of the platinum mine metals are suggested to be exhausted in the few next decades.^[28] Noble metal free catalysts are proposed to potentially replace noble metal compositions,[29] unfortunately with significantly lower intrinsic activities. [30-32] Manganese-containing materials have been rapidly identified as most promising systems among transition metal containing materials for formaldehyde oxidation.^[18,33] Xu et al. demonstrated that tunnel type cryptomelane is highly efficient for the reaction,^[34] with complete and selective conversion of formaldehvde since 140°C (400 ppmv formaldehyde, GHSV of 18,000 mL g⁻¹ h⁻¹). Birnessite, a manganese layered-type material, has been reported to present high activity for the reaction, due to adequate textural properties in addition to highly active Mn(IV) surface oxidation sites:^[35] conversion to CO₂ starts from 100°C (460 ppmv formaldehyde, GHSV of 30000 mL g⁻¹ h⁻¹). Manganese-cerium mixed oxide is also an efficient material to convert formaldehyde, with comparable activities than those obtained for channel-type structures,^[36] but with an important effect of the preparation route on the activity.^[37] Indeed, preparation impacts (i) textural characteristics (surface area, pore size and pore volume), (ii) homogeneity, (iii) mean manganese oxidation state, (iv) surface composition, all parameters having an effect, positive or negative, on the material surface reactivity.

In this work, Activated Reactive Synthesis (ARS) is proposed as an alternative Top-Down approach to produce efficient oxidation materials. The approach is, in its principle, considered as sustainable since no solvent is used during the whole production process,^[38] and abundant and cheap inorganic precursors can be used for final material production.^[39-41] A two steps grinding process is then developed, based on our experience for the preparation of perovskite and hexaaluminate,^[40-43] to produce nanocrystalline α -MnO₂ material, starting from commercial sample. The study evidenced the potential of the two-step ARS to modify material morphology, in order to produce material with adequate properties for low temperature oxidation reaction.

Results and Discussion

Structural properties

X-ray diffraction patterns obtained for the different materials are presented in Figure 1 for the ball milled materials, and in Figure S1 for the reference Mn/SBA-15 sample. The commercial sample

(Mn-C) presents a α-MnO₂ structure (ICDD file n°44-0141), along with weak reflections attributed to KOH as low content impurity (identified by an * in Figure 1). Upon grinding process, significant modifications of the diffractogram are observed. After HEBM (Mn-LEBM-0), the maintaining of the initial crystal structure is observed, with only α -MnO₂ phase detected. However, a significant broadening and decrease in intensity of the reflections are observed, with mean crystal domain size, as calculated by the Scherrer equation, decreasing from >50 nm (commercial Mn-C) to 6 nm (Mn-LEBM-0) (Table 1). Whatever the LEBM duration, comparable diffractograms are observed. Indeed, only the a-MnO₂ phase is detected (Figure 1), while diffraction peaks widths and intensities being only slightly altered by the LEBM step time. While the Mn-LEBM-0 solid presents a crystal domain size of 6.0 nm, the mean crystal size remains in the 4.9-5.8 nm range whatever the HEBM duration (Table 1).

 Table 1. Selected properties of commercial and synthesized materials.

Sample	XRD phase ^[a]	D _c ^[b]	S _{BET} ^[c]	$V_{P}^{[c]}$	$D_{P}^{[c]}$	XPS AON ^[d]	TPR AON ^[e]
Mn-C	α- MnO2, KOH	>50	10.2	0.03	11.2	3.5	3.6
Mn- LEBM-0	α-MnO ₂	6.0	14.6	0.03	3.9 - 12.3	3.5	3.4
Mn- LEBM-1	α-MnO ₂	5.0	52.5	0.08	3.6 - 23.0	-	-
Mn- LEBM-2	α-MnO ₂	4.9	57.0	0.08	3.9 - 22.8	3.3	3.5
Mn- LEBM-5	α-MnO ₂	5.1	65.2	0.11	3.9 - 30.9	3.3	3.4
Mn- LEBM-10	α-MnO ₂	5.8	78.0	0.13	4.0 - 24.0	3.3	3.4
SBA-15	-	-	829	1.21	6.1	-	-
Mn/SBA- 15	β-MnO ₂	12.0	610	0.83	4.5- 5.8	-	4.0

[a] crystalline phase detected; [b] calculated crystal domain size (D_c) using X-ray line broadening, after correction of the instrumental broadening; [c] specific surface area (S_{BET}), pore volume (V_p) and B.J.H. pore size (D_p) evaluated from N₂ physisorption isotherms; [d] average oxidation number evaluated from the Mn 3s core level; [e] average oxidation number of manganese, issued from H₂ consumption of TPR-H₂ experiments.

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The impact of the two steps of grinding over α -MnO₂ structure is comparable to precedent results obtained over perovskites and hexaaluminates.^[41-44] For these last two kinds of material, the reduction of crystal size occurred during the HEBM step, and only surface area was enhanced during LEBM step. Similarly, significant decrease in crystal size proceeds during the HEBM step (decrease in crystal size from >50 nm to 5-6 nm), and mean crystal domain size remains constant during LEBM.



Figure 1. High angles diffraction patterns for α -MnO₂ prepared by Ball Milling process; Bottom: ICDD file n°44-0141 for α -MnO₂.

Diffractogram obtained over Mn/SBA-15 is presented in Figure S1. Material presents reflections attributed to β-MnO₂ (ICCD file n°81-2261) with no other crystalline phases detected. Only a broad and poorly intense additional signal, at 20 ranging from 17° to 32°, is observed. However, this signal is originating from the amorphous character of the silica support. Mean crystal domain size of 12 nm is calculated for the Mn/SBA-15. This size can be easily explained by the confinement of nanoparticles (NPs) occurring in ordered solids during thermal treatment. The precursor is located in the ordered silica pores after the drying step of the impregnation. The following thermal decomposition, performed in our case at 300°C, results in the formation of NPs of β -MnO₂ confined in mesopores for which crystal growth is limited by the space available between the walls.^[45] The mean crystal size calculated for the SBA-15 supported β -MnO₂ phase, in this study, is higher than the mean pore size of the silica host (Table 1). This result suggests that a part of the manganese precursor remains out of the ordered porosity, or migrates out upon drying. Thermal activation leads to a part of the manganese oxide not suggested to physical hindering during calcination. Large external particle formation contributes to the increase in mean crystal domain size as calculated by the Scherrer equation.

Textural properties

Results of N_2 physisorption are presented in Figure 2 for the ball milled materials, and Figure S2 for the Mn/SBA-15 reference sample. Textural properties, obtained by treatment of the isotherms, are gathered in Table 1.

First of all, the commercial cryptomelane (Mn-C) presents very low surface area and pore volume (Table 1), values classically reported in the literature, and related to inter-aggregate porosity (isotherm of type II with small H3 hysteresis - Figure 2(a)). Note that the microporosity, located inside the tunnel structure of the cryptomelane is not probed by N₂ due to the too large size of the dinitrogen molecule.



Figure 2. (a) N₂ adsorption/desorption isotherms and (b) pore size distributions for ball milled materials. Isotherms are shifted by 10 cm³ g⁻¹ for clarity.

After HEBM treatment, only limited modifications in either isotherm shape or textural properties are observed. The isotherm recorded for the Mn-LEBM-0 sample remains of Type II, with small H3 hysteresis, suggesting the maintaining of an external porosity. The surface area and pore volume remain limited and comparable to those obtained for the commercial material (14.6 $m^2\,g^{\text{-1}}$ and 0.03 $cm^3\,g^{\text{-1}},$ respectively - Table 1). The lack in surface area enhancement despite the crystal size reduction upon HEBM is suggested to originate from the formation of dense, poorly porous, aggregates of nanoparticles. The main difference between non-milled material and HEBM material (Mn-LEBM-0) consists in a modification of the pore size distribution. The Mn-C material presents a broad pore size centered at ~ 11 nm (Table 1). The Mn-LEBM-0 sample presents an additional pore contribution at lower size, e.g. ~4.0 nm (Table 1, Figure 2(b)). The formation of such low pore size could be related to the decrease in crystal domain size (Figure 1) leading to changes in the internal porosity of the aggregates.[43,44]

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Figure 3. Evolution of the specific surface area of ball milling materials with LEBM time.

With LEBM duration increase, an increase in pore volume is observed, in parallel with a significant surface area enhancement (Figure 3), up to a factor 4 when compared with commercial sample (Table 1). However, the isotherm and hysteresis shapes remain unchanged, of type 2 with H3 hysteresis type (Figure 2). An important increase of the surface area is observed during the first 60 min of LEBM. At prolonged time of LEBM, a roughly linear slow increase in surface area is observed (from 2 h, 57.0 m² g⁻¹ to 10 h, 78.0 m² g⁻¹). Such evolution could be related to a first period in which the material microarchitecture is significantly modified (milling time < 60 min). During this short period, XRD did not show significant differences in mean crystal domain sizes, and then, only important modifications of the aggregate size and internal porosity can explain this evolution in surface area. The discrepancy of evolution between crystal size and specific surface area during HEBM and LEBM processes could be related to the mode of milling applied. Under HEBM process, the generated surface of crystals, chemically unstable, will cold-weld (no gain in surface area). However, attrition conditions (LEBM process) ensure the separation of the elementary crystals and surface stabilization leading to the formation of aggregates with smaller size and more porous (increase of SSA - Figure 3; additional low size pore population - Figure 2(b)). After 60 min of LEBM, the increase in surface area becomes less rapid, showing that the process of disaggregation / modification of intra-aggregate porosity becomes slower. In addition to the increases in surface area and in pore volume, pore size distribution continues to evolve, with (i) the increase in ~4 nm pore contribution (intra-aggregate porosity), and (ii) the increase in the broad 15-40 nm pore contribution (inter-aggregate porosity) (Figure 2(b)).

N₂ physisorption isotherms and pore size distributions of SBA-15 and derived Mn-containing catalysts are presented in Figure S2. As awaited, SBA-15 shows type IV isotherm with H1 hysteresis loop, characteristic of mesostructured solid with cylindrical pores.^[45] SBA-15 displays sharp pore size distribution, centered at ~6.0 nm (Table 1). Isotherm obtained for Mn/SBA-15 only differs on the desorption branch, with a visible forced closure step at P/P₀ = 0.53, which highlights the formation of constriction in the tubular pores of the SBA-15 after manganese oxide particle formation. Pore size distribution consequently shows the presence of a pore contribution around 4.5 nm. Finally, upon formation of the MnO₂ particles in the SBA-15 support, surface area and pore volume are observed to decrease (Table 1), an evolution coherent with the pore filling of the support by the manganese phase.^[45,46]

Material microstructure

Morphology of the materials are observed by SEM (Figure 4) and TEM (Figure 5). The commercial low surface area α -MnO₂ sample present fibrillar / rod-like shaped cristals (Figure 4(a) and Figure 6(a)). The lengths of the fibers are not homogeneous, and are observed to vary from 100 nm to 500 nm. These elongated crystals are assembled into large aggregates, of wide size population from slightly less than 1 μ m to 10 μ m.

Visible modification of the morphology is observed after HEBM step. First, the micrometric assembly of crystal, after HEBM (presented for Mn-LEBM-2 sample, exactly similar representative images being recorded for Mn-LEBM-0 sample) is always from one to several micrometers (Figure 4(b)). Elongated particles are always visible, with a core of the aggregate observed to be more dense. This observation is confirmed by higher resolution TEM analysis (Figure 5(c)), for which we observed two different shapes for the elementary particles. The first population of particles presents elongated shape, with comparable size as in Mn-C, and they are located on the periphery of the aggregates. A second population of particle, majoritary, present pseudo-spherical shape with size down to 25 nm. Then, HEBM process is observed to induce a breaking of the elongated particles to form more isotropic shaped particles (with length of formed particles close to their width). However, the conversion of the fibrillar particle into pseudo-spherical is not complete at the end of the HEBM step, and some of the initial elongated particles remain. The elementary particle evolution induced during HEBM is coherent with the observed evolution on pore size distribution (Figure 2(b)). Indeed, lower size elementary particle will obviously lead to lower pore diameter inside the aggregates (intra-aggregate porosity, the porosity observed below 10 nm in Figure 2(b)).



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Figure 4. Evolution of the α -MnO₂ microstructure upon ball milling process, as observed by SEM. (a) Mn-C; (b) Mn-LEBM-2; (c) Mn-LEBM-5; (d) Mn-LEBM-10.



Figure 5. Evolution of the α -MnO₂ microstructure upon ball milling process, as observed by TEM. (a) Mn-C; (b) Mn-LEBM-0; (c), Mn-LEBM-2; (d) Mn-LEBM-5; (e-f) Mn-LEBM-10.

Morphology evolves significantly upon LEBM process. A first visible mobification is observed by SEM analysis (Figure 4(c-d), at different milling times), with the complete disparition of the elongated particles (characteristic of cryptomelane microstructure) when LEBM time is above 2 h. Also, a significant

decrease in aggregate size is observed, with most of the aggregates being below 300 nm. By TEM, some residual elongated crystals are always visible for Mn-LEBM-2 (Figure 5(c)). However, such particles are no more observed for Mn-LEBM-5 and Mn-LEBM-10 (Figure 5(d-f)). LEBM step achieves the crystal

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size and shape modification, to obtain after 5 h, only pseudospherical particles. By TEM analysis, the reduction of aggregate size is also observed, as well as the formation of the <10 nm porosity (visible between elementary particles in Figure 5(d-e)). This observation is in agreement with N₂ physisorption results.

Surface properties

Impact of milling process on the material surface characteristics is evaluated by XPS. When exposed to the atmosphere, surface of materials contains a noticeable amount of adventitious carbon contamination. C 1s contamination spectrum classically presents C-C (285 eV, used as a charge reference), C-O-C (~286 eV) and O-C=O (~289 eV) components.[47] The three components are observed at the surface of all materials, commercial and milled (Figure S3). However, the quantity of carbon increases significantly after HEBM treatment while it remains constant during LEBM treatment (Figure S3). O 1s signals are presented in Figure S4. The O 1s signal can be decomposed in four components OI (530.0 eV), OII (531.2 eV), OIII (532.2 eV) and OIV (534.2 eV) (Figure S3). The O₁ component is attributed to O²⁻ lattice oxygen, while the presence of O_{II} component can be explained by the presence of oxygen vacancies or defects.^[48] The OII peak has an area contribution of 18% for Mn-C and Mn-LEBM-0 and 26% for Mn-LEBM-2, Mn-LEBM-5, Mn-LEBM-10 samples suggesting that LEBM induces the formation of little more oxygen defective surface. The OIII component is ascribed to oxygen atoms in OH and/or O=C groups, while the presence of OIV component arises from physisorbed water and/or O-C group.^[48,49] It is noticeable that the O_{III} peak area contribution increases from 8% for Mn-C to 18-22% for all ball-milled samples. This increase can be explained by the CO₂ adsorption from ambient air on unsaturated metal sites produced during the milling processes.



Figure 6. XPS signal registered in the 705-740 eV B.E. region for materials prepared by ball milling process. (a) Mn-LEBM-0; (b), Mn-LEBM-2; (c) Mn-LEBM-5; (d) Mn-LEBM-10.

Mn 3s photopeak presents two multiplet split components, due to the coupling of non-ionized 3s electron with 3d valence-band electrons. Manganese average oxidation number (AON) can be extracted from the magnitude of the peak splitting (Δ Es) applying the correlation established by Galakhov *et al.*.^[50] AON = 8.956 -1.13(Δ Es). Calculated values of AON values are listed in Table 1. They range between 3.3 and 3.5, showing the presence of Mn⁴⁺ and Mn³⁺ ions on the material surface, as awaited from XRD results, with a very limited impact of the milling process (type of milling and time of milling) on the AON value.

Figure 6 shows the Fe 2p signal, registered in the BE region 705-740 eV, for selected materials issued from ball milling. First of all, HEBM step does not induce iron contamination. After LEBM treatment, two main photopeaks at binding energies ~710 eV and ~723 eV are clearly observed. The two photopeaks can be assigned to Fe 2p_{3/2} (710 eV) and Fe 2p1/2 (723 eV) core levels. The 2p doublet separation is 13.6 eV. The two peaks with low intensity at ~718 eV and ~732 eV can be assigned to Fe³⁺ Fe 2p_{3/2} and Fe³⁺ Fe 2p_{1/2} satellites, respectively.^[51] Spectra decomposition (Figure S5), using the Fe 2p_{3/2} spectral fitting parameters proposed by Biesinger et al.,[52] confirms the formation of only Fe³⁺ cation in oxide environment, Fe₂O₃. The LEBM treatment then induces a surface contamination with iron. even at low milling time (Figure 6(b), Mn-LEBM-2). This surface contamination increases with time of milling since the ratio Fe/Mn is observed to increase from Mn-LEBM-2 to Mn-LEBM-10 (Figure 7). However the transition metals (Mn+Fe) surface content, as evaluated by XPS, remains unchanged, with almost constant value obtained for (Fe+Mn)/O whatever the milling type and time (Figure 7). It can be concluded that Fe is mainly segregating on the material surface, progressively replacing Mn surface species.



Figure 7. Evolution of Fe/Mn and (Fe+Mn)/O XPS ratio upon ball milling process (a) Mn-C (b) Mn-LEBM-0; (c), Mn-LEBM-2; (d) Mn-LEBM-5; (e) Mn-LEBM-10.

Redox properties

Reducibility of manganese species are evaluated by H_2 -TPR. Thermograms are presented in Figure 8(a) for the ball milled

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materials, and comparison with reference sample is given in Figure 8(b).

The commercial sample Mn-C exhibits two main reduction peaks located at 304°C and 370°C, with a shoulder peak at lower temperature (~280°C) (Figure 8(a)). The low temperature reduction process (280°C) is assigned to the reduction of Mn⁴⁺ species in the cryptomelane structure into Mn³⁺ species leading to the Mn₂O₃ phase formation. The further two-step reduction process is attributed to the reduction of Mn₂O₃ into Mn₃O₄, followed by the reduction of Mn₃O₄ into MnO. Indeed in the temperature range studied, MnO is the final state obtained after reduction of higher valence manganese oxide phase.^[53,54] Similar H₂ reduction profiles are obtained for the ball milled materials. The temperatures of the two main peaks are shifted to higher temperatures. After HEBM treatment (Mn-LEBM-0), the manganese reduction processes take place at temperatures increased by ~30°C compared to temperatures recorded for Mn-C. The reduction temperatures are also observed to shift to higher temperature after 2 hours of LEBM treatment, and remains thereafter unchanged for longer milling times. Over Mn-LEBM-10 material, an additional reduction shoulder at 456°C, and a broad peak between 500 and 800°C, are clearly observed. These new contributions, especially at the 500-800°C temperature range, are also visible for Mn-LEBM-2 and Mn-LEBM-5. They are ascribed to the reduction of Fe³⁺ species, identified by XPS analysis and originating from steel vial and balls contamination. Besides, temperatures observed in thermograms for this additional hydrogen consumption matches well with those recorded for the of a-Fe₂O₃ material reduction.[55]



Figure 8. H₂-TPR profiles obtained for (a) ball milled materials and (b) comparison with reference sample.

From hydrogen consumption, and assuming that Mn²⁺ is the final oxidation state in the material after reduction at 800°C, Mn average oxidation numbers (AON) are calculated (Table 1). Calculated values range between 3.4 and 3.6, in agreement with AON values issued from XPS analysis (Table 1). These results confirm that milling conditions used for the modification of

cryptomelane does not significantly affect the global manganese oxidation number, in agreement with the preservation of the cryptomelane structure observed by XRD.

The H₂-TPR profile for the impregnated sample is quite similar, showing two reduction steps, with maximum of H₂ consumption located at ~345°C and ~445°C (Figure 8(b)). The hydrogen consumption allowed to conclude in a Mn AON of 4.0 in the reference sample (Table 1). This value is consistent with the stoichiometric β -MnO₂ formation, phase identified by XRD. Then the first reduction peak centered at ~340°C is ascribed to the reduction of MnO₂ into Mn₃O₄ (3MnO₂ + 2H₂ = Mn₃O₄ + 2H₂O) and account for the two-thirds of the total H₂ consumed quantity while the second peak at higher temperature is assigned to the reduction of Mn₃O₄ into MnO (Mn₃O₄ + H₂ = 3MnO + 2H₂O).

Catalytic properties

Figure 9 and Figure S6 show the evolution of the formaldehyde conversion into CO_2 as a function of the reaction temperature for the different catalysts. Whatever the catalyst used, HCHO oxidation is fully selective into CO_2 and H_2O , and no other products have been detected during reaction.



Figure 9. HCHO conversion into CO_2 plotted as a function of the reaction temperature for commercial and ball milled catalysts.

In comparison with catalytic properties displayed by Mn-C, the catalytic activity is not enhanced after HEBM treatment (Figure 9). When LEBM process is applied with moderate time of milling from 10 minutes to 1 hour, the materials becomes much more active for the HCHO oxidation. A decrease in T_{50} (temperature at which 50% of formaldehyde is converted into CO₂) of ~60°C is measured between Mn-LEBM-1 and Mn-C (Figure 9). This result could be directly related to the important increase in specific surface area observed during the first 60 min of LEBM (Figure 3). After 1 h of LEBM (Mn-LEBM-1), the material presents similar activity than the silica supported manganese oxide reference

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catalyst (Figure S6) that confirms the beneficial effect of the milling approach on the catalytic performance of commercial α -MnO₂. However when the milling time is further increased, from 1 h to 10 h, no significant enhancement in the catalytic activity is observed (Figure 9), although the SSA always increases (Figure 3). A reason for the difference in evolution between the catalytic activity and the accessible surface can be the observed alteration of the redox properties when LEBM time increases (Figure 8(a)) issued from Fe surface contamination (Figure 6). Indeed, an increase in reduction temperature is observed when LEBM time increases, that means a decrease in Mn⁴⁺ site reducibility. Indeed, XPS shows the presence of iron surface contamination after only 2 h of LEBM, and the iron surface content in observed to increase with LEBM (Figure 6 and Figure 7).



Figure 10. Intrinsic activity of ball milled catalyst for formaldehyde oxidation (at 100°C) plotted as a function of the Fe/Mn surface atomic ratio (XPS).





The good correlation between the intrinsic activity (number of HCHO converted into CO_2 h⁻¹ m⁻²) and the Fe/Mn atomic ratio (Figure 10) supports this interpretation. When the milling time increases, more iron species are deposited at the material surface. The intrinsic activity decreases because of the Fe³⁺ species progressive surface covering, considering a redox mechanism for HCHO oxidation over transition metal oxides, Fe³⁺ being less reducible than Mn⁴⁺ species will lead to lower activity (Figure 8 (a)).

Formaldehyde oxidation, a surface mechanism?

From precedent results, it seems obvious that formaldehyde reacts with surface Mn^{4+} sites to produce CO_2 , and that the progressive covering of the surface by less reactive Fe^{3+} sites leads to a decrease in material activity when normalized per surface unit. The carbon balance evolution with reaction temperature is shown in Figure S7 for ball milled catalysts and Mn/SBA-15 reference catalyst. U-shapes curves are observed for all catalysts. When the reaction temperature decreases, the carbon balance decreases below 100%, showing that, in parallel with the oxidation reaction, formaldehyde is retained on the material surface. When material surface is saturated, the carbon balance increases to 100%, at low temperature. This observation is valid for either milled materials and reference supported material.

The IR analysis of Mn-LEBM-2 after catalytic test is performed in order to identify residual adsorbed species (Figure S8). After subtraction of the DRIFTS spectrum (post reaction Mn-LEBM-2 and fresh Mn-LEBM-2), five characteristic absorption bands, at 1354, 1373, 1578, 2347 and 2857 cm⁻¹, are observed. These bands are attributed to formate species.^[56]

The quantity of adsorbed formate species is evaluated by integration of the area of the U-shape curve of Figure S7, and values plotted as a function of the specific surface area of α -MnO₂ ball milling materials (Figure 11). A linear correlation between specific surface area and quantity of adsorbed formate species is obtained. The dependence of the formate adsorption capacity with the material surface area, in addition to the evolution of the activity with redox and surface properties of material is in line with a pure suprafacial mechanism for which only surface species are involved during reaction.

Conclusions

Activated Reactive Synthesis is proposed as an efficient approach to produce α -MnO₂ nanopowder, starting from low surface area, commercial, α -MnO₂ material. The approach consists in two successive grinding steps. The first step, performed at high energy, allows to decrease mean crystal domain size (with significant modifications of the particle shape, evolving from elongated cylindrical shape to pseudo spherical shape). Despite the measured elementary particle size reduction, surface area remains low, and a second grinding step, at low energy, is needed to increase accessible surface. Surface areas up to 60 m² g⁻¹ are easily obtained. Surface area generation

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during low energy ball milling occurs through the rearrangement of the aggregates, with observed size decrease and increase in intra-aggregated porosity.

Improvement in catalytic activity is measured for milled materials, which reach comparable activity than obtained for reference silica supported MnO_2 material. However, increasing the milling time at low energy above 1 h does not allow to increase activity despite the significant increase in surface area. This discrepancy is paralleled with the contamination of the material surface by iron when milling duration increases. Contamination induces a decrease in redox capability at low temperature, with partial replacement of active Mn^{4+} surface sites by less active Fe^{3+} surface sites.

Experimental Section

Material syntheses

Raw material: A commercial, microcrystalline, α -MnO₂ sample (denoted Mn-C thereafter) is used as starting material. α -MnO₂, or cryptomelane-type manganese oxide, is a channel-type microporous material. Channels, with size of 4.7 Å x 4.7 Å, are formed by 2 x 2 {MnO₆} octahedra connected by their edges and corners.^[57] Channel presents an *XMn*₈O₁₆, *nH*₂O global formula in which *X* is a compensation cation (potassium in our case). In cryptomelane-type solid, manganese mean oxidation state varies between 3.6 and 3.8,^[58] demonstrating the presence of either Mn(IV) and Mn(III) in the structure. α -MnO₂ phase is among the most active phases for formaldehyde low temperature oxidation,^[18,34] justifying the use of α -MnO₂ as starting raw material for Activated Reactive Synthesis process.

ARS-derived materials: the ARS process consists in a two-step grinding process. The Mn-C material is first calcined at 400°C to remove adsorbed water. 7 g of calcined Mn-C are introduced in 50 mL WC crucibles with 3 WC balls of 0.11 cm diameter. The powder is then subjected to a High Energy Ball Milling (HEBM) in a SPEX 8000 mixer (conditions: 1000 rpm for 2 h). The objective of this step, at high energy, is to reduce crystal domain size down to the nanometer length. After HEBM step, the material is denoted Mn-LEBM-0. Mn-LEBM-0 material is then subjected to a second step of grinding, at low energy (Low Energy Ball Milling – LEBM) in an attritor type grinder. Different materials are produced at different LEBM times: 10 min (Mn-LEBM-0.16), 30 min (Mn-LEBM-0.5), and from 1 h (Mn-LEBM-1) to 10 h (Mn-LEBM-10) each hour.

Reference supported material: Ground material properties are compared with those displayed by a β-MnO₂ supported mesoporous silica (SBA-15) catalyst. Since the preferential growth of a-MnO₂ crystal leads to channel type morphology, the synthesis in the confined space of the tubular porosity of the SBA-15 silica is not reliable and would result in significant pore plugging. Consequently, and due to the excellent properties displayed by silica supported β -MnO₂ catalyst, it has been selected as noble metal free reference catalyst.^[46] The reference is obtained by wet impregnation of hydrated manganese nitrate precursor over mesostructured SBA-15 silica support. SBA-15 is prepared following previously published procedure.^[59] 4 g of triblock copolymer is dissolved in 1.6 mol L⁻¹ HCl solution. After heating of the solution at 40 °C, 8.5 g of tetraethylorthosilicate is added dropwise to the solution under stirring. After 24 h of ageing, the solution is transferred into a Teflon-lined autoclave for hydrothermal treatment at 100°C for 24 h. After cooling down to room temperature, the sample is filtered, washed with water, dried at 100°C for 12 h, and calcined at 550°C for 4 h (temperature increase rate of 1.5 °C min⁻¹). Manganese precursor impregnation procedure is as follow: 1 g of the calcined SBA-15 support is immersed in 20 mL of water containing the dissolved nitrate precursor (amount of precursor is calculated to achieve a 20 wt.% loading in MnO₂ in the final material). After 30 min of mixing, the solvent is evaporated at 40 °C. Then, the dry solid is calcined at 300°C for 4 h (temperature increase rate of 1 °C min⁻¹). The following material is obtained: Mn-SBA-15.

Characterization of solids

Powder X-ray diffraction: X-ray diffraction patterns are recorded over a D8 Advance instrument from Brucker, equipped with a Cu K α X-ray source (λ = 1.54184 Å). Diffractograms are recorded for 2.0 values comprised from 10° and 80°, with a step size of 0.04° and an acquisition time for each step of 2 s. Identification of crystalline phases is performed by comparison with references issued for PDF database. Cristal domain sizes are calculated using the Scherrer equation, after correction of the FWHM to account for the instrumental broadening.

 N_2 physisorption: Physisorption experiments are performed at -196°C, on a Micromeritics Tristar II instrument. Before analysis, a known mass of ~50-200 mg of solid is heat-treated under vacuum at 150°C for 6 h. Specific surface area (S_{BET}) is calculated using the B.E.T. algorithm, on the linear part of the B.E.T. plot (P/P_0 = 0.1-0.25). Pore volume (V_p) is measured on the adsorption branch of the isotherm, at P/P_0 value of 0.98. Pore diameter (D_p) is calculated applying the B.J.H. model on the desorption branch of the isotherm.

Scanning Electronic Microscopy: Morphology of material is evaluated by Scanning Electron Microscopy. Micrographs are recorded on a Hitachi S-4700 instrument, with a 20k magnification.

Transmission Electronic Microscopy: Samples morphology evolution is evaluated by transmission electron microscopy over a JEOL 2100 UHR instrument, operated at 200 kV with a LaB₆ source and equipped with a Gatan Ultra scan camera. All the samples were embedded in a polymeric resin (spurr), and cut into sections of 50 nm thick using an ultramicrotome. Samples are deposited on a carbon grid for observation.

X-ray Photoelectron Spectroscopy: Material surface composition and surface manganese Average Oxidation State (AOS) are both extracted from X-ray Photoelectron Spectroscopy (XPS). Analysis are performed on a KRATOS AXIS Ultra instrument equipped with an electron beam of low energy for charge compensation. X-ray source is of AI K α (hv = 1486.6 eV) type. Irradiation is performed at ambient temperature, under ultra-vacuum conditions (P ~ 10⁻⁹ mbar). Determination of the binding energies for the different elements is performed using binding energy of 1s level of contamination carbon, arbitrarily positioned at 285.0 eV.

Redox properties

Manganese reducibility is evaluated by Temperature Programmed Reduction under H₂ (TPR) experiments. Manipulations are performed on a Micromeritics Autochem instrument. A known amount of catalyst (~150 mg) is inserted in a U-shaped tubular reactor. The catalyst is activated under simulated air, up to the material calcination temperature (1 h, applying a temperature increase rate of 5 °C min⁻¹). After cooling down to room temperature, a 50 mL min⁻¹ flow composed of 5 vol.% H₂ in Ar is stabilized, and a temperature increase ramp of 10 °C min⁻¹ is applied. Hydrogen consumption is on-line monitored using a Thermal Conductivity Detector (TCD) previously calibrated. In order to obtain reliable TPR results, the sensibility factor, K, as well as the shape and resolution parameter, P, are verified to be in the recommended values with the applied experimental conditions.^[60,61] From the hydrogen consumption are

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extracted manganese Average Oxidation Number (AON), supposing that the final oxidation state of manganese, at the end of the TPR experiment, is +II, according to Eq. (1):

$$Mn^{y+} + \left(\frac{y-2}{2}\right) \cdot H_2 = Mn^{2+} + (y-2) \cdot H^+$$
(1)

Catalytic oxidation of formaldehyde

The catalytic properties are measured in a fixed-bed type catalytic reactor. Total flow rate for all experiments is fixed at 100 mL min⁻¹, with 120 ppmv of formaldehyde in 20 vol.% O2 - He flow. Generation of formaldehyde in flow gas is performed using a permeation system from VICI Metronics (Dynacalibrator Model 150), loaded with paraformaldehyde. Gas phase formaldehyde concentration is adjusted by control of the permeation chamber temperature at a selected gas flow rate. Catalytic tests are performed with 0.200 g of catalyst loaded in a glass tubular reactor (I.D. = 10 mm). Before catalytic reaction, the catalyst is activated under simulated air at 250°C (total flow rate = 100 mL min⁻¹) for 2 h. At the end of the activation period, the reaction flow, containing 120 ppmv of HCHO, is stabilized. When stabilized, the reaction is started, with a temperature decrease rate of 1 °C min-1 applied to the reactor. Formaldehyde abatement (calculated from the gas phase concentration of formaldehyde) and conversion of formaldehyde into CO2 (calculated from gas phase CO2 concentration) are both calculated. CO is also analyzed. From initial formaldehyde, residual formaldehyde, CO and CO2 concentrations are calculated carbon balances to evidence possible adsorption of formaldehyde over catalyst surface. Quantification of reactant and products is performed by gas chromatography, using a micro-GC CP4900 from VARIAN, equipped with a TCD and CP-Sil 5 CB column for separation (8 m). Experimental Details.

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Keywords: Manganese oxide • formaldehyde • heterogeneous catalysis • activated reactive synthesis • oxidation

- [1] https://www.irsst.qc.ca/media/documents/PubIRSST/RG2-473.pdf
- [2] Recommendation from the Scientific Committee on Occupational Exposure Limits for Formaldehyde, SCOEL/SUM/125, 2008.
- [3] E. Roffael, Formaldehyde release from particleboard and other wood based panel, Forest Research Institute Malaysia, Kuala Lumpur, 1993.
- [4] M. Hayashi and H. Osawa, Build. Environ. 2008, 43, 329-336.
- [5] T. Godish, Indoor Air Pollution Control, Lewis Published, Chelsea, 1989.
- [6] B. Virote, S. Srisuda, T. Wiwut, Sep. Purif. Technol. 2005, 42, 159-168.
- [7] K. J. Lee, N. Shiratori, G. H. Lee, J. Miyawaki, I. Mochida, J. Jang, *Carbon* 2010, 48, 4248-4255.
- [8] Q. Wen, C. Li, Z. Cai, W. Zhang, H. Gao, L. Chen, G. Zeng, X. Shu, Y. Zhao, *Bioresource Technol.* 2011, *102*, 942-947.
- [9] Y. Song, W. Qiao, S.-H. Yoon, I. Mochida, Q. Guo, L. Liu, J. Appl. Polymer Sci. 2007, 106, 2151-2157.
- [10] E. M. Carter, E. L. Katz, G. E. Speitel, D. Ramirez, *Environ. Sci. Technol.* 2011, 45, 6498-6503.

- [11] T. Okachi and M. Onaka, J. Am. Chem. Soc. 2004, 126, 2306-2307.
- [12] M.D.C. Cazorla and A.M. Grutzeck, *Ceramics Trans.* 2006, *176*, 3-13.
 [13] I. Hideyuki, O. Yasunori, S. Tsuneji, *J. Antibacterial Antifungal Agents*
- 2005, 33, 453-461. [14] J.P. Bellat, I. Bezverkhyy, G. Weber, S. Royer, R. Averlant, J.M.
- Giraudon, J.F. Lamonier, J. Hazard. Mater. 2015, 300, 711-717.
- [15] S. Srisuda, B. Virote, *J. Environ. Sci.* **2008**, *20*, 379-384.
- [16] Z. Xu, J. Yu, G. Liu, B. Cheng, P. Zhou, X. Li, *Dalton Trans.* 2013, 42, 10190-10197.
- [17] Z. Xu, J. Yu, W. Xiao, Chem. A Eur. J. 2013, 19, 9592-9598.
- [18] J. Quiroz Torres, S. Royer, J.P. Bellat, J.M. Giraudon, J.F. Lamonier, *ChemSusChem* 2013, 6, 578-592.
- [19] T. Chen, H. Dou, X. Li, X. Tang, J. Li, J. Hao, *Micro. Meso. Mater.* 2009, 122, 270-274.
- [20] J. X. Peng, S. W. Wang, Appl. Catal. B 2007, 73, 282-291.
- [21] C. Zhang, H. He, Catal. Today 2007, 126, 345-350.
- [22] C. Zhang, F. Liu, Y. Zhai, H. Ariga, N. Yi, Y. Liu, K. Asakura, M. Flytzani-Stephanopoulos, H. He, Angew. Chem. Int. Ed. 2012, 124, 9766-9770.
- [23] B. Liu, C. Li, X. Zhang, Y. Iiu, W. Hu, Q. Wang, L. Han, F. Zhang, *Appl. Catal. B* 2012, 111-112, 467-475.
- [24] X. F. Tang, J. L. Chen, X. M. Huang, Y. Xu, W. J. Shen, Appl. Catal. B 2008, 81, 115-121.
- [25] Q. Xu, Y. Zhang, J. Mo, X. Li, Environ. Sci. Technol. 2011, 45, 5757-5760.
- [26] L. Nie, J. Yu, X. Li, B. Cheng, G. Liu, M. Jarionec, *Environ. Sci. Technol.* 2013, 47, 2777-2783.
- [27] Q. Xu, W. Lei, X. Li, X. Qi, J. Yu, G. Liu, J. Wang P. Zhang, *Environ. Sci. Technol.* 2014, 48, 9702-9708.
- [28] The Raw Materials Initiative, European commission, COM(2008)297 2008.
- [29] S. Royer, D. Duprez, F. Can, X. Courtois, C. Batiot-Dupeyrat, S. Laassiri, H. Alamdari, *Chem. Rev.* 2014, 114, 10292-10368.
- [30] L. Zhou, J. He, J. Zhang, Z. He, Y. Hu, C. Zhang, H. He, J. Phys. Chem. C 2011, 115, 16873-16878.
- [31] M. Alvarez-Galvan, B. Pawelec, V. de La Pena O'Shea, J. Fierro, P. Arias Appl. Catal. B 2004, 51, 83-91.
- [32] L. Bai, F. Wyrwalski, J. F. Lamonier, A. Y. Khodakov, E. Monfiler, A. Ponchel, Appl. Catal. B 2013, 138-139.
- [33] Y. Sekine, Atmos. Environ. 2002, 36 5543-5547.
- [34] T. Chen, H. Dou, X. Li, X. Tang, J. Li, J. Hao, Micro. Meso. Mater. 2009, 122, 270-274
- [35] H. Tian, J. He, L. Liu, D. Wang, Z. Hao, C. Ma, *Micro. Meso. Mater.* 2012, 151, 397-402.
- [36] X. Tang, Y. Li, X. Huang, Y. Xu, H. Zhu, J. Wang, W. Shen, *Appl. Catal. B* 2006, 62, 265-273.
- [37] J. Quiroz Torres, J.M. Giraudon, J. F. Lamonier, *Catal. Today* 2011, *176*, 277-280.
- [38] S. Royer, H. Alamdari, in *Perovskites and Related Oxides*, Vol. 1 (Eds.: P. Granger, V.I. Parvulescu, W. Prellier), Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, **2015**, pp.25-49.
- [39] R. Zhang, A. Villanueva, H. Alamdari, S. Kaliaguine, J. Catal. 2006, 237, 368-380.
- [40] R. Zhang, H. Alamdari, S. Kaliaguine, Appl. Catal. A 2008, 340, 140-151.
- [41] S. Laassiri, D. Duprez, S. Royer, H. Alamdari, Catal. Sci. Technol. 2011, 1, 1124-1127.
- [42] S. Laassiri, N. Bion, F. Can, X. Courtois, D. Duprez, S. Royer, H. Alamdari, *CrystEngComm* **2012**, *14*, 7733-7743.
- [43] S. Laassiri, N. Bion, D. Duprez, H. Alamdari, S. Royer, *Catal. Sci. Technol.* 2013, 3, 2259-2269.
- [44] S. Laassiri, N. Bion, D. Duprez, S. Royer, H. Alamdari, PCCP 2014, 16, 4050-4060.
- [45] A. Ungureanu, B. Dragoi, A. Chireac, C. Ciotonea, S. Royer, D. Duprez, A.S. Mamede, E. Dumitriu, ACS Appl. Mater. & Interf. 2013, 5, 3010-3025.

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- [46] R. Averlant, S. Royer, J.M. Giraudon, J.P. Bellat, I. Bezverkhyy, J.F. Lamonier, *ChemCatChem* 2014, 6, 152-161.
- [47] L. Islas, J.-C. Ruiz, F. Munoz-Munoz, T. Isoshima and G. Burillo, *Appl. Surf. Sci.* 2016, 384, 135-142.
- [48] X. Zhang, J. Qin, Y. Xue, P. Yu, B. Zhang, L. Wang and Riping Liu, Scientific Reports 2014, 4, article n°4596.
- [49] D. Briggs and G. Beamson, Anal. Chem. 1993, 65, 1517-1523.
- [50] V.R. Galakhov, M. Demeter, S. Bartkowski, M. Neumann, N.A. Ovechkina, E.Z. Kurmaev, N.I. Lobachevskaya, Y.M. Mukovskii, J. Mitchell, D.L. Ederer, *Phys. Rev. B: Condens. Matter* **2002**, 65, 113102-113105.
- [51] T. Yamashita and P. Hayes, Appl. Surf. Sci. 2008, 254, 2441-2449.
- [52] M.C. Biesinger, B.P. Payne, A.P. Grosvenor, L.W.M. Lau, A.R. Gerson, R.St.C. Smart, *Appl. Surf. Sci.* 2011, 257, 2717-2730.
- [53] B. R. Strohmeier and D. M. Hercules, J. Phys. Chem. 1984, 88, 4922-4929.

- [54] A. Baylet, S. Royer, C. Labrugère, H. Valencia, P. Marécot, J. M. Tatibouët and D. Duprez, *Phys. Chem. Chem. Phys.* **2008**, *10*, 5983-5992.
- [55] Z. Qu, L. Miao, H. Wanga et Q. Fub, Chem. Commun. 2015, 51, 956-958.
- [56] C. Li, K. Domen, K. Maruya and T. Onishi, J. Catal. 1990, 125, 445-455.
- [57] H. Perez, P. Navarro, J.J. Delgado and M. Montes, Appl. Catal. A 2011, 400, 238-248.
- [58] I. Attibak, A. Bueno-Lopez, A. Garcia-Garcia, P. Navaro, D. Frias and M. Montes, Appl. Catal. B 2010, 93, 267-273.
- [59] C. Ciotonea, A. Ungureanu, B. Dragoi, A. Chireac, S. Petit, S. Royer, E. Dumitriu, *Chem. Commun.* 2013, 49, 7665-7667.
- [60] D.A.M. Monti and A. Baiker, J. Catal. **1983**, 83, 323-335.
- [61] P. Malet, A. Caballero, J. Chem. Soc., Faraday Trans. 1988, 84(7), 2369-2375.

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Entry for the Table of Contents

Layout 1:

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Activated Reactive Synthesis is proposed as an efficient, solvent free, top-down approach for the production of nanocatalysts. Starting from microcrystalline – low surface area – manganese oxide, nanocrystalline high surface area - material, highly active for the low temperature catalytic oxidation of formaldehyde, is produced.



Carmen Ciotonea, Rémy Averlant, Guillaume Rochard, Anne-Sophie Mamede, Jean-Marc Giraudon, Houshang Alamdari, Jean-François Lamonier* and Sébastien Royer*

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A simple and green procedure to prepare efficient manganese oxide nanopowder for the low temperature removal of formaldehyde