Crystalline-phase-dependent catalytic performance of MnO₂ for aerobic oxidation reactions

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ABSTRACT Knowledge of the catalytic performances of different crystalline phases of a material is vital for the development of superior catalysts. In this study, different phases of MnO₂ (α , β , γ , and δ) have been prepared by the oxidation of Mn²⁺, and their catalytic performances were evaluated using the aerobic oxidation of benzyl alcohol to benzaldehyde as a model reaction. α -MnO₂ promoted the reaction to the highest yield. However, when the yields were normalized by the corresponding surface areas, δ -MnO₂ exhibited the highest specific activity and α -MnO₂ the lowest, indicating that the diverse microstructures resulting from the crystalline phase have a profound effect on catalytic performance. α -MnO₂ showed the highest catalytic stability, resulting from its unchanged composition and morphology after use. Informed by the experimental results, a possible reaction mechanism involving the Mars-van Krevelen process was proposed. This work provides useful information for the development of effective catalysts for aerobic oxidation.

Keywords: crystalline phase, MnO₂, aerobic oxidation

INTRODUCTION

It is well known that the performance of a catalyst is dependent on its microstructure [1–4]. Accordingly, adjusting the structure of materials is an effective way to optimize their catalytic performances and develop new catalysts with high activities and stabilities [1–4]. The crystal phase of a material is a fundamental factor that influences its microstructure [5]. Therefore, if a substance can exist in more than one crystalline form, it may be possible to tune its catalytic behavior simply by controlling its crystalline phase.

MnO₂ is a typical multiple-phase oxide [6–8] that has

attracted considerable attention in the field of catalysis owing to its low cost and high stability [9–13]. Specifically, it has been widely employed as a heterogeneous catalyst in organic synthesis [10–13]. However, most of the studies on MnO₂ catalysis have not investigated the influence of its crystalline phase on its catalytic performance. In most studies, the catalyst was purchased from a reagent company or synthesized without phase control, resulting in the use of materials with undetermined phase characteristics. Therefore, the relationship between the phase of MnO₂ and its catalytic performance for a certain reaction is required.

Selective oxidation of an alcohol is a fundamental reaction in pharmaceutical chemistry and industrial manufacturing because the corresponding aldehydes or ketones serve as key intermediates in the synthesis of fine chemicals [14–18]. However, many conventional reactions require oxidants such as chromium trioxide (i.e., the Sarret reagent) or oxalyl chloride, which are dangerously toxic and lead to the formation of large amounts of by-products [19–21]. Therefore, intense efforts have been devoted to developing efficient heterogeneous catalysts that employ molecular oxygen as the primary oxidant in order to meet the requirements of green synthesis [14–16,18,22–27].

Several noble metals and alloy catalysts have shown highly effective for this kind of reaction [14–18,22–25]. However, MnO₂, which is a promising catalyst for the oxidation of aromatic alcohols and their derivatives, is a more economical choice. Furthermore, like other heterogeneous catalysts, MnO₂ also has the advantages of facile post-reaction removal and recyclability. Consequently, it is necessary to investigate the catalytic prop-

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erties of the different crystalline phases of MnO_2 in a given alcohol oxidation reaction.

In the current study, the phase of MnO_2 (α , β , γ , or δ) was controlled by using different oxidants and reagent equivalencies in its preparation. The products were all of high phase purity. All the phases catalyzed the aerobic oxidation of benzyl alcohol to benzaldehyde, and α - MnO_2 afforded the highest yield. When the yields were divided by the corresponding catalyst surface areas, δ - MnO_2 showed the highest specific activity and α - MnO_2 the lowest. This indicates that microstructural differences resulting from different crystalline phases determine catalytic performance. Reusability of the catalysts experimentally revealed that α - MnO_2 had the highest catalytic stability. Based on the above results, a possible reaction mechanism involving the Mars-van Krevelen process was proposed.

EXPERIMENTAL SECTION

Preparation of MnO_2 with different phases

The syntheses were carried out based on the method reported by Li *et al.* [6–8] with some modifications. For the preparation of α - MnO_2 , $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ (3.200 g) and KMnO_4 (8.000 g) were dissolved in deionized water (140 mL) with stirring to form a homogeneous solution, which was then transferred into a Teflon-lined stainless-steel autoclave with a volume of 250 mL. Then, the autoclave was sealed and maintained at 180°C for 24 h. After the reaction was completed, the mixture was centrifuged and washed several times with deionized water until no ions were detected using $\text{Ba}(\text{NO}_3)_2$, followed by drying in air. The preparation of δ - MnO_2 was conveniently performed by adjusting the mass of $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ and KMnO_4 to 0.507 g and 4.583 g, respectively, with other conditions unchanged.

For the synthesis of β - MnO_2 , $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ (10.818 g) and an equimolar amount of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (14.814 g) were mixed in deionized water (140 mL) to form a homogeneous solution, which was then heated at 140°C for 24 h in a Teflon-lined stainless-steel autoclave (250 mL). Additionally, when the solution was treated at 90°C for 12 h in a vessel (500 mL) under ambient atmosphere, γ - MnO_2 was obtained.

Catalytic performance tests

The aerobic oxidation of benzyl alcohol was performed in a 50-mL three-necked flask. First, 44.0 mg of the catalyst was dispersed in 10 mL dimethylformamide (DMF) and sonicated for 10 min. Then, 1 mmol benzyl alcohol and

an equal amount of biphenyl (used as an internal standard) were mixed with the catalyst and the mixture was transferred into a flask after ultrasonication for 1 min. The reaction was carried out at 120°C for 6 h in the presence of dioxygen under normal pressure. Samples were taken periodically during the reaction to monitor the conversion of benzyl alcohol. The final mixture was diluted with acetone and centrifuged to remove the catalyst. The supernatant was analyzed by a gas chromatographer (GC, Agilent 7890A) fitted with an HP-5 capillary column and a flame ionization detector (FID). For recycling tests, the catalyst was recovered after the reaction was completed by washing several times with ethanol, followed by drying overnight at 50°C.

Characterization

The composition of the products was characterized by X-ray diffraction (XRD) on Bruker D8-Advance X-ray diffractometer with Cu K α radiation ($\lambda = 0.15418$ nm) in the range of 10–80°. The operating voltage and current were maintained at 40 kV and 40 mA, respectively. The morphologies of the samples were investigated using a scanning electron microscope (SEM, Nova NanoSEM 200) operating at an accelerating voltage of 10 kV and a transmission electron microscope (TEM, JEOL JEM-1200EX) operating at an accelerating voltage of 200 kV. The Brunauer-Emmett-Teller (BET) surface areas of the four catalysts were determined at 196°C by nitrogen adsorption using a Micromeritics ASAP2020 HD88 after degassing at 300°C.

RESULTS AND DISCUSSION

Fabrication and characterization of MnO_2 with different phases

All the preparations were based on the oxidation of Mn^{2+} by strong oxidants (KMnO_4 or $\text{K}_2\text{S}_2\text{O}_8$). The crystallographic phases of the as-prepared MnO_2 samples were determined by XRD. All the diffraction peaks in Fig. 1a can be indexed to a structure with tetragonal symmetry in the space group $P42/mnm$, which is in good agreement with the reported data for pure-phase α - MnO_2 (JCPDS, 44-0141). No impurities are detected. This demonstrates that the pure α - MnO_2 is obtained when Mn^{2+} is oxidized by KMnO_4 at a molar ratio of 1:2.67. If this ratio is adjusted to 1:9.67, phase-pure δ - MnO_2 forms, as evidenced by the XRD pattern shown in Fig. 1d (JCPDS, 52-0556). The pattern in Fig. 1b confirms that the pure β - MnO_2 (JCPDS, 24-0735) is synthesized when $\text{K}_2\text{S}_2\text{O}_8$ is employed as the oxidant in a hydrothermal system, while

Figure 1 XRD patterns of (a) α - MnO_2 , (b) β - MnO_2 , (c) γ - MnO_2 , and (d) δ - MnO_2 .

Figure 2 Representative SEM images of the samples. (a) α - MnO_2 , (b) β - MnO_2 , (c) γ - MnO_2 , (d) δ - MnO_2 .

Fig. 1c shows that γ - MnO_2 (JCPDS, 14-0644) is formed when the same mixture is treated under atmospheric conditions in a flask. Thus, the XRD results verify that all the samples are sufficiently pure for use as single-phase catalysts.

The morphologies and microstructures of the as-prepared samples were examined by SEM, TEM, and high-resolution TEM (HRTEM), as shown in Figs 2–4, respectively. The SEM (Fig. 2a) and TEM (Fig. 3a) images of the α - MnO_2 sample reveal a large amount of solid

Figure 3 Representative low-magnification TEM images of (a) α - MnO_2 , (b) β - MnO_2 , (c) γ - MnO_2 , and (d) δ - MnO_2 .

Figure 4 HRTEM images of MnO_2 with different phases: (a) α - MnO_2 , (b) β - MnO_2 , (c) γ - MnO_2 , and (d) δ - MnO_2 .

nanowires with diverse lengths and diameters. The lattice fringes with spacings of 0.49 and 0.23 nm shown in the corresponding HRTEM image (Fig. 4a) can be assigned to the (200) and (330) facets of α - MnO_2 , respectively. Thus, the wires prefer to grow along the $\langle 010 \rangle$ direction.

Figs 2b and 3b show the SEM and TEM images of β -

Figure 5 Kinetic profiles of the aerobic oxidation of benzyl alcohol catalyzed by α -, β -, γ -, and δ -MnO₂. Reaction conditions: 44 mg catalyst, 108 mg substrate, 10 mL DMF, 0.1 MPa oxygen, 393 K, 6 h. (a) Y-axis indicates the yield of benzaldehyde, (b) Y-axis indicates the surface-area-normalized yield.

MnO₂, revealing that the sample has nanorod-like morphology. Most of the nanorods are wider than the α -MnO₂ wires. The lattices with spacings of 0.30 and 0.22 nm indicated in Fig. 4b correspond to the (110) and (200) planes of β -MnO₂, respectively. Thus, the growth direction of the rods is along the $\langle 110 \rangle$ direction.

The SEM result in Fig. 2c shows that the as-obtained γ -MnO₂ sample consists of many short rods that aggregate to form urchin-like structures. Fig. 3c shows the TEM image of these rods, which were separated by the intensive ultrasonication used for TEM sample preparation. The lattice spacing of 0.21 nm measured from the HRTEM image (Fig. 4c) can be ascribed to the (211) planes of γ -MnO₂, further confirming its crystalline phase.

The structure of δ -MnO₂ is quite different from that of the other samples, comprising hierarchical flower-like shapes (Fig. 2d) constructed by several thin sheets (Fig. 3d). Furthermore, its porous structure can be clearly seen. Lattice fringes with spacing of 0.25 nm for the (101) facets of δ -MnO₂ are clearly observed (Fig. 4d). Furthermore, another wider lattice spacing of 0.66 nm can be seen in the HRTEM image, which is from the (003) facets and reflects the number of K⁺ and H₂O species intercalating between the planes [28].

The nitrogen adsorption/desorption isotherms of the four as-prepared materials are presented in Fig. S1. Only the δ -MnO₂ sample exhibits a type-IV isotherm, which has a broad hysteresis loop with an appearance between those of H3- and H4-type loops. This is due to the stacking of sheets or lamellar pores.

A prominent increase occurs in the relative pressure range of 0.45–0.9 (P/P_0), which is attributed to the capillary condensation of nitrogen inside the primary pores.

The other samples show type III isotherms in the same range, indicating that only δ -MnO₂ has a typical mesoporous structure. Calculations using the isotherms of the four catalysts reveal that α -MnO₂ has the highest BET surface area (53.8 m² g⁻¹), while γ -MnO₂ has the second highest (42.4 m² g⁻¹). δ -MnO₂ and β -MnO₂ present the lowest surface areas of 14.4 and 14.3 m² g⁻¹, respectively. The size-distribution profiles (Fig. S2) indicate that α -, β -, and γ -MnO₂ do not have porous structures, while δ -MnO₂ has typical pores with a broad size distribution in the 10–100 nm range.

Catalytic performances of the as-prepared MnO₂ catalysts in the aerobic oxidation of benzyl alcohol

In order to systematically investigate the catalytic performances of the four catalysts, we focused on the aerobic oxidation of benzyl alcohol because it is a very common reaction that is frequently used in the chemical industry. Thin-layer chromatography (TLC) combined with GC-MS results revealed that benzaldehyde was obtained as the unique product. Fig. 5 shows the kinetic profiles of this conversion reaction, from which it can be seen that the reaction rates are very high during the initial stage and decrease with reaction time (Fig. 5a). All the phases of MnO₂ except β -MnO₂ are effective catalysts for this reaction, affording yields of > 90% after 6 h. However, under the same conditions, β -MnO₂ only achieves a yield of 42.1% and the reaction rate deduced from the kinetic profile is clearly lower than that of other phases.

In order to compare the real catalytic activities of the four phases, the yields were normalized by surface area to eliminate its influence. As shown in Fig. 5b, the per-area yield of δ -MnO₂ increases more rapidly and reaches a higher value than those of the other phases. Clearly, it is

Figure 6 XRD patterns of the fresh and used MnO_2 catalysts.

the most active catalyst among the four samples for the oxidation of benzyl alcohol. Although $\beta\text{-MnO}_2$ affords the lowest yield, it has the second-highest surface-area-normalized catalytic activity because of its low specific surface area. Conversely, $\alpha\text{-MnO}_2$ affords the highest conversion, but it has the lowest specific activity owing to its large surface area. The order of the specific activities are $\delta\text{-MnO}_2 > \beta\text{-MnO}_2 > \gamma\text{-MnO}_2 > \alpha\text{-MnO}_2$. Thus, the different phases have distinctive microstructures, which causes variation in their specific activity.

After the first catalytic reaction, the used catalysts were isolated and recovered for XRD analysis, as shown in Fig. 6. All the diffraction peaks for α - and $\delta\text{-MnO}_2$ are in accordance with those of the fresh catalysts and the corresponding standard PDF cards. Therefore, it is clear that no compositional transformations occur in α - and $\delta\text{-MnO}_2$ during the reaction. Conversely, all the XRD peaks of the used $\gamma\text{-MnO}_2$ sample are slightly shifted to the high-angle region compared to those of the fresh samples. However, the pattern does not change and there are no extra diffraction signals. This indicates that the interplanar spacings of the main facets of $\gamma\text{-MnO}_2$ decrease slightly during the catalytic process, but its crystalline phase and composition do not change. The XRD results

for $\beta\text{-MnO}_2$ show that a small extra peak at 26.2° from an unknown substance appears after use, but the pattern remains largely unchanged, even after six further uses.

These results clearly demonstrate that the four samples act as catalysts rather than oxidants during the oxidation process. If the reactions were stoichiometric rather than catalytic, the MnO_2 (0.5 mmol) would have been completely consumed, resulting in a 50% maximum yield of benzaldehyde, as 1.0 mmol benzyl alcohol was used (see the Experimental section). Clearly, this hypothesis conflicts with the experimental results, and there is no doubt that the reaction is a catalytic conversion.

When O_2 was absent from the reaction (with other conditions fixed), the conversion of benzyl alcohol was lower than 5% ($\alpha\text{-MnO}_2$ was used). Furthermore, the XRD profile (Fig. S3) of the used catalyst indicates that MnO_2 does not oxidize benzyl alcohol without O_2 because the phase and composition have not changed. This result further confirms that the oxidation of benzyl alcohol in this work is not a stoichiometric reaction between MnO_2 and benzyl alcohol but a catalytic reaction. More importantly, O_2 plays a very important role in the completion of the catalytic cycle.

Furthermore, the reusability of the four catalysts was

Figure 7 Recyclability of the four phases of MnO₂ catalysts in the oxidation of benzyl alcohol. Reaction conditions: 44 mg catalyst, 108 mg benzyl alcohol, 10 mL DMF, 0.1 MPa oxygen, 393 K, 6 h.

evaluated after recovery. Each catalyst was used six times under the same reaction conditions. From Fig. 7, it can be seen that α-MnO₂ is the most stable catalyst for this reaction, affording space >90% yield after six runs. δ-MnO₂ is quite stable for the first three runs, but the yields decrease significantly from the fourth cycle. In addition, the two other samples exhibit apparent loss of catalytic activity throughout the tests. These results further confirm that the reaction between MnO₂ and benzyl alcohol is not stoichiometric as, in a stoichiometric reaction, and the MnO₂ would be completely exhausted in the first run.

After the sixth use, the catalysts were recovered and re-characterized to check their compositions and structures. As illustrated in Fig. S4, the XRD results are consistent with those for the first-use samples. The only difference among them is that the peaks for all the catalysts are less intense, indicating that their degrees of crystallinity are lower after use.

The used catalysts were examined by SEM to assess their morphology changes. Fig. 8a shows that the size and shape of α-MnO₂ is very close to those of the fresh samples. This is a vital reason for its excellent catalytic stability, as well as the lack of compositional change. Similar to α-MnO₂, β-MnO₂ also maintains its morphology (Fig. 8b) upon repeated uses. Thus, its poor reusability is caused by slight compositional change upon use (Fig. 6b). Unlike the α- and β-samples, γ- and δ-MnO₂ exhibit apparent morphological changes. Significant aggregation occurs, resulting in greater resistance of mass transfer. Thus, they become less active after recycling.

Fig. 9 illustrates the possible mechanism of this catalytic

Figure 8 SEM images of each phase of MnO₂ after the 6th use.

Figure 9 Possible catalytic mechanism of the four catalysts for benzyl alcohol oxidation in the presence of oxygen.

reaction by the Mars-van Krevelen process in detail [29–32]. This process begins with the diffusion and adsorption of benzyl alcohol at the Lewis acid sites (Mn⁴⁺). After adsorption, the hydroxyl oxygen atoms, which exhibit Lewis basicity, generate new bonds with Mn⁴⁺ to form a coordinate intermediate. This weakens the O–H bonds in the hydroxyl groups. Simultaneously, the α-hydrogens on the methylene are attacked by lattice oxygen (O^{2–}). Subsequently, carbon-oxygen double bonds are formed to produce benzaldehyde as a result of electron migration. Mn²⁺ is simultaneously oxidized into Mn⁴⁺ in the presence of O₂ with the production of H₂O₂, which quickly decomposes to H₂O [29–32].

Finally, using δ-MnO₂ as the catalyst, several derivatives of benzyl alcohol and 4-pyridylcarbinol were subjected to the oxidation reaction to further examine its catalytic performance. Table 1 lists the yields of the five deriva-

Table 1 Yield of substrates with different substituent groups

Entry	Substrate	Product	Time (h)	Yield (%)
1			6	98.4%
2			6	77.6%
3			6	80.6%
4			6	35.5%
5			6	<10%

tives. All derivatives except 2-chlorobenzyl alcohol give lower yields of the corresponding aldehyde in comparison with that of benzaldehyde. This indicates that the substituent groups decelerate the reaction because of steric hindrance. 4-Pyridylcarbinol provides the lowest yield because the higher nucleophilicity of the N atom compared to that of the O atom leads to it preferentially interacting with Mn^{4+} . This result provides indirect evidence for the proposed mechanism.

CONCLUSIONS

In summary, MnO_2 with different phases (α , β , γ , and δ) were prepared by the oxidation of Mn^{2+} . The products were of high phase purity. The aerobic oxidation of benzyl alcohol was employed as a model reaction to reveal the influence of the phase on the catalytic performance of MnO_2 . The results reveal that, of the four catalysts, α - MnO_2 catalyzes the reaction with the highest yield. When the yields were normalized by the corresponding surface areas of the catalysts, δ - MnO_2 was found to exhibit the highest specific activity and α - MnO_2 the lowest. This is due to the different microstructures presented by the different crystalline phases. Neither the composition nor the morphology of α - MnO_2 changed

after use, thus demonstrating its excellent catalytic stability. A possible reaction mechanism on the basis of the Mars-van Krevelen process was proposed. The results of this work will provide useful information for the development of effective catalysts for aerobic oxidation.

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Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Experimental details are available in the online version of the paper.

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MnO₂晶相对耗氧反应的催化性能的影响

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摘要 研究同种物质不同晶相材料的催化性能对于遴选最佳的催化剂十分重要。本文利用Mn²⁺的氧化反应制备了高纯度的不同晶相MnO₂ (α, β, γ, δ相), 通过苯甲醇耗氧氧化成苯甲醛的反应对其催化性能进行了评估。结果显示, 在相同条件下, α-MnO₂催化该反应的产率最高。如果用表面积归一化产率, 则δ-MnO₂具有最高的面积比活性, 而α-MnO₂的却最低。不同晶相导致的不同微观结构决定了它们的催化性能。经过多次催化反应后, 只有α-MnO₂的成分和形貌均未改变, 显示出最高的催化稳定性。因此提出了一种基于Mars-van Krevelen过程的可能的反应机理。此工作可为发展有效的耗氧氧化反应催化剂提供有利支持。