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1. Introduction

Volatile organic compounds (VOCs), a major group of significant atmospheric pollutants, usually come from various industrial processes, automobiles and municipal incineration, which not only seriously harm human health but also threaten environmental quality due to their extremely toxic and malodorous nature.^{1–5} Driven by the more and more rigorous environmental legislation of VOC emission, several end-of-pipe techniques, e.g. adsorption, condensation, non-thermal plasma, thermal incineration, biotechnology, photocatalysis and catalytic oxidation,¹⁻⁶ have been widely implemented for VOC elimination, among which catalytic oxidation is generally believed to be one of the most efficient and cost-effective techniques for VOC elimination because it is energy saving, has high efficiency and does not produce secondary pollutants.¹⁻⁵ However, the vital challenge of such a technique is still to design and acquire highly efficient catalysts.

During the last few decades, two representative kinds of catalysts, mainly including supported noble metals (Pt, Pd, Au, Rh,...) and transition metal oxides (V, Mn, Co, Cu, Fe,...),^{1-5,7-12} have been extensively developed for VOC elimination by using a

Boosting acetone oxidation efficiency over MnO₂ nanorods by tailoring crystal phases[†]

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Developing metal oxides with tailored crystal phases has become a research hotspot in environmental catalysis. In this work, three kinds of MnO₂ nanorods with different crystal phases, e.g. α -, β - and γ -MnO₂, have been prepared by a one-pot hydrothermal method with goals to explore their crystal-phase dependent catalytic performances for acetone elimination. The results attest that α -MnO₂ gave the optimal acetone oxidation activity as compared with β - and γ -MnO₂, completely achieving 100% acetone conversion and 100% CO₂ selectivity at 120 °C under the reaction conditions of acetone concentration = 1000 ppm, 20 vol% O₂/N₂ and WHSV = 90 000 mL g_{cat}⁻¹ h⁻¹. This superior activity of α -MnO₂ mainly originated from its unique crystal phase that resulted in the synergistic effect by combining the largest crystal tunnel size, the highly enhanced chemical nature originating from more Mn⁴⁺ cations, the highly improved low-temperature redox properties and the weakest Mn–O bond strength. Meanwhile, three kinds of MnO₂ nanorods also demonstrated strong long-term stability and good water tolerance for acetone elimination, showing good potential in practical applications.

catalytic oxidation technique. It has been generally admitted that noble metal catalysts are catalytically more active at lowoperating temperature and exhibit higher catalytic activities than metal oxides for VOC elimination,^{1,7} but the high cost and rapid deactivation of noble metal catalysts inevitably limit their wide applications. Therefore, great efforts have recently been devoted to developing metal oxide catalysts, especially transition metal oxides,⁸⁻¹⁴ which are expected to be a better alternative to replace noble metal catalysts. Among various transition metal oxides, MnO₂ is widely considered as one of the most effective candidates for VOC elimination, which has received extensive concern of widespread applications in catalytically eliminating various VOCs.^{3,5,15-19} Intrinsically, MnO₂ commonly exists in different crystal phases, mainly including α -, β -, γ - and δ -MnO₂ crystal phases,¹⁵⁻²⁵ in which the basic [MnO₆] octahedral units are linked in different modes. Meanwhile, it is usually accepted that the difference in crystal-phase structures can significantly affect the physicochemical properties, which in turn influence the catalytic reactivity of MnO2. Accordingly, many studies have revealed the crystal-phase dependent catalytic reactivity of MnO₂ in the field of VOC elimination.¹⁵⁻¹⁹ For instance, Yu et al. reported that the catalytic activities of MnO2 with different crystal phases for dimethyl ether oxidation distinctly varied in the order of β - $< \gamma$ - $< \alpha$ -MnO₂, fairly agreeing well with their low-temperature reducibility order.15 Shangguan et al. found that the catalytic activities of MnO₂ with different crystal phases for both acetaldehyde and benzene oxidations ranked in the same sequence of β - < γ - < α -MnO₂, mainly attributed to their different numbers of OH groups and VOC adsorption



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capacities together with their distinguishing oxygen mobility.¹⁶ Lu et al. revealed that the difference in the crystal phases of MnO₂ apparently affected the catalytic activity for propane oxidation and the catalytic activity arranged in the trend of δ - < β - < γ - $\approx \alpha$ -MnO₂, which was significantly associated with their different exposed facets that influenced the active adsorption of propane on the surface of MnO₂.¹⁷ Wang et al. studied MnO₂ with different crystal phases for toluene oxidation in a combined plasma-catalytic process and disclosed that the catalytic activity increased gradually in the order of β - $< \delta$ - < γ - < α -MnO₂, primarily ascribed to their different Mn–O bond strengths and surface-chemisorbed active oxygen species.18 Hu et al. discovered that the catalytic activities of MnO₂ with different crystal phases for benzene oxidation ranked in the sequence of δ - < α - < β - < γ -MnO₂, which was mainly related to their differences in the surface adsorbed oxygen species ratio and low-temperature O₂ desorption amount.¹⁹ Despite the contribution of considerable efforts to explore the crystal-phase dependent catalytic reactivity of MnO₂ for VOC elimination, the essential mechanism has not yet been clearly elucidated and remains even partly contradictory. The reactivity order of MnO2 with different crystal phases for VOC elimination is usually different from different researchers,¹⁵⁻¹⁹ and a similar phenomenon is also observed in other application fields, e.g. CO oxidation, NO oxidation, water oxidation, catalytic ozonation, selective catalytic reduction of NO_x with NH₃, electrochemical oxygen reduction, electrochemical energy storage and pollutant degradation in aqueous medium.²⁰⁻²⁹ The possible reason is that previous studies of the crystal-phase dependent catalytic reactivity of MnO₂ for VOC elimination normally accompany different morphological structures, exposed facets and preparation conditions. Hence, further studies are extremely urgent to reveal the essence of the crystal-phase dependent catalytic reactivity of MnO₂ for VOC elimination.

Herein, three kinds of MnO₂ nanorods with different crystal phases, e.g. α -, β - and γ -MnO₂, have been fabricated by a one-pot hydrothermal method, aiming to reveal their crystalphase dependent catalytic performances for acetone elimination. The results indicate that α -MnO₂ presented the optimal acetone oxidation activity in comparison with β - and γ -MnO₂, completely achieving 100% acetone conversion and 100% CO₂ selectivity at 120 $^{\circ}$ C under the reaction conditions of acetone concentration = 1000 ppm, 20 vol% O_2/N_2 and WHSV = 90 000 mL g_{cat}^{-1} h⁻¹. This superior activity of α -MnO₂ was mainly associated with its unique crystal phase that resulted in the synergistic effect by integrating the largest crystal tunnel size, the highly enhanced chemical nature originating from more Mn4+ cations, the highly improved low-temperature redox properties and the weakest Mn-O bond strength. Meanwhile, three kinds of MnO₂ nanorods also displayed strong long-term stability and good water tolerance for acetone oxidation, showing good potential in practical applications. It can be believed that the findings from this study can deliver some new insights for guiding the rational design of high-efficient catalysts applied in VOC elimination.

2. Experimental section

2.1. Catalyst preparation

All chemical reagents employed in this work were of analytical grade and used as received without further treatment. Three kinds of MnO₂ nanorods with different crystal phases were successfully fabricated by a one-pot hydrothermal process according to previous studies with minor revisions.^{25,30} For synthesizing α-MnO₂, 7.5 mmol KMnO₄ and 7.5 mmol NH₄Cl were completely dissolved in 80 mL distilled water, then poured into a 100 mL Teflon-lined autoclave and kept at 200 °C for 24 h. Afterwards, the solid sediment was thoroughly washed with distilled water and absolute alcohol several times, then dried at 100 °C for 12 h, and finally calcinated at 350 °C for 3.0 h. Similarly, for preparing β -MnO₂, 10 mmol MnSO₄·H₂O and 10 mmol (NH₄)₂S₂O₈ were dissolved in 80 mL distilled water and kept at 120 °C for 12 h. For fabricating γ -MnO₂, 20 mmol MnSO₄·H₂O and 20 mmol (NH₄)₂S₂O₈ were dissolved in 80 mL distilled water and kept at 90 °C for 24 h.

2.2. Catalyst characterization

The crystal phase characterized by the powder X-ray diffraction (XRD) technique was achieved on BRUKER D2 PHASER with CuK α radiation and 2θ values ranging from 10° to 70° under the conditions of 40 kV and 30 mA. Raman spectra measured on HORIBA LabRAM HR Evolution were acquired using an excitation wavelength of 532 nm at room temperature. Electron paramagnetic resonance (EPR) analysis achieved on a JEOL JES-FA200 was conducted at 77 K. The morphological features of catalysts captured by using a field emission scanning electron microscope (FESEM) and a high-resolution transmission electron microscope (HRTEM) were analysed on Hitachi-S4800 and JEOL JEM-2100, respectively. The physical structural parameters of the catalysts, mainly including the specific surface area (S_{BET}), pore diameter (D_{P}) and pore volume $(V_{\rm P})$, were obtained from N₂ adsorption–desorption isotherms using Micromeritics ASAP 2460 at a temperature of 77 K. Elemental compositions and chemical value states of catalysts analyzed using X-ray photoelectron spectroscopy (XPS) were determined on PerkinElmer PHI-5000C with AlKa radiation and calibrated with the reference of C_{1s} = 284.6 eV. The reducibility of the catalysts determined by using a hydrogen temperatureprogrammed reduction (H2-TPR) technique was determined on Micromeritics Auto-chemisorbed II 2920 with a thermal conductivity detector (TCD) to quantify the H2 consumed amount in the temperature range of 100–350 °C, and 50 mg catalyst placed into a U-shaped quartz tube was initially purged at 300 °C for 1.0 h in highly pure Ar, then cooled to 50 °C, and finally heated up to 600 °C with a 10 °C min⁻¹ ramp in a 30 mL min⁻¹ 10% H_2/Ar stream. An oxygen temperature-programmed desorption (O2-TPD) test was performed in the same H2-TPR apparatus to quantify the desorption amount of oxygen species in the temperature range of 50-350 °C, and 50 mg catalyst was firstly pretreated at 350 °C for 1.0 h in a 30 mL min⁻¹ 10% O_2 /He stream, then cooled to 50 °C, and finally heated up to 900 $^{\circ}$ C with a 10 $^{\circ}$ C min⁻¹ ramp in highly pure He stream.

2.3. Activity evaluation

The catalytic activities of MnO₂ nanorods with different crystal phases for acetone oxidation were evaluated in a continuous flow fixed-bed tubular quartz reactor ($\phi = 6.0$ mm) by the temperature-programmed oxidation (TPO) reaction using 100 mg catalyst (40-60 mesh) at atmospheric pressure as schemed in Fig. S1 (ESI⁺). Each TPO reaction runs from 50 °C to 250 °C together with a K-thermocouple projecting into the catalyst bed for guaranteeing the temperature raising ramp at 2.0 °C min⁻¹. Feed gases, mainly including 1000 ppm acetone, 20 vol% O_2 and major N_2 as the balance gas, flowed through the catalyst bed with a total stream of 150 mL min⁻¹ corresponding to a weight hourly space velocity (WHSV) of 90 000 mL g_{cat}^{-1} h⁻¹. To study the effect of WHSVs on catalytic activity, the total streams of feed gases were changed into 300 mL min $^{-1}$ and 400 mL min $^{-1}$ corresponding to WHSVs of 180000 mL g_{cat}^{-1} h⁻¹ and 240 000 mL g_{cat}^{-1} h⁻¹, respectively. To investigate the effect of water on catalytic activity, 8.0 vol% and 16 vol% H₂O vapor generated by pumping distilled water into a gasification chamber at 180 °C were separately introduced into the reaction system along with feed gases. The concentrations of reactants and products were analyzed online using a gas chromatograph (Shimadzu GC-2014C) equipped with TCD and FID detectors. The catalytic activities were determined by using the reaction temperatures of T_{10} , T_{50} and T_{90} corresponding to achieved acetone conversions ($\eta_{acetone}$) of 10%, 50% and 90%, respectively, where $\eta_{acetone}$ was defined as the following equation: $\eta_{acetone}$ = $[(C_{\text{acetone-in}} - C_{\text{acetone-out}})/C_{\text{acetone-in}}] \times 100\%.$

3. Results and discussion

3.1. Physicochemical characteristics

The XRD patterns in Fig. 1 reveal that three MnO_2 catalysts demonstrated distinctly different diffraction peaks, all of which could be indexed to the respective pure crystal phase, *e.g.* α -MnO₂ (JCPDS Card No. 44-0141), β -MnO₂ (JCPDS Card No. 24-0735)



Fig. 1 XRD patterns of MnO₂ with different crystal phases.

and γ -MnO₂ (JCPDS Card No. 14-0644).¹⁸⁻²³ The diffraction peaks located at 2θ values of 12.8° , 18.1° , 28.8° , 37.5° , 41.9° , 49.9° and 60.3° were assigned to the (110), (200), (310), (211), (301), (411) and (521) planes of α -MnO₂ in the tetragonal phase, the diffraction peaks centered at 2θ values of 28.7° , 37.3° , 42.8° , 56.7°, 59.4° and 64.8° were well identified as the (110), (101), (111), (211), (220) and (002) planes of β -MnO₂ in the tetragonal phase, and the diffraction peaks situated at 2θ values of 22.4° , 37.1° , 42.6° , 56.1° and 65.6° were fairly associated with the (120), (131), (300), (160) and (421) planes of γ -MnO₂ in the orthorhombic phase.²³ All the diffraction peaks of three MnO₂ catalysts corresponded to a single phase and no other peaks ascribable to impurities were detected, indicating that they were present in a highly pure single phase. Meanwhile, the diffraction peaks of α- and γ-MnO2 were much weaker and broader than β -MnO₂, implying that both of them had a lower crystallization degree. Based on the principal (310) peak of α -MnO₂, the (110) peak of β -MnO₂ and the (131) peak of γ -MnO₂, their respective crystallite size has been calculated using Scherrer's equation as listed in Table 1. It can be clearly observed that the crystallite size of β -MnO₂ was much bigger than those of α - and γ -MnO₂, especially γ -MnO₂, signifying its high crystallization degree, which could be mainly attributed to their different preparation processes.

The crystal structures in Fig. 2 show that three MnO₂ catalysts with different crystal phases were constructed by different interlinking modes of edge-sharing basic [MnO₆] octahedral units. For α -MnO₂, one-dimensional structure was constructed from the double chains of edge-sharing basic $[MnO_6]$ octahedral units by forming (2×2) and (1×1) tunnels that extended along the crystallographic *E* axis of a tetragonal unit cell, and their corresponding sizes were 4.6 imes 4.6 Å and 2.3 \times 2.3 Å,^{15,18} respectively. β -MnO₂ possessed a rutile-type structure with tetragonal symmetry (P42/mnm), in which the basic [MnO₆] octahedral units build up strings of edge-sharing octahedral units extending along the crystallographic c axis of a tetragonal unit cell, and then linked with neighboring chains by sharing common corners, finally leading to the formation of (1×1) tunnels with a size of 2.3 \times 2.3 Å in the crystal structure of β -MnO₂.^{18,20} For γ -MnO₂, the crystal structure was recognized as a random intergrowth of pyrolusite (1×1) tunnel and ramsdellite (2×1) tunnel structures with corresponding sizes of 2.3 \times 2.3 Å and 4.6 \times 2.3 Å, respectively, in which the basic [MnO₆] octahedral units shared the edges and corners.^{21,23} Therefore, γ -MnO₂ can be considered to be a most complex and highly disordered material, which can be sufficiently validated by its much weaker and broader diffraction peaks of XRD patterns as shown in Fig. 1. Hence, it can be speculated that the difference in the crystal structures of three MnO₂ catalysts resulted in different tunnel structures and sizes, and the tunnel size of the three MnO2 catalysts distinctly varied in the order of β - $< \gamma$ - $< \alpha$ -MnO₂.

The Raman spectra in Fig. 3a further reveal the different crystal structures and local Mn environments of three MnO_2 catalysts in more detail. Generally, the Raman bonds in the range of 200–500 cm⁻¹ are associated with the Mn–O–Mn

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Table 1 Physical structural parameters of MnO_2 with different crystal phases

Catalysts	Crystal phase	Crystallite size (nm)	Mn–O length ^a (Å)	$S_{ m BET}~({ m m^2~g^{-1}})$	$V_{\rm p} \left({\rm cm}^3 {\rm g}^{-1} ight)$	$D_{\rm p}~({\rm nm})$
α -MnO ₂ β -MnO ₂	Tetragonal Tetragonal	20 27	1.98 1.88	60 16	0.12 0.027	26 17
γ -MnO ₂	Orthorhombic	16	1.91	46	0.15	17

^a The value of Mn–O length cited from ref. 18 and 20.



Fig. 2 Crystal structures of MnO₂ with different crystal phases.



Fig. 3 Raman spectra (a) and EPR spectra (b) of ${\rm MnO}_2$ with different crystal phases.

bending vibrations in the MnO_2 octahedral lattice while the Raman bonds in the range of 500–700 cm⁻¹ are related to the typical Mn–O stretching of the [MnO₆] octahedral unit.^{15,17,18,20} The results in Fig. 3a show that α -MnO₂ featured four major peaks located at approximately 188 cm⁻¹, 389 cm⁻¹, 580 cm⁻¹ and 633 cm⁻¹. The strong peak at 580 cm⁻¹ was definitely assigned to the deformation modes of the Mn–O–Mn chain in the MnO₂ octahedral lattice while the peak at 633 cm⁻¹ was assigned to the Mn–O stretching modes, and both of them distinctly indicated a well-developed tetragonal structure with a (2 × 2) tunnel in α -MnO₂.^{15,17,18} The peak at 188 cm⁻¹ of α -MnO₂ represented an external mode that is derived from the translational motion of basic [MnO₆] octahedral units,^{17,18}

signifying the high mobility of surface oxygen species in α -MnO₂. β -MnO₂ demonstrated two main peaks centered at around 539 cm⁻¹ and 667 cm⁻¹. The peak at 539 cm⁻¹ corresponded to the Mn–O stretching of the [MnO₆] octahedral unit and the peak at 667 cm⁻¹ was indexed to the characteristic A_{1g} mode, indicating a well-developed rutile-type tetragonal structure with a (1 \times 1) tunnel in $\beta\text{-MnO}_2.^{15,18}$ The $\gamma\text{-MnO}_2$ also displayed two major peaks situated at about 579 cm⁻¹ and 669 cm⁻¹. The former peak at 579 cm⁻¹ suggested a welldeveloped orthorhombic structure with a (2×1) tunnel in $\gamma\text{-}MnO_2$ and the latter peak at 669 cm^{-1} was ascribed to the stretching mode of the Mn-O bond in the [MnO₆] octahedral unit.^{15,18} It should be noticed that no peaks located at less than 200 cm⁻¹ can be observed in β - and γ -MnO₂, possibly implying the weaker mobility of surface oxygen species as compared with α -MnO₂. Meanwhile, it can be noted that the full width at the respective half-maximum values of the three MnO₂ catalysts ranked in the sequence of α - < γ - < β -MnO₂ corresponding to the increased number or concentration of defective sites, which seemingly contradicted with their variation in the crystallization degree as revealed by XRD analysis. This phenomenon can be interpreted by the fact that the Raman technique is surface sensitive while the XRD technique is an indication of bulk materials.31

To ascertain the chemical nature of defective sites in three MnO₂ catalysts, the EPR characterization has been employed and the corresponding results have been shown in Fig. 3b. Clearly, it can be seen that all of the three MnO₂ catalysts exhibited a sharp and strong EPR signal located at approximately g = 1.995, which was mainly related to the Zeeman effect of the unpaired electrons trapped at the sites of oxygen vacancies,^{32,33} distinctly attesting that the chemical nature of defective sites in three MnO₂ catalysts was due to oxygen vacancies. To the best of our knowledge, the number or concentration of oxygen vacancies can be generally proportional to the peak intensity of the EPR signal according to previous studies.^{32,33} It can be noted that the peak intensity of EPR signals increased gradually in the order of α - $< \gamma$ - <β-MnO₂, indicating the increased number or concentration of oxygen vacancies, which agreed well with the results of Raman analysis.

The FESEM images in Fig. 4 demonstrate that the morphological structures of three MnO_2 catalysts were uniform nanorods with different lengths and diameters. The respective lengths and diameters of the three MnO_2 catalysts were calculated to be around 0.30–1.5 µm and 50–80 nm for α -MnO₂, 0.20–2.5 µm and 30–90 nm for β -MnO₂, 0.50–2.0 µm and 15–60 nm for γ -MnO₂, respectively. Meanwhile, their corresponding TEM



Fig. 4 FESEM, TEM and HRTEM images of MnO₂ with different crystal phases.

images also showed that the three MnO₂ catalysts were present in uniform nanorods, apparently exhibiting the consistent morphology and corresponding size distribution of the three MnO₂ catalysts as disclosed by FESEM analysis. Moreover, the distinct reflections with *d*-spacing values of 0.69 nm, 0.31 nm and 0.24 nm in their respective HRTEM image for three MnO₂ catalysts were assigned to the typical (110) plane of the tetragonal α -MnO₂ crystal phase, the principal (110) plane of the tetragonal β -MnO₂ crystal phase and the principal (131) plane of the orthorhombic γ -MnO₂ crystal phase,^{17,30} obviously attesting that α -, β - and γ -MnO₂ preferentially exposed the (110), (110) and (131) facets, respectively.

The N₂ sorption isotherms in Fig. 5 display that all of the three MnO₂ catalysts showed the typical type-IV N₂ adsorptiondesorption isotherms along with a small H1 hysteresis loop in the relative pressure (P/P_0) range of 0.7–1.0, implying the existence of mesoporous structures in three MnO₂ catalysts that are generally related to the slit-shaped pores according to the classic IUPAC definitions.^{19,32,34,35} The slit-shaped pores usually originated from the sheet-like or rod-like feature of materials,^{32,34,35} coinciding well with the results of FESEM and TEM analysis. Meanwhile, it can be found that no saturated adsorption in a high P/P_0 range of three MnO₂ catalysts was achieved up to $P/P_0 = 1.0$, signifying the existence of partial large mesopores.36,37 This speculation can be evidenced by their respective pore size distribution curve in which a wide pore size distribution could be observed in the range of 3.0-50 nm, mainly stemming from the aggregated voids by the accumulation of the nanorod units. Based on N2 sorption isotherms, the surface area (S_{BET}) , pore volume (V_{P}) and pore size $(D_{\rm P})$ of the three MnO₂ catalysts have been acquired by using the classic BET and BJH models from the desorption branches, respectively. From Table 1, one can obviously see that the S_{BET} increased greatly in the order of β - $< \gamma$ - $< \alpha$ -MnO₂, indicating that α -MnO₂ had the highest S_{BET} among the three MnO₂ catalysts. This observation was mainly attributed to their



Fig. 5 N_2 adsorption-desorption isotherms (a) and pore size distribution curves (b) of MnO₂ with different crystal phases.

different tunnel sizes as revealed by crystal structures in Fig. 2. It can be seen that the tunnel size of the three MnO₂ catalysts increased gradually in the order of β - $< \gamma$ - $< \alpha$ -MnO₂, agreeing well with the variation order in S_{BET} . It can be noted that the larger the tunnel size is, the higher the S_{BET} is. This fact can be mainly related to the size confinement of N₂ molecules (3.05 Å) in a certain scope during the testing process of S_{BET} .

The surface chemical compositions and chemical valence states of the three MnO_2 catalysts have been studied by employing an XPS technique as shown in Fig. 6. The survey spectra in Fig. S2 (ESI[†]) revealed that all of the three MnO_2 catalysts only contained Mn and O elements and no other impurities were detected, suggesting their high purity. The high-resolution spectrum of the Mn2p region in Fig. 6a demonstrated two spin–orbit doublets with binding energies of around 641.7 eV and 653.4 eV corresponding to $Mn2p_{3/2}$ and $Mn2p_{1/2}$,^{18,19} respectively. The signals of Mn^{4+} and Mn^{3+} cations can be observed after the decomposition of Mn2p spectra by using Gaussian fitting methods. Two distinct peaks with binding energies of about 642.8 eV and 654.2 eV were



Fig. 6 XPS spectra of MnO_2 with different crystal phases: Mn2p of (a) and O1s of (b).

indexed to the typical Mn4+ cations while two major peaks with binding energies of approximately 641.6 eV and 652.8 eV were assigned to the characteristic Mn³⁺ cations.¹⁹ The presence of Mn³⁺ cations is generally linked to the formation of oxygen vacancies. To identify the origin of oxygen vacancies, the highresolution spectrum of the O1s region for three MnO2 catalysts in Fig. 6b has been deconvoluted into two major peaks at binding energies of around 529.9 eV and 531.7 eV corresponding to the lattice oxygen (Olatt) species and surface chemisorbed oxygen (O_{ads}) species (e.g. O_2^{2-} , O_2^{-} , OH^- or O^-),³²⁻³⁶ respectively. Usually, the number or concentration of oxygen vacancies can be normally reflected by the peak intensity of surface chemisorbed oxygen (O_{ads}) species according to previous reports.^{32,33} Interestingly, the peak intensity of Oads in Fig. 6b increased slightly in the sequence of α - < γ - < β -MnO₂, indicating the increased number or concentration of oxygen vacancies. Based on the XPS analysis, the quantified surface chemical compositions and chemical valence states of three MnO₂ catalysts have been calculated and are listed in Table 2. It can be seen that the Mn^{4+}/Mn^{3+} molar ratio increased gradually in the order of β - γ - < α -MnO₂, effectively attesting that α -MnO₂ had the highest number or concentration of Mn4+ cations, which was in good accordance with previous studies.^{18,19} Taking into account the fact that the Mn species with higher chemical value states were more conductive to the oxidation reactions over a Mn-based catalyst, $^{14,38-40}$ it can be speculated that α -MnO₂ will show higher catalytic activity in acetone oxidation. However, the Oads/Olatt

Table 2 Surface elemental compositions and chemical value states of MnO_2 with different crystal phases

	Mn2p envelope			O1s envelope			
Catalysts	Mn ⁴⁺ (%)	Mn^{3+} (%)	Mn ⁴⁺ /Mn ³⁺	O _{ads} (%)	O_{latt} (%)	O _{ads} /O _{latt}	
α-MnO ₂	47	53	0.89	21	79	0.27	
β -MnO ₂	37	63	0.59	25	75	0.33	
γ-MnO ₂	39	61	0.64	23	77	0.30	

molar ratio increased gradually in the sequence of α - $\langle \gamma$ - $\langle \beta$ -MnO₂, obviously manifesting β -MnO₂ with the highest number or concentration of oxygen vacancies and also showing an inverse trend to the variation order in the Mn⁴⁺/Mn³⁺ molar ratio, which can be ascribed to the reason that the formation of oxygen vacancies was mainly contributed by the presence of characteristic Mn³⁺ cations. Meanwhile, the above results were in good accordance with the characterization as revealed by Raman and EPR analysis.

The reducibility of the three MnO₂ catalysts has been evaluated by using H₂-TPR experiments as depicted in Fig. 7a. Generally, the reduction of MnO₂ often undergoes threestepwise reduction processes of $MnO_2 \rightarrow Mn_2O_3 \rightarrow Mn_3O_4 \rightarrow$ MnO.^{15,17-20} In this study, it should be emphasized that the reduction products of the three MnO₂ catalysts were green powder, indicating that the final reduction products of the three MnO₂ catalysts were MnO. Clearly, β-MnO₂ demonstrated three distinct reduction peaks situated at about 327 °C, 385 °C and 475 °C, which can be associated with the simultaneous reductions of $MnO_2 \rightarrow Mn_2O_3$, $Mn_2O_3 \rightarrow Mn_3O_4$ and $Mn_3O_4 \rightarrow$ MnO,^{15,17,18} respectively. In contrast, the H₂-TPR profiles of α - and γ -MnO₂ were greatly different from that of β -MnO₂. α-MnO2 only exhibited two reduction peaks centered at around 264 °C and 325 °C. Similarly, γ-MnO₂ displayed two reduction peaks located at approximately 325 °C and 485 °C. The reduction process giving rise to these peaks of α - and γ -MnO₂ could not be elucidated in detail, but probably involved the reduction of $MnO_2 \rightarrow MnO$ with the simultaneous reductions of Mn₂O₃ and Mn₃O₄.^{18,20} Interestingly, it should be noted that the former peaks of α - and γ -MnO₂ shifted dramatically to the lower temperature as compared with β -MnO₂, unquestionably signifying their enhanced low-temperature reducible ability. The amount of H₂ consumed below 350 °C has been acquired by quantitatively calculating the reduction peaks in the H2-TPR profiles of the three MnO₂ catalysts as listed in Table 3. It can be observed that the H₂ consumed amount increased greatly in the trend of β - < γ - < α -MnO₂, apparently indicating that



Fig. 7 H_2 -TPR (a) and O_2 -TPD (b) profiles of MnO₂ with different crystal phases.

Table 3Chemical structural parameters and special activities of MnO_2 with different crystal phases

	Consumption (mmol g^{-1})		Special activity (°C) ^a			P at 160 °C
Catalyst	H_2	O ₂	T_{10}	T_{50}	T ₉₀	$(\text{mol m}^{-2} \text{ s}^{-1})$
$\begin{array}{l} \alpha\text{-MnO}_2\\ \beta\text{-MnO}_2\\ \gamma\text{-MnO}_2 \end{array}$	7.81 2.07 5.11	0.22 0.07 0.11	72 93 85	93 144 122	104 159 133	$\begin{array}{c} 6.94 \times 10^{-6} \\ 6.53 \times 10^{-6} \\ 6.79 \times 10^{-6} \end{array}$

 $\alpha\text{-MnO}_2$ possessed the highest low-temperature reducibility. This observation can be mainly attributed to the fact that $\alpha\text{-MnO}_2$ contained more Mn^{4+} cations than $\beta\text{-}$ and $\gamma\text{-MnO}_2$ since the reduction of $Mn^{4+} \rightarrow Mn^{2+}$ required much more H_2 than the reduction of $Mn^{3+} \rightarrow Mn^{2+}$, fairly agreeing well with the results of XPS analysis. Meanwhile, from Table 1, it can be seen that the average Mn–O bond length in MnO_2 ranked in the order of $\beta\text{-} < \gamma\text{-} < \alpha\text{-MnO}_2.^{18,20}$ Usually, the longer the average Mn–O bond length is, the easier the Mn–O bond can be reduced. This might be also responsible for the highest low-temperature reducibility of $\alpha\text{-MnO}_2$.

The adsorption and activation potentials of the three MnO₂ catalysts towards different oxygen species have been studied by performing O₂-TPD experiments as presented in Fig. 7b. Obviously, one can see that all the MnO₂ catalysts demonstrated three kinds of desorption peaks with respect to oxygen species as follows: the low-temperature desorption peak located at less than 400 °C, the medium-temperature desorption peak situated in the range of 400-600 °C and the high-temperature desorption peak exceeding 600 °C, which were mainly assigned to the desorption of chemisorbed surface active oxygen species (e.g. O_2 , O_2^- and O^-), the liberation of sub-surface lattice oxygen (O²⁻) and the release of bulk lattice oxygen (0²⁻),^{17,19,41} respectively. Meanwhile, it can be found that the desorption peaks below 600 $^\circ C$ of $\alpha\text{-}$ and $\gamma\text{-}MnO_2,$ especially α -MnO₂, shifted slightly to the lower temperature in comparison with β -MnO₂, distinctly suggesting α -MnO₂ with the highest adsorption and activation potentials towards surface active oxygen species. Based on the O2-TPD profiles of the three MnO2 catalysts, the desorption amount of surface active oxygen species below 350 °C has been quantitatively calculated and is listed in Table 3. Clearly, it can be seen that the desorption amount of surface active oxygen species increased significantly in the order of β - < γ - < α -MnO₂, further confirming α -MnO₂ with the highest adsorption and activation potentials towards surface active oxygen species. However, the above result seems to contradict the characterization as disclosed by EPR and XPS analysis. Usually, the more the oxygen vacancies and the surface chemisorbed oxygen (Oads) species of catalysts are, the higher the adsorption and activation potentials of catalysts towards surface active oxygen species are.⁴² α-MnO₂ showed the highest adsorption and activation potentials towards active oxygen species although it had the relatively lowest number of oxygen vacancies and the surface chemisorbed oxygen (O_{ads}) species as evidenced in Fig. 3b and 6b. This observation could be possibly attributed to the reason that α -MnO₂ had the largest tunnel size (see Fig. 2 and Table 1) as compared with β- and γ-MnO₂, which facilitated the enhanced adsorption and diffusion of active oxygen species due to its less mass transfer and diffusion resistance, thereby improving its adsorption and activation potentials towards active oxygen species effectively. Meanwhile, the average Mn–O bond length in MnO₂ increased slightly in the sequence of β - $\langle \gamma$ - $\langle \alpha$ -MnO₂, which might also account for the highest desorption amount of surface active oxygen species of α -MnO₂ due to the fact that the longer the average Mn–O bond length is, the easier the Mn–O bond is broken.¹⁸

3.2. Catalytic performance

The catalytic performances of the three MnO₂ catalysts have been evaluated by using acetone oxidation as a model reaction at atmospheric pressure ranging from 50 °C to 200 °C under the reaction conditions of acetone concentration = 1000 ppm, 20 vol% O_2/N_2 and WHSV = 90000 mL g_{cat}^{-1} h⁻¹. Blank experiments revealed that no measurable acetone oxidation can be found to take place without catalysts in the examined temperature range, and only CO₂ and H₂O as the final products can be detected over three MnO₂ catalysts under the experimental conditions employed. As shown in Fig. 8a, one can clearly see that the acetone conversion over the three MnO₂ catalysts increased dramatically along with the increasing reaction temperature, albeit to their greatly distinguishing degrees. Complete acetone conversion can be achieved at reaction temperatures of approximately 120 °C, 190 °C and 150 °C for α -, β - and γ -MnO₂, respectively. The produced CO₂ concentrations over the three MnO₂ catalysts have been also monitored and quantitatively analyzed as plotted in Fig. 8b. Notably, the produced CO_2 concentrations over three MnO_2 catalysts also increased significantly along with the rise in the reaction temperature regardless of their different degrees, almost showing the same trend as the acetone conversion curves. Combining the normalization of acetone conversion



Fig. 8 Acetone conversion curves (a), the produced CO₂ concentration curves (b) and the corresponding T_{10} , T_{50} and T_{90} (c) of MnO₂ with different crystal phases based on the same mass basis at WHSV = 90 000 mL g_{cat}⁻¹ h⁻¹.

and the produced CO_2 concentration, the CO_2 /acetone molar ratio was calculated to be around 2.97, which was very close to the theoretical value of 3.0, attesting that acetone was completely oxidized to CO₂ and H₂O under the present conditions. For intuitively comparing the catalytic performances of the three MnO₂ catalysts, the reaction temperatures of T_{10} , T_{50} and T_{90} corresponding to the achieved acetone conversion of 10%, 50% and 90%, respectively, are employed as the evaluation criteria for acetone oxidation. From Table 3 and Fig. 8c, it is obvious that the T_{10} , T_{50} and T_{90} of the three MnO₂ catalysts ranked in the same sequence of α - $< \gamma$ - $< \beta$ -MnO₂, undeniably showing that α -MnO₂ gave the optimal acetone oxidation activity in this study. Meanwhile, from Table S1 (ESI⁺), it should be emphasized that the catalytic activity of α -MnO₂ was also much higher than those of many previously reported catalysts for acetone oxidation, mainly including noble metal-based, Co-based, Fe-based, Cu-based, Ce-based, Ti-based and V-based catalysts together with some multi-component metal oxides, which further confirmed the excellent acetone oxidation activity of α -MnO₂.

Importantly, it should be pointed out that the activity data in Fig. 8 were acquired by performing acetone oxidation over the three MnO₂ catalysts based on the same catalyst mass basis rather than simultaneously on the same surface area basis. Therefore, the effect of surface area on the acetone oxidation activity must be considered, mainly due to the fact that acetone oxidation as a typical gas-solid heterogeneous catalytic reaction usually occurs at the binary-phase contact interface or boundary.^{8,43-45} Accordingly, the activity evaluation of acetone oxidation over the three MnO2 catalysts has been carried out on the basis of the same surface area by using β -MnO₂ as a reference: the S_{BET} fixed at 1.6 m² is equal to 100 mg of β -MnO₂, 26.7 mg of α -MnO₂ and 34.8 mg of γ -MnO₂, respectively. As shown in Fig. 9a and b, the acetone conversion and the produced CO₂ concentration of the three MnO₂ catalysts also increased greatly along with the increasing reaction temperature irrespective of their



Fig. 9 Acetone conversion curves (a), the produced CO₂ concentration curves (b) and the corresponding T_{10} , T_{50} and T_{90} (c) of MnO₂ with different crystal phases based on the same surface area basis at WHSV = 90 000 mL g_{cat}⁻¹ h⁻¹.

distinctly different degrees, completely achieving acetone conversion at 160 °C, 200 °C and 180 °C for α -, β - and γ -MnO₂, respectively, which demonstrated the same variation trend as the obtained results as revealed in Fig. 8a and b. Meanwhile, as shown in Fig. 9c, it can be observed that the respective T_{10} , T_{50} and T_{90} of the three MnO₂ catalysts also increased significantly in the order of α - $< \gamma$ - $< \beta$ -MnO₂, further reconfirming α -MnO₂ with the optimal acetone oxidation activity in this study. For guaranteeing the activity order more accurately, the acetone conversion rate at 160 °C over the three MnO₂ catalysts has been calculated by using the activity data in Fig. 9a according to the equation of R_s (mol m⁻² s⁻¹) = $\eta QC_f/S$, where η , Q, C_f and S referred to the acetone conversion, the volumetric flow rate (mL min $^{-1}$), the feed of acetone concentration (ppm) and the surface area of the catalyst (m^2) , respectively. As listed in Table 3, it can be noticed that α -MnO₂ showed the highest acetone conversion rate among the three MnO₂ catalysts, further validating α -MnO₂ with the optimal acetone oxidation activity in this study.

Considering the above results in Fig. 8 and 9 together with the R_s in Table 3, it can be concluded that α -MnO₂ had the optimal acetone oxidation activity owing to the fact that the acetone oxidation activity increased gradually in the order of β - < γ - < α -MnO₂ in this work. Meanwhile, it can be said that the surface area of the three MnO₂ catalysts did not play a crucial role in catalyzing acetone oxidation in this work. Hence, the distinguishing acetone oxidation activities of the three MnO₂ catalysts can be mainly correlated with their different crystal phases together with their caused different physicochemical properties as follows. Firstly, the three MnO₂ catalysts possessed different crystal phases, which resulted in different crystal tunnel structures and tunnel sizes. The tunnel size of the three MnO₂ catalysts increased gradually in the sequence of β - < γ - < α -MnO₂, indicating that α -MnO₂ possessed the relatively largest tunnel size. The largest tunnel size favored the enhanced adsorption and diffusion of acetone molecules, which in turn enlarged the contact interface or the contact frequency of acetone molecule-catalyst and thus, effectively improved the acetone oxidation activity of α-MnO₂. Secondly, the Mn^{4+}/Mn^{3+} molar ratio (see Table 2) of the three MnO_2 catalysts varied in the sequence of β - $< \gamma$ - $< \alpha$ -MnO₂, attesting that α-MnO₂ contained the relatively highest amount of Mn⁴⁺ cations. As mentioned in previous studies,^{14,38-40} it is well known that the Mn species with higher chemical value states were more conductive to the oxidation reactions over a Mn-based catalyst. Thus, the relatively highest amount of Mn⁴⁺ cations in α-MnO₂ facilitated its enhanced acetone oxidation activity. Thirdly, the low-temperature reducibility and the amount of surface active oxygen species (see Table 3) for three MnO₂ catalysts also increased gradually in the trend of β - < γ - < α -MnO₂, validating the highest low-temperature redox potential of α -MnO₂, which also accounted for the enhanced acetone oxidation activity of α-MnO2. Moreover, it has been reported that the Mn-O bond strength of MnO₂ catalysts can play an important role in determining their catalytic performances according to previous reports.18,20 The longer

the average Mn–O bond length is, the weaker the Mn–O bond strength is. It can be noted that the average Mn–O bond length of the three MnO₂ catalysts increased slightly in the order of β - < γ - < α -MnO₂, suggesting the longest average Mn–O bond length and the weakest Mn–O bond strength of α -MnO₂. Accordingly, the Mn–O bond can be most easily broken in α -MnO₂ for acetone oxidation, which can also endow α -MnO₂ with the improved catalytic performance. Therefore, it can be concluded that all the above factors through the synergistic effect simultaneously contributed to endow α -MnO₂ with the highest acetone oxidation activity.

The effect of WHSV on the acetone oxidation activity over the three MnO₂ catalysts has been investigated as shown in Fig. 10. Obviously, it can be seen that the acetone conversion over the three MnO₂ catalysts decreased dramatically and a much higher reaction temperature of three MnO₂ catalysts was required for completely achieving acetone conversion with the increase in the WHSV value from 90 000 mL g_{cat}^{-1} h⁻¹ to 240 000 mL g_{cat}^{-1} h⁻¹. In other words, the increase in the WHSV value lead to the lower acetone conversion at the same reaction temperature, which can be further validated by the evidence that the respective T_{10} , T_{50} and T_{90} of acetone conversion over the three MnO₂ catalysts were increased to higher temperatures along with the increase in the WHSV value. These distinguishing acetone oxidation activities of the three MnO₂ catalysts with respect to the WHSV value were mainly attributed to the shorter retention time of acetone molecules in the catalyst bed at a higher WHSV value,^{8,43-45} which significantly shorten the contact time or reduced the contact frequency of acetone molecule-catalyst and thus, decreased the acetone oxidation activity.

The catalyst deactivation is a big challenge that urgently requires addressing for practical applications. Meanwhile, it is well-known that water is often produced during the VOC oxidation process and also has an adverse effect on the catalytic activity.43-45 Thus, the long-term stability and water tolerance of catalysts for VOC oxidation are generally considered as two important evaluation criteria for their potential in practical applications. Accordingly, the long-term stability over the three MnO₂ catalysts for testing 48 h has been evaluated under the reaction conditions of acetone concentration = 1000 ppm, 20 vol% O_2/N_2 and WHSV = 90 000 mL g_{cat}^{-1} h⁻¹ at two selected different reaction temperatures corresponding to the acetone conversions of approximately 60% and 100%, respectively. As shown in Fig. 11, it can be noticed that all of the three MnO₂ catalysts demonstrated strong long-term stability at the two selected different reaction temperatures, acetone conversions being almost unchanged and stable at around 60% and nearly 100% in the entire catalytic oxidation test. The effect of H₂O vapor on the acetone oxidation activity over the three MnO2 catalysts has also been studied by separately introducing 8.0 vol% and 16 vol% H₂O vapor into the reaction system. The experimental results in Fig. 11 revealed that the acetone conversions at the selected different reaction temperatures for reacting 12 h apparently decreased gradually from nearly 100% to around 95%, 91% and 82% for α -, β - and γ -MnO₂, respectively, when 8.0 vol% H₂O vapor was introduced. Subsequently, the acetone conversion further decreased to about 78%, 87% and 79% for α -, β - and γ -MnO₂, respectively, when 16 vol% H₂O vapor was introduced. This observation validated that the H₂O vapor had a detrimental effect on the acetone oxidation activity of the three MnO₂ catalysts, which was mainly due to the presence of competitive adsorption between the



Fig. 10 Acetone conversion curves and the corresponding T_{10} , T_{50} and T_{90} of MnO₂ with different crystal phases at different WHSVs.



Fig. 11 Long-term stability test and the effect of H₂O vapor on catalytic activity for MnO₂ with different crystal phases at WHSV = 90 000 mL g_{cat}^{-1} h⁻¹.

acetone molecule and H₂O vapor on the surface of catalysts.⁴³⁻⁴⁵ Interestingly, it can be noticed that the acetone conversion over the three MnO₂ catalysts could immediately recover back to almost 100% in several hours once the H₂O vapor was interrupted, indicating that three MnO₂ catalysts had good tolerance for H₂O vapor at a certain content. However, it should be emphasized that the acetone conversion of β-MnO₂ (87%) decreased much smaller than those of α - (78%) and γ -MnO₂ (79%) when 16 vol% H₂O vapor was introduced, indicating its relatively higher water tolerance, which could be possibly ascribed to its higher stable crystal phase.

4. Conclusions

In summary, three kinds of MnO₂ nanorods with different crystal phases have been successfully fabricated by a one-pot hydrothermal method and their crystal-phase dependent catalytic performances for acetone oxidation have been investigated in detail. The results reveal that α -MnO₂ gave the optimal acetone oxidation activity as compared with β - and γ -MnO₂, which was attributed to its unique crystal phase that resulted in the synergistic effect by combining the largest crystal tunnel size, the highly enhanced chemical nature originating from more Mn⁴⁺ cations, the highly improved low-temperature redox properties and the weakest Mn-O bond strength. Meanwhile, they also presented strong long-term stability and good water tolerance for acetone elimination, showing good potential in practical applications. We believe that the findings from this study can deliver some new insights for guiding the rational design of highly efficient catalysts applied in VOC elimination.

Conflicts of interest

There are no conflicts to declare.

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