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Insights into the solar light driven thermocatalytic oxidation of VOCs over tunnel structured manganese oxides

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Different tunnel structured manganese oxides (1*1, 2*2, and 3*3) have been synthesized *via* a facile hydrothermal strategy. The three catalysts exhibit high photothermal performance, resulting in considerable increase of temperature above the light-off temperature for VOCs oxidation. On this point, aerobic oxidations of propane and propylene under simulated sunlight and infrared light irradiation were selected as probe reactions to explore the light driven thermocatalytic activity. Furthermore, the light-off curves of the manganese oxides for propane and propylene were carefully investigated, which clearly explained the possibility of combining both the efficient photothermal effect and excellent thermocatalytic activity of the manganese oxides. Results show that the catalytic effects follow the order of 1*1 < 3*3 < 2*2. 2*2 exhibited the best catalytic properties due to better low-temperature reducibility, suitable tunnel structure and the presence of more Mn⁴⁺. This work suggests new applications for traditional catalysts with intense photoabsorption and provides the insights into the overall utilization of solar energy.

1. Introduction

Volatile organic compounds (VOCs) as major air pollutants are not only hazardous to human health but also harmful to the environment.¹ Among the strategies for the elimination of VOCs, catalytic oxidation using transition metal oxides has been highly promising because of its technical and economic feasibility.² However, high operating temperature in this process means low energy efficiencies, and will compromise the long-term stability of catalysts, decrease the selectivity for the desired products.^{3, 4} At present, The efficient removal of VOCs at mild temperature is becoming a crucial but challenging issue in the context of increasingly serious air pollution.⁵

The recently emerged photothermal effect of catalysts suggests a new means for harvesting solar energy. The infrared light, accounting for almost half of the solar energy, has not been utilized effectively by traditional semiconductor-based solar energy conversion technology that is mainly active in the region from ultraviolet to visible light.⁶ As most light sources supply full spectrum irradiation, suitable catalysts can efficiently transform the absorbed solar energy (typically the

1295 Dingxi Road, Shanghai 200050, P. R. China. E-mail: <u>wzwang@mail.sic.ac.cn</u> ^{b.} University of Chinese Academy of Science, Beijing 100049, People's Republic of China. infrared part) to thermal energy, resulting in a considerable increase of temperature, which is just enough to stimulate the thermocatalytic oxidation of VOCs.^{7, 8} Recently, Meng *et al.*⁹ investigated the *Group VIII* nanocatalysts, which showed effective energy utilization over the whole range of the solar spectrum, excellent photothermal performance, and unique activation abilities, thus realizing a two-step water-based CO_2 conversion driven by solar energy. Furthermore, we have previously shown that the maximum utilization of photothermal conversion can be realized through amorphous MnO_x modified Co_3O_4 ¹⁰ or conductive substrate supported Co_3O_4 systems.⁴

Manganese oxides are among the prominent candidates for catalytic reactions due to their outstanding structural uniformity, low cost, and environmental compatibility.^{11, 12} More importantly, they possess strong photoabsorption ability and exhibit excellent photothermal effect. Manganese oxides have very diverse structures, depending on the connectivity between the [MnO₆] units via sharing corners or edges.¹³ Among them, considerable attentions have been paid to the tunnel structured manganese oxides due to their distinguished catalytic performances.¹⁴ Typically, three types of square tunnel structures of manganese oxides including pyrolusite, cryptomelane and todorokite are showed in Fig. 1. Pyrolusite $(\beta-MnO_2)$ is featured for its corner-shared MnO₆ in its structural unit and forms a small tunnel structure (1 * 1, ca. $0.23\,\times\,0.23\,$ nm²) absent of extra water and cations. 12 The accessibility to β -MnO₂ is limited due to small voids in the structure,¹⁵ which further deteriorates the activity. The crystal structure of cryptomelane consists of two double edge-sharing MnO₆ octahedral chains, which are corner-connected to form one-dimensional tunnels (2 * 2, ca. 0.46×0.46 nm²).¹⁶ Because

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Electronic Supplementary Information (ESI) available: [Fig. S1-S6 displayed the N₂ adsorption-desorption isotherm, pore size distributions, blank experiments for C₃H₈ and C₃H₆ oxidation, C₃H₈ and C₃H₆ oxidation under Xe lamp and IR lamp irradiation, UV-Vis-IR spectra and HCHO degradation for the 1*1, 2*2, and 3*3 catalysts during the three cycles]. See DOI: 10.1039/X0xX00000x

temperature. The resulting black slurry was filtered, washed with deionized water and then freeze-dried.

The todorokite manganese oxide (3*3) was prepared through two steps. Briefly, buserite was initially prepared by the co-precipitation method. MnCl₂·4H₂O (0.2969 g) and MgCl₂·6H₂O (0.5083 g) were dissolved into 25 ml deionized water to form a mixed solution, to which the 8.8 M NaOH (25 ml) was rapidly added. Then 0.025 M KMnO₄ (25 ml) solutions were successively added to the above solution with a speed of 62.5 mL/h. The mixture was aged at 60 °C for 24 h and then washed by the deionized water to obtain buserite. 3*3 was prepared by the addition of the buserite above into 40 mL deionized water, and charged into a 50 mL Teflon-lined autoclave at 160 °C for 24 h. The system was allowed to cool down to room temperature. The resulting black slurry was filtered, washed with deionized water and then freeze-dried.

2.2 Characterization

The purity and crystallinity of the manganese oxides was measured by X-ray diffraction (XRD) using a Rigaku D/MAX 2250 V diffractometer with monochromatized Cu Ka radiation (λ =0.15418 nm) under 40 kV, 100 mA and with the 2 θ ranging from 10° to 80°. The morphologies and structures of the samples were characterized by transmission electron microscope (TEM), high-resolution transmission electron microscopy (HRTEM) (TecnaiG2 F20 S-Twin, accelerating voltage 200 kV), and N₂ adsorption-desorption measurements using a V-sorb 2800P surface area analyzer. The specific surface areas were calculated by the Brunauer-Emmett-Teller (BET) method. Pore volume and pore size distribution plots were obtained by the Barrett-Joyner-Halenda (BJH) method. X-ray photoelectron spectroscopy (XPS) were obtained by irradiating every sample with a 320 μ m diameter spot of monochromated aluminum Ka X- rays at 1486.6 eV under ultrahigh vacuum conditions (performed on ESCALAB 250, THERMO SCIENTIFIC Ltd.). Charging effects were corrected by adjusting the binding energy of C 1s to 284.6 eV. UV-vis diffuse reflectance spectra (DRS) of the samples were measured using a Hitachi UV-3010PC UV-vis spectrophotometer. Hydrogen temperature-programmed reduction (H₂-TPR) measurements were performed (for each sample, 50 mg) on a ChemiSorb 2750 instrument equipped with a thermal conductivity detector, under a 4 vol% H_2/Ar flow (25 mL min⁻¹) at a heating rate of 10 °C min⁻¹.

2.3 Light driven catalytic oxidation of C_3H_8 and C_3H_6

The catalytic activities of all the samples were evaluated by the gas-phase aerobic oxidation of C_3H_8 (50 ppm) and C_3H_6 (50 ppm). The apparatus used was described in earlier papers²². Experiments were operated in a gas-closed vitreous reactor (capacity 600 mL) with a quartz window, and a 500 mW cm⁻² Xe lamp was lighted to simulate the optical excitation and thermal activation. Before the catalytic test, a thermocouple was placed on the catalyst to measure the temperature of the catalyst under the irradiation of the Xe lamp. During the oxidation process, a GC analysis (GC 7900, Techcomp) equipped with two detective channels was used to detect the



of its unique structural characteristics such as porous structure, mixed valency of Mn, easy release of lattice oxygen, *etc.*, cryptomelane has been extensively investigated for diverse applications of catalytic oxidation.¹ The todorokite crystals possess a specific oxide-type structure with a framework consisting of triple chains of edge-sharing MnO₆ octahedra that corner-share to form tunnels of *ca*. 0.69 × 0.69 nm² (3 * 3).^{17, 18} The todorokite shows significantly larger adsorptive capacity for molecules with size dimensions close to its tunnel size, *e.g.* C₆H₁₂ and CCl₄.¹⁹

Specifically, herein we report three kinds of tunnel structured manganese oxides via hydrothermal synthesis, which show strong absorption in the entire solar spectrum region and transform the absorbed solar energy to thermal energy. Aerobic oxidations of propane (C_3H_8) and propylene (C_3H_6) under simulated sunlight and infrared light irradiation were selected as probe reactions to explore the light driven thermocatalytic activity for the first time. The surface area, tunnel structure, degree of crystallinity, Mn^{4+} species, and reducibility of the catalyst has been integrally discussed. In addition, this work offers a new way for the overall utilization of solar energy, by combining both the efficient photothermal effect and excellent thermocatalytic activity of the tunnel structured manganese oxides.

2. Experimental

2.1 Material preparation

Preparation of pyrolusite (1*1).²⁰ For a typical synthesis, MnCl₂·4H₂O (8 mmol) and an equal amount of $(NH_4)_2S_2O_8$ were added to 40 mL distilled water at room temperature to form a homogeneous solution, which was then transferred into a 50 mL Teflon-lined stainless steel autoclave, sealed and maintained at 140 °C for 12 h. The system was allowed to cool down to room temperature. The resulting black slurry was filtered, washed with deionized water and then freeze-dried.

The cryptomelane (2*2) sample was prepared according to the similar procedure reported by Hou *et al.*: ²¹ MnCl₂·4H₂O (1.25 mmol) and KMnO₄ (2.5 mmol) were added to 40 mL distilled water at room temperature to form a homogeneous solution, which was then transferred into a 50 mL Teflon-lined stainless steel autoclave, sealed and maintained at 100 °C for 24 h. The system was allowed to cool down to room DOI: 10.1039/C6CP02776H

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decrease of C_3H_6 , C_3H_8 and the increase of CO_2 simultaneously. The channel for C_3H_8 and C_3H_6 detection consists of a TM plot-Al₂O₃/S capillary column and a flame ionization detector (FID). Another channel for CO_2 detection consists of a TDX-01, 80–100 mesh packed column followed by a methane conversion furnace and a FID. In addition, an infrared (IR) lamp was also used as the light source to simulate the thermal activation.

2.4 Thermocatalytic oxidation of C_3H_8 and C_3H_6

The thermocatalytic activities of all the samples for C_3H_8 and C_3H_6 oxidation were tested in a quartz tube reactor with an inner diameter of 10mm at atmospheric pressure. 200 mg of the manganese oxides were used as catalyst. The reagent gas consisted of 100 ppm C_3H_6 + 50 ppm C_3H_8 +20% O_2 + the balance made up of N_2 at a steady flow rate of 200 SCCM, thus giving a weight hourly space velocity (WHSV) of 60 L h⁻¹ g⁻¹. The reactants and products were analyzed online by gas chromatograph (GC) equipped with a TCD. The activity of the catalysts was characterized by T_{10} , T_{50} , and T_{90} , which represent the temperature of target gas conversion at 10, 50, and 90%, respectively.

2.5 Room temperature oxidation of formaldehyde (HCHO)

The catalytic oxidation activity of the as-prepared samples (50 mg) for HCHO degradation (260 ppm) was tested in a gasclosed vitreous reactor (capacity 650 mL) with a double-walled jacket with water for temperature control. During the experiment, the reaction temperature was kept at 25 °C by circulating water. The activity of the catalysts on HCHO oxidation was estimated by the concentration change of HCHO before and after the 60 min oxidation process. HCHO concentration in the reactor was analyzed by phenol spectrophotometric method. 10 mL gas sample containing trace HCHO was absorbed by 15 mL phenol reagent solution $(1 \times 10^{-4} \text{ wt \%})$ for 5 min. Then, 1.2 mL (1 wt %) ammonium ferric sulfate solution was added as the coloring reagent. After being shaken and waiting for 15 min in the dark, HCHO concentration was determined by measuring light absorbance at 630 nm with a spectrophotometer (Hitachi U-3010 UV-vis spectrophotometer). CO and CO₂ were monitored by GC analysis (GC 7900, Techcomp).



3. Results

3.1 Textural characterization of the catalysts

Fig. 2 gives the XRD patterns of the manganese oxides. The diffraction patterns of the 1*1 prepared by the reaction of MnCl₂ with (NH₄)₂S₂O₈ match standard diffraction for pyrolusite (β -MnO₂, JCPDS 24-0735). The 2*2 obtained from the reaction of MnCl₂ with KMnO₄ showed intense diffraction peaks at 2 θ = 12.8°, 17.9°, 28.7°, 37.7°, 41.9°, 49.9°, and 56.1°, which can be attributed to the crystalline phase of pure tetragonal cryptomelane (KMn₈O₁₆, JCPDS 29-1020).²³ XRD pattern for the synthesized 3*3 is in agreement with the previous reports.^{12, 24} The diffraction peaks can be indexed to the orthorhombic phase of the todorokite MnO₂ (JCPDS 38-0475). To take the intensities and half-widths of the diffraction peaks into account, the degree of the crystallinity decreases in the sequence: 1*1> 2*2 > 3*3.

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The morphology and size of the as-prepared manganese oxides were estimated by TEM. Fig. 3 shows the TEM images of the manganese oxides with different magnifications. It can be clearly seen that both 1*1 and 2*2 can be characterized by the morphology of nanorods with lengths of ca. 0.5~2 µm and diameters of ca. 15~50 nm. Generally, the diameter of 1*1 is much larger than 2*2. 3*3 displays a completely different morphology. As shown in Fig. 3, 3*3 is characterized by the morphology of hexagon nanosheets with side lengths of ~30 nm. More notably from the high resolution TEM image, homogeneous worm-like pores distributed among nanoparticulates can be observed within every nanosheet, suggesting the mesoporous structure of 3*3. $^{\rm 25}$

 $N_{\rm 2}$ adsorption-desorption isotherms of different manganese oxides catalysts and their corresponding pore size distribution



Fig. 3	TEM	images	of	1*1	(A1-3),	2*2	(B1-3),	and	3*3
(C1-3).								

Table 1.	Pore	structural	parameters	of	the	manganese
oxides.						

catalysts	1*1	2*2	3*3	
BET surface area(m ² /g)	8.7	35.8	61.9	
pore volume(cm ³ /g)	0.109	0.163	0.532	
Average pore				
diameter(nm)	25.5	16.6	26	

are shown in. Fig S1 (supporting information (SI)). BET surface areas of the 1*1, 2*2, and 3*3 are 8.7, 35.8, and 61.9 m²g⁻¹, respectively (Table 1). The surface area increases with the increase of tunnel sizes of the three samples. 1*1 possesses the lowest surface area, which may be due to its smallest tunnel size as a result of the densely packed manganese octahedra.²⁶

3.2 Surface composition and reducibility of the catalysts

XPS was performed to further investigate the surface compositions and elementary oxidation states. The XPS spectra of Mn 2p and O 1s for 1*1, 2*2, and 3*3 are displayed in Fig. 4A, 4B. The oxidation state of Mn and the relative levels of the Mn⁴⁺/Mn³⁺ atomic ratio are analyzed by studying the Mn 2p_{3/2} spectra (Table 2). Fig. 4A shows that Mn 2p_{3/2} has two components displayed in binding energy at 642.1 and 643.2 eV, which are due to the surface Mn³⁺ and Mn⁴⁺ ions, respectively.²⁷ From Table 2, the surface Mn⁴⁺/Mn³⁺ molar ratios of 1*1, 2*2, and 3*3 are 0.877, 0.961, and 0.639, respectively. The 2*2 catalyst possess the highest ratio of Mn⁴⁺/Mn³⁺ on the surface, and the 3*3 displays the lowest



<u>1*1, 2*2, and 3*3.</u>

 Table 2. Summary of area percentages of different

 elemental components obtained from the deconvoluted

 spectra

sample	01		02		03		Mn ⁴⁺ /Mn ³⁺
	eV	%	eV	%	eV	%	
1*1	529.9	69.9	531.6	30.1			0.877
2*2	530	66.6	531.1	33.4			0.961
3*3	529.9	33.6	531.1	60.2	532.8	6.2	0.639

ratio. Different surface oxygen species have been identified by the deconvoluted O 1s spectrum. Fig. 4B revealed the fitted O1s peaks. In detail, the peak at 529.4-529.8 eV (O1) is originated from lattice oxygen,²⁷ the peak at 531.1–531.8 eV (O2) is attributed to a high number of defect sites with a low oxygen coordination, ⁸ and the peak at 532.8 eV (O3) is associated with hydroxyl species of surface-adsorbed water molecules.²⁸ As reported in Table 2, the percentages of different surface oxygen species are nearly the same for 1*1 and 2*2. The area of the peak of O2 is the largest for the 3*3 among the three samples, which indicates that the 3*3 with mesoporous structure possess more oxygen vacancies than the other counterparts. These oxygen vacancies are related to the coexistence of Mn³⁺ and Mn⁴⁺ ions.²⁰ XPS can only quantify elements on the surface of a material. However, if the channel structure and specific surface area in the bulk phase of mesoporous 3*3 is considered, 3*3 should possess many more surface adsorbed oxygen species (typically O2).

Reducibility of the manganese oxide catalysts, an important factor known to be correlated with their redox activity, was investigated by means of H₂-TPR (Fig. 5). The TPR profile of manganese oxides usually presented two well-resolved reduction peaks, which indicated a two-step reduction for MnO₂: MnO₂ \rightarrow Mn₃O₄, Mn₂O₃ \rightarrow MnO.^{29, 30} Among all the samples, 1*1 showed a low reduction temperature of 288 °C with a two-step reduction (the second locates at 389 °C). 3*3 also showed a two-step reduction (at 359 and 476 °C) and the ratio of the lower temperature peak to the higher temperature peak was around 2. The lower temperature reduction was attributed to the reduction of MnO₂ to Mn₃O₄ and the higher







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temperature peak was attributed to the reduction of Mn_3O_4 to MnO. Similar reduction profiles were previously observed for MnO_2 which supports our assignments.^{28, 31} On the other hand, 2*2 only showed one broad reduction peak centered at 306 °C , which is typical for large and nonporous particles.^{31, 32} What's more, the temperature where the reduction peak of 2*2 starts is lower than that of 1*1. When the three manganese oxides are compared based on their lowest temperature reduction peaks and terminated temperature ranges, the enhanced reducibility of the samples is in the order 1*1 < 3*3< 2*2.

3.3 Catalyst activity evaluation

The light-off temperature for C_3H_8 oxidation is significantly higher than that for $C_3H_6^{33,34}$, which can be easily understood on the basis of the generally higher activity of alkenes compared to alkanes. The light driven catalytic activity of the manganese oxides were investigated by evaluating the aerobic oxidation of C_3H_8 (50 ppm) and C_3H_6 (50 ppm) under the simulated solar irradiation from the Xe lamp. The C_3H_8 and C_3H_6 catalytic oxidation cannot proceed at room temperature without being irradiated. Besides, blank tests in the absence of any catalyst were performed (Fig. S2, SI). The photolysis of



Fig. 7 (A) (B) The light-off curves of the manganese oxides for C_3H_8 and C_3H_6 .

Table 3. Reaction Temperatures at which the C_3H_8 and C_3H_6 conversions are 10, 50, and 90%.

sample	T ₁₀ (°0	T ₅₀	(°C)	T ₉₀ (°C)		
ID	C₃H ₈	C_3H_6	C_3H_8	C_3H_6	C_3H_8	C_3H_6
1*1	251	185	300	223	350	263
2*2	191	119	227	168	263	205
3*3	233	170	276	210	312	245

C₃H₆ contributed to less than 14% of C₃H₆ decrease under Xe lamp irradiation, while changes in C_3H_8 content were not distinct, indicating the indispensable role of the catalyst. The concentration variations (C_t/C_0) of C_3H_6 against the irradiation time over various catalysts are shown in Fig. 6, while all the catalysts display no catalytic activity towards C₃H₈ (results not shown). A rapid decrease of the C3H6 concentration was observed in the presence of the 2*2 catalyst. About 78.1% C₃H₆ oxidation was achieved within 20 min. Meanwhile, after the Xe lamp irradiation for 20 min, the C_3H_6 oxidation of 1*1 and 3*3 is only 28.2% and 55.4%, respectively. In general, 2*2 exhibits the highest light driven catalytic activity in comparison to the behavior of the other two. Cutoff filter (> 690 nm) had been used to determine the catalytic activity of the manganese oxides under the infrared irradiation of the Xe lamp, related results were shown in Fig. S3. For 2*2, about 50% C₃H₆ oxidation were achieved within 20 min, which accounted for nearly 60% of the catalytic activities under the irradiation of Xe lamp with full spectrum. Specifically, much enhanced catalytic activities were realized for all the catalysts when an extra IR lamp was used for the same experiments (Fig. S2 and S4, SI), especially the 2*2, 20.3% C₃H₈ and 98% C₃H₆ oxidation was achieved within 20 min.

Moreover, C_3H_8 and C_3H_6 were chosen for the individual thermocatalytic oxidation tests to determine the temperature when the catalytic activity of the manganese oxides starts (T_s). Fig. 7A, 7B show the light-off curves of the manganese oxides for C_3H_8 and C_3H_6 . The reaction temperatures of T_{10} , T_{50} , and T_{90} (corresponding to the target gas conversion = 10%, 50%, and 90%, respectively) for the catalysts is compared (Table 3). As shown in Fig. 7A, 7B and Table 3, all the measured T_{10} , T_{50} , and T_{90} temperatures follow the order of 1*1 > 3*3 > 2*2. The performance of 3*3 is relatively close to 1*1. For the same conversion (C_3H_6), the temperature 3*3 needed is just *ca*. 15 °C lower than that of 1*1. Remarkably, as compared to 3*3 and 1*1, 2*2 shows a tremendous decrease (for C_3H_6 , $\Delta T_{10} = 51-66$ °C, $\Delta T_{50} = 42-55$ °C, $\Delta T_{90} = 40-58$ °C) at the reaction temperature of T_{10} , T_{50} , and T_{90} .

4. Discussion

4.1 Photothermal effect

The photoabsorption ability is quite important for efficient photothermal conversion. We measured the UV-Vis-IR spectra of 1*1, 2*2, and 3*3. All the three samples show strong absorption in the entire solar spectrum region (Fig. S5). Before the catalytic tests, the photothermal effect was measured. The temperature evolution profiles of 1*1, 2*2, and 3*3 under the irradiation of the Xe lamp are shown in Fig. 8A. Generally, the temperature of the samples quickly increases from room temperature to more than 100 °C in 120 s with the lamp on. When the temperature reaches a plateau, an equilibrium is established between the absorption of light energy and the energy dissipation from the catalyst to the surroundings⁷. The plateau temperatures (T_p) of 1*1, 2*2, and 3*3 are 157°C, 142 °C and 165 °C, revealing their efficient photothermal

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structure and possessed more Mn⁴⁺, which may be the major

general, more readily reduced surface species have higher

redox activities because their reduction occurs at lower

temperature. It is well known that low-temperature reducibility is one of the critical factors for the oxidation reaction. Secondly, despite its medium degree of crystallinity and surface area, the tunnel structure of 2*2 takes a great

effect for its catalytic activity. The manganese oxides with the

tunnel structure show molecular-sieve properties.¹² The

accessibility to 1*1 is limited due to small voids in the

structure,¹⁵ while 3*3 shows significantly larger adsorptive

capacity for molecules with size dimensions close to its tunnel

size.¹⁹ Considering of the size dimensions of the C_3H_8 and C_3H_6 molecules (0.40~0.43 nm), tunnel structure of 2*2 is suitable

for the adsorption of C₃H₈ and C₃H₆. The tunnel diameter of

2*2 was reported to be a major factor that gave rise to its high catalytic activity.¹² Similar results occurred for the catalytic oxidation of HCHO without light or heat source (fig. S6), while

Firstly, 2*2 shows the highest reducibility (H₂-TPR, Fig. 5). In

factors that lead to its excellent activity.

A Xe lamp 160 140 120 100 T (°C) 120 180 240 300 360 420 480 t (s) 300 в IR lamp 250 200 T (°C) 150 2*2 3*3 100 120 180 240 420 300 360 t (s) Fig. 8 Temporal change of the temperature on the

catalysts under the irradiation of the Xe lamp (A) and IR lamp (B).

conversion. When IR lamp was used as the light source, the temperature of the samples quickly increases from room temperature to more than 150 °C in 120 s (Fig. 8B). The values of T_p are 226 $^{\circ}C$ (1*1), 258 $^{\circ}C$ (2*2), and 244 $^{\circ}C$ (3*3), much larger than that under the Xe irradiation.

The manganese oxides did not exhibit photocatalytic activity via the traditional photocatalytic route at room temperature. The efficient catalytic activity of the three tunnel structured manganese oxides under the Xe or IR lamp irradiation originates from the light (typically the infrared part) driven thermocatalysis.⁷ Integrating the results of Fig. 7B and Fig. 8A, apparently, the light off temperature (T_s) of 1*1 (~150 °C), 2*2 (~80 $^{\circ}$ C), and 3*3 (~120 $^{\circ}$ C) for C₃H₆ oxidation is lower than their corresponding $T_{\rm p}$ no matter under Xe or IR lamp irradiation. Thus, the high $T_{\rm p}$ induced by efficient photothermal conversion is enough to trigger off thermocatalytic C₃H₆ oxidation for the catalysts in the light irradiation experiments. As for the C_3H_8 oxidation, the situation is opposite. Considering the much higher T_p when the IR lamp is used, there is no doubt for the much higher catalytic activity.

4.2 Mechanism discussion

It is believed that catalytic activities are associated with the surface area, tunnel structure, degree of crystallinity, oxygen defect, and transition-metal ion redox ability (reducibility) of the catalyst. $^{\rm 35}$ So the question is why the 2*2 catalyst shows much higher activities. It can be concluded that the influence induced by the photothermal effect can be ignored on account of the smaller T_n of 2*2 compared to that of 1*1 and 3*3 under Xe irradiation. From the characterization results, 2*2 exhibited higher low-temperature reducibility, suitable tunnel





either a small amount of Mn³⁺ or a large amount of Mn⁴⁺ (or both together) are important for high activity of CO oxidation catalysts,³⁷ which is consistent with the present study. For 3*3 with the lowest degree of crystallinity, highest surface area, and more surface adsorbed oxygen species (table 2), its catalytic activity is clearly not as expected. In this regard, the larger 0.69 \times 0.69 nm² tunnel size of 3*3, the poorer reducibility, and the presence of higher Mn³⁺ content is considered to be responsible for diminished activity. 5. Conclusions In summary, tunnel structured manganese oxides (1*1, 2*2,

and 3*3) have been synthesized through a facile hydrothermal method. The three kinds of catalysts exhibit strong absorption in the entire solar spectrum and shows strong solar heating effect, resulting in a considerable increase of temperature above the light-off temperature for VOCs oxidation. Aerobic oxidations of C_3H_8 and C_3H_6 under simulated sunlight were performed, while rapid decreases of the C_3H_6 concentration were observed. Enhanced catalytic activities were realized for all the catalysts when the IR lamp was used for the same experiments. Much higher T_p can be realized under the infrared light irradiation, resulting in better catalytic activities. Furthermore, the light-off curves of the manganese oxides for C_3H_8 and C_3H_6 clearly explained the mechanism of the light driven thermocatalytic oxidation. The catalytic activities under all the test conditions followed the order 1*1 < 3*3 < 2*2. The excellent catalytic property of the 2*2 catalyst is primarily due to better low-temperature reducibility, suitable tunnel

structure and the presence of more Mn⁴⁺. On the basis of this study, a brand new strategy for catalyst design toward the fully use of both the efficient photothermal effect and excellent thermocatalytic activity is suggested.

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