

Complete Formaldehyde Removal over 3D Structured Na_{1.1}Mn₄O₈@Mn₅O₈ Biphasic-Crystals

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With the increasing concerns on the formaldehyde (HCHO) hazard, the efficient oxidation of HCHO over affordable and harmless catalyst is of significant practical interest. Herein, the intermediate state of $Mn_5O_8-Na_{1.1}Mn_4O_8$ ($Na-Mn_5O_8$) biphasic-crystal catalyst, which features $Na_{1.1}Mn_4O_8$ -nanosheet@ Mn_5O_8 -nanorod interconnected 3D structure, is successfully fabricated through the anaerobic calcination of manganite followed by alkali treatment. The resultant $Na-Mn_5O_8$ exhibits 100% conversion of HCHO (150 ppm and 60000 h⁻¹) and reliable stability (50 h) at 90°C under demanding water-free feed conditions, which is superior to that of the reference samples of Mn_5O_8 ,

1. Introduction

Formaldehyde (HCHO), a major pollutant among volatile organic compounds and one of the 1st group human carcinogens, released from modern building materials, furniture and consumables poses a serious threat to our living quality and health.^[1] It is urgent to develop appropriate technologies for efficient HCHO removal. Catalytic oxidation of HCHO to harmless CO₂ and H₂O is the most promising approach for the HCHO elimination due to its continuous and facile operation.^[2] Although the noble metal-based catalysts, such as Pt/PbO,^[3] Pt/ $ZrO_{27}^{[4]}$ Au/FeO_x^[5] and Pd/TiO₂₇^[6] exhibited complete oxidation of HCHO even at room temperature, the unaffordable cost limits their practical application in large scale. Thus, there are many interests in developing highly efficient HCHO oxidation catalysts using the transition metal oxides such as MnO_{2i} ^[7] Co₃O₄,^[8] CeO₂,^[1b] MnO₂–CeO₂,^[1b,9] TiO₂^[10] and FeO_x.^[11] Among them, manganese oxide (MnOx) catalysts, a serial of environ-

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 $Na_{1.1}Mn_4O_{87}$, MnO_2 and $Na-MnO_2$. The experimental results demonstrate that the abundant structure defects (oxygen vacancies) on $Na-Mn_5O_{87}$, which may locate along the phase interfaces / shared-edges of Mn_5O_8 nanorods and $Na_{1.1}Mn_4O_8$ nanosheets, significantly enhance the active oxygen species and finally contribute to the high activity for HCHO oxidation. Furthermore, the 3D structure of $Na-Mn_5O_8$ favors mass transfer and fully exposing active sites for the HCHO adsorption and conversion. These findings reveal a way to enhance the catalytic activity of metal oxides via controlling the intermediate state of heteropical crystals.

mental-friendly materials, were widely studied due to their excellent reactivity in many catalytic oxidation reactions e.g. ethyl acetate and CO oxidation.^[12] Compared with the noble metal based catalysts, however, MnO_x is still challenged by the relatively low reactivity for HCHO oxidation.

MnO_x could compose by a wide range of stoichiometry of Mn and O in the formation of various crystal phases like β -MnO₂, γ -MnO₂, α -Mn₂O₃, γ -Mn₂O₃ and α -Mn₃O₄ due to the special electronic structure of Mn 3d⁵4s^{2,[13]} To improve the reactivity of MnO_x, many efforts have been made by investigating the effects of valance state, crystal structure, defects and heteroatoms on the HCHO oxidation. Zhang et al. found that δ -MnO₂ is more active than α -, β - and γ -MnO₂ due to its special 2D layered structure and high lattice oxygen migration rate.^[14] Rong et al. demonstrated that 3D structure MnO₂ has high reactivity in HCHO conversion owing to the increased amount of active sites and the intensified mass transfer over the catalysts.^[15] Furthermore, the heteroatoms also play an important role on the reactivity of MnO_x. With doping Ce atoms into MnO₂ lattice, the surface adsorbed oxygen species and the migration rate of surface lattice oxygen were improved, led to an enhanced HCHO oxidation performance.^[1b,16] Xu et al. introduced K⁺ ions into the lattice of manganese oxide to form d-sp hybrid orbitals, which improved the activity of lattice oxygen and the surface adsorbed oxygen species in the HCHO oxidation.^[17] On the other hand, it is well known that the mixed valency catalysts have higher reactivity in the catalytic oxidation because that the high-low valences cycling benefits to the oxidation of reagent and recovery of catalyst.^[11] However, MnO_x studied for HCHO oxidation mostly focus on MnO₂ with Mn(IV) in the catalysts. Thus, it is highly attractive to improve the catalytic performance by developing Mn mixed valency catalysts. Mn₅O₈ has the chemical formula of Mn(II)₂Mn(IV)₃O₈, possessing a mixed valency of Mn. It has a similar crystal structure to Cd₂Mn₃O₈ and Ca₂Mn₃O₈ which is a highly



asymmetric monoclinic structure. In addition, Mn_5O_8 has a layered structure composed of a $[Mn_3O_8]^{4-}$ anionic layer with a MnO_6 octahedron and a Mn^{2+} cationic layer, which would be easy for the heteroatom intercalation. $^{[18]}$ According to the aforementioned effects of valency, crystal structure and heteroatom on the reactivity of MnO_2 based catalysts, these special features of Mn_5O_8 signs a great potential in catalytic oxidation of HCHO.

In the present work, we designed and demonstrated a facile strategy to fabricate 3D Mn_5O_8 – $Na_{1.1}Mn_4O_8$ mixed-crystalline catalyst, comprised of $Na_{1.1}Mn_4O_8$ -nanosheet@ Mn_5O_8 -nanorod hybrid structure and large and accessible surface area, through the anaerobic calcination of manganite followed by alkali treatment. The resultant co-crystal catalysts exhibited excellent activity and reliable stability for the complete oxidation of HCHO. The structure, surface chemistry, redox properties and oxidation performance of the intermediate phase of Mn_5O_8 – $Na_{1.1}Mn_4O_8$, pure phases of Mn_5O_8 and $Na_{1.1}Mn_4O_8$ as well as the reference samples of MnO_2 and Na– MnO_2 were investigated in detail. Concomitantly, the role of the unique features of Mn_5O_8 – $Na_{1.1}Mn_4O_8$ on HCHO oxidation mechanism was also evaluated.

2. Results and Discussion

2.1. Structure and texture of MnO_x based catalysts

Figure 1A illustrates the preparation procedure of manganese oxides. Mn₅O₈ and MnO₂ (reference sample) nanorods could be obtained by heating the precursor of manganite (MnOOH) in inert atmosphere and air, respectively. In sequence, the Na-Mn₅O₈ biphasic-crystals (i.e. Mn_5O_8 -Na_{1.1} Mn_4O_8) and pure phase of Na_{1.1}Mn₄O₈ are prepared by the different strength of alkali treatments on Mn₅O₈. The structure transformation of the manganese oxide species in preparation was monitored by Xray diffractometry (XRD), as shown in Figure 1B. The uncalcinated precursor is assigned to the manganite i.e. Mn³⁺O (OH) species (JCPDS 41-1379), which transferred to Mn₅O₈ (JCPDS 39-1218) upon the calcination in N₂. After the 1st alkali treatment on Mn₅O₈, interestingly, additional two sharp and intense peaks at 12.5 and 25.2°, ascribed to $Na_{1.1}Mn_4O_8\cdot 3H_2O$ (JCPDS 43–1456), were observed. It suggests that partial Mn_5O_8 transferred to Na_{1.1}Mn₄O₈·3H₂O, resulting in Mn₅O₈-Na_{1.1}Mn₄O₈ (Na-Mn₅O₈) biphasic-crystals. Further treating the Na-Mn₅O₈ biphasic-crystals with harsher conditions, the residual Mn₅O₈ in Na-Mn₅O₈ biphasic-crystals were completely convert into the pure phase Na_{1.1}Mn₄O₈, as only Na_{1.1}Mn₄O₈ pattern was observed.

As control, β -MnO₂ (JCPDS 24-0735) could be obtained by calcining MnOOH in air. In addition, β -MnO₂ kept stable upon the alkali treatment because of no visual structure changes were observed from the XRD pattern of alkali treated β -MnO₂ (Figure S1). The structure analysis indicates that the intermediate phase between pure Mn₅O₈ and Na_{1.1}Mn₄O₈ can be fabricated through an appropriate alkali treatment of Mn₅O₈. On the other hand, it also reveals that Na ions are easily

intercalate into the $[Mn_3O_8]^{4-}/Mn^{2+}$ layered structure of Mn_5O_8 in compared with MnO_2 .

The morphology and microstructure of these samples were measured by scanning electron microscopy (SEM) and transmission electron microscopy (TEM), as shown in Figure 2. As MnOOH prefers to grow along the [0 0 1] direction, the precursor MnOOH exhibited a tetragonal nanorod structure with a high aspect ratio (Figure 2A and B). Under the high resolution, MnOOH displayed the ordered microstructure with an interplanar spacing of 0.263 nm (Figure 2C), which can be assigned to MnOOH (0 2 0). The nanorod morphology of MnOOH was well remained for the obtained Mn₅O₈ (Figure 2D and E). The interplanar spacings are 0.486 and 0.501 nm, matching the (2 0 0) and (-1 1 0) facets of Mn_5O_8 , respectively (Figure 2F). Interestingly, the Na–Mn₅O₈ biphasic-crystals display two kinds of morphology, in which the ultrathin 2D nanosheets formed along the edges of Mn₅O₈ nanorods to build an interconnected 3D structure (Figure 2G). As the single nanorod shown in Figure 2I, the ultrathin nanosheet sprouted along the longitudinal direction of Mn₅O₈ nanorod. This epitaxiaL growth nanosheet was proved as Na1.1Mn4O8 due to the interplanar spacing of 0.242 nm is ascribed to $Na_{1.1}Mn_4O_8$ (2 0 –2). For the Na_{1.1}Mn₄O₈ sample, the nanorod structure disappeared and only wrinkling nanosheets were observed (Figure 2J). The nanosheet of Na_{1.1}Mn₄O₈ displayed a scroll structure with the nanorod as an axis (Figure 2K). The unchanged interplanar spacing (0.242 nm) proves the formation of $Na_{11}Mn_4O_8$ pure phase. This is consistent with the XRD analysis. During the phase transition from Mn_5O_8 to $Na_{1,1}Mn_4O_8$, it is reasonable that a part of Mn_5O_8 nanorod was firstly dissolved in the alkali solution and then rearranged and epitaxially grew on the defect surface of Mn₅O₈ until the whole Mn_5O_8 nanorod was used up. Generally, high index plane contains the highly discordant electron distribution, which leads to the high reactivity.^[19] Herein, the higher index planes exposed on Na-Mn₅O₈ may benefit to its activity in the HCHO oxidation. In addition, catalytic reaction active site tends to be the structural defects, such as edges and corners. The intermediate phase of Na-Mn₅O₈ potentially have higher defects density due to the uncomplete phase transition and thus high reactivity in HCHO oxidation. On the other hand, the phase transition from 1D nanorod of Mn₅O₈ to 2D nanosheet of Na1.1Mn4O8 and 3D nano-sheet/rod significantly increased the specific surface areas from 27.6 to 50.8 and 47.1 m^2g^{-1} , respectively (Table 1).

Table 1. Physicochemical properties of Mn_5O_8,MnO_2 and their derivatives.							
Samples	S _{BET} [m²/g]	XPS Na [at.%]	Mn/O	O_{ads}/O_{latt}	Mn^{4+}/Mn^{2+}	AOS	
Mn₅O ₈	27.6	0	0.50	0.50	0.6	2.8	
Na–Mn₅O ₈	47.1	5.1	0.25	0.61	1.7	3.4	
Na _{1.1} Mn ₄ O ₈	50.8	10.7	0.32	0.43	_[a]	3.7	
MnO ₂	10.7	0	0.36	0.21	_[a]	3.9	
Na-MnO ₂	14.1	2.1	0.27	0.39	_[a]	3.9	
[a] Only Mn (IV) was indicated by the XPS results.							

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Figure 1. (A) Scheme of MnO_x preparation; (B) XRD patterns of MnOOH, Mn_5O_8 , $Na-Mn_5O_8$ mixed-crystal and $Na_{1.1}Mn_4O_8$.

As comparison, the as-prepared MnO₂ also exhibited a nanorod morphology (Figure S2). The interplanar spacing, 0.318 nm, was ascribed to β -MnO₂ (1 1 0), in line with the XRD measurements. Unlike the morphology change for alkali treated Mn₅O₈, Na–MnO₂ remained the nanorod morphology of MnO₂ and the almost same interplanar spacing of 0.316 nm, which confirms the structure stability of MnO₂ in the alkali treatment.

2.2. Surface chemistry of MnO_x catalysts

The surface chemical states of catalysts were elucidated by Xray photoelectron spectroscopy (XPS). The Mn2p spectrum of Mn₅O₈ shows typically two components of Mn 2p3/2 and Mn 2p1/2, in which the binding energies 642.9/654.7 eV and 641.0/ 652.8 eV could be ascribed to Mn (IV) and Mn (II), respectively (Figure S3). In comparison, the Mn2p peaks of Na–Mn₅O₈ and Na_{1.1}Mn₄O₈ shifted to higher binding energies, indicating a more oxidic state of Mn and an increased content of Mn(IV).^[20]





Figure 2. SEM (A, D, G, J) and TEM (B, C, E, F, H, I, K, L) images of MnOOH (A–C), Mn₅O₈ (D–F), Na–Mn₅O₈ (G–I) and Na_{1.1}Mn₄O₈ (J–L).

Similarly, the Mn 3 s XPS also displayed the oxidation state of surface Mn atoms. Two peaks appear in the Mn 3 s spectra because of the coupling of Mn 3 s electron with Mn 3d electron giving rise to parallel or antiparallel spin configuration.^[21] The magnitude of the splitting energy of Mn 3 s peaks increase approximately linearly as the Mn oxidation state decreases, which can be described as the empirical Equation 1:^[22]

 $\Delta E \approx 7.88 - 0.85n \tag{1}$

Where ΔE is the Mn 3 s binding energy difference and n ($2 \le n \le 4$) is the average oxidation state (AOS) of the Mn atoms. The value of ΔE decreased from 5.50 eV for Mn₅O₈ to 4.98 and 4.74 eV for Na–Mn₅O₈ and Na_{1.1}Mn₄O₈, respectively (Figure 3A). Correspondingly, the AOS of Mn increased from 2.8 for Mn₅O₈ to 3.4 for Na–Mn₅O₈ and further to 3.7 for Na_{1.1}Mn₄O₈ (Table 1), in line with the Mn2p results. It is reasonable that the surface electron density on the treated samples was decreased by the intercalation of Na⁺, leading to the increase of valence state of Mn. It has been reported that the Mn mixed oxide with higher Mn (IV) content possess higher reactivity in the oxidation.^[23] Therefore, it suggests that alkali treated samples would more active in the HCHO oxidation. In contrast, the valence state of MnO₂ kept unchanged at Mn (IV) before and after the alkali

treatment due to the stable structure of MnO_2 (Table 1 & Figure S4).

The O 1s XPS spectrum of Mn₅O₈ can be deconvoluted into three peaks at 529.78 eV, 531.03 eV and 532.88 eV, corresponding to lattice oxygen (O_{latt}), surface adsorbed oxygen (O_{ads}) species (such as $\mathrm{O_2^-}$ and $\mathrm{O^-}$ groups) and adsorbed -OH group (O_{OH}), respectively (Figure 3B).^[24] O_{latt} and O_{ads} were the predominant O species on Mn₅O₈. Compared with Mn₅O₈, the peaks of O_{latt} and O_{ads} of $Na-Mn_5O_8$ and $Na_{1.1}Mn_4O_8$ shifted to higher binding energies, which might be contributed to the changes in the chemical environment of oxygen atoms after rearrangement of crystal. The formation of atom vacancy would reduce the electron density around \boldsymbol{O}_{latt} and therefore increase the binding energies of O_{latt}.^[7c] Owing to the lower valence state of Na⁺ than Mn (II) / Mn (IV), furthermore, the O atoms around the Mn defects are unsaturated, which are easy to be hydroxylated.^[24] Therefore, the content of O_{OH} increased from 7.7% for Mn_5O_8 to 11.8-13.2% for the alkali treated samples (Figure 3B). In addition, the O vacancies and /or unsaturated O atoms are migratable as active oxygen species due to the weak interaction between O and Na⁺. The active oxygen species play a key role in the oxidation of HCHO. On one hand, the O_{ads} tends to participate into the oxidation reaction due to its high activity and the interaction between catalyst surface and

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Figure 3. (A) Mn 3 s, (B) O 1s and (C) Na 1s XPS spectra and (D) FT-IR spectra of Mn₅O₈, Na–Mn₅O₈ and Na_{1,1}Mn₄O₈.

reactant. On the other hand, O_{latt} with high mobility enhances the formation of surface active oxygen species through the complex migration between surface lattice oxygen and oxygen vacancies.^[7c] In this case, Na–Mn₅O₈ owned the highest O_{ads} content, i.e. 32.9% and the largest O_{ads}/O_{latt} ratio of 0.61 among these samples (Table 1 and Figure 3B), suggesting that Na–Mn₅O₈ contains abundant atom (oxygen) vacancies and thus possesses high reactivity for HCHO oxidation.

The Na content on sample surface increased from 0 for Mn_5O_8 to 5.1 and 10.7 at.% for Na $-Mn_5O_8$ and Na_{1.1}Mn₄O₈, respectively (Figure 3C and Table 1), in line with the observation of XRD. Compared with the Mn_5O_8 based samples, the Na⁺ content in Na $-MnO_2$ is much lower (Figure S5 and Table 1), confirming the relative inertness of MnO_2 in the alkali

conditions. Both experimental and simulation have suggested that alkali metal ions can facilitate the activation of oxygen molecules and lattice oxygen.^[17] The surface groups of catalysts were measured by FT–IR (Figure 3D and Figure S6). The bands at 3250–3,500 cm⁻¹ and 1650 cm⁻¹ can be ascribed to the stretching vibration of –O–H and the bending vibration of –OH groups in water, respectively.^[25] Among these samples, Na–Mn₅O₈ possesses more –OH groups, which is consistent with the O1s XPS analysis.

The local structure state and the lattice oxygen activity of Mn_5O_8 , $Na-Mn_5O_8$ and $Na_{1,1}Mn_4O_8$ were analyzed by Raman spectroscopy (Figure 4A). The Raman band located around 270 cm⁻¹ could be attributed to the stretching vibration of Mn_5O_8 ,^[22] which is weakened for $Na-Mn_5O_8$ and then disap-





Figure 4. (A) Raman spectra and (B) Mn–O bond force constant of Mn₅O₈, Na–Mn₅O₈ and Na_{1.1}Mn₄O₈.

peared for Na_{1.1}Mn₄O₈. In contrast, there is no signal around 270 cm⁻¹ for MnO₂ and its alkali treated sample (Figure S7), suggesting that it is a characteristic band for Mn₅O₈. It is clear that Na-Mn₅O₈ is an intermediate mixed-crystal containing unconverted Mn₅O₈ while Na_{1.1}Mn₄O₈ is single phase without Mn₅O₈ residues. The Raman band around 640 cm⁻¹ can be attributed to the [MnO₆] symmetric stretching vibrations.^[26] The band intensity gradually weakened with the alkali treatment. In addition, the Raman shift moved from 643 cm⁻¹ of Mn₅O₈ and $Na_{1.1}Mn_4O_8$ to 638 cm⁻¹ of Na–Mn₅O₈, which may be contributed by the oxygen vacancies in Na–Mn₅O₈.^[27] The Raman band around 570 cm⁻¹ is assigned to the stretching vibration caused mainly by Mn⁴⁺ in the basal plane of the [MnO₆] sheet.^[28] This band was found as a tiny shoulder signal for Na-Mn₅O₈ but a strong peak for Na1.1Mn4O8. It confirms that more Mn (IV) formed in sequence for $Na-Mn_5O_8$ and $Na_{1.1}Mn_4O_8$, in agreement with the XPS results. In addition, no band ascribed to Na⁺ /O interaction was found in the Raman results. It reveals that no strong bond of Na-O was formed and the unrestricted Na⁺ and lattice oxygen would help to adsorb and activate oxygen and HCHO molecules.[13]

Based on the Hooke's law, on the other hand, the Mn–O bond force constant (k) can be calculated from the Raman results by using the following equation (2).^[29]

$$\omega = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}}$$
(2)

where ω is the Raman shift (cm⁻¹) around 640 cm⁻¹, *c* is the velocity of light (ms⁻¹), and μ is the effective mass (g). As shown in Figure 4B, Na–Mn₅O₈ owned the lowest Mn–O force constant (*k*). However, the *k* value of pure Na_{1.1}Mn₄O₈ even a little bit higher than Mn₅O₈. This reveals that the decreased k of

Na–Mn₅O₈ is mostly caused by the intermediate state of Na–Mn₅O₈. In other words, the existence of oxygen vacancies in Na–Mn₅O₈ contributes to the decline of Mn–O force constant. Furthermore, all Mn₅O₈ based samples displayed lower *k* than that of MnO₂ and Na–MnO₂ (Figure S9). It means that MnO₂ structure is more stable than Mn₅O₈ as already proved by XRD and XPS results, and correspondingly, Mn₅O₈ is more active than MnO₂, which will be confirmed by the following HCHO oxidation. According to the above analysis, the uncomplete phase transition from Mn₅O₈ to Na_{1.1}Mn₄O₈ left abundant oxygen vacancies in Na–Mn₅O₈, which impacts the interactions of Mn–O and then the oxidation activity for HCHO.

Figure 5A shows the hydrogen temperature programmed reduction (H₂-TPR) profiles of the Mn₅O₈ based samples. The profile of Mn₅O₈ reveals two peaks between 230 and 390°C, representing the initial reduction of adsorbed active oxygen species and the reduction of Mn_5O_8 to MnO_v (y < 1.6), respectively.^[30] For Na-Mn₅O₈ and Na_{1.1}Mn₄O₈, the reduction of active oxygen species slightly shifted from 235 °C for Mn₅O₈ to 268 and 278 $^\circ\text{C},$ respectively. This reveals that the intercalation of Na⁺ contributed to the activation and adsorption of oxygen and then reinforce the interaction force of active oxygen on the sample.^[31] With the decrease of Mn₅O₈ content in the sample, on the other hand, the peak intensity of Mn₅O₈ reduction gradually declined for Na-Mn₅O₈ and Na_{1.1}Mn₄O₈. As the new generated Mn (IV) is easier reduced, furthermore, the reduction temperature slightly decreased from 384°C for Mn₅O₈ to 377 and 368 °C for Na–Mn₅O₈ and Na_{1.1}Mn₄O₈, respectively, due to the increase of Mn (IV) content in these samples.

The oxygen activation of the samples was measured by oxygen temperature programmed desorption (O_2 -TPD) analysis (Figure 5B). The signals in the O_2 -TPD profiles at low temperature (<300 °C), moderate temperature (300–600 °C), and high temperature (>600 °C) correspond to the release of surface





Figure 5. (A) H₂-TPR and (B) O₂-TPD of Mn₅O₈, Na–Mn₅O₈ and Na_{1.1}Mn₄O₈.

chemisorbed oxygen molecules / active surface oxygen, subsurface lattice oxygen and bulk lattice oxygen, respectively.^[32] Oxygen that released at low temperature was considered as labile oxygen species, which was highly active for HCHO oxidation. $\mathsf{Mn}_{\mathsf{5}}\mathsf{O}_8$ shows only one peak at the moderate temperature, reflecting to a high content of sub-surface lattice oxygen on Mn₅O₈ and a relatively low capacity for oxygen molecule activation. In contrast, the alkali treated samples offer significantly enhanced activation capacity for oxygen molecules because that both of them displayed down-shifted signals at ~130 °C. Importantly, the low temperature signal of Na–Mn₅O₈ is sharper and more intensive than that of Na_{1.1}Mn₄O₈, confirming the high capacity for oxygen activation and adsorption. For the moderate temperature signal, in addition, it decreased from ~540 $^{\circ}$ C for Mn₅O₈ to ~380 $^{\circ}$ C for Na–Mn₅O₈, indicating that the sub-surface lattice oxygen of Na-Mn₅O₈ were well activated. As a reference, only signals at the temperature higher than 500 °C were observed from the O2-TPD measurements of MnO₂ and Na–MnO₂ (Figure S9).

2.3. Catalytic oxidation of HCHO over MnO_x

The catalytic oxidation of HCHO on the catalysts was tested via the continuous flow method in a fixed-bed micro-reactor, as illustrated in Figure S10. Figure 6A shows the temperature dependence of HCHO conversion over the MnO_x catalysts at 50–150 °C. The conversion of HCHO were increased with the rise of reaction temperature. The activity of different samples followed the order: Na–Mn₅O₈ > Na_{1.1}Mn₄O₈ ≈ Mn₅O₈ > Na–MnO₂ ≈ MnO₂. T₁₀₀ (corresponding to the complete conversion temperature of HCHO) of Mn₅O₈ is 110 °C, which is much lower than that of MnO₂ (140 °C). It may be contributed

by the special 2D layered structure, the low Mn-O interaction force and the mixed valency of Mn₅O₈ that have been proved by the measurements above. For the intermediate phase of Na-Mn₅O₈, it exhibited the highest HCHO conversion in the whole range of temperature and the T_{100} value was further declined to 90°C, demonstrating the highest activity among these samples. In comparison, the pure Na_{1.1}Mn₄O₈ exhibited a similar activity to Mn₅O₈. The HCHO oxidation performance of Na-Mn₅O₈ is also compared with the literature results, as shown in Table 2.^[7c,15,24,28,30a,33] Under the similar feeding conditions, $Na-Mn_5O_8$ offers the lowest $T_{100},$ which is even better than the supported metal (e.g. Ag and Ir) catalysts. It is noted that the powder paraformaldehyde was used as HCHO resource in this work, and to keep the HCHO concentration of feedstock stable and reliable, the dehydrated cylinder air was introduced as sweep gas for HCHO feedings. Therefore, the humidity of the feedstock is much lower than the real environment and that used in literature. It has been reported that water/humidity plays a very important role in the promotion of HCHO catalytic oxidation.^[3,34] Therefore, Na-Mn₅O₈ exhibited highly efficient HCHO removal under low humidity conditions. Combination with the structure and chemistry analysis above, the intermediate phase state of Na-Mn₅O₈, which led to a heteropical 3D structure of Na1.1Mn4O8-nanosheet@Mn5O8-nanorod and especially the abundant structure defects (e.g. oxygen vacancies), contributed to the high activity of this material in HCHO oxidation because that both mass transfer of reagents and oxygen/HCHO activation were intensified.

The apparent activation energy (*Ea*) of HCHO oxidation over the catalysts was also calculated by using the Arrhenius equation (Figure 6B). *Ea* for Na–Mn₅O₈, Na_{1.1}Mn₄O₈, Mn₅O₈, Na–MnO₂ and MnO₂ were 44.7, 45.3, 45.7, 53.5 and 58.9 kJ mol⁻¹, respectively, which means HCHO was most easily





Figure 6. (A) HCHO conversion over various MnO_x at different temperature ($\delta_{HCHO} = 150$ ppm, GHSV = 60000 mL g⁻¹ h⁻¹); (B) Temperature dependence of HCHO conversion on various $MnO_{x'}$ (C) Effects of GHSV on the HCHO conversion over Na– Mn_5O_8 at different temperature ($\delta_{HCHO} = 150$ ppm); (D) Temperature cycling of Na– Mn_5O_8 in 50–90 °C and the stability of Na– Mn_5O_8 at 90 °C ($\delta_{HCHO} = 150$ ppm, GHSV = 60000 mL g⁻¹ h⁻¹).

Table 2. Catalytic performance of reported catalysts for the oxidation of HCHO.						
Catalyst	Feeding conditions $[ppmmLg^{-1}h^{-1}]$	T ₁₀₀ [°C]	Ref.			
1 K/MnO ₂	9000	90	[28]			
K ₁ /HMO	8400	120	[30a]			
V _{Mn} -3	4800	100	[24]			
Ag ₁ /HMO	8400	130				
Ir/TiO ₂ –R	12000	125	[31]			
α-MnO ₂ -110	9000	130	[7c]			
3D-MnO ₂	18000	90	[15]			
m-NiO-s	3600	100	[33b]			
Mn–Cu–Ce	6000	170	[33c]			
MnO _x -C-Co ₃ O ₄ -CeO ₂	7200	100	[37]			
Na–Mn ₅ O ₈	9000	90	This work			

activated and oxidized by Na–Mn₅O₈. It is well consistent with the reactivities of these catalysts. Furthermore, the effect of GHSV on the HCHO oxidation was evaluated over Na–Mn₅O₈ in the range of 30,000 to 120,000 mLg_{cat}⁻¹ h⁻¹ (Figure 6C). The value of T₁₀₀ dropped to 75 °C at GHSV = 30000 mLg_{cat}⁻¹ h⁻¹ and then increased to 105 °C under 120000 mLg_{cat}⁻¹ h⁻¹, suggesting that higher GHSV would inhibit the oxidation process. The stability of Na–Mn₅O₈ for HCHO oxidation was tested by temperature cycling in the range of 50–90 °C and long-term operation at 90 °C (Figure 6D). The catalyst displayed stable

performance during the four-time temperature cycling. During 50 h operation, furthermore, the HCHO conversion maintained at ~100% without deactivation. After reaction, no visual change of microstructure was observed from Na–Mn₅O₈ (Figure S10). These indicated the good stability of Na–Mn₅O₈ for the elimination of HCHO.



2.4. Catalytic mechanism of HCHO over $Na-Mn_5O_8$

To gain insights into the reaction, the HCHO oxidation on Na–Mn₅O₈ was investigated by *in situ* diffuse reflectance infrared Fourier transform spectra (DRIFTS) in a flow of HCHO-O₂ mixture at room temperature. As shown in Figure 7A, the absorption bands at 1120, 1340, 1367, 1448, 1518, 1668, 2347, 2846 and 3200–3650 cm⁻¹ were observed from Na–Mn₅O₈. The band at around 1120 cm⁻¹ was corresponded to molecularly adsorbed HCHO.^[11] As the conversion of adsorbed HCHO into its intermediates is a fast step, the intensity of this signal is relatively weak.^[11] The band at 1448 cm⁻¹ was assigned to δ (CH₂) of dioxymethylene species (H₂CO₂, DOM), which are the intermediates of HCHO oxidation and can be easily converted to formate species.^[35] Otherwise, the bands at 1340, 1367, 1518 and 2846 cm⁻¹ could be attributed to v_s (COO), δ (CH), v_{as} (COO)

and v(CH) from the intermediates of formate species $(HCOO^{-})^{[24]}$ Carbonyl carbon in HCHO is electrophilic, which tends to adsorb on nucleophilic surface oxygen atom to form DOM, which will be further oxidized to formate. With the exposure time, the peaks of DOM decreased while the signals of formate increased. It reveals that the conversion of DOM species is a relatively fast step but the further conversion of formate to carbonate species (CO_3^{2-}) is a limited step. The carbonate species were observed at the band of 1668 cm⁻¹, which would finally convert into CO_2 (2347 cm⁻¹). In addition, the negative peak of hydroxyLgroups (~3480 cm⁻¹) was ascribed to the loss of surface –OH, suggesting that –OH groups were involved and consumed in the HCHO oxidation.^[3]

According to the obtained findings, a possible process of HCHO removal on $Na-Mn_5O_8$ is proposed, as shown in Figure 7B. HCHO is firstly adsorbed on the surface of catalyst and



Figure 7. (A) In situ DRIFTS spectra of Na–Mn₅O₈ exposed to the flow of HCHO-O₂ (δ_{HCHO} = 30 ppm) at room temperature; (B) The proposed mechanism of HCHO oxidation over Na–Mn₅O₈.



the adsorption is enhanced by –OH groups via forming hydrogen bonding with HCHO. The adsorbed HCHO would be oxidized by surface active oxygen species into DOM, formate, carbonate and CO₂, in sequence,^[11] as proved by the DRIFTS. On one hand, the surface active oxygen species are released by the redox cycle of Mn(IV)/Mn(II). On the other hand, the oxygen molecules in the feedstock would be adsorbed on the oxygen species. With the consumption of active oxygen, the oxygen vacancies would be recovered for the next cycle. In this process, Na⁺ would enhance the stability of active oxygen species through Na⁺/oxygen species interactions. The consumed –OH groups would be replenished by the reaction between water and active oxygen species.

3. Conclusions

The pure phase of Mn₅O₈ nanorod and Na_{1.1}Mn₄O₈ nanosheet as well as their intermediate phase of Mn₅O₈-Na_{1.1}Mn₄O₈ $(Na-Mn_5O_8)$ were synthesized by anaerobic calcination of manganite with and without alkali treatments. During the phase transformation from Mn₅O₈ to Na_{1,1}Mn₄O₈, the morphology changed from nanorod to ultrathin nanosheet. The intermediate phase of Na- Mn₅O₈ kept both morphologies of these pure phases, resulting in a heteropical 3D structure building by Na1.1Mn4O8-nanosheet@Mn5O8-nanorod. The resultant Na-Mn₅O₈ enables complete conversion of HCHO and reliable stability at low temperature under demanding HCHO feed conditions, which is superior to that of Mn₅O₈, Na_{1.1}Mn₄O₈ and the reference of MnO₂ and Na–MnO₂ in this work as well as that of the reported manganese oxide catalysts. The experimental results demonstrated that the abundant structure defects (oxygen vacancies) on Na-Mn₅O₈, which may locate along the interface of Mn₅O₈ nanorods and Na_{1.1}Mn₄O₈ nanosheets, significantly enhanced the surface active oxygen species and finally contributed to better activity for HCHO oxidation. Furthermore, Na–Mn₅O₈ exhibited continuous interconnected 3D structure, which favors mass transfer and fully expose reaction-active sites for the HCHO adsorption and conversion.

Experimental Section

Preparation of MnO_x

Potassium permanganate (KMnO₄), polyethylene glycol (PEG 400), and sodium hydroxide (NaOH, \geq 96%) were purchased from Aladdin Chemicals (China). All the reagents were analyticaL grade and used without further purification. The MnO_x precursor, MnOOH, was firstly prepared through a hydrothermal method.^[36] In detail, the well mixed solution, containing PEG 400 (2 mL), KMnO₄ (0.1 g) and deionized water (80 mL), was placed into a Teflon-lined autoclave (100 mL) and then heated at 160°C for 5 h. The resultant precipitates were washed with deionized water and ethanol for several times and then dried at 70°C overnight. Mn₅O₈ was obtained by calcining the as-prepared precursor MnOOH at 280°C in N₂ for 2 h. As a reference, MnO₂ was prepared under the air atmosphere at 280°C for 5 h. The Na⁺ doped MnO_x, i.e.

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 $Na_{1.1}Mn_4O_8\cdot 3H_2O-Mn_5O_8$ biphasic-crystals (denoted as $Na-Mn_5O_8$) and $Na-MnO_2$ were synthesized through the reaction between NaOH and the corresponding manganese oxides. In a typical procedure, 0.1 g of as-synthesized manganese oxides was added to 100 mL NaOH solution (40 g L^{-1}) and stirred for 20 h at 100 °C. The resultant solid was then washed with water and dried at 70 °C overnight. For the preparation of pure $Na_{1.1}Mn_4O_8\cdot 3H_2O$ (denoted as $Na_{1.1}Mn_4O_8$), 0.1 g of $Na-Mn_5O_8$ biphasic-crystals was further thermal-treated in NaOH solution (200 g L^{-1}) in autoclave for another 20 h at 160 °C.

Formaldehyde oxidation

The HCHO oxidation over the packed catalyst (100 mg, 40– 60 mesh) was carried out in a tubular fixed-bed quartz reactor under atmospheric pressure (Figure S11). The HCHO feedstock (~ 150 ppm) is generated by passing a stream of pure air (Pujiang Gas Co., Shanghai) through paraformaldehyde powders at room temperature. The gaseous hourly space velocity (GHSV) was controlled in the range of 30,000 and 120,000 mLg_{cat}⁻¹h⁻¹ by adjusting the flux of air. The HCHO concentration of inlet was controlled by the amount of paraformaldehyde and the GHSV, which was confirmed firstly by gas chromatography (GC) for each test. The relative humidity of the feedstock was measured by a psychrometer (i.e. ~30% in this work). The HCHO concentration in the reactant or product gas stream was analyzed by a GC with a thermal conductivity detector (TCD). The HCHO conversion (η_{HCHO}) was calculated by the Equation 3.

$$\eta_{HCHO} = \frac{\delta_{feed} - \delta_{outlet}}{\delta_{feed}} * 100\%$$
(3)

Where $\delta_{\textit{feed}}$ and $\delta_{\textit{outlet}}$ is the HCHO concentration before and after reaction. The reliability of GC method was also confirmed by the phenol spectrophotometric method.^[3] To calculate the apparent activation energy (E_a) of HCHO oxidation on the catalysts, the η_{HCHO} was controlled below 15 % by adjusting GHSV.

Characterization

The crystal structure of catalysts was determined by XRD (Rigaku Ultima IV) using Cu K α radiation (α = 0.15406 nm, 40 kV, 40 mA). The morphology of the catalysts was characterized by a transmission electron microscopy (TEM, JEM-2100, 200 kV) and a scanning electron microscopy (SEM, Zeiss SUPRA 55 SAPPHIRE, 2-20 kV). The near-surface chemical state and elemental composition of catalysts were analyzed by an X-ray photoelectron spectroscopy (XPS, K-Alpha, Al K α radiation, 1486.6 eV, 12 kV, 3 mA). XPS peak positions were calibrated with the help of the C 1s peak at 284.8 eV. The specific surface area of the samples was derived from N₂ sorption measurements carried out on an automatic micropore physisorption analyzer (TriStar II 3020), using the multipoint Brunauer-Emmet-Teller (BET) analysis method. Raman spectroscopy measurements were performed using a Renishaw Raman spectrometer using a 12.5 mW laser source at an excitation wavelength of 532 nm. The chemical information of samples was measured by Fourier transform infrared (FTIR) spectroscopy (Shimadzu IRAffinity-1). A Micromeritics AutoChem II 2920 apparatus, equipped with a thermal conductivity detector (TCD), was used for H₂ temperatureprogrammed reduction (H₂-TPR) and O₂ temperature programmed desorption (O2-TPD) analysis. In situ diffuse reflectance infrared Fourier transform spectra (DRIFTS) of catalysts were recorded in Thermo Fisher 6700. Samples were pretreated by N₂ for 1 min under room temperature before exposing to HCHO containing gas



(~30 ppm at a flow rate of 20 $\rm mL\,min^{-1}$ balanced by pressured oxygen).

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: $Mn_5O_8 - Na_{1.1}Mn_4O_8$ biphasic-crystal \cdot defects formation \cdot nanosheet-nanorod three-dimensional structure \cdot formaldehyde oxidation \cdot low temperature activity

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FULL PAPERS

Formaldehyde oxidation: Complete HCHO removal was achieved at 90 °C under demanding conditions over the interconnected 3D structure of Na_{1.1}Mn₄O₈-nanosheet@ Mn₅O₈nanorod biphasic-crystals. Structure defects on the nano-rod/-sheet shared-edges significantly enhance the activity.



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Complete Formaldehyde Removal over 3D Structured Na_{1.1}Mn₄O₈@Mn₅O₈ Biphasic-Crystals