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Highly Efficient MnO₂/AlOOH Composite Catalyst for Indoor Low-Concentration Formaldehyde Removal at Room Temperature

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ABSTRACT: Indoor formaldehyde from substandard furniture and decorative materials seriously endangers human health. How to remove effectively indoor formaldehyde with low concentration at room temperature is a challenging problem. Using a $MnO_2/$ AlOOH composite by the MnO_2 modification as a catalyst provides an effective approach to solve this challenge. Here, a new type of $MnO_2/AlOOH$ composite catalyst with high ability to remove indoor low-concentration formaldehyde was prepared by redox reaction at room temperature. A $MnO_2/AlOOH$ composite with a homogeneous dispersion of MnO_2 has high specific surface



area and a large amount of surface hydroxyl (-OH) which plays a major role in the adsorption of formaldehyde. A partially crystalline structure was observed in the composite, which contains multivalent Mn ions and a large number of vacancy defects. The surface -OH of composite shows strong oxidation activity through the charge exchange of multivalent Mn ions and vacancy defects. The composite has a higher ability to remove indoor low-concentration formaldehyde compared to the birnessite MnO_2 at room temperature. This study proposes a new idea for the improvement of catalytic performance in the structure and composition of the catalyst.

■ INTRODUCTION

Formaldehyde (HCHO) is known as one of the most common pollutants in the indoor environment. Long-term exposure to an environment containing a certain concentration of formaldehyde will have a serious impact on human health. Indoor formaldehyde is generally derived from substandard furniture and decorative materials, of which formaldehyde evaporates slowly for up to 10 years.¹⁻³ This requires an efficient and long-term effective method to remove formaldehyde, especially the indoor low-concentration formaldehyde. Catalytic oxidation is a promising method which can decompose HCHO into H_2O and CO_2 with less restriction. In relevant reports,^{4–} noble-metal-based catalysts have the best ability to oxidize formaldehyde, maintaining high catalytic activity at relatively low temperatures. Au, Pt, Pd and other noble metal nanoparticles are dispersed on the surface of (hydro-) oxides such as TiO₂, FeO_x, CeO₂, AlOOH, and MnO₂. These supports generally have high specific surface area, which facilitates the dispersion of noble metal particles and the adsorption of formaldehyde molecules. However, the high cost of noble metal catalysts has always been a barrier to its commercialization. It is necessary to develop an inexpensive room-temperature catalyst.

Another type of catalyst for formaldehyde oxidation is a transition-metal oxide catalyst, represented by Co_3O_4 and MnO_2 .^{12–17} Most transition-metal oxide catalysts require relatively high temperature (about 80-140 °C) to be catalytically active, among which the birnessite-type MnO_2

performs best.^{18–25} Birnessite is a kind of layered manganese dioxide built by edge-sharing octahedral MnO_6 . A certain number of cations like Na⁺ and K⁺ are located in the layers for charge balance. Birnessite-type MnO_2 can only partly oxidize formaldehyde at room temperature. Therefore, many meaningful researches^{26–30} have been carried out in order to further enhance catalytic activity of birnessite-type MnO_2 . Both of these studies showed that high specific surface area and defects, which act as adsorption and active sites in catalytic reactions, are closely related to the high activity of formaldehyde oxidation.

Nanostructured AlOOH was widely used in the fields of adsorption and catalysis as a low-cost and environmentally friendly material. AlOOH has nanosheet structure with high specific surface area and a large number of surface hydroxyl (-OH) groups. The Pt/AlOOH prepared by dispersing and depositing nano Pt particles on the AlOOH nanosheets exhibited a remarkable catalytic activity as well as stability for elimination of formaldehyde at room temperature.^{7,8} High catalytic activity does not depend on the amount of noble

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metal depositing, but rather by higher dispersion.³¹ Therefore, we venture to guess that using MnO_2 particles with high dispersity instead of Pt to complex with AlOOH which has high specific surface area and a large amount of surface –OH groups may provide a low-cost and highly efficient formaldehyde-removal catalyst. The removal of indoor high-concentration formaldehyde has been widely studied in recent years.^{10,18,26,28} However, how to effectively remove indoor low-concentration formaldehyde has rarely been explored.

In this work, we prepared MnO₂/AlOOH composites by reacting KMnO₄ with a large number of surface -OH groups from AlOOH and applied it in indoor low-concentration formaldehyde removal at room temperature. MnO2 was dispersed uniformly in the MnO₂/AlOOH composites. The composite has a heterogeneous structure with partially crystalline structure containing a large number of surface -OH and vacancy defects. This composite catalyst has a significantly higher activity than the birnessite MnO₂ and has an advantage in indoor low-concentration formaldehyde removal. We found that -OH on the catalyst surface plays an important role in the oxidation of formaldehyde, and a new explanation of its reaction mechanism was given. Unlike most studies that focus on improving the performance of MnO₂ through various methods, this is a new type of catalyst obtained through MnO₂ modification.

EXPERIMENTAL SECTION

Catalyst Synthesis. All chemicals used for preparation were of analytical grade. $KMnO_4$ and ammonium hydroxide were purchased from Beijing Chemical Reagent Co., Ltd. Other chemicals were all purchased from Aladdin Reagent Co., Ltd. AlOOH was synthesized by simplified microemulsion-assisted method.⁸ The detailed procedure is as follows: A mixture containing 100 mL of cyclohexane and 20.46 g of polyethylene glycol (PEG 400) was magnetically stirred over 900 rpm in room temperature. After stirring for 10 min, 20 mL of Al(NO₃)₃ solution (0.32 M) and 3.85 mL of NH₃ solution (27 wt %) were added stepwise to the above mixture and then aged about 6 h to make precipitation of aluminum oxyhydroxide. The precipitation was collected after centrifuging and washing with deionized water (four times) to remove possible residual organics.

The AlOOH precipitate was dispersed in 150 mL of deionized water by ultrasonic. Then a 0.1 M KMnO₄ solution (5 mL, 10 mL, 15 mL, 20 mL, 25 mL, 30 mL) was added to the mixture and stirred about 12 h until the solution faded. MnO₂/AlOOH powders were obtained by washing and air-drying precipitations at room temperature. With the mole ratio of Al/Mn, the obtained samples were labeled as $A_{10}M_x$ (for x = 1-6). Powders obtained by air-drying the AlOOH without Mn at room temperature were denoted as AlOOH. As a comparison, pure MnO₂ powder was obtained by the reaction of methanol with KMnO₄ and air-dried at room temperature, denoted as MnO₂.

Characterization. X-ray diffraction (XRD) analysis was performed by an X-ray diffractometer (D8 Advance Davinci, Bruker, Germany) with Cu target. SEM photographs were taken at 10 kV by a field emission scanning electron microscope (Sirion200, FEI, USA) and EDS elemental mapping was performed at 20 kV. High-magnification TEM photographs were taken by transmission electron microscopy (Tecnai F20, FEI, USA). Samples were all ultrasonically dispersed in ethanol and then placed on copper grids for TEM characterization. The specific surface area ($S_{\rm BET}$) of the samples was tested by a fully automatic specific surface area and a micropore analyzer (ASAP2020HD88, Micromeritics, USA). Samples were degassed at 30 °C.

The X-ray absorption data at the Mn K-edge of the powder samples were measured at room temperature by using transmission mode at beamline BL14W1 of the Shanghai Synchrotron Radiation Facility (SSRF), China. The station was operated with a Si (111) double

crystal monochromator. The photon energy was calibrated with the first inflection point of Mn K-edge in Mn metal foil. Data analysis was performed with the Athena software packages. XPS analysis was carried out on an X-ray photoelectron spectrometer (AXIS ULTRA, Kratos, UK) with Al target. The full spectrum of the sample and the fine spectrum of each element were scanned separately. The binding energy was calibrated by C 1s peak (284.8 eV). Fourier transform infrared spectroscopy (FT-IR) was recorded on Nexus (Thermo Nicolet, U.S.A.) from 450 to 4000 cm⁻¹. In situ diffuse reflectance infrared Fourier transform spectroscopy (in situ DRIFTS) was performed on a Tensor II FTIR spectrometer (Bruker) equipped with an in situ diffuse reflectance cell (Harrick) to clarify the intermediate species during HCHO oxidation and its mechanism. The catalyst samples in powder are loaded in the DRIFT cell. There are three gas ports and two coolant ports on the reaction chamber. Then, highpurity O2, high-purity He, and 100 ppm of HCHO mixtures were introduced into the cell. Under dark conditions, HCHO adsorption on the catalysts was carried out for 20 min, and the total gas flow rate was 100 mL/min. Next, the catalysts were illuminated by a visible light source (MUA-210) for 30 min under room temperature.

Evaluation of HCHO Removal Activity. To simulate indoor conditions, a static test of the catalyst's ability to remove low-concentration formaldehyde was performed in a self-constructed reaction facility, as shown in Figure 1. The sealed reaction chamber



Figure 1. Self-constructed reaction facility for formaldehyde removal.

made of glass has a volume of 5 L and three air holes that can be switched. First, 0.1 g of composite catalyst powder was spread on a 6 cm diameter glass wafer and placed at the bottom of the reaction chamber. The wafer was covered by a glass cover with a thin wire which could pass through the air hole to easily lift the glass cover. Next, the air was pumped through a certain concentration of formaldehyde solution into the reaction chamber. The initial concentration of formaldehyde in the reaction chamber was adjusted by the pump-down time and the concentration of the formaldehyde solution. Then, the glass cover was pulled up, and then all the air holes were closed. The catalyst was contacted with low-concentration formaldehyde gas in the reaction chamber and started to react at room temperature. A formaldehyde detector (MEF500, Sensology, China) was used to record the initial concentration of formaldehyde in the reaction chamber and the change within 1 h. The formaldehyde removal rate was calculated as the following:

$$P_{\rm T} = \frac{C_0 - C_{\rm T}}{C_0} \times 100\%$$

where C_0 is the initial HCHO concentration and $C_{\rm T}$ is the concentration at T min.

RESULTS AND DISCUSSION

The crystal structure of the samples was detected by XRD measurement (Figure 2). The XRD peaks located at 14.5° , 28.1° , 38.3° , 49.2° , 65.0° , and 71.9° of pure AlOOH samples assigned to (020), (120), (031), (200), (002), and (251) of AlOOH (JCPDS no. 21-1307), respectively. It can be seen that AlOOH synthesized at room temperature by a simplified



Figure 2. (a) XRD patterns of as-prepared AlOOH, $A_{10}M_{xv}$ and MnO₂ samples and (b) enlarged XRD patterns in the 2θ range of $60-70^{\circ}$.

method also has good crystallinity. The XRD peaks located around 36.5° (100) and 65.5° (110) of pure MnO₂ can be assigned to the birnessite structure (JCPDS no. 80-1098) with poor crystallinity.²⁶ Poor crystallinity may be due to the low synthesis temperatures and the different raw materials (CH₃OH) used. With the increasing proportion of Mn in the compound, the crystallinity of the material appears to be continuously reduced, which is mainly reflected by the continuous decrease of the diffraction peaks of AlOOH. The addition of Mn may damage the ordered structure of AlOOH or mask the characteristic peaks. Meanwhile, there was no obvious diffraction peak of MnO₂ found in A₁₀M_x patterns on account of the poor crystallinity of MnO2. In order to confirm the presence of MnO₂ in the composite catalyst, the XRD patterns were amplified in the 2θ range of $60-70^\circ$, as shown in Figure 2b. It can be clearly seen that one peak (2θ about 66°) of $A_{10}M_6$ sample coincides with (110) peak of MnO₂ from the amplified XRD patterns. This indicates that MnO₂ is present in the composite catalyst. However, no peaks of MnO2 were found in the amplified XRD patterns of A₁₀M₁ sample, which was due to the lower content of MnO₂.

The microscopic morphology of samples was surveyed by SEM and is shown in Figure 3. The observed powder samples



Figure 3. SEM images of as-prepared AlOOH, MnO_2 , and $A_{10}M_x$ samples: (a) AlOOH, (b) MnO_2 , (c) $A_{10}M_1$, (d) $A_{10}M_2$, (e) $A_{10}M_5$, and (f) $A_{10}M_6$.

were prepared by hand-grinding after drying and therefore were all larger particles. Pure AlOOH has a loose layered structure (Figure 3a) and a high specific surface area of 488 m^2/g (specific surface area data are listed in Table 1). Birnessite MnO_2 was nanospheres composed of nanosheets.²² The MnO_2 sample shown in the Figure 3b appears as nanoclusters. The specific surface area was found to be 98 m²/

Table 1. Combined Results of BET and XPS of As-Prepared Samples

samples	$S_{\rm BET}~(m^2/g)$	Mn/Al (molar)	O_{surf} / O_{latt}	Al 2p (eV)
Alooh	488	_	6.15	74.3
$A_{10}M_1$	424	0.11	6.12	74.4
$A_{10}M_6$	293	0.44	3.04	74.3
MnO_2	98	-	4.5	-

g, which is similar to other reports.²⁸ The samples with different ratios of AlOOH and MnO_2 still microscopically composed of nanosheets (Figure 3c–f). No obvious MnO_2 particles can be found in $A_{10}M_x$ samples. However, it can be visibly seen that the high MnO_2 ratio samples are denser than the low MnO_2 ratio samples. This was also consistent with the test results of the specific surface area of the samples. Even though the microstructure appears to be a dense block, the specific surface area of $A_{10}M_x$ is still far higher than that of birnessite MnO_2 . In general, the higher specific surface was believed to be beneficial to reduce transfer resistance and improve catalytic performance.³² Catalytic oxidation of formaldehyde was usually interpreted as the "adsorption-oxidation" cycle. Xu et al.³³ studied composites of MnO_2 grown on carbon spheres. Its high specific surface area and abundant surface oxygen played a major role in Hg⁰ removal.

In the initial design idea, the synthesized MnO_2 will grow on the AlOOH surface and form MnO_2 nanoclusters. However, the results of the elemental mappings (Figure 4) show that Mn



Figure 4. SEM image and elemental mapping of as-prepared (a-d) $A_{10}M_1$ sample and (e-h) $A_{10}M_6$ sample.

and K were in a pretty high dispersion degree as well as Al. Mn ions were distributed between layers of AlOOH or had already been incorporated into the bulk phase. Mn and K still maintain a high dispersion degree in the samples with a high Mn ratio (Figure 4e-h).

In order to further explore the specific structure and existing form of MnO_2 hybridized with AlOOH, TEM characterization was performed (Figure 5). As shown in high-resolution TEM (HRTEM) images, composite samples have poor crystallinity and consist of microcrystals and a noncrystal structure. The lattice spacing of 0.21 nm observed on all samples was assigned to the (031) planes of AlOOH, as the content of Mn was too small and no MnO_2 crystal can be found in $A_{10}M_1$. In $A_{10}M_6$ (Figure 5c,d), the lattice spacings of 0.35 and 0.24 nm correspond to the (002) and (100) lattice planes of birnessite,²⁶ which indicate that Mn ions also participated in the formation of the interface structure with the increase of Mn ratio. Observed crystallites were small in size and disorderly in distribution, while amorphous phases account for a large proportion. This further confirms the Mn ions were dispersed



Figure 5. TEM and HRTEM images of as-prepared $A_{10}M_x$ samples: (a, b) $A_{10}M_1$ and (c, d) $A_{10}M_6$.

in AlOOH lattice matrix forming a partially crystalline structure, which encourages the occurrence of the lattice defects and the exposure of inner atoms.^{32,34–36} In addition, it is interesting to find some annular lattice planes in $A_{10}M_{6}$, which need further research.

In order to analyze the influence of the fine structure and chemical valence of the composite catalyst on the catalytic performance, the as-synthesized samples were performed by Xray absorption fine structure (XAFS). Photoelectrons which were excited by X-ray are scattered by the surrounding coordinating atoms, leading to X-ray absorption intensity oscillating with energy. The electronic and geometric local structures of the system can be obtained by studying these oscillating signals. XAFS includes two parts, extended X-ray absorption fine structure (EXAFS) and XANES. The near-edge X-ray fine structures (XANES) of the samples MnO_{2} , $A_{10}M_6$ and $A_{10}M_5$ are shown in Figure 6a. The MnO₂, A10M6 and A10M5 lines do not coincide, which means that the chemical valence of Mn has changed due to the loading of MnO₂ in AlOOH, and the Mn ions tend to be multivalent. It is beneficial to the electron exchange process of manganese ions, which may activate more active sites to improve the performance for HCHO decomposition. The EXAFSs of different samples are shown in Figure 6b. The intensity of the oscillating peak in the high-energy region is weakened, implying AlOOH reduced the grain size of MnO₂, which increased the contact of formaldehyde molecules with MnO₂. As we can see from Figure 6c, Mn K-edge XAFS transformed

its Fourier into R space by using IFEFFIT software. $A_{10}M_6$ and A10M5 did not perform significant Al-Mn peaks, indicating that manganese oxide and aluminum oxide were phaseseparated. Meanwhile, the peaks of $A_{10}M_6$ and $A_{10}M_5$ are slightly lower than pure MnO₂, which means the O coordination number decreased around Mn, and the Mn valence state changed. It is consistent with the change of Mn valence state observed from the result of the XANES (Figure 6a). Thus, the compounding of MnO₂ with AlOOH can make Mn ions tends to be in different valence states and can also reduce the grain size of MnO_2 , leading to high catalytic activity for low-concentration HCHO removal. In addition, the decrease of the O coordination number may also show the existence of Mn vacancies (V_{Mn}) . Due to the existence of $V_{Mn'}$ K⁺ ion compensates its charge imbalance, facilitating the formation of surface active oxygen, which in turn acts as the active site for HCHO oxidation.²⁶

In order to further confirm the existence of the multivalent state of Mn in the composite catalyst, XPS measurements were also performed to analyze surface chemical compositions and chemical states, as shown in Figures 7 and 8. The Mn 3s



Figure 7. Mn 3s XPS spectra of (a) MnO₂ and (b) A₁₀M₆ samples.

spectra of MnO₂ and A₁₀M₆ samples are shown in Figure 7. It is possible to distinguish Mn oxidation states using Mn 3s peak.^{37–40} As we can see from Figure 7, the Mn 3s peaks of MnO₂ and A₁₀M₆ samples have two multiple split components, which may be caused by coupling of non-ionized 3s electron with 3d valence-band electrons.^{37,38} Magnitude of peak splitting (ΔE) is diagnostic of Mn oxidation state, ΔE for MnO (Mn²⁺) 6.0 eV, Mn₂O₃ (Mn³⁺) \geq 5.3 eV, MnO₂ (Mn⁴⁺) 4.7 eV.^{37,38} Magnitude of Mn 3s peaks splitting of MnO₂ sample is 4.79 eV (Figure 7a), which corresponds to the Mn⁴⁺ oxidation state. Magnitude of Mn 3s peaks splitting of A₁₀M₆ sample is 5.15 eV (Figure 7b). Compared with the MnO₂ sample, the peak splitting of the A₁₀M₆ sample is more obvious. This indicates that A₁₀M₆ sample has a multivalent state of Mn (Mn³⁺, Mn⁴⁺) in the composite catalyst. It should be noted



Figure 6. Fourier-transformed XAFS spectra of different samples (MnO_2 , $A_{10}M_6$ and $A_{10}M_5$). (a) The XANES of the different samples. (b) The EXAFS of the different samples. (c) The Fourier transform R-space of the Mn K-edge XAFS spectra of different samples.



Figure 8. O 1s XPS spectra of as-prepared samples.

that the Mn 3s spectra for $A_{10}M_1$ sample are absent because the Mn content in this sample was low and the signal was very weak. The results of Mn 3s XPS analysis are consistent with the previous Fourier-transformed XAFS spectra analysis. Therefore, there must have been some reactions in the composite catalyst to produce multivalent Mn ions (Mn³⁺, Mn⁴⁺) and vacancy defects (such as oxygen vacancies). These reactions may occur in the catalytic process of composites, as shown in eqs 1–3.

$$A-OH \to A^{+} + e^{-}/-OH \tag{1}$$

$$2Mn^{4+} + 2e^{-}/-OH \leftrightarrow 2Mn^{3+} + H_2O + 0.5O_2$$
(2)

$$4Mn^{4+} + O_2^- \rightarrow 4Mn^{4+} + 2e^-/V_0 + 0.5O_2$$

$$\rightarrow 2Mn^{4+} + 2Mn^{3+} + V_0 + 0.5O_2$$

Multivalent Mn ions and a large number of vacancy defects are conducive to charge exchange, which in turn makes these chemical reactions possible to finish. According to the eq 3, oxygen vacancies (V_{Ω}) were generated in composite catalyst due to the presence of multivalent Mn ions. In addition, oxygen vacancies may also occur due to the existence of V_{Mn}. The bond between K^+ and unsaturated oxygen around V_{Mn} is not as strong as the bond Mn-O, thus these unsaturated oxygens are more easily mobile and act as active oxygen species.²⁶ It has been reported that oxygen vacancies were generated with the presence of Mn³⁺ in the catalyst to balance the charge.^{27,41} The electron exchange of Mn ions involves the primary oxidation of formaldehyde and the generation of reactive oxygen ions.⁴² Oxygen vacancies can migrate to the surface of the catalyst and act as the active site for the oxidation of formaldehyde,⁴³ so its content significantly affects catalytic performance. In addition, dioxygen molecules in air would be adsorbed on V_O and dissociated $(O_2 + V_O \rightarrow O_2)$ O⁻). The consumed surface -OH is replenished via the reaction with H₂O (O₂⁻ + H₂O \rightarrow 2OH). Surface active oxygen $(O_2^-, O^-, or -OH groups)$ has strong catalytic oxidation ability.

The O 1s XPS patterns shown in Figure 8 can be divided into three peaks at 529.2–530.4 eV, 531.6–531.8 eV, and 533.0–533.2 eV, corresponding to lattice oxygen (O_{latt}), surface adsorbed oxygen species (O_{surf}), and adsorbed molecular H₂O.³² The content of adsorbed molecular H₂O in AlOOH and its composites was small, while MnO₂ showed strong water absorption. The crystallinity of AlOOH and its composites was better, so their binding energy of Olatt was higher than that of MnO₂. The content of surface adsorbed oxygen species directly reflects the surface -OH group content of the sample, which plays an important role in the oxidation of formaldehyde. In all four samples, the peaks of O_{surf} were dominant and the O_{surf}/O_{latt} ratio was calculated by their peak areas. AlOOH is a material rich in surface -OH groups. The ratio of O_{surf}/O_{latt} was similarly high in AlOOH and $A_{10}M_1$ but small in A10M6, which was consistent with the previously described synthesis of MnO₂ by depleting surface -OH. On one hand, -OH can adsorb formaldehyde molecules through hydrogen bonds to provide sites for reactions. On the other hand, a large amount of -OH can help accelerate the oxidation of formaldehyde. It has been pointed out in the literature that -OH will directly oxidize the intermediate formate produced by the initial oxidation of formaldehyde to CO_2 and H_2O .^{44,45} However, there were also some reports that low O_{surf}/O_{latt} ratio was beneficial to Mars-van Krevelen mechanism for formaldehyde oxidation.^{46,47} It must be pointed out that O_{surf} contains a large number of -OH originally present on the surface of AlOOH, which means that not all of the -OH has a catalytic reaction activity. In addition, the peak position of Al 2p remained at 74.3 eV (see Figure S1 and Table 1), indicating that the Al 2p peak did not split and Al remained unchanged as AlOOH.

The FT-IR spectra of AlOOH, MnO_2 and $A_{10}M_x$ samples were measured in order to investigate the surface functional groups of different samples, as shown in Figure 9. The strong



Figure 9. FT-IR spectra of as-prepared samples.

peak at 3412-3424 cm⁻¹ was attributed to the stretching vibrations of adsorbed water molecules and structural OH group.48 The content of -OH reflected by the intensity of -OH absorption peak of each sample is roughly consistent with the O_{surf} content of the samples from the XPS measurement. It is noteworthy that the difference between -OH content of $A_{10}M_x$ samples and AlOOH is large according to the FT-IR spectra. However, there is not a big difference between the O_{surf} contents of AlOOH and A₁₀M_r samples according to the XPS spectra. There are two main reasons for this situation: (i) the relative ratio of O_{surf}/O_{latt} obtained in XPS needs to consider the crystallinity of the material and the content of the Olatt; and (ii) the surface adsorbed oxygen of $A_{10}M_x$ samples in XPS peak contains not only the O_{surf} but also a certain amount of active O^{2-} and O^{-} ions.^{43,49} In addition, the small absorption peaks at 1053–1072 cm⁻¹ in AlOOH and

(3)

 $A_{10}M_x$ samples show that there may be residual alcohols in the preparation process.

To test the ability of the catalyst to remove indoor formaldehyde with low concentration at room temperature, a static reaction for the enclosed space was designed. Considering the indoor formaldehyde level of ordinary residents, the initial concentration was 0.5 mg/m³ (lower concentration), and the degradation curve of formaldehyde over time is shown in Figure 10. The concentration of



Figure 10. Curve of formaldehyde concentration over time with asprepared catalysts.

formaldehyde dropped fastest in the first 10 min and tended to be gentle after 20 min. At 20 min, the formaldehyde removal rate (P_{20}) of each sample was 32%, 38%, 40% and 52%, respectively. $A_{10}M_1$ and $A_{10}M_4$ had similar removal rates and were higher than MnO₂, while $A_{10}M_6$ had the best removal rate. The change trend of formaldehyde concentration conforms to the "adsorption—oxidation" formaldehyde removal mechanism. The formaldehyde molecules were first adsorbed by the catalyst and then degraded on the surface. After a long time, the degradation curve tends to be flat and cannot remove completely due to the fact that the catalyst has poor activity at low temperatures and the formaldehyde cannot be oxidized in time so that there is a dynamic balance of "adsorption—desorption" on the catalyst surface. Catalysts with

In order to clarify the intermediate species of the catalysts in the reaction of formaldehyde at room temperature, in situ DRIFTS spectra of the MnO2 and A10M6 materials were performed. The reaction gas is 100 ppm of formaldehyde gas, and the equilibrium gas is O_2 and He. The total gas flow rate is 100 mL/min. The DRIFTS spectra of the MnO_2 and $MnO_2/$ AlOOH composite catalysts after exposure to HCHO for 50 min are shown in Figure 11. A series of infrared absorption peaks appear on the surface of the birnessite manganese dioxide during catalytic oxidation. According to previous studies, the bands located around $1343-1360 (v_{c}(COO-))$, 1542–1592 (v_{as} (COO–)), and 2824–2844 cm⁻¹ (v(CH)) can be attributed to the formate species, ^{51,52} indicating that the HCHO adsorbed on the surface of the catalyst is converted into a formate species. The band at 1657 cm⁻¹ can be ascribed to water adsorbed on the surface of the catalyst,⁵³ which may be derived from water in the reaction gas or products of HCHO decomposition. The infrared absorption peaks at 1234, 2343, and 3684 cm⁻¹ correspond to v_{as} (COO-) of the carbonate species, carbon dioxide (CO₂) adsorbed on the surface, and hydroxyl species on the surface, respectively. In the dark conditions and the light-on conditions, the infrared absorption peak of CO₂ appeared, indicating that HCHO is continuously oxidized after the adsorption process and adsorption equilibrium. It is worth noting that the intensity of the infrared peak of CO2 at 2343 cm⁻¹ for the composite catalyst $(A_{10}M_6)$ is significantly stronger than that of MnO₂ at the adsorption equilibrium (Figure 11b,d). This indicates that the catalytic performance of the composite catalyst is better than that of MnO₂, which is consistent with the analysis result from Figure 10. The peak around 1475–1479 cm⁻¹ can be ascribed to $\delta(CH_2)$ in dioxymethylene (DOM).⁵⁴ Therefore, in the process of formaldehyde adsorption and oxidation, the intermediate species of dioxymethylene, formate, and carbo-



Figure 11. In situ DRIFTS spectra of (a) HCHO adsorption process of MnO_2 , (b) HCHO adsorption equilibrium of MnO_2 , (c) HCHO adsorption process of $A_{10}M_{62}$ and (d) HCHO adsorption equilibrium of $A_{10}M_6$.



Figure 12. Reaction pathway of HCHO on MnO₂/AlOOH composite catalyst.

nate were produced on the surface of the MnO₂. A negative peak of $36\overline{8}4$ cm⁻¹ appeared, indicating that the surface -OHparticipates in the catalytic oxidation reaction and gradually would be consumed as the reaction progresses. The infrared absorption peak of the intermediate species of A₁₀M₆ during HCHO adsorption oxidation is about the same as that of MnO₂, however, lower accumulation of dioxymethylene species appear on in situ infrared spectrum of $A_{10}M_6$. The absorption peak indicates that HCHO has a faster oxidation rate on the surface of A10M6. Moreover, compared with infrared spectrum of MnO2, the accumulation of carbonate species on the surface of A10M6 was also lower, indicating that the intermediate species had a faster conversion rate on the surface of the A10M6 catalyst. In situ infrared spectra of two catalysts were observed to be gradually consumed by surface hydroxyl species, which is consistent with the conclusion that the catalyst surface -OH accelerates catalytic oxidation of formaldehyde in XPS. A₁₀M₆ has a lower negative peak, indicating that surface hydroxyl group participates in the catalytic oxidation reaction at room temperature, A10M6 catalyst plays a synergistic role by modifying AlOOH, and surface -OH is activated by the advantage of high specific surface area of AlOOH. Therefore, the HCHO decompose rate on the surface of $A_{10}M_6$ becomes high, and the conversion rate of the intermediate species also changes accordingly, thereby facilitating the catalytic oxidation process of formaldehyde.

The catalytic cycle of HCHO oxidation over MnO₂/AlOOH composite catalyst with high specific surface area and a large amount of -OH groups is summarized in Figure 12. HCHO is first adsorbed on composite catalyst, which is enhanced by water contained in the composite catalyst via forming hydrogen bonding with formaldehyde. Adsorbed HCHO and its hydrate (methanediol, $CH_2(OH)_2$) would be oxidized by surface active oxygen $(O_2^-, O^-, or -OH groups)$ of composite catalyst into DOM, formate, carbonate and CO₂ sequentially according to the analysis results of in situ DRIFTS spectra (Figure 11). Based on the analysis of Mn 3s and O 1s XPS spectra (Figures 7 and 8), oxygen vacancies were generated in the composite catalyst with the presence of multivalent Mn ions and V_{Mn} in the catalyst. Then, a dioxygen molecule in air would be adsorbed on V_O and dissociated ($O_2+V_O \rightarrow O_2^-$, O⁻). The consumed surface OH is replenished via the reaction with H_2O ($O_2^- + H_2O \rightarrow 2OH$). Thus, the catalytic cycle is finished. Due to the existence of multivalent Mn ions and V_{Mn} in the catalyst, the K⁺ ion may compensate its charge imbalance, facilitating the formation of surface active oxygen, which in turn acts as the active site for HCHO oxidation.

The compounding of MnO₂ with AlOOH effectively improved the catalytic activity, and the mechanism can be explained by the following factors. First, the composite catalyst has a high specific surface area and a large number of surface -OH groups, which facilitate the adsorption of formaldehyde molecules and provide a large number of reaction sites. Adsorption is an important part of the formaldehyde removal process and exhibits a more pronounced effect at low temperatures and low HCHO concentrations. Second, the synthesized complex has good dispersibility and partially crystalline structure. This amorphous structure produces a large number of multivalent states of Mn ions and vacancy defects which facilitates charge exchange (eqs 1-3). The exchange of charge between Mn ions and vacancy defects makes the nearby -OH highly oxidizing (eq 2). The catalytically active -OH serves as the active site for oxidation of formaldehyde. Mn in A10M6 has more morphology (crystalline MnO₂ and amorphous Mn ions), which makes $A_{10}M_6$ have a higher oxidation activity -OH, explaining its optimal catalytic activity. The report mentioned that the combination of active oxygen ions (O^{-}, O_{2}^{-}) generated by the complex exchange of O₂, oxygen vacancies, and lattice oxygen with H₂O molecules can generate -OH as a supplement to -OH and self-recovery of the catalyst (Figure 12). The active -OH which can directly oxidize formaldehyde can also be regarded as an existing form of active oxygen ion. In addition, the existence of multivalent Mn ions and V_{Mn} in the composite catalyst makes it possible for the K⁺ ion to compensate its charge imbalance, facilitating the formation of surface active oxygen. These surface active oxygen species in turn act as the active site for HCHO oxidation.

Unlike most studies that focus on improving the performance of MnO_2 , this is a new type of highly efficient formaldehyde catalyst obtained through MnO_2 modification. AlOOH has a large number of surface -OH but does not have the ability to oxidize formaldehyde. By combining with MnO_2 , part of the surface -OH has the ability to oxidize formaldehyde, and its comprehensive catalytic performance exceeds MnO_2 itself. The $A_{10}M_6$ sample with a partially crystalline structure has better performance. The $MnO_2/$ AlOOH composite catalyst takes advantage of the high specific surface area of AlOOH and stimulates the activity of surface -OH, providing a new idea for the improvement of the catalytic activity of transition-metal oxides such as MnO_2 .

The MnO₂/AlOOH composite catalyst was prepared successfully by redox reaction of potassium permanganate KMnO₄ and surface -OH of AlOOH at room temperature. Various proportions of MnO₂ were uniformly dispersed in AlOOH, forming a partially crystalline structure. In the static test that simulated indoor formaldehyde removal at room temperature, the $A_{10}M_6$ sample showed the best ability to remove indoor low-concentration formaldehyde. Removal of indoor formaldehyde should be divided into "adsorption-oxidation" processes. The composite has a higher specific surface area and a large amount of surface -OH which facilitates the adsorption and fixation of formaldehyde. The partially crystalline structure formed by the complex has a variety of valence states of Mn ions and a large number of vacancy defects. Through the charge exchange of Mn ions and vacancy defects, the nearby -OH can have a strong oxidizing activity. MnO₂/AlOOH composite catalyst has a strong catalytic effect on indoor formaldehyde with low concentration by a strong oxidation activity from the nearby -OH. This study proposes new ideas for the improvement of catalytic performance in the structure and composition of the catalyst. It is expected that this modification strategy may be effective for the other materials, except AlOOH to remove indoor low-concentration formaldehyde.

ASSOCIATED CONTENT

③ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c00852.

Al 2p XPS spectra of as-prepared samples (PDF)

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Notes

The authors declare no competing financial interest.

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