Performance and characterization of MnOx-NiO catalysts for removing formaldehyde at room temperature

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Abstract. The effects of the hydrothermal co-precipitation factors of hydrothermal temperature, hydrothermal time, calcination temperature and calcination time on the crystal structure, microstructure, lattice defect and formaldehyde removal properties at indoor temperature of MnOx-NiO composite oxide catalysts were investigated by using the X-ray diffractiono (XRD), scanning electron microscope (SEM), transmission electron microscope (TEM), X-ray photoelectron spectroscopy (XPS) and the catalytic activity testing apparatus. The results showed that the formaldehyde removal rate of the catalysts would increase first and then decrease with increasing in the hydrothermal temperature, or hydrothermal time, calcination temperature, calcination time. The maximum formaldehyde removal rate at indoor temperature is 95.57% with the best technology of the catalysts is as the following: 0.0125 mol potassium permanganate, 0.005 mol nickel nitrate, 5 ml sodium oxalate solution, 0.5 ml ammonia solution, hydrothermal 5 h at 130 °C and then calcination 5 h at 200 °C, the loose spherical accumulation specimen was composed of amorphous and crystal, and existed abundant Mn4+ species and lattice oxygen on the catalyst surface.

1. Introduction
Formaldehyde is a typical indoor air pollutant, and prolonged exposure to formaldehyde could bring many adverse human symptoms, such as headaches, eye irritation, respiratory diseases, etc., even leading to cancer and malformations in severe cases[1,2]. It is urgent to find a kind of appropriate method for the effective removal of indoor formaldehyde. Some conventional methods for formaldehyde remove have been well reported in previous literatures, such as ventilation, physical adsorption[3,4], photocatalytic[5] and catalytic oxidation[6]. Among them, catalytic oxidation is considered to be the most effective method to remove indoor formaldehyde pollution due to its high catalytic efficiency, simple operation, and no secondary pollution[7]. Therefore, the preparation of a high efficiency catalyst sensitive to low concentration of formaldehyde is the focus of current research.

The current research on catalysts mainly focuses on precious metal catalysts and transition metal catalysts. Catalysts doped with precious metals, such as platinum[8], gold[9] and silver[10], exhibit good low-temperature catalytic activity. However, the high price greatly limits the application of precious...
mental. In contrast, the transition metal catalysts with relatively low cost, abundant resources, stability and good tolerance has aroused the increasingly interest of researchers. Common transition metal catalysts including manganese dioxides (MnO$_2$)[11,12], NiO[13], Co$_3$O$_4$[14] and so on. MnO$_2$ shows excellent catalytic performance for HCHO oxidation at room temperature[15]. The MnO$_2$/PG catalysts have uniform distribution of MnO$_2$, abundant hydroxyl species, and good formaldehyde catalytic performance[16]. MnO$_2$ catalysts with three-dimensional ordered mesoporous can completely convert formaldehyde into carbon dioxide and water at 130 °C[17]. When the Cu-Mn oxides supported on palygorskite at 207-258 °C, the conversion rate of formaldehyde is 90%[18]. Therefore, it is of great practical value and social significance to study transition metal catalysts with good catalytic performance at room temperature.

Till now, there are many researches on catalyst preparation, and the preparation methods include precipitation, hydrothermal, gel sol method and so on[19-21]. Precipitation has been widely applied among these preparation methods, owing to the catalyst materials prepared by precipitation method have a small particle size and uniform distribution[22]. It has been reported in previous literature, Pt/ZrO$_2$-Al$_2$O$_3$ catalysts were prepared with different doping amounts by co-precipitation method. When the doping amount of ZrO$_2$ was 40 wt%, the complete oxidation temperature of CO and C$_3$H$_6$ were reduced by 20 °C and 25 °C, respectively[23]. Tang reported that MnO$_x$-CeO$_2$ catalysts were prepared by sol-gel method, co-precipitation method and modified co-precipitation method. Among them, the catalyst sample prepared by modified co-precipitation method has the highest catalytic activity. At 100 °C, formaldehyde can be reduced completely converted into carbon dioxide and water[24].

In this study, potassium permanganate and nickel nitrate were used as raw materials to prepare MnO$_x$-NiO catalysts by hydrothermal co-precipitation method, to explore the influence of different hydrothermal temperatures and times as well as calcination temperatures and times on the catalytic performance of the catalyst, optimize the preparation process, and provide ideas for removing indoor formaldehyde more economically and effectively.

2. Experimental

2.1. Catalyst preparation

The MnO$_x$-NiO catalysts were prepared by the hydrothermal co-precipitation method. Firstly, 0.0125 mol potassium permanganate (99.5%, Xilong chemical) and 0.005 mol nickel nitrate (99%, Xilong chemical) were dissolved in 50 ml deionized water with stirring at room temperature. Then, 5 ml of 0.1 mol/L sodium oxalate solution was added to the mixture with continuous stirring for 15 min. After that, 0.5 ml of 5 mol/L ammonia water were adding into the stirring process with stirring for 15 min, and the resulting mixed solution was transferred in a hydrothermal reactor and placed in condition at a certain temperature for a certain time. After cooling to room temperature, the products were washed with water and ethanol, centrifuged at 3500 rpm several time, and dried in air at 70 °C. Finally, the powder was calcined in a muffle furnace at a certain temperature for a certain time to obtain the MnO$_x$-NiO catalysts. Pure MnO$_2$ samples were also prepared by the same method with potassium permanganate as precursor.

2.2. Catalytic activity test

The oxidation of formaldehyde was performed in a reaction device as shown in Fig 1. The formaldehyde gas was produced by heating the powder paraformaldehyde, when the concentration of formaldehyde in the reaction system stabilized at 0.45-0.46 mg/m$^3$, weighed 0.1 g of the catalyst sample and placed it in the sealed tank. The formaldehyde concentration was measured using an acetylacetone spectrophotometer, and the measurement was continued for 3 hours. The calculation method of the sample's formaldehyde removal rate is as follows:
HCHO removal rate (%) = \frac{C_{\text{in}} - C_{\text{out}}}{C_{\text{in}}} \times 100\% \quad (1)

Where $C_{\text{in}}$ is the initial concentration of formaldehyde, and $C_{\text{out}}$ is the concentration of formaldehyde after the reaction.

**Figure 1.** The schematic diagram of activity test device.

### 3. Characterization

The MnO$_x$-NiO catalysts were characterized by X-ray Diffraction (XRD, Rigakudiffractometer), FT-IR spectra (PerkinElmer), Raman spectrum (Renishawspectrometer), scanning electron microstructure (SEM, FEI Corporation), high-resolution transmission electron microscope (HR-TEM, FEI Tecnai G2 F20) and X-ray energy spectrometer (XPS, ESCALAB 250Xi). XRD was carried with CuKα as the radiation source ($\lambda=0.15418$ nm) at 40 kV and 15 mA with 10°-80° $2\theta$ range. The FT-IR spectra of samples were obtained in the range of 4000-400 cm$^{-1}$. The Raman spectra of samples were recorded with the 514 nm laser beam in the range of 300-1000 cm$^{-1}$. SEM and TEM were used to analyze the microstructure, morphology and lattice spacing of the samples. The TEM was carried with 200 kV of voltage condition and the camera length was 200. XPS (ESCALAB 250xi, America) was performed to analyze the element composition and valence state of the catalyst samples with Al Kα X-ray excitation source.

### 4. Results and discussion

Figure 2 shows the effect of hydrothermal temperature, hydrothermal time, calcination temperature and calcination time on formaldehyde removal efficiency of MnO$_x$-NiO catalysts. Among them, other process parameters were: 0.0125 mol potassium permanganate, 0.005 mol nickel nitrate, 5 ml sodium oxalate solution, 0.5 ml ammonia solution, hydrothermal temperature was 100-140 °C, hydrothermal time was 3-7 h, calcination temperature was 100-300 °C and calcination time was 4-8 h. It can be found that with the increase of hydrothermal temperature, hydrothermal time, calcination temperature and calcination time the formaldehyde removal efficiency increased rapidly, as the temperature continues to rise, formaldehyde removal rate dropped dramatically. The maximum formaldehyde removal rate at indoor temperature appeared at hydrothermal temperature was 130 °C, hydrothermal time was 5 h, calcination temperature was 200 °C and calcination time was 5 h, respectively.
As a conclusion, the optimized operation parameters for preparing MnO$_x$-NiO catalysts were as follows: 0.0125 mol potassium permanganate, 0.005 mol nickel nitrate, 5 ml sodium oxalate solution, 0.5 ml ammonia solution, hydrothermal temperature 130 °C, hydrothermal time 5 h, calcination temperature 200 °C, calcination time 5 h. The formaldehyde removal rate of the samples prepared under this condition was 95.57%, which was 30% higher than that of the pure MnO$_2$ samples prepared under the same condition.

Figure 3 shows the XRD patterns of the MnO$_x$-NiO catalysts, pure MnO$_2$ samples were as control group to be detected. It can be seen from the XRD patterns that the diffraction peaks of the pure MnO$_2$ samples at 2θ of 12.7° (001), 24.6° (002), 36.5° (100) and 65.5° (110), which were attributed to the birnessite structure (PDF72-1982). Compared with the pure MnO$_2$ samples, the MnO$_2$ crystal diffraction peak of the MnO$_2$-NiO catalysts at 2θ = 12.7° was disappeared, and the NiO crystal (PDF 47-1049) diffraction peak appeared at 2θ = 37.28°. But the others peaks related to MnO$_2$ (2θ =24.6°, 36.5°)[24] and Ni (2θ = 44.4°, 51.8°, 76.4°)[25]/NiO (2θ = 43.3°, 62.8°, 75.3°) [26] were not observed, indicating Mn-Ni-O solid solution formation. For the MnO$_2$-NiO catalysts, the diffraction peak of amorphous phase was more obvious. The MnO$_x$-NiO samples were composed of amorphous and MnO$_2$, NiO crystalline phases. The addition of Ni affected the crystal structure of MnO$_x$-NiO samples [27,28], increasing lattice defects and producing amorphous substances that were conducive to the conversion of formaldehyde, thus improving the removal rate of formaldehyde.

The FR-IR spectrums of the MnO$_x$-NiO and MnO$_2$ samples are shown in Figure 4. It was obvious that both samples had vibration peaks corresponding to adsorbed water (O-H) and surface hydroxyl group (-OH) near 3445 cm$^{-1}$ and 1635 cm$^{-1}$. The MnO$_2$ sample showed asymmetric C-H bending vibration at the wavenumber of 1398 cm$^{-1}$[29]. Compared with the pure MnO$_2$ samples, the absorption peaks intensity of the MnO$_x$-NiO catalysts became lower, and the wave number at 580 cm$^{-1}$ was the fingerprint area, which could reflect the subtle structural changes of the molecules. The vibration peaks appearing near 580 cm$^{-1}$ were related to the lattice vibration of Mn-O, Ni-O, Mn-O-Mn, Ni-O-Ni, O-Mn-O and O-Ni-O. It showed that the addition of Ni had a certain effect on the lattice vibration and
surface functional groups of the sample, thereby promoting the removal rate of formaldehyde at room temperature.

![Figure 4](image1)

**Figure 4.** FT-IR spectrums analysis of MnO$_x$-NiO catalysts (a, MnO$_x$-NiO; b, MnO$_2$)

The Raman spectrums of the MnO$_x$-NiO samples are shown in Figure 5. For comparison, the Raman spectrums of the pure MnO$_2$ sample are also shown in the figure. The Raman peaks near 585 cm$^{-1}$ and 646 cm$^{-1}$ were caused by the stretching vibration and symmetrical stretching vibration of the Mn-O lattice base plane of the MnO$_6$ sheet. Both Raman peaks belonged to birnessite MnO$_2$$^{[30]}$. It can be seen from Figure 5 that compared with the Raman spectrums of the pure MnO$_2$ samples, the blue-shift phenomenon was observed in the spectrum of MnO$_x$-NiO, which was the result of the interaction of MnO$_x$-NiO oxides$^{[31]}$. In addition, the intensity of the Raman peak of the samples became relatively weaker, indicating that the addition of Ni distorted the crystal lattice of the catalysts and produced more crystal lattice defects, which was beneficial to the catalytic oxidation of formaldehyde. It was consistent with the above XRD analysis results.

![Figure 5](image2)

**Figure 5.** Raman spectrums of MnO$_x$-NiO catalysts (a, MnO$_x$-NiO; b, MnO$_2$).

Figure 6 shows the SEM analysis results of MnO$_x$-NiO and pure MnO$_2$ samples. It can be seen from the figure that the MnO$_x$-NiO and MnO$_2$ samples were all flocculent spherical deposits, and the distribution was relatively uniform. Compared with the MnO$_2$ samples, the MnO$_x$-NiO particles had a more developed pore structure, a loose surface and a larger specific surface area, which were beneficial to improve the catalyst's formaldehyde removal activity. That is, the MnO$_x$-NiO samples had better dispersibility and activity$^{[32]}$. 

![Figure 6](image3)
Figure 6. SEM images of MnOx-NiO catalysts (a, MnOx-NiO; b, MnO2).

Figure 7. TEM and HRTEM images of MnOx-NiO catalysts.

Figure 7 shows the TEM images of the MnOx-NiO catalyst samples. It can be seen from 7(a) that the catalysts showed a thick fold accumulation in the middle and a thin fold accumulation in the edge, which was beneficial to increase the specific surface area of MnOx-NiO catalysts and enhance the catalytic performance of the samples. It can be seen from 7(b) that the lattice spacing of the samples were 0.209 nm and 0.241 nm, corresponding to the NiO (200) crystal plane and MnO2 (101) crystal plane, respectively. In addition, the existence of a lattice spacing of 0.253 nm was also found, which was the (012) crystal plane of the layered double hydroxide of nickel[8]. It may be that the manganese-nickel ions on the surface of the sample reacted with adsorbed water on the surface to form a manganese-nickel layered bimetal oxide. The above results confirmed the existence of MnO2 and NiO, and also explained the possible reasons for the formation of amorphous substances in the samples.

Figure 8 shows the Ni2p, Mn2p and O1s X-ray photoelectron spectroscopy of samples. It can be seen from Figure 8(a) the spectrum of Mn2p which was apparently divided into two peaks, attributed to Mn2p3/2 and Mn2p1/2. The signal peaks appeared at the binding energy of 642.1 eV and 643 eV were attributed to Mn3+ and Mn4+ (642.5-643 eV) species in the catalyst samples[33], Mn4+ ions were dominant species in the MnOx-NiO catalysts. The abundant Mn4+ particles on the sample surface could provide sufficient active sites for formaldehyde oxidation, which was beneficial to enhance the catalytic activity of the catalysts[24]. It can be seen from Figure 8(b) that Ni2p had two main peaks, Ni2p3/2 and Ni2p1/2, and there were corresponding satellite peaks near the main peak. The MnOx-NiO samples showed two peaks on the Ni2p3/2 and Ni2p1/2 orbitals, 855 eV and 872.6 eV respectively, indicating the existence of Ni2+ compounds, such as NiO and Ni(OH) species, and no characteristic peaks of Ni3+ (856.1-856.7 eV) were found[34,35].
Figure 8. XPS spectrums of MnO$_x$-NiO samples (a) Mn2p, (b) Ni2p, (c) O1s.

Figure 8(c) was obtained by fitting the O1s spectrum of the MnO$_x$-NiO samples. It can be seen from the figure that the samples had the corresponding lattice oxygen (O$_I^-$) and surface adsorbed oxygen (O$_{II}^-$) at the binding energy of 529.7 and 531.1 eV [36]. The formation of lattice oxygen may be related to lattice defects, which were conducive to the catalytic oxidation of formaldehyde. The above content was consistent with the results of the Raman test.

5. Conclusions
The MnO$_x$-NiO catalysts synthesized by hydrothermal co-precipitation method performed excellent catalytic activity. Exploring the influence of reaction conditions on catalyst formaldehyde removal rate, keeping the other process parameters were 0.0125 mol potassium permanganate, 0.005 mol nickel nitrate, 5 ml sodium oxalate solution, 0.5 ml ammonia solution unchanged, the formaldehyde removal rate of MnO$_x$-NiO catalysts increased first and then decreased with the increase of hydrothermal temperature and time as well as calcination temperature and time. The optimum process parameters obtained in the experiment were the hydrothermal temperature was 130 °C, hydrothermal time was 5 h, calcination temperature was 200 °C, and the calcination time was 5 h. The samples prepared under these conditions had the highest catalytic activity and the formaldehyde removal rate was 95.57% at room temperature, which was 30% higher than that of pure MnO$_2$ catalysts. MnO$_x$-NiO catalysts were composed of amorphous and crystal, and the presence of more amorphous substances was conducive to promoting the removal of formaldehyde. Compared with pure MnO$_2$, the addition of Ni had a certain effect on the surface functional group and lattice vibration of the catalysts. The microscopic morphology of the samples was spherical accumulation, the surface was loose, and the average particle diameter was 888.94 nm. The presence of Mn$^{4+}$ particles and lattice oxygen were more conducive to the room temperature oxidation of formaldehyde.
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