Selective Catalytic Reduction of NO with NH₃ over High Purity Palygorskite-supported MnO₂ with Different Crystal Structures

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ABSTRACT

In order to find efficient catalysts for low-temperature selective catalytic reduction with ammonia (NH₃-SCR), several MnO₂ with different crystal structure have been supported on high-purity palygorskite (Pal) by a hydrothermal method. The effect of MnO₂ crystal structures on the NH₃-SCR performance of the catalysts was investigated. All catalysts were characterized by X-ray diffraction (XRD), N₂ adsorption-desorption, Raman spectrum, Thermo gravimetric analysis/Differential thermo gravimetric (TG/DTG), ammonia-temperature programmed desorption (NH₃-TPD), hydrogen-temperature programmed reduction (H₂-TPR), Transmission electron microscope (TEM) and X-ray energy dispersive spectroscopy (EDS) and X-ray photoelectron spectrometer (XPS). The presented results suggested that α-MnO₂/Pal catalyst exhibit the highest catalytic activity among four type MnO₂/Pal catalysts in the temperature range of 50–400°C, own promising stability during a 24 h continuous denitration experiment. Furthermore, the crystal structure affords α-MnO₂/Pal with the highest specific surface area and more acidic sites, which is beneficial for the SCR reaction. It has improved the NH₃ adsorption ability and catalytic activity of the catalyst.

Keywords: Palygorskite; MnO₂; Selective catalytic reduction; NO; Crystal structure.

INTRODUCTION

Nitrogen oxides (NOₓ) can result in acid rain, photochemical smog and ozone depletion, it has become a global environmental concern question (Yung et al., 2007; Liu et al., 2015a; Yu et al., 2015). NH₃-SCR is the most commonly used and effective denitration technology in modern thermal power plants, accounting for about 95% of the worldwide flue gas denitration devices, with NO conversion reaching over 90% (Pappas et al., 2016; Boningari et al., 2018; Wang et al., 2019a). Transition metal catalysts gradually show bright prospects because of their high resistant performance to poisoning and sintering (Du et al., 2019; He et al., 2019; Wang et al., 2020). In order to reduce costs, it is necessary to develop composite catalysts with higher catalytic activity at low temperatures. The Mn based catalysts own substantial low-temperature activity, besides, the material sources are world wide access, so the catalysts have a good prospect of industrial application (Hua et al., 2020; Wu et al., 2020). In addition, as the valence state of Mn species in the catalyst increases, its SCR catalytic activity becomes better. An earlier report showed that MnO₃ own the highest NO conversion among the MnO₃ catalyst include of MnO₂, Mn₅O₈, Mn₂O₃ and Mn₃O₄ (Kapteijn et al., 1994). Moreover, the morphology and pore structure of MnO₃ have significant influence on its catalytic activity, there are several kinds of crystal structures in MnO₂, and the most common ones are α-, β-, γ- and δ-MnO₂. Different crystal structures have different functions in adsorption ability, oxygen functional groups and redox activity (Cheng et al., 2006; Liang et al., 2008; Zhang et al., 2015). In the past few decades, different forms of manganese dioxide have received attention and research in catalytic conversion of CO, NO, formaldehyde and ethanol (Liang et al., 2008; Zhang et al., 2015; Chen et al., 2016; Liu et al., 2016; Yang et al., 2020). However, there is less research on the relationship between the crystal structure and catalytic activity of SCR catalysts. Importantly, the substantial porous structure, is a vital factor in SCR reaction (Wang et al., 2019b). Palygorskite is recognized as a typical low-cost clay mineral. Its well-developed pore structure and large specific surface area make it a potential catalyst support for many catalytic reactions and a good carrier for many catalysts (Lin et al., 2017b; Liu et al., 2018; Liu et al., 2019). It may be implied that manganese dioxides loaded Palygorskite...
catalyst may have a greatly improved removal efficiency for NOx. Furthermore, the main composition of raw Pal clay were Pal, quartz, dolomite and a few impurities (Qiu et al., 2015).

Therefore, there is great need to study: 1) the purification effect of raw Palygorskite; 2) the relationship between the SCR activity and crystal structures of MnO2 in MnO2/Pal catalysts to synthesize a novel MnO catalyst for SCR. In this study, four crystal forms of manganese dioxide were loaded on highly purified Palygorskite, subsequently the denitration performance and N2 selectivity of Pal-supported catalyst in NH3-SCR were evaluated, and the characterizations were applied for the catalyst, the reaction mechanism was investigated. In order to further study with Pal as the carrier, is expected to achieve industrial application of forming low temperature SCR denitration catalyst preparation.

EXPERIMENTAL SECTION

Purified Palygorskite

200 g of raw Pal mine powder (guanshan Palygorskite clay mine, mingguang city, anhui province) was added into 1.5 L deionized water, ultrasonic dispersion 30 min. Then added 2 L deionized water, removed the magnetic material with the magnetic bar until there is no obvious trace on the magnetic bar. The following 2 g sodium hexametaphosphate and 1.5 L deionized water were added, stirring 30 min, then static settlement 12 h. The upper mixed liquid was placed in the 5 L measuring cylinder, then added deionized water to 5 L, and the substratum sedimentation was poured and settled for 12 h. The mixture was transferred from the measuring cylinder to the large beaker, 2 g CaCl2 was added and stirred until it is sticky, centrifugal, and took the sediment into the oven to dry. After that, 1% mass ratio of dilute hydrochloric acid was added for acidification, the mixed solution was stirred for 24 h at 60°C. Subsequently, the purified Palygorskite clay (In the following sections, the purified Palygorskite clay was labeled as Pal) was acquired after filtration, washing and drying at 100°C for 2 h.

Preparation of Catalysts

The synthetic method of α-MnO2/Pal, 5.09 g Pal was added into 100 ml deionized water, stirring 2 h ensure Pal spread evenly, then 0.53 g MnSO4·H2O, 1.25 g KMnO4 were dissolved in deionized water and then 2 ml concentrated HNO3 added slowly, after that stirring overnight. The solution was transferred into a Teflon reactor (200 mL) then heated to 100°C and held isothermally for 24 h. After cooling down, the sediment was centrifuged, washed five times, then dried at 100°C overnight, and finally calcined in a muffle furnace at 400°C for 2 h. Ultimately, α-MnO2/Pal was achieved by grinding to 40 to 60 mesh sieving for the following experiment. The procedures for the preparation of other crystal structures catalysts were similar to that of α-MnO2/Pal:

For β-MnO2/Pal, 4.63 g Pal was added into 100 mL deionized water, stirring 2 h, then 1.69 g MnSO4·H2O and 2.28 g (NH4)2S2O8 were added slowly, subsequently heated to 140°C and held isothermally at 140°C for 12 h in an oven.

For γ-MnO2/Pal, 9.26 g Pal was added into 100 mL deionized water, stirring 2 h, then 3.37 g MnSO4·H2O and 4.57 g (NH4)2S2O8 were added slowly, subsequently heated to 90°C and held isothermally at 90°C for 24 h in an oven.

For δ-MnO2/Pal, 5.86 g Pal was added into 100 mL deionized water, stirring 2 h, then 0.80 g (NH4)2C2O4 and 2.00 g KMnO4 were added slowly, subsequently heated to 90°C and held isothermally at 90°C for 10 h in an oven.

Characterization

In order to test the purification effect of Palygorskite clay, a X-ray fluorescence (XRF, Shimadzu XRF-1800) catalysis was carried out for Palygorskite clay before and after purification. X-ray diffraction (XRD) was investigated by a DX-2700 diffractometer fitted with a nickel-filtered Cu Ka radiation source and operating at a voltage of 40 kV and 30 mA. The specific area (BET) analyses of the catalysts were determined by a Quantachrome NOVA 3000e apparatus. The pore size distribution and pore volume were calculated from the desorption branch of N2 adsorption isotherm using the BJH method. TG curves were performed on a TG/DTA7300 instrument (EXSTA-SII, Seiko Instruments Inc. Japan). H2-TPD analyses was carried out in a quartz tube reactor with a mass spectograph for detection of H2, 0.1 g catalyst was heated from 50 to 800°C under 5% H2/Ar. NH3-TPD was also tested using the above equipment. Raman scattering spectra were recorded on HORIBA HR spectrometer with 532 nm line of argon ion laser as an excitation source. XPS data were acquired by an ESCALAB 250Xi electron spectrometer using Mg K radiation (1253.6 eV). All element binding energies were calibrated relative to the C 1s peak from carbon contamination at 284.6 eV. The physicochemical properties of the catalysts were determined by the micrographs obtained on a JEM-2100F transmission electron microscope (TEM). Elemental distribution mapping for the particles was obtained with the aid of TEM integrated with X-ray energy dispersive spectroscopy (EDS).

Activity Test

The SCR activity of different structural MnO2/Pal catalysts were evaluated in a fixed-bed quartz tubular reactor (i.d. 8 mm) and catalyst (100 mg, 40–60 mesh) was placed in the center of the reactor. The mixture gas consisted of 500 ppm NO, 500 ppm NH3, 3 vol% O2 and with Ar as balance gas. The total flow rate was 300 mL min−1 and keeping a gas hourly space velocity (GHSV) of 64000 h−1 in the whole time. In detail, the procedure is as follows: the system was firstly inlet the reaction gas for 20 min at room temperature. Then the samples were heated to 50°C and maintain 20 min. After that, the catalysts were heated at 10°C min−1 from 50°C up to 400°C. The concentrations of NOx in inlet and outlet gas were measured by a flue gas analyzer (KANE, KM9106), respectively. NO conversion is defined as:

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\text{NO conversion} = \frac{\text{NOinlet} - \text{NOoutlet}}{\text{NOinlet}} \times 100\% \quad (1)
\]

(NO and NO2 were the only nitrogen-containing oxides detected).
RESULTS AND DISCUSSION

XRF

The purification result investigated by XRF was shown in Table 1. From the table, we found that after the acid leaching purification, the content of SiO₂ increased while the content of MgO decreased; besides the CaO was completely removed and the burning loss decreased. After the hydrostatic sedimentation and acid leaching purification, dolomite and other impurities can be effectively removed and the sample of Pal with a higher purity can be obtained. It can be used as the catalyst carrier for the subsequent study of NH₃ SCR denitration.

XRD

The XRD patterns of purified Pal and MnO₂/Pal were shown in Fig. 1. After purification, we found that the diffraction peak ascribed to dolomite disappeared while the intensity of the quartz diffraction peak decreased significantly. In the meantime, the Pal exhibited more prominent diffraction peaks compared with the raw Palygorskite mineral, indicating that the purification had a good efficiency. The diffraction peaks in 8.4°, 13.7°, 16.3°, 19.8°, 20.9°, 27.6° and 34.4° were in good agreement with the characteristic peaks of Palygorskite (JSPDS 31-783). The XRD patterns of the four catalysts have no obvious corresponding crystal manganese dioxide peaks, and compared with purified Pal, the reflections strength of MnO₂/Pal catalysts significantly decreased. It may be related to the hydrothermal synthesis method destroying the structure of Pal and highly distribution manganese dioxide with poor crystallinity. The purification had a good efficiency. The diffraction peaks into the MnO₂ pore channel, reducing the stability of its crystalline structure (Meher and Rao, 2012). The δ-MnO₂, α-MnO₂, γ-MnO₂, and β-MnO₂ show layered structure, 2 × 2 tunneled structure, 2 × 1 tunneled structure, and 1 × 1 tunneled structure, respectively. The main reason of δ-MnO₂ and α-MnO₂ less stable than β-MnO₂ was due to the easy collapse of layer or large tunnel.

Raman

Raman spectroscopy was applied to further identify the crystal structure of MnO₂ among MnO₂/Pal catalysts. The Raman spectra of MnO₂/Pal catalysts was shown in Fig. 3, several bands were recognized from α-MnO₂/Pal at 149, 400, 510, 560 and 641 cm⁻¹. The band at 560 cm⁻¹ was attributed to the Mn–O lattice vibration in α-MnO₂, while the other two catalysts, β-MnO₂ and δ-MnO₂ less stable than β-MnO₂ was due to the easy collapse of layer or large tunnel.

TG/DTG

Thermogravimetric analysis can be used to identify the phase of manganese dioxides loaded onto Pal. TG-DTG analyses were respectively performed on the Pal after purification and the four prepared catalysts, as shown in Fig. 2. below. The typical TG curves show four weight losses in 91°C, 212°C, 437°C and 668°C respectively. It indicates that there are four states of dehydration in Pal, named, caused by loss of water adsorbed on outer surface, pore channel, water of coordination crystal and structure respectively (Frost and Ding, 2003). In general typical MnO₂ within the scope of room temperature to 900°C will react through two-step pyrolysis, namely MnO₂ is decomposed into Mn₂O₃ at first, and then decomposed to Mn₃O₄, corresponding to the decomposition temperature of about 483°C and 799°C (Terayama and Ikeda, 1983). The weight loss ratios of the two catalysts, α-MnO₂/Pal and δ-MnO₂/Pal, with potassium permanganate as the precursors, are significantly higher than the other two catalysts. This may be related to some K⁺ ions into the MnO₂ pore channel, reducing the stability of its crystalline structure (Meher and Rao, 2012). The δ-MnO₂, α-MnO₂, γ-MnO₂, and β-MnO₂ show layered structure, 2 × 2 tunneled structure, 2 × 1 tunneled structure, and 1 × 1 tunneled structure, respectively. The main reason of δ-MnO₂ and α-MnO₂ less stable than β-MnO₂ was due to the easy collapse of layer or large tunnel.

Fig. 1. The XRD patterns of purified Pal and MnO₂/Pal.

Fig. 2. The TG-DTA spectra of purified Pal and MnO₂/Pal.

Table 1. The element content in Palygorskite clay before and after purification (LOI: Loss on ignition).

|                | SiO₂ (%) | MgO (%) | Al₂O₃ (%) | Fe₂O₃ (%) | CaO (%) | K₂O (%) | TiO₂ (%) | P₂O₅ (%) | Others (%) | LOI (%) |
|----------------|----------|---------|-----------|-----------|---------|---------|---------|----------|-----------|--------|
| before         | 49.57    | 9.29    | 7.11      | 4.07      | 1.65    | 1.19    | 0.55    | 0.25     | 0.27      | 26.05  |
| after          | 59.03    | 8.39    | 8.03      | 4.81      | 0       | 1.22    | 0.51    | 0.32     | 0.19      | 17.5   |
A BET analysis was performed on different MnO$_2$/Pal catalysts and Pal after purification. The analysis results were summarized in the following Table 2. From this table, we find α-MnO$_2$/Pal owns the maximum specific surface area, β-MnO$_2$/Pal owns the highest total pore volume and average pore size while the lowest specific surface area. Compared with the purified Pal, MnO$_2$/Pal catalysts own higher total pore volume and average pore size. Except α-MnO$_2$/Pal, the specific surface area of other MnO$_2$/Pal catalysts were reduced. After purification, we found that Pal owns large specific surface area and was suitable as a catalyst carrier.

The loading of different crystal structures of MnO$_2$ onto Pal can explain the decrease of BET surface area. However, compared with the BET characterization results of pure MnO$_2$ with different crystal structures, MnO$_2$/Pal owns larger specific surface area (Lin et al., 2017a), which may be related to the contribution of purified Pal (Zhao et al., 2016).

**Catalyst Activity Test and the Selective of N$_2$**

As shown in Fig. 4, after purification, it can be seen that Pal almost have no catalytic effect in low temperature, until at 250°C the catalytic effect appears, then starts to rise, up to 20% at 400°C. All the four catalysts loaded with manganese
The catalytic activity of manganese dioxide have good catalytic performances at medium temperature, and their catalytic activity reaches the highest at 250°C, which is consistent with previous researches (Chen et al., 2016; Jia et al., 2016; Yang et al., 2020). In the temperature ranging from 150–300°C, the α-MnO2/Pal shows promising catalytic activity (NO conversion rate was over 97%) towards NO reduction with O2. Interestingly, except δ-MnO2/Pal, the other MnO2/Pal catalysts during 250–300°C are all close to 100% NO conversion. In comparison to the above catalysts, δ-MnO2/Pal shows higher NO conversion before 250°C. Yet, the NO conversion of δ-MnO2/Pal decreases significantly at high temperature period. Compared with pure phase manganese dioxide, the activity intensity was close, and the order of activity intensity of different crystal forms of manganese dioxide was consistent (Luo et al., 2016). The catalytic activity was similar to pure manganese dioxide, which was achieved by using Pal supported manganese dioxide. According to the comprehensive characterization analysis, the catalytic activity of α-MnO2/Pal is higher than the other three catalysts.

Fig. 5 shows the results of N2 selectivity of purified Pal and MnO2/Pal catalysts. Purified Pal afforded highly impressive N2 selectivity, which were over 99% at different temperatures. Therefore, we can infer that Pal as the catalyst carrier had no effect on the N2 selectivity of catalyst. N2 selectivity of four Pal supported catalysts decreased before 350°C then increased with the rising of temperature, obviously α-MnO2/Pal exhibited the better N2 selectivity than others. Fig. 6 shows the stability experiment of α-MnO2/Pal catalyst at 250°C. After 24 h continuous denitration experiment, the denitration efficiency of the catalyst can still be maintained at about 99%, which shown that the MnO2 supported on high-purity Pal own satisfactory stability.

Through the above experiments, it was found that the optimal catalyst was α-MnO2/Pal among the four catalysts. Therefore, it was tested for sulfur dioxide and water vapor tolerance. The results are shown in Fig. 7. The experimental conditions were used as follows: 250°C, 500 ppm NH3 and NO, 3% O2, Ar balance, and GHSV of 64000 h–1. After 200 ppm SO2 was introduced in, NO conversion dropped rapidly to below 40% after 20 minutes and then gradually decreased to about 3%. After switching SO2 off, NO removal rate slightly increased to about 5%. When 6% volume fraction of water vapor was introduced, the NO removal rate gradually decreased, and finally reached a steady state at about 70%. When cutting off water vapor, NO removal rate gradually restored to the initial value. It can be seen that the deactivation effect of SO2 on the catalyst is irreversible, while water vapor is reversible. Finally, we investigated the combined impacts of H2O and SO2 on SCR activity of α-MnO2/Pal. The NO conversion rate has a slight decrease at first and could maintain NO conversion above 90% after 1 hour. Nevertheless, the NO removal rate gradually decreased until it reached to 0%. When the H2O and SO2 inlet gas were turn off, the NO conversion rate gradually increases to about 10%.

### NH3-TPD and H2-TPR

As we known that the surface acid sites of the catalysts make an important impact in the removal of NO by NH3-SCR at low temperature (Liu et al., 2015b). As shown in Fig. 8, the NH3-TPD curves of the α-MnO2/Pal only contained one single main peak in 150°C. Compared with other catalysts, the peak position shifted to right for an offset of 20°C and the intensity was far more than other kinds of catalysts. According to previous reports, 130–150°C of NH3 desorption peak attributed to weak acid Bronsted acid sites of adsorption, 480–665°C of NH3 desorption peak assigned to acid adsorption Lewis acid sites (Jin et al., 2010; Lee et al., 2012; Zhang et al., 2014). As a Pal supported catalyst, in 480 and 665°C, δ-MnO2/Pal had two obvious acid sites, compared with the front weak acid sites its strength lower, δ-MnO2/Pal showed a peak in 640°C belong to strong acid site, β- and γ-MnO2/Pal both own one peak in 560°C belong to strong acid site. The desorption peak position in the NH3-TPD curve reflected the strength of the acid site of the catalyst, while the peak area corresponds to the adsorption amount of ammonia (Bates et al., 2014; Cao et al., 2015). The peak area of α-MnO2/Pal was significantly greater than that of the other three catalysts, and the weak acidic site was mainly responsible for it, which was more favorable for NH3-SCR reaction.

### Table 2. BET analyses of different crystal structures MnO2/Pal catalysts and Pal after purification.

| Catalysts       | BET specific surface area (m² g⁻¹) | Total pore volume (mL g⁻¹) | Average pore diameter (nm) |
|-----------------|-----------------------------------|----------------------------|----------------------------|
| Pal after purification | 144.45                            | 0.34                       | 9.44                       |
| α-MnO2/Pal      | 162.09                            | 0.45                       | 11.01                      |
| β-MnO2/Pal      | 124.91                            | 0.46                       | 14.76                      |
| γ-MnO2/Pal      | 131.57                            | 0.43                       | 13.09                      |
| δ-MnO2/Pal      | 125.05                            | 0.43                       | 13.67                      |
Fig. 4. Catalytic activities of purified Pal and MnO₂/Pal.

Fig. 5. The N₂ selectivity for purified Pal and MnO₂/Pal.

Fig. 6. The stability experiment of α-MnO₂/Pal catalyst at 250°C.

Fig. 7. Effect of H₂O and SO₂ on the selective catalytic reduction activity of α-MnO₂/Pal catalysts.

Fig. 8. NH₃-TPD patterns of purified Pal and MnO₂/Pal.

The H₂-TPR patterns of MnO₂/Pal catalysts were showed in Fig. 9. We can find all catalysts have two obvious H₂ reduction peaks, which can be explained by the gradual reduction of MnO₂ to MnO (Tong and Huang, 2012). By contrast, the following ellipticity-temperature profiles are shown to evaluate the abundant Mn⁴⁺, Mn³⁺ and Oα species. β-MnO₂/Pal and γ-MnO₂/Pal catalysts own two reduction peaks appear in similar positions of 367°C and 376°C, meanwhile high-temperature reduction peaks were located at 521°C and 526°C, respectively. According to the characterization results of XRD, TG and Raman, the typical process of reduction was MnO₂ to Mn₃O₄ and then to MnO (Alvarez-Galvan et al., 2003). The reduction peaks of δ-MnO₂/Pal were observed at 414°C, 517°C, respectively, and the strength of the two peaks were lower than former catalysts. α-MnO₂/Pal had a main reduction peak at 300°C while a weak peak at 462°C. It should be attributed to the reduction of MnO₂ to Mn₂O₃ and Mn₃O₄, finally transformed to MnO. Due to the lowest reduction temperature, α-MnO₂/Pal was regarded as the optimal catalyst.
TEM

Figs. 10(a)–10(d) showed the TEM images of the different catalysts. For these images, the one-dimensional rod-shaped substance was ascribed to Pal, at the same time the surface of Pal was coated by flocculent MnO$_2$. We can find although MnO$_2$ particles were in nano size, nonetheless, their dispersion in MnO$_2$/Pal were different. It is clear that α-MnO$_2$ (Fig. 10(a)) has good dispersibility on the surface of Pal. Compared with Figs. 10(b) and 10(d), there was a certain degree of agglomeration of MnO$_2$ on surface of β- and γ-MnO$_2$/Pal catalysts, with the particle size between 50 and 200 nm. Then, δ-MnO$_2$ was also highly dispersed on the surface of Pal as shown in Fig. 10(c). In addition, it was found that the pores on the surface of catalysts could be seen more clearly after purification, which might be due to the fact that the impurities were removed. The dispersion of different crystal forms of manganese dioxide just confirms the direction of special surface area values with different loaded MnO$_2$ as shown in Table 2. The high-resolution image and EDS spectrum of α-MnO$_2$/Pal is shown in Figs. 10(e) and 10(f), where the crystal edge of α-MnO$_2$ is found, and the lattice spacing is 2.1 Å. This is consistent with Raman spectrum characterization (Fig. 3). Through Raman spectroscopy and TEM analysis, we confirmed the successful synthesis of α-MnO$_2$. The EDS result (Fig. 10(f)) confirmed that Si, Mg,
Al, Fe, O and other elements were attributed to Pal, Mn and O elements attributed to MnO₂, and Cu element to the TEM sample slide. We calculated loading content of Mn element reaches the theoretical value.

**XPS**

XPS spectroscopy analyze was used to identify the MnO₂/Pal catalysts surface species of Mn and O. It is clear that the Mn 2p 3/2 peaks of β-MnO₂/Pal right shift about 0.5 eV while other catalysts were located near 642.2 eV (Fig. 11(a)), and similar shift was occurred in the following O 1s peak (Fig. 11(c)). This is caused by the unique crystal structure of β-MnO₂ (Zhang et al., 2015; Chen et al., 2016). The percents of surface Mn³⁺/Mn⁴⁺ molar ratios were listed in Table 3. α-MnO₂/Pal own the highest Mn³⁺/Mn⁴⁺ molar ratio whereas the δ-MnO₂/Pal showed the lowest, which is consistent with the H₂-TPR result in section 3.7.

XPS spectra of O 1s was shown in Fig. 11(c), the profiles of MnO₂/Pal catalysts were fitted to three peaks. Binding energies at 529.6 ± 0.1 eV was ascribed to surface adsorbed

![XPS spectra](image)

**Fig. 11.** XPS spectra of α-, β-, γ- and δ-MnO₂/Pal catalysts: (a) Mn 2p and (b) Mn 2p 3/2 (c) O 1s.
oxygen (denoted as O₉) and 531.0 ± 0.2 eV belong to lattice oxygen with manganese (denoted as O₉). Peaks near 532.4 eV were assigned to surface hydroxyl species and chemisorbed water (denoted as O₉OH) (Li et al., 2016). Unlike the high content of lattice oxygen in pure phase MnO₂ (Liang et al., 2008), the surfaces of the prepared different crystalline MnO₂/Pal catalysts are covered by mostly hydroxyl oxygen, because the carrier Pal contains a large amount of hydroxyl oxygen (Chen et al., 2011; Xie et al., 2016; Yang et al., 2020). As we known that O₉ performs high activities and makes an important impact in reduction reaction because of its higher mobility than O₉ (Zhao et al., 2018). Table 3 showed the percent of molar ratios O₉/O₉OH. The value was decrease in the following sequence: α > β > γ > δ-MnO₂, which consistent with the catalytic activity results in section 3.6. This indicating that the catalytic activity was nearly correlated with the surface O₉ species concentration.

### CONCLUSIONS

Considering the catalytic performance, selecting an optimum support for MnO₂ catalysts plays a major role in NO reduction behaviour. In our work, after the hydrostatic sedimentation and acid leaching purification, impurities can be effectively removed and a higher-purity palygorskite can be obtained. After the purification process, several MnO₂ with different crystal structure have been supported on high-purity palygorskite by hydrothermal method. All four catalysts show good NO removal efficiency at 150–300°C, purity palygorskite by hydrothermal method. All four catalysts show good NO removal efficiency at 150–300°C, which is consistent with the catalytic activity results in section 3.6. This indicating that the catalytic activity was nearly correlated with the surface O₉ species concentration.

### DECLARATION OF COMPETING INTEREST

The authors declare no competing interests.

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### REFERENCES

Alvarez-Galvan, M., De la Peña O’Shea, V., Fierro, J. and Arias, P. (2003). Alumina-supported manganese-and manganese-palladium oxide catalysts for VOCs combustion. \*Catal. Commun.* 4: 223–228.

Bates, S.A., Delgass, W.N., Ribeiro, F.H., Miller, J.T. and Gounder, R. (2014). Methods for NH₃ titration of Brønsted acid sites in Cu-Zeolites that catalyze the selective catalytic reduction of NO with NH₃. \*J. Catal.* 312: 26–36.

Bonigari, T., Pappas, D.K. and Smirniotis, P.G. (2018). Metal oxide-confined interweaved titania nanotubes M/TNT (M=Mn, Cu, Ce, Fe, V, Cr, and Co) for the selective catalytic reduction of NO in the presence of excess oxygen. \*J. Catal.* 365: 320–333.

Cao, F., Chen, J., Lyu, C., Ni, M., Gao, X. and Cen, K. (2015). Synthesis, characterization and catalytic performances of Cu-and Mn-containing ordered mesoporous carbons for the selective catalytic reduction of NO with NH₃. \*Catal. Sci. Technol.* 5: 1267–1279.

Chen, H., Wang, Y. and Lv, Y.K. (2016). Catalytic oxidation of NO over MnO₂ with different crystal structures. \*RSC Adv.* 6: 54032–54040.

Chen, T., Liu, H., Li, J., Chen, D., Chang, D., Kong, D. and Frost, R.L. (2011). Effect of thermal treatment on adsorption-desorption of ammonia and sulfur dioxide on palygorskite: Change of surface acid-alkali properties. \*Chem. Eng. J.* 166: 1017–1021.

Cheng, F., Zhao, J., Song, W., Li, C., Ma, H., Chen, J. and Shen, P. (2006). Facile controlled synthesis of MnO₂ nanostructures of novel shapes and their application in batteries. \*Inorg. Chem.* 45: 2038–2044.

Du, Y., Liu, L., Feng, Y., Yang, B. and Wu, X. (2019). Enhancement of NH₃-SCR performance of LDH-based MnMnAl(M=Cu, Ni, Co) oxide catalyst: influence of dopant M. \*RSC Adv.* 9: 39699–39708.

Frost, R.L. and Ding, Z. (2003). Controlled rate thermal analysis and differential scanning calorimetry of sepiolite and palygorskites. \*Thermochim. Acta* 397: 119–128.

Gao, T., Fjellvåg, H. and Norby, P. (2009). A comparison study on Raman scattering properties of α-and β-MnO₂. \*Anal. Chim. Acta* 648: 235–239.

He, S., Li, Q., Zhang, Q., Zhang, Z. and Wang, L. (2019). High efficiency of Ce-modified MnO₃/TiO₂-ZrO₂-based low-temperature selective catalytic reduction denitration catalysts. \*J. Environ. Eng.* 145: 1–8.

Hua, H., Zeng, J., Wang, G., Zhang, J., Zhou, J., Pan, Y., Liu, Q., Xu, Y., Qian, G. and Xu, Z.P. (2020). Understanding of the high hydrothermal stability of a catalyst prepared from Mn slag for low-temperature...

### Table 3. XPS results of surface Mn and O elements.

| Catalyst          | Mn²⁺ (%) | Mn³⁺ (%) | Mn²⁺/Mn³⁺ | O₉ (%) | O₉OH (%) | O₉/O₉OH (%) | O₂/O₃ |
|-------------------|----------|----------|-----------|--------|----------|-------------|-------|
| α-MnO₂/Pal        | 49.13    | 50.87    | 0.96      | 20.03  | 6.20     | 73.77       | 3.23  |
| β-MnO₂/Pal        | 32.19    | 67.81    | 0.47      | 14.85  | 7.53     | 77.62       | 1.97  |
| γ-MnO₂/Pal        | 33.83    | 66.17    | 0.51      | 9.08   | 6.56     | 84.36       | 1.38  |
| δ-MnO₂/Pal        | 21.47    | 78.53    | 0.27      | 5.56   | 4.95     | 89.49       | 1.12  |
selective catalytic reduction of NO. J. Hazard. Mater. 381: 120935.

Jia, J., Zhang, P. and Chen, L. (2016). Catalytic decomposition of gaseous ozone over manganese dioxides with different crystal structures. Appl. Catal., B 189: 210–218.

Jin, R., Liu, Y., Wu, Z., Wang, H. and Gu, T. (2010). Low-temperature selective catalytic reduction of NO with NH3 over MnCe oxides supported on TiO2 and Al2O3: A comparative study. Chemosphere 78: 1160–1166.

Kapteijn, F., Vanlangeveld, A.D., Moulijn, J.A., Andreini, A., Vuurman, M.A., Turek, A.M., Jehng, J.M. and Wachs, I.E. (1994). Alumina-supported manganese oxide catalysts: I. Characterization: effect of precursor and loading. J. Catal. 150: 94–104.

Lee, S.M., Park, K.H. and Hong, S.C. (2012). MnOx/CeO2-TiO2 mixed oxide catalysts for the selective catalytic reduction of NO with NH3 at low temperature. Chem. Eng. J. 195: 323–331.

Li, J., Zhang, P., Wang, J. and Wang, M. (2016). Birnessite-type manganese oxide on granular activated carbon for formaldehyde removal at room temperature. J. Phys. Chem. C 120: 24121–24129.

Liang, S., Teng, F., Bulgan, G., Zong, R. and Zhu, Y. (2008). Effect of phase structure of MnO2 nanorod catalyst on the activity for CO oxidation. J. Phys. Chem. C 112: 5307–5315.

Lin, H., Chen, D., Liu, H., Zou, X. and Chen, T. (2017). Effect of MnO2 crystalline structure on the catalytic oxidation of formaldehyde. Aerosol Air Qual. Res. 17: 1011–1020.

Liu, J., Song, W., Xu, C., Liu, J., Zhao, Z., Wei, Y., Duan, A. and Jiang, G. (2015a). The selective catalytic reduction of NOx over a Cu/ZSM-5/SAPO-34 composite catalyst. RSC Adv. 5: 104923–104931.

Liu, P., He, H., Wei, G., Liang, X., Qi, F., Tan, F., Tan, W., Zhu, J. and Zhu, R. (2016). Effect of Mn substitution on the promoted formaldehyde oxidation over spinel ferrite: Catalyst characterization, performance and reaction mechanism. Appl. Catal., B 182: 476–484.

Liu, P., Wei, G., Liang, X., Chen, D., He, H., Chen, T., Xi, Y., Chen, H., Han, D. and Zhu, J. (2018). Synergetic effect of Cu and Mn oxides supported on palygorskite for the catalytic oxidation of formaldehyde: Dispersion, microstructure, and catalytic performance. Appl. Clay Sci. 161: 265–273.

Liu, P., Wei, G., He, H., Liang, X., Chen, H., Xi, Y. and Zhu, J. (2019). The catalytic oxidation of formaldehyde over palygorskite-supported copper and manganese oxides: Catalytic deactivation and regeneration. Appl. Surf. Sci. 464: 287–293.

Liu, Y., Xu, J., Li, H., Cai, S., Hu, H., Fang, C., Shi, L. and Zhang, D. (2015b). Rational design and in situ fabrication of MnO4@NiCo3O4 nanowire arrays on Ni foam as high-performance monolith de-NOx catalysts. J. Mater. Chem. A 3: 11543–11553.

Luo, S., Zhou, W., Xie, A., Wu, F., Yao, C., Li, X., Zuo, S. and Liu, T. (2016). Effect of MnO2 polymorphs structure on the selective catalytic reduction of NOx with NH3 over TiO2-palygorskite. Chem. Eng. J. 286: 291–299.

Meher, S.K. and Rao, G.R. (2012). Enhanced activity of microwave synthesized hierarchical MnO2 for high performance supercapacitor applications. J. Power Sources 215: 317–328.

Pappas, D.K., Boningari, T., Boolchand, P. and Smirniotis, P.G. (2016). Novel manganese oxide confined interweaved titania nanotubes for the low-temperature selective catalytic reduction (SCR) of NOx by NH3. J. Catal. 334: 1–13.

Qiu, G., Xie, Q., Liu, H., Chen, T., Xie, J. and Li, H. (2015). Removal of Cu(II) from aqueous solutions using dolomite–palygorskite clay: Performance and mechanisms. Appl. Clay Sci. 118: 107–115.

Sinha, A.K., Pradhan, M. and Pal, T. (2013). Morphological evolution of two-dimensional MnO2 nanosheets and their shape transformation to one-dimensional ultralong MnO2 nanowires for robust catalytic activity. J. Phys. Chem. C 117: 23976–23986.

Terayama, K. and Ikeda, M. (1983). Study on thermal decomposition of MnO2 and MnO by thermal analysis. J. Jpn. Inst. Met. 24: 754–758.

Tong, H. and Huang, Y. (2012). The effects of manganese precursors on Mn-based/TiO2 catalysts for catalytic reduction of NO with NH3, J. Air Waste Manage. Assoc. 62: 271–277.

Wang, D., Luo, J., Yang, Q., Yan, J., Zhang, K., Zhang, W., Peng, Y., Li, J. and Crittenden, J. (2019a). Deactivation mechanism of multipoisons in cement furnace flue gas on selective catalytic reduction catalysts. Environ. Sci. Technol. 53: 6937–6944.

Wang, R., Hao, Z., Li, Y., Liu, G., Zhang, H., Wang, H., Xia, Y. and Zhan, S. (2019b). Relationship between structure and performance of a novel highly dispersed MnO2 on Co-Al layered double oxide for low temperature NH3–SCR. Appl. Catal., B 258: 117983.

Wang, Z.Y., Guo, R.T., Shi, X., Liu, X.Y., Qin, H., Liu, Y.Z., Duan, C.P., Guo, D.Y. and Pan, W.G. (2020). The superior performance of CoMnOx catalyst with ballflower-like structure for low-temperature selective catalytic reduction of NOx by NH3, Chem. Eng. J. 381: 122753.

Wu, X., Shi, Q., Xu, Y., Wang, J. and Zhang, X. (2020). Synthesis and catalytic performances of manganese oxides-loaded porous halloysite/carbon composites for the selective catalytic reduction of NO with NH3, Appl. Clay Sci. 185: 105200.

Xie, J., Chen, T., Xing, B., Liu, H., Xie, Q., Li, H. and Wu, Y. (2016). The thermochemical activity of dolomite occurred in dolomite-palygorskite. Appl. Clay Sci. 119: 42–48.

Yang, W., Su, Z.a., Xu, Z., Yang, W., Peng, Y. and Li, J. (2020). Comparative study of α-, β-, γ- and δ-MnO2 on toluene oxidation: oxygen vacancies and reaction intermediates. Appl. Catal., B 260: 118150.

Yu, F., Xu, X., Peng, H., Yu, H., Dai, Y., Liu, W., Ying, J., Sun, Q. and Wang, X. (2015). Porous NiO nano-sheet as an active and stable catalyst for CH4 deep oxidation. Appl. Catal., A 507: 109–118.

Yung, M.M., Holmgreen, E.M. and Ozkan, U.S. (2007).
Cobalt-based catalysts supported on titania and zirconia for the oxidation of nitric oxide to nitrogen dioxide. *J. Catal.* 247: 356–367.

Zhang, J., Li, Y., Wang, L., Zhang, C. and He, H. (2015). Catalytic oxidation of formaldehyde over manganese oxides with different crystal structures. *Catal. Sci. Technol.* 5: 2305–2313.

Zhang, R., Zhong, Q., Zhao, W., Yu, L. and Qu, H. (2014). Promotional effect of fluorine on the selective catalytic reduction of NO with NH3 over CeO2-TiO2 catalyst at low temperature. *Appl. Surf. Sci.* 289: 237–244.

Zhang, X., Wu, Q., Diao, Q., Wang, J., Xiao, K., Yang, B. and Wu, X. (2019). Performance study for NH3-SCR at low temperature based on different methods of Mnx/SEP catalyst. *Chem. Eng. J.* 370: 364–371.

Zhao, B., Ran, R., Wu, X. and Weng, D. (2016). Phase structures, morphologies, and NO catalytic oxidation activities of single-phase MnO2 catalysts. *Appl. Catal., A* 514: 24–34.

Zhao, X., Niu, C., Zhang, L., Guo, H., Wen, X., Liang, C. and Zeng, G. (2018). Co-Mn layered double hydroxide as an effective heterogeneous catalyst for degradation of organic dyes by activation of peroxymonosulfate. *Chemosphere* 204: 11–21.

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