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 (NO_x) 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 MnO₂ own the highest NO conversion among the MnO_x catalyst include of MnO₂, Mn₅O₈, Mn₂O₃ and Mn₃O₄ (Kapteijn *et al.*, 1994). Moreover, the morphology and pore structure of MnO₂ 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

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catalyst may have a greatly improved removal efficiency for NO_x . 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 MnO_2 in MnO_2/Pal catalysts to synthesize a novel MnO_x catalyst for SCR. In this study, four crystal forms of manganese dioxide were loaded on highly purified Palygorskite, subsequently the denitration performance and N_2 selectivity of Pal-supported catalyst in NH_3 -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 CaCl_2 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 $\alpha\text{-MnO}_2/\text{Pal}$, 5.09 g Pal was added into 100 ml deionized water, stirring 2 h ensure Pal spread evenly, then 0.53 g $\text{MnSO}_4\cdot\text{H}_2\text{O}$, 1.25 g KMnO_4 were dissolved in deionized water and then 2 ml concentrated HNO_3 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, $\alpha\text{-MnO}_2/\text{Pal}$ 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 $\alpha\text{-MnO}_2/\text{Pal}$:

For $\beta\text{-MnO}_2/\text{Pal}$, 4.63 g Pal was added into 100 mL deionized water, stirring 2 h, then 1.69 g $\text{MnSO}_4\cdot\text{H}_2\text{O}$ and 2.28 g $(\text{NH}_4)_2\text{S}_2\text{O}_8$ were added slowly, subsequently heated to 140°C and held isothermally at 140°C for 12 h in an oven.

For $\gamma\text{-MnO}_2/\text{Pal}$, 9.26 g Pal was added into 100 mL deionized water, stirring 2 h, then 3.37 g $\text{MnSO}_4\cdot\text{H}_2\text{O}$ and 4.57 g $(\text{NH}_4)_2\text{S}_2\text{O}_8$ were added slowly, subsequently heated to 90°C and held isothermally at 90°C for 24 h in an oven.

For $\delta\text{-MnO}_2/\text{Pal}$, 5.86 g Pal was added into 100 mL deionized water, stirring 2 h, then 0.80 g $(\text{NH}_4)_2\text{C}_2\text{O}_4$ and 2.00 g KMnO_4 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 K α 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 N_2 adsorption isotherm using the BJH method. TG curves were performed on a TG/DTA7300 instrument (EXSTA-SII, Seiko Instruments Inc. Japan). H_2 -TPR analyses was carried out in a quartz tube reactor with a mass spectrograph for detection of H_2 , 0.1 g catalyst was heated from 50 to 800°C under 5% H_2/Ar . NH_3 -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 MnO_2/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 NH_3 , 3 vol% O_2 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 $10^\circ\text{C min}^{-1}$ from 50°C up to 400°C . The concentrations of NO_x in inlet and outlet gas were measured by a flue gas analyzer (KANE, KM9106), respectively. NO conversion is defined as:

$$\text{NO}_{\text{conversion}} = (\text{NO}_{\text{inlet}} - \text{NO}_{\text{outlet}}) / \text{NO}_{\text{inlet}} \times 100\% \quad (1)$$

(NO and NO_2 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 SiO_2 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 NH_3 SCR denitration.

XRD

The XRD patterns of purified Pal and MnO_2/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 MnO_2/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 on Pal. Combined with TEM and Raman spectroscopy analysis below, the main reason is that manganese dioxide has uniform load on Pal and poor crystallinity.

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, namely, 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 MnO_2 within the scope of room temperature to 900°C will react through two-step pyrolysis, namely MnO_2 is decomposed into Mn_2O_3 at first, and then decomposed to Mn_3O_4 , corresponding to the decomposition temperature of about 483°C and 799°C (Terayama and Ikeda, 1983). The weight loss ratios of the two catalysts, $\alpha\text{-MnO}_2/\text{Pal}$ and $\delta\text{-MnO}_2/\text{Pal}$, with potassium

Fig. 1. The XRD patterns of purified Pal and MnO_2/Pal .

permanganate as the precursors, are significantly higher than the other two catalysts. This may be related to some K^+ ions into the MnO_2 pore channel, reducing the stability of its crystalline structure (Meher and Rao, 2012). The $\delta\text{-MnO}_2$, $\alpha\text{-MnO}_2$, $\gamma\text{-MnO}_2$, and $\beta\text{-MnO}_2$ show layered structure, 2×2 tunneled structure, 2×1 tunneled structure, and 1×1 tunneled structure, respectively. The main reason of $\delta\text{-MnO}_2$ and $\alpha\text{-MnO}_2$ less stable than $\beta\text{-MnO}_2$ was due to the easy collapse of layer or large tunnel.

Raman

Raman spectroscopy was applied to further identify the crystal structure of MnO_2 among MnO_2/Pal catalysts. The Raman spectra of MnO_2/Pal catalysts was shown in Fig. 3, several bands were recognized from $\alpha\text{-MnO}_2/\text{Pal}$ at 149, 400, 510, 560 and 641 cm^{-1} . The band at 560 cm^{-1} was attributed to the Mn-O lattice vibration in $\alpha\text{-MnO}_2$ (Gao et al., 2009; Sinha et al., 2013). The weak band at 641 cm^{-1} belonged to Mn_3O_4 , which was due to the local overheating of the samples during the spectrum acquisition (Chen et al., 2016). Through the special diffraction bands measured by Raman spectroscopy and the lattice spacing measured by TEM result in section 3.8 below, we confirmed the synthesis of $\alpha\text{-MnO}_2$. For $\beta\text{-MnO}_2/\text{Pal}$, the band at 640 cm^{-1} was attributed to MnO_6 octahedral stretching vibration (Liang et al., 2008). $\gamma\text{-MnO}_2$ was considered to be formed by the random symbiosis of pyrolusite ($\beta\text{-MnO}_2$) and ramsdellite (R-MnO_2). From the Raman spectra of $\gamma\text{-MnO}_2/\text{Pal}$, we could find the band at 637 cm^{-1} was similar to above $\beta\text{-MnO}_2$. In addition, the bands at 382, 486 and 577 cm^{-1} were attributed to the R-MnO_2 (Zhang et al., 2015). The weak band at 502 cm^{-1} and two strong bands at 639 and 561 cm^{-1} were belong to $\delta\text{-MnO}_2$ of $\delta\text{-MnO}_2/\text{Pal}$ (Chen et al., 2016).

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

	SiO_2 (%)	MgO (%)	Al_2O_3 (%)	Fe_2O_3 (%)	CaO (%)	K_2O (%)	TiO_2 (%)	P_2O_5 (%)	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

Fig. 2. The TG/DTG patterns of purified Pal and MnO₂/Pal, (a) α-MnO₂/Pal, (b) β-MnO₂/Pal, (c) γ-MnO₂/Pal, (d) δ-MnO₂/Pal, (e) Pal.

BET

A BET analysis was performed on different MnO₂/Pal catalysts and Pal after purification. The analysis results were summarized in the following Table 2. From this table, we find α-MnO₂/Pal own the maximum specific surface area, β-MnO₂/Pal own the highest total pore volume and average pore size while the lowest specific surface area. Compared with the purified Pal, MnO₂/Pal catalysts own higher total pore volume and average pore size. Except α-MnO₂/Pal, the specific surface area of other MnO₂/Pal catalysts were reduced. After purification, we found that Pal own large specific surface area and was suitable as a catalyst carrier.

The loading of different crystal structures of MnO₂ onto Pal can explain the decrease of BET surface area. However, compared with the BET characterization results of pure MnO₂ with different crystal structures, MnO₂/Pal own 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 N₂

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

Fig. 3. The Raman spectra of MnO₂/Pal catalysts.

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 (m ² g ⁻¹)	Total pore volume (mL g ⁻¹)	average pore diameter (nm)
Pal after purification	144.45	0.34	9.44
α -MnO ₂ /Pal	162.09	0.45	11.01
β -MnO ₂ /Pal	124.91	0.46	14.76
γ -MnO ₂ /Pal	131.57	0.43	13.09
δ -MnO ₂ /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 O_a 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.

Fig. 9. H₂-TPR patterns of MnO₂/Pal catalysts.

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 MnO₂. We can find although MnO₂ particles were in nano size, nonetheless, their dispersion in MnO₂/Pal were different. It is clear that α-MnO₂ (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 MnO₂ on surface of β- and γ-MnO₂/Pal catalysts, with the particle size between 50 and 200 nm. Then, δ-MnO₂ 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 MnO₂ as shown in Table 2. The high-resolution image and EDS spectrum of α-MnO₂/Pal is shown in Figs. 10(e) and 10(f), where the crystal edge of α-MnO₂ 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-MnO₂. The EDS result (Fig. 10(f)) confirmed that Si, Mg,

Fig. 10. TEM images pattern of MnO₂/Pal catalysts (a) α-MnO₂/Pal, (b) β-MnO₂/Pal, (c) γ-MnO₂/Pal, (d) δ-MnO₂/Pal, (e) the high-resolution image and (f) EDS spectrum of α-MnO₂/Pal.

Al, Fe, O and other elements were attributed to Pal, Mn and O elements attributed to MnO_2 , 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 MnO_2/Pal catalysts surface species of Mn and O. It is clear that the Mn 2p 3/2 peaks of $\beta\text{-MnO}_2/\text{Pal}$ 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 $\beta\text{-MnO}_2$ (Zhang *et al.*, 2015; Chen *et al.*, 2016). The percents of surface $\text{Mn}^{3+}/\text{Mn}^{4+}$ molar ratios were listed in Table 3. $\alpha\text{-MnO}_2/\text{Pal}$ own the highest $\text{Mn}^{3+}/\text{Mn}^{4+}$ molar ratio whereas the $\delta\text{-MnO}_2/\text{Pal}$ showed the lowest, which is consistent with the $\text{H}_2\text{-TPR}$ result in section 3.7.

XPS spectra of O 1s was shown in Fig. 11(c), the profiles of MnO_2/Pal catalysts were fitted to three peaks. Binding energies at 529.6 ± 0.1 eV was ascribed to surface adsorbed

Fig. 11. XPS spectra of $\alpha\text{-}$, $\beta\text{-}$, $\gamma\text{-}$ and $\delta\text{-MnO}_2/\text{Pal}$ catalysts: (a) Mn 2p and (b) Mn 2p 3/2 (c) O 1s.

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

Catalyst	Mn 2p 3/2			O 1s			
	Mn ³⁺ (%)	Mn ⁴⁺ (%)	Mn ³⁺ /Mn ⁴⁺	O _a (%)	O _β (%)	O _{OH} (%)	O _a /O _β
α-MnO ₂ /Pal	49.13	50.87	0.96	20.03	6.20	73.77	3.23
β-MnO ₂ /Pal	32.19	67.81	0.47	14.85	7.53	77.62	1.97
γ-MnO ₂ /Pal	33.83	66.17	0.51	9.08	6.56	84.36	1.38
δ-MnO ₂ /Pal	21.47	78.53	0.27	5.56	4.95	89.49	1.12

oxygen (denoted as O_a) and 531.0 ± 0.2 eV belong to lattice oxygen with manganese (denoted as O_β). Peaks near 532.4 eV were assigned to surface hydroxyl species and chemisorbed water (denoted as O_{OH}) (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 O_a performs high activities and makes an important impact in reduction reaction because of its higher mobility than O_β (Zhao *et al.*, 2018). Table 3 showed the percent of molar ratios O_a/O_β. 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 O_a 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, the α-MnO₂/Pal exhibits the best SCR catalytic performance (NO conversion rate was over 97%) and N₂ selectivity. Besides, α-MnO₂/Pal after the addition of SO₂ and H₂O in the feed gas could exert an adverse effect on the NO_x conversion. TG analysis revealed that different hydroxyl structures of catalysts in SCR reaction. NH₃-TPD and H₂-TPR analysis indicated that α-MnO₂/Pal catalyst own more weak acid sites and redox ability than other catalysts. The higher specific surface areas of catalyst, uniformly distributed MnO₂ particles, and percentage of Mn³⁺/Mn⁴⁺ molar ratio, oxygen-containing groups and surface adsorbed oxygen, which results in the excellent catalytic performance of α-MnO₂/Pal.

DECLARATION OF COMPETING INTEREST

The authors declare no competing interests.

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