Non-thermal Plasma Assisted Preparation of MnCeO_x , MnO_x and CeO_2 Catalysts for Enhancement of Surface Active Oxygen and NO Oxidation Activity

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ABSTRACT

Non-thermal plasma was used to enhance the synthesis of nanostructured manganese oxide, cerium oxides and MnCeO_x composite oxide catalysts via the decomposition of organics and nitrates in an integrated network gel. Pure oxides prepared with plasma formed larger crystallites and exhibited more crystallization. The active oxygen species in the plasma were adsorbed through interaction with ions on the catalyst surface; compared to calcined catalysts, the percentage of active oxygen was 33%, 7% and 20% higher for the plasma-treated MnO_x , CeO_2 and MnCeO_x , respectively. The percentage of unsaturated Ce^{3+} was also 10% higher on the plasma-treated MnCeO_x . Furthermore, the NO oxidation efficiency at 275°C for plasma-treated MnO_x and MnCeO_x was 28% and 21% higher, respectively, than for their calcined counterparts. Due to the lack of significant thermal effects during preparation, the plasma-treated catalysts better retained the structures of their precursors, the even mixtures of manganese oxides and ceria in gel. Additionally, the plasma-treated MnO_x and MnCeO_x displayed higher formation and decomposition rates for nitrates. The continuous and rapid transformation of NO into nitrates and of nitrates into NO_2 contributes to the excellent oxidation efficiency of these catalysts.

Keywords: Catalyst; Non-thermal plasma; MnO_x ; MnCeO_x ; NO oxidation.

INTRODUCTION

Nitrogen oxides (NO_x) are one of the primary pollutants in the atmosphere, which contribute to acid rain, photochemical smog and ozone depletion (Chen *et al.*, 2017). Increasing public awareness on environmental issues in recent years boosts the introduction of more rigorous and stringent environmental regulations, which drive the development of highly efficient technologies for NO_x removal (Kuwahara *et al.*, 2016; Wang *et al.*, 2018). NO oxidation to NO_2 , which has tremendous value (Zheng *et al.*, 2016), has received extensive attention as NO_2 can be more easily absorbed in wet flue gas desulfurization system (Gao *et al.*, 2010, 2011), where SO_2 and NO_2 can be removed simultaneously.

For the NO oxidation process, manganese oxides (MnO_x) were found to be suitable for the substitution of noble metal catalysts due to their superior catalytic activity and relatively low cost (Tang *et al.*, 2012; Wang *et al.*, 2012; Liu *et al.*, 2017). CeO_2 is usually used as an assistant component in MnO_x catalyst because CeO_2 has large oxygen storage

capacity and unique redox couple $\text{Ce}^{3+}/\text{Ce}^{4+}$ (Li *et al.*, 2011). The MnO_x - CeO_2 mixed oxides present a kind of solid solution structure with high redox ability (Tikhomirov *et al.*, 2006; Li *et al.*, 2012; Liu *et al.*, 2018b). Previous studies indicated that the preparation method significantly affected the final phase distribution and therefore the resulting properties and the catalytic performance of MnO_x - CeO_2 (Arena *et al.*, 2008; Perez-Omil *et al.*, 2010). However, in most preparation methods, thermal calcinations are needed to form oxides, which lead to the phase separation and sintering of metal oxides, reduce the synergistic interaction between manganese and cerium oxides, and further cause the decrease of catalytic activity for the MnO_x - CeO_2 mixed oxides (Tang *et al.*, 2006).

Non-thermal plasma (NTP) can decompose various organics by reactive species including ions, radicals and activated molecules without heating the macroscopic, because in non-thermal plasma only electrons are at a high temperature (about 10^4 K), whereas the ions and neutrals are at a low temperature (about 400 K). Non-thermal plasma treatment is becoming a novel route to prepare highly efficient catalysts. Previous studies have shown that plasma treatment could modify both chemical and physical properties of catalysts, resulting in low activation temperature, high activity and stability (Liu *et al.*, 2004; Zou *et al.*, 2007; Zhang *et al.*, 2010; Tu *et al.*, 2013). The surface morphology

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of catalysts can be tuned, and new types of active sites with unusual but valuable catalytic properties may form after plasma treatment (Jun *et al.*, 2004; Zhu *et al.*, 2005). The plasma-treated samples have higher specific surface areas because it is performed at a low temperature, whereas the traditional catalysts are prepared at a high temperature, which is a major drawback of thermal methods (Zhang *et al.*, 2010; Cui *et al.*, 2013). It has been noticed that the formation of ultrafine particles with higher specific surface and crystal lattice variation will have a large number of vacancies (Diebold, 2003). The oxidation state of pure metal oxides can be influenced when exposed to plasma discharge, which was evidenced by observing Mn_3O_4 after exposing the Mn_2O_3 catalyst to NTP (Guo *et al.*, 2006).

Because of the advantage of plasma in catalyst preparation, several studies have attempted to develop preparation methods using plasma based on impregnation method and co-precipitation method (Zou *et al.*, 2007; Zhang *et al.*, 2010; Tang *et al.*, 2012; Tu *et al.*, 2013). Khataee *et al.* (2016) treated clinoptilolite by corona discharge plasma and found that the catalytic performance of the plasma-modified clinoptilolite was greater than the natural clinoptilolite. Zou *et al.* (2007) used glow discharge plasma to modify the impregnation method to prepare Pt/TiO_2 photocatalysts and found that an enhanced metal-support interaction are produced. Zhu *et al.* (2005) used dielectric barrier discharge (DBD) to treat $\text{Ni}/\text{Al}_2\text{O}_3$ and $\text{Pt}/\text{Al}_2\text{O}_3$ catalysts and found the metal species dispersion increased after plasma treatment. Yan *et al.* (2015) found that DBD plasma decomposed Ni catalysts possessed improved coke resistance.

It is clear to see that plasma can effectively decompose the precursor to prepare highly efficient catalysts. Sol-gel process is a superior and common method to prepare catalysts, because other elements can be easily incorporated into the final product. If the non-thermal plasma is used to remove the components in samples prepared by sol-gel

process, higher catalytic activity may be achieved. In this work, we adapted a plasma-assisted sol-gel method for the synthesis of pure manganese oxide, cerium oxides and MnCeO_x composite oxides catalysts. Their catalytic performances were evaluated by the NO oxidation and compared with the catalyst synthesized by traditional thermal method. A range of methods were used to further research the effect of plasma treatment on the physical and chemical properties.

EXPERIMENTAL SECTION

Catalyst Preparation

In our test of the activity of MnCeO_x catalysts with different Mn:Ce atom ratio, catalyst with a ratio of 3:1 had the highest activity. So MnO_x , CeO_2 and MnCeO_x with an Mn:Ce atom ratio of 3:1 were prepared by the sol-gel method. The nitrates of cerium or/and manganese were mixed in deionized water. The citric acid was used as the complexing agent with a 1.3:1 ratio of the acid to metal ions. Appropriate amount of polyglycol was followed with 10 wt.% citric acid added. The blended solution was sufficiently mixed by a magnetic stirrer and heated at 80°C till the gel was formed. The sample was dried at 110°C overnight, and then divided into two portions. One portion was decomposed and calcined at 300°C for 5 h in air. The obtained sample was denoted as $\text{MnO}_x\text{-C}$, $\text{CeO}_2\text{-C}$ and $\text{MnCeO}_x\text{-C}$.

The other portion of the sample was treated by plasma. The sample was put into the discharging tube for 90 min by dielectric barrier discharge plasma in the air atmosphere, as shown in Fig. 1. The DBD reactor included a quartz tube acted as the dielectric material, a steel rod along the axis of the quartz tubes acted as the ground electrode connected to the power supply and a copper sheet that wrapped around the outer surface of the quartz tube acted as the ground electrode. The length of the plasma

Fig. 1. Schematic illustration of preparation process of $\text{MnO}_x\text{-P}$, $\text{CeO}_2\text{-P}$ and $\text{MnCeO}_x\text{-P}$ catalysts.

discharge zone was 100 mm, in which the samples were packed into the gap between the quartz tube and the rod. The DBD reactor was energized by an AC high-voltage power with a frequency of 9 kHz and a discharge voltage of 10 kV. The voltage was measured by a voltage probe (P6015A; Tektronix, Inc., USA) and monitored with an oscilloscope (DPO4034; Tektronix, Inc., USA). A 1 μ F capacitor connected to the DBD reactor was used for discharge power measurement, which was about 185 W. These samples were designated as MnO_x-P, CeO₂-P and MnCeO_x-P.

Catalyst Characterization

Thermogravimetric analysis (TGA) was performed by a TGA Q500 analyzer (TA Instruments, USA). The samples (2 mg) were heated from 50 to 800°C in nitrogen at a heating rate of 10°C min⁻¹.

Fourier-transform infrared spectroscopy (FTIR) was carried out using a Nicolet 5700 spectrometer (Thermo Fisher Scientific, USA). The spectrum was generated and collected 32 times and the background line obtained was automatically subtracted. The spectra were recorded from 400 to 4000 cm⁻¹.

The powder X-ray diffraction (XRD) was carried out on a D/MAX-RA system (Rigaku Corporation, Japan) using monochromated Cu K α radiation (40 kV, 200 mA) at a scan rate of 4° min⁻¹ with a 0.0167° step size in the 2 θ range between 10° and 90°.

The BET surface area and pore size distribution were obtained by measuring N₂ adsorption and desorption at liquid nitrogen temperature (77 K) with ASAP 2020 system (Micromeritics Instrument Corp., USA). Prior to N₂ adsorption, the samples were degassed at 250°C for 3 h.

Temperature programmed reduction (TPR) of hydrogen was performed on a custom-made TCD setup using 100 mg catalysts. Prior to each measurement, the samples were pretreated under flowing pure Ar at 200°C for 30 min, and this was followed by cooling to 50°C in atmosphere of Ar containing 10% H₂ at a flow rate of 30 mL min⁻¹. TPR runs were carried out from 50°C to 700°C with linear heating rate (10°C min⁻¹) in the same atmosphere.

The X-ray photoelectron spectra (XPS) measurement of O 1s, Mn 2p, and Ce 3d regions was performed using a Thermo ESCALAB 250 electron spectrometer (Thermo Fisher Scientific, USA) equipped with an Al K α X-rays (h ν = 1486.6 eV) and a hemispherical electron analyzer being operated at a constant pass energy (20 eV). Sample charging effects were eliminated by correcting the observed spectra with a C1s binding energy (BE) value of 284.6 eV.

High-resolution transmission electron microscopy (HR-TEM) were obtained using a Tecnai G² F20 S-Twin (FEI Co., USA) operated at 300 kV. Samples were dispersed in alcohol using supersonic waves, and they were put on Cu grids for TEM observation under air atmosphere.

In situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) experiments of NO adsorption were performed on a Nicolet NEXUS 6700 Fourier-transform infrared spectrometer (Thermo Fisher Scientific, USA), equipped with an MCT/A detector. The samples were pretreated at 350°C for 1 h in N₂ with a flow of 100 mL min⁻¹ before each experiment. All the IR spectra were recorded

by collecting 64 scans with a resolution of 4 cm⁻¹.

Activity Measurement

Experiments of NO catalytic oxidation were carried out at atmospheric pressure in the temperature range of 100–350°C in a cylindrical fixed-bed quartz reactor (diameter = 8 mm) containing 0.2 g catalyst of 60–80 mesh. The reactor was connected to testo 350 gas analyzer (Testo SE & Co. KGaA, Germany) for NO and NO₂ measurement. The gas flow and gas hourly space velocity (GHSV) in all experiments were 1200 mL min⁻¹ and 360,000 mL g⁻¹ h⁻¹. The reactive gas mixtures used contained 400 ppm NO, 5% O₂ and balance N₂. During our test, the sum of NO and NO₂ concentration generally remained at a level of 400 ppm. To avoid the deviation caused by the fluctuation of the inlet NO concentration, the NO oxidation efficiency was calculated by the outlet NO and NO₂ concentration:

$$\eta (\%) = \frac{[\text{NO}_2]_{\text{out}}}{[\text{NO}]_{\text{out}} + [\text{NO}_2]_{\text{out}}} \times 100\% \quad (1)$$

RESULTS AND DISCUSSION

Plasma Treatment

In order to obtain the lowest temperature of the removal of the organics and nitrates, TGA analyses, as shown in Fig. 2, were carried out over samples before plasma treatment and calcinations, which was denoted as MnO_x-BEF P/C, CeO₂-BEF P/C and MnCeO_x-BEF P/C. With increasing temperature, the weight decreases and there is negligible weight loss after 300°C. The weight loss before the temperature of 200°C is attributed to desorption of absorbed water and decomposition of nitrates, while the weight loss at 200–270°C contributed to the decomposition of the organics. Therefore, 300°C is chosen as the calcination temperature in the traditional preparation method. The DBD plasma treatment effectively decomposes the organics and nitrates on the gel particles. After plasma treatment, the weight loss of the sample was negligible before 600°C, almost the same as the calcined sample. The temperature of the DBD reactor was measured by infrared imaging. As shown in Fig. 3, the highest macro temperature of the discharge zone is about 180°C, which is lower than the decomposition temperature of the organics. However, based on the TGA results on the gel particles, which is displayed in Fig. 2, 300°C is the lowest calcinations temperature to ensure complete decomposition of the organics and nitrates, and proper catalytic activities. This demonstrates that the organics and nitrates are removed by reacting with active species in plasma, rather than thermal effect.

FTIR was used to determine if the organics and nitrates can be removed completely by air plasma treatment. As shown in Fig. 4, the surface of the precursor without treatment has many groups including –COOH, –NO₃⁻ (Li et al., 2010), –OH (Oh et al., 2005), C–O–C (Oh et al., 2005) and C=O (Kang and Xing, 2007; Ibrahim et al., 2009). The peak at 1388 cm⁻¹ is corresponding to the nitrates. The peak at 1734 cm⁻¹ is assigned to the C=O in –COOH, and the

Fig. 2. TG curves of the catalyst precursors before calcinations

Fig. 3. The temperature distribution of the DBD reactor surface.

Fig. 4. The FTIR spectra of the samples without treatment, after plasma treatment and after calcinations.

peak at 1073 cm^{-1} is assigned to C–O–C in polyethylene glycol (PEG). The infrared spectroscopy of the sample treated by air plasma is almost the same with that of the sample after calcination, except trace amount of residue

nitrate. It indicates that air plasmas could decompose organic matters completely and gain pure oxides. That is because the oxidative active components including O and O_3 formed in air plasma can decompose organics in the

precursor of catalyst efficiently. It is important to note that the existence of residue nitrates in $\text{MnO}_x\text{-P}$ is not because the nitrates in the precursor have not been decomposed, but caused by adsorption and desorption equilibrium of nitrates and NO_x in air plasma environment (Yu *et al.*, 2018). In our previous study (Liu *et al.*, 2018a), it is observed that nitrates were easier to be removed than organics in the precursor. They could be decomposed at $\sim 200^\circ\text{C}$ by heat and even can be removed by N_2 plasma.

The sol-gel method converts metal ions into an integrated network (the gel), in which the metal ions are evenly mixed at the molecular level (Lakshmi *et al.*, 1997). To form metal oxides, organics and salts in the gel need to be decomposed. At present, the most commonly method used to remove the organics and salts is thermal calcination under strictly controlled conditions (Cividanes *et al.*, 2010). Although the gel can be removed effectively, the thermal calcination may cause agglomeration of the metal oxides, reducing the degree of homogeneity. Plasma treatment is an alternative to the conventional calcination because of its low macro temperature.

Characterization of the Catalysts

To compare the structure and surface morphology of the catalysts prepared by plasma and calcination method, the XRD patterns and the TEM images of the samples are measured and displayed in Figs. 5 and 6. The two CeO_2 samples present typical diffraction peaks of cubic fluorite structural CeO_2 phase. The diffraction peaks of $\text{CeO}_2\text{-P}$ are stronger and narrower than those of $\text{CeO}_2\text{-C}$, indicating the larger crystallites and better crystallinity in the catalyst prepared by plasma. The crystallite size calculated from

the peak of $2\theta = 28.5^\circ$ using Scherrer's equation is 6.8 nm for $\text{CeO}_2\text{-C}$ and 9.4 nm for $\text{CeO}_2\text{-P}$. CeO_2 crystallites can be observed clearly in the HR-TEM images shown in Fig. 6(a). The crystallite sizes of CeO_2 are close to those calculated by the XRD results, and the size is smaller in $\text{CeO}_2\text{-C}$ than in $\text{CeO}_2\text{-P}$.

In the case of $\text{MnO}_x\text{-C}$ sample, the diffraction pattern can be assigned to Mn_3O_4 and Mn_5O_8 . HR-TEM images are consistent with the XRD results. The interplanar spacings of ~ 0.28 nm, ~ 0.31 nm and ~ 0.49 nm correspond to tetragonal Mn_3O_4 oxide and monoclinic Mn_5O_8 oxide. In the case of $\text{MnO}_x\text{-P}$ sample, two different diffraction patterns can be obtained. One of them can be assigned to Mn_3O_4 and Mn_5O_8 , and another one can be assigned to MnO(OH) and Mn_2O_3 . The HR-TEM images are convincing proof of the XRD results. Different from $\text{MnO}_x\text{-C}$, the HR-TEM images of $\text{MnO}_x\text{-P}$ display mainly crystallite rods which are MnO(OH) and Mn_2O_3 , while the crystallites of Mn_3O_4 and Mn_5O_8 are granular. The $\text{MnO}_x\text{-P}$ displays larger crystallites and better crystallinity than $\text{MnO}_x\text{-C}$.

$\text{MnCeO}_x\text{-C}$ displays weak diffraction peaks, indicating a low crystallinity of mixed oxides. The incremental shift of diffraction peak to higher angles compared with that of CeO_2 suggests considerable decrease of the lattice constant, which implies the formation of solid solution between MnO_x and CeO_2 (Machida *et al.*, 2000). Compare to $\text{MnCeO}_x\text{-C}$, the peaks for Mn_3O_4 vanish and the formation of $\alpha\text{-Mn}_2\text{O}_3$ can be observed in $\text{MnCeO}_x\text{-P}$. The diffraction peaks of $\text{MnCeO}_x\text{-P}$ are weaker and broader than $\text{MnCeO}_x\text{-C}$, demonstrating smaller crystallites, better formation of solid solution, which is favorable to increase surface area and essential to oxidation ability of the catalyst.

Fig. 5. XRD patterns of the catalysts.

Fig. 6. TEM images of the catalysts (a) CeO₂, (b) MnO_x and (c) MnCeO_x.

According to the results, plasma preparation shows different effect on Mn or Ce pure oxides and Mn-Ce mixed oxides. Compared with catalysts prepared by traditional method, pure oxides prepared by plasma have larger crystallite size, while Mn-Ce mixed oxides prepared by

plasma show smaller crystallite size. During the decomposition of organics and nitrates using DBD plasma, the highest macro temperature of the discharge zone is about 180°C, so there is no significant thermal effect on the samples during the plasma treatment and the change in

structure after the plasma treatment is less dramatic than that after the thermal calcination. Therefore, the pure oxides and the solid solution in plasma prepared catalysts are both better formed than those in calcined catalysts.

Table 1 gives the specific surface area of the catalysts prepared by plasma and traditional method which was calculated according to the BET method. The specific surface areas of $\text{MnO}_x\text{-P}$ and $\text{CeO}_2\text{-P}$ catalysts are a little lower than $\text{MnO}_x\text{-C}$ and $\text{CeO}_2\text{-C}$, respectively. The influence of plasma treatment on MnCeO_x is obvious. $\text{MnCeO}_x\text{-P}$ exhibits the highest surface area ($101.5 \text{ m}^2 \text{ g}^{-1}$), much higher than $\text{MnCeO}_x\text{-C}$ ($68.9 \text{ m}^2 \text{ g}^{-1}$). These results coincide with the XRD and TEM analysis. For MnCeO_x catalyst, the plasma treatment can promote the formation of Mn-Ce-O solid solution, so it has higher specific surface area than that prepared by calcination method. The pure oxides prepared by plasma have larger crystallite size, leading to a decline in specific surface area.

The great influence of plasma on structure and surface morphology of the catalysts may result in considerable changes of oxidation state of Mn and Ce, which will further affect the behavior of oxygen on catalyst surface, NO oxidation activities and NO adsorption/desorption ability. In order to analyze the oxidation states of cerium and manganese, XPS spectra of Mn 2p, Ce 2p and O 1s of the samples were measured. As given in Fig. 7(a), the O 1s spectra are deconvoluted into two or three overlapping peaks. The peak at 529.4 eV corresponds to lattice oxygen (O^{2-}) (denoted as O_β) whereas another shoulder peaks at 530.8 eV and 532.5 eV corresponds to the surface adsorbed oxygen (denoted as O_α) such as O_2^{2-} or O^- belonging to defect-oxide or a hydroxyl-like group (Holgado *et al.*, 2000; Kang *et al.*, 2007). O_α species have higher mobility than lattice oxygen, actively take part in the oxidation process and greatly contribute to the catalytic activity (Liu *et al.*, 2014; Lin *et al.*, 2017). It can be seen that the intensity of the O_α peaks has an obvious increase in catalysts prepared by plasma, which is quantified by the relative concentration ratio of $\text{O}_\alpha/(\text{O}_\alpha + \text{O}_\beta)$. Table 2 summarizes the calculated values of quantitative analysis. The $\text{O}_\alpha/(\text{O}_\alpha + \text{O}_\beta)$ ratio of $\text{MnO}_x\text{-P}$ is about 56.5%, which is 33% higher than that of $\text{MnO}_x\text{-C}$ (23.5%), and $\text{MnCeO}_x\text{-P}$ and $\text{CeO}_2\text{-P}$ is 19.8% and 7% higher than that of $\text{MnCeO}_x\text{-C}$ and $\text{CeO}_2\text{-C}$, respectively. This implies that catalysts prepared by plasma have more oxide vacancies and oxygen molecules can be adsorbed at the oxygen vacancies to form active surface oxygen (Liu *et al.*, 2019). Furthermore, the ratio of O on catalysts surface prepared by plasma is relatively high. There are many kinds of active oxygen in the plasma, such as O and O_3 .

Although the active oxygen species in plasma are short-living and unstable, they can be adsorbed by the catalyst and interact with the ion on the catalysts surface. For example, when O_3 reaches the catalysts surface, O atoms, O_2 and OH radicals are formed on the surface (Sekiguchi *et al.*, 2017). Therefore, the ratio of O and $\text{O}_\alpha/(\text{O}_\alpha + \text{O}_\beta)$ on catalysts surface prepared by plasma is relatively high.

According to the deconvolution of the Mn 2p_{3/2}, the binding energies around 643.6, 641.9 and 640.4 eV could be ascribed to the presence of Mn^{4+} , Mn^{3+} and Mn^{2+} species, respectively (He *et al.*, 2016). In the Ce 3d spectra, the U, U', U'', V, V' and V'' peaks are contributed to Ce^{4+} , while the U' and V' peaks are attributed to Ce^{3+} (Wu *et al.*, 2007a; He *et al.*, 2016). The proportion of Ce^{3+} ions with regard to the total cerium species is calculated, as shown in Table 2. The proportion of Ce^{3+} in $\text{MnCeO}_x\text{-P}$ is 22.4%, which is 9.6% higher than that of $\text{MnCeO}_x\text{-C}$. The proportion of Ce^{3+} in $\text{CeO}_2\text{-P}$ is higher than that in $\text{CeO}_2\text{-C}$, too.

The formation of Ce^{3+} is important to the active oxygen on catalyst surface, because Ce^{3+} can lead to charge imbalance, oxygen vacancies and unsaturated chemical bonds (Chen *et al.*, 2011). Due to more solid solution is formed by plasma pretreatment, as discussed above and in XRD results, the portion of the relative amount of $\text{Ce}^{3+}/(\text{Ce}^{3+} + \text{Ce}^{4+})$ is increased. As a result, oxygen vacancies and surface active oxygen in plasma-assisted prepared catalysts increase, which is confirmed by the results of relative concentration ratios of $\text{O}_\alpha/(\text{O}_\alpha + \text{O}_\beta)$. Therefore, the well-formed solid solution results in the increase of relative amount of Ce^{3+} and the increase of oxygen vacancies and surface active oxygen, which has higher mobility than lattice oxygen. And all of these lead to the enhanced oxidation efficiency of plasma pretreated catalysts.

The oxidation catalytic properties of the catalysts can be determined by their redox properties, which were measured by temperature-programmed reduction with H_2 . The H_2 -TPR profiles of the studied catalysts are displayed in Fig. 8. Mn-containing samples exhibit two groups of reduction peaks centered at about 200°C and 400°C, respectively. The first set of peaks attribute to the reduction of Mn^{4+} to Mn^{3+} , and the peak at higher temperature corresponded to the reduction of Mn^{3+} to Mn^{2+} (Kapteijn *et al.*, 1994; Arena *et al.*, 2001). Compare to catalysts prepared by thermal method, the catalysts prepared by plasma treatment display lower reduction temperature. For $\text{MnCeO}_x\text{-P}$, compared to $\text{MnCeO}_x\text{-C}$, intensity of the first peak increases and intensity of the second peak decreases, accordingly, indicating the reduction occurs more at lower temperature. As discussed above in XPS results, there is more oxygen species and

Table 1. The physical characteristics of the catalysts.

Samples	S_{BET} ($\text{m}^2 \text{ g}^{-1}$)	Pore volume ($\text{cm}^3 \text{ g}^{-1}$)	Pore size (nm)
$\text{MnO}_x\text{-C}$	21.8	0.132	18.02
$\text{MnO}_x\text{-P}$	21.7	0.105	19.76
$\text{MnCeO}_x\text{-C}$	68.9	0.131	6.78
$\text{MnCeO}_x\text{-P}$	101.5	0.228	8.96
$\text{CeO}_2\text{-C}$	77.6	0.060	3.49
$\text{CeO}_2\text{-P}$	63.2	0.086	4.61

Fig. 7. XPS spectra for (a) O 1s, (b) Mn 2p, and (c) Ce 2p.

Table 2. Surface contents of O and composition of O and Ce species derived by XPS.

Samples	O (%)	$O_{\alpha}/(O_{\alpha} + O_{\beta})$ (%)	Ce^{3+}/Ce (%)
MnO _x -C	63.4	23.5	
MnO _x -P	69.8	56.5	
MnCeO _x -C	65.9	26.2	12.8
MnCeO _x -P	68.9	46.0	22.4
CeO ₂ -C	74.4	33.5	13.2
CeO ₂ -P	76.8	40.5	13.7

Fig. 8. H₂-TPR profiles of the catalysts.

higher portion of surface adsorbed oxygen on plasma pretreated catalysts, which is easier to be reduced by H₂ and has an important influence on catalytic oxidation. This suggests that catalysts prepared by plasma have not only improves the oxygen storage capacity, but also enhances the oxidation-reduction ability at low temperature.

Catalytic Activities

Fig. 9(a) illustrates the catalytic performance for NO oxidation to NO₂ over prepared catalysts. It is obvious that the oxidation activity of the catalysts prepared by plasma is much higher than that of the catalysts prepared by traditional method. At 275°C, the MnCeO_x-P catalyst presents an oxidation efficiency of 74.3%, which is 21% higher than that of MnCeO_x-C. And compared with MnO_x-C, the oxidation efficiency of MnO_x-P is 28% higher at 275°C. The NO oxidation efficiency of the CeO₂-P prepared by plasma has only a little increase compared to CeO₂-C, because the oxidation activities of CeO₂ is low itself. In order to test the stabilities of the two kinds of catalysts, we re-measured the NO oxidation during the temperature dropped down to the room temperature, and found that the catalytic activities were the same as that during the temperature raised up. It is also confirmed that the catalysts exhibited superior catalytic stabilities. The results of catalytic activity are consistent with the catalyst property analysis.

The activity of MnCeO_x-P catalyst was also tested for 24 h at 300°C with 10 vol.% H₂O in the flue gas and the results are shown in Fig. 9(b). Before adding H₂O, the oxidation has been stabilized for 5 h. The presence of H₂O decreases the NO oxidation efficiency of MnCeO_x-P from 80% to about 69% in 0.5 h, and then the oxidation activity is stable after that. The oxidation activity was able to restore to the original level with the removal of H₂O. The reason that the inhibition effect of H₂O is reversible should

be the competitive adsorption of the gas phase water vapor and reactant on catalyst surface.

In-situ DRIFTS

In order to clarify the NO oxidation behaviors with the catalysts prepared by plasma and calcinations, the *in-situ* DRIFTS measurements of MnO_x and MnCeO_x, which can provide useful information of the adsorption of NO, redox reactions on catalyst surface, and desorption capacity of the catalysts, were performed at 275°C. Prior to NO adsorption, the samples were treated at 300°C in N₂ for 0.5 h to remove adsorbed species. After the sample was cooled to 275°C, 1000 ppm NO were introduced to the IR cell and IR spectra were recorded for various times. Fig. 10(a) shows the spectra of MnO_x-C after the introduction of 1000 ppm NO at 275°C. After the feeding of NO, bands at 1627, 1544, 1335, 1272, 1248, and 1218 cm⁻¹ appeared. The band at 1544 cm⁻¹ can be assigned to bidentate nitrate (Tang *et al.*, 2011; Liu *et al.*, 2012); the band at 1248 cm⁻¹ is typical of monodentate nitrate (Liu *et al.*, 2012); the band at 1335 cm⁻¹ is attributed to NO₂⁻ species (Liu *et al.*, 2012); bands at 1272 and 1218 cm⁻¹ are due to bridge nitrate (Chen *et al.*, 2010; Liu *et al.*, 2012); the band at 1627 cm⁻¹ can be assigned to weakly adsorbed NO₂ (Chen *et al.*, 2010; Jin *et al.*, 2010). A weak bond at 1913 cm⁻¹ is attributed to nitrosyl. In the OH stretching region, a negative band at 3627 cm⁻¹ and a broad absorption between 3600 and 3250 cm⁻¹ are also observed. The negative band can be assigned the consumption of isolated surface OH groups, whereas the broad band is associated with the absorption of H-bonded hydroxyls (Wu *et al.*, 2007b; Tang *et al.*, 2011). When 10% O₂ was added, these bands assigned to nitrates, NO₂ and hydroxyls increased rapidly, indicating that the presence of O₂ could enhance the NO adsorption significantly. Finally, when using carrier gas to purge the nitrates, the intensity of the bands reduced quickly, indicating all the nitrates are active and can decompose to NO_x. Fig. 10(b) shows the DRIFT spectra of NO adsorption on MnO_x-P. Compared with MnO_x-C, the bands at 1544, 1272 and 1239 cm⁻¹ due to various nitrates are stronger under the condition of NO and NO + O₂ demonstrating more active sites was involved in the reaction with NO. The band at 1218 cm⁻¹ due to bridge nitrate is much weaker and the band at 1335 cm⁻¹ is due to NO₂⁻ shifts to 1353 cm⁻¹ in all condition. The band at 1672 cm⁻¹ shows weaker intensity than the band in MnO_x-C in the condition of NO + O₂. In the OH stretching region, the consumption of isolated surface OH groups and formation of H-bonded hydroxyls are weak as well. These were very different with MnO_x-C. These results strongly suggest that different nitrate species and weakly adsorbed NO_x would appear over MnO_x catalysts prepared by plasma treatment, compared with that prepared by the conventional method. Furthermore, the bands in MnO_x-P after N₂ purge are much weaker than those in MnO_x-C, indicating that the various kinds of nitrates are less stable and produce more gaseous NO₂ molecule on plasma prepared MnO_x than on MnO_x-C. Because the outlet NO₂ mainly came from the decomposition of nitrates, easier decomposition of formed nitrates can lead

Fig. 9. Catalytic performance of the catalysts (a) NO oxidation as function of temperature and (b) NO oxidation as function of time at 300 °C with 10 vol.% H₂O in the flue gas.

to a high production of NO₂ and make active sites for further formation of nitrates. The continuous and rapid transformation of nitrates to NO₂ is the reason for excellent oxidation efficiency of plasma prepared catalysts.

The spectra of MnCeO_x are very different from that of MnO_x, as displayed in Fig. 10(c) for MnCeO_x-C. Several bands at 1593, 1577, 1542, 1509, 1424, 1266, 1242, and 1203 cm⁻¹ were detected. The bands at 1577 and 1542 cm⁻¹ can be assigned to bidentate nitrate (Chen *et al.*, 2010; Tang *et al.*, 2011); the band at 1593 cm⁻¹ correspond to nitrite species (Eng and Bartholomew, 1997); the band at 1242 cm⁻¹ is due to monodentate nitrate (Liu *et al.*, 2012); the bands at 1266 and 1203 cm⁻¹ are due to bridge nitrate (Chen *et al.*, 2010; Liu *et al.*, 2012). The bands assigned to adsorbed NO₂ species are not detected. The weak bond attributed to nitrosyl also appeared. For MnCeO_x-P, the

bands at 1593, 1577 and 1203 cm⁻¹ shifted to 1595, 1574 and 1215 cm⁻¹, respectively. The bands in MnCeO_x-P are much stronger than those in MnCeO_x-C, indicating that more nitrates are formed on MnCeO_x-P. As discussed in XPS and H₂-TPR results, plasma pretreated catalysts get relatively rich in oxygen species, higher portion of surface active oxygen, and more species which can be reduced by H₂ at low temperature, therefore, more NO is adsorbed and participate in reactions. To further clarify the amount of nitrates decomposed during N₂ purge, the subtraction spectra after adsorption of NO + O₂ and after N₂ purge were considered and shown in Fig. 10(e). It was observed that the subtraction spectra of MnCeO_x-P is stronger than that of MnCeO_x-C, indicating more nitrates are decomposed during N₂ purge and higher production of NO₂. Tang *et al.* (2011) proposed that NO was first adsorbed on Mn sites to

Fig. 10. DRIFTS spectra of (a) MnO_x-C, (b) MnO_x-P, (c) MnCeO_x-C and (d) MnCeO_x-P under exposure to 1000 ppm NO at 275°C for 5 min and 20 min, and followed by exposure to 1000 ppm NO + 5% O₂ for 5 min and 20 min, and finally purged by N₂ for 30 min; (e) DRIFTS subtraction spectra obtained from (c) and (d).

form nitrosyls, and then nitrosyls were readily oxidized to nitrates by active lattice oxygen. Subsequently, nitrates were decomposed to NO_2 , and the consumed lattice oxygen was supplemented by gaseous O_2 . Cen *et al.* (2012) found that substitution of surface Ce atom with an Mn atomic dopant makes the first oxygen vacancy form spontaneously and greatly promotes the adsorbed oxygen molecule activation. As discussed in the XPS results, well formed solid solution structure of MnCeO_x prepared by plasma provides more surface active oxygen which can participate in the formation of nitrates. The oxygen vacancy caused by the formation of NO_2 is also easier to be filled by adsorbed oxygen molecule. Thus, the plasma prepared catalysts get accelerated redox cycle in oxidation of NO.

CONCLUSIONS

Compared to their traditionally calcined counterparts, plasma-treated MnO_x and MnCeO_x catalysts displayed higher concentrations of surface active oxygen and higher NO oxidation efficiency. Preparing the pure oxide catalysts with plasma increased the exposure of active manganese components and oxygen species on the surface and enhanced the formation of pure oxides. For the mixed oxide catalysts, plasma treatment promoted interaction between the MnO_x and CeO_2 , resulting in an increased amount of Mn-Ce-O solid solution, larger specific surface area and smaller crystallites. However, pure oxides prepared with plasma formed larger crystallites and exhibited more crystallization. The active oxygen species in the plasma were adsorbed through interaction with ions on the catalyst surface. Therefore, the total percentage of O and active oxygen on the surface of the plasma-treated catalysts was higher. Compared to the calcined catalysts, the NO oxidation efficiency at 275°C for the plasma-treated MnCeO_x and MnO_x was higher by 21% (resulting in an oxidation efficiency of 74.3%) and 28%, respectively. Because the plasma treatment did not cause significant thermal effects, structural changes in the catalysts were less dramatic than those following thermal calcination.

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