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Article

Promotional effect of spherical alumina loading with manganese-based bimetallic oxides on nitric-oxide deep oxidation by ozone

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ABSTRACT

Nitric oxide (NO) deep oxidation to dinitrogen pentoxide (N_2O_5) by ozone together with wet scrubbing has become a promising technology for nitrogen-oxide (NO_x) removal in industrial boilers. Catalysts were introduced to enhance the N_2O_5 formation rate with less ozone injection and leakage. A series of monometallic catalysts (manganese, cobalt, cerium, iron, copper, and chromium) as prepared by the sol-gel method were tested. The manganese oxides achieved an almost 80% conversion efficiency at an ozone (O_3)/NO molar ratio of 2.0 in 0.12 s. The crystalline structure and porous parameters were determined. The thermodynamic reaction threshold of NO conversion to N_2O_5 is oxidation with an O_3 /NO molar ratio of 1.5. Spherical alumina was selected as the support to achieve the threshold, which was believed to improve the catalytic activity by increasing the surface area and the gas-solid contact time. Based on the manganese oxides, cerium, iron, chromium, copper, and cobalt were introduced as promoters. Cerium and iron improved the deep-oxidation efficiency compared with manganese/spherical alumina, with less than 50 mg/m^3 of outlet NO + nitrogen oxide, and less than 25 mg/m^3 of residual ozone at an O_3 /NO molar ratio of 1.5. The other three metal oxides inhibited catalytic activity. X-ray diffraction, nitrogen adsorption, hydrogen temperature-programmed reduction, and X-ray photoelectron spectroscopy results indicate that the catalytic activity is affected by the synergistic action of NO_x oxidation and ozone decomposition.

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1. Introduction

Nitrogen oxides (NO_x) are one of the main sources of haze [1,2] and are toxic to human health. They contain mainly nitric oxide (NO) and nitrogen oxide (NO_2). The main NO_x exhaust from power-plant boilers, industrial boilers, and automotive vehicles is NO, which accounts for more than 95% of the total NO_x [3]. Exhausted NO_x gases are eliminated by selective catalytic reduction (SCR) [4] and non-SCR with ammonia-based reducing agents [5]. However, these two technologies may be

uneconomic and unable to match increasingly strict emissions legislation, especially for ultra-low Chinese emissions (particle matter < 5 mg/m^3 , SO_2 < 35 mg/m^3 , NO_x < 50 mg/m^3 , oxygen (O_2) = 6%). Because of their low capacity and wide distribution, the control of emission from small-scale industry boilers is a significant challenge [6]. Temperature windows of typical industrial boilers that can be used for emissions treatment are usually lower than 200 °C, which is unsuitable for SCR and non-SCR technologies. Extremely complex flue-gas compositions hinder the SCR application in different industries such as

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glass, carbon black, and cement. Therefore, a development of alternative economic and effective new technologies for NO_x control in complex industry boilers is required urgently.

NO is nearly insoluble in water whereas the other NO_x gases, NO_2 and dinitrogen pentoxide (N_2O_5), have a higher solubility. N_2O_5 can be removed easily by water spraying without any additives [7,8]. NO peroxidation can achieve the simultaneous removal of SO_2 and NO_x in a wet flue-gas desulfurization tower. Low-temperature oxidation by ozone combined with wet flue-gas desulfurization, which has been studied by researchers, may be a good choice to deal with NO_x removal in special cases [3,9–12]. Previous work [13,14] has focused on the conversion of NO to N_2O_5 , which is defined as NO deep oxidation. According to the mechanism [13], deep oxidation is a slow reaction that requires more than a 3–5-s residence and a large ozone dosage (O_3/NO molar ratio > 2.0). If we consider the overall reaction for N_2O_5 formation, $2\text{NO} + 3\text{O}_3 = \text{N}_2\text{O}_5 + 3\text{O}_2$, theoretically, NO could be converted completely to N_2O_5 with an O_3/NO molar ratio of 1.5. In the latest research [14], catalyst introduction into NO deep oxidation was attempted. The NO deep-oxidation efficiency could be improved significantly with a short residence time and a lower ozone dosage with catalyst introduction.

Ozone is a strong oxidant [15] and it has been used extensively in water purification [16], volatile-organic-compounds treatment [17], and disinfection [18]. In these applications, catalysts were added to improve the ozonation efficiency [19–21]. Transition-metal oxides displayed an excellent performance for catalytic ozonation in previous studies [22–24]. Manganese oxides exhibited the best activity among these transition-metal oxides because of their various oxidation states and high oxygen-storage capacity. The transition of oxidation states during the redox reaction cycles plays a critical role in catalytic ozonation.

In our latest work, manganese oxides that were supported on spherical alumina (SA) exhibited excellent performance for catalytic NO deep oxidation by ozone. An increase in NO deep-oxidation efficiency resulted for a stoichiometric ratio of $\text{O}_3/\text{NO} = 1.5$. Catalyst stabilities and the resistance to SO_2 and water vapor, which coexist in flue gas, need to be improved. Based on previous catalytic-ozonation studies [14], catalytic activity is related to the adsorption ability of reactants and the ozone decomposition activity. Therefore, the objective of catalyst modification is to increase the NO_x adsorption ability and improve ozone decomposition.

The redox abilities of manganese oxides can be enhanced by combining them with other metal oxides [25]. The NO_x adsorption ability [26] and the ozone decomposition activity [27] can also be improved. Thus, five metal oxides were selected to load the manganese (Mn)-based catalyst that was supported on SA to investigate the catalytic activity. The catalytic activities of monometallic metal oxides have not been determined. In this work, oxides of Mn, cobalt (Co), cerium (Ce), iron (Fe), copper (Cu), and chromium (Cr) were prepared by the sol-gel method and were tested for NO deep oxidation. Subsequently, the NO oxidation ability of the metal oxides that were supported on SA was investigated.

2. Experimental

2.1. Catalyst preparation

Monometallic metal oxides were prepared by the sol-gel method. Desirable amounts of metal nitrates ($\text{Mn}(\text{NO}_3)_2$, 49.0%–51.0%; $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\geq 99.0\%$; $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\geq 98.5\%$; $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, $\geq 99.0\%$; $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\geq 99.0\%$; $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\geq 98.5\%$; all from Sinopharm) and citrate ($\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$, Sinopharm, $\geq 99.5\%$) were dissolved in deionized water to achieve a 0.5 mol/L solution. A citrate solution was poured into the metal-nitrate solution with a citrate/metal-nitrate molar ratio of 2. After 48 h stirring, the mixed solution was transferred to an oven overnight at 110 °C. The resultant fluffy gel was calcined at 400 °C for 3 h in a tube furnace in air at 5 °C/min.

Hereafter, SA (Sinopharm, 2–3 mm diameter) was used as the support. Bimetallic oxides were loaded on SA by coimpregnation. Manganese acetate, as a precursor, exhibited a better performance than manganese nitrate [25,28]. $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ (Aladdin, $\geq 99.0\%$) was dissolved in 10 mL of deionized water with the desired metal nitrate. Then 10 g of SA was immersed in the mixed solution, and left unstirred at room temperature for 24 h. The Mn loading was fixed at 5 wt%, and the doped metal was fixed at an M/Mn molar ratio of 1/5, where M represents the doped metal. The coated SA was dried at 110 °C for 12 h and calcined at 400 °C for 3 h in air at 5 °C/min. Catalyst samples were labelled M-Mn/SA.

2.2. Catalyst characterization

The X-ray diffraction (XRD) patterns of the monometallic catalysts and the manganese-oxide-based catalysts were recorded on a Rigaku D/max 2550PC diffractometer at 4°/min using $\text{Cu-K}\alpha$ radiation.

Nitrogen (N_2) adsorption-desorption isotherms were recorded using Micromeritics ASAP 2020 equipment at a liquid N_2 temperature (–196 °C). The samples were degassed at 200 °C for 5 h prior to analysis. Specific surface areas were calculated by the Brunauer-Emmett-Teller (BET) method. The total pore volume and average pore diameter were obtained from pore-size distributions by using the Barret-Joyner-Halenda (BJH) method to desorb the cumulative surface area of the pores.

Hydrogen temperature-programmed reduction (H_2 -TPR) analysis was carried out by using an automatic temperature-programmed chemisorption analyzer (Micromeritics AutoChem II 2920). Catalyst samples (50 mg) were pretreated at 200 °C in helium for 1 h prior to testing. Subsequently, H_2 -TPR patterns were obtained by measuring the H_2 consumption from 100 to 800 °C at 10 °C/min in 5% H_2 -95% argon (20 mL/min).

X-ray photoelectron spectroscopy (XPS) spectra were collected originally on a photoelectron spectrometer (Thermo Scientific Escalab 250Xi) with a standard $\text{Al-K}\alpha$ source (1486.6 eV). All binding energies were referenced to the C 1s line at 284.5 eV before data analysis. These results were treated after peak-fit processing.

2.3. Activity tests

A detailed experimental procedure and calculation formula can be found in our previous work [14]. NO deep oxidation was carried out in a fixed-bed reactor with an internal diameter of 5.8 mm and a length of 120 mm. The total gas flow rate was 2 L/min, with an oxygen concentration of 2.5 vol%, and the corresponding residence time in the reactor was ~ 0.12 s. The initial NO concentration was fixed at 410 mg/m³ with a small amount of residual NO₂ in the cylinder. The O₃-O₂ mixture that was generated from a dielectric-barrier-discharge ozone generator (HTU-500, 1 g/h, AZCO, Canada) was injected separately into the catalyst bed to avoid a reaction between the NO and O₃ before catalyst contact. The inlet and residual ozone concentrations were detected by a high- (BMT-964 BT, OSTI Inc.; 0–200000 mg/m³, ± 100 mg/m³) and a low-concentration ozone analyzer (Model 205, 2B Technologies; 0–430 mg/m³ ± 0.002 mg/m³), respectively. The initial and outlet concentrations of the gas components, including NO, NO₂, and O₂, were measured by using a Fourier transform infrared spectroscopy gas analyzer (Gasmeter, O₂ was measured by the external oxygen analyzer). Because of the short lifetime of N₂O₅, no commercial instrument exists to measure the quantitative N₂O₅ concentration. Previous work [13,14] has indicated that N₂O₅ is the only remaining product during deep oxidation. The catalytic activity was expressed by the residual concentration of NO + NO₂. The conversion efficiency (NO and NO₂ to N₂O₅) was calculated from a previous equation [14].

Firstly, 0.3 g of monometallic metal oxides were arranged in the deep-oxidation reactor without any dilution. The conversion efficiencies at 70 °C varied with O₃/NO ratio. All results were recorded after a 10-min stabilization period. Then, 2.2 g of manganese oxide-based catalysts were arranged in the same reactor, and the catalytic reaction temperature was fixed at 100 °C, unless otherwise noted. The ozone injection amount was fixed at 642 mg/m³ to ensure an O₃/NO molar ratio of 1.5. Because of the spherical design, some space was excluded between these catalyst pellets. This resulted in a longer catalytic reaction time (0.12 s) or gas-solid contact time, compared with traditional powder catalysts, which are believed to play a critical role to improve performance.

3. Results and discussion

3.1. Catalytic activity with monometallic catalysts

3.1.1. Catalytic deep oxidation results

The catalytic activities of monometallic catalysts were tested at 70 °C as we have found this reaction optimal for N₂O₅ formation [13]. The results are shown in Fig. 1. The presence of a catalyst enhanced the NO deep oxidation compared with the blank results. Overall, the catalytic activity decreased as Mn > Fe > Cr > Co > Cu > Ce. Mn is the best catalyst for ozone decomposition [18,29]. Manganese oxides showed excellent performance for NO_x storage [30], oxidation [31], and reduction [32]. Catalytic NO deep oxidation can be regarded as a combination of ozone decomposition, NO_x storage, and oxidation.

Fig. 1. NO deep-oxidation efficiencies varied with O₃/NO molar ratios by monometallic catalysts.

Therefore, Mn displayed the best performance among these transition-metal oxides, as was expected.

It has been proven that NO is transferred mainly to NO₂ with an O₃/NO molar ratio that is lower than 1.0 [3]. But the conversion efficiency of NO and NO₂ to N₂O₅ increased gradually from a lower O₃/NO molar ratio. Especially for monometallic Mn, the conversion efficiency reached nearly 15% at an O₃/NO molar ratio of 0.9. Under this condition, NO was not converted completely to NO₂. This result indicates that the NO₂ from NO oxidation was oxidized partly by O₃ to promote N₂O₅ formation, which precedes the total oxidization of NO. As mentioned above, the activation energy for NO₂ oxidation is much higher than that for NO oxidation. So N₂O₅ cannot form before NO is converted completely into NO₂ in the homogeneous gaseous reactor without catalysts. This phenomenon indicates that the presence of catalyst reduces the activation energy of NO₂ oxidation, and results in NO₂ and NO oxidation.

The N₂O₅ formation efficiency reached the highest level after an O₃/NO molar ratio of 2.0 as shown in Fig. 1. Although N₂O₅ formation was promoted significantly compared with the blank results, the ozone usage was still as high as before. The required residence time was reduced by these catalysts. This result indicates that not only the N₂O₅ formation rate, but also the O₃ decomposition rate were accelerated by these catalysts, which resulted in too much O₃ being decomposed without a participating reaction. It is believed that these results can be attributed to a less specific surface area and a compact arrangement. The former is unfavorable for reactant adsorption and ozone decomposition. The latter would lead to an accumulation of reaction intermediates and a rapid O₃ decomposition, which inhibits the catalytic reaction progress [14,21]. Although the activation energy for NO₂ oxidation has been reduced to some extent by catalyst addition, it is still higher than that of NO oxidation, which can be verified by the fact that N₂O₅ cannot be detected for an O₃/NO molar ratio of 0.5.

The goal of catalyst introduction is to achieve a theoretical threshold at an O₃/NO molar ratio of 1.5. We introduced spher-

ical arrangements to extend the reactant residence time on the catalyst surface, and to allow for sufficient time to facilitate NO₂ oxidation. Hereafter, SA was used as a support and doped with other transition-metal oxides.

3.1.2. Crystallite structure of monometallic catalysts

The XRD patterns of the monometallic catalysts are shown in Fig. 2. For each sample, only one crystalline phase was detected. CeO₂, Mn₂O₃, Fe₂O₃, CuO, CoO, and Cr₂O₃ diffraction peaks are visible for the monometallic Ce, Mn, Fe, Cu, Co, and Cr catalysts, respectively.

3.1.3. Porous structure parameters of monometallic catalysts

The N₂ adsorption-desorption isotherms and pore-size distribution curves of the monometallic catalysts are shown in Fig. 3. Catalysts Mn, Co, Fe, Cu, and Cr showed a characteristic type-IV isotherm according to the IUPAC classification, with the H3 hysteresis loop at $P/P_0 = 0.8\text{--}1.0$ indicating a mesoporous structure [33,34]. This corresponds to the broader pore-size distribution and slit-shaped pores [35]. A characteristic type-IV isotherm with an H1 hysteresis loop at $P/P_0 = 0.4\text{--}1.0$ was visible for the monometallic Ce, which exhibited a narrow pore-size distribution.

The BET surface area, pore volume, and average pore diameter are shown in Table 1. Monometallic Cr had the highest surface area (38.1 m²/g) and pore volume (0.27 cm³/g). Monometallic Cu had the lowest surface area (0.5 m²/g) and pore volume (0.002 cm³/g). The higher surface area and pore volume improve the adsorption ability. This result could explain why monometallic Cr displayed a better catalytic activity, whereas monometallic Cu showed a very low catalytic activity.

Fig. 2. XRD patterns of monometallic catalysts.

Ceria (CeO₂) has a large oxygen capacity and is always used as an excellent support or promotor. However, literature [18,36] has shown that CeO₂ exhibits a very low activity for ozone decomposition. Thus, the surface area of monometallic Ce was similar to Mn, but it was the worst catalyst for NO deep oxidation.

3.2. Catalytic activity with Mn-based bimetallic catalysts

3.2.1. Catalytic deep-oxidation results

Alumina has been used widely as a catalyst support because

Fig. 3. N₂ adsorption-desorption isotherms and pore-size distribution curves of monometallic catalysts.

Table 1

Pore-structure parameters of monometallic catalysts.

Catalyst	BET surface area (m ² /g)	Pore volume ^a (cm ³ /g)	Average pore diameter ^b (nm)
Mn	15.4	0.13	27.0
Ce	18.2	0.06	10.3
Co	1.6	0.01	38.8
Fe	12.2	0.15	45.1
Cu	0.5	0.002	33.7
Cr	38.1	0.27	23.2

^a BJH desorption cumulative pore volume.^b BJH desorption average pore diameter.

of its high surface area [17,37]. Bimetallic catalysts that were supported on SA were prepared to conduct catalytic deep-oxidation tests. The bimetallic catalytic activities are shown in Fig. 4. Ozone was injected at time zero. The concentration of NO + NO₂ decreased immediately after ozone injection, which indicated the formation of N₂O₅. Among these catalysts, Fe-Mn/SA and Ce-Mn/SA displayed the highest catalytic activity. After 20 min of ozone injection, the concentrations of NO + NO₂ tended to stabilize at a concentration lower than 20 mg/m³ for Fe-Mn/SA and 50 mg/m³ for Ce-Mn/SA. The corresponding conversion efficiencies were higher than 95% and 88%, respectively, which were all higher than the monometallic catalyst Mn/SA (83%). The ultra-low emission standard (NO_x < 50 mg/m³) has been reached. This shows that catalysts that are doped with Fe and Ce could improve the NO deep-oxidation efficiency, and could be applied for ultra-low emissions control. However, for the other three catalysts, the average stable concentration of NO + NO₂ was higher than 100 mg/m³. The average stable concentration of NO + NO₂ was higher than 200 mg/m³ for Co-Mn/SA. This indicates that Mn/SA doping with Cu, Cr, and Co inhibited the catalytic NO deep-oxidation activity.

Another interesting phenomenon in Fig. 4 is that the stable results required a long time. Especially for Cr-Mn/SA, Cu-Mn/SA, and Co-Mn/SA, the concentration of NO + NO₂ always showed a certain degree of volatility. This is because

Fig. 4. Variation in NO + NO₂ concentration with reaction time for Mn-based catalysts doped with different metal oxides. **Fig. 5.** Concentration of residual ozone after catalytic NO deep oxidation for Mn-based catalysts doped with different metal oxides.

newly formed N₂O₅ was adsorbed on the catalyst surface, and was desorbed slowly until saturation adsorption. The metal-atom valence state was increased by ozone injection before reacting with the reactants (NO, NO₂) [14]. Therefore, the concentrations of NO + NO₂ decreased continuously at the beginning of ozone injection and then reached equilibrium. This also explains why the concentrations of residual ozone increased continuously initially as shown in Fig. 5.

The concentration of residual ozone in Fig. 5 was not of the same order as the concentration of NO + NO₂ as shown in Fig. 4. Catalyst Cu-Mn/SA exhibited the highest concentration of residual ozone, whereas Co-Mn/SA exhibited the lowest ozone concentration. This demonstrates that the catalytic activity of the NO deep oxidation by ozone was not only affected by the ozone decomposition ability of the catalyst. The results in Fig. 5 that relate to NO_x oxidation do not represent the complete catalyst activity order of the ozone decomposition. Co-Mn/SA displayed the lowest catalytic potential for NO deep oxidation, with the lowest ozone residual. Perhaps because of this, large amounts of NO + NO₂ that were adsorbed on the catalyst surface would reduce the oxidized atom continuously, whereas the ozone residual was insufficient to recover the reduced atom. Thus, the concentration of NO + NO₂ for Co-Mn/SA exhibited a large volatility.

The residual ozone concentrations were less than 25 mg/m³ for Ce-Mn/SA and Fe-Mn/SA. As mentioned above, the concentrations of NO + NO₂ without deep oxidation were less than 50 mg/m³ for these two samples, which were close to twice the residual ozone. The equivalence ratio of NO₂/O₃ for N₂O₅ formation was 2.0. It can be concluded that ozone participated efficiently in NO deep oxidation.

3.2.2. Effect of reaction temperature on catalytic activity

Temperature is critical for N₂O₅ formation [13] and catalyst activity. Because of the better resistance to SO₂ and water vapor [38], Ce-Mn/SA was used to study the effect of reaction temperature on catalytic activity. The concentration of NO + NO₂ varied with time at different temperatures as shown in Fig. 6. There was no obvious difference between these four tem-

Fig. 6. NO + NO₂ concentration variation with time at different reaction temperatures (Ce-Mn/SA).

peratures (70, 100, 130, and 160 °C). When the temperature increased from 100 to 130 °C, the stable concentration of NO + NO₂ was relatively lower than that with the former two temperatures (70 and 100 °C). This result can be attributed to the increasing decomposition rate of the intermediates, which would recover more active sites. Therefore, the catalytic activity can be enhanced to some extent by an increase in temperature. The decrease in concentration at higher temperatures (130 and 160 °C) became slower compared with the lower temperatures (70 and 100 °C). More than 80 min was required to reach a stable state at 160 °C. As mentioned above, N₂O₅ has a short life time, and its decomposition rate will be accelerated at a higher temperature. Therefore, the N₂O₅ residence time on the catalyst surface was longer than 0.12 s before saturation adsorption was reached, which may lead to N₂O₅ decomposition to NO₂ and NO before it is desorbed from the catalyst surface. This may be another reason for the small higher stable concentration compared with that at 130 °C. Catalytic NO deep oxidation by ozone over Ce-Mn/SA can be applied in industrial applications at a reasonable temperature.

3.2.3. Crystallite structures

The XRD patterns of these five catalyst samples are shown in Fig. 7. Only the alumina diffraction peaks are visible in the samples, which indicates that the doped metals were highly dispersed in the support. The diffraction peaks of gibbsite Al(OH)₃ disappeared and the diffraction peaks of bohmite AlO(OH) weakened after loading with Mn. The diffraction peaks of bohmite AlO(OH) almost disappeared after loading with bimetallic oxides. This indicates that impregnation resulted in the removal of OH species. The diffraction peaks of Cu-Mn/SA were relatively higher than that for other samples, which indicated that crystallization occurred.

3.2.4. Physicochemical properties

The N₂ adsorption-desorption isotherms of the SA support and Mn-based catalysts in Fig. 8 show that the alumina sub-

Fig. 7. XRD patterns of Mn-based catalysts doped with different metal oxides.

strate catalysts exhibited IV isotherms with H1 hysteresis loops. The bigger hysteresis loop at $P/P_0 = 0.4$ –1.0 indicates a larger surface area compared with previous monometallic catalysts. Fig. 8 and Table 2 show that after impregnation, the surface area decreased for all samples, except for Ce-Mn/SA. These metal oxides were immersed into the pores of the SA, which led to the occupation of some pores. The average pore diameter increased after impregnation, which indicates a decrease in pore numbers. The increase in average pore diameter most likely results because OH is removed during impregnation, as is shown in the XRD results. As is shown in Fig. 10 and Table 3, the ratio of chemisorbed oxygen species decreased significantly after loading with Mn (Mn/SA compared with SA) and decreased again for the bimetallic catalysts. This could provide evidence for the decrease in OH during impregnation. The pore-blockage position by OH of the SA was recovered. Ce-Mn/SA had the highest surface area (318.7 m²/g), which may result in an improved catalytic activity. The increase in

Fig. 8. N₂ adsorption-desorption isotherms of Mn-based catalysts.

Table 2

Pore-structure parameters of Mn-based catalysts.

Catalyst	BET surface area (m ² /g)	Pore volume ^a (cm ³ /g)	Average pore diameter ^b (nm)
SA	294.3	0.37	4.5
Mn/SA	268.3	0.37	5.0
Ce-Mn/SA	318.7	0.43	4.8
Fe-Mn/SA	228.9	0.32	5.0
Cu-Mn/SA	264.0	0.36	4.9
Cr-Mn/SA	281.8	0.36	4.7
Co-Mn/SA	246.1	0.34	4.9

^a BJH desorption cumulative volume of pores.^b BJH desorption average pore diameter.**Table 3**

Binding energies and distribution of Mn and oxygen species.

Sample	Mn ³⁺ (eV)	Mn ⁴⁺ (eV)	Mn ⁴⁺ /Mn	O _α (eV)	O _β (eV)	O _β /O
SA	—	—	—	530.3	531.3	0.80
Mn/SA	641.7	644.5	0.33	530.2	531.1	0.57
Ce-Mn/SA	642.1	643.6	0.55	530.6	531.6	0.43
Fe-Mn/SA	641.7	643.8	0.46	530.4	531.3	0.50
Cu-Mn/SA	642.3	645.2	0.26	530.7	531.7	0.39
Cr-Mn/SA	642.2	644.3	0.42	530.7	531.6	0.47
Co-Mn/SA	642.4	644.8	0.35	530.7	531.6	0.52

surface area after doping with Ce may result because of the H1 hysteresis loop of the monometallic Ce sample as shown in Fig. 3. Although the quantity of adsorbed monometallic Ce sample was lower than for the other samples, the hysteresis loop was broader than for the other samples. This may favor the interaction between Ce and the supports. The BET surface area for these five samples decreased as Ce-Mn/SA > Cr-Mn/SA > Cu-Mn/SA > Co-Mn/SA > Fe-Mn/SA. Surface area is not the only determining factor for catalytic activity, which resulted in a different order of catalytic activity.

H₂-TPR measurements were carried out to compare the redox abilities of these catalysts, and the results are shown in Fig. 9. Because the pure SA support [14] showed almost no redox ability in the temperature range, all the reduction peaks in Fig.

Fig. 9. H₂-TPR profiles for Mn-based catalysts.

9 should be attributed to transition-metal oxides. Ce-Mn/SA, Fe-Mn/SA, and Co-Mn/SA exhibited little difference from Mn/SA. When these three profiles are overlapped, the reduction peak area decreases slightly after doping with Fe. This may be related to the reduced surface area of Fe-Mn/SA. The first reduction region between 100 and 450 °C was attributed mainly to a two-step reduction of MnO_x → Mn₃O₄ → MnO [39], whereas the second reduction peak between 600 and 700 °C, which represented the reduction of MnO_x species with larger particles [40], almost disappeared. This result indicates that the amounts of larger particles of MnO_x species decreased visibly after doping with these metal oxides. For the other two catalyst samples, Cu-Mn/SA and Cr-Mn/SA, the reduction peaks became sharper and the intensities increased significantly. The first reduction peak of Cu-Mn/SA occurred at a lower temperature (220 °C). This suggests that the introduction of Cu enhanced the redox ability by a strong synergistic effect between Mn and Cu. Cu possessed a higher reducibility than Mn, and therefore the first reduction peak at 220 °C corresponds mainly to the reduction of Cu²⁺ [41,42]. The reduction peak at 281 °C for Cr-Mn/SA most likely resulted because of the reduction of CrO₆ to Cr₂O₃ [43]. However, this result does not imply an absence of reduction for MnO_x species. The better redox abilities of Cu-Mn/SA and Cr-Mn/SA contributed to the better catalytic activity.

3.2.5. Surface properties

The Mn 2p spectra in Fig. 10 show that the asymmetrical signals of all samples included a spin orbit doublet with Mn 2p_{3/2} and Mn 2p_{1/2} at BE = 642 and 653 eV, respectively. The Mn 2p_{3/2} region could be resolved into two main peaks that are ascribable to the surface of Mn³⁺ and Mn⁴⁺ species [44,45] using an optimum combination of the Gaussian peaks method. The specific binding energy of these Mn species and the molar ratio of Mn⁴⁺ as calculated by the quantitative-area integration method are listed in Table 3. Ce-Mn/SA and Fe-Mn/SA possessed the highest molar ratio of Mn⁴⁺ among these samples. It has been reported that Mn species with a higher valence could enhance the oxidizing power and benefit the NO oxidation reaction [46,47]. The higher distribution ratio of Mn⁴⁺ can induce a more active oxygen bonding with Mn⁴⁺ to stabilize the chemical states and structure [48]. Therefore, the higher Mn⁴⁺ ratio of these two catalysts resulted in a better catalytic activity for NO deep oxidation. However, it has been reported that Mn³⁺ species could enhance the formation of oxygen vacancies [27,29]. The density of the oxygen vacancies affects the catalytic activity of the ozone decomposition significantly [49]. Mn⁴⁺ favors NO oxidation, whereas Mn³⁺ favors ozone decomposition. Therefore, the relative balance distribution between Mn⁴⁺ and Mn³⁺ is better for the catalytic activity of NO deep oxidation by ozone.

The O 1s spectra of these five samples can be deconvoluted into two peaks that are ascribable to lattice oxygen O_α and chemisorbed oxygen O_β [49,50]. The specific binding energy and the molar ratios are listed in Table 3. Co-Mn/SA exhibited the most chemisorbed oxygen on the catalyst surface among these samples. The corresponding Mn³⁺ ratio was high. This

Fig. 10. Mn 2p, O 1s, and doped metal atomic XPS spectra of Mn-based catalysts.

probably resulted in the lowest concentration of residual ozone in Fig. 5. But, as the catalytic-activity test results show in Fig. 4, Co-Mn/SA displayed the worst activity. It can be concluded that the excellent ozone decomposition activity of Co-Mn/SA resulted in insufficient ozone for NO deep oxidation. The higher ratio of chemisorbed oxygen that is associated with the higher Mn^{4+} contributed to a better NO oxidation activity [48]. Ce-Mn/SA and Fe-Mn/SA possessed these two factors and therefore, they displayed excellent activity.

The Ce 3d, Fe 2p, Cu 2p, Cr 2p, and Co 2p XPS spectra are given and the chemical states are labelled in Fig. 10. Two chemical states of Ce species exist on the catalyst surface: Ce^{4+} and Ce^{3+} , and the integrated area ratio of Ce^{4+}/Ce was 0.47, which could be attributed to a strong interaction between manganese and cerium oxides [51]. The transition between

Ce^{4+} and Ce^{3+} of cerium oxides results in large amounts of labile oxygen vacancies and oxygen species [52,53]. The higher ratio of Ce^{3+} creates more chemisorbed oxygen species on the catalyst surface because of the charge imbalance, labile oxygen vacancies, and unsaturated chemical bonds [54,55]. Therefore, abundant Ce^{3+} species exist on the catalyst surface, which are critical for the excellent catalytic activity.

The Fe 2p spectra was relatively simple compared with the Ce 3d spectra. Only two main peaks are visible from the XPS signal, which are ascribable to Fe^{3+} at a lower binding energy and Fe^{2+} at a higher binding energy [56]. The corresponding integrated area ratio of $\text{Fe}^{3+}/\text{Fe}_{\text{total}}$ was 0.51. This result indicates that Fe^{3+} and Fe^{2+} had a nearly average distribution on the catalyst surface.

The Cu 2p spectra included two main regions of Cu 2p_{1/2} at

BE = 947–960 eV and Cu $2p_{3/2}$ at BE = 930–940 eV, along with two satellite peaks as shown in Fig. 10. The Cu $2p_{1/2}$ signal can be deconvoluted into two peaks that are ascribable to Cu⁺ (932.2 eV) (stabilized by Cu-Mn interactions) and Cu²⁺ (934.6 eV) [57–59], respectively. The interaction between Cu and Mn species, $\text{Cu}^{2+} + \text{Mn}^{3+} \rightarrow \text{Cu}^+ + \text{Mn}^{4+}$, favors the catalytic reaction [60]. Electronic transfer between these two species is associated with oxygen-species adsorption [39]. However, according to the XPS results of Cu-Mn/SA, Mn³⁺ and Cu²⁺ are dominant species of Mn and Cu, respectively. This indicates that the interaction between Cu and Mn in Cu-Mn/SA was weak, and resulted in less chemisorbed oxygen on the catalyst surface, which may be a reason for the highest ozone residual in Fig. 5 for Cu-Mn/SA.

The two main peaks in the Cr $2p$ spectra represent Cr $2p_{3/2}$ at BE = 579.4 eV and Cr $2p_{1/2}$ at BE = 587.5 eV, which can be assigned to CrO₃ and Cr₂O₃, respectively [61]. The integrated area ratio of Cr⁶⁺/Cr was 0.72. The enrichment in Cr⁶⁺ on the catalyst surface contributed to its higher catalytic activity [62].

Because of the spin-orbit-splitting energy, the Co $2p$ spectra exhibited two main peaks that correspond to Co $2p_{3/2}$ at BE = 781.3 eV and Co $2p_{1/2}$ at BE = 797.3 eV, respectively, along with two satellite peaks. After peak fitting, the Co $2p_{3/2}$ and Co $2p_{1/2}$ regions were decomposed into two kinds of peaks that are ascribed to Co³⁺ (782.3 and 797.8 eV) and Co²⁺ (780.8 and 796.0 eV) [27,56,63]. The integrated area ratio of Co³⁺/(Co²⁺ + Co³⁺)

was 0.47. This result indicates that Co³⁺ and Co²⁺ existed with a nearly average distribution on the catalyst surface.

4. Conclusions

A series of monometallic catalysts (Mn, Co, Ce, Fe, Cu, and Cr) was prepared by the sol-gel method to effect catalytic NO deep oxidation by ozone. The manganese oxides displayed the highest conversion efficiency (almost 80% at an O₃/NO molar ratio of 2.0) among the samples. Only one type of crystalline phase was detected by XRD measurements for all samples and these were CeO₂, Mn₂O₃, Fe₂O₃, CuO, CoO, and Cr₂O₃. The porous structure parameters results showed that the catalytic activity is related to surface area and pore parameters, but these are not the only determining factors. A significant difference resulted for these monometallic samples: Cr possessed the highest surface area (38.1 m²/g) and Cu exhibited the lowest surface area (0.5 m²/g).

The manganese-oxide-based bimetallic catalysts that were supported on SA were studied by using the same procedure. Ce, Fe, Cr, Cu, and Co were selected as promoters, respectively. Ce-Mn/SA and Fe-Mn/SA showed the best performance and an excellent stability at a molar ratio of O₃/NO = 1.5, with less than 50 mg/m³ of NO + NO₂, and less than 25 mg/m³ of ozone residual, which had reached the ultra-low emission standard. The other three metal oxides inhibited the catalytic activity. XRD, N₂

Graphical Abstract

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Promotional effect of spherical alumina loading with manganese-based bimetallic oxides on nitric-oxide deep oxidation by ozone

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This paper focused on catalytic NO deep oxidation to N₂O₅. The Mn oxides exhibited the best activity. The lowest left concentration of NO+NO₂ was less than 20 mg/m³ by Fe-Mn/SA under the O₃/NO molar ratio of 1.5.

adsorption, H₂-TPR, and XPS were conducted to study the crystalline structure, physicochemical, and surface properties of these catalysts. A higher surface area and better pore parameters favored reactant adsorption. More oxygen vacancies benefited ozone adsorption and decomposition. The relative balance distribution between Mn⁴⁺ and Mn³⁺ was better for NO oxidation and ozone decomposition, and this favored N₂O₅ formation. The synthetic action of surface area, pore parameters, atomic chemical states, and oxygen vacancies affects the catalytic activity.

References

- [1] R. J. Huang, Y. L. Zhang, C. Bozzetti, K. F. Ho, J. J. Cao, Y. M. Han, K. R. Daellenbach, J. G. Slowik, S. M. Platt, F. Canonaco, P. Zotter, R. Wolf, S. M. Pieber, E. A. Brunns, M. Crippa, G. Ciarelli, A. Piazzalunga, M. Schwikowski, G. Abbaszade, J. Schnelle-Kreis, R. Zimmermann, Z. S. An, S. Szidat, U. Baltensperger, I. E. Haddad, A. S. H. Prévôt, *Nature*, **2014**, 514, 218–222.
- [2] Q. Zhang, Y. Huang, S. Q. Peng, Y. F. Zhang, Z. X. Sheng, J. J. Cao, W. K. Ho, S. C. Lee, D. Y. H. Pui, *Appl. Catal. B*, **2017**, 204, 346–357.
- [3] Z. H. Wang, J. H. Zhou, Y. Q. Zhu, Z. C. Wen, J. Z. Liu, K. F. Cen, *Fuel Process. Technol.*, **2007**, 88, 817–823.
- [4] D. Mráček, P. Kočí, J. S. Choi, W. P. Partridge, *Appl. Catal. B*, **2016**, 182, 109–114.
- [5] D. Q. Dao, L. Gasnot, K. Marschall, A. El Bakali, J. F. Pauwels, *Energy Fuels*, **2010**, 24, 1696–1703.
- [6] Q. Ma, Z. H. Wang, F. W. Lin, M. Kuang, R. Whiddon, Y. He, J. Z. Liu, *Energy Fuels*, **2016**, 30, 2302–2308.
- [7] W. L. Chang, P. V. Bhav, S. S. Brown, N. Riemer, J. Stutz, D. Dabdub, *Aerosol Sci. Technol.*, **2011**, 45, 665–685.
- [8] K. Skalska, J. S. Miller, S. Ledakowicz, *Sci. Total Environ.*, **2010**, 408, 3976–3989.
- [9] I. Jogi, E. Stamate, C. Irimiea, M. Schmidt, R. Brandenburg, M. Holub, M. Bonislawski, T. Jakubowski, M. L. Kääriäinen, D. C. Cameron, *Fuel*, **2015**, 144, 137–144.
- [10] S. L. Ding, Q. Yu, Y. Z. Zhang, Y. Liu, C. X. Xie, G. Yu, *J. Adv. Oxid. Technol.*, **2015**, 18, 114–122.
- [11] K. Li, X. L. Tang, H. H. Yi, P. Ning, D. J. Kang, C. Wang, *Chem. Eng. J.*, **2012**, 192, 99–104.
- [12] K. Skalska, J. S. Miller, S. Ledakowicz, *Chem. Eng. Sci.*, **2011**, 66, 3386–3391.
- [13] F. W. Lin, Z. H. Wang, Q. Ma, Y. He, R. Whiddon, Y. Q. Zhu, J. Z. Liu, *Energy Fuels*, **2016**, 30, 5101–5107.
- [14] F. W. Lin, Z. H. Wang, Q. Ma, Y. Yang, R. Whiddon, Y. Q. Zhu, K. F. Cen, *Appl. Catal. B*, **2016**, 198, 100–111.
- [15] D. Y. Yuan, Z. H. Wang, C. Ding, Y. He, R. Whiddon, K. F. Cen, *J. Phys. D*, **2016**, 49, 455203/1–455203/12.
- [16] U. Roland, F. Holzer, F. D. Kopinke, *Appl. Catal. B*, **2005**, 58, 217–226.
- [17] A. Ikhlaiq, B. Kasprzyk-Hordern, *Appl. Catal. B*, **2017**, 200, 274–282.
- [18] B. Dhandapani, S. T. Oyama, *Appl. Catal. B*, **1997**, 11, 129–166.
- [19] J. Nawrocki, B. Kasprzyk-Hordern, *Appl. Catal. B*, **2010**, 99, 27–42.
- [20] M. T. N. Dinh, J. M. Giraudon, A. M. Vandenbroucke, R. Morent, N. De Geyter, J. F. Lamonier, *Appl. Catal. B*, **2015**, 172–173, 65–72.
- [21] E. Rezaei, J. Soltan, N. Chen, *Appl. Catal. B*, **2013**, 136–137, 239–247.
- [22] S. Dimitrova, G. Ivanov, D. Mehandjiev, *Appl. Catal. A*, **2004**, 266, 81–87.
- [23] P. C. C. Faria, J. J. M. Órfão, M. F. R. Pereira, *Appl. Catal. B*, **2009**, 88, 341–350.
- [24] H. C. Wang, H. S. Liang, M. B. Chang, *J. Hazard. Mater.*, **2011**, 186, 1781–1787.
- [25] M. S. Jin, J. H. Kim, J. M. Kim, J. K. Jeon, J. Jurng, G. N. Bae, Y. K. Park, *Catal. Today*, **2013**, 204, 108–113.
- [26] A. Bueno-López, D. Lozano-Castelló, J. A. Anderson, *Appl. Catal. B*, **2016**, 198, 189–199.
- [27] J. Z. Ma, C. X. Wang, H. He, *Appl. Catal. B*, **2017**, 201, 503–510.
- [28] J. H. Ko, S. H. Park, J. K. Jeon, S. S. Kim, S. C. Kim, J. M. Kim, D. Chang, Y. K. Park, *Catal. Today*, **2012**, 185, 290–295.
- [29] C. X. Wang, J. Z. Ma, F. D. Liu, H. He, R. D. Zhang, *J. Phys. Chem. C*, **2015**, 119, 23119–23126.
- [30] Z. S. Zhang, B. B. Chen, X. K. Wang, L. Xu, C. Au, C. Shi, M. Crocker, *Appl. Catal. B*, **2015**, 165, 232–244.
- [31] F. W. Lin, Y. He, Z. H. Wang, Q. Ma, R. Whiddon, Y. Q. Zhu, J. Z. Liu, *RSC Adv.*, **2016**, 6, 31422–31430.
- [32] S. J. Yang, F. H. Qi, S. C. Xiong, H. Dang, Y. Liao, P. K. Wong, J. H. Li, *Appl. Catal. B*, **2016**, 181, 570–580.
- [33] Y. X. Wang, H. Q. Sun, H. M. Ang, M. O. Tadé, S. B. Wang, *Appl. Catal. B*, **2015**, 164, 159–167.
- [34] B. Y. Bai, J. H. Li, J. M. Hao, *Appl. Catal. B*, **2015**, 164, 241–250.
- [35] F. S. Ding, A. F. Zhang, M. Liu, Y. Zuo, K. Y. Li, X. W. Guo, C. S. Song, *Ind. Eng. Chem. Res.*, **2014**, 53, 17563–17569.
- [36] C. Heisig, W. H. Zhang, S. T. Oyama, *Appl. Catal. B*, **1997**, 14, 117–129.
- [37] F. Gunnarsson, J. A. Pihl, T. J. Toops, M. Skoglundh, H. Härelind, *Appl. Catal. B*, **2017**, 202, 42–50.
- [38] F. W. Lin, Z. H. Wang, J. M. Shao, D. K. Yuan, Y. He, Y. Q. Zhu, K. F. Cen, *RSC Adv.*, **2017**, 7, 25132–25143.
- [39] W. X. Tang, X. F. Wu, S. D. Li, X. Shan, G. Liu, Y. F. Chen, *Appl. Catal. B*, **2015**, 162, 110–121.
- [40] V. A. de la Peña O'Shea, M. C. Alvarez-Galvan, J. L. G. Fierro, P. L. Arias, *Appl. Catal. B*, **2005**, 57, 191–199.
- [41] D. A. Aguilera, A. Perez, R. Molina, S. Moreno, *Appl. Catal. B*, **2011**, 104, 144–150.
- [42] M. R. Morales, B. P. Barbero, L. E. Cadús, *Appl. Catal. B*, **2006**, 67, 229–236.
- [43] R. H. Ma, P. J. Hu, L. Y. Jin, Y. J. Wang, J. Q. Lu, M. F. Luo, *Catal. Today*, **2011**, 175, 598–602.
- [44] L. L. Zhang, J. J. Tu, L. Lyu, C. Hu, *Appl. Catal. B*, **2016**, 181, 561–569.
- [45] D. Delimaris, T. Ioannides, *Appl. Catal. B*, **2008**, 84, 303–312.
- [46] D. M. Meng, W. C. Zhan, Y. Guo, Y. L. Guo, L. Wang, G. Z. Lu, *ACS Catal.*, **2015**, 5, 5973–5983.
- [47] M. Q. Shen, Z. Zhao, J. H. Chen, Y. G. Su, J. Wang, X. Q. Wang, *J. Rare Earths*, **2013**, 31, 119–123.
- [48] J. H. Chen, M. Q. Shen, X. Q. Wang, G. S. Qi, J. Wang, W. Li, *Appl. Catal. B*, **2013**, 134–135, 251–257.
- [49] J. B. Jia, P. Y. Zhang, L. Chen, *Appl. Catal. B*, **2016**, 189, 210–218.
- [50] V. P. Santos, M. F. R. Pereira, J. J. M. Órfão, J. L. Figueiredo, *Appl. Catal. B*, **2010**, 99, 353–363.
- [51] P. Sudarsanam, B. Hillary, M. H. Amin, S. B. A. Hamid, S. K. Bhargava, *Appl. Catal. B*, **2016**, 185, 213–224.
- [52] X. H. Li, S. L. Zhang, Y. Jia, X. X. Liu, Q. Zhong, *J. Nat. Gas Chem.*, **2012**, 21, 17–24.
- [53] G. S. Qi, R. T. Yang, *J. Catal.*, **2003**, 217, 434–441.
- [54] X. Gao, Y. Jiang, Y. Zhong, Z. Y. Luo, K. F. Cen, *J. Hazard. Mater.*, **2010**, 174, 734–739.
- [55] B. Guan, H. Lin, L. Zhu, Z. Huang, *J. Phys. Chem. C*, **2011**, 115, 12850–12863.
- [56] R. Tholkappian, K. Vishista, *Appl. Surf. Sci.*, **2015**, 351, 1016–1024.

- [57] J. L. Ayastuy, A. Gurbani, M. P. González-Marcos, M. A. Gutiérrez-Ortiz, *Int. J. Hydrogen Energy*, **2012**, 37, 1993–2006.
- [58] M. Konsolakis, S. A. Carabineiro, P. B. Tavares, J. L. Figueiredo, *J. Hazard. Mater.*, **2013**, 261, 512–521.
- [59] X. Q. Qiu, M. Miyauchi, K. Sunada, M. Minoshima, M. Liu, Y. Lu, D. Li, Y. Shimodaira, Y. Hosogi, Y. Kuroda, K. Hashimoto, *ACS Nano*, **2012**, 6, 1609–1618.
- [60] S. A. Kondrat, T. E. Davies, Z. L. Zu, P. Boldrin, J. K. Bartley, A. F. Carley, S. H. Taylor, M. J. Rosseinsky, G. J. Hutchings, *J. Catal.*, **2011**, 281, 279–289.
- [61] L. Zhong, Q. Zhong, W. Cai, S. Zhang, Y. Yu, M. Ou, F. J. Song, *RSC Adv.*, **2016**, 6, 21056–21066.
- [62] A. Y. Wang, Y. L. Guo, F. Gao, C. H. F. Peden, *Appl. Catal. B*, **2017**, 202, 706–714.
- [63] L. Y. Wang, X. X. Cheng, Z. Q. Wang, C. Y. Ma, Y. K. Qin, *Appl. Catal. B*, **2017**, 201, 636–651.

球形氧化铝负载锰基双金属氧化物催化剂催化臭氧深度氧化NO

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摘要: 在工业锅炉烟气处理领域, 由于锅炉容量低, 烟气温度往往无法满足传统选择性催化还原(SCR)所需温度窗口. 工业锅炉烟气成分的复杂性也给氮氧化物治理带来了严峻考验. 臭氧深度氧化NO结合湿法洗涤同时脱硫脱硝技术具有独特的应用优势. 传统臭氧氧化技术中, NO被臭氧氧化为NO₂, 进而在脱硫塔中实现一体化脱硫脱硝. 但由于NO₂溶解度相对较低, 需要在脱硫浆液中加入添加剂提高脱硝效率, 造成运行成本增加. NO经臭氧深度氧化后, NO₂进一步转化为溶解度高的N₂O₅, 传统脱硫石膏浆液即可实现高效吸收N₂O₅, 从而有效提高氮氧化物吸收效率. 但由于N₂O₅生成反应速率低, 深度氧化存在臭氧投入量大、反应时间长及臭氧残留多的缺点. 臭氧耦合催化剂深度氧化NO可有效解决以上问题.

首先, 本文采用溶胶-凝胶法合成一系列单金属氧化物(Mn, Co, Ce, Fe, Cu, Cr)作为臭氧深度氧化NO的催化剂. 结果发现锰氧化物表现出最高的催化活性, 在70 °C下, O₃/NO摩尔比为2.0时经过0.12 s的反应时间催化剂即可实现80%以上的转化效率. 但根据N₂O₅生成的总包反应(2NO + 3O₃ = N₂O₅ + 3O₂)可以看出, O₃/NO摩尔比为1.5时即可实现N₂O₅的完全转化. 由于催化臭氧氧化反应温度较低, 中间产物在催化剂表面聚集, 占据大量活性位, 进而导致无法实现1.5摩尔比的高效转化. 通过采用球形氧化铝作为载体, 避免粉末状催化剂紧凑型布置, 增加换热面积, 可有效降低催化剂表面中间产物聚集; 同时延长了气体与催化剂的接触时间, 提高反应效率. 在球形氧化铝载体上负载锰基双金属氧化物(Ce-Mn, Fe-Mn, Cr-Mn, Cu-Mn和Co-Mn), 在初始NO浓度为410 mg/m³, 反应温度100 °C, O₃/NO摩尔比1.5, 催化反应时间0.12 s的工况下, 催化剂最终实现95% (Fe-Mn)和88% (Ce-Mn)的转化效率, 剩余NO和NO₂的浓度分别低于20 mg/m³ (Fe-Mn)和50 mg/m³ (Ce-Mn), 臭氧残留浓度低于25 mg/m³. 同负载单一锰氧化物(83%转化率)相比, 双金属氧化物进一步提高了N₂O₅生成效率. 因此, 臭氧耦合催化剂深度氧化NO结合湿法吸收在工业锅炉超低排放(NO_x < 50 mg/m³)领域具有广泛应用前景.

通过XRD、氮气吸附、H₂-TPR和XPS等手段研究了催化剂的晶体结构、孔结构参数、氧化还原性能和表面原子价态. 催化臭氧深度氧化NO主要与催化剂对臭氧的分解性能和对NO的氧化性能有关. 较大的比表面积和孔容有利于催化剂的吸附. 氧空位有利于臭氧的吸附和分解. Mn⁴⁺和Mn³⁺的均衡分布既有利于NO的吸附氧化又有利于臭氧的吸附分解, 最终提高了N₂O₅生成效率.

关键词: 一氧化氮; 深度氧化; 催化剂; 臭氧; 过渡金属氧化物

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