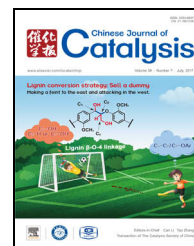


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## Article

# 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<sub>2</sub>O<sub>5</sub>) by ozone together with wet scrubbing has become a promising technology for nitrogen-oxide (NO<sub>x</sub>) removal in industrial boilers. Catalysts were introduced to enhance the N<sub>2</sub>O<sub>5</sub> 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<sub>3</sub>)/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<sub>2</sub>O<sub>5</sub> is oxidation with an O<sub>3</sub>/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<sup>3</sup> of outlet NO + nitrogen oxide, and less than 25 mg/m<sup>3</sup> of residual ozone at an O<sub>3</sub>/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<sub>x</sub> oxidation and ozone decomposition.

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## 1. Introduction

Nitrogen oxides (NO<sub>x</sub>) are one of the main sources of haze [1,2] and are toxic to human health. They contain mainly nitric oxide (NO) and nitrogen dioxide (NO<sub>2</sub>). The main NO<sub>x</sub> exhaust from power-plant boilers, industrial boilers, and automotive vehicles is NO, which accounts for more than 95% of the total NO<sub>x</sub> [3]. Exhausted NO<sub>x</sub> 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<sup>3</sup>, SO<sub>2</sub> < 35 mg/m<sup>3</sup>, NO<sub>x</sub> < 50 mg/m<sup>3</sup>, oxygen (O<sub>2</sub>) = 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<sub>x</sub> control in complex industry boilers is required urgently.

NO is nearly insoluble in water whereas the other NO<sub>x</sub> gases, NO<sub>2</sub> and dinitrogen pentoxide (N<sub>2</sub>O<sub>5</sub>), have a higher solubility. N<sub>2</sub>O<sub>5</sub> can be removed easily by water spraying without any additives [7,8]. NO peroxidation can achieve the simultaneous removal of SO<sub>2</sub> and NO<sub>x</sub> 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<sub>x</sub> removal in special cases [3,9–12]. Previous work [13,14] has focused on the conversion of NO to N<sub>2</sub>O<sub>5</sub>, 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<sub>3</sub>/NO molar ratio > 2.0). If we consider the overall reaction for N<sub>2</sub>O<sub>5</sub> formation, 2NO + 3O<sub>3</sub> = N<sub>2</sub>O<sub>5</sub> + 3O<sub>2</sub>, theoretically, NO could be converted completely to N<sub>2</sub>O<sub>5</sub> with an O<sub>3</sub>/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 O<sub>3</sub>/NO = 1.5. Catalyst stabilities and the resistance to SO<sub>2</sub> 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<sub>x</sub> 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<sub>x</sub> 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 (Mn(NO<sub>3</sub>)<sub>2</sub>, 49.0%–51.0%; Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O, ≥99.0%; Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, ≥98.5%; Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O, ≥99.0%; Cr(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, ≥99.0%; Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, ≥98.5%; all from Sinopharm) and citrate (C<sub>6</sub>H<sub>8</sub>O<sub>7</sub>·H<sub>2</sub>O, Sinopharm, ≥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]. Mn(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O (Aladdin, ≥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 Cu-K<sub>α</sub> radiation.

Nitrogen (N<sub>2</sub>) adsorption-desorption isotherms were recorded using Micromeritics ASAP 2020 equipment at a liquid N<sub>2</sub> 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<sub>2</sub>-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<sub>2</sub>-TPR patterns were obtained by measuring the H<sub>2</sub> consumption from 100 to 800 °C at 10 °C/min in 5% H<sub>2</sub>-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 Al-K<sub>α</sub> 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.

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