LaO_x modified MnO_x loaded biomass activated carbon and its enhanced performance for simultaneous abatement of NO and Hg^0

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Abstract

A battery of agricultural straw derived biomass activated carbons supported LaO_x modified MnO_x (LaMn/BACs) was prepared by a facile impregnation method and then tested for simultaneous abatement of NO and Hg^0. 15%LaMn/BAC manifested excellent removal efficiency of Hg^0 (100%) and NO (86.7%) at 180 °C, which also exhibited splendid resistance to SO_2 and H_2O. The interaction between Hg^0 removal and NO removal was explored; thereinto, Hg^0 removal had no influence on NO removal, while NO removal preponderated over Hg^0 removal. The inhibitory effect of NH_3 was greater than the accelerative effect of NO and O_2 on Hg^0 removal. The physicochemical characterization of related samples was characterized by SEM, XRD, BET, H_2-TPR, NH_3-TPD, and XPS. After incorporating suitable LaO_x into 15%Mn/BAC, the synergistic effect between LaO_x and MnO_x contributed to the improvement of BET surface area and total pore volume, the promotion of redox ability, surface active oxygen species, and acid sites, inhibiting the crystallization of MnO_x. 15%LaMn/BAC has the best catalytic oxidation activity at low temperature. That might be answerable for superior performance and preferable tolerance to SO_2 and H_2O. The results indicated that 15%LaMn/BAC was a promising catalyst for simultaneous abatement of Hg^0 and NO at low temperature.

Keywords

Simultaneous removal · NO · Elemental mercury (Hg^0) · SO_2 tolerance · H_2O resistance

Introduction

With the implementation of the ultra-low emission and energy saving of coal-fired power plant plan since 2015 in China, electrostatic precipitator (ESP) or fabric filter (FF) system, wet flue gas desulfurization (WFGD) unit, and selective catalytic reduction (SCR) devices have been extensively adopted for corresponding pollutants abatement (Liu et al. 2018; Zhao et al. 2019a; Gao et al. 2018a). Consequently, following SO_2, NO_x, and dust, mercury emission has triggered tremendous concerns due to its severe toxicity, high persistence, toilless biological fluidity, and strong biomagnification in the food chain and ecosystem after it is converted into more venomous methylmercury (Gao et al. 2018a; Xue et al. 2016; Shen et al. 2018a; Jiang et al. 2018). It is well recognized that elemental mercury (Hg^0), oxidized mercury (Hg^2+), and particle-bound mercury (Hg^0) coexist in coal-fired flue gas (Wang et al. 2017; Liu et al. 2019a). It is well recognized that elemental mercury (Hg^0), oxidized mercury (Hg^2+), and particle-bound mercury (Hg^0) coexist in coal-fired flue gas (Wang et al. 2017; Liu et al. 2019a). Thereinto, Hg^{2+} and Hg^0 can be readily captured by WFGD and ESP or FF, respectively (Xu et al. 2018a; Chi et al. 2017; Shan et al. 2019). However, Hg^0 (the major mercury form) is untoward to remove by existing environmental protection devices in consideration of its water insolubility and strong volatility (Gao et al. 2018b; Xu et al. 2016; Shen et al. 2018a; Jiang et al. 2018). Thus, the emphasis and difficulty of eliminating mercury pollution lie in controlling Hg^0 emission.
In response to increasing environmental consciousness and rigorous mercury emission regulations, plentiful technologies, including catalytic oxidation and adsorption, have been tremendously researched for Hg\textsubscript{0} removal in recent years (Gao et al. 2018a; Zhang et al. 2017a; Yang et al. 2019a). To date, activated carbon injection (ACI) for Hg\textsubscript{0} abatement is a commercial technology (Shen et al. 2018b; Zhao et al. 2018; Shi et al. 2019). However, it suffers from some intractable bottlenecks, such as potential secondary contamination, huge operating costs, tardy regeneration rates, and the value deterioration of fly ash (Zhang et al. 2017a, 2018; Zhao et al. 2018). Furthermore, controlling NO and Hg\textsubscript{0} emissions by utilizing SCR and ACI independently confronts several inevitable shortcomings such as large equipment investment, high land requirement, huge maintaining, and operating costs (Gao et al. 2018a, b; Chen et al. 2020). It is essential to use the ameliorative SCR catalyst to achieve efficient reduction of NO\textsubscript{x} and oxidation of Hg\textsubscript{0} without subjoining equipment for considering comprehensive benefits; various SCR catalysts have been abundantly investigated for this purpose (Li et al. 2018; Zhang et al. 2021). It is well accepted that vanadium-based SCR catalyst can make part Hg\textsubscript{0} oxidize to Hg\textsuperscript{2+}, but the converting ability from Hg\textsubscript{0} to Hg\textsuperscript{2+} is relatively limited in low chlorine flue gas (Jiang et al. 2018; Zhao et al. 2018; Chen et al. 2018). However, such catalyst has to operate at a temperature range of 300–400 °C and that urges SCR unit to be placed upstream of desulfurization and dedusting devices where catalyist is readily impaired by SO\textsubscript{2} and dust (Jiang et al. 2018; Zhang et al. 2021). Moreover, V\textsubscript{2}O\textsubscript{5} itself poses certain threat to the environment and human health (Li et al. 2018; Zhang et al. 2021). Notably, to overcome the abovementioned deficiencies, it is significantly needful to exploit preferable cryogenic catalysts with outstanding demercurization and denitrification efficiencies, realizing simultaneous removal of Hg\textsubscript{0} and NO by the existing gas purification devices.

Notably, in order to achieve these objectives, numerous novel catalysts, such as Mn-Ce/TiO\textsubscript{2}, CuO-MnO\textsubscript{x}/AC-H, La\textsubscript{0.8}Ce\textsubscript{0.2}MnO\textsubscript{3}, have been researched for simultaneous abatement of NO and Hg\textsuperscript{0} (Shen et al. 2018b; Zhao et al. 2019a, b, c; Zhang et al. 2017b). Thereinto, manganese oxides (MnO\textsubscript{x}) catalysts with splendid cryogenic performance have been extensively investigated for NO and Hg\textsuperscript{0} removal in view of preeminent properties of Mn species, such as the nature of labile oxygen, outstanding redox properties, diversiform oxidation states, and high oxygen storage/release capacity as well as environmental friendliness, abundant reserves, and cheap price (Zhao et al. 2019b; Xu et al. 2018b; Fan et al. 2018). Nevertheless, some MnO\textsubscript{x}-based catalysts especially unsupported ones often bore with several shortcomings, such as poor tolerance to SO\textsubscript{2} and H\textsubscript{2}O, low thermal stability, and little specific surface area. These shortcomings impeded their actual applications (Zhang et al. 2018; Fan et al. 2018). Furthermore, La\textsubscript{2}O\textsubscript{3} can be used as an effective promoter to improve the dispersion of active components to obtain a catalyst with high stability and activity (Shen et al. 2018b). Studies have shown that the addition of La promotes the low temperature activity to Hg\textsubscript{0} and NO (Gao et al. 2018b; Yang et al. 2018a). Therefore, the manganese-based catalyst modified by lanthanum species may exhibit excellent performance.

As shown in literature, numerous carbon-based catalysts with activated carbon/biomass activated carbon (AC/BAC) carriers not only exhibited good performances for Hg\textsubscript{0} and NO simultaneous abatement at low temperature, but also often demonstrated great resistance to SO\textsubscript{2} and H\textsubscript{2}O (Gao et al. 2018a; Ren et al. 2017). That preeminent manifestations were possibly attributed to the excellent physicochemical characteristics of carbonaceous materials, and the good SO\textsubscript{2} tolerance was related to the large surface areas and abundant oxygen-containing functional groups (Ren et al. 2017; Guo et al. 2015), while the high H\textsubscript{2}O resistance might be associated with hydrophobic property of carbon materials (Abdelouahab-Reddam et al. 2015; Joung et al. 2014). As we well know, traditional ACs mainly come from non-renewable and relatively expensive resources such as wood and coal. Meanwhile, China suffers from intractable challenges from handling renewable agriculture straws in enormous quantities every year, owing to lack of reasonable approaches. As a result, BACs derived from agriculture straws have drawn attention with excellent application prospect. Until now, carbon materials including BACs have stimulated their potential in simultaneous removal of NO and Hg\textsubscript{0}, due to its sustainability, adjustable surface chemistry, and outstanding surface area (Shen et al. 2018a; Li et al. 2019). In addition, BACs with hierarchical porous structure usually show the advantages of excellent gas absorption and rapid mass transfer, which were also in favor of simultaneous removal of NO and Hg\textsubscript{0}. Therefore, manganese oxides loaded on BAC derived from agricultural straw wastes may be a promising catalyst for Hg\textsubscript{0} and NO simultaneous removal at low temperature. To the best of our knowledge, few studies related to LaO\textsubscript{x} modified MnO\textsubscript{x}/BAC for simultaneous abatement of Hg\textsubscript{0} and NO have been reported in publications, in which the synergistic effect between MnO\textsubscript{x} and LaO\textsubscript{x} might have a positive role on aggrandizing performance and tolerance to SO\textsubscript{2} and H\textsubscript{2}O. Consequently, a battery of systematic tests is performed to elucidate its performance for NO and Hg\textsubscript{0} simultaneous abatement over LaMn/BAC catalysts in this work.

**Materials and methods**

**Materials preparation**

The manufacture method of BAC carrier was detailedly presented in our previous paper (Gao et al. 2018a). Lanthanum...
nitrates or manganese acetates acted as the precursors of LaO\(_x\) and MnO\(_x\), respectively. The preparation steps of La/BAC, Mn/BAC, and LaMn/BAC were shown below. First, lanthanum nitrates or manganese acetates were dissolved into moderate deionized water to generate corresponding precursor solutions. Second, desired BACs were soaked in aforesaid precursor solutions for 24 h. Third, impregnated samples dried at 105 °C and therewith calcined at 500 °C for 4 h under N\(_2\) atmosphere. The atomic ratios of La/Mn in XLaMn/BACs were 1:4 based on our preliminary experiments, where X corresponded to the mass fraction of LaMn mixed oxides. Meanwhile, for comparison, XMn/BAC and XLa/BAC were synthesized by the same procedures.

**Materials characterization**

The ASAP2460 volumetric sorption analyzer (Micromeritics Instrument Corp., USA) was applied to determine the specific surface areas and pore parameters of samples. Scanning electron microscopy photographs were taken to analyze sample surface structures and morphologies on the Hitachi S-4800 analyzer (Hitachi Limited, Japan). The X-ray diffraction (XRD) results embodying component crystallinity and dispersivity were collected on a Bruker D8-Advance X-ray diffraction device. NH\(_3\)-TPD and H\(_2\)-TPR (the abbreviations for ammonia-temperature programmed desorption and H\(_2\)-temperature programmed reduction, respectively) were carried out using the Tianjin Xianquan TP-5080 automatic chemical adsorption instrument. The element chemical composition and chemical state of samples were conducted on the K-Alpha 1063 X-ray photoelectron spectrometer (Thermo Fisher Scientific, USA).

**Experimental setup and procedure**

Figure 1 displays the experimental apparatus diagram. In each test, 250 mg sample was placed in the reactor with a quartz tube (600 mm length \(\times\) 10 mm inner diameter). The total flow rate of simulated flue gas (SFG) was sustained at 500 mL/min (gas hourly space velocity (GHSV) = approximately 80,000 h\(^{-1}\)), which mainly consisted of 5%O\(_2\), 500 ppm NO, 100 μg/m\(^3\) Hg\(^0\) (g), 500 ppm NH\(_3\), and N\(_2\).

The mercury conversion tests were carried out to distinguish mercury speciations (Gao et al. 2018a; Ma et al. 2015a), in which the outlet gas of the reactor could be divided into two freely switching branches: one got through 10% SnCl\(_2\) + HCl aqueous solution to reduce Hg\(^{2+}\) to Hg\(^0\) for measuring total mercury (Hg\(_{\text{out}}^0\)), whereas the other passed 10% KCl aqueous solution to dislodge Hg\(^{2+}\) in order to accurately measure Hg\(^0\). Therefore, \(E_{\text{oxy}}\) denoting the oxidation efficiency of Hg\(^0\) could be determined by Eq. (1). Similarly, \(E_{\text{NO}}\) and \(E_{\text{Hg}}\) expressing their removal efficiencies were respectively calculated by Eqs. (2) and (3). Meanwhile, NO and Hg\(^0\) concentrations were measured by Germany MGA 5 flue gas analyzer and Russia Lumex RA-915 M mercury analyzer, respectively.

\[
E_{\text{oxy}} = \frac{\text{Hg}_{\text{out}}^0 - \text{Hg}_{\text{in}}^0}{\text{Hg}_{\text{in}}^0} \times 100\% \tag{1}
\]

\[
E_{\text{NO}} = \frac{\text{NO}_{\text{in}} - \text{NO}_{\text{out}}}{\text{NO}_{\text{in}}} \times 100\% \tag{2}
\]

\[
E_{\text{Hg}} = \frac{\text{Hg}_{\text{in}}^0 - \text{Hg}_{\text{out}}^0}{\text{Hg}_{\text{in}}^0} \times 100\% \tag{3}
\]
In which, NO_{in} and NO_{out} respectively indicated inlet and outlet NO concentrations. Likewise, inlet Hg^{0} concentration and outlet Hg^{0} concentration were independently represented as Hg^{0}_{in} and Hg^{0}_{out}. Moreover, in order to lessen test errors, E_{NO} and E_{Hg} were the average data of several parallel tests, and their relative errors were confined to 5%.

Results and discussion

Characterization of samples

BET analysis

The average pore diameters, total pore volumes, and BET surface areas of modified BACs and virgin BAC are summarized in Table 1. Further, their pore size distribution curves and N_{2} adsorption-desorption isotherms are displayed in Fig. 2. According to IUPAC, these samples shared type IV isotherm with slit shaped pores, implying the presence of H3 hysteresis loops (Chen et al. 2017). As shown in Fig. 2b, 15%La/BAC and 15%Mn/BAC exhibited bimodal peaks centered at around 2.4 nm and 3.9 nm, while other samples possessed unimodal and narrow peaks located at about 2.4 nm. That clearly indicated these samples owned most mesopores and some micropores, which could provide more active sites and inner surface areas for SCR reaction (Guan et al. 2012). Virgin BAC owned the largest total pore volume (0.485 cm^{3}/g) and the highest BET surface area (745.935 m^{2}/g). Nevertheless, both total pore volume and BET surface area demonstrated noticeable decreases after loading metal oxides, and the descending trend became more and more severe with the augment of metal oxide impregnation. Especially, 30%LaMn/BAC exhibited the smallest total pore volume (0.306 cm^{3}/g) and the poorest BET surface area (474.657 m^{2}/g). That could be interpreted as the deposition of metal oxides in preexisting pores and the destruction of thin pore walls in the impregnation and calcination processes (Ma et al. 2015a; Xie et al. 2015). It was worth mentioned that 15%LaMn/BAC revealed bigger total pore volume and BET surface area than those of 15%La/BAC and 15%Mn/BAC, which might be ascribed to a strong interaction derived between LaO_{x} and MnO_{x}; the phenomenon indicated that the addition of LaO_{x} expresses a certain promotion effect on the BET surface area of the catalyst, which promoted a progressive dispersion of crystallites (Liotta et al. 2013). Similar appearance was found in other report (Jampaiah et al. 2015).

Table 1: The BET specific surface area and pore parameters of virgin BAC and modified BACs

| Sample          | BET surface area (m^{2}/g) | Total pore volume (cm^{3}/g) | Average pore diameter (nm) |
|-----------------|----------------------------|------------------------------|-----------------------------|
| Virgin BAC      | 745.935                    | 0.485                        | 2.605                       |
| 7.5%LaMn/BAC    | 679.127                    | 0.440                        | 2.589                       |
| 15%LaMn/BAC     | 646.049                    | 0.420                        | 2.601                       |
| 22.5%LaMn/BAC   | 520.463                    | 0.336                        | 2.585                       |
| 30%LaMn/BAC     | 474.657                    | 0.306                        | 2.580                       |
| 15%La/BAC       | 516.055                    | 0.345                        | 2.673                       |
| 15%Mn/BAC       | 610.447                    | 0.402                        | 2.634                       |

SEM analysis

Figure 3 revealed these SEM micrographs of virgin BAC and modified BACs with different loading values. The dark smoothness areas demonstrated carbon en-riched zones, while light pelleting areas represented the presence of metal oxides. As you could see clearly, the introduction of metal oxides changed overwhelmingly pristine surface properties of virgin BAC. As shown in Fig. 3b, with regard to 7.5%LaMn/BAC, only a handful of agglomerates were discovered, and most metal oxides were highly dispersed. However, the presence of large dark areas indicated that 7.5%LaMn/BAC’s surface could not obtain full application, and additional catalytic sites could be further provided through enhancing metal oxides loading (Gao et al. 2018a). For 15%LaMn/BAC, abundant metal oxides scattered plenarily on the BAC surface, although some agglomerates were still found. With regard to 22.5%LaMn/BAC and 30%LaMn/BAC, apparent and even serious agglomerates emerged, respectively. Consequently, metal oxide accumulation got more and more worse, resulting in the disappearance of available pores and catalytic active sites, exerting negative effect on its catalytic activity. This phenomena were in line with BET results.

XRD analysis

Figure 4 depicts the XRD patterns of modified BACs and virgin BAC. For virgin BAC, two strong diffraction peaks located at about 26.60° and 44.46° were detected, which were deemed to be the characteristic peaks of BAC (Gao et al. 2018b).
2018a; Xie et al. 2015). Nevertheless, they weakened and even vanished with loading LaO\textsubscript{x} or MnO\textsubscript{x}, indicating the presence of a strong interaction between BAC and metal species (Gao et al. 2018b; Du et al. 2018). Besides, the fact that the peak intensity of metal oxides was much stronger than BAC might be also responsible for this phenomenon. With regard to 15%La/BAC, the diffraction peaks corresponded to La\textsubscript{2}O\textsubscript{3} (JCPDS 24-0508) and La(OH)\textsubscript{3} (JCPDS 05-0602) were found (Xu et al. 2016; Tang et al. 2004). For 15%Mn/BAC, the diffraction peaks ascribed to different crystalline manganese oxides were detected, indicating the coexistence of Mn\textsuperscript{4+}, Mn\textsuperscript{3+}, and Mn\textsuperscript{2+} in the sample (Xu et al. 2016; Forzatti 2001; Cimino and Scala 2016; Kang et al. 2007). Comparatively speaking, the peaks of LaMn/BAC representing different Mn and La species weakened significantly and even disappeared. This results might indicate the presence of a strong interaction originated between LaO\textsubscript{x} and MnO\textsubscript{x}, thus resulting in smaller crystal sizes of metal oxides and higher surface areas due to the modification of LaO\textsubscript{x}, which might be favorable for catalytic reactions (Gao et al. 2018a; Li et al. 2012).

**H\textsubscript{2}-TPR analysis**

It was noteworthy that the redox properties of catalysts usually played crucial roles in catalytic activities. The H\textsubscript{2}-TPR profiles of modified BACs and virgin BAC are illustrated in Fig. 5. As regards virgin BAC, the distinct reduction peak approximately at 680 °C might be reasonably assigned to the gasification of BAC (Zhang et al. 2015), which also existed in other
samples. As for modified BACs, the introduction of metal oxides would generate lattice oxygen. As a result, the broad higher peak at 675 °C of modified BACs might be partly attributed to the reduction of lattice oxygen (Zhao et al. 2016; Li et al. 2014). Therefore, the peak at round 700 °C was greatly enhanced for modified BACs due to the superposition of BAC gasification and lattice oxygen reduction. With regard to 15%Mn/BAC, three remarkable reduction peaks located at 335 °C, 439 °C, and 517 °C were observed in the low temperature range, which might belong to the stepwise reduction of MnO$_2$ → Mn$_2$O$_3$ → Mn$_3$O$_4$ → MnO (Ma et al. 2015a; Boningari et al. 2015; Zhang et al. 2014). By contrast, these reduction peaks of 15%LaMn/BAC slidden into lower temperature regions, which were discovered at 323 °C, 425 °C, and 505 °C, respectively (Boningari et al. 2015; Zhang et al. 2014; Li et al. 2017). That suggested 15%LaMn/BAC obtained better redox ability than 15%Mn/BAC, which was beneficial to catalytic activity through introduction of LaO$_x$ (Zhang et al. 2014; Li et al. 2017). Meanwhile, these profile shifts might implicate the presence of La-Mn complexes, which was largely due to a synergistic effect stemmed from La species and Mn species (Gao et al. 2018a; Li et al. 2010). Thus, it was reasonable to infer that 15%LaMn/BAC embodied better catalytic activity than 15%Mn/BAC (Li et al. 2017, 2010).

NH$_3$-TPD analysis

The surface acidity properties of modified BACs and virgin BAC were estimated by NH$_3$-TPD. As shown in Fig. 6, virgin BAC exhibited a feeble peak at high temperature range,
indicating that it also had a handful of acid sites for NH$_3$ adsorption and activation. The NH$_3$ desorption peak at high temperature range dramatically increased with the introduction of La, indicating that the introduction of La could significantly enhance its amount and strength of acidic sites. This phenomenon was plausibly assigned to that La could adjust the intensity distribution and amount of acid sites, stemming from its lanthanide contraction and 4f orbitals without full electron occupancy (Zhan et al. 2014; Liu et al. 2017), in which medium temperature peaks were in line with Brønsted acid sites, while high temperature peaks belonged to Lewis acid sites (Lónyi et al. 1996; Gu et al. 2010; Fang et al. 2018).

It was conjectured that Brønsted acid sites might be stemmed from surface hydroxyl groups (Gu et al. 2010; Ma et al. 2015b), while Lewis acid sites possibly originated from unsaturated metal sites (Gu et al. 2010; Zhu et al. 2017). Meanwhile, the intensity and areas of desorption peaks were associated with the strength and amount of acid sites (Gao et al. 2018b), which followed a descending trend: 15%LaMn/BAC > 15%La/BAC > 15%Mn/BAC > virgin BAC. Even more noteworthy was the fact that 15%LaMn/BAC displayed the most acid sites for NH$_3$ adsorption and its succedent activation, thus boosting SCR activity, which was largely due to a synergistic effect stemmed between La
and Mn species (Zhu et al. 2017; Moreno-Tost et al. 2002). Hence, it was reasonable to infer that 15%LaMn/BAC could behave the best NO removal efficiency.

**XPS analysis**

Figure 7 elucidates the XPS spectra of O 1s, Mn 2p, La 3d, and Hg 4f. The O 1s XPS spectra of uncirculated and used 15%LaMn/BAC were rendered in Fig. 7a, which were deconvoluted into three components centered 529.8 ~ 530.1 eV, 531.3 ~ 531.4 eV, and 532.7 ~ 532.9 eV. The lower binding energy peaks were put down to lattice oxygen (O α), the medium binding energy peaks were regarded as weakly bonded oxygen and/or chemisorbed oxygen (O β), and the higher binding energy peaks represented adsorbed water species and/or hydroxyl groups (O γ) (Li et al. 2010, 2015a). However, virgin BAC only exhibited two kinds’ peaks of O 1s; one peak was located at 531.61 eV, and the other one was sited at 533.9 eV. The former peak could be ascribed to O β, while the latter one might correspond to either-type oxygen, which was the primary product for carbonate-based electrolytes, stemming from reaction/reduction of carbonate-based solvents (Ma et al. 2015a; Veith et al. 2012; Freunberger et al. 2011). It was easy to accept that the introduction of metal oxides could provide abundant O α for modified BACs, which was beneficial for oxidizing NO to NO2 to boost E NO at low temperature (Kang et al. 2007; Zhan et al. 2014; Li et al. 2015c). In addition, the interaction between LaO x and MnO x could contribute to more oxygen vacancies and chemisorbed oxygens, which facilitated Hg 0 adsorption and oxidation (Xie et al. 2015). Combined with the analyses of BET and SEM, the introduction of metal oxides and its precursors (metal nitrates) could cover the surface of virgin BAC in the calcination and foregoing loading processes, resulting in the formation of lattice oxygen and disappearance of either-type oxygen (Gao et al. 2018a; Ma et al. 2015a). The tiny amounts of either-type oxygen of virgin BAC could be fully overspread with metal oxides forming lattice oxygen. Compared with fresh 15%LaMn/BAC, the ratios of O α and O β both demonstrated palpable downward trends, while the ratio of O γ raised from 37.24 to 40.86% after reactions, suggesting both O α and O β might participate in the reactions. In this regard, we could conjecture that 15%LaMn/BAC with affluent O α and O β along with well-dispersed active species might probably be very efficient for NO and Hg 0 elimination (Xie et al. 2015; Deng et al. 2015; Liu et al. 2016). So its unique advantages were proved for the use of LaO x to modify MnO x/BAC for NO and Hg 0 abatement.

As elucidated in Fig. 7b, the Mn 2p regions of uncirculated and used 15%LaMn/BAC consisted of two main peaks including Mn 2p3/2 and Mn 2p1/2 centered at around 641.8 eV and 653.5 eV, respectively. Moreover, the latter could be deconvoluted into three peaks at 641.1–641.5 eV, 642.5–643 eV, and 644.6–644.7 eV, which were ascribed to Mn 2+, Mn 3+, and Mn 4+, respectively (Du et al. 2018; Zhang et al. 2014; Li et al. 2015c). It could be seen that the proportion of Mn 4+ descended distinctly from 23.7 to 19.1%, while the percentage of Mn 3+ enhanced slightly from 21.2 to 21.5%, and the ratio of Mn 2+ increased from 20.9 to 25.5%, indicating that some Mn 2+ generated from consumed Mn 4+ in reactions. It was demonstrated that Mn 2+ species and its redox cycle could boost the oxidation process from NO to NO2, which was beneficial for both NO conversion and Hg 0 oxidation (Boningari et al. 2015; Zhang et al. 2014; Li et al. 2015c).
Furthermore, it was speculated that the large-span valence change from Mn$^{4+}$ to Mn$^{3+}$ and whereafter to Mn$^{2+}$ over Mn-based catalysts might be beneficial to NO and Hg$^0$ elimination; meanwhile, Mn$^{4+}$ was deemed to be the most active species (Yang et al. 2018b; Liu et al. 2019b).

The La 3d XPS spectra of uncirculated and used 15%LaMn/BACs are illustrated in Fig. 7c. Two essentially identical doublet peaks including main peaks and its satellite peaks were observed, where the peaks at 834.1 eV (834.4 eV) were the main peaks for La 3d$^{5/2}$, 838.1 eV (838.3 eV) for the satellite peaks of La 3d$^{5/2}$, and the peaks located at 851.1 eV (851.2 eV) were the main peaks of La 3d$^{3/2}$, 855.0 eV (855.3 eV) for its satellite peaks of La 3d$^{3/2}$ (Tholkappiyan and Vishista 2014). Meanwhile, the main peaks ascribed to 3d$^9$ 4f$^0$ arose from the spin-orbit interaction whereas their satellite peaks due to the 3d$^9$ 4f$^1$ final state were attributed to the electron transfer between the empty La 4f orbit and the oxygen valence (Dudric et al. 2014). The appearance of satellite peaks located at a higher binding energy of approximate 4 eV was a diagnose feature for confirming the presence of La$^{3+}$ compounds coordinated by other ligands (Rudyk et al. 2011). The energy separations between La 3d$^{5/2}$ and La 3d$^{3/2}$ core levels were approximately 17 eV, which was inconsistent with that of standard La$_2$O$_3$ (Tholkappiyan and Vishista 2014). Moreover, the binding energy value of La 3d$^{5/2}$ was 834.1 eV (834.4 eV), which was higher than that of bulk La$_2$O$_3$ with the binding energy value of 831.9 eV (Rudyk et al. 2011). In addition, these binding energy values of La 3d were in concert with that in perovskites (Gao et al. 2018b; Rudyk et al. 2011; Blanchard et al. 2010). These phenomena indicated the transformation of La$_2$O$_3$ into a perovskite-type structure of LaMnO$_x$ (Craciun and Dulamita 1997), which was in well accordance with H$_2$-TPR analysis. It means that the addition of LaO$_x$ can control the morphological structure of the catalyst.

The Hg 4f XPS spectra of used 15%LaMn/BAC are presented in Fig. 7d; four peaks centered at 99.9 eV, 101.44 eV, 102.65 eV, and 104.6 eV were recorded. The medium peak at
102.65 eV corresponded to Si 2p (Tao et al. 2012). The weakest peak at 99.9 eV was attributed to the characteristic peak of adsorbed Hg\(^0\) (Tao et al. 2012; Hutson et al. 2007). The strongest peak located at 104.6 eV belonged to Hg 4f5/2, and the other medium peak at 101.44 eV represented Hg 4f7/2, which was associated with HgO (Tao et al. 2012; Hutson et al. 2007; Li et al. 2015b). As illustrated in Fig. 8, mercury conversion tests demonstrated that catalytic oxidation with the product of HgO and adsorption worked together for Hg\(^0\) removal, in which their contributions varied with reaction time.

**The performance of samples**

**Effect of active ingredient**

Figure 9a, b reveals the effect of active ingredients on E\(_{\text{NO}}\) and E\(_{\text{Hg}}\) at 60 ~ 340 °C, respectively. It was clearly to see that both reaction temperature and active ingredients exerted significant influences on NO and Hg\(^0\) removal. Apparently, E\(_{\text{NO}}\) and E\(_{\text{Hg}}\) enhanced significantly after loading Mn or La species onto virgin BAC, indicating that active ingredients were conducive to NO and Hg\(^0\) removal. Particularly, 15%LaMn/BAC exhibited preferable E\(_{\text{NO}}\) and E\(_{\text{Hg}}\) than those of 7.5%LaMn/BAC and 30%LaMn/BAC. Besides, 15%LaMn/BAC also yielded better performance and broader active temperature window compared with 15%Mn/BAC and 15%La/BAC, which exerted the highest E\(_{\text{Hg}}\) of 100% at 100 ~ 180 °C and the best E\(_{\text{NO}}\) of 88.6% at 220 °C with a second-best E\(_{\text{NO}}\) of 86.7% at 180 °C. The former appearance demonstrated that active ingredients could not always display decisive role in NO and Hg\(^0\) removal, which might be also affected by BET surface areas and total pore volumes (Gao et al. 2018a, b). The later appearance could be assigned to a synergistic effect originated from La and Mn species derived from the LaO\(_x\) modified Mn supported catalyst, which contributed to smaller crystal sizes and better dispersion of metal oxides, bigger BET surface area, bigger total pore volume, higher redox ability, and more acid sites, and those properties were responsible for better performance and broader active temperature window (Xie et al. 2015; Liotta et al. 2013; Zhang et al. 2014). Notably, the E\(_{\text{Hg}}\) of La/BAC and Mn/BAC significantly decreased after 220 °C in Fig. 9b, which was probably ascribed to their relatively poorer catalytic activity for Hg\(^0\) oxidation than that of LaMn/BAC, due to Hg\(^0\) oxidation dominating for Hg\(^0\) removal at that time since this samples had suffered from uninterrupted tests of 20 h. Simultaneously, incorporating La\(_2\)O\(_3\) into MnO\(_x\) lattice could generate more bulk oxygen species and oxygen vacancies with high mobility, which were beneficial to Hg\(^0\) oxidation. (Liu et al. 2017; Hou et al. 2020). Similar appearances were also discovered in previous works (Gao et al. 2018a, b).

In addition, E\(_{\text{NO}}\) and E\(_{\text{Hg}}\) of modified BACs showed similar trends with increasing reaction temperature, respectively. Meanwhile, E\(_{\text{Hg}}\) exhibited a slight increase in the temperature range of 60 to 180 °C and whereafter declined dramatically with further elevating reaction temperature, whereas E\(_{\text{NO}}\) yielded an apparent increase from 60 ~ 220 °C and afterwards displayed a very slight dip except for 15%La/BAC. That phenomenon demonstrated that elevating reaction temperature often boosted Hg\(^0\) and specially NO abatement until a certain
temperature, after which further enhancing reaction temperature exerted negative effects on \( \text{Hg}^0 \) and NO abatement. With respect to 15% LaMn/BAC, \( E_{\text{NO}} \) aggrandized from 78.5 to 88.6% until reaction temperature augmented from 60 to 220 °C, and further increasing reaction temperature resulted in \( E_{\text{NO}} \) declining to 83.8% at 340 °C, while \( E_{\text{Hg}} \) reached 100% from originally 98.3% at 60 °C and maintained 100% removal efficiency at 100 ~ 180 °C, and therewith, it decreased slightly from 100 to 90.1% at 340 °C. It was recognized that increasing reaction temperature would boost catalytic activity at low temperature owing to enhancing catering activation energy and chemisorption stemmed from generating more chemical bonds (Tao et al. 2012; Zeng et al. 2004). Moreover, the manifest declines of \( E_{\text{Hg}} \) and \( E_{\text{NO}} \) at high temperatures might be interpreted by two reasons. On the one hand, the adsorption of reactant molecules like \( \text{Hg}^0 \) onto adsorption sites would be inhibited by high temperature (Li et al. 2011). On the other hand, the structures of carbon-based catalysts might be destroyed by high temperature due to active ingredients catalytic oxidizing carbon matrix (Gao et al. 2018a, b; Lu et al. 2011).
It was noteworthy that 15%LaMn/BAC respectively exhibited 100% and 86.7% removal efficiency for Hg⁰ and NO at 180 °C, indicating it has excellent application potential at low temperature compared with 15%Mn/BAC without LaOₓ modification.

### Effect of flue gas components

The effects about flue gas components on NO and Hg⁰ simultaneous abatement over 15%LaMn/BAC are presented in Fig. 10. It could be seen that both E₇g and especially ENO declined dramatically when 5% O₂ was removed from SFG. The poor performance might be profited from preexisted Oα and Oβ on the sample surface (Gao et al. 2018a, b; Xie et al. 2015), as demonstrated in the O 1s XPS analysis. Nevertheless, compared with that under SFG, additional 5% O₂ joining the SFG engendered negligible influences on NO and Hg⁰ removal. This phenomenon indicated that O₂ could play a positive effect on E₇₉ and E₇g under oxygen-poor conditions. It was well-known that Oα and Oβ would be expended in NO reduction and Hg⁰ oxidation reactions; meanwhile, active metal species were reduced in that processes. Noteworthily, gaseous O₂ could supplement consumed Oα and Oβ through oxidizing aforesaid reduced metal species, thus facilitating these reactions continuing (Bueno-López et al. 2005; Grabowski et al. 2002).

As shown in Figs. 10 and 11, both SO₂ and H₂O restrained ENO and EHg, and the synchronous presence of SO₂ and H₂O aroused more serious declines of EHg and ENO than that under separate SO₂ and H₂O. The prohibitive influences of SO₂ and H₂O could be interpreted by several reasons. First of all, the existence of SO₂ and H₂O might compete with Hg⁰, NH₃, NO, and O₂ for adsorption and catalytic sites (Li et al. 2011, 2008; Casapu et al. 2009). Secondly, the emerging ammonium sulfates or bisulfates could cover activated sites and destroy porous structure; additionally, the possible generating metal sulfates stemmed from metal oxides reacting with SO₂ might lead activated adsorption or catalytic sites to inactive ones (Li et al. 2015b), thus suppressing E₇₉ and EHg. Most notably, 15%LaMn/BAC exhibited better tolerance to SO₂ and H₂O than that of 15%Mn/BAC in preliminary experiments because of introduction of LaOₓ, which might be ascribed to bigger BET surface area and higher metal oxides dispersion as well as other advantageous synergistic effects between LaOₓ and MnOₓ species (Zhang et al. 2014, 2015).

### The interaction between NO removal and Hg⁰ removal

It was indispensable to inspect the possible interaction effects between NO removal and Hg⁰ removal allowing for practical application. As illustrated in Fig. 12, ENO seemed hardly changed when 100 μg/m³ Hg⁰ was suddenly removed from SFG, and ENO only manifested some indistinctive changes even if additional 100 μg/m³ Hg⁰ was added into SFG. That suggested Hg⁰ removal exerted almost no impact over NO removal, which might be explained by that Hg⁰ concentration was too small to have little impact on NO removal. On the contrary, EHg elevated remarkably when 500 ppm NO and 500 ppm NH₃ were concurrently subtracted from SFG, indicating NO removal displayed detrimental influence on Hg⁰ removal. It was inferred that NO removal might take precedence of Hg⁰ removal in high NO and NH₃ concentrations (Zhang et al. 2017c; Niksa and Fujiwara 2005).

To further investigate the separate effect of NO and NH₃ on Hg⁰ removal, systematic tests were performed, as presented in Fig. 12. EHg manifested an obvious drop when 500 ppm NO was precluded from the SFG, and the similar result was also
observed when additional 500 ppm NH$_3$ was joined in the SFG. Clearly, that indicated NH$_3$ had evidently suppressive influence on Hg$^0$ abatement, which was probably assigned to rapidly adsorbed NH$_3$ occupying some active sites; therewith, part active oxygen was expended, thus restraining Hg$^0$ removal (Chen et al. 2017; Qi et al. 2004; He et al. 2016). Moreover, EHg exhibited significant increase when 500 ppm NH$_3$ was precluded from SFG, and the positive appearance was also detected when additional 500 ppm NO was added into the SFG, which demonstrated NO displayed promotional role on Hg$^0$ removal. That appearance might be attributed to the fact that some weakly adsorbed NO could be oxidized to NO$_2$, which was in favor of Hg$^0$ oxidation (Zhao et al. 2019b; Li et al. 2010).

**Mechanism exploration**

According to the analyses of the experimental results, the feasible mechanism of simultaneous removal of NO and Hg$^0$
on LaMn/BACs was speculated. The total low-temperature activity of the catalyst was facilitated as the introduction of La species (Wang et al. 2019a), which is consistent with the results of H2-TPR. It was indicated that La2O3 promoted the electron movement between Mn4+, Mn3+, and Mn2+ attributed to the synergistic effect emerged between La and Mn. The XPS characterization of Mn 2p demonstrated that the conversion of Mn4+ to Mn2+ was facilitated under the catalytic reaction; LaOx might existed as an electron promoter in the catalyst. This alteration in the valence state of manganese species on the catalyst is a possible mechanism for NO reduction and Hg0 oxidation (Yang et al. 2018a; Liu et al. 2019b; Yang et al. 2019b; Gao et al. 2019). The possible NH3-SCR reaction process of NO could be summarized as follows: gaseous NH3 was adsorbed on the Lewis and Brønsted acid sites on the surface of the catalyst, and formative coordinated NH3 and NH4+ reacted with gaseous NO and adsorbed NO2 via the Langmuir-Hinshlwood mechanism to convert into innocuous N2 and H2O (Zhang et al. 2017a; Zhao et al. 2018; Fu et al. 2014). Moreover, we detected tiny amount of CO2 and CO in the outlet gas, as shown in Eqs. (19)–(21) (where KO was denoted as lanthanum-manganese composite metal oxide). Notably, this phenomenon of some side reactions might occur during the NH3-SCR process on the carbon-supported metal oxide because of the carbon support as reducer had also been reported in other studies (Shen et al. 2018b; Li et al. 2018; Lu et al. 2010). Notwithstanding, the dominance of reactions (8)–(18) relative to reactions (19)–(21) was not affected. The specific reaction formulas were as follows:

\[
\begin{align*}
2\text{Mn}^{4+} & \rightarrow 2\text{Mn}^{3+} + \text{O}_\alpha \quad (4) \\
2\text{Mn}^{3+} & \rightarrow 2\text{Mn}^{2+} + \text{O}_\alpha \quad (5) \\
2\text{Mn}^{3+} + 1/2\text{O}_2 & \rightarrow 2\text{Mn}^{4+} \quad (6) \\
2\text{Mn}^{3+} + 1/2\text{O}_2 & \rightarrow 2\text{Mn}^{2+} \quad (7) \\
\text{O}_2(g) & \rightarrow \text{O}_2(\text{ad}) \quad (8) \\
\text{O}_2(\text{ad}) & \rightarrow 2\text{O}_\beta \quad (9) \\
\text{KO} + \text{O}_\beta & \rightarrow \text{KO}_2^* \quad (10) \\
\text{KO}_2^* + \text{NO}_0(g) & \rightarrow \text{KO} + \text{NO}_2(\text{ad}) \quad (11) \\
\text{NO}_0(g) & \rightarrow \text{NO}_0(\text{ad}) \quad (12) \\
\text{NO}_0(\text{g}) + \text{O}_\beta & \rightarrow \text{NO}_2(\text{ad}) \quad (13) \\
\text{NO}_0(\text{ad}) + \text{O}_\alpha & \rightarrow \text{NO}_2(\text{ad}) \quad (14) \\
\text{NH}_3(g) & \rightarrow \text{NH}_3(\text{ad}) \quad (15) \\
\text{NH}_3(\text{g}) + \text{H}^+_{\text{surf}} & \rightarrow \text{NH}_4^+(\text{ad}) \quad (16) \\
2\text{NH}_3(\text{ad}) + \text{NO}_2(\text{ad}) + \text{NO}_0(g) & \rightarrow 2\text{N}_2 + 3\text{H}_2\text{O} \quad (17) \\
2\text{NH}_4^+(\text{ad}) + \text{NO}_2(\text{ad}) + \text{NO}_0(g) & \rightarrow 2\text{N}_2 + 3\text{H}_2\text{O} + 2\text{H}^+ \quad (18)
\end{align*}
\]

\[
\begin{align*}
\text{KO}_2^* + \text{BAC} & \rightarrow \text{KO} + \text{CO} \quad (19) \\
\text{KO}_2^* + \text{CO} & \rightarrow \text{KO} + \text{CO}_2 \quad (20) \\
2\text{NO} + 2\text{CO} & \rightarrow \text{N}_2 + 2\text{CO}_2 \quad (21)
\end{align*}
\]

The conversion pathway of Hg0 on the catalyst prepared in this work can be divided into adsorption including physisorption, chemisorption, and catalytic oxidation, which have also been noted in our previous researches (Gao et al. 2018a, b). As shown in Fig. 8, the contribution of the two modes of mercury conversion varied with the reaction time. It was potty to observe from Fig. 8 that the contribution of catalytic oxidation was relatively small at the beginning, but Hg0 oxidation prevailed gradually with the increase of reaction time. The oxidation of Hg0 was ascribed to the Mars-Maessen mechanism under the atmosphere of N2 + O2 that both Oα and Oβ participated in Hg0 oxidation (Zhao et al. 2019b; Wang et al. 2019b). Oα and Oβ were easy to combine with adsorbed Hg0 to form HgO (Zhao et al. 2019c) (as shown in Eq. (23)). However, the oxidation of Hg0 was mainly attributed to the consumption of Oα, which was also consistent with the analysis results of XPS O 1s (Gao et al. 2018a; Shen et al. 2018b). Therefore, the oxidation path of Hg0 was speculated that Hg0(g) was first adsorbed on the sample surface and oxidized with Oα and Oβ to generate HgO(ads)- Nevertheless, part of HgO(ads) might be converted into HgO(g). The reaction process was summarized as follows:

\[
\begin{align*}
\text{Hg}_0(g) & \rightarrow \text{Hg}_0(\text{ad}) \quad (22) \\
\text{Hg}_0(\text{g}) + \text{O}_\alpha/\text{O}_\beta & \rightarrow \text{HgO}(\text{ad}) \quad (23) \\
\text{HgO}(\text{ad}) & \rightarrow \text{HgO}(g) \quad (24)
\end{align*}
\]

Furthermore, it is very valuable to explore the possible mechanisms about the effect of gas components on Hg0 removal. Figure 10 indicates that both H2O and SO2 had inhibitory effects on the removal of Hg0. The inhibitory effect of H2O was due to its competitive adsorption with Hg0, hindering the adsorption of Hg0 (Liu et al. 2020; Xu et al. 2016). Similarly, SO2 also possessed the competitive adsorption with Hg0. In addition, SO2 not only reduced HgO(ads) to Hg0(g) but also reacted with active metal oxides MnO and Mn2O3 to form Mn-SO42− with the participation of Oβ, which caused the active sites to be covered and reduced the removal efficiency of Hg0 (Liu et al. 2021; Zhao et al. 2017; Zhang et al. 2017d). Therefore, the possible reaction of SO2 could be described as follows; Eqs. (25)–(27) were shown. Moreover, Fig. 12 reveals that NH3 had an adverse effect on E_{Hg}. On one hand, this might also be related to the competitive adsorption between NH3 and Hg0. On the other hand, NH3 was adsorbed on the sample surface and reacted with SO3(ads) or H2O(ads) to form (NH4)2SO4 or NH4HSO4 crystals, which would block the microporous structure of the sample, thereby reducing the
removal efficiency of Hg\(_0\) (as shown in Eq. (28)) (Xu et al. 2016, 2019; Sun et al. 2020). On the contrary, NO showed a promotional effect on the removal of Hg\(_0\); it could be attributed to the NO\(_2\)/NO active species formed by the oxidation of NO via Eqs. (29)–(30), which would promote Hg\(_0\) oxidation (Zhu et al. 2019). In summary, the possible mechanisms about the effect of gas components on Hg\(_0\) removal could be described as follows:

\[
\begin{align*}
\text{HgO}_2(g) + \text{SO}_2(g) & \rightarrow \text{Hg}_2(g) + \text{SO}_3(g) \tag{25} \\
\text{MnO}_2 + \text{SO}_2 + \beta \text{Mn} \rightarrow \text{Mn}_2\text{SO}_4 & \tag{26} \\
\text{Mn}_2\text{O}_3 + \text{SO}_2 + \beta \text{Mn} \rightarrow \text{Mn}_2\text{SO}_4 & \tag{27} \\
\text{NH}_3(ad) + \text{H}_2\text{O}(ad) + \text{SO}_2(ad) & \tag{28} \\
+ \alpha \text{Mn} \rightarrow \text{NH}_4\text{SO}_4/\text{NH}_4\text{HSO}_4 & \tag{29} \\
\text{NO}_2(ad) + \text{Hg}_0(ad) \rightarrow \text{HgO(ad) + NO(ad)} & \tag{30} \\
\text{NO}_2(ad) + \text{Hg}_0(ad) + \alpha \text{Mn} \rightarrow \text{Hg(NO)}_3 & \tag{31}
\end{align*}
\]

### Conclusions

A battery of LaMn/BACs adopting a facile ultrasound-assisted impregnation method was prepared for simultaneous abatement of NO and Hg\(_0\). 15\%LaMn/BAC manifested excellent performance for NO and Hg\(_0\) simultaneous removal and superior resistance to SO\(_2\) and H\(_2\)O at low temperature due to bringing LaO\(_x\) in the catalyst; meanwhile, it exhibited splendid Hg\(_0\) removal efficiency (100\%) and extraordinary NO removal efficiency (86.7\%) at 180 °C. The interaction between Hg\(_0\) removal and NO removal was explored; thereinto, Hg\(_0\) removal had no influence on NO removal, while NO removal preponderated over Hg\(_0\) removal. The accelerative effects of NO and O\(_2\) on Hg\(_0\) removal could not offset the inhibitory influence of NH\(_3\). SEM, XRD, BET, H\(_2\)-TPR, NH\(_3\)-TPD, and XPS were exploited to characterize the physicochemical properties of relevant samples. After incorporating suitable LaO\(_x\) into 15\%Mn/BAC, the synergistic effect between LaO\(_x\) and MnO\(_x\) emerged in 15\%LaMn/BAC, which contributed to the enhancement of BET surface area and total pore volume, the improvement of redox ability, surface active oxygen species, and acid sites, suppressing the crystallization of MnO\(_x\). That might be answerable for superior performance and preferable tolerance to SO\(_2\) and H\(_2\)O under the modified effect of LaO\(_x\). The results indicated that 15\%LaMn/BAC was a promising catalyst for simultaneous abatement of Hg\(_0\) and NO at low temperature.

### Author contribution

Conceptualization: Lei Gao; methodology: Lei Gao and Caiting Li; formal analysis and investigation: Lei Yi and Jinke Xie; writing—original draft preparation: Jian Shan and Yingyun Liu; writing—review and editing: Junwen Lv and Mi Li; funding acquisition, resources, and supervision: Lei Gao.

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### Data availability

The datasets used and analyzed during the current study are available from the corresponding author on reasonable request.

### Competing interests

The authors declare no competing interests.

### References

Abdelouahab-Reddam Z, El Mail R, Coloma F, Sepúlveda-Escribano A (2015) Platinum supported on highly-dispersed ceria on activated carbon for the total oxidation of VOCs. Appl Catal A Gen 494:87–94

Blanchard PER, Slater BR, Cavell RG, Mar A, Grosvenor AP (2010) Electronic structure of lanthanum transition-metal oxyarsenides LaMAsO(M = Fe, Co, Ni) and LaFe\(_x\)\_\_AsO (M\(_x\) = Co, Ni) by X-ray photoelectron and absorption spectroscopy. Solid State Sci 12:50–58

Boninatti T, Ettireddy PR, Somogyvari A, Liu Y, Vorontsov A, McDonald CA, Smirniotis PG (2015) Influence of elevated surface texture hydrated titania on Ce-doped Mn/TiO\(_2\) catalysts for the low-temperature SCR of NO\(_x\) under oxygen-rich conditions. J Catal 325:145–155

Bueno-López A, Krishna K, Makkee M, Mouljin JA (2005) Enhanced soot oxidation by lattice oxygen via La\(_{\text{3+}}\)-doped CeO\(_2\). J Catal 230:237–248

Casapu M, Kröcher O, Elsener M (2009) Screening of doped MnO\(_x\)–CeO\(_2\) catalysts for low-temperature NO-SCR. Appl Catal B Environ 88:413–419

Chen H, Xia Y, Huang H, Gan Y, Tao X, Liang C, Luo J, Fang R, Zhang J, Zhang W, Liu X (2017) Highly dispersed surface active species of Mn/Co/TiW catalysts for high performance at low temperature NH\(_3\)-SCR. Chem Eng J 330:1195–1102

Chen C, Jia W, Liu S, Cao Y (2018) The enhancement of CuO modified V\(_2\)O\(_5\)-WO\(_3\)/TiO\(_2\) based SCR catalyst for Hg\(_0\) oxidation in simulated flue gas. Appl Surf Sci 436:1022–1029

Chen X, Hu X, Jiang N (2020) Kinetics and reaction mechanism of NO removal from simulated flue with peroxymonosulfate solution activated by high temperature and metal ions (Fe\(_{\text{3+}}\), Co\(_{\text{3+}}\) and Fe\(_{\text{3+}}\)). Chem Eng J 383:123139

Chi G, Shen B, Shen R, He C, Zhang X (2017) Simultaneous removal of NO and Hg\(_0\) over Ce-Cu modified V\(_2\)O\(_5\)/TiO\(_2\) based commercial SCR catalysts. J Hazard Mater 333:83–92

Ciminó S, Scala F (2016) Removal of elemental mercury by MnO\(_x\) catalysts supported on TiO\(_2\) or Al\(_2\)O\(_3\). Ind Eng Chem Res 55:5133–5138

Craciun R, Dulamita N (1997) Influence of La\(_2\)O\(_3\) promoter on the structure of MnO\(_x\)/SiO\(_2\) catalysts. Catal Lett 46:229–234
Liu Z, Liu D, Zhao B, Feng L, Ni M, Jin J (2020) Mercury removal based on adsorption and oxidation by fly ash: a review. Energy Fuel 34: 11840–11866

Liu Z, Liu D, Jin J, Feng L, Ni M, Zhao B, Wu X (2021) Impact of gas impurities on the Hg0 oxidation on high iron and calcium coal ash for chemical looping combustion. Environ Sci Pollut Res. https://doi.org/10.1007/s11356-020-11872-z

Lönn Y, Valyon J, Engelhardt J, Mizukami F (1996) Characterization and catalytic properties of sulfated ZrO2−TiO2 mixed oxides. J Catal 160:279–289

Lu P, Li C, Zeng G, He L, Peng D, Li HC, Zhai Y (2010) Low temperature selective catalytic reduction of NO by activated carbon fiber loading lanthanum oxide and ceria. Appl Catal B Environ 96:157–161

Ma J, Li C, Zhao L, Zhang J, Song J, Zeng G, Zhang X, Xie Y (2015a) Study on removal of elemental mercury from simulated flue gas over activated coke treated by acid. Appl Surf Sci 329:292–200

Ma Z, Wu X, Si Z, Weng D, Weng J, Weng T (2015b) Impacts of niobia loading on active sites and surface acidity in NbOx−CeO2−ZrO2 NH3−SCR catalysts. Appl Catal B Environ 179:380–394

Moreno-Tost R, Santamaria-González J, Maireles-Torres P, Rodriguez-Castellon E, Jiménez-López A (2002) Cobalt supported on zirconia doped mesoporous silica: a selective catalyst for reduction of NO with ammonia at low temperatures. Appl Catal B Environ 38:51–60

Niksa S, Fujiwara N (2005) A predictive mechanism for mercury oxidation on selective catalytic reduction catalysts under coal-derived flue gas. J Air Waste Manage Assoc 55:1866–1875

Qi G, Yang RT, Chang R (2004) MnOx−CeO2 mixed oxides prepared by co-precipitation for selective catalytic reduction of NO with NH3 at low temperatures. Appl Catal B Environ 51:93–96

Ren S, Guo F, Yang J, Yao L, Zhao Q, Kong M (2017) Selection of carbon materials and modification methods in low-temperature sintering flue gas denitrisation. Chem Eng Res Des 126:278–285

Rudyk BW, Blanchard PER, Cavell RG, Mar A (2011) Electronic structure of lanthanum copper oxycarboxigenides CuLaOCh(C=C=S, Se, Te) by X-ray photoelectron and absorption spectroscopy. J Solid State Chem 184:1649–1654

Shan Y, Wang Y, Chen H, Liu Y (2019) Removal of elemental mercury from flue gas using microwave/ultrasound-activated Ce−Fe magnetoporous carbon derived from biomass straw. Energy Fuel 33:8394–8302

Shen F, Liu J, Dong Y, Wu D (2018a) Mercury removal by biomass-derived porous carbon: experimental and theoretical insights into the effect of H2S. Chem Eng J 348:409–415

Shen B, Zhu S, Zhang X, Chi G, Patel D, Si M, Wu C (2018b) Simultaneous removal of NO and Hg0 using Fe and Co co-doped Mn−Ce−TiO2 catalysts. Fuel 224:241–249

Shi M, Luo G, Xu Y, Zou R, Zhu H, Hu J, Li X, Yao H (2019) Using H2S plasma to modify activated carbon for elemental mercury removal. Fuel 254:115549

Sun X, Sun L, Liu Y, Li K, Wang C, Song X, Ning P (2020) Research on reaction conditions and mechanism for simultaneous removal of NO and Hg0 over Cu−Fe modified activated carbon at low temperature. J Energy Inst 93:87–98

Tang B, Ge J, Wu C, Zhuo L, Niu J, Chen Z, Shi Z, Dong Y (2004) Sol–solvothermal synthesis and microwave evolution of La(OH)3 nanorods to La2O3 nanorods. Nanotechnology 15:1273–1276

Tao S, Li C, Fan X, Zeng G, Lu P, Zhang X, Wen Q, Zhao W, Luo D, Fan C (2012) Activated coke impregnated with cerium chloride used for elemental mercury removal from simulated flue gas. Chem Eng J 210:547–556

Tholkappiyar R, Vishista K (2014) Influence of lanthanum on the optomagnetic properties of zinc ferrite prepared by combustion method. Physica B 448:177–183

Veith GM, Nanda J, Delmaur LH, Dudney NJ (2012) Influence of lithium salts on the discharge chemistry of Li-air cells. J Phys Chem Lett 3:1242–1247

Wang H, Wang B, Sun Q, Xu W, Li J (2017) New insights into the promotional effects of Cu and Fe over V2O5−WO3/TiO2 NH3−SCR catalysts towards oxidation of Hg0. Catal Commun 100:169−172

Wang X, Kang Y, Cui D, Li J, Li D (2019a) Influence of lanthanum promoter on vanadium catalyst for sulfur dioxide oxidation. Catal Commun 118:39–45

Wang H, Wang B, Zhou J, Li G, Zhang D, Ma Z, Xiong R, Sun Q, Xu W (2019b) CuO modified vanadium-based SCR catalysts for Hg0 oxidation and NO reduction. J Environ Manag 239:17–22

Xie Y, Li C, Zhao L, Zhang J, Zeng G, Zhang X, Wang T, Tao S (2015) Experimental study on Hg0 removal from flue gas over columnar MnOx−CeO2/activated coke. Appl Surf Sci 333:59–67

Xu H, Qu Z, Zong C, Quan F, Mei J, Yan N (2016) Catalytic oxidation and adsorption of Hg0 over low-temperature NH3−SCR LaMnO3 perovskite oxide from flue gas. Appl Catal B Environ 186:30–40

Xu H, Jia J, Guo Y, Qu Z, Liao Y, Xie J, Shangguan W, Yan N (2018a) Design of 3D MnO2 carbon sphere composite for the catalytic oxidation and adsorption of elemental mercury. J Hazard Mater 342:69–76

Xu W, Zhang G, Chen H, Zhang G, Han Y, Chang Y, Gong P (2018b) Mn beta and Mn/ZSM-5 for the low-temperature selective catalytic reduction of NO with ammonia: effect of manganese precursors. Chin J Catal 39:118–127

Xu W, Pan J, Fan B, Liu Y (2019) Removal of gaseous elemental mercury using seaweed chars impregnated by NH4Cl and NH4Br. J Clean Prod 216:277–287

Yang J, Zhang M, Li H, Qu W, Zhao Y, Zhang J (2018a) Simultaneous NO reduction and Hg0 oxidation over La0.95Ce0.05Mn0.5 perovskite catalysts at low temperature. Ind Eng Chem Res 57:9374–9385

Yang Z, Li H, Liu X, Li P, Yang J, Lee P, Shih K (2018b) Promotional effect of CuO loading on the catalytic activity and SOx resistance of MnOx−TiO2 catalyst for simultaneous NO reduction and Hg0 oxidation. Fuel 227:79–88

Yang W, Adewuyi YG, Hussain A, Liu Y (2019a) Recent developments on gas−solid heterogeneous oxidation removal of elemental mercury from flue gas. Environ Chem Lett 17:19−47

Yang R, Mei C, Wu X, Yu X, Shl Z (2019b) Mn − Cu binary metal oxides with molecular-scale homogeneity for Hg0 removal from coal-fired flue gas. Ind Eng Chem Res 58:19292−19201

Zeng H, Jin F, Guo J (2004) Removal of elemental mercury from coal combustion flue gas by chloride-impregnated activated carbon. Fuel 83:143−146

Zhan W, Guo Y, Gong X, Guo Y, Wang Y, Lu G (2014) Current status and perspectives of rare earth catalytic materials and catalysis. Chin J Catal 35:1238−1250

Zhang L, Shi L, Huang L, Zhang J, Gao R, Zhang D (2014) Rational design of high-performance deNOx catalysts based on MnxCo3−xO4 nanocages derived from metal–organic frameworks. ACS Catal 4:1753−1763

Zhang G, Li Z, Zheng H, Zheng T, Lu Y, Wang Y (2015) Influence of the surface oxygenated groups of activated carbon on preparation of a nano Cu/AC catalyst and heterogeneous catalysis in the oxidative carbonylation of methanol. Appl Catal B Environ 179:95−95

Zhang X, Cui Y, Wang J, Tan B, Li C, Zhang H, He G (2017a) Simultaneous removal of Hg0 and NO from flue gas by Co0.3−xCoxO3−z/ Zr0.35Ti0.65O2 impregnated with MnOx. Chem Eng J 326:1210−1222

Zhang X, Shen B, Shen F, Zhang X, Si M, Yuan P (2017b) The behavior of the manganese-cerium loaded metal-organic framework in elemental mercury and NO removal from flue gas. Chem Eng J 326:551−560
Zhang J, Li C, Zhao L, Wang T, Li S, Zeng G (2017c) A sol-gel Ti-Al-Ce-nanoparticle catalyst for simultaneous removal of NO and Hg⁰ from simulated flue gas. Chem Eng J 313:1535–1547
Zhang X, Li Z, Wang J, Tan B, Cui Y, He G (2017d) Reaction mechanism for the influence of SO₂ on Hg⁰ adsorption and oxidation with Ce₀.₁-Zr-MnO₂. Fuel 203:308–315
Zhang S, Zhao Y, Yang J, Zhang J, Zheng C (2018) Fe-modified MnOₓ/TiO₂ as the SCR catalyst for simultaneous removal of NO and mercury from coal combustion flue gas. Chem Eng J 348:618–629
Zhang Z, Li R, Wang M, Li Y, Tong Y, Yang P, Zhu Y (2021) Two steps synthesis of CeTiOₓ oxides nanotube catalyst: enhanced activity, resistance of SO₂ and H₂O for low temperature NH₃-SCR of NOₓ. Appl Catal B Environ 282:119542
Zhao L, Li C, Li S, Wang Y, Zhang J, Wang T, Zeng G (2016) Simultaneous removal of elemental mercury and NO in simulated flue gas over V₂O₅/ZrO₂-CeO₂ catalyst. Appl Catal B Environ 198:420–430
Zhao S, Duan Y, Yao T, Liu M, Lu J, Tan H, Wang X, Wu L (2017) Study on the mercury emission and transformation in an ultra-low emission coal-fired power plant. Fuel 199:653–661
Zhao L, Li C, Du X, Zeng G, Gao L, Zhai Y, Wang T, Zhang J (2018) Effect of Co addition on the performance and structure of V/ZrCe catalyst for simultaneous removal of NO and Hg⁰ in simulated flue gas. Appl Surf Sci 437:390–399
Zhao Y, Yuan B, Zheng Z, Hao R (2019a) Removal of multi-pollutant from flue gas utilizing ammonium persulfate solution catalyzed by Fe/ZSM-5. J Hazard Mater 362:266–274
Zhao B, Yi H, Tang X, Li Q, Liu D, Gao F (2019b) Using CuO-MnOₓ/AC-H as catalyst for simultaneous removal of Hg⁰ and NO from coal-fired flue gas. J Hazard Mater 364:700–709
Zhao L, Li C, Li S, Du X, Zhang J, Huang Y (2019c) Simultaneous removal of Hg⁰ and NO in simulated flue gas on transition metal oxide M' (M' = Fe₂O₃, MnO₂, and WO₃) doping on V₂O₅/ZrO₂-CeO₂ catalysts. Appl Surf Sci 483:260–269
Zhu L, Zhu Y, Zhang S, Deng J, Zhong Q (2017) Effects of synthesis methods on catalytic activities of CoOₓ–TiO₂ for low-temperature NH₃-SCR of NO. J Environ Sci (China) 54:277–287
Zhu Y, Hou Y, Wang J, Guo Y, Huang Z, Han X (2019) Effect of SCR atmosphere on the removal of Hg⁰ by a V₂O₅-CeO₂/AC catalyst at low temperature. Environ Sci Technol 53:5521–5527

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