

Full Length Article

Simultaneous removal of Hg^0 and NO from simulated flue gas over columnar activated coke granules loaded with La_2O_3 - CeO_2 at low temperature



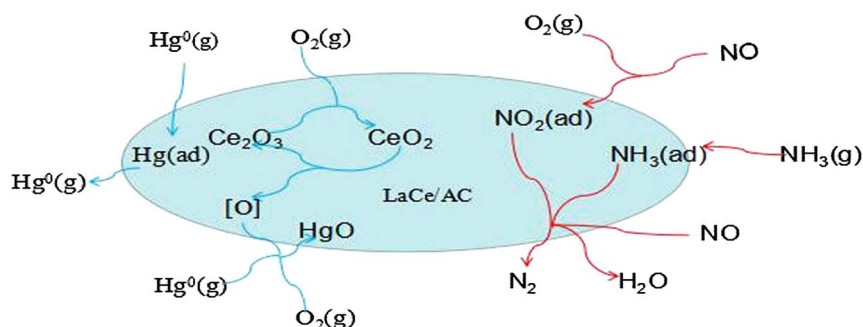
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GRAPHICAL ABSTRACT



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ABSTRACT

A series of industrial desulfuration activated cokes loaded La_2O_3 and CeO_2 (LaCe/AC) were employed for simultaneous NO and Hg^0 removal from simulated flue gas. The physicochemical characteristics of samples were characterized by BET, XRD, SEM, NH_3 -TPD, TGA and XPS. 25% LaCe/AC exhibited outstanding NO removal efficiency (91.3%) and superior Hg^0 removal efficiency (94.3%) at 180 °C. The effects of Hg^0 on SCR reaction and SCR atmosphere on Hg^0 oxidation were investigated. The results demonstrated that Hg^0 had negligible impact on NO removal efficiency while NO evidently promoted Hg^0 removal efficiency. Meanwhile, NH_3 had an adverse effect on Hg^0 removal efficiency. The slightly inhibitive effect derived from the existence of H_2O or SO_2 was also detected. The NO removal mainly followed the Langmuir-Hinshwood mechanism while the Hg^0 removal mechanism was attributed to the combination of physisorption and chemisorption and catalytic oxidation. Especially, the relative contributions of physisorption and chemisorption and catalytic oxidation were distinguished and calculated by designed mercury conversion and desorption tests, the results indicated chemisorption displayed the predominant role. In addition, the stability test of 27 h was carried out and eventually the sample maintained 84.5% Hg^0 removal efficiency and 89.5% NO removal efficiency, indicating its potentially large-scale industrial application at low temperatures in the foreseeable future.

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1. Introduction

Nitrogen oxides (NO_x) and elemental mercury emitted from coal-fired power plants have attracted extensive attentions due to their adverse effects on human health and the environment [1,2]. Consequently, more and more national or federal laws and regulations have been implemented to control NO_x and Hg^0 emissions [3,4]. Notably, some strict regulations aiming to achieve ultra low emission in coal-fired power plants are put forward in China, in which the emission concentrations of NO_x and Hg^0 are limited to 5 mg/m^3 and 0.002 mg/m^3 , respectively [5]. Therefore, enormous efforts contribute to various technologies for reducing NO_x and Hg^0 emissions from coal-fired power plants to meet these laws and regulations. Among them, selective catalytic reduction of NO_x with NH_3 ($\text{NH}_3\text{-SCR}$) has been the most widely employed technique while activated carbon injection for Hg removal has been the most successful and mature method [3,6]. The traditionally separate NO_x and Hg^0 control technology brought out many problems such as large footprint requirement, high equipment investment and large operation cost [7]. With the spread of SCR system in coal-fired power plant, how to make good use of SCR installation for simultaneous NO_x and Hg^0 removal has aroused wide interests. However, the conventional SCR catalyst was not effective enough for Hg^0 conversion in the flue gas burnt the low chlorine coal [8,9], in addition, to reduce reaction costs and avoid deactivation, the SCR system was desired to be loaded downstream of the particle control devices where the temperature was lower than 200°C beyond the active temperature range of $\text{V}_2\text{O}_5\text{-WO}_3(\text{MoO}_3)/\text{TiO}_2$ catalyst [5]. Therefore, low temperature SCR catalysts have been widely studied, many transition metal oxides such as MnO_x , CeO_2 , V_2O_5 and CoO_x demonstrate good performance and appear to be the potential alternative for NO removal [10–12]. Consequently, novel low temperature SCR catalyst with the ability of simultaneous removal NO_x and Hg^0 is of significantly practical interest.

It has been reported that the absorption method is one promising process for simultaneously removing SO_2 , NO_x and Hg^0 , in which activated coke (AC) is effective at low temperatures of $100\text{--}200^\circ\text{C}$ [6,13,14]. AC as a catalyst or an adsorbent owns many special aspects, such as physical and chemical stability, adsorption and catalytic properties, abundant structure characteristics and the tremendous potential for further modification [15]. It was easy to understand that virgin AC could not own constantly good NO_x removal efficiency and modified AC with active metal oxides could exhibit better performance [16]. In our previous works, virgin AC showed poor Hg^0 removal ability and modified AC with different acids and metal oxides or chlorides could promote Hg^0 removal and achieve the agelong excellent performance [17–20]. Consequently, it is of enormously practical interest to modify AC with active metal oxides for NO_x and Hg^0 simultaneous control at low temperatures. However, to the authors' knowledge, systematic researches with respect to modified AC with active metal oxides for NO_x and Hg^0 simultaneous removal are rarely reported.

Up to date, CeO_2 has been successfully widely used in a variety of heterogeneous reactions as an effective catalyst, a promoter, a support as well as active species for NO reduction and Hg^0 oxidation respectively because of its unique redox couple $\text{Ce}^{4+}/\text{Ce}^{3+}$, large oxygen storage capacity, nontoxic and high efficiency [2,8,16,21]. The redox shift between Ce^{4+} and Ce^{3+} may result in labile oxygen vacancies and bulk oxygen species with high mobility [20]. In addition, the combination of CeO_2 with other metal oxides including La_2O_3 could produce a synergistic effect, which was conducive to the promotion of NO reduction and Hg^0 oxidation [16,19,20,22]. In this work, La_2O_3 and CeO_2 with the precursors of lanthanum nitrate and cerium nitrate supported on cylindrical activated coke granular (LaCe/AC) by the impregnation method were investigated for NO and Hg^0 simultaneous removal.

2. Materials and methods

2.1. Materials preparation

The cylinder commercial desulfuration ACs possess an average diameter of 6 mm and length of 15 mm. Virgin ACs were washed with deionized water to remove possible impurities and then dried at 105°C overnight for further study. The detailed prepared steps of LaCe/AC were as follows. First, the 24 h water adsorption of AC was measured. Second, calculated lanthanum nitrate and cerium nitrate were dissolved in deionized water to form corresponding aqueous solution, and then the calculated amount of AC was impregnated in the solution for 24 h. Third, the mixture was dried in an electric blast oven at 105°C and then calcined in an electric tube furnace at 550°C for 4.5 under N_2 protection. Finally, the products were cooled to room temperature in N_2 . The mole ration of La/Ce was 1:4 in all LaCe/AC samples, which was demonstrated to be the optimal ration in our preliminary experiments. The mass percentage of LaCe mixed oxides of LaCe/AC samples were 5%, 10%, 15%, 20%, 25%, 30%, respectively, which was denoted as xLaCe/AC, where x represented the LaCe mass percentage. Meanwhile, the same mass percentages of La/AC and Ce/AC were prepared by the same method when needed.

2.2. Materials characterization

Brunauer–Emmett–Teller (BET) surface area, pore volume and average pore diameter of the samples were acquired by N_2 adsorption with an automatic Micromeritics ASAP2460 volumetric sorption analyzer (Micromeritics Instrument Corp., USA). Scanning electron microscopy (SEM) photographs were obtained by an Hitachi S-4800 analyzer (Hitachi Limited, Japan) to further analyze the morphology and surface structure of the samples. X-ray diffraction (XRD) measurements were employed to examine the dispersivity and crystallinity of active metal oxides on the AC, which was carried out on a Bruker D8-Advance X-ray diffraction device with CuK α radiation ($\lambda = 0.1543 \text{ nm}$) in the range of $10\text{--}80^\circ(2\theta)$. The thermogravimetric analysis (TGA) was conducted with a DTG-60 thermal analyzer (Shimadzu, Japan) to determine the speciation of mercury formed on spent LaCe/AC. The ammonia-temperature programmed desorption ($\text{NH}_3\text{-TPD}$) was performed using the TP-5080 automatic chemical adsorption instrument (Tianjin Xianquan, China). X-ray photoelectron spectroscopy (XPS) was carried out on a K-Alpha 1063 X-ray photoelectron spectrometer (Thermo Fisher Scientific, USA) with 72 W Al K α radiation.

2.3. Experimental setup and procedure

The schematic diagram of the experimental setup was shown in our previous works [17–20]. The normal simulated flue gas (SFG) with a total flow rate of 500 mL/min contained $80 \mu\text{g/m}^3 \text{ Hg}^0$, 6% O_2 and N_2 as the carrier gas and balanced gas. NO, NH_3 , SO_2 and H_2O (g) and other concentrations of O_2 and Hg^0 were provided when needed. Each individual flue gas component (N_2 , O_2 , NO, NH_3 and SO_2) from cylinder gases was accurately controlled by mass flow controllers, which was mixed with each other and Hg^0 or H_2O (g) in a gas mixing chamber. Calculated H_2O (g) was generated through a peristaltic pump which transferred liquid H_2O into Teflon tube wrapped with temperature-controlled heating band which made liquid H_2O be fully vaporized. Gaseous Hg^0 was generated by the elemental mercury permeation tube (VICI Metronics, USA) placed in a U-shaped quartz tube which was immersed in a water bath. During each test, 18 g sample corresponding to a space velocity of around 5000 h^{-1} was laid in the central part of a quartz tube with an inner diameter of 52 mm and a length of 950 mm, which was placed horizontally in an electric tube furnace for the reaction temperature regulation. The gas analyzer system contained an on-line mercury analyzer (Lumex RA-915 M, Russia, detection limit = 2 ng/m^3) with a data acquisition computer and a flue gas

analyzer (MGA5, Germany).

Before the activity test, the blank test of the system was conducted and the effect of the pipes and the reactor on NO and Hg⁰ removal was proved to be negligible. The mercury conversion test and designed desorption test were conducted to distinguish the possible relative contributions of catalytic oxidation and physisorption and chemisorption. In the mercury conversion system, gas released from the reactor was firstly divided into two branches, one went to 10% KCl aqueous solution to remove Hg²⁺ for Hg⁰ measurement, and the other went to 10% SnCl₂ aqueous solution to reduce Hg²⁺ to Hg⁰ for total elemental mercury (Hg_{out}⁰) measurement. Then they went through 10% NaOH aqueous solution to remove acidic gas in the front of the mercury analyzer. Thence, the oxidation efficiency of Hg⁰ (E_{oxi}) could be calculated by the Eq. (1). It is assumed that physisorption is reversible while chemisorption is irreversible under the conditions (up to 180 °C), thus the relative contributions of physisorption and chemisorption could be determined by the reversibility of Hg uptake [23]. After the activity test and the mercury conversion test proceeded several hours, the desorption test was conducted when pure N₂ of 500 mL/min was introduced and the outlet Hg⁰ concentration was detected until the detection limit was exceeded. The definition of NO removal efficiency (E_{NO}) and Hg⁰ removal efficiency (E_{Hg0}) were given below by Eqs. (2) and (3), respectively. Thence, as shown in Eq. (4), E_{Hg0} was loosely thought that consisted of E_{oxi}, E_{phy} and E_{che} which represented the mean Hg⁰ removal efficiency derived from catalytic oxidation, physisorption and chemisorption, respectively, in which E_{phy} and E_{che} could be obtained by the approximate integral.

$$E_{\text{oxi}} = \frac{Hg_{\text{out}}^{\text{0T}} - Hg_{\text{out}}^{\text{0}}}{Hg_{\text{in}}^{\text{0}}} \times 100\% \quad (1)$$

$$E_{\text{NO}} = \frac{NO_{\text{in}} - NO_{\text{out}}}{NO_{\text{in}}} \times 100\% \quad (2)$$

$$E_{\text{Hg}^0} = \frac{Hg_{\text{in}}^{\text{0}} - Hg_{\text{out}}^{\text{0}}}{Hg_{\text{in}}^{\text{0}}} \times 100\% \quad (3)$$

$$E_{\text{Hg}^0} = E_{\text{phy}} + E_{\text{che}} + E_{\text{oxi}} \quad (4)$$

where NO_{in} and NO_{out} are the NO concentration of the inlet and outlet of the reactor, respectively. Hg_{in}⁰ and Hg_{out}⁰ are the Hg⁰ concentration of the inlet and outlet of the reactor, respectively.

3. Results and discussion

3.1. Materials characterization

3.1.1. BET analysis

The physical properties including BET surface area, pore volume and average pore diameter of virgin AC and LaCe/AC are shown in Table 1, and the pore distribution curves of these samples are shown in Fig. 1. Based on the figure, the pore diameters of these samples were changed with the different loading value. It can be clearly seen that LaCe/AC possessed higher total pore volume and bigger average pore

Table 1
The specific surface area, pore volume and average pore diameter of the samples.

Samples	BET surface area (m ² /g)	Total pore volume (cm ³ /g)	Average pore diameter (nm)
Virgin AC	234.73	0.120	2.055
5%LaCe/AC	261.83	0.140	2.136
10%LaCe/AC	260.88	0.150	2.306
15%LaCe/AC	248.68	0.141	2.276
20%LaCe/AC	239.03	0.147	2.472
25% LaCe/AC	225.15	0.154	2.728
30%LaCe/AC	216.71	0.136	2.507

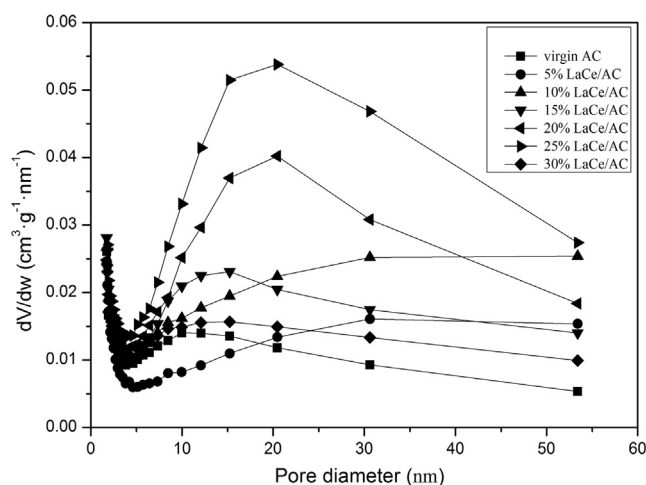


Fig. 1. The pore size distribution curves of virgin AC and LaCe/AC.

diameter than that of virgin AC to a certain extent. In particular, 25% LaCe/AC owned the largest pore volume and the biggest average pore diameter, which might be one reason for that it exhibited the outstanding performance, indicating adsorption played an important role in Hg⁰ and NO removal. Interestingly, compared with virgin AC, LaCe/AC with low loading value showed bigger BET surface area but LaCe/AC with high loading value owned lower BET surface area. And the BET surface area of LaCe/AC decreased with the increase of the loading value. The similar trend was also found in other reports [19,24,25]. Although some old pores might be covered in the impregnation process, more new pores could generate during the decomposition of active components in the calcination process as well as the reaction between active components and AC in the loading process, which were responsible for that LaCe/AC exhibited higher pore volume and bigger average pore diameter than that of virgin AC. That might be also the reason for that LaCe/AC with low loading (5–20%) exhibited bigger BET. It was easy to understand that the agglomerated metal oxides on the external and the internal surfaces of the samples increased with the increase of the loading value, causing the destruction of pore walls and the blockage of internal porosity [26]. The agglomerated effect increased with the increase of loading value, which might account for that the BET surface area of LaCe/AC decreased with the increase of the loading value.

3.1.2. XRD analysis

Fig. 2 displayed the XRD patterns of virgin AC and LaCe/AC samples. As to virgin AC, two strong diffraction peaks at 26.60° and 44.46° attributed to AC were detected [19]. However, the intensity of the two peaks evidently decreased with the increase of the loading value of LaCe mixed oxides. Nevertheless, when the loading value of LaCe mixed oxides exceeded 15%, the peaks belonged to AC vanished, indicating that La₂O₃ and CeO₂ interacted with AC intensely in these samples. For 25%LaCe/AC and 30%LaCe/AC, three peaks attributed to CeO₂ were detected at 2θ = 27.88°, 46.98° and 56.14°, respectively [17]. In contrast, no obvious peak belonged to CeO₂ was observed in 10%LaCe/AC, the monolayer dispersion theory might account for that, in which the metal oxide whether in a crystalline phase or not depended on the oxide content and its threshold value [27]. Interestingly, there was no apparent peak attributed to lanthanum oxides discovered among all samples while lanthanum assuredly existed in the LaCe/AC samples despite its low content, suggesting that lanthanum oxide might exist as an amorphous phase or highly dispersed on the surface of AC [28]. The similar phenomenon was also observed in other XRD results, for example, the peaks attributed to manganese oxides didn't appear in the XRD results of Mn-Ce/AC and Mn-Ce/Ti catalyst [19,29].

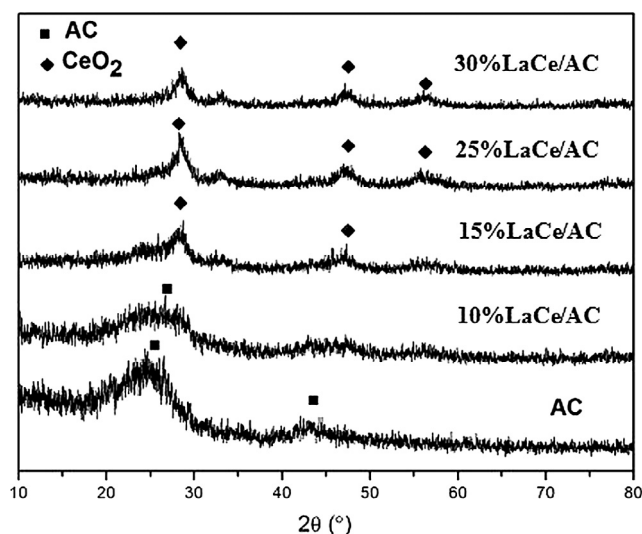


Fig. 2. XRD patterns of virgin AC and LaCe/AC.

3.1.3. SEM analysis

The results of SEM photographs of virgin AC and LaCe/AC were shown in Fig. 3. It was clearly seen that the surface characteristics of AC were changed by loading LaCe mixed oxides, in which the dark zone represented carbon enriched area while the light zone indicated the existence of metal oxides. It should be noted that metal oxides of 5% LaCe/AC had the best dispersity among the samples and only a few small agglomerates were observed. But the surface of LaCe/AC with low loading value existed some bare places, suggesting the active metal oxide failed to cover their surfaces adequately and failed to supply enough active centers which wasn't favorable for their catalytic ability. More and more metal oxide agglomerates formed on the surface of AC with further increase of the loading value, in addition, the agglomerates became bigger and the bare place disappeared gradually, which were in agreement with the results of BET.

3.1.4. NH_3 -TPD analysis

NH_3 -TPD was performed to estimate the number of surface acidities of virgin AC, Ce/AC, La/AC and LaCe/AC, and the curves were shown in Fig. 4. There were several peaks because of the NH_3 ammonia species of various thermal stability, in which the peaks at 166.42–183.37 °C were ascribed to the desorbed NH_3 from the weak acid sites; the peaks at 225.8–241.68 °C were assigned to the desorbed coordinated NH_3 bound to Brønsted sites; the peaks at 295.72–308.12 °C were attributed to the desorbed coordinated NH_3 bound to Lewis acid sites [3,30,31]. Compared with virgin AC, the addition of metal oxides broadened the desorption temperature range, and the desorption peak areas representing the number of acid amount followed a ascending order: virgin AC < La/AC < Ce/AC < LaCe/AC. Clearly, the coexistence of La and Ce created the biggest desorption temperature range and desorption peaks areas, indicating LaCe/AC had the most acid amount and possessed the most Lewis acid sites and Brønsted sites. It was well known that both Lewis acid sites and Brønsted sites could contribute to NH_3 -SCR reactions and the number of them could be considered as one most important criteria for apperceiving the catalytic ability of NH_3 -SCR systems [30,31]. Thus, we had reason to believe that LaCe/AC had the best catalytic performance among these samples.

3.1.5. TGA analysis

Fig. 5 illustrated the TGA results of fresh and spent 25% LaCe/AC. Compared with the fresh sample, the spent sample demonstrated two obviously excess weight loss range at 50–150 °C and 350–550 °C. The obviously excess weight loss at 50–150 °C could be ascribed to elemental mercury from physisorption, meanwhile, the initial excess

weight loss below 100 °C was attributed to the combination of the loss of desorbed water and the loss of elemental mercury from physisorption [19,23,32]. The other obviously excess weight loss at 350–550 °C was mainly attributed to the mercury species from chemisorption and catalytic oxidation which might exist as a mixture of HgO , HgSO_4 or other mercury species because M. Antonia Lopez-Anton [33] reported the thermal decomposition profile of a mixture of HgCl_2 , HgS , HgSO_4 , and HgO (2:2:1:1) mainly occurred at the temperature range of 400–600 °C, in which the thermal decomposition of HgO and HgSO_4 often took place in the temperature intervals of 430–560 and 500–600 °C, respectively [33,34]. This appearance was in accordance with Zhao et al. [35]. The results verified that the removal mechanism of Hg^0 was ascribed to the combined contribution of physisorption and chemisorption and catalytic oxidation.

3.1.6. XPS analysis

XPS measurements were used to analyze the chemical states and the surface interaction of elements on the surface of virgin AC, fresh Ce/AC, fresh and used LaCe/AC. Fig. 6 displayed the spectra of O 1s, C 1s, Ce 3d and La 3d. The XPS spectra of O 1s were shown in Fig. 6a, the peaks at 529.3–529.6 eV were attributed to lattice oxygen (O_α), the peaks at 531.5–531.8 eV were assigned to chemisorbed oxygen or/and weakly bonded oxygen (O_β), and the peak at 533.3 eV was ascribed to hydroxyl groups or/and adsorbed water species (O_γ) [3,19,36]. The ratio of $\text{O}_\beta/\text{O}_\gamma$ ($\text{O}_\gamma = \text{O}_\alpha + \text{O}_\beta + \text{O}_\gamma$ (when needed)) of fresh LaCe/AC increased evidently compared to that of fresh Ce/AC. The reason for that could be explained by that the introduction of La resulted in the increase of Ce^{3+} related chemisorbed and/or weakly bonded oxygen, which were the most active oxygen in oxidation reactions [16,37]. Besides, the ratio of $\text{O}_\beta/\text{O}_\gamma$ of LaCe/AC decreased from 61.3% to 56.1% after the reaction, while the ratio of $\text{O}_\alpha/\text{O}_\gamma$ was almost no changed. This clearly indicated some O_β was consumed in the reaction processes, suggesting that O_β participated in the reactions.

As shown in Fig. 6b, the C 1s spectra can be assigned to five component peaks representing graphitic carbon (denoted as C–C, 284.6–285.1 eV), carbon present in ether or alcohol groups (denoted as C–O, 286.3–287.0 eV), carbonyl groups (denoted as C=O, 287.5–288.1 eV) and ester or carboxyl groups (denoted as O=C–O) [38]. After virgin AC loaded metal oxides, all peaks shifted slightly to higher binding energy. In addition, the total oxygen-contained groups reduced and specially the ratio of C–O decreased from 19.46% to 9.74%, whereas the ratio of O=C–O increased from 4.22% to 10.86%. This former might be attributed to the desorption of surface oxygen in the process of high temperature calcination under N_2 atmosphere, and the later could be ascribed to the doping nitrate precursors [39]. In the used sample, the total oxygen-contained groups raised, in which the ratio of C–O and C=O increased from 9.74% and 5.69% to 19.54% and 10.62%, respectively. That phenomena could be explained by the addition of O_2 , thus resulting in the increase of oxygen-contained groups which could oxidize Hg^0 to HgO [17–18]. On the contrary, the ratio of O=C–O decreased from 10.86% to 6.43%.

The XPS spectra of Ce 3d of fresh Ce/AC, fresh and used LaCe/AC were displayed in Fig. 6c. The curves of Ce 3d spectra were comprised of four pairs of spin-orbit doublets, the peaks labeled v_1 , v_2 and v_3 represented Ce^{4+} 3d $_{5/2}$, whereas those peaks labeled u_1 , u_2 and u_3 arose from Ce^{4+} 3d $_{3/2}$. The other two peaks labeled v_1 and u_1 were attributed to Ce^{3+} species. The u/v , u_2/v_2 and u_3/v_3 represented Ce^{4+} and u_1/v_1 corresponded to Ce^{3+} [19]. It was noteworthy that Ce^{4+} and Ce^{3+} species coexisted, and Ce^{4+} was the primary valence among these samples. However, the ratio of $\text{Ce}^{3+}/\text{Ce}^{4+}$ of fresh LaCe/AC was 46%, which was much higher than that of fresh Ce/AC (29.5%), manifesting the introduction of La facilitated the reduction of cerium oxide to produce Ce^{3+} . The presence of Ce^{3+} was confirmed to create a charge imbalance, more unsaturated chemical bonds and oxygen vacancies on the catalyst surface, leading to more surface active oxygen species formed, which were beneficial for the reduction of NO and the

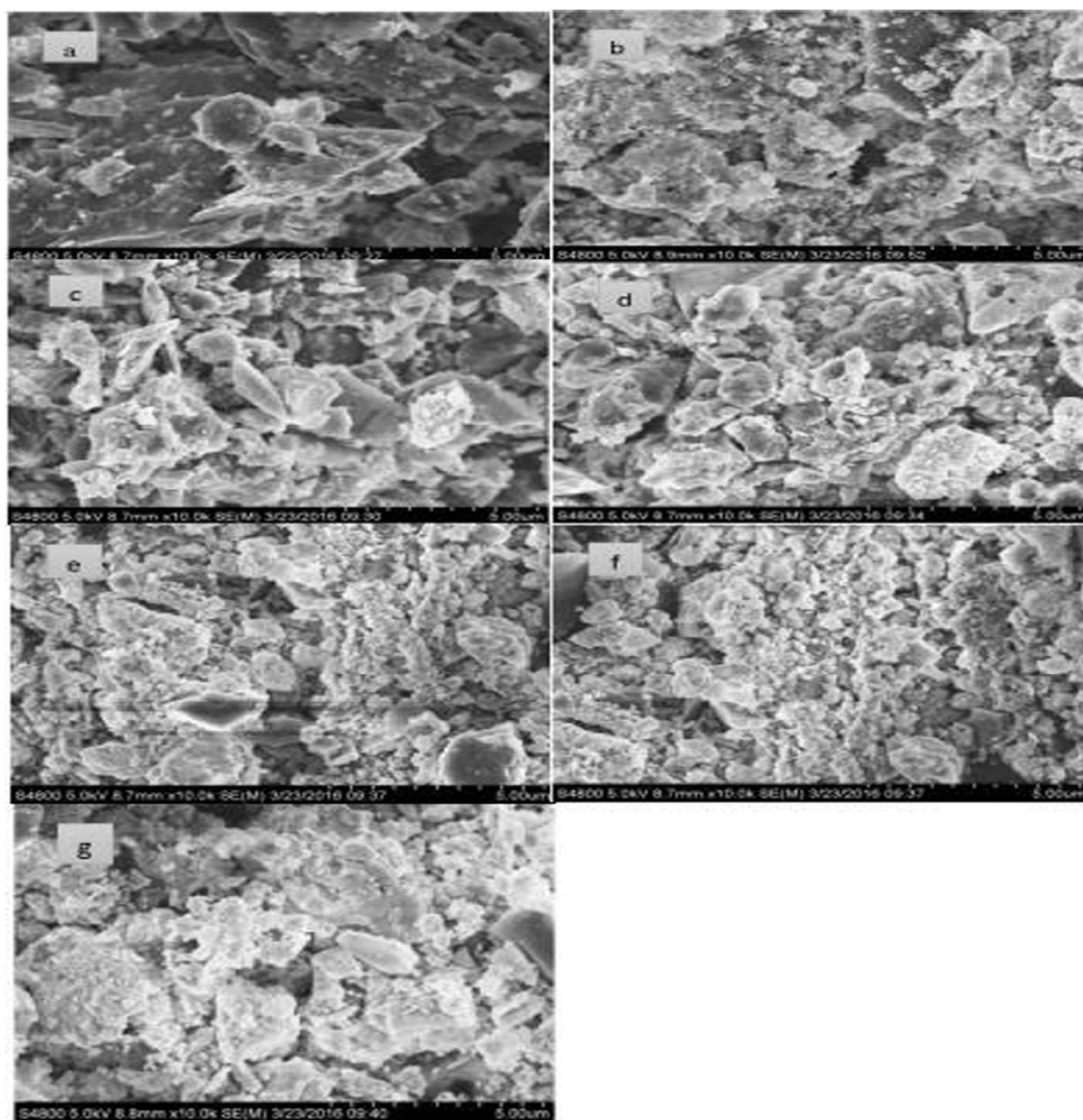


Fig. 3. SEM images of virgin AC and LaCe/AC: (a) Virgin AC, (b) 5%LaCe/AC, (c) 10%LaCe/AC, (d) 15%LaCe/AC, (e) 20%LaCe/AC, (f) 25%LaCe/AC, (g) 30%LaCe/AC. 5000 multi-pulter.

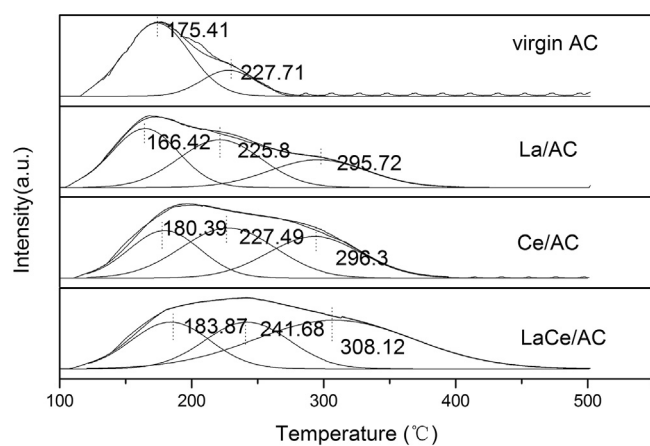


Fig. 4. NH_3 -TPD curves of virgin AC, La/AC, Ce/AC and LaCe/AC.

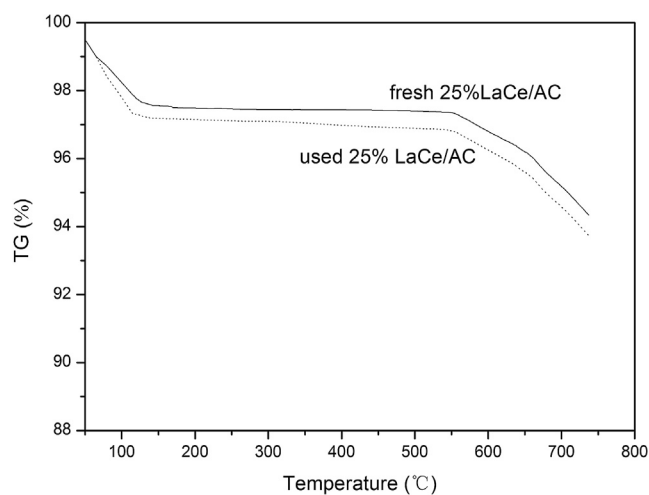


Fig. 5. TGAs of the fresh and spent 25%LaCe/AC.

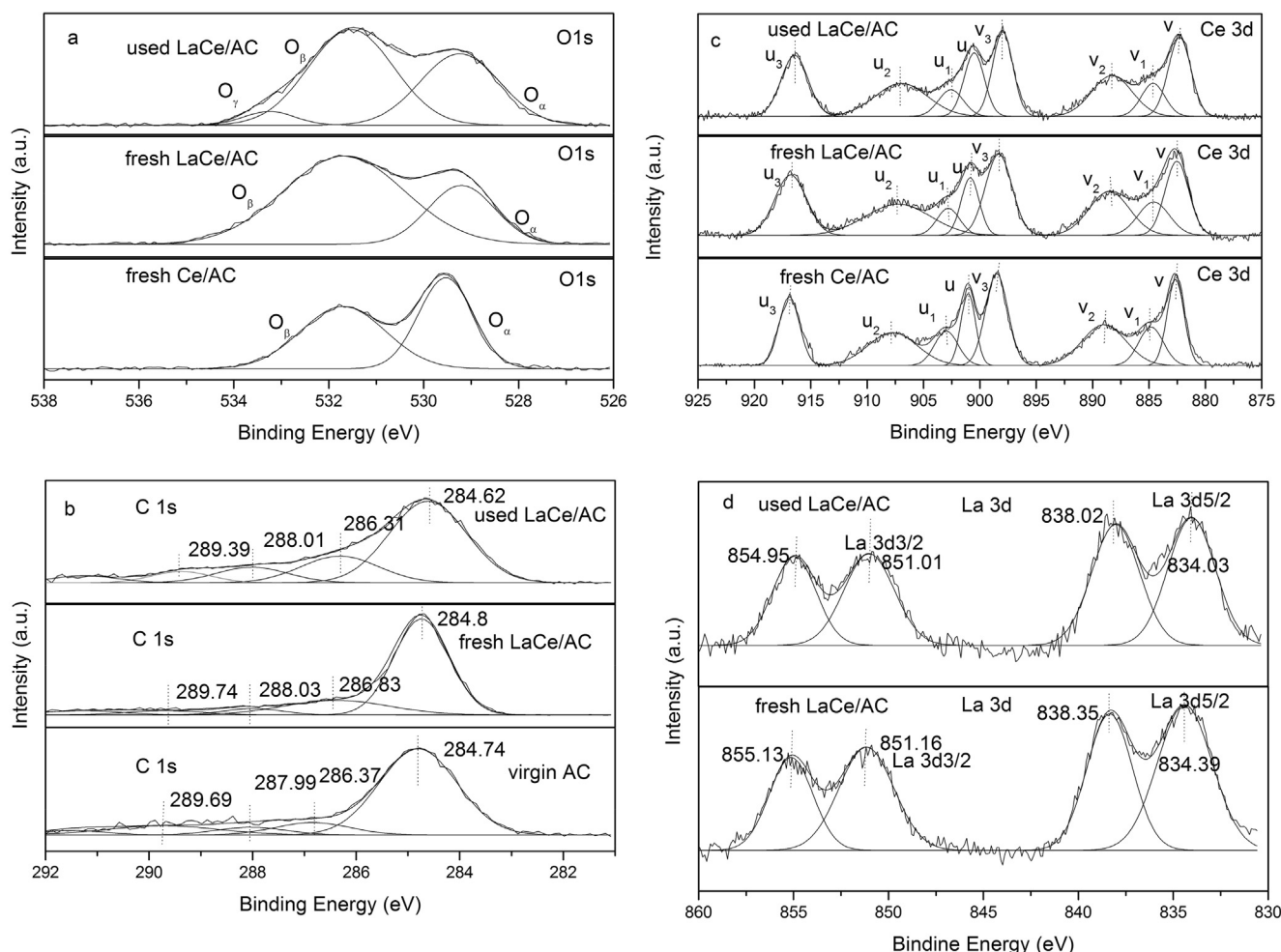


Fig. 6. XPS spectra of virgin AC, fresh Ce/AC, fresh and used LaCe/AC over the spectral regions of (a) O 1s, (b) C 1s, (c) Ce 3d and (d) La 3d.

oxidation of Hg [3,40]. In addition, the ratio of Ce^{3+}/Ce^{4+} decreased from 46% to 34.9% after the reactions, indicating that Ce^{3+} participated in the catalytic processes and Ce species shifted between Ce^{4+} and Ce^{3+} with simultaneously storing and releasing oxygen.

The XPS spectra of La 3d of fresh and used LaCe/AC are shown in Fig. 6d. They both exhibit a doublet splitting, one is attributed to the spin-orbit interaction and the other one is due to the electron transfer from the oxygen valence to the empty La 4f orbit [41]. The peaks at binding energy values of around 834 eV and 851 eV are for La 3d_{5/2} and La 3d_{3/2}, while the satellite peaks at binding energy values of around 838 eV and 855 eV are for La 3d_{5/2} and La 3d_{3/2}. The binding energy values are in agreement with that of La in perovskites and they are higher than that of standard La₂O₃ (for example, the binding energy value of La 3d_{5/2} of La₂O₃ is 831.9 eV) [42,43], combined with the above XPS analysis, suggesting that lanthanum-cerium complex oxide is formed at the sample.

3.2. Activity and stability test

3.2.1. Effect of the loading value

Fig. 7 showed the effect of the loading value on E_{NO} and E_{Hg^0} . Compared to virgin AC, the modified AC promoted NO and Hg⁰ removal remarkably, which suggested the loading of La₂O₃ and CeO₂ was propitious for NO and Hg⁰ removal. However, E_{NO} and E_{Hg^0} had different trends with the increase of the loading value. E_{NO} kept a sustainable growth with the increase of the loading value, which displayed a rapid growth from 0 to 20% and exhibited a slow growth from 25% to 30%, and 30%LaCe/AC yielded the best E_{NO} of 90.3%. While E_{Hg^0}

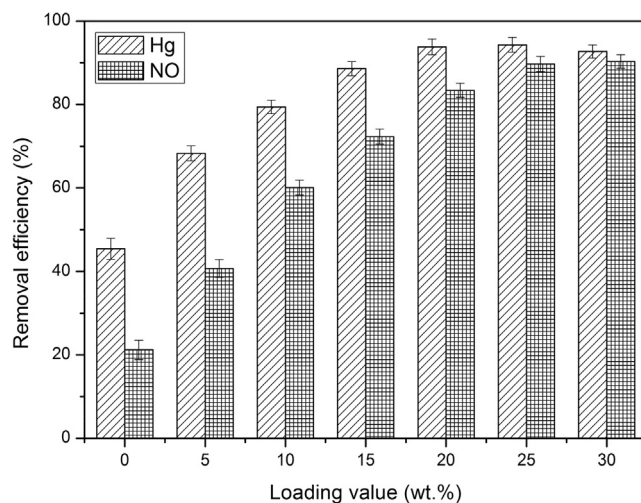


Fig. 7. Effect of the loading value on Hg⁰ and NO removal efficiency. Reaction conditions: T = 180 °C, 6% O₂, 80 μg/m³ Hg⁰, 800 ppm NO, 800 ppm NH₃, N₂ as balance.

increased with the increase of the loading value when it was below 25% and then decreased as the loading value was further increased to 30%, in which 25% LaCe/AC yielded the highest E_{Hg^0} of 94.3%. From the above phenomena and aforementioned results of BET, it was obvious that E_{NO} and E_{Hg^0} were not invariably consistent with the total pore volume and BET surface areas, indicating that physisorption played a certain role but not the dominant role in NO and Hg⁰ removal. In the

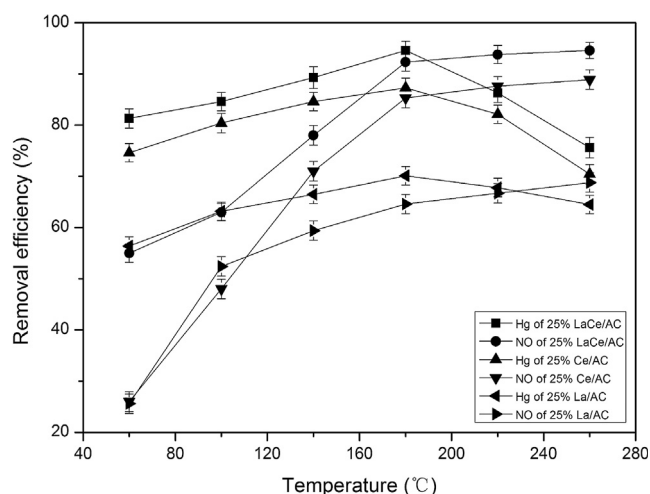


Fig. 8. Effect of the reaction temperature on Hg^0 and NO removal efficiency of 25%LaCe/AC, 25%La/AC and 25%Ce/AC. Reaction conditions: $T = 60\text{--}260^\circ\text{C}$, 6% O_2 , $80\text{ }\mu\text{g}/\text{m}^3$ Hg^0 , 800 ppm NO, 800 ppm NH_3 , N_2 as balance.

subsequent study, 25% LaCe/AC was chosen as the optimal LaCe/AC sample due to comprehensive consideration among all the samples.

3.2.2. Effect of reaction temperature

To investigate the effects of active components and reaction temperature, systematic tests on NO and Hg^0 removal over 25%LaCe/AC, 25%La/AC and 25% Ce/AC were carried out and the results were shown in Fig. 8. It could be clearly seen that both active components and reaction temperature played an important role on both NO and Hg^0 performance. Interestingly, the NO and Hg^0 performance of 25% LaCe/AC exhibited better than that of 25% Ce/AC and 25% La/AC at different temperatures. Specially, 25%LaCe/AC showed good low temperature performance on both NO and Hg removal, and obtained much improvement compared with 25%La/AC and 25% Ce/AC. This phenomenon might be caused by the synergistic effect between La and Ce, and this similar appearance was observed in other reports [19,20]. The effect of reaction temperature over different active components demonstrated the similar trend. With increasing reaction temperature, E_{NO} increased continuously and eventually reached the maximum. However, E_{Hg^0} showed some different tendency, which first achieved the best E_{Hg^0} at about 180°C and then declined with further increasing reaction temperature. These results indicated that although the elevated temperature benefited the NO removal, it was unfavorable for the Hg^0 removal when the temperature exceeded 180°C . With respect to 25% LaCe/AC, E_{Hg^0} augmented from 81.3% to 94.6% when the reaction temperature increased from 60°C to 180°C . The analysis of TGA indicated that the removal of Hg^0 was attributed to the combined contribution of physisorption and chemisorption and catalytic oxidation. In which catalytic oxidation would boost due to the increase of the catering activation energy with the increase of reaction temperature [17,18], and chemisorption would yet enhance with the increase of the reaction temperature due to the formation of more and more chemical bonds [44]. Thus the decline of E_{Hg^0} after 180°C could be explained by that the Hg^0 removal from physisorption was inhibited with the increase of the reaction temperature [45]. In addition, E_{NO} reached about 91% at 180°C and the growth would be slower with further increase reaction temperature. These phenomena were consistent with our previous works [19,22]. It was noteworthy that 25%LaCe/AC exhibited 91.3% NO removal efficiency and 94.3% Hg^0 removal efficiency at 180°C , and the performance shown better than many reported catalysts for simultaneous NO and Hg^0 removal [2,3]. For example, Zhao et al. [3] recently reported that their best V/ZrCe_{0.6} catalyst yielded 87.3% SCR activity and 77.6% Hg^0 oxidation efficiency.

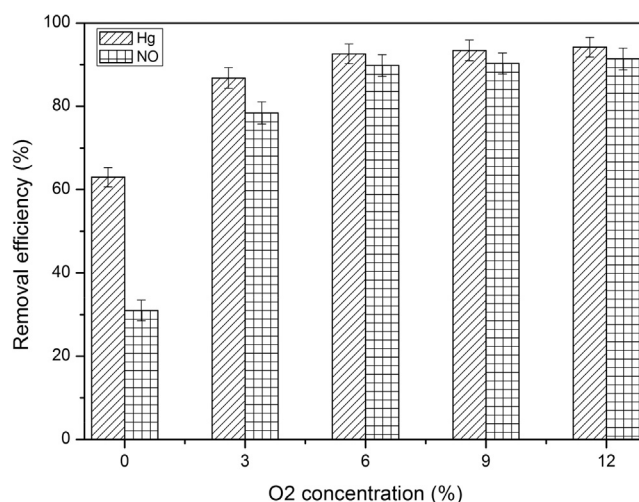


Fig. 9. Effect of the concentration of O_2 on simultaneous NO and Hg^0 removal over 25% LaCe/AC. Reaction conditions: $T = 180^\circ\text{C}$, 0–12% O_2 , $80\text{ }\mu\text{g}/\text{m}^3$ Hg^0 , 800 ppm NO, 800 ppm NH_3 , N_2 as balance.

3.2.3. Effect of the concentration of O_2

Fig. 9 showed the changes in E_{NO} and E_{Hg^0} with respect to O_2 concentration, it could be seen that an increased O_2 concentration enhanced E_{NO} and E_{Hg^0} . In the absence of O_2 , only about E_{NO} of 31% and E_{Hg^0} of 63% were achieved, but in the presence of 6% O_2 , the NO and Hg^0 removal efficiencies were raised to 89.8% and 92.6%, respectively. The relative high E_{Hg^0} yielded under reaction conditions without O_2 because of the relative strong adsorption capacity of AC and abundance existing chemisorbed oxygen and lattice oxygen on 25% LaCe/AC [19]. The chemisorbed oxygen and lattice oxygen would be consumed in the NO and Hg^0 removal reactions, which could be replenished due to the gaseous O_2 and the redox shift between Ce^{3+} and Ce^{4+} [2,3,46], and the replenished ratio varied with the O_2 concentration of the environment to some degree, thus O_2 displaying a promotional effect on NO and Hg^0 removal. However, it could be noted that E_{NO} and E_{Hg^0} remained almost the same when the concentration of O_2 increased to 9% and even to 12%, indicating that, for 25% LaCe/AC, 6% O_2 was sufficient to replenish the consumed oxygen.

3.2.4. Effect of the concentration of Hg^0

Hg^0 was one of the key components in the SFG, which might affect

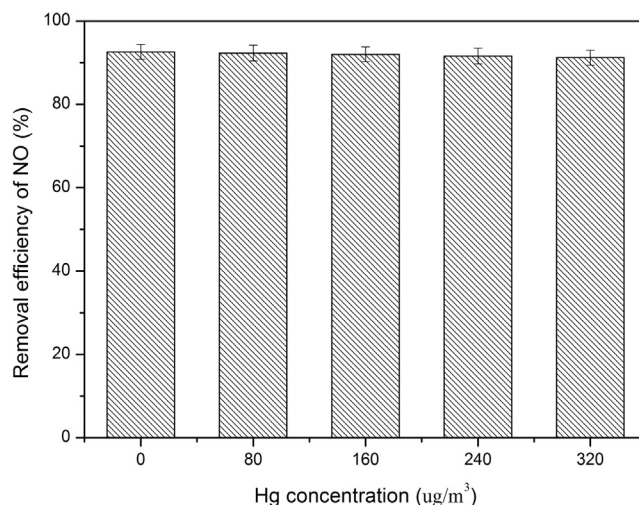


Fig. 10. Effect of the concentration of Hg^0 on NO removal over 25% LaCe/AC. Reaction conditions: $T = 180^\circ\text{C}$, 6% O_2 , 0–320 $\mu\text{g}/\text{m}^3$ Hg^0 , 800 ppm NO, 800 ppm NH_3 , N_2 as balance.

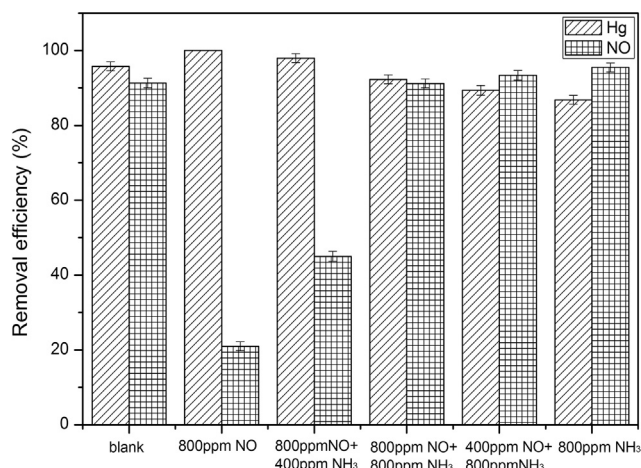


Fig. 11. Effect of NH₃ and NO on simultaneous NO and Hg⁰ removal over 25%LaCe/AC. Reaction conditions: T = 180 °C, 6% O₂, 80 μg/m³ Hg⁰, 0–800 ppm NO, 0–800 ppm NH₃, N₂ as balance.

the NO removal. Thus, the effect of the concentration of Hg⁰ on NO removal over 25% LaCe/AC was performed. As shown in Fig. 10, when 80 μg/m³ Hg⁰ was added into the Hg-free flue gas, E_{NO} didn't display any change. Nevertheless, E_{NO} decreased slightly with further increase of the concentration of Hg⁰, which indicating that Hg⁰ had slightly prohibitive effect on NO removal. The phenomenon might be probably explained by two reasons. On the hand, Hg⁰ might compete with NO for adsorption or catalytic sites in spite of its relative lower concentration compared to that of NO. On the other hand, the existing Hg⁰ might be oxidized to HgO accumulated on the surface of the sample resulting in slightly affecting the NO removal [2,47], in which HgO was confirmed by TGA and the mercury conversion test. It was worth mentioning that the actual Hg⁰ concentration was much lower than the tested concentrations and the SCR process for NO removal wouldn't be affected significantly by Hg⁰ in the real application.

3.2.5. Effect of NH₃ and NO

As shown in Fig. 11, the individual or joint effect of NH₃ and NO on simultaneous NO and Hg⁰ removal over 25%LaCe/AC was investigated. The blank test of Hg⁰ removal was carried out when the flue gas was normal SFG while the blank test of NO removal was performed when there was no Hg⁰ in the SFG. It was easy to find that E_{Hg0} of the blank test exhibited better than that in SCR conditions, suggesting that the co-presence of NH₃ and NO had an obviously inhibitory effect on Hg⁰ removal, which was in accordance with the previous works [2,3,8]. In the simultaneous NO and Hg⁰ removal, SCR reaction played the dominant role under high concentrations of NH₃ and NO [48]. However, E_{NO} of SCR conditions didn't show any change comparing with that of the blank test, which validated again that Hg⁰ had slightly prohibitive effect on NO removal. The individual NO displayed very markedly stimulative effect on Hg⁰ removal and this appearance was also observed when excess NO existed in the flue gas. The excess NO could react with O₂ producing NO₂, which was reported to be active for Hg⁰ oxidation [49]. The individual NH₃ displayed some inhibitory effect on Hg⁰ removal and this phenomenon yet existed in excess NH₃ conditions. Which might be attributed to that NH₃ could rapidly adsorb and react on the catalyst surface generating some adsorbed species which could consume surface active oxygen and occupy the surface active sites, inhibiting Hg⁰ oxidation and resulting in the decline of E_{Hg0} [50,51].

3.2.6. Effect of SO₂ and H₂O

The effects of SO₂ and H₂O on NO and Hg⁰ removal over 25%LaCe/AC were shown in Fig. 12. It could be seen that SO₂ had negative influence on both NO and Hg⁰ removal, and the inhibitory effect

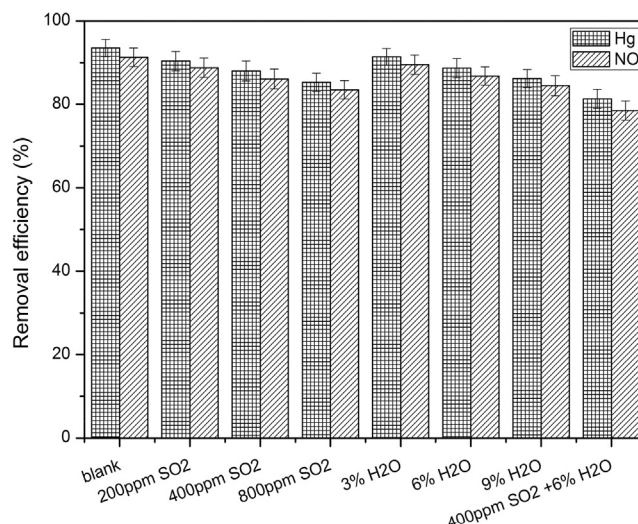


Fig. 12. Effect of SO₂ and H₂O on simultaneous NO and Hg⁰ removal over 25%LaCe/AC. Reaction conditions: T = 180 °C, 6% O₂, 80 μg/m³ Hg⁰, 800 ppm NO, 800 ppm NH₃, 0–800 ppm SO₂, 0–9% H₂O, N₂ as balance.

increased with the increase of the concentration of SO₂. When the concentration of SO₂ changed from 0 to 800 ppm, E_{NO} decreased from 91.3% to 83.5%, similarly, E_{Hg0} decreased to 85.3% from the initial level of 93.5%. Two possible reasons were responsible for this results, on one hand, SO₂ could compete with NO, NH₃ and Hg⁰ for active sites [52]. Besides, the adsorbed SO₂ reacted with the surface oxygen of the sample, thus hindering the reaction between Hg⁰ and surface oxygen, which might play a key role in the inhibitive effect for Hg⁰ removal [19]. On the other hand, the possible formation of ammonium sulfates in the presence of NH₃ and SO₂, which might block the activated centers and destroy the sample's porous structure due to its sediment.

Fig. 12 also demonstrated that both NO and Hg⁰ removal were inhibited by H₂O(g), and the inhibitory effect became more worse with the increase of the content of H₂O(g). E_{NO} fell by 6.8% from 91.3% to 84.5% while E_{Hg0} fell by 7.3% from 93.5% to 86.2% when 9% H₂O (g) was added into the dry SFG. This results indicated that 25%LaCe/AC exhibited good H₂O resistance, which might be ascribed to the hydrophobic property of the carbon material supports [53,54]. The decline of E_{NO} and E_{Hg0} could be explained by the competitive adsorption of H₂O (g) with other compositions in consequence of failing to easily reach the adsorption or catalytic oxidation sites [55,56], thus resulting in the decrease of E_{NO} and E_{Hg0}. Furthermore, the coinstantaneous addition of 400 ppm SO₂ and 6% H₂O gave rise to a giant drop of E_{NO} and E_{Hg0} derived from the combined influence of SO₂ and H₂O. The synergistic competition effects and the possible formation of ammonium sulfates (bisulfates) or other sulfates because of the coexistence of SO₂ and H₂O and other gas components were responsible for the giant drop of E_{NO} and E_{Hg0}.

3.2.7. Stability test

The stability of a given catalyst or sorbent is an important factor for its industrial application. The stability tests of virgin AC and 25% LaCe/AC under clean conditions, and 25% LaCe/AC under the conditions with 200 ppm SO₂ and 3% H₂O were shown in Fig. 13. Both E_{NO} and E_{Hg0} of virgin AC decreased more quickly than that of 25% LaCe/AC with time under clean conditions. 25% LaCe/AC could eventually maintain E_{Hg0} of 84.5% and E_{NO} of 89.5%, respectively, suggesting that E_{Hg0} obtained more obvious decrease than E_{NO}. The difference might be ascribed to the different removal mechanisms of NO and Hg⁰ because both adsorption and catalytic oxidation contributed to Hg⁰ removal in which adsorption with limited adsorption capacity accounted for the main contributions while adsorption wasn't mainly responsible for NO removal [16]. Both E_{NO} and E_{Hg0} of 25% LaCe/AC demonstrated a

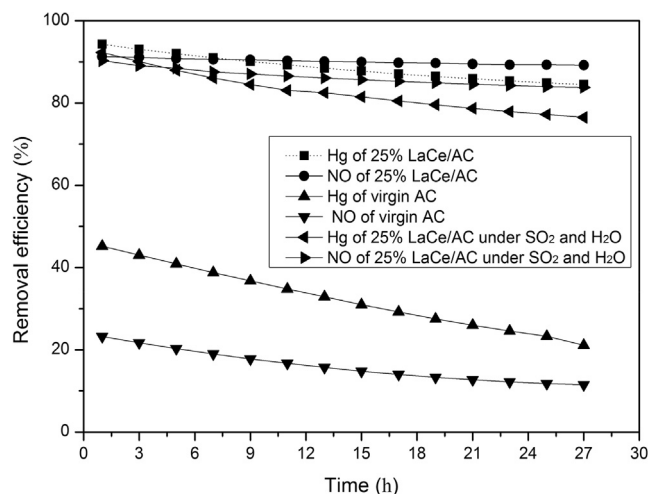


Fig. 13. The stability tests on simultaneous NO and Hg⁰ removal over virgin AC under clean conditions, and 25%LaCe/AC under the clean conditions with or without 200 ppm SO₂ and 3% H₂O. Clean conditions: T = 180 °C, 6% O₂, 80 µg/m³ Hg⁰, 800 ppm NO, 800 ppm NH₃, N₂ as balance.

rapid decline under the conditions with 200 ppm SO₂ and 3% H₂O than that under clean conditions, which was attributed to the inhibitive effect from H₂O and SO₂. Notably, the relatively good final E_{Hg0} and E_{NO} even under 200 ppm SO₂ and 3% H₂O indicated the sample's potentially industrial application.

3.3. Mechanism study

For NH₃-SCR of NO over metal oxides loaded catalysts or sorbents, it was recognized that catalytic centers were metal oxides which acted as the electron transfer station among NO, O₂ and NH₃ [16,22,57,58]. Based on these literatures and our previous and current works, thus possible main NH₃-SCR reaction pathways over 25%LaCe/AC were proposed as follows: NH₃ coordinated to the Lewis acid sites or Brønsted sites which acted as crucial active sites, and then reacted with adsorbed NO₂ and gaseous NO, thus generating the final products of N₂ and H₂O, which mainly followed the Langmuir-Hinshwood mechanism [16,59]. The reactions were simplified as reactions (5–11), in which MO representing lanthanum-cerium complex oxides acted as catalytic centers. At the same time, some researchers referred that some side reactions in the NH₃-SCR process over carbon-supported metal oxides might take place due to the carrier of carbon as a reducing agent [22,45], as reactions (12)–(14) showed. That did occur in our tests because very little amount CO₂ was detected in the outlet gases. Notwithstanding, reactions (12)–(14) were a little weaker compared with reactions (5)–(11).

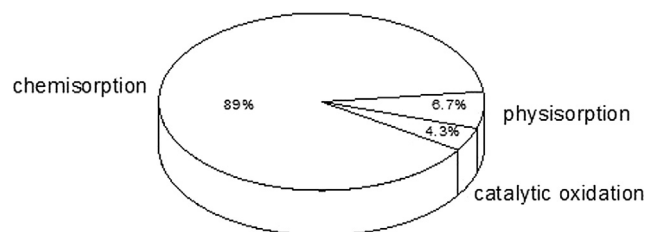
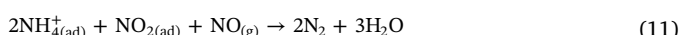
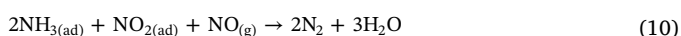


Fig. 14. Different contributions in overall Hg⁰ uptake over 25%LaCe/AC. Reaction conditions: T = 180 °C, 6% O₂, 80 µg/m³ Hg⁰, 800 ppm NO, 800 ppm NH₃, N₂ as balance.

As for Hg⁰ removal, the mercury conversion test and the desorption test demonstrated that the Hg⁰ removal mechanism of 25%LaCe/AC was attributed to combination of physisorption and chemisorption and catalytic oxidation, which was in accordance with the TGA analysis. Their relative contributions in overall Hg⁰ uptake were shown in Fig. 14, in which chemisorption played the predominant role. It was easy to understand that the Hg capture by the physisorption and chemisorption due to the abundant pore structure of the AC. The reversible Hg⁰ capture derived from the physisorption was due to the van de Waals force while the irreversible chemisorption mercury was because of the formation of chemical bonds [44,45]. Our previous work confirmed that both adsorption oxygen (O_(ad)) and lattice oxygen [O] participated in the catalytic process of Hg⁰ oxidation, in which the consumed O_(ad) was compensated by gaseous oxygen (O_{2(g)}) while the consumed [O] was replenished by the redox shift between Ce³⁺ and Ce⁴⁺ [2,3,19,20]. XPS analysis indicated that the presence of La benefited the generation of Ce³⁺ in the process, and Ce³⁺ was confirmed to create a charge imbalance, more unsaturated chemical bonds and oxygen vacancies on the catalyst surface, leading to more surface active oxygen species formed, which were beneficial for the oxidation of Hg [3,40]. Based on the characterizations, the tests and the literatures [2,3,60], the main catalytic oxidation process was possibly proposed as below:



4. Conclusion

A series of industrial desulfuration activated cokes loaded La₂O₃ and CeO₂ (LaCe/AC) were employed for simultaneous NO and Hg⁰ removal from simulated flue gas. 25%LaCe/AC exhibited outstanding NO removal efficiency (91.3%) and superior Hg⁰ removal efficiency (94.3%) at 180 °C. The results demonstrated that Hg⁰ had negligible impact on NO removal efficiency while NO evidently promoted Hg⁰ removal efficiency. Meanwhile, NH₃ had an adverse effect on Hg⁰ removal efficiency. The slightly inhibitive effect derived from the existence of H₂O or SO₂ was also detected. The NO removal mainly followed the Langmuir-Hinshwood mechanism while the Hg⁰ removal mechanism was attributed to the combination of physisorption and chemisorption and catalytic oxidation. Especially, the relative contributions of physisorption and chemisorption and catalytic oxidation were distinguished and calculated by designed mercury conversion and desorption tests, the results indicated chemisorption displayed the predominant role. In addition, the stability test of 27 h was carried out and eventually the sample maintained 84.5% Hg⁰ removal efficiency and 89.5% NO removal efficiency, indicating its potentially large-scale industrial application at low temperatures in the foreseeable future.

Acknowledgements

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