#### **RESEARCH ARTICLE**

# Adsorption and oxidation of elemental mercury from coal-fired flue gas over activated coke loaded with Mn–Ni oxides



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#### Abstract



A series of Mn–Ni/AC (AC, activated coke) catalysts were synthesized by the impregnation method for the removal of elemental mercury ( $Hg^0$ ) from simulated flue gas. The samples were characterized by BET, ICP-OES, SEM, XRD, XPS, H<sub>2</sub>-TPR, FT-IR, and TGA. Mn<sub>6</sub>Ni<sub>0.75</sub>/AC exhibited optimal removal efficiency of 96.6% in the condition of 6% O<sub>2</sub> and balanced in N<sub>2</sub> at 150 °C. The experimental results showed that both O<sub>2</sub> and NO facilitated Hg<sup>0</sup> removal. SO<sub>2</sub> could restrain the Hg<sup>0</sup> removal in the absence of O<sub>2</sub>, while the inhibitory effect of SO<sub>2</sub> was weakened with the aid of 6% O<sub>2</sub>. In addition, H<sub>2</sub>O exhibited a slightly negative influence on Hg<sup>0</sup> removal. The characterization of the samples indicated that Mn<sub>6</sub>Ni<sub>0.75</sub>/AC possessed larger specific surface area, higher dispersion of metal oxides, and stronger redox ability. In the meantime, the results of XPS and FT-IR demonstrated that the lattice oxygen and chemisorbed oxygen made contributions to Hg<sup>0</sup> removal and the consumed oxygen could be compensated by the redox cycle of metal oxides and gas-phase O<sub>2</sub>. Meanwhile, the mechanisms of Hg<sup>0</sup> removal were proposed based on the above studies.

Keywords Elemental mercury · Mn-Ni oxides · Activated coke · Adsorption · Oxidation

## Introduction

As a hazardous and toxic pollutant of coal combustion, mercury has attracted considerable concern in recent years because of its high toxicity, long-range mobility in the atmosphere, persistence and bioaccumulation, and neurotoxic influence on human health (Dranga et al. 2012; Li et al. 2016b; Wang et al. 2014). Nowadays, a great number of countries have been trying to control mercury emissions. The U.S. Environmental Protection Agency (EPA) finalized the national standard Final Mercury and Air Toxics Standards for

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<sup>2</sup> Key Laboratory of Environmental Biology and Pollution Control (Hunan University), Ministry of Education, Changsha 410082, People's Republic of China mercury control and hazardous pollutants on April 19, 2012 (Tao et al. 2012). In China, the Emission Standard of Air pollution for Thermal Power Plants has been issued by the government department, which limited mercury emission to  $0.03 \text{ mg/m}^3$  (Shen et al. 2017). To enforce the severe mercury control laws and regulations, it is urgent to adopt more effective emission reduction technologies.

The forms of mercury have an important influence on the removal efficiency of mercury. Generally, three main forms of mercury existed in coal combustion flue gas: particle-bound mercury (Hg<sup>p</sup>), elemental mercury (Hg<sup>0</sup>), and oxidized mercury (Hg<sup>2+</sup>) (Galbreath and Zygarlicke 1996). The existing air pollution control devices (APCDs) can easily remove the Hg<sup>p</sup> and Hg<sup>2+</sup>. For instance, Hg<sup>p</sup> can be captured by electrostatic precipitators (ESPs) or fabric filters (FFs), and Hg<sup>2+</sup> can be removed by wet flue gas desulfurization devices (WFGDs) because of its water solubility. Conversely, Hg<sup>0</sup> has higher volatility and lower water solubility, which is difficult to remove directly by APCDs and WFGDs (Li et al. 2008; Mei et al. 2008). Therefore, developing viable and effective technologies for removing Hg<sup>0</sup> is the main aim and mission in controlling mercury. So far, there are several ways that have been applied to remove Hg<sup>0</sup>, including catalytic oxidation, sorbent injection, and photochemical oxidation (Pitoniak

et al. 2005; Portzer et al. 2004; Vidic and Siler 2001). Thereinto, the technology of activated carbon injection (ACI) has been used to remove  $Hg^0$  at present (Sjostrom et al. 2010). However, the ACI practical application is not widely used due to high operating cost, low mechanical strength, and low utilization rate, as well as adverse impact on the utilization of fly ash (Jones et al. 2007; Sun et al. 2013).

Activated coke (AC), a type of porous material, is effective for SO<sub>2</sub>, NO, and Hg<sup>0</sup> removal (Tsuji and Shiraishi 1997b; Wu et al. 2015). Compared with the traditional activated carbon, AC is cheaper and can be regenerated to further reduce costs. In addition, AC possesses high mechanical strength, which can resist abrasion and squashing during the disposing process (Tsuji and Shiraishi 1997a). Meanwhile, AC can provide abundant active sites to Hg<sup>0</sup> removal due to the relatively higher surface area and different functional groups (Xie et al. 2015). These advantages indicated that AC is a promising prospect for Hg<sup>0</sup> removal in practical application. However, virgin AC exhibits lower removal capacity of Hg<sup>0</sup>. Some reports said that loading metal oxides on AC can enhance the Hg<sup>0</sup> removal ability of AC (Hua et al. 2010; Wang et al. 2010). Therefore, various metal oxides and bimetallic oxides, including CeO<sub>2</sub> (He et al. 2011),  $MnO_x$  (Li et al. 2010), CuO (Xu et al. 2014), FeO<sub>x</sub> (Yang et al. 2011), CoO<sub>x</sub> (Zhang et al. 2014), MnO<sub>x</sub>-CeO<sub>2</sub> (Li et al. 2017), and CuO- $ZrO_2$  (Tang et al. 2018), have been broadly studied and had the potential for Hg<sup>0</sup> removal. In previous works, we have used AC loaded with different metal compounds to remove  $Hg^0$  (Tao et al. 2012; Wang et al. 2016; Wu et al. 2015; Xie et al. 2015). Manganese oxide is one of the optimal choices because of its superior catalytic activities at low temperatures and lower cost. Moreover, Hg<sup>0</sup> could be oxidized to form HgO by manganese oxides (Li et al. 2012). Manganese oxides can enhance the oxygen storage ability of the sample which resulted from the capacity to convert higher oxidation states, which causes high removal efficiency of Hg<sup>0</sup>. At the same time, Ni-based catalyst is one of the most active transition metal catalysts and, compared to noble metals, are lowpriced (Kambolis et al. 2010; Luisetto et al. 2015), but there are few reports about Ni-based materials for Hg<sup>0</sup> removal. Therefore, the Mn-Ni-mixed oxides over activated coke (Mn-Ni/AC) may be a valid method to promote the activity for Hg<sup>0</sup> removal.

In this study, samples of Mn–Ni/AC synthesized by the impregnation method and their activity for Hg<sup>0</sup> removal were studied. The effect of the Mn–Ni molar ratio on the removal efficiency of Hg<sup>0</sup> was researched, as well as the effect of reaction temperature (90–240 °C) and gas constituents (O<sub>2</sub>, NO, SO<sub>2</sub>, and H<sub>2</sub>O). Methods such as Brunauer–Emmett–Teller (BET), inductively coupled plasma optical emission spectrometry (ICP-OES), scanning electron microscopy (SEM), X-ray diffraction (XRD), temperature-programmed reduction of hydrogen (H<sub>2</sub>-TPR), X-ray photoelectron

spectroscopy (XPS), Fourier transform infrared spectroscopy (FT-IR), and thermogravimetric analysis (TGA) were carried out to investigate the characterization of different samples. Furthermore, the mechanisms concerned with  $Hg^0$  removal were discussed based on the results and characterization of experiment.

## **Experimental section**

## Sample preparation

The virgin AC (columnar particle, diameter = 5 mm and length = 7-10 mm) was obtained from Alxa League Ke'xing Carbon Industry, China. Firstly, the AC was washed several times with deionized water and subsequently dried in an electric blast oven at 105 °C overnight. Then, the required solution consisted of a certain amount of 50% Mn(NO<sub>3</sub>)<sub>2</sub> solutions, Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, and deionized water. The virgin AC was added to the obtained solutions at ambient temperature for 24 h. The resulting precursors were dried at 105 °C for 12 h, then calcined at 500 °C for 4 h in the condition of pure N<sub>2</sub>. The total Mn-Ni oxide mass percentage of the whole samples was 6%, which was proven to be the best mass percentage in the preliminary experiments. And the Mn/(Mn + Ni) molar ratios of the samples were 0, 0.25, 0.4, 0.5, 0.6, 0.75, and 1, respectively. Therefore, the obtained samples were noted as  $Mn_6Ni_1$ AC, where 6 represents the Mn-Ni oxide mass percentage, and x represents the molar ratio of Mn/(Mn + Ni).

## Sample characterization

The BET surface area, pore volume, and pore size of the samples were obtained from the  $N_2$  adsorption isotherm with a Quadrasorb SI-3MP analyzer (Quantachrome Instrument Crop, USA).

An ICP-OES was employed to measure the actual content of loaded metal over virgin AC, which was carried out on SPECTRO BLUE SOP (Germany).

To study the microstructure and morphology of the samples, SEM images were performed on the MIRA3 LMU (Tescan, Czech Republic). The images of each catalyst were magnified to  $\times 10,000$  and  $\times 50,000$ .

XRD patterns were employed to examine the dispersivity and crystalline phase of the samples, which was conducted by a Rigaku D/Max 2550 XRD (Rigaku, Japan) apparatus with Cu-K $\alpha$  radiation in a 2 $\theta$  range of 10–80°.

 $H_2$ -TPR was measured on an AutoChem 2920 automated adsorption analyzer (Micromeritics Instrument Crop, USA), which was used to determine the redox abilities of the samples.

The X-ray photoelectron spectroscopy (XPS) measurements were implemented using a Thermo K-Alpha 1063 spectrometer (Thermo Fisher Scientific, UK) equipped with an Al K $\alpha$  X-ray radiation source. The binding energy was referenced to C 1s at 284.6 eV.

FT-IR experiments were conducted on a Tensor27 (Bruker, Germany) device in the range of 400–4000 cm<sup>-1</sup> at a spectral resolution of 4 cm<sup>-1</sup>. The prepared samples were exposed to the corresponding reaction conditions:  $O_2$  ( $N_2$  and 6%  $O_2$ ) at 150 °C, NO +  $O_2$  (700 ppm NO,  $N_2$ , and 6%  $O_2$ ) at ambient temperature, SO<sub>2</sub> +  $O_2$  (1200 ppm SO<sub>2</sub>,  $N_2$ , and 6%  $O_2$ ) at ambient temperature, and  $H_2O + O_2$  (8 vol%  $H_2O$ ,  $N_2$ , and 6%  $O_2$ ) at ambient temperature. Each sample was saturated for 2 h.

TGA was used to evaluate the thermal stability of the sample, which was performed by a DTG-60 thermal analyzer (Shimadzu, Japan). Approximately 15 mg sample was used and warmed up to 600 °C with a heating rate of 10 °C/min under the atmosphere of pure  $N_2$ .

#### **Evaluation of mercury removal activity**

The Hg<sup>0</sup> removal activity was studied by a fixed-bed reactor, and the schematic plot of the Hg<sup>0</sup> removal apparatus is exhibited in Fig. 1. For every test, 20 g AC sample was placed in the quartz tube reactor (52 mm inner diameter  $\times$  850 mm length)

and the temperature controlled by the tube furnace. The Hg<sup>0</sup> permeation tube (VICI Metronics, USA) generated Hg<sup>0</sup> vapor being carried by high purity N<sub>2</sub>. Different gas components including N2, O2, SO2, NO, CO2, and gas-phase H2O would be added to the gas mixer inlet when used (SFG =  $6\% O_2 +$  $12\% \text{ CO}_2 + 400 \text{ ppm SO}_2 + 350 \text{ ppm NO} + \text{N}_2$ ). The inlet flow rate was controlled by a mass flow controller (MFC) and the total flow rate was maintained at 500 mL/min (GHSV = 1500  $h^{-1}$ ). The inlet and outlet Hg<sup>0</sup> concentrations were monitored using an online RA-915M mercury analyzer (LUMEX Ltd., Russia). In order to comprehend the adsorption and oxidation efficiency during the removal process, mercury speciation experiments were conducted by the conversion system, which consists of three gas washing bottles containing 10% NaOH solution, 10% SnCl<sub>2</sub> solution, and 10% KCl solution. The  $Hg^{2+}$  could be reduced by SnCl<sub>2</sub> solution and the Hg<sup>T</sup> was measured, while the KCl solution could capture the Hg<sup>2+</sup> and Hg<sup>0</sup> was detected by the mercury analyzer. Hence, Hg<sup>2+</sup> concentrations could be calculated according to the differential of Hg<sup>T</sup> and Hg<sup>0</sup>. Meanwhile, the regenerability of Mn<sub>6</sub>Ni<sub>x</sub>/AC was also investigated. The spent sample was heated to 500 °C and maintained for 3 h under the atmosphere of pure N<sub>2</sub> to decompose the mercury species on the surface of the sample. Then, the regenerated sample was



Fig. 1 Schematic diagram of the experimental setup

used for the next experiment of Hg<sup>0</sup> removal. For each test, the desired inlet Hg<sup>0</sup> concentration needs to be stabilized for more than 1 h, and the outlet concentration was recorded after the variation of Hg<sup>0</sup> concentration less than 5% for longer than 1 h. The Hg<sup>0</sup> removal efficiencies, namely total efficiencies ( $E_{T}$ ), oxidation efficiencies ( $E_{oxi}$ ), and adsorption efficiencies ( $E_{ads}$ ) were calculated by Eqs. (1–3):

$$E_{\rm T} = \frac{\rm Hg_{in}^0 - \rm Hg_{out}^0}{\rm Hg_{in}^0} \times 100\%$$

$$\tag{1}$$

$$E_{\text{oxi}} = \frac{\text{Hg}_{\text{out}}^{\text{T}} - \text{Hg}_{\text{out}}^{0}}{\text{Hg}_{in}^{0}} \times 100\%$$
<sup>(2)</sup>

$$E_{\rm ads} = \frac{\mathrm{Hg}_{\rm in}^{0} - \mathrm{Hg}_{\rm out}^{\mathrm{T}}}{\mathrm{Hg}_{\rm in}^{0}} \times 100\% \tag{3}$$

Where  $Hg_{in}^0$  and  $Hg_{out}^0$  denote the inlet and outlet  $Hg^0$  concentrations ( $\mu g/m^3$ ), respectively, and  $Hg_{out}^T$  denotes the outlet  $Hg^T$  concentrations ( $\mu g/m^3$ ).

# **Results and discussion**

#### **Removal performance**

The removal efficiencies of elemental mercury over different samples were carried out at 90–240 °C. From Fig. 2, the virgin AC exhibited lower efficiency of Hg<sup>0</sup> removal, only 65–80%. And the addition of MnO<sub>x</sub> and/or NiO improved the Hg<sup>0</sup> removal activity of samples significantly, indicating that the modification of MnO<sub>x</sub> and NiO could supply abundant active sites for Hg<sup>0</sup> adsorption and oxidation (Du et al. 2018). For the Mn<sub>6</sub>Ni<sub>x</sub>/AC samples, the change of  $E_T$  exhibited similar trends



Fig. 2 Removal of  $Hg^0$  on  $Mn_6Ni_{\rm x}/AC$  samples in simulated flue gas (reaction condition 100  $\mu$ g/m<sup>3</sup> Hg<sup>0</sup>, 6% O<sub>2</sub>, 20 g sample, total flow rate 500 mL/min)

from 90 to 240 °C. The Hg<sup>0</sup> removal efficiencies increased with the reaction temperature increased from 90 to 150 °C; subsequently, the removal efficiencies reduced as the temperature further increased. However, the removal efficiencies of Hg<sup>0</sup> were higher than 80% over all modified samples at the broad temperature window from 90 to 240 °C. Among these samples, Mn<sub>6</sub>Ni<sub>0.75</sub>/AC showed the best performance in Hg<sup>0</sup> removal, which achieved the maximum removal efficiency of 96.6% at 150 °C. Hence, Mn<sub>6</sub>Ni<sub>0.75</sub>/AC, as the sample with the highest removal efficiency, was employed in flue gas experiments.

## Effect of flue gas components

For the purpose of investigating the effects of each flue gas constituent on  $Hg^0$  removal process and reaction approaches, flue gas experiments (O<sub>2</sub>, NO, SO<sub>2</sub>, H<sub>2</sub>O) were conducted over the sample of Mn<sub>6</sub>Ni<sub>0.75</sub>/AC at 150 °C.

## Effect of O<sub>2</sub>

Figure 3 exhibits the roles of different  $O_2$  concentrations in  $Hg^0$  removal. The sample of  $Mn_6Ni_{0.75}/AC$  exhibited relatively high removal performance for  $Hg^0$  under pure  $N_2$ . This result might be due to the sample modified by  $MnO_x$  and NiO, which promoted the redox abilities and the activity of the surface oxygen on the sample (Du et al. 2018). The  $E_T$  increased to 96.6% after introducing 6%  $O_2$ , while there was no obvious increase of  $E_T$  with the  $O_2$  concentration further increased to 12%. Thereinto, the adsorption efficiencies of



**Fig. 3** Effect of flue gas components on  $Hg^0$  removal over  $Mn_6Ni_{0.75}/AC$  and mercury speciation conversion experiment (reaction condition 100  $\mu g/m^3 Hg^0$ , 0–12% O<sub>2</sub>, 0–700 ppm NO, 0–1200 ppm SO<sub>2</sub>, 0–8 vol% H<sub>2</sub>O, SFG = 6% O<sub>2</sub> + 12% CO<sub>2</sub> + 400 ppm SO<sub>2</sub> + 350 ppm NO + N<sub>2</sub>, 20 g sample, total flow rate 500 mL/min, reaction temperature 150 °C)

 $Hg^0$  were basically unchanged as the  $O_2$  concentration increased from 6 to 12%. However, it was observed that the oxidation efficiencies increased with the  $O_2$  concentration increased, suggesting that gas-phase  $O_2$  was involved in the process of  $Hg^0$  oxidation, which might be attributed to the gaseous  $O_2$  that could replenish the surface oxygen consumed by  $Hg^0$  (Zeng et al. 2017). In the meantime, 6%  $O_2$  was adequate for  $Hg^0$  removal.

#### Effect of NO

Compared to the condition of pure  $N_2$ , the positive influence on Hg<sup>0</sup> removal was observed after adding 350 ppm NO (Fig. 3), which illustrated that the ability of  $Mn_6Ni_{0.75}/AC$  for  $Hg^0$ removal was improved in the presence of NO. However, there was no significant change as the NO concentration further increased. It was reported that NO could adsorb on the active sites of Mn<sub>6</sub>Ni<sub>0.75</sub>/AC and react with the surface oxygen of the sample to form  $NO_x$  species (Li et al. 2008). On one hand, NO consumed the surface oxygen and occupied the active sites of the sample surface under pure N2, leading to the decrease of  $Hg^0$  removal efficiency. On the other hand, the formed NO<sub>x</sub> species from the reactions of NO and surface oxygen were beneficial to Hg<sup>0</sup> oxidation (Fuente-Cuesta et al. 2012). Hence, compared to pure N<sub>2</sub>, the oxidation efficiencies of  $Hg^0$  increased in the presence of NO. Meanwhile, the  $Hg^0$ removal efficiency increased obviously after introducing 6% O2, which was due to the gas-phase O2 that could supplement the consumed surface oxygen.

## Effect of SO<sub>2</sub>

It was observed that SO<sub>2</sub> displayed the obvious inhibitory effects on Hg<sup>0</sup> removal (Fig. 3). Compared to pure N<sub>2</sub>,  $E_{T}$ values declined obviously to 76.54 and 65.82%, corresponding to 400 and 800 ppm SO<sub>2</sub>, respectively, while the removal efficiency was basically unchanged under 1200 ppm SO<sub>2</sub>. On one side, SO<sub>2</sub> could adsorb on the surface of the sample, then competed with the active sites of Hg<sup>0</sup> and reacted with the surface oxygen, which would affect the reaction of Hg<sup>0</sup> and the surface oxygen (Casapu et al. 2009; Xie et al. 2015). On the other side, SO<sub>2</sub> was easy to react with metal oxides to form sulfites and sulfates, which could hinder the oxidation of Hg<sup>0</sup> (Li et al. 2017). The above two aspects might be the reason for the negative effect of SO<sub>2</sub>. Besides, the oxidation efficiencies of Hg<sup>0</sup> removal gradually decreased with the SO<sub>2</sub> concentration increased due to the competitive effect between  $SO_2$  and  $Hg^0$  (Li et al. 2012). When 6%  $O_2$  was introduced, the inhibitory effects of SO2 were weakened and the oxidation efficiency of Hg<sup>0</sup> increased slightly, which was attributed to the supplement of surface oxygen consumed by SO<sub>2</sub>.

#### Effect of H<sub>2</sub>O

Water vapor, as an unavoidable component that existed in coal combustion flue gas, usually exhibits an opposite influence on Hg<sup>0</sup> removal (Li et al. 2011; Wan et al. 2011; Zhang et al. 2017). The addition of 8 vol% gas-phase H<sub>2</sub>O which inhibited Hg<sup>0</sup> removal was observed (Fig. 3). The removal efficiencies decreased from 92.5 to 88.33%, which could be interpreted that water vapor competed with the active sites of Hg<sup>0</sup> on the surface of Mn<sub>6</sub>Ni<sub>0.75</sub>/AC (Li et al. 2008). Nevertheless, a slight decline of  $E_{\rm T}$  also implied that the Mn<sub>6</sub>Ni<sub>0.75</sub>/AC exhibited good resistance to H<sub>2</sub>O, which had great potential for practical application on Hg<sup>0</sup> removal.

## Mercury speciation conversion experiment and stability test

To study the effects of adsorption and oxidation on Hg<sup>0</sup> removal, the mercury speciation conversion experiment was conducted in different flue gas conditions, and the results are shown in Fig. 3. It could be clearly seen that the adsorption efficiency was much larger than the oxidation efficiency under different flue gas conditions, which indicated that adsorption ability played the most important role in the removal process. Meanwhile, the effect of oxidation also existed. In addition, Fig. 4 presents the stability result of Mn<sub>6</sub>Ni<sub>0.75</sub>/AC in the removal of Hg<sup>0</sup>, which was performed at 150 °C for 24 h. It should be noted that the removal efficiencies were unstable in the first 2 h, and then decreased slightly to reach the lower removal efficiency of 76.49% at 24 h. Except for the removal efficiencies of Hg<sup>T</sup>, Hg<sup>0</sup> oxidation efficiencies in flue gas were also probed. At 2, 6, 12, 18, and 24 h, Hg<sup>2+</sup> removal efficiencies were 2.16, 5.68, 8.82, 10.96, and 12.24%, respectively. The observation suggested that the adsorption ability of the



**Fig. 4** Stability test of  $Mn_6Ni_{0.75}/AC$  for  $Hg^0$  removal (reaction condition 100 µg/m<sup>3</sup> Hg<sup>0</sup>, SFG (6% O<sub>2</sub> + 12% CO<sub>2</sub> + 400 ppm SO<sub>2</sub> + 350 ppm NO + N<sub>2</sub> + 8 vol% H<sub>2</sub>O, 20 g sample, total flow rate 500 mL/min, reaction temperature 150 °C)

 $Mn_6Ni_{0.75}/AC$  was excellent at the beginning and active sites of the sample were sufficient; thus, the efficiency decreased slowly.  $Hg^0$  oxidation gradually replaced  $Hg^0$  adsorption as the reaction proceeded, owing to the consumption of adsorption sites and the competitive adsorption of  $SO_2$  and  $Hg^0$  (Li et al. 2008, 2012; Zeng et al. 2017). Moreover, the adsorption efficiency gradually decreased and oxidation efficiency became higher, suggesting the importance of oxidation effect in  $Hg^0$  removal.

#### Characterization of samples

## **BET and ICP-OES**

The BET-specific surface area, pore volume, and pore size of the samples are shown in Table 1. It was clearly seen that the samples of Mn-Ni-modified AC possessed higher surface area and larger pore volumes compared with virgin AC. The reaction of AC and metal oxides could generate a number of new pores during the preparation process, which was responsible for the higher surface area of the modified samples (Wang et al. 2016). Besides, with the increase of the manganese content, the BET surface area and total pore volumes of Mn<sub>6</sub>Ni<sub>x</sub>/AC increased. In particular, Mn<sub>6</sub>Ni<sub>0.75</sub>/AC possessed the largest BET surface area and total pore volumes, which provided more active sites for Hg<sup>0</sup> adsorption, resulting in the outstanding removal performance of the sample. Additionally, the pore distribution curves of AC, Ni<sub>6</sub>/AC, Mn<sub>6</sub>/AC, and Mn<sub>6</sub>Ni<sub>0.75</sub>/AC were obtained by the Horvath-Kawazoe (HK) method and the Barrett-Joyner-Halenda (BJH) method. As implied in Fig. 5, the average pore size of all samples was approximately 2.0 nm, close to the micropore range, indicating that impregnation with Mn-Ni oxides made a negligible effect on the average pore size. It should be noted that more micropores with pore size lower than 2 nm were observed in the sample of Mn<sub>6</sub>Ni<sub>0.75</sub>/AC, which resulted in a higher BET surface area, thereby facilitating the adsorption and the succeeding oxidation of the gas reactant.



Fig. 5 The pore size distribution curves of virgin AC, Ni $_6$ /AC, Mn $_6$ Ni $_{0.75}$ /AC, and Mn $_6$ /AC

ICP-AES measurements were employed to test the actual contents of loaded metal over the samples. From the results of Table 2, the calculated contents of loaded metal were higher than the actual contents for all the samples, which was possibly due to the loss of the manganese precursor and nickel precursor during the process of impregnation and calcination.

#### SEM

The SEM micrographs of the virgin AC and the prepared samples are displayed in Fig. 6. The surface features of AC were changed to a certain extent through loading of Mn–Ni metal oxides, which were mainly dispersed on the surface of AC at the micrometric scale. However, more agglomerates appeared on the surface of Mn<sub>6</sub>/AC and Ni<sub>6</sub>/AC. Furthermore, it could be clearly observed that a flake-like morphology appeared on the surface of Ni/AC, and some fine lines that are rod-like covered the surface of Mn/AC in Fig. 6b, and the active metal oxides were dispersed well like a mesh on the surface of Mn<sub>6</sub>Ni<sub>x</sub>/AC, indicating that there might exist synergistic effects between MnO<sub>x</sub> and NiO over Mn<sub>6</sub>Ni<sub>x</sub>/AC, thus improving the dispersion of active

Samples	BET surface area (m <sup>2</sup> /g)	Total pore volume $(cm^3/g)$	Average pore diameter (nm)	Pore distribution (%)	
				Micropore	Mesopore
AC	96.523	0.060	2.468	67.25	32.75
Ni <sub>6</sub> /AC	108.008	0.072	2.665	62.20	37.80
Mn <sub>6</sub> Ni <sub>0.25</sub> /AC	198.029	0.100	2.024	79.81	20.19
Mn <sub>6</sub> Ni <sub>0.4</sub> /AC	217.055	0.113	2.077	77.90	22.10
Mn <sub>6</sub> Ni <sub>0.5</sub> /AC	235.615	0.123	2.089	77.13	22.87
Mn <sub>6</sub> Ni <sub>0.6</sub> /AC	255.860	0.131	2.046	78.82	21.18
Mn <sub>6</sub> Ni <sub>0.75</sub> /AC	257.123	0.136	1.965	82.81	17.19
Mn <sub>6</sub> /AC	134.078	0.087	2.595	62.23	37.77

Table 1BET surface and poreparameters of the differentsamples

**Table 2** The contents of Mn andNi in samples obtained by ICP-AES (unit: wt%)

Samples	Mn		Ni		
	Calculated content	Actual content	Calculated content	Actual content	
Ni <sub>6</sub> /AC	_	_	4.71	4.35	
Mn <sub>6</sub> Ni <sub>0.25</sub> /AC	1.06	0.92	3.40	3.25	
Mn <sub>6</sub> Ni <sub>0.4</sub> /AC	1.66	1.47	2.65	2.44	
Mn <sub>6</sub> Ni <sub>0.5</sub> /AC	2.04	1.91	2.18	2.09	
Mn <sub>6</sub> Ni <sub>0.6</sub> /AC	2.41	2.16	1.71	1.51	
Mn <sub>6</sub> Ni <sub>0.75</sub> /AC	2.95	2.72	1.05	0.94	
Mn <sub>6</sub> /AC	3.79	3.50	_	_	

components over the samples (Tang et al. 2018). These results could cause the increase of the BET surface area, which was in accordance with the BET results.

## XRD

Figure 7 shows the results of the XRD measurements, which was conducted to determine the crystal species of the virgin AC and selected samples. It was found that there were diffraction patterns for SiO<sub>2</sub> ( $2\theta = 36.040^{\circ}$  and  $68.089^{\circ}$ ) in the virgin AC (Du et al. 2018). The typical peak of carbon at  $2\theta =$ 26.603° and 44.464° was detected in all the samples (Xie et al. 2015), indicating that the microstructures of AC were not changed partly after the process of impregnation. However, the intensity of carbon characteristic peaks reduced after adding the Mn-Ni oxides, indicating there might exist an interaction of metal oxides and AC, which was consistent with the results of BET, SEM, and H2-TPR. For the Ni6/AC, the peaks at  $2\theta = 37.158^\circ$ ,  $43.238^\circ$ , and  $62.839^\circ$  appeared, which corresponded to the NiO phase (Xia et al. 2016). In addition, the peaks at  $2\theta = 32.520^{\circ}$ ,  $36.085^{\circ}$ ,  $43.036^{\circ}$ ,  $60.037^{\circ}$ , and 62.275° were ascribed to Mn<sub>3</sub>O<sub>4</sub>, and the diffraction peaks at  $2\theta = 35.082^\circ$ ,  $40.822^\circ$ , and  $58.859^\circ$  were attributed to MnO (Du et al. 2018; Yi et al. 2018), while no apparent peaks assigned to NiO were detected in the sample of Mn<sub>6</sub>Ni<sub>x</sub>/AC, demonstrating that the nickel oxides were well dispersed over the samples or existed as an amorphous phase (Wu et al. 2008). In the meantime, compared with  $Mn_6/AC$ , the intensity of peaks that corresponded to Mn<sub>3</sub>O<sub>4</sub> weakened apparently after introducing the nickel oxide, indicating that the crystallinity of MnO<sub>x</sub> was lower or crystallite size became smaller in the presence of NiO, which was favorable for Hg<sup>0</sup> removal.

# H<sub>2</sub>-TPR

The H<sub>2</sub>-TPR analysis was performed to study the redox behaviors of different samples and the results obtained are depicted in Fig. 8. The reduction peak of virgin AC appeared at approximately 670 °C, which was attributed to the gasification of the carbon support (Zhang et al. 2015), whereas for Mn<sub>6</sub>/AC, the sample

showed another peak located at 526 °C, corresponding to the reduction of  $Mn_3O_4$  to MnO, and the broad shoulder peak at 691 °C might be ascribed to the gasification of the carbon support and the reduction of lattice oxygen due to the fact that the peak area was larger than that of virgin AC (Du et al. 2018; Zhao et al. 2016). The peak of Ni<sub>6</sub>/AC at 382 °C corresponded to the reduction of  $Ni^{2+}$  to  $Ni^{0}$  (Wang et al. 2018). However, it could be seen that the three peaks of Mn<sub>6</sub>Ni<sub>0.75</sub>/AC occurred at around 403, 509, and 675 °C, corresponding to the reduction of Ni<sup>2+</sup> to Ni<sup>0</sup>, Mn<sub>3</sub>O<sub>4</sub>  $\rightarrow$ MnO, and the lattice oxygen, respectively. It was worth noting that the peak assigned to the  $Mn_3O_4 \rightarrow MnO$  transferred to relatively low temperature, suggesting that the synergetic effects of Mn and Ni species could promote the mobility of surface oxygen and enhance the redox ability (Chen et al. 2018). Therefore, Mn<sub>6</sub>Ni<sub>0.75</sub>/AC possessed more formation of oxygen vacancies, which was conducive for catalytic activity (Li et al. 2016a).

## XPS

To understand the chemical states of the elements (O, Mn, Ni, and Hg) on the surface of different samples, XPS measurements were conducted and the results are exhibited in Fig. 9. The XPS O 1s spectra are presented in Fig. 9a, and the three peaks at 529.5-530.3, 531.1-532.0, and 532.5-533.6 eV could be ascribed to the lattice oxygen  $(O_{\alpha})$ , chemisorbed oxygen and/or weakly bonded oxygen  $(O_{\beta})$ , and hydroxyl groups and/or adsorbed water species  $(O_{\gamma})$ , respectively (Deng et al. 2015; Kang et al. 2007; Zhao et al. 2016). As shown in Table 3, the ratio of  $O_{\beta}/O_{T}$  ( $O_{T} = O_{\alpha} + O_{\beta} + O_{\gamma}$ ) over  $Mn_6Ni_{0.75}/AC$  (54.78%) was higher than that over  $Mn_6/$ AC (38.02%) and Ni<sub>6</sub>/AC (41.00%), suggesting the higher amount of  $O_{\beta}$  on the sample of  $Mn_6Ni_{0.75}/AC$  because of the interaction of  $MnO_x$  and NiO. Hence, the higher  $O_\beta$  content and more oxygen vacancies over the sample of Mn<sub>6</sub>Ni<sub>0.75</sub>/AC could contribute to the prominent removal

**Fig. 6** SEM images (× 10,000) of **a** virgin AC, **b** Ni<sub>6</sub>/AC, **c** Mn<sub>6</sub>/AC, **d**  $\blacktriangleright$  Mn<sub>6</sub>Ni<sub>0.25</sub>/AC, **e** Mn<sub>6</sub>Ni<sub>0.4</sub>/AC, **f** Mn<sub>6</sub>Ni<sub>0.5</sub>/AC, **g** Mn<sub>6</sub>Ni<sub>0.6</sub>/AC, **h** Mn<sub>6</sub>Ni<sub>0.75</sub>/AC. SEM images (× 50,000) of **i** Ni<sub>6</sub>/AC, **j** Mn<sub>6</sub>/AC, **k** Mn<sub>6</sub>Ni<sub>0.5</sub>/AC, **l** Mn<sub>6</sub>Ni<sub>0.75</sub>/AC



performance of Hg<sup>0</sup> (Xie et al. 2015). Furthermore, in contrast to the fresh Mn<sub>6</sub>Ni<sub>0.75</sub>/AC, the ratio of O<sub> $\alpha$ </sub> and O<sub> $\beta$ </sub> over the used Mn<sub>6</sub>Ni<sub>0.75</sub>/AC all decreased to some extent, indicating the lattice oxygen and chemisorbed oxygen were involved in the process of Hg<sup>0</sup> removal.

Figure 9b shows the broad and asymmetric peaks at approximately 642.0 and 653.3 eV ascribed to Mn 2p<sub>3/2</sub> and Mn  $2p_{1/2}$ , respectively. The Mn  $2p_{3/2}$  had been reconstructed by three peaks at 641.2, 642.6, and 645.0 eV, corresponding to Mn<sup>3+</sup>, Mn<sup>4+</sup>, and Mn<sup>2+</sup>, respectively (Guo et al. 2012; Liu et al. 2016). As shown in Table 3, the ratio of  $Mn^{4+}/Mn^{3+}$ increased with the addition of NiO, suggesting that the incorporation of NiO was beneficial for the formation of highvalence Mn atoms on the surface of the sample. Besides, the ratio of Mn<sup>4+</sup>/Mn<sup>3+</sup> on the used Mn<sub>6</sub>Ni<sub>0.75</sub>/AC decreased from 2.27 to 0.99 compared with that of the fresh  $Mn_6Ni_{0.75}/AC$ . Thereinto, the adsorbed Hg<sup>0</sup> could be oxidized by Mn<sup>4+</sup> directly; meanwhile, Mn<sup>3+</sup> also played a significant role in the effect of oxidation when O<sub>2</sub> existed (Li et al. 2015). This result also indicated that the higher content of Mn<sup>4+</sup> over the  $Mn_6Ni_{0.75}/AC$  was beneficial to  $Hg^0$  oxidation.

The XPS results of Ni 2p and Ni  $2p_{3/2}$  are shown in Fig. 9c. The Ni 2p pattern consists of four distinct features: the main peak of Ni  $2p_{3/2}$  and its satellite peak at ~854 and ~862 eV and the Ni  $2p_{1/2}$  peak and its satellite peak at ~872 and ~879 eV, respectively (Wang et al. 2018). The surface structure behind the data revealed by the XPS was more intricate, especially for Ni  $2p_{3/2}$ , because of the complicated effects between diverse electron configurations in the final state (Bonomo et al. 2017; Marrani et al. 2014). According to the reference (Wang et al. 2018), the Ni  $2p_{3/2}$  region had been deconvoluted into six different Voigt peaks with a Gaussian/Lorentzian (G/L) ratio of

**Fig. 7** XRD patterns of the samples



Fig. 8  $\,H_2\mbox{-}TPR$  profiles of virgin AC,  $Mn_6/AC,\,Ni_6/AC,\,and\,Mn_6Ni_{0.75/}AC$ 

0.85, and the six peaks were called as simplicity A, B, C, D, E, and F in the order of increasing binding energy (BE). The peaks at 861.0 eV (D), 864.1 eV (E), and 866.6 eV (F) were assigned to the  $cd^{10}L^2$ ,  $cd^8$ , and shake-up transition states, respectively. For Ni<sub>6</sub>/AC, the lowest BE peak at 854.0 eV (A) associated with NiO corresponded to  $cd^9L$  (Jiménez-González et al. 2013; Marrani et al. 2014). The peaks at 855.4 eV (B) and 856.6 eV (C) were ascribed to the intersite charge transfer screening process ( $d^8:cd^9L$ ) and a nonlocal screening electronic state ( $cd^9:d^7$ ), respectively. Both peaks B and C were assigned to Ni<sup>2+</sup> ions (Jiménez-González et al. 2013; Marrani et al. 2014). However, when the MnO<sub>x</sub> was introduced, the peak of lower BE values at 853.4 eV was observed, indicative of metallic Ni





Fig. 9 XPS spectra for O1s, Mn 2p, Ni 2p, Ni 2p<sub>3/2</sub>, and Hg 4f of the as-prepared samples: a O 1s, b Mn 2p, c Ni 2p and Ni 2p<sub>3/2</sub>, and d Hg 4f



Fig. 9 continued.

(Luisetto et al. 2015), which further proved that the possible reaction of  $Mn^{3+} + Ni^{2+} \leftrightarrow Mn^{4+} + Ni^0$  took place during the process of Hg<sup>0</sup> removal.

Figure 9d depicts the XPS pattern of Hg 4f. The characteristic peak at 102.3 eV could be ascribed to Si 2p (Chen et al. 2018). The peak at 99.2 eV corresponded to Hg<sup>0</sup> (Tang et al. 2018), and another peak assigned to Hg 4f<sub>7/2</sub> at 101.2 eV corresponded to HgO (Tao et al. 2012). These results demonstrate that the primary mercury species of the sample surface was HgO. Moreover, the reaction of oxidation occurred during the process of Hg<sup>0</sup> removal, which was consistent with the results of the mercury speciation conversion experiment.

# FT-IR

Figure 10 shows the FT-IR spectra of the  $Mn_6Ni_{0.75}/AC$  catalyst at different gas components for 2 h. From Fig. 10(a), a number of bands were detected over the sample. The bands at 3740 and 3426 cm<sup>-1</sup> corresponded to the hydroxyl group bonding on the surface of the sample and O–H stretching vibration of water, respectively (Kwon et al. 2015), which were beneficial for Hg<sup>0</sup> removal. The band at 1515 cm<sup>-1</sup> could be assigned to the formation of bidentate formate (Ivanov et al. 2009). The bands occurring near 2919 and 2300–2400 cm<sup>-1</sup> were attributed to the CH stretch of bidentate formate and vibration of CO<sub>2</sub>,

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Table 3	The relative XPS
intensity	of the samples

Relative intensity	AC	Mn <sub>6</sub> /AC	Ni <sub>6</sub> /AC	Mn <sub>6</sub> Ni <sub>0.75</sub> /AC	Used Mn <sub>6</sub> Ni <sub>0.75</sub> /AC
O <sub>α</sub> (%)	_	47.02	49.89	39.23	34.71
O <sub>β</sub> (%)	59.37	38.02	41.00	54.78	46.34
$O_{\gamma}(\%)$	40.63	14.96	9.11	5.99	18.95
$Mn^{2+}$ (%) <sup>a</sup>	—	19.82	_	25.14	20.43
$Mn^{3+}$ (%) <sup>a</sup>	—	23.75	_	14.33	25.51
$Mn^{4+}$ (%) <sup>a</sup>	_	25.03	_	32.53	25.36
$Mn^{4+}/Mn^{3+}$	_	1.05	_	2.27	0.99
Ni <sup>2+</sup> (%) <sup>b</sup>	_	_	51.11	44.80	57.23
$\mathrm{Ni}^{0}\left(\% ight)^{\mathrm{b}}$	—	_	_	6.34	-

 $^{a}$  The percent of different valence of Mn in Mn  $2p_{3/2}$ 

<sup>b</sup> The percent of different state of Ni in Ni 2p<sub>3/2</sub> and shake-up satellite

respectively (Du et al. 2018; Ma et al. 2011). The bands at 1600– 1800 and 1076 cm<sup>-1</sup> were ascribed to the stretching vibration of carbonyl and to the asymmetric stretching vibration of SiO<sub>2</sub>, respectively, while the bands at 500–1000 cm<sup>-1</sup> corresponded to the bending vibration of Si–O (Chen et al. 2018), in line with the XRD results. In the curve of Fig. 10(b), the band at 1383 cm<sup>-1</sup> was attributed to nitrate (NO<sub>3</sub><sup>-</sup>) species (Zhang et al. 2017), indicating the surface of the sample was loaded with the nitrate species and led to increased removal efficiency (Fuente-Cuesta et al. 2012). After SO<sub>2</sub> + O<sub>2</sub> adsorption, the band at 1089 cm<sup>-1</sup> was detected, which could correspond to the stretching motion of the adsorbed sulfate and/or bisulfate (Tang et al. 2018). In addition, the adsorption spectrum of H<sub>2</sub>O + O<sub>2</sub> was also performed. The main difference was the bands at 1640 and 1390 cm<sup>-1</sup> were detected. And the band at 1640 cm<sup>-1</sup> was ascribed to  $\delta_{\rm HOH}$  of H<sub>2</sub>O, which indicated that there existed the formation of water on the surface of the sample (Chen et al. 2014). And the two bands could be ascribed to the vibration of the surface hydroxyl species (OH), suggesting the active oxygen and hydroxyl could be easily formed by gasphase H<sub>2</sub>O and O<sub>2</sub> on the surface of the sample (Zhao et al. 2016).

## **TGA** analysis

TGA was carried out to investigate the thermal stability of the fresh and used  $Mn_6Ni_{0.75}/AC$ , as depicted in Fig. 11. It was observed that there was a significant weight loss between 50 and 150 °C, which was attributed to the loss of adsorbed water and the loss of physisorption of Hg<sup>0</sup> (Gao et al. 2018). The

Fig. 10 FT-IR spectra of  $Mn_6Ni_{0.75}/AC$  under different conditions: (a) 100 µg/m<sup>3</sup> Hg<sup>0</sup> + 6% O<sub>2</sub> + N<sub>2</sub> at 150 °C; (b) 100 µg/m<sup>3</sup> Hg<sup>0</sup> + 700 ppm NO + 6% O<sub>2</sub> + N<sub>2</sub> at room temperature; (c) 100 µg/m<sup>3</sup> Hg<sup>0</sup> + 1200 ppm SO<sub>2</sub> + 6% O<sub>2</sub> + N<sub>2</sub> at room temperature; (d) 100 µg/m<sup>3</sup> Hg<sup>0</sup> + 8 vol% H<sub>2</sub>O + 6% O<sub>2</sub> + N<sub>2</sub> at room temperature





Fig. 11 TGA curves of the fresh and the used Mn<sub>6</sub>Ni<sub>0.75</sub>/AC

other excess weight loss range at 370–500 °C could be ascribed to HgO from the chemical adsorption and oxidation of Hg<sup>0</sup>, which was due to the thermal decomposition of HgO that mainly took place at the temperature range of 430–560 °C (Lopez-Anton et al. 2010). These results were consistent with the XPS results and proved that physisorption, chemisorption, and oxidation were involved in the removal mechanism of Hg<sup>0</sup>. Moreover, the weight loss at the temperature above 500 °C might be owing to the decomposition of AC functional groups and other factors (Wu et al. 2015). Therefore, the sample of Mn<sub>6</sub>Ni<sub>0.75</sub>/AC possessed excellent thermal stability.

# Mechanism for Hg<sup>0</sup> removal

Based on the above studies and previous studies, the reaction mechanisms about  $Hg^0$  removal over the sample of  $Mn_6Ni_{0.75}$ / AC were proposed. According to the characterization results, the sample of Mn<sub>6</sub>Ni<sub>0.75</sub>/AC was synthesized successfully by using metal oxides, which possessed higher BET surface area, more active sites, higher dispersion of active components, and higher reducibility. The reaction mechanisms of Hg<sup>0</sup> removal were attributed to the adsorption and oxidation. On one hand, the adsorption consisted of physisorption and chemisorption. From the results of XPS and TGA, vapor-phase Hg<sup>0</sup> could collide with the surface of the samples and was adsorbed on the surface of  $Mn_6Ni_{0.75}/AC$  to form  $Hg^0(ad)$  because of the van de Waals force, corresponding to the physisorption (Fan et al. 2012). The physisorption was primarily related to the active sites of the sample. Then, the adsorbed Hg<sup>0</sup> could be oxidized to mercury oxide by the metal oxides on the surface of the sample, which was ascribed to the irreversible chemisorption. The physisorption was weakened with the increase of the reaction temperature, while the chemisorption could play a dominant role as the

temperature increased (Fan et al. 2012). On the other hand, the Hg<sup>0</sup> oxidation on the sample could be explained by the Mars-Maessen mechanism (Zhao et al. 2015). And the lattice oxygen  $(O_{\alpha})$  and chemisorbed oxygen  $(O_{\beta})$ were involved in the  $Hg^0$  removal. The consumed  $O_{\beta}$ was supplemented by gas-phase  $O_2$ , while the  $O_{\alpha}$  was compensated by the redox shift of  $Mn^{4+}/Mn^{3+}/Mn^{2+}$  and  $Ni^{2+}/Ni^{0}$  (Du et al. 2018; Gao et al. 2018). Meanwhile, the incorporation of NiO was beneficial for the formation of high-valence Mn atoms, which was favorable for Hg<sup>0</sup> oxidation. Then, with the progress of the Hg<sup>0</sup> removal reaction, the oxidation of Hg<sup>0</sup> could displace a part of adsorption removal, which was in accordance with the stability experiment. Additionally, the FT-IR results exhibited that NO and SO<sub>2</sub> reacted with active oxygen to form nitrate species and sulfate and/or bisulfate, respectively. The main mechanisms of Hg<sup>0</sup> removal could be described as follows:

 $Hg^{0}(g) \rightarrow Hg^{0}(ad) \tag{4}$ 

 $Hg^{0}(ad) + O_{\alpha} {\rightarrow} HgO(ad) \tag{5}$ 

 $Hg^{0}(ad) + O_{\beta} {\rightarrow} HgO(ad) \tag{6}$ 

$$O_2(g) \rightarrow 2O_\beta$$
 (7)

 $\langle \alpha \rangle$ 

$$2MnO_2 \rightarrow Mn_2O_3 + O_\alpha \tag{8}$$

$$Mn_2O_3 \rightarrow 2MnO + O_{\alpha} \tag{9}$$

$$NiO \rightarrow Ni^0 + O_{\alpha} \tag{10}$$

$$HgO(ad) \rightarrow HgO(g) \tag{11}$$

$$2MnO + 1/2 O_2 \rightarrow Mn_2O_3 \tag{12}$$

$$Mn_2O_3 + 1/2 O_2 \rightarrow 2MnO_2$$
(13)

 $Ni^0 + 1/2 O_2 \rightarrow NiO$  (14)

$$Mn_2O_3 + NiO \rightarrow 2MnO_2 + Ni^0$$
<sup>(15)</sup>



Fig. 12 Regeneration performance of  $Mn_6Ni_{0.75}/AC$  in simulated flue gas (reaction condition 200  $\mu$ g/m<sup>3</sup> Hg<sup>0</sup>, 6% O<sub>2</sub>, 20 g sample, total flow rate 500 mL/min)

## Regeneration performance of Mn<sub>6</sub>Ni<sub>0.75</sub>/AC

Except for the Hg<sup>0</sup> removal activity, regeneration and reuse of the spent catalysts are also indispensable to practical application. To investigate the regeneration performance of the sample,  $Mn_6Ni_{0.75}/AC$  was used for the regeneration experiments. As shown in Fig. 12, the removal efficiencies of the regenerate samples were not significantly lower than those of the fresh sample, which indicated that the spent sample of  $Mn_6Ni_{0.75}/AC$  could be efficiently regenerated by the thermal desorption treatment. Hence, the sample of  $Mn_6Ni_{0.75}/AC$  possessed excellent regenerability and remarkable industrial application prospects.

## Conclusion

The samples of Mn-Ni/AC were prepared by the impregnation method for Hg<sup>0</sup> removal in simulated flue gas. The experimental results exhibited that the Hg<sup>0</sup> removal efficiencies of Mn<sub>6</sub>Ni<sub>x</sub>/AC were more superior to virgin AC, Mn<sub>6</sub>/AC, and  $Ni_6/AC$ . The highest  $Hg^0$  removal efficiency (96.6%) was acquired over Mn<sub>6</sub>Ni<sub>0.75</sub>/AC at 150 °C, which was due to the remarkable synergistic effects between  $MnO_x$  and NiO. In addition, the sample of Mn<sub>6</sub>Ni<sub>0.75</sub>/AC showed excellent stability for Hg<sup>0</sup> removal during 24 h and possessed outstanding regeneration performance, which was adapted to practical applications. NO promoted the efficiencies of Hg<sup>0</sup> removal whether O2 existed or not, while SO2 showed a negative impact on Hg<sup>0</sup> removal without O<sub>2</sub> because of the competitive adsorption. However, the inhibitory effect of SO2 was weakened owing to the addition of gas-phase O2 that could replenish the surface oxygen consumed by SO<sub>2</sub>. Moreover,  $Mn_6Ni_{0.75}/AC$  also displayed good resistance to  $H_2O$ . Besides, the results of characterization showed that the features of Mn<sub>6</sub>Ni<sub>0.75</sub>/AC, such as the larger BET surface area, higher dispersion of metal oxides, higher reducibility, and high active hydroxyl group, were favorable for Hg<sup>0</sup> removal. XPS results also exhibited that the lattice oxygen and chemisorbed oxygen played important roles in the removal of  $Hg^0$ , as well as the redox cycle of  $MnO_x$  and NiO. Further studies need to investigate the removal of Hg<sup>0</sup> and VOCs simultaneously, such as toluene.

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