Elemental mercury (Hg^0) removal over spinel LiMn$_2$O$_4$ from coal-fired flue gas

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HIGHLIGHTS

- Spinel LiMn$_2$O$_4$ was used as heterogeneous catalyst.
- LiMn$_2$O$_4$ had higher Hg^0 removal efficiency than Mn$_2$O$_3$ and Li$_2$O–Mn$_2$O$_3$.
- The mechanisms for Hg^0 removal over spinel LiMn$_2$O$_4$ were discussed.

ARTICLE INFO

ABSTRACT

Spinel LiMn$_2$O$_4$ was prepared using a sol–gel method to investigate gaseous elemental mercury (Hg^0) removal performance from coal-fired power plants. The physical and chemical characterization results indicated that LiMn$_2$O$_4$ had a basic MnO$_6$ unit and Li ions in the spinel λ-MnO$_2$ structure. LiMn$_2$O$_4$ exhibited better Hg^0 removal performance than that of pure Mn$_2$O$_3$ and mixed oxides of Li$_2$O–Mn$_2$O$_3$. Hg^0 removal efficiency of LiMn$_2$O$_4$ was 93.09% (600 min reaction) at an optimum temperature of 150 °C. Higher temperature (>200 °C) was not favorable for Hg^0 removal. O$_2$ enhanced the Hg^0 removal efficiency of LiMn$_2$O$_4$, while SO$_2$ and H$_2$O inhibited the reaction, and the co-existence of them had a poison effect on Hg^0 removal. The primary Hg^0 removal mechanism was chemical-adsorption, Hg^0 was firstly catalytic oxidized to Hg^{2+} along with the reduction of high valance of Mn (Mn^{4+}/Mn^{3+}) to low valance (Mn^{3+}/Mn^{2+}). Hg^{2+} was combined with adsorbed oxygen and existed as Hg–O on LiMn$_2$O$_4$ surface. The existence of Li ions constructs a λ-MnO$_2$ structure and benefits the oxidation process. Furthermore, based on the Hg-TPD results, the desorption activation energy was 58.82 kJ/mol.

1. Introduction

Elemental mercury (Hg^0) emitted from coal-fired power plants is hazardous in the atmosphere [1]. Up to now, many approaches had been developed to control the emission of Hg^0 [2–6]. According to the Hg^0 removal mechanism, it can be classified to two Hg^0 control methods: (1) catalytic oxidation of Hg^0 to oxidized mercury (Hg^{2+}) and (2) adsorption of Hg^0 by sorbents. Although the Hg^{2+} in the flue gas can be removed by wet flue gas desulfurization (WFGD) devices, mercury enriched in the slurry could cause mercury secondary contamination [7]. However, the adsorption of Hg^0 on the sorbents was not stable by physical-adsorption [8]. Enhancement of catalytic oxidation of Hg^0 to Hg^{2+}, followed by

chemical-adsorption was a potential method for the efficient mercury control.

Among various Hg^0 catalysts or sorbents, manganese-based oxides (MnO$_x$) were potential materials due to their higher redox potential, low cost and environmental friendliness. Bulk metal oxides have long been an interest as heterogeneous catalytic oxidation catalysts. To enhance Hg^0 removal performances of MnO$_x$, lots of manganese-based oxides have been developed and evaluated in the laboratory. Ce–MnO$_x$ [9,10], Sn–MnO$_x$ [11], Fe–MnO$_x$ [11,12] and other binary metal oxides were synthesized to enlarge Hg^0 adsorption capacities, to enlarge reaction temperature window and to enhance SO$_2$ resistance performance, etc. It was accepted that the Hg^0 removal mechanism can be described as follows: Hg^0 first adsorbed on the surface of MnO$_x$, followed the catalytic oxidation by high valance of Mn (Mn^{4+}/Mn^{3+}), after that the oxidized mercury combined with adsorbed oxygen to form Hg–O species. The primary Hg^0 removal process was ascribed to a

chemical-adsorption process. During this process, the higher surface area, sufficient adsorbed oxygen and higher valance state of Mn are beneficial for Hg^0 removal.

MnO_x occur naturally as minerals in at least 30 different crystal structures. Our recent studies found that the crystal structures of MnO_2 significantly affects Hg^0 catalytic oxidation and adsorption [13]. The Hg^0 removal performance over α-, β- and γ-MnO_2 has an order of α-$MnO_2 > \gamma$-$MnO_2 \geqslant \beta$-MnO_2. It has been acknowledged that high crystallinity would increase the stability and enhance the catalytic performance. Mn-based perovskite oxides have indicated to have high gas-phase heterogeneous catalytic oxidation performance [14,15]. Moreover, among Mn-based perovskite oxides, $LaMnO_3$ had superior catalytic removal performance for Hg^0 [16,17]. The effects of crystal structure of manganese oxides on the catalysis activity showed be further developed.

Spinel $LiMn_2O_4$ was an interesting cathode material for lithium-ion batteries due to its low cost, low toxicity and high voltage [18]. $LiMn_2O_4$ exhibited three-dimensional frameworks, comprising MnO_6 octahedral units and coexisting Li ions. In general, Li ions can be fully extracted from the spinel framework of $LiMn_2O_4$ to produce a spinel-type λ-MnO_2 that $LiMn_2O_4$ often acted as Li^+ ion selective adsorbent. And it has been reported that $LiMn_2O_4$ had a water oxidation performance because the role of λ-MnO_2 [19,20]. However, to our knowledge, there were still no reports about using spinel $LiMn_2O_4$ for the gas-phase heterogeneous catalytic oxidation.

In this study, $LiMn_2O_4$ was synthesized to investigate the Hg^0 removal performance. The BET, XRD, Raman, H_2-TPR and XPS were employed for the chemical and physical characterization. The Hg^0 removal performance was evaluated in a fixed-bed adsorption system. The effects of gas components and the mechanism for Hg^0 removal was discussed. Furthermore, the mercury release performance was evaluated and the desorption energy was calculated.

2. Experimental section

2.1. Materials preparation

$LiMn_2O_4$ was synthesized according to the citrate complexation procedure. Stoichiometric amounts of the metallic nitrates ($LiNO_3$ and $Mn(NO_3)_3$) were firstly dissolved in the distilled water. Thereafter, an aqueous solution of citric acid (CA), was slowly added to the precursor solution under gentle stirring. The molar ratio of Li:Mn:CA was 1:1:2. Solvent evaporation was performed at 80 °C until the formation of gel. After vigorous stirring and evaporation, a transparent gel was formed, which was dried at 100 °C overnight. The obtained precursor was calcined at 300 °C for 1 h in air to completely decompose citric acid followed by calcination at 500 °C for 5 h at a rate of 10 °C/min. Mn_2O_3 and Li_2O were also synthesized according to the same sol–gel method. Additionally, the physical mixed oxides of Li_2O–Mn_2O_3 were synthesized for comparison.

2.2. Materials characterization

X-ray diffraction (XRD) was carried out using X-ray diffractometer equipped with a Cu–Kα radiation (APLX-DUO, BRUKER, Germany). Diffractograms were collected in the 2θ range from 10° to 80° with a scanning velocity of 5°/min. Raman spectroscopy was used for the determination of the crystallinity degree of the materials. The analyses were performed in a SENTERRA R200 microscope. The 633 nm line of Ar^+ laser was used for the excitation. The multipoint Brunauer–Emmett–Teller (BET) surface areas and pore analysis were performed using a N_2 sorption measurement (Nova-2200e) at 77 K. The pore size and pore volume were

calculated based on the Barrett–Joyner–Halenda (BJH) method. X-ray photoelectron spectroscopy (XPS) was used to analyze the surface characteristics of as-prepared materials. The XPS system contained an AXIS Ultra DLD (Shimadzu–Kratos) spectrometer with Al–Kα as the excitation source. The C 1 s line at 284.6 eV was taken as a reference for the binding energy calibration. The reducibility of the samples was determined using H_2-TPR experiments, and these experiments were performed on a Chemisorp TPx 290 instrument. The samples were degassed at 200 °C for 3 h under an Ar atmosphere prior to the tests, and the reducing gas consisted of 10% H_2/Ar.

A mercury-temperature programmed desorption (Hg-TPD) method was employed to investigate the regeneration characteristics of the as-prepared materials. After mercury adsorption at 150 °C with 4% O_2 for 30 min, the sorbents were regenerated by heating from 100 to 700 °C in a pure N_2 carrier gas. Hg-TPD curves under different heating rates (2 °C/min, 5 °C/min and 10 °C/min) on the $LiMn_2O_4$ surfaces were collected. The desorption activation energy was also calculated according to the results.

2.3. Hg^0 fix-bed adsorption

A lab-scale fixed-bed adsorption system was assembled, as shown in Fig. 1, to explore the uptake capacity of Hg^0 by the as-prepared materials. The experimental method was similar to our previous studies [21]. The fixed-bed reactor was constructed to allow for a total gas flow of 500 ml/min. Temperature control devices were installed to control the mixed gas and the reactor temperature. The reaction temperatures range from 100 to 300 °C. 20 mg of as-prepared materials were used for each experiment and it was put in a quartz tube with a diameter of 4 cm. During the Hg^0 removal experiments, the mercury inlet gas bypassed the as-prepared material and then passed into the analytical system until the desired inlet mercury concentration was established. The mercury analyzer was CVASS in this study. Before each test, the Hg^0 concentration was adjusted by Lumex RA 915. In addition, active carbon was used for the off-gas cleaning. It can adsorb the mercury (Hg^{2+} and Hg^0) in the flue gas. $KMnO_4$ was used for adsorbed the oxidized mercury.

To investigate the effect of temperature on the flue gas, the area under the breakthrough curves corresponding to Hg^0 on the prepared sorbents during the test time was integrated. To investigate the effects of various gas components, 4% O_2, 500 ppm SO_2 and 4% H_2O were chosen when needed. These gases were firstly get through a mixed gas tank.

The Hg^0 removal efficiency was calculated according to Eq. (1):

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$$x\mathrm{Hg} = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$Hg^0 \text{ removal efficiency} = \frac{Hg_{in}^0 - Hg_{out}^0}{Hg_{in}^0} \tag{1}$$

where Hg_{in}^0 was the inlet concentration of Hg^0, and Hg_{out}^0 was the outlet concentration of Hg^0.

3. Results and discussion

3.1. Physicochemical properties

Fig. 2 presented X-ray diffraction (XRD) patterns of the as-prepared samples. The XRD patterns of Li_2O, Mn_2O_3 $LiMn_2O_4$ and Li_2O–Mn_2O_3 samples was collected. For Li_2O, it existed in an amorphous phase. The peaks in the pure manganese oxide was ascribed
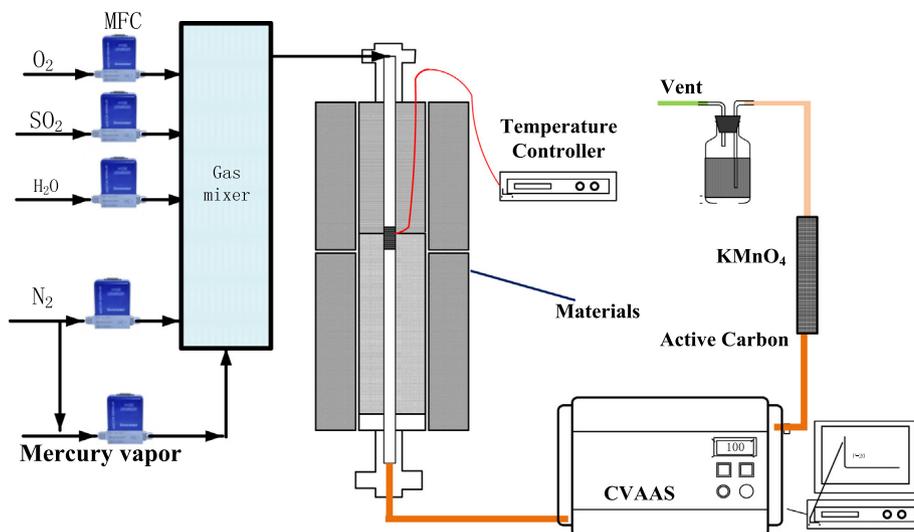
Fig. 1. Process flow diagram for mercury removal assessment.

to Mn_2O_3 in accordance with PDF card of No. 24-0508. For $LiMn_2O_4$, the peaks at 18°, 35°, 43°, 58°, 63° and 67° were well-defined structure in good agreement with spinel $LiMn_2O_4$ with PDF card of No. 35-0782 [22]. There were no other phases in the patterns of $LiMn_2O_4$. It indicated that the spinel $LiMn_2O_4$ was successfully synthesized. For comparison, the XRD pattern of $Li_2O–Mn_2O_3$ mixed oxide was collected. Interestingly, $Li_2O–Mn_2O_3$ has mixed phases of Mn_2O_3 and spinel $LiMn_2O_4$. There were no patterns can be ascribed to Li_2O. It could be speculated that the flexible Li^+ ions could enter into manganese oxide to form $LiMn_2O_4$, and residual Mn_2O_3 still remain its own crystal phase.

To further investigate the structural features of as-prepared samples, Raman spectra was employed and the results are shown in Fig. 3. In the spinel $LiMn_2O_4$, it had a wide peak centered at 641 cm^{-1}, it was the characteristic of vibrations involving motion of oxygen atoms inside the octahedral MnO_6 unit. The basic structure of manganese oxides was MnO_6 octahedral unit, and that the Raman shift was at about 600–700 cm^{-1} [23,24]. The vibrations were detected at 689 and 615 cm^{-1} for Mn_2O_3 and $Li_2O–Mn_2O_3$, respectively. However, the intensity of $LiMn_2O_4$ was stronger than that of Mn_2O_3 and $Li_2O–Mn_2O_3$, which indicated a better
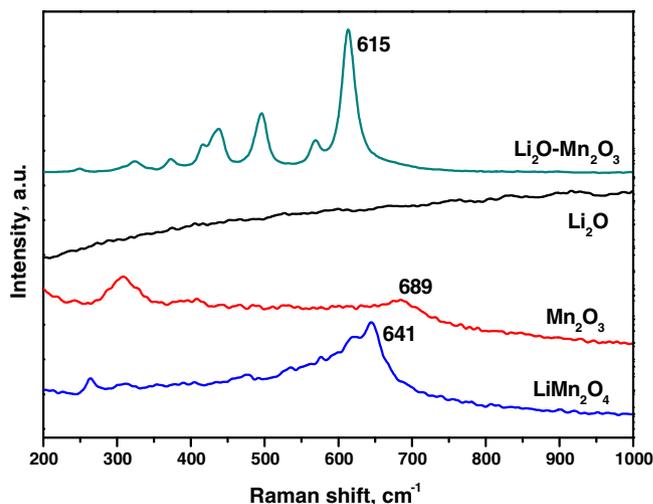
Fig. 3. Raman spectra of as-prepared samples.

crystallization. The bands of $LiMn_2O_4$ and $Li_2O–Mn_2O_3$ broadened and down-shifted when the particles became smaller. For instance, the distinct features at 689 cm^{-1} for bulk Mn_2O_3 shifted to 641 cm^{-1} for $LiMn_2O_4$, accompanied by broadening of the bands. The formation of $Li_2O–Mn_2O_3$ had smaller particle size than $LiMn_2O_4$.

As presented in Table 1, the BET surface areas and pore properties of the as-prepared materials were analyzed. Mn_2O_3 had a small BET surface area of 11.2 m^2/g. It is smaller than that of Li_2O (40.1 m^2/g). For $LiMn_2O_4$, the BET surface area (41.2 m^2/g) which was much larger than that of Mn_2O_3. The pore size of $LiMn_2O_4$ and Mn_2O_3 were 3.618 and 3.825 nm, respectively. However, the pore volume of $LiMn_2O_4$ was three times larger than that of Mn_2O_3. The sufficient pores in $LiMn_2O_4$ resulted in the higher surface area. In addition, $Li_2O–Mn_2O_3$ had the largest BET surface area (53.2 m^2/g) among the as-prepared samples. The physical mixed oxides had large pore volume which was 0.812 m^3/g. After Li^+ ions entered into the basic octahedral MnO_6 unit, the surface area of prepared Mn-based material was enlarged.

The chemical compositions of $LiMn_2O_4$ were analyzed by X-ray photoelectron spectra (XPS). As XPS spectra shown in Fig. 4(a), in the region of O 1 s, Li_2O had only one peak at 531.3 eV, the high
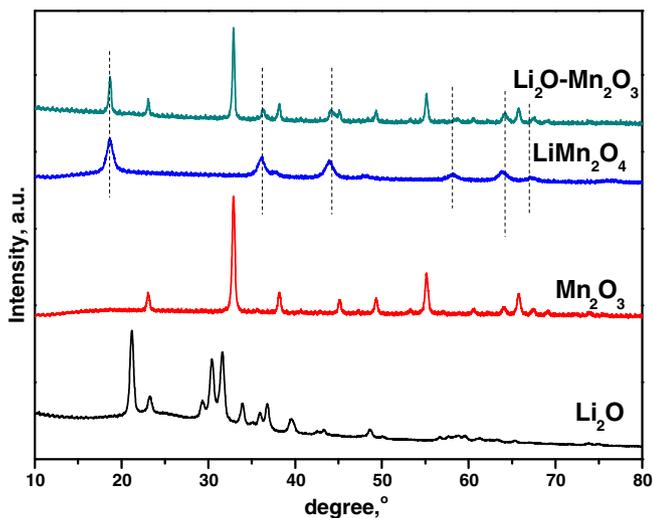
Fig. 2. XRD patterns of as-prepared samples.

Table 1
BET surface area, BJH pore properties and XPS analysis of as-prepared materials.

Materials	BET surface area (m^2/g)	Pore volume (m^3/g)	Pore size (nm)	O (%)		Mn (%)	
				O_{ads}	O_{latt}	Mn^{4+}	Mn^{3+}
Li_2O	40.1	0.073	3.825	100	–	–	–
Mn_2O_3	11.2	0.051	3.301	44.24	55.76	–	100
$LiMn_2O_4$	41.2	0.154	3.618	39.32	60.68	21.88	78.12
$Li_2O–Mn_2O_3$	53.2	0.812	3.646	55.92	44.08	–	100
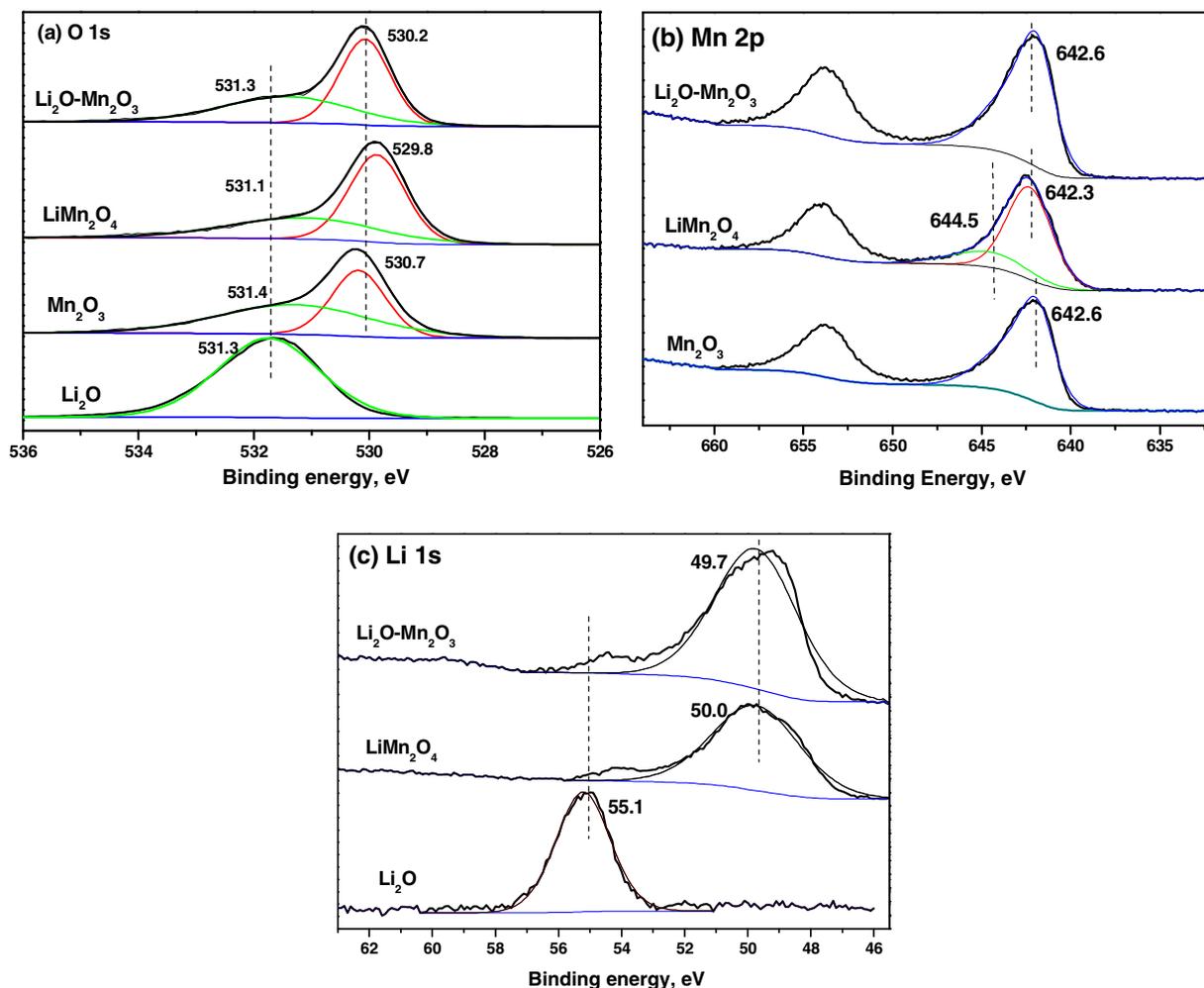
Fig. 4. XPS profiles for $LiMn_2O_4$, Mn_2O_3, Li_2O and $Li_2O–Mn_2O_3$.

binding energy of such oxygen indicated the instability of Li_2O. For Mn_2O_3, two peaks at 531.4 and 530.7 eV were corresponded to the surface adsorbed oxygen (O_{ads}) and lattice oxygen (O_{latt}), respectively [21]. Similarly, $LiMn_2O_4$ and $Li_2O–Mn_2O_3$ had these two character peaks which can be ascribed to O_{ads} and O_{latt}. However, the ratio of O_{ads}/O_{latt} was quite a different. From the results listed in Table 1, the ratio of O_{ads}/O_{latt} for Mn_2O_3 and $LiMn_2O_4$ were 44.24/55.76 and 39.32/60.68, respectively. $Li_2O–Mn_2O_3$ had the highest ratio of 55.92/45.08. It had been proven that O_{ads} was the adsorption site for the oxidized mercury. The higher concentration of surface adsorbed oxygen was due to the mobility of Li ions. Li ions entered into Mn_2O_3 and formed spinel $LiMn_2O_4$, resulted in the residual oxygen on its surface.

As shown in Fig. 4(b), in the spectra of Mn 2p, for $LiMn_2O_4$, the peaks at 644.5 and 642.3 eV were corresponded to Mn^{4+} and Mn^{3+}, respectively. The ratio of Mn^{4+}/Mn^{3+} was 21.88/78.12. for

Mn_2O_3, the peaks detected at 642.6 eV was ascribed to Mn^{3+}. $Li_2O–Mn_2O_3$ had one peak at 642.6 eV and it was ascribed to Mn^{3+}. The spinel $LiMn_2O_4$ had higher valance of Mn which was due to the unstable of Li^+ in $LiMn_2O_4$. Generally, with the addition of Li ions in the manganese oxides, the reaction of "$2Mn^{3+} = Mn^{4+} + Mn^{2+}$" occurred. Therefore, the binding energy of Mn^{3+} for $LiMn_2O_4$ was lower than that of Mn_2O_3. Li ions ascend the valance of Mn in $LiMn_2O_4$ which was beneficial for catalytic oxidation.

In the region of Li 1 s, as shown in Fig. 4(c), for Li_2O, the line has a binding energy centered at 55.1 eV, the low binding energy indicated that Li has low electron binding capacity. But for $LiMn_2O_4$ and $Li_2O–Mn_2O_3$, they presented two peaks on their spectra. One small peak at 55.1 eV and another primary peak at approximately 50.0 eV. The co-existence of Li and Mn resulted in the higher mobility of Li ions in the spinel $LiMn_2O_4$ structure.

Based on the above discussion, $LiMn_2O_4$ was synthesized using simple sol–gel method, it existed a basic spinel structure. With the addition of Li ions in the Mn-base structure, the surface area was enlarged and the valance of Mn was increased.

3.2. Hg^0 removal performances over $LiMn_2O_4$

3.2.1. Hg^0 removal efficiencies over as-prepared samples

The Hg^0 removal performances over the as-prepared materials were tested, and the results are shown in Fig. 5. Obviously, Li_2O had nearly no activity for Hg^0. Mn_2O_3 had 90% Hg^0 removal efficiency in the initial 100 min. But it gradually lost its activity for Hg^0, it had only approximately 23% Hg^0 removal efficiency after 600 min reaction. For $LiMn_2O_4$, it presented excellent performance for Hg^0 removal, the Hg^0 removal efficiency was higher than 99% even after 600 min reaction. $LiMn_2O_4$ showed quite a different performance compared to that of Mn_2O_3. In order to further indenfy the effect of crystal structure, the performance of the mixed oxide ($Li_2O–Mn_2O_3$) was investigated. The Hg^0 removal performance was not as well as $LiMn_2O_4$, even was worse than Mn_2O_3. The Hg^0 removal efficiency drop rapidly, and the Hg^0 removal efficiency was only approximately 30% after 600 min reaction. As discussed above, the mixed oxide of $Li_2O–Mn_2O_3$ had largest surface area among the as-tested materials, and it had a mixed phase of Mn_2O_3 and spinel $LiMn_2O_4$. However, it didn't showed a better performance for Hg^0 removal. The bulk partiles of $Li_2O–Mn_2O_3$ resulted in the larger pore volume and surface area. However, the primary Mn active sites was occupied and the catalytic effect of $LiMn_2O_4$ can't exhibit. The results confirmed that spinel $LiMn_2O_4$ was favorable for Hg^0 removal.

3.2.2. Effect of temperature on Hg^0 removal efficiencies over $LiMn_2O_4$

The effect of reaction temperature on Hg^0 removal efficiencies over $LiMn_2O_4$ were investigated at a wide reaction temperature window (100–300 °C). For comparison, the performances of Mn_2O_3 and $Li_2O–Mn_2O_3$ were also investigated. The Hg^0 removal efficiencies were calculated based on the total 600 min reaction. As shown in Fig. 6, $LiMn_2O_4$ had higher than 90% removal efficiencies at 100 and 150 °C, and the highest removal efficiency was 93.09% at 150 °C. However, the Hg^0 removal efficiencies decreased sharply as the reaction temperature increased to 200 °C, it had only 52.4% Hg^0 removal efficiency. As the temperature rising, the Hg^0 removal efficiencies further decreased. For Mn_2O_3, the highest Hg^0 removal efficiency was 80.1% at 100 °C. The Hg^0 removal effi-

Fig. 6. Effect of temperature on Hg^0 removal efficiencies.

Fig. 7. Effect of O_2, SO_2 and H_2O on Hg^0 removal efficiencies. (b) N_2, (b) 4% O_2, (c) 8% O_2, (d) 500 ppm SO_2 + 4% O_2, (e) 4% H_2O + 4% O_2 and (f) 500 ppm SO_2 + 4% H_2O + 4% O_2.

ciency decreased sharply as the temperature increased, and it had only approximately 32% Hg^0 removal efficiency when the temperature was 300 °C. The mixed oxide $Li_2O–Mn_2O_3$ had approximately 40% Hg^0 removal efficiencies at 100–150 °C. And the Hg^0 removal efficiencies were decreased as the temperature rising. Obviously, as-prepared Mn-based material lost their activities when the temperature was higher than 200 °C, $LiMn_2O_4$ had the best performance at 150 °C. The material can be used downstream of the electrostatic precipitator/fan filter (ESP/FF) units in a coal-fired power plant.

3.2.3. Effect of O_2, SO_2 and H_2O on Hg^0 removal efficiencies over $LiMn_2O_4$

Furthermore, the effects of gas components on Hg^0 removal efficiencies over $LiMn_2O_4$ were investigated and the results are presented in Fig. 7. In the absence of O_2, Hg^0 removal efficiency was 79.1%, which is the average removal efficiency of total 600 min. When the simulated gas had 4% O_2, the Hg^0 removal performance was enhanced, the calculated Hg^0 removal efficiency was 93.09%. To further investigate the effect of O_2 on Hg^0 removal, 8% O_2 was added in the simulated gas, the Hg^0 removal efficiency was increased to 95.45%. Obviously, O_2 was favorable for Hg^0 removal and it was in accordance with previous studies [21,25]. The effect of H_2O and SO_2 were also investigated. In the presence of

Fig. 5. Hg^0 removal efficiencies over different materials.
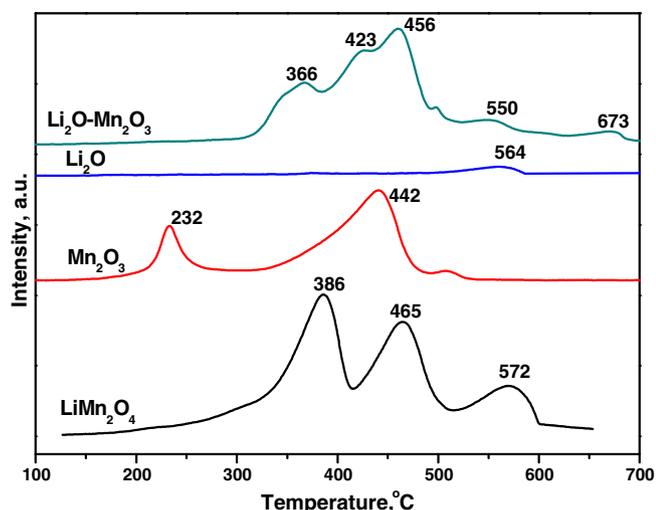
Fig. 8. H_2-TPR profiles of as-prepared samples.

500 ppm SO_2 + 4% O_2, the Hg^0 removal efficiency decreased to 81.35%. The Mn based materials suffer from the poison of SO_2, the sulfate generated on the surface, resulted in the inactivation of Mn active sites. When the gas component was 4% H_2O + 4% O_2, the Hg^0 removal efficiency was only 51.98%. H_2O also had higher poison effect on Hg^0 removal compared to that of SO_2. With 500 ppm SO_2 + 4% H_2O + 4% O_2, the Hg^0 removal efficiency decreased to only 20.72%. The co-existence of SO_2 and H_2O had a severe poisoning effect on Hg^0 removal.

3.3. Hg^0 removal mechanism over $LiMn_2O_4$ spinel oxide

As discussed above, $LiMn_2O_4$ presented excellent performance for Hg^0 removal. The large surface area and the special spinel structure was beneficial for Hg^0 removal. The Hg^0 removal mechanism was generally ascribed to catalytic oxidation and chemical-adsorption process. The reducibility of the as-prepared samples was analyzed using H_2-temperature programmed reduction (H_2-TPR) (Fig. 8). For Mn_2O_3, two obvious peaks were detected at 232 and 442 °C, the peak at low temperature was ascribed to the reduction of surface oxygen and the peak at higher temperature were assigned to $Mn^{3+} \rightarrow Mn^{2+}$.[13] In the profile of Li_2O, there is a weak peak at high temperature of 564 °C and it can be ascribed to $Li^+ \rightarrow Li^0$. For $LiMn_2O_4$, three characteristic peaks were presented, the peaks at 386 and 465 °C could ascribed to $Mn^{4+} \rightarrow Mn^{3+}$ and $Mn^{3+} \rightarrow Mn^{2+}$, respectively. As the temperature rising, a peak at 572 °C can be ascribed to $Li^+ \rightarrow Li^0$. With the addition of Li ions in $LiMn_2O_4$, the valance of Mn was increased, resulted in the higher reducibility. For $Li_2O–Mn_2O_3$, it presented five character peaks in its profile, these peaks were ascribed to the reduction of $Mn^{4+} \rightarrow Mn^{3+}$, $Mn^{3+} \rightarrow Mn^{2+}$, $Li^{2+} \rightarrow Li^0$ and the interaction between Li and Mn ions (such as $Li^+ + Mn^{3+} \leftrightarrow Li^0 + Mn^{4+}$ and $Li^+ + Mn^{2+} \leftrightarrow Li^0 + Mn^{3+}$). Based on the H_2-TPR results, with the addition of Li, $LiMn_2O_4$ showed better reducibility than Mn_2O_3. The valance of Mn was increased based on the XPS results, and that the reduction of $Mn^{4+} + e^- \rightarrow Mn^{3+}$ offered an electrons for Hg^0 oxidation. The active Li^+ can acted as a good electron acceptor in the process which benefited catalytic oxidation.

After adsorption, the XPS spectra were presented in Fig. 9. For O 1 s, the peaks at 531.2 and 530.0 eV were corresponded to O_{ads} and
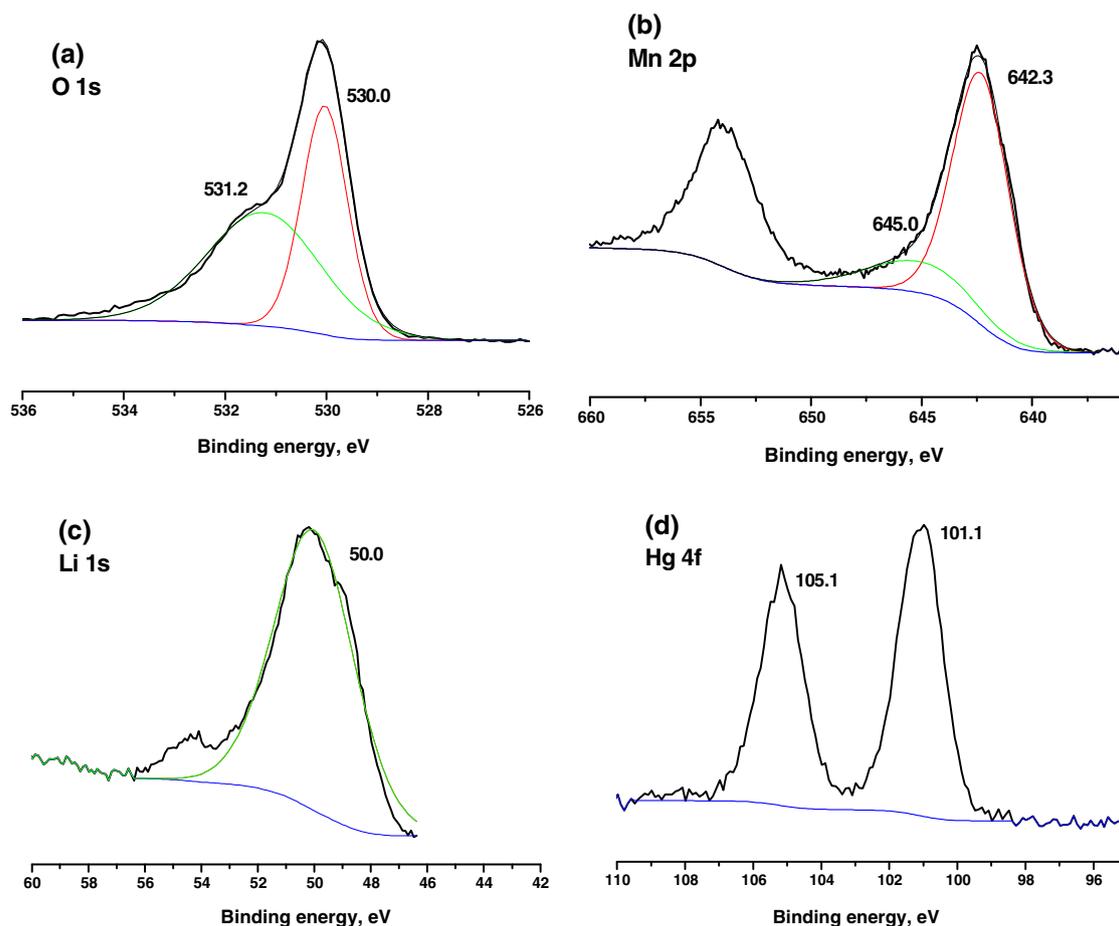
Fig. 9. XPS spectra of after adsorption $LiMn_2O_4$.
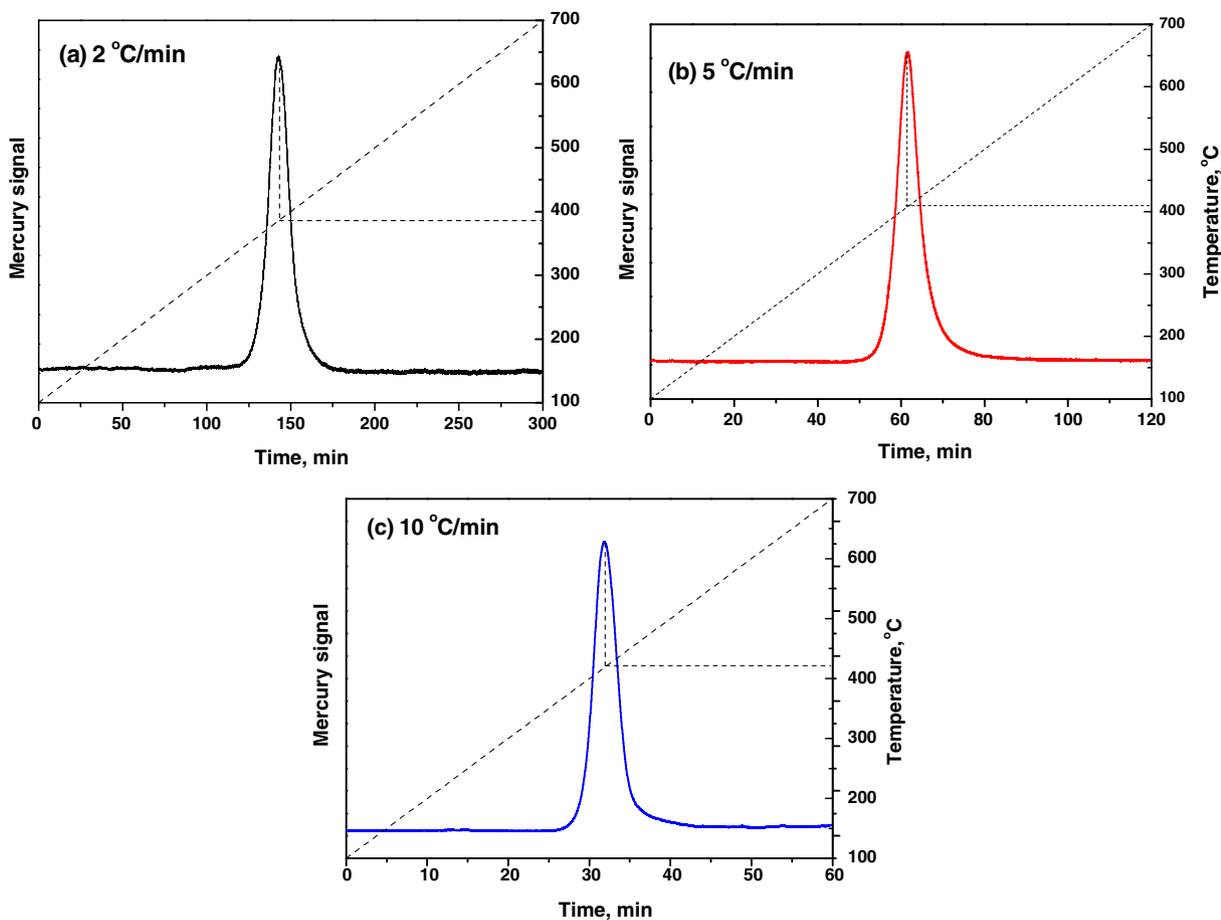
Fig. 10. Hg-TPD curves of LiMn$_2$O$_4$ at different heating rates.

O_{latt}. The ratio of O_{ads}/O_{latt} was 55.32/44.68. The ratio was a slight increase compared to that of the fresh sample. This could be the reason that LiMn$_2$O$_4$ had oxygen adsorption performance. For the spectrum of Mn 2p, the peaks at 645.0 and 642.3 eV were corresponded to Mn^{4+} and Mn^{3+}, respectively. But the ratio of Mn^{4+}/Mn^{3+} decreased from 21.88/78.12 to 18.86/81.14. Mn was the primary active sites for the catalytic oxidation. During the Hg^0 removal process, the high valance of Mn was reduced to the lower valance. In the spectrum of Li 1 s, it had nearly no change. But on the surface of after adsorption sample, mercury was detected. In the spectrum of Hg 4f, the peaks at 105.1 and 101.1 eV can be ascribed to Hg–O bond. This indicated that the Hg^0 removal process was a chemical-adsorption process.

Gaseous Hg^0 was firstly adsorbed on the surface of Mn-based materials. And then the Hg^0 was oxidized to Hg^{2+} along with the reducing of Mn^{4+} to Mn^{3+} or Mn^{3+} to Mn^{2+}. The Hg^{2+} was finally chemical-adsorbed by surface oxygen. The processed is attributed to the Mars–Maessen mechanism [26], were described as follows:

$$Hg^0(g) \leftrightarrow \equiv Hg^0(ads) \tag{2}$$

$$2\equiv Mn^{4+} + \equiv Hg^0(ads) \leftrightarrow 2\equiv Mn^{3+} + \equiv Hg^{2+} \tag{3}$$

$$2\equiv Mn^{3+} + \equiv Hg^0(ads) \leftrightarrow 2\equiv Mn^{2+} + \equiv Hg^{2+} \tag{4}$$

$$\equiv O^{2-} + \equiv Hg^{2+} \leftrightarrow \equiv Hg-O \tag{5}$$
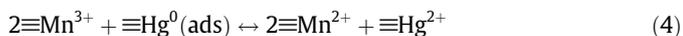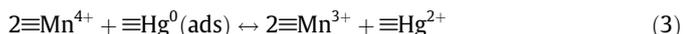
During the Hg^0 removal process, the free Li$^+$ in the MnO$_6$ units was beneficial for electron transfer.

$$LiMn_2O_4 \leftrightarrow Li_{1-x}Mn_2O_4 + xLi^+ + xe^- \tag{6}$$
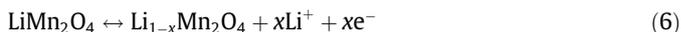
Base on H$_2$-TPR results, the Li$^+$ in the λ-MnO$_2$ was beneficial for the interaction with higher valance of Mn. So Mn keep the higher valance state. MnO$_2$ had higher valance of Mn compared to that of Mn$_2$O$_3$ or the mixed Li$_2$O–Mn$_2$O$_3$ which was beneficial for the higher catalytic performance.

3.4. Regeneration test

As shown in Fig. 10, the property of regeneration was tested using the Hg-TPD method, and the activation energy for desorption was calculated. The results of the Hg-TPD curves under different rates of heating on LiMn$_2$O$_4$ are shown in Fig. 10. During the desorption process at each heating rate, one primary peak emerged on the Hg-TPD curves, suggesting that Hg-O bond the main specie on the LiMn$_2$O$_4$ surface. According to the results, mercury could be released at approximately 400 °C under pure N$_2$ conditions.

Based on the desorption data under different rates of heating, the desorption activation energy was calculated according to Eq. (7):

$$2LnT_p - Ln\beta = \frac{E_d}{RT_p} - Ln\frac{E_d}{AR} \tag{7}$$

where T_p is the maximum value at a certain temperature (K), β is the heating rate (K/min), Ed is the desorption activation energy (kJ/mol), R is the gas constant, T is the temperature (K), and A is a pre-exponential factor. According to the Eq. (7), the desorption activation energies was 58.82 kJ/mol.

4. Conclusions

In summary, $LiMn_2O_4$ was synthesized the catalytic removal performance for Hg^0 was investigated. $LiMn_2O_4$ exhibited better performance compared to that of Mn_2O_3 and $Li_2O–Mn_2O_3$ mixed oxides. $LiMn_2O_4$ presented a spinel structure, with the addition of Li^+ ions, the surface area was enlarged. And the reducibility was enhanced. The Hg^0 removal mechanism can be described into two steps: (1) physical-adsorption: Hg^0 first adsorbed on $LiMn_2O_4$, the larger surface area benefited physical-adsorption; (2) catalytic oxidation-adsorption: Hg^0 was oxidized by the reduction of Mn and adsorbed with oxygen. Furthermore, after adsorption, the mercury on $LiMn_2O_4$ surface can release using thermal decomposition method. The released mercury can be collected which protected from mercury secondary contamination.

Acknowledgments

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