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Conversion of elemental mercury with a novel membrane catalytic system at low temperature

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ABSTRACT

A unique assembly, which integrated membrane delivery for oxidants with catalytic oxidation (MDCOs), was employed to convert elemental mercury (Hg^0) to its oxidized form at low temperature (around 150 °C). MnO_x was used as the main catalytic component in MDCOs with Mo and/or Ru to improve the catalytic activity. The MDCOs was proved to be very effective for the conversion of Hg^0 compared with the traditional catalytic oxidation mode (TCO). The analysis of speciation for Hg after catalytic oxidation showed that there was mainly mercury (II) chloride. The addition of transition metals of Mo and Ru obviously improved the conversion of Hg^0 to Hg^{2+} and enhanced the activity of the MDCOs at low temperature, and the conversion efficiency of Hg^0 reached 95% with Mo-Ru-Mn catalyst and 8 ppmv HCl. The inhibition of SO_2 to Hg^0 conversion in the MDCOs was insignificant. The Hg^0 removal exceeded 80% even if the concentration of SO_2 reached 1000 ppmv. The results also indicated that the Deacon reaction with the yield of Cl_2 were significantly improved after modified, and MDCOs with Mo-Ru-Mn catalyst can work efficiently at low temperature.

1. Introduction

Mercury (Hg) is one of the most concerned heavy metal contaminants, and coal combustion is an important emission source for atmospheric mercury [1,2]. Hg emission from coal-fired flue gas often presents in three main forms: elemental (Hg^0), gaseous divalent (Hg^{2+}) and particulate-associated (Hg(p)) [3], in which Hg^0 is the most difficult to be captured with the existing air pollution control devices [4].

Hg^0 in flue gases can be oxidized by HCl in the presence of certain catalysts. However, most of the investigated catalysts for this purpose can only work efficiently at higher temperature, such as above 523 K [5,6]. Thus these catalysts have to work upstream of air-preheater and particulate collection devices to meet such temperature window, where the deterioration of the catalyst by the high content of flyash in flue gas was often encountered [7]. In addition, the traditional catalytic oxidation mode (TCO) exists some shortcomings for Hg^0 oxidation [8,9]. First of all, Hg^0 in flue gas is just at the trace level (1–5 $\mu g\,m^{-3}$) [10], but the large amount of oxidants are needed to obtain high removal efficiency. Therefore, the efficiency of oxidants is rather low now for the most tested TCO modes. Moreover, introducing too much of oxidants into flue gas may bring the risk of secondary effect.

In order to overcome the shortcomings of TCO mentioned above, we have put forward a unique technology that integrated the membrane delivery and catalytic oxidation (MDCOs) for Hg^0 conversion at low temperature. The MDCOs used porous ceramic membrane doped with transition metals as catalyst. Based on the series of our previous experiments [11], it is found that the MDCOs system with MnO_x as the main catalytic component was very effective for Hg^0 conversion and displayed excellent sulfur-tolerant at the temperature of 573 K [11]. And the employed efficiency of oxidants is higher in the MDCOs. However, the performance of the MDCOs at low temperature is still unclear.

Furthermore, although some transition metal oxides (e.g., MnO_x) showed excellent performance for Hg^0 conversion at high temperature [11–15], most were less active at low temperature and SO_2 had significantly negative effect on Hg^0 conversion. Based on our preliminary tests [13], the activity of transition metal catalysts could be significantly enhanced by doping some metal oxides, such as molybdenum (Mo) or ruthenium (Ru).

Therefore, in order to well understand the performance of the MDCOs at low temperature, the conversion efficiency of Hg^0, efficiency of oxidants, the influence of catalyst composition and the different components of flue gas were mainly investigated. Meanwhile, the catalysts of MnO_x and MnO_x modified with Mo and/or

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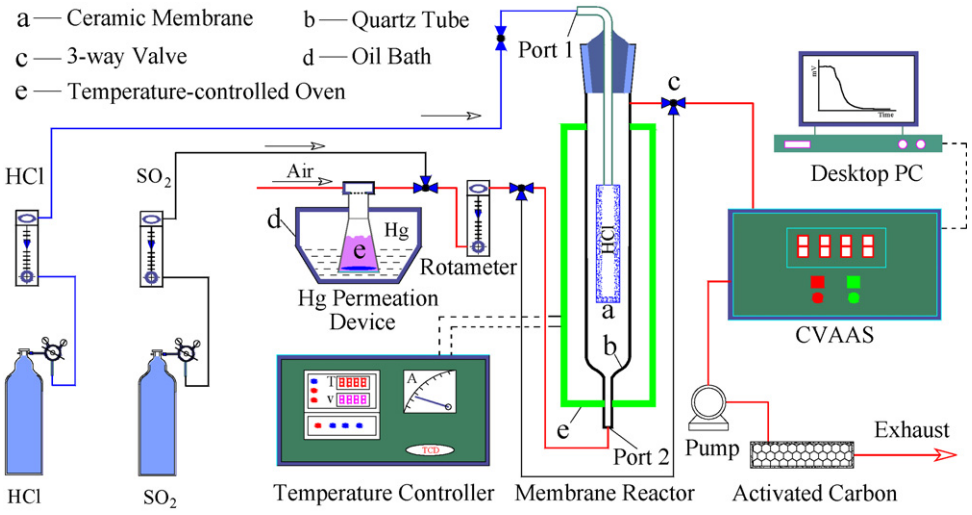

Fig. 1. Experimental scheme of the MDCOs system.

Ru were prepared and characterized together with their catalytic properties.

2. Experimental

2.1. Experimental assembly

The experimental assembly is shown in Fig. 1, which was used to evaluate the performance of Hg^0 conversion in the MDCOs system. The MDCOs reactor consisted of a quartz tube (360 mm in length with an inner diameter of 16 mm) and a tubular ceramic membrane mounted coaxially. The CVAAS (SG-921, Jiangfen Ltd.) was used to continuously monitor and acquire the inlet (C_0) or outlet (C) Hg^0 concentration of the reactor. The measurement for HCl, Cl_2 and SO_2 was carried out with the recommended method of gas detector tubes (Gastec, Japan).

As shown in Fig. 1, the injection of HCl from port 1 was considered as the MDCOs process. In addition, the process can be regarded as the TCO mode if HCl was injected from port 2, where HCl would be premixed with the simulated flue gas before contacting with catalysts.

2.2. Catalyst preparation

The MDCOs system employed a porous tubular membrane that was made of alumina (Al_2O_3, Hefei Great Wall Co. Ltd.), with pore diameter of 4.7 μm, inner diameter of 8 mm, outer diameter of 12 mm, Brunauer–Emmett–Teller (BET) surface of 4.1 $m^2\,g^{-1}$ and length of 50 mm. The catalysts were prepared by wet impregnation method and expressed as M or M-Mn, in which M represented the doped metals, i.e., Mn, Mo, Ru, Mo-Mn, Ru-Mn or Mo-Ru-Mn. The loading value of manganese to Al_2O_3 was set at 8 (±0.2) wt.% as default value in later experiments. The loading values of Mo and Ru to Mn were set at 1 mol% and 0.5 mol%, respectively. All chemicals, including the precursors of $Mn(NO_3)_2$, $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ and $RuCl_3{\cdot}3H_2O$, used for catalyst preparation were of analytical grade, and purchased from Sino-pharm Chemical Reagent Co.

2.3. Test conditions

The experiments were performed in the MDCOs at the temperature of 423 K with the simulated flue gas of SO_2 and/or HCl. Air was mixed as the source of O_2. All the gases were monitored with rotameters, and the total flow rate was set at 25.0 L h^{-1}. The flow rates of SO_2 and HCl were set at 2.0 and 1.0 L h^{-1}, respectively. The continuous operation time before acquire the data was set at 4 h at all tests if it was not clearly stated.

2.4. Analysis of sample characterization

The X-ray diffractometer (XRD, D/max-2200/PC, Rigaku Co., Japan) was used to determine the crystal structures of catalysts at 40 kV and 20 mA using Cu Kα radiation in the range of 20–80° (2θ) with a step size of 0.02°. The analysis of oxide specimens was performed with an X-ray photoelectron spectroscopy (XPS, PHI-5000C ESCA). The morphology of catalysts was scanned by a field emission scanning electron microscope (FE-SEM, SIRION 200, USA). An energy dispersive X-ray spectrometer (EDX, INCA OXFORD) was used to examine the distribution of doped element in catalysts.

3. Results

3.1. Removal of Hg^0 in MDCOs and TCO mode with Mn catalyst

Fig. 2 illustrates the removal of Hg^0 in the MDCOs and TCO mode with Mn catalyst under various conditions. The results showed that the removal efficiencies of Hg^0 in the TCO mode were far less than that in the MDCOs mode both at 423 K and 573 K. The removal efficiency of Hg^0 in the TCO mode hardly reached 60% even if 20 ppmv HCl was used at 573 K (Fig. 2(b)). In Fig. 2(a), it also shows that the removal efficiency of Hg^0 can reach 80% or higher in the MDCOs mode with the presence of 12 ppmv HCl. Compared with the removal of Hg^0 in the two modes, it was obvious that the MDCOs mode had obvious superiority at the removal of Hg^0 over the TCO mode at low temperature. However, Hg^0 conversion efficiency in MDCOs just with Mn as the catalyst was not high enough at low temperature even increasing the concentration of HCl to 20 ppmv. Therefore, it was necessary to further enhance the catalyst activity in MDCOs at low temperature.

3.2. Performance of catalytic oxidation with modified Mn catalysts

The elemental mercury conversion efficiencies with various transition metals are shown in Fig. 3. It can be seen that the activity of Mn catalyst was greatly improved after modification with Mo or Ru, and Mo-Ru-Mn catalyst had an optimal improvement on the removal of Hg^0 with efficiency of 95%. The analysis of Hg speciation

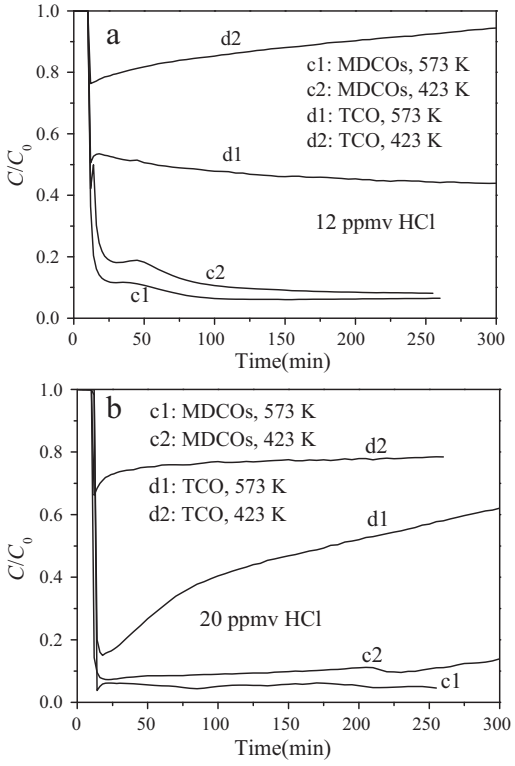

Fig. 2. Removal efficiencies of Hg^0 with Mn catalyst in the MDCOs and TCO mode at different conditions. Reaction conditions: $[SO_2] = 0$, C_0 was about 24.2 ppbv, and air was used as carrier gas.

showed that the proportion of mercury (II) chloride on the catalysts of Mn, Mo-Mn, Ru-Mn and Mo-Ru-Mn accounted for 63%, 71%, 91% and 93%, respectively. The results showed that the addition of transition metals of Mo and Ru can obviously increase the conversion of Hg^0 to Hg^{2+} in the MDCOs. Compared with Mn catalyst, the conversion of Hg^0 with Mo-Ru-Mn catalyst increased by 30%. As shown in Figs. 2 and 3, the removal of Hg^0 in MDCOs with Mo-Ru-Mn cannot only improve the conversion of Hg^0 but also save the amount of oxidants at low temperature of 423 K. It was also found that O_2 played an important role on the Hg^0 removal. When high purity N_2 was used as the carrier gas without oxygen, weak Hg removal was detected with efficiency of about 8% with Mn catalyst being present.

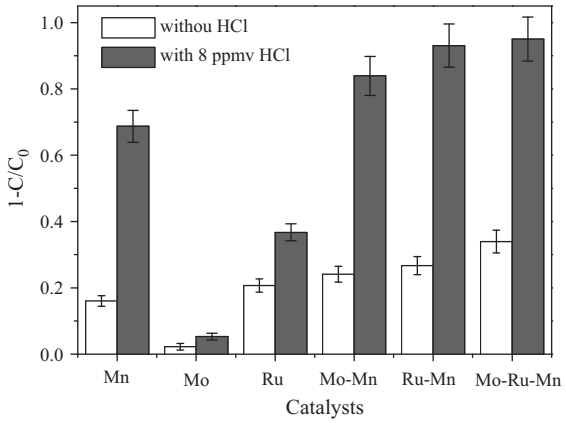

Fig. 3. Removal efficiencies of Hg^0 with the catalysts doped with various transition metals in the MDCOs mode. Reaction conditions: $[HCl] = 8$ ppmv, $[SO_2] = 0$, $T = 423$ K, C_0 was about 23.5 ppbv, and air was used as carrier gas.

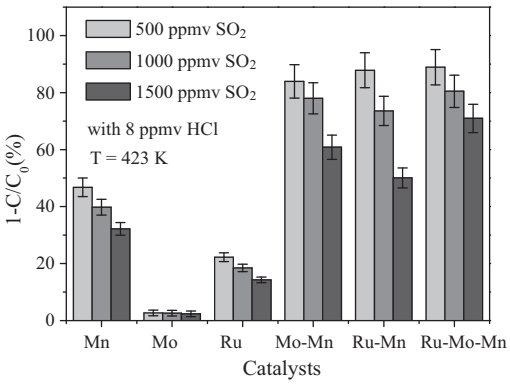

Fig. 4. Influence of SO_2 on the removal of Hg^0 with the catalysts doped with various transition metals at 423 K. Reaction conditions: $[HCl] = 8$ ppmv, C_0 was about 23 ppbv, and air was used as carrier gas.

3.3. *Effect of SO_2 on Hg^0 removal*

The results of gas-phase studies indicated that Mo and Ru had a promoting function for Mn catalyst on sulfur-tolerance to SO_2 at the test conditions. Compared with Mn catalyst, the modified catalysts with Mo or Mo/Ru showed good sulfur-tolerance to SO_2 (Fig. 4). The removal of Hg^0 reached about 90% when 500 ppmv SO_2 was introduced. The efficiency was far higher than that in the TCO mode shown in Fig. 2. Fig. 4 shows that the presence of SO_2 suppressed the capacity of the MDCOs for Hg^0 removal. However, the inhibition of SO_2 was insignificant. The removal of Hg^0 exceeded 80% even with 1000 ppmv of SO_2.

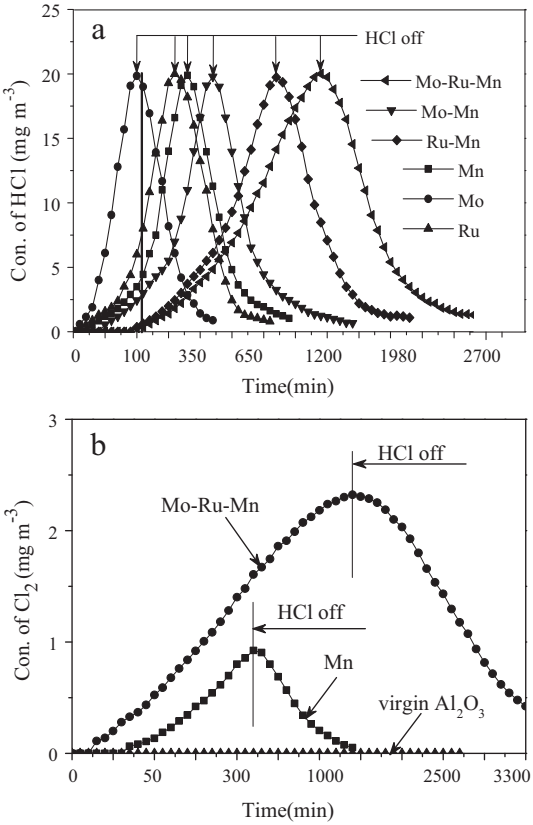

Fig. 5. Penetration curves of (a) HCl and (b) Cl_2 produced in the MDCOs at 423 K without Hg^0 in the gas. Reaction conditions: initial HCl concentration was about 20 mg m^{-3} with flow rate of 2.0 L h^{-1}.

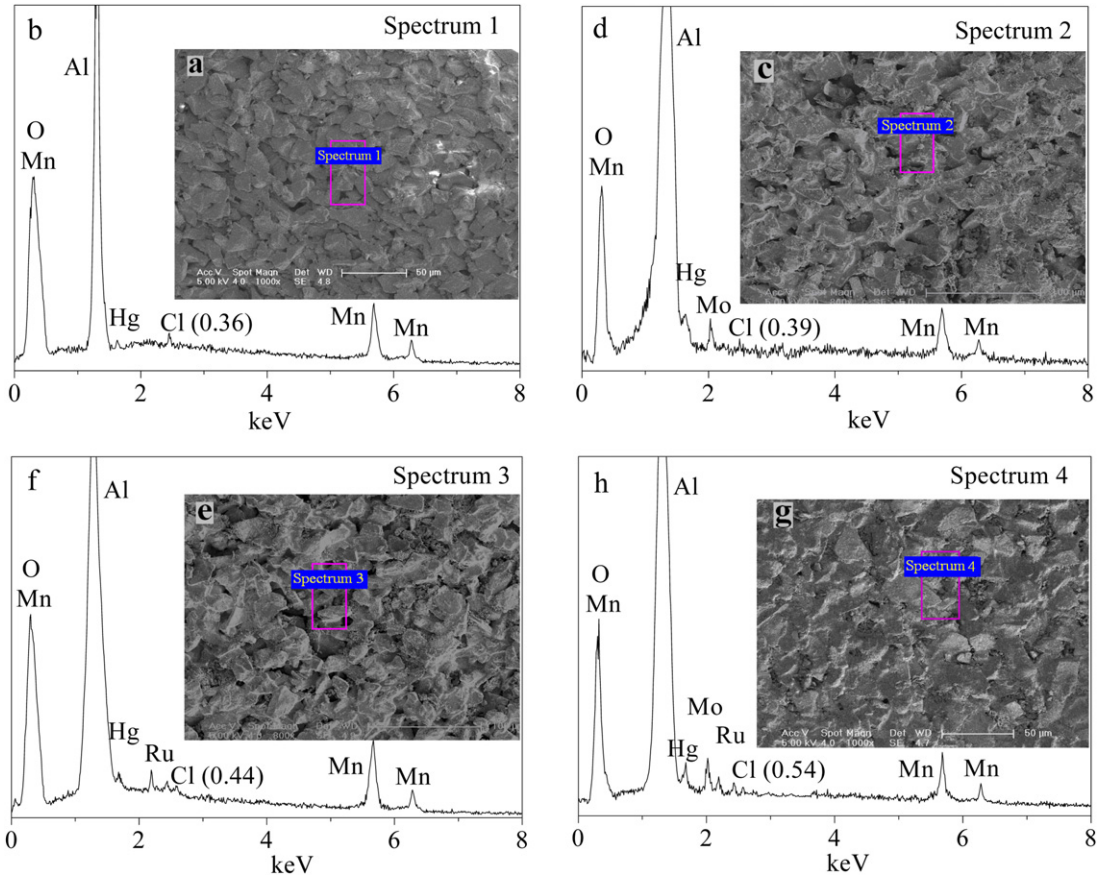

Fig. 6. FE-SEM and EDX spectra of the catalysts after HCl used. (a) and (b) Mn catalyst, (c) and (d) Mo-Mn catalyst, (e) and (f) Ru-Mn catalyst, and (g) and (h) Mo-Ru-Mn catalyst. The numbers in bracket are the contents of Cl (wt.%) on the surface of the catalysts. Reaction conditions: [HCl] = 8 ppmv, [SO_2] = 0, C_0 was about 24 ppbv, and air was used as carrier gas.

According to the literature, the formation of $HgSO_{4(ad)}$ may be occur due to the chemical adsorption of SO_2 and further conversion [16]. To confirm the presence of $HgSO_4$, the test analyzed the XPS spectrum of S 2p after SO_2 was used. On the basis of the result of S 2p XPS and combined with the spectra of Hg 4f and O 1s, it can be confirmed that Hg specie was assigned to $HgSO_4$ (BE 168.7 eV) by the XPS database of the National Institute of Standards and Technology (NIST) [17] and pervious literature [18].

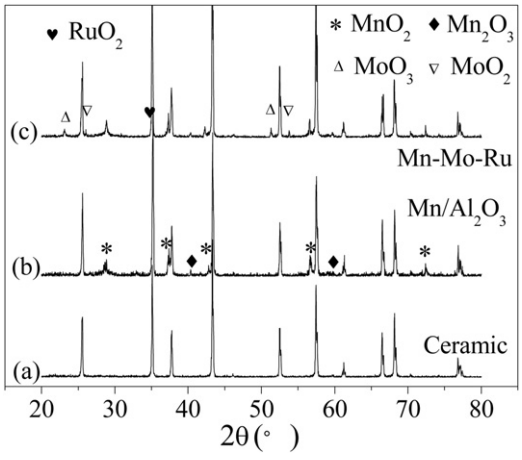

Fig. 7. X-ray diffraction patterns of (a) virgin ceramic tube, (b) Mn catalyst and (c) Mo-Ru-Mn catalyst.

3.4. Retainability and conversion of HCl

Previous studies have indicated that the Deacon process might be the predominant pathway for Hg^0 oxidation by HCl in the presence of catalysts [19,20], especially in the presence of Ru [21,22]. Moreover, chlorine (Cl_2) and Cl atom (hydrogen abstracted from HCl) are active intermediates [5,23], and their yield can be used as an identifier to evaluate the efficiency of the Deacon process in the MDCOs. Even though Cl_2/Cl concentration in coal-fired flue gas is very low, it is likely that Cl_2 is still in excess over Hg^0.

In addition, the penetration curves of HCl in the MDCOs were investigated, and the results were shown in Fig. 5. As shown in Fig. 5(a), the ceramic membrane doped with unmodified MnO_x displayed a significant retainability for HCl. The complete breakthrough time for Mn catalyst was about 6 h. And the retainability of ceramic membrane for HCl varied along with doped transition metals. Fig. 5(a) shows that Mo-Ru-Mn catalyst had the longest breakthrough time of 21 h, which might be favorable for the yield of Cl_2 and the conversion of Hg^0. The adsorbed equilibrium amount of HCl on the surface of Mn and Mo-Ru-Mn catalysts were 28 and 98 μg-HCl/g-tube at 423 K, respectively.

On the basis of the tests in Fig. 5, the sorbed HCl in MDCOs with various catalysts can be evaluated. When Hg^0 removal reached stable (about 120 min, the vertical solid line in Fig. 5(a)), the amount of escaped HCl for Mn, Mo, Ru, Mo-Mn, Ru-Mn and Mo-Ru-Mn catalysts were 4.4, 19.0, 8.0, 3.0, 0.6 and 0.4 mg m^{-3}, respectively. It can be seen that Mo-Ru-Mn catalyst had the lowest amount of escaped HCl (less than 2%).

The production of Cl_2(g) in the MDCOs was also monitored along with HCl penetration across the membrane (Fig. 5(b)). It was

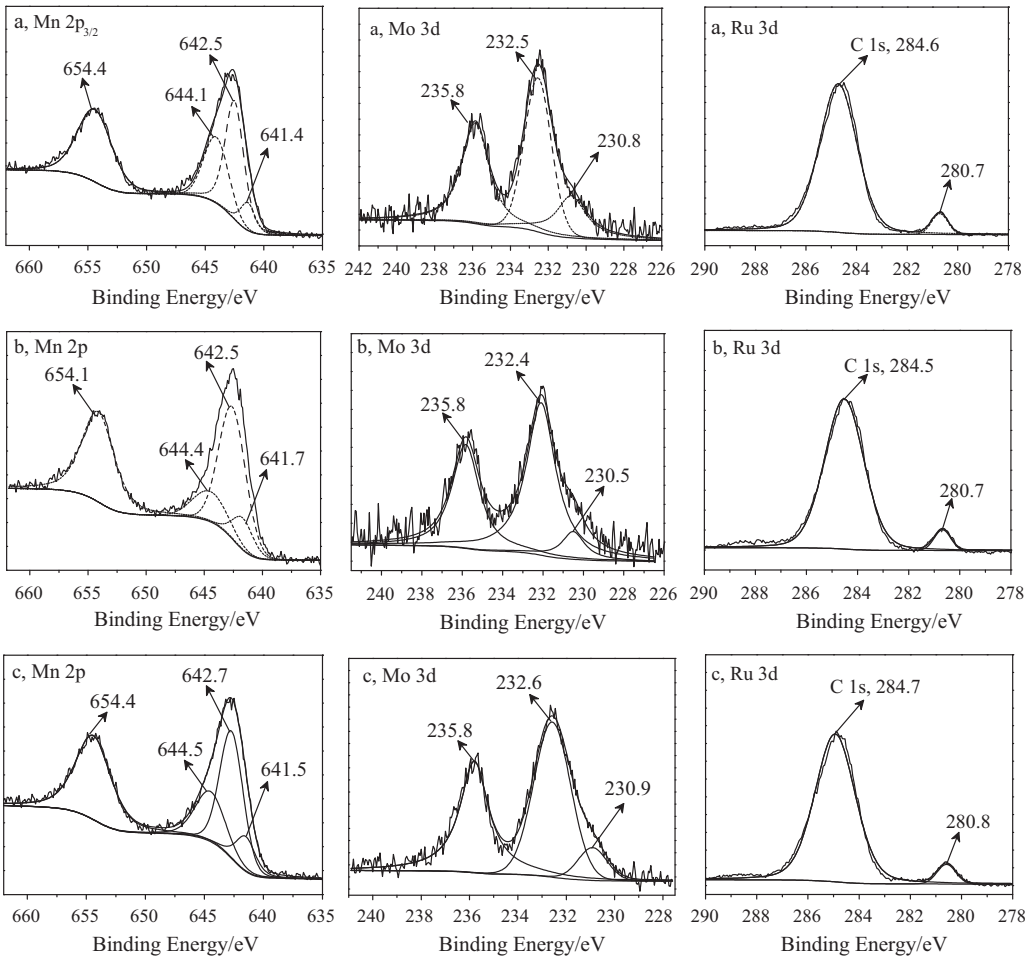

Fig. 8. XPS spectroscopes of Mn 2p, Mo 3d and Ru 3d (dash is fitted results). (a) Sample a, (b) sample b and (c) sample c. Mo-Ru-Mn catalyst was used. Air was used as carrier gas.

indicates that virgin ceramic membrane had no catalysis to the Deacon process. Though Cl_2 can be hardly detected out in the TCO mode, a higher Cl_2 yield was measured in the MDCOs and the maximum concentration of Cl_2 was about 2.3 mg m^{-3} (curve of Mo-Ru-Mn in Fig. 5(b)). By Comparison with Mn and virgin Al_2O_3 curves in Fig. 5(b), the Cl_2 yield from Mn catalyst doubled after modified with Mo and Ru. The results show that the Deacon process was greatly accelerated after the MDCOs was modified with Mo and Ru, resulting in the increasing of Cl_2 yield.

However, it is difficult to determine in situ the contents of atomic chlorine (reactive activated $[Cl]^*$ produced from the Deacon process) or adsorbed $HgCl_{(ad)}$ at the tested conditions. The EDX spectra of the different catalysts after catalytic oxidation for Hg^0 were used to analyze approximately the contents of atomic chlorine, and the results were shown in Fig. 6.

To eliminate the influence of chlorine derived from $RuCl_3$, the prepared catalysts were washed with 10 wt.% NH_4OH solution until both the XPS and EDX did not detected the existence of chlorine [24]. Fig. 6 shows that the amount (0.54 wt.%) of adsorbed Cl or Cl^- on Mo-Ru-Mn catalyst were more than that on Mn catalyst (0.26 wt.%), although we could not conclusively distinguish the speciation of Cl. It validates that the Deacon process was indeed accelerated after the MDCOs was modified with Mo or Ru.

3.5. Structural properties

The XRD patterns in Fig. 7(b) and (c) illustrate the primary diffraction peaks of manganese oxides, which are uniform with those of MnO_2 at $2\theta = 28.68^\circ$, 37.33°, 42.83°, 56.65°, and 72.26° (JCPDS 24-0735), respectively [25]. It is obvious that MnO_x mainly presented in the form of MnO_2 though the weak peak for Mn_2O_3 could also been observed. The presence of MoO_3 was confirmed by the diffraction peaks of the molybdenum (VI) at $2\theta = 23.12^\circ$ and 51.32°, (JCPDS 47-1081). Simultaneously, the MoO_2 was found at $2\theta = 26.04^\circ$ and 53.76° (JCPDS 50-0739). Fig. 7(c) shows that the ruthenium speciation was attributed to RuO_2, based on the characteristic peaks of ruthenium at $2\theta = 28.01^\circ$ (hardly shown) and 35.05° (JCPDS 40-1290 and 43-1027).

3.6. XPS analysis

In order to obtain the valence states of the catalysts after catalytic oxidation, three samples of Mo-Ru-Mn catalysts were analyzed with XPS technique. The results are shown in Fig. 8 and the binding energies of C 1s, Mn 2p, Mo 3d, Ru 3d, O 1s, Cl 2p and Hg 4f are listed in Table 1.

As shown in Fig. 8, the XPS results show that the Mn 2p peaks were not clearly changed after modified. The Mn $2p_{3/2}$ spectra in these samples indicated two peaks at 642.5 and 641.5 eV (listed in Table 1). By comparison with the Mn 2p XPS spectrum database in the NIST [17], MnO_x in these samples were determined to be mainly present in the states of Mn (IV) and Mn (III). The XPS spectra data showed that Mn (II) cation was not present. It was in good agreement with the XRD results.

The Mo 3d XPS spectra exhibited three characteristic peaks, including BEs of 232.5 eV, 235.8 eV and 230.8 eV. The former two

Table 1
XPS spectra data of C1s, Mn 2p, Mo 3d, Ru 3d, O 1s, Cl 2p and Hg 4f.

Samples	Binding energy (eV)								
	C 1s	Mn $2p_{3/2}$	Mo $3d_{5/2}$	Mo $3d_{3/2}$	Ru $3d_{5/2}$	O 1s	Hg $4f_{5/2}$	Hg $4f_{7/2}$	Cl 2p
a	284.6	642.5 641.4	232.5 230.8	235.8	280.7	532.5 530.6 529.8	–	–	–
b	284.5	642.5 641.7	232.4 230.5	235.8	280.7	532.3 530.6 529.6	104.5	100.8	–
c	284.7	642.7 641.5	232.6 230.9	235.8	280.8	532.4 530.8 529.6	–	101.6	198.7

peaks were attributed to Mo (VI), and the latter one corresponded to Mo (IV). The ratio of Mo (VI) to Mo (IV) in the samples b and c had little change, compared with that in the fresh catalysts. Based on the XPS data of Mn and Mo-Ru-Mn catalysts, the peak area ratio of Mn (IV) to Mn (III) had a slight increase after Mn catalyst was modified, with the value increased from 1.63 to 2.52 (shown in Table 1).

The O 1s spectra (shown in Fig. 9) of the three catalysts showed three fitted O 1s peaks, including O_a (mainly attributed to Al_2O_3, including little hydroxyl groups), O_b (mainly attributed to RuO_2, Mn_2O_3 and lattice oxygen O_d) and O_c (mainly attributed to MnO_2, MoO_x and chemisorbed O_e) [18]. Noticeably, the peak area of O 1s slightly increased after modified with Mo and Ru.

Fig. 10(b) shows that the Hg 4f spectrum of the sample b showed two peaks of 104.5 and 100.8 eV. Combined with the spectra of Hg 4f and O 1s, it can be confirmed that Hg speciation was assigned to HgO by the NIST XPS database [17]. However, the spectrum of the catalyst c was different from that of the sample b shown in Fig. 10(c). It had only one peak at 101.6 eV. Considering the spectra of Cl 2p and the BE of 101.6 eV (Hg $4f_{7/2}$), it can be confirmed that mercury was present in its bivalent state ($HgCl_2$) on the surface of the Mo-Ru-Mn catalyst after HCl was used.

The XPS spectrum (BE 281.9 eV) of ruthenium chloride was not observed. It indicates that almost all $RuCl_3$ were activated, which was in accordance with the above results of the EDX. The BEs of ruthenium and oxygen (Ru $3d_{5/2}$ at 280.7 eV and O 1s at 529.7 eV) were the characteristic of polycrystalline RuO_2 [26] and were identical to those in the fresh and used catalysts. The result was consistent with previous studies [24].

4. Discussion

4.1. Catalytic performance

Compared with the data shown in Fig. 2, the results indicated the catalytic performance of the MDCOs can be enhanced obviously for Hg^0 conversion with the addition of Mo or Ru. The efficiency was increased to 95% with Mo-Ru-Mn catalyst vs 68% for just with Mn catalyst at 423 K. The analysis of speciation for Hg after catalytic oxidation showed that there was mainly mercury (II) chloride on the surface of Mo-Ru-Mn catalyst. The distinctive difference between the unmodified and modified catalysts after contacting HCl was the obvious increase of chlorine in the latter as shown in Fig. 6. Besides, combined with the XPS analysis of spectra of Cl 2p and Hg 4f (shown in Table 1 and Fig. 10), there were much more amount of mercury (II) chloride on the surface of Mo-Ru-Mn catalyst. It was suggested that the atomic chlorine ($[Cl]^*$) produced from the Deacon process played a critical role during the process of Hg^0 conversion. Thus, the function of $[Cl]^*$ is supposed to be able to accelerate and improve the conversion of Hg^0 to Hg^{2+}.

To further verify the effect of $[Cl]^*$ on Hg^0 removal, a test was carried out with 0.5 ppmv Cl_2 (employed concentration in the simulated flue gas) as a substitute for HCl. The Cl_2 concentration of 0.5 ppmv was equal in the amount of Cl_2 produced from the Deacon process with 8 ppmv HCl. The results indicate that the mean efficiency of three replicate tests was below 50%, far less than that in the presence of HCl. The results further verified the activity of $[Cl]^*$ or the Deacon process in the MDCOs.

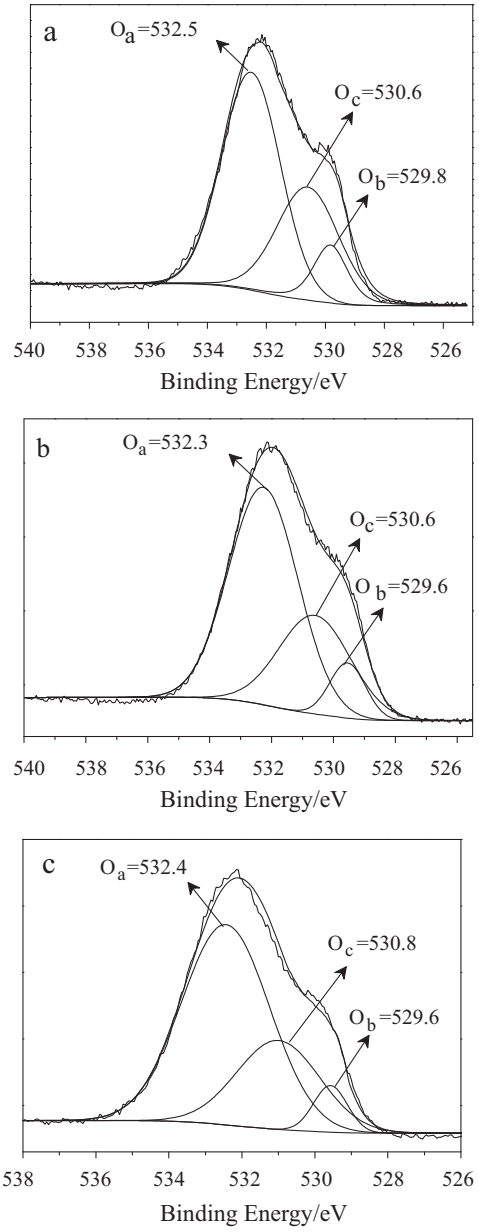

Fig. 9. O 1s XPS narrow scan spectra of Mo-Ru-Mn catalyst. (a) Sample a, (b) sample b and (c) sample c.

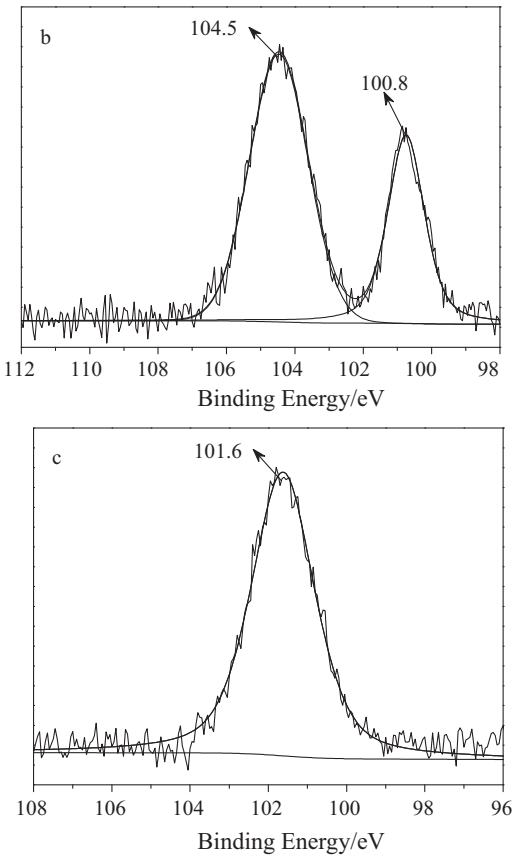

Fig. 10. Hg XPS spectroscopes of the Mo-Ru-Mn catalyst (dash is fitted results). (b) Sample b and (c) sample c.

The reaction between adsorbed $Hg_{(ad)}$ and O_2 (resulting in the formation of HgO) occurs at the temperature of 423 K [10]. However, the reaction process of $Hg_{(ad)}$ and $[Cl]^*$ has low energy barrier at room temperature, which is close to the collision limitation. Its Gibbs free energy at 423 K is highly negative, and its rate constant shows little temperature dependence [27]. An average rate constant for this reaction, 1.5×10^{13} cm^3 mol^{-1} s^{-1}, was suggested by Senior et al. [28]. So based on the spectrum database of Hg 4f XPS (Fig. 10(b)), it can be deduced that the formation of HgO was existent, although it may not be the main production.

From Fig. 5(b), it can be seen that the addition of transition metals, especially Ru, improved greatly the conversion of HCl to Cl/Cl_2, resulting in the increase of the proportion of mercury (II) chloride. The results indicate that the addition of transition metals changed obviously the speciation of Hg after catalytic oxidation. Therefore, it is evident that the Deacon process played an important role during the process of Hg^0 conversion. The results further confirmed the higher efficiencies of the MDCOs with Mo-Ru-Mn catalyst at low temperature.

Fig. 5(a) shows that most of injected HCl were retained in the MDCOs, which would be helpful to the sequential reactions for Hg^0 oxidation. Therefore, the retainability for oxidants and the mode of mass delivery in the MDCOs had a notable advantage for both the conversion of HCl and the conversion efficiency of oxidants. This can be used to partly explain the higher efficiency for Hg^0 removal and utilization for oxidants in the MDCOs.

That the conversion of HCl to Cl_2 was rather effective in the MDCOs, can be tentatively explained from the following aspects. Firstly, the concentration of adsorbed HCl on the surface of the catalysts in the MDCOs was supposed to be higher by far than that in the TCO mode [11], accordingly, the rate of Cl_2 produced from the Deacon process became rapid. Secondly, HCl could be adequately exposed to the catalysts as it was delivered across the porous wall of the membrane, resulting in the occurrence of the Deacon process.

Fig. 4 indicates that the addition of Mo and Ru was beneficial to the MDCOs ability for sulfur-tolerance. The previous results indicated that the amount of SO_2 adsorbed on the surface of catalysts decreased dramatically in the MDCOs, compared with that in the TCO mode with HCl being present [11].

Fig. 4 shows that the addition of Mo on Mn-base material greatly increased the removal efficiencies of Hg^0 and the efficiencies almost doubled compared to that in the presence of only Mn. The results and our previous studies all indicate that the larger affinity of Mo to sulfur would minimize the chance of the contact between sulfur and Mn, which was very beneficial for decreasing the deactivation or the coverage by SO_2 for Mn-base active sites [13]. Meanwhile, the affinity of Mo to sulfur could diminish the competitive adsorption between SO_2 and Hg^0 on active sites to some extent, which would result in the increase of removal efficiency by adsorption. Fig. 4 also confirms the above results, i.e., the addition of Mo had obvious exhibition for sulfur-tolerance, which would promote the contact between whether Hg^0 and Mn-base active sites or the catalysts and oxidants. Moreover, the HCl delivery mode in the MDCOs ensures its exposure to the catalyst preferentially. Therefore the Deacon process was accelerated because of preferential contact between oxidants and catalysts. All these improved the ability of the MDCOs for sulfur-tolerance, resulting in the occurrence of high removal of Hg^0 in the MDCOs, compared with that in the TCO mode.

Fig. 4 also shows obviously that the presence of SO_2 suppressed Hg^0 removal. However, the influence of SO_2 was insignificant. The influence of SO_2 on the removal of Hg^0 can be analyzed from the following aspects. Firstly, when SO_2 contacted with the catalysts, it would be adsorbed on the surface and active sites of the catalysts, resulting in the competitive adsorption for catalyst active sites between HCl and SO_2 or SO_2 and Hg^0. Secondly, the Deacon process was interfered by the competitive adsorption. This may be the main cause for reducing the efficiencies of the MDCOs. Thirdly, $HgSO_{4(ad)}$ could be formed and was too tightly adsorbed on the surface of the catalysts to escape along with flue gas, which hampered the adsorption of the catalysts for Hg^0, resulting in the decline of Hg^0 removal.

The previous studies have shown that the Al_2O_3 support can be sulfated upon SO_2 adsorption [29]. SO_2 strongly chemisorbs at basic surface hydroxyls and O^{2-} sites, resulting in the formation of adsorbed (bi) sulfites, which can be converted to sulfates upon oxidation. Due to the formation of sulfate on the surface of the catalysts, there might be the sulfation of active phase, e.g., $MnSO_4$. The sulfation of Mn-base active phase would result in the decreased efficiency of the Deacon reaction. The test also found the presence of $HgSO_4$, which might inhibit the Deacon reaction and adsorption of Hg^0 on the active sites because of the firm combination between the sulfate and active phase.

The formation of $HgSO_4$ could occur through two pathways at the test conditions. One was that SO_2 firstly reacted with HgO to form Hg_2SO_4, and then Hg_2SO_4 was converted to $HgSO_4$ upon oxidation. Another was that SO_2 reacted firstly with $H_2O_{(ad)}$ to form H_2SO_4, and then H_2SO_4 reacted with HgO to form $HgSO_4$. Based on the test results, the former process could be achieved. However, the latter might be present when air was used as carrier gas. Based on the analysis above, the reaction pathway could be written as:

$$SO_{2(g)} \rightarrow SO_{2(ad)} \quad (R1)$$

$$Hg_{(g)} \rightarrow Hg_{(ad)} \quad (R2)$$

$$O_{2(g)} \rightarrow O_{2(ad)} \quad (R3)$$

$$Hg_{(g)} + O_{2(ad)} \rightarrow HgO_{(ad)} \quad (R4)$$

$$SO_{2(ad)} + 2HgO_{(ad)} \rightarrow Hg_2SO_{4(ad)} \quad (R5)$$

$$2Hg_2SO_{4(ad)} + O_{2(ad)} \rightarrow 2HgSO_{4(ad)} + 2HgO_{(ad)} \quad (R6)$$

$$2SO_{2(ad)} + 2H_2O_{(ad)} + O_{2(ad)} \rightarrow 2H_2SO_{4(ad)} \quad (R7)$$

$$H_2SO_{4(ad)} + HgO_{(ad)} \rightarrow HgSO_{4(ad)} + H_2O_{(ad)} \quad (R8)$$

Besides the inhibition for Hg^0 removal by $HgSO_4$, based on the previous literatures [30], SO_2 had an inhibitory effect on homogeneous oxidation of Hg^0 by combination with Cl-base, resulting in the decreased efficiency of reactive activated chlorine.

4.2. Redox behaviors

It is usually considered that the capture of elemental mercury mainly occurs via a Mars–Maessen redox mechanism [3,9,27,31]. In this mechanism, Hg^0 firstly absorbed on the surface of the catalysts and then reacted with the lattice oxygen to form HgO-MO_x. It was reported that certain Hg^0 removal efficiencies could be found and decreased in the absence of O_2. After introducing O_2, the Hg^0 removal efficiencies recovered again [31]. The XPS results presented above also indicated that Hg^0 was oxidized to mercury oxide by the Mn-base catalysts in the presence of gaseous oxygen, supporting the Mars–Maessen mechanism.

The phase of Mn had a critical role on the conversion of Hg^0 in this test. The XRD results show the presence of mixed MnO_2 and Mn_2O_3 phases on the surface of the fresh catalysts. The test also showed that the ratio of Mn (IV) to Mn (III) decreased greatly after catalytic oxidation under the condition of high pure N_2. On the contrary, according to Fig. 8, the ratio of Mn (IV) to Mn (III) increased markedly after modified. So it can be concluded that the reduced Mn (IV) could be completely regenerated during the process of the reaction with air as carrier gas. The results could be used to partly explain the reason why the Mo-Ru-Mn catalyst showed excellent catalytic activity at low temperature.

According to Fig. 8, the ratio of Mo (VI) to Mo (IV) on the surface of catalysts before and after catalytic oxidation had little change. The valence state of Ru was identical to the fresh and used catalysts and presented in the form of Ru (IV). It indicates that the Deacon process unaltered practically the state of Mo, especially Ru, which highlighted the stability of the catalysts [26,32]. Moreover, it is thought that mercury oxidation with HCl requires the assistance of O_2/O, and the Deacon reaction also needs the ambience of O_2/O. So, the above results show clearly that O_2 played a crucial role in stabilizing the speciation of the catalysts, improving the efficiency of the Deacon reaction and promoting the oxidation of Hg^0.

During the process of the oxidation of Hg^0, the exhausted lattice oxygen of the catalysts could be supplied by the gas-phase oxygen [3,27,31]. Fig. 9 indicates that the oxygen content (mainly from O_d and O_e) on the surface of the catalysts increased after modified. The result was beneficial to both the regeneration of transition metal oxides and the conversion of Hg^0. The reasons could be explained from the following two aspects. On the one hand, O_d and O_e (derived from adsorbed oxygen $O_{2(ad)}$) on the surface of the catalysts would be helpful to the reduction of Mn (III) to Mn (IV), and the reduction of Mo (IV) to Mo (VI). On the other hand, the reaction between $O_{2(ad)}$ and adsorbed Hg^0 ($Hg_{(ad)}$) could be promoted to some extent. The results were consistent with the literatures [27,31].

5. Conclusions

The catalytic activities of the MDCOs system for conversion of Hg^0 to Hg^{2+} were examined with different transition metals as catalysts at low temperature of 423 K. The results show that the conversion efficiencies of Hg^0 were largely improved with modified catalysts in the presence of 8 ppmv HCl. Mo-Ru-Mn catalyst had excellent performance during the process of Hg^0 conversion and the Deacon reaction. The experiment also indicated that the species of transition metals of Mn, Mo and Ru were mainly MnO_2, MoO_3 and RuO_2, respectively, according to the XRD and XPS analysis. After modified with Mo and Ru, Mn catalyst had better performance for chlorine yield and sulfur-tolerance to SO_2.

In addition, the high removal efficiency of Hg^0 was mainly attributed to the formation of activated $[Cl]^*$ derived from the Deacon process. Compared with the TCO mode, the MDCOs had absolute predominance at the conversion of Hg^0, improvement of the Deacon process, ability of sulfur-tolerance, catalytic activity of catalysts and utilization of oxidants.

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