



Research article

Significance of Fe₂O₃ modified SCR catalyst for gas-phase elemental mercury oxidation in coal-fired flue gasWen-Jun Huang, Hao-Miao Xu, Zan Qu ^{*}, Song-Jian Zhao, Wan-Miao Chen, Nai-Qiang Yan ^{*}

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ABSTRACT

To improve the ability of commercial selective catalytic reduction (SCR) catalyst to catalyze the oxidation of gaseous elemental mercury, Fe₂O₃ was introduced. Modifying with Fe₂O₃ can significantly enhance the elemental mercury oxidation ability of SCR catalyst. Fe₂O₃/SCR prepared by an impregnation method was employed as mercury oxidation catalysts in the simulated flue gas, and the role of Fe₂O₃ was investigated. The temperature window was from 150 to 450 °C. In this study, Fe₂O₃/SCR (1% Fe, wt.) was found to be an optimal catalyst with a mercury oxidation efficiency of higher than 90% at 350 °C using a simulated flue gas. The catalysts were characterized by X-ray diffraction (XRD), Brunauer Emmet Teller (BET) measurements, and X-ray photoelectron spectroscopy (XPS). The results indicated that the Fe₂O₃ was well-dispersed on the surface of SCR. The surface areas and catalytic oxidation activity were not consistent patterns, and the diameter of the mercury atom was much smaller than the pore diameter of the Fe₂O₃/SCR catalysts. Loading content of Fe₂O₃ was a very important factor for the removal of mercury. HCl was the most effective flue gas component responsible for the Hg⁰ oxidation. However, SO₂ had a slight inhibition effect on Hg⁰ oxidation. Furthermore, change experiment of a mercury valence state was performed. And the mechanism of Hg⁰ oxidation was also discussed.

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1. Introduction

In October 2013, the world's first legally binding treaty aimed at limiting the industries to use mercury had been adopted in Kumamoto, Japan. The mercury emissions to the atmosphere had drawn more and more attention. Coal-fired power plants are recognized as one of the major anthropogenic sources of mercury emission [1,2]. Especially, China was regarded as one of the largest contributors of mercury emission. To reduce the emission from coal-fired plants, lots of work had been done on recognizing the mercury fate in the coal-fired flue gas and development novel technologies for mercury control [3–7]. Generally, mercury exists in three forms in the coal-fired flue gas, elemental mercury (Hg⁰), oxidized mercury (Hg²⁺) and particulate-bound mercury (Hg^p). It is hard to remove Hg⁰ from flue gas due to its insolubility and high volatility. By contrast, the Hg²⁺ and Hg^p can be efficiently removed by typical air pollution control devices (APCDs), such as electrostatic precipitators and fabric filter (ESP/FF), flue gas desulfurization (FGD) and scrubber systems [4,8–11]. In addition, mercury mainly exists in Hg⁰ in the combustion zone of the boilers, but it can be oxidized to Hg²⁺ by oxidizing components in the flue gas by thermo-chemical processes [9]. However, there still remains about 60–80% Hg⁰ of total mercury (Hg^T) emitted into the atmosphere [8,12]. Because of the

intractability of Hg⁰, the study on Hg⁰ removal from flue gas is becoming increasingly important.

The most widely used and effective technologies for the control of the element mercury in flue gas are as following: the halogen injecting coal technology, activated carbon injection (ACI), and catalytic oxidation or direct oxidation technology [13–17]. However, the ACI technology was limited for usage due to its high cost and collection of the mercury in the fly ashes. Halogen injected technology could generate secondary pollution (such as halogenated polycyclic aromatic hydrocarbons) which was harmful for the environment. Catalytic oxidation technology seemed as a potential method through oxidizing Hg⁰ to Hg²⁺. Following by Hg²⁺ in the flue gas can be removed by WFGD. Currently, certain noble metal or metal oxides, such as V, Mn, Co, Ru, and Ag, had been identified to be effective for the oxidation of Hg⁰ to Hg²⁺ [18–20]. The transition metal oxide catalysts were often studied as the substitutes of noble metals and they exhibited high oxidation activity, but the activation could be affected by high temperature. Usually, the operating temperature of SCR catalyst is 300–400 °C. Thus, we focus on catalysts with high Hg⁰ catalytic oxidation efficiency at 350 °C. We founded that the Fe₂O₃ modified SCR catalyst was good at enhancing Hg⁰ oxidation. Several theoretical and experimental studies about mercury adsorption or capture on Fe₂O₃ were reported [21–25]. Borderieux et al. researched the Hg⁰ removal performance of Fe₂O₃ nanoparticles and found that Fe₂O₃ nanoparticles could act as an adsorbent of Hg⁰ vapor and catalyst [26]. Tan et al. studied the Hg⁰ removal of the Fe₂O₃/SiO₂ composite and found that chemisorption played an important role in removal of

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Hg⁰ with the presence of O₂ [27]. It has been reported that TiO₂ is a good carrier for many catalysts, supporting such reaction as the SCR reaction and Hg⁰ oxidation. However, there have been few studies reporting the use of a Fe₂O₃ catalyst loaded on commercial SCR catalyst as a system for Hg⁰ oxidation.

Based on the above discussion, the aim of this study was to investigate the Hg⁰ oxidation efficiencies over the metal oxide catalysts loaded onto commercial SCR. The catalysts were prepared using an ambient-temperature impregnation method. The physical and chemical properties of the catalysts, as well as the Hg⁰ oxidation efficiency were investigated. XRD, BET, and XPS were used to characterize the catalysts. Additionally, factors (reaction temperature and SO₂) affecting the oxidation efficiency of Hg⁰ by Fe₂O₃/SCR catalyst were evaluated. Furthermore, the catalytic mechanism was discussed based on the experimental and characterization results. This study provided information regarding the industrial application of Fe₂O₃/SCR catalysts.

2. Experimental section

2.1. Materials and catalyst preparations

Commercially available SCR (Shanghai Liangjiang Titanium White Product Co., Ltd.) was mainly used as the carrier for the various catalysts. All chemicals used for the preparation of catalysts were analytical and purchased from Sigma-Aldrich Co. or Sino-pharm Chemical Reagent Co. The SO₂ (5000 ppmv), NH₃ (5000 ppmv) and HCl (1000 ppmv) gases were supplied by Dalian Date Gas Co.

The catalysts were prepared by using impregnation method, which included ZnO/SCR, Y₂O₃/SCR, NiO/SCR, ZrO₂/SCR, Co₃O₄/SCR, MnO₂/SCR, and Fe₂O₃/SCR. Appropriate amount of commercial SCR and metal nitrates was mixed and dissolved in deionized water by stirring for 2 h to guarantee uniform loading. After heating at 110 °C, the excess water was evaporated. Then the solid obtained was calcined at 400 °C in a muffle furnace for 4 h in air, and cooled to the room temperature to obtain the M_xO_y/SCR catalysts. All the catalysts were sized to 40–60 mesh for testing. The catalysts were denoted as x% M_xO_y/SCR, where x represented the weight ratio of M in M_xO_y/SCR. The concentration of each metal in this study was 1%. The temperature of the reactor

was kept at 350 °C, which was near to the actual temperature of SCR operation (300–400 °C) in the coal-fired power plant.

2.2. Catalytic activity measurement

The catalytic activity evaluation of the catalysts was in a fixed-bed reactor (Fig. 1) containing 0.05 mL of catalyst (~25 mg). It consisted of a simulated gas preparation system, catalytic reaction device, cold vapor atomic fluorescence spectrometry (CVAFS) and an online data acquisition system. Steady-state Hg⁰ vapor was prepared from the Tekran Model 3310 Calibration Source (Tekran Instruments Corp., USA) and blended with the gases in the mixing tank before entering the reactor. The flow rate of gas was 600 mL·min⁻¹, corresponding to a gas hourly space velocity (SV) of 7.2 × 10⁵ h⁻¹, which was greater than that of the actual SCR operation (4000–8000 h⁻¹) due to the catalyst configuration differences (e.g. small particles vs. honeycomb). The flue gas consisted of 120 µg m⁻³ Hg⁰, 8 ppmv HCl and 5% O₂, with the balance gas of N₂ from nitrogen generator. 500 ppmv SO₂ was used if it was necessary. The concentrations of Hg⁰ and Hg^T were continuously monitored using the 3300RS local dilution mercury emissions monitoring system. The detection limit of mercury was 0.1 ng·m⁻³. All lines that mercury passed through were heated to 120 °C to prevent mercury deposition, especially the Hg²⁺, on the inner surface. The definition of Hg⁰ oxidation efficiency (E_{oxi}) over the catalyst was quantified by the following formula:

$$E_{\text{oxi}}(\%) = \Delta\text{Hg}^0 / \text{Hg}^0_{\text{in}} = (\text{Hg}^0_{\text{in}} - \text{Hg}^0_{\text{out}}) / \text{Hg}^0_{\text{in}}$$

where Hg⁰_{in} (µg m⁻³) and Hg⁰_{out} (µg m⁻³) are the concentrations of Hg⁰ measured at the inlet and outlet of the reactor, respectively.

2.3. Catalyst characterization

X-ray diffraction (XRD) patterns were recorded with a diffractometer (XRD-6100, SHIMADZU, Japan) with Cu Kα radiation (40 kV and 20 mA) to determine the distribution of crystalline species in the catalysts. The scanning range was from 10 to 80° at a step of 7° min⁻¹. X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250) measurements were conducted with Al Kα radiation as the excitation

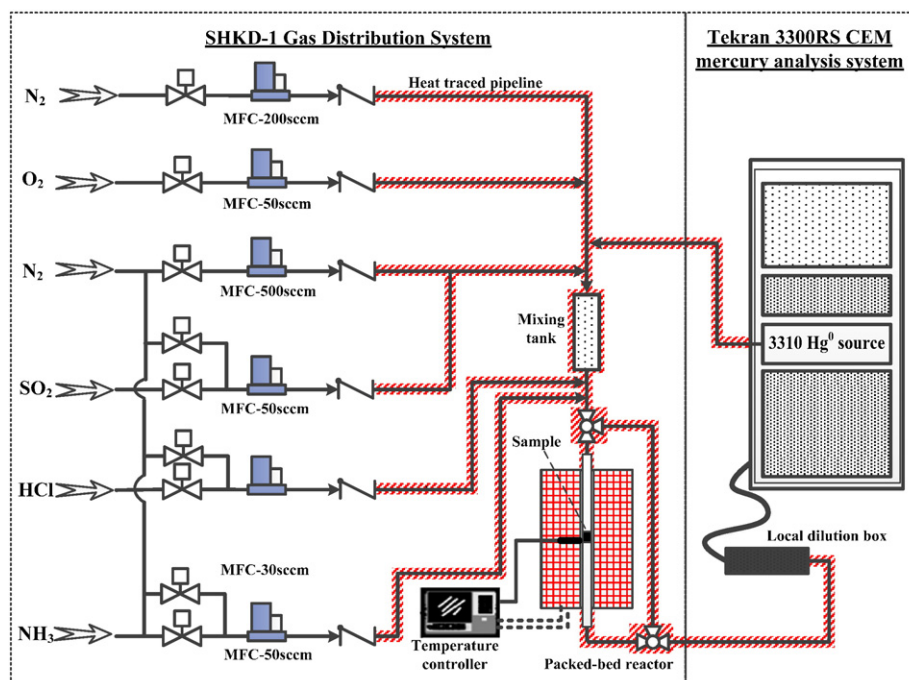


Fig. 1. Schematic diagram of setup for SCR modified with the transition metals.

source. The C 1s line at 284.8 eV was taken as a reference for binding energy calibration. The specific surface area of the catalyst was determined using BET method, and the pore volume and pore sizes were calculated by the Barrett-Jioner-Halenda (BJH) method.

3. Results and discussion

3.1. Effect of different transition metal oxides on Hg^0 catalytic oxidation

The catalytic oxidation performance of Hg^0 over various metal oxides modified catalysts was investigated. The significant difference of activity among the catalysts was shown in Fig. 2. The Hg^0 oxidation efficiencies of ZnO-, Y_2O_3 -, NiO-, and ZrO_2 -modified commercial SCR catalysts were lower than that of blank SCR catalyst. Meanwhile, the oxidizing Hg^0 efficiencies of Co_3O_4 -, MnO_2 -, and Fe_2O_3 -catalyst were higher than that of blank SCR catalyst, and the following order of activity was obtained at 350 °C as following: $Fe_2O_3 > MnO_2 > Co_3O_4$. Therefore, Fe_2O_3 /SCR catalyst could enhance Hg^0 oxidation effectively. For the sample of Fe_2O_3 /SCR, above 90% Hg^0 oxidation was observed at 350 °C.

Obviously, Fe_2O_3 /SCR exhibited the highest activity for Hg^0 oxidation which could be ascribed to Fe_2O_3 . Some researched have proven that iron oxides can promote the catalyst to have high oxidation activity for the removal of Hg^0 [27]. In addition, the outer shell of the Fe ion is a type of unfilled orbital structure, which has a more effective nuclear charge. This type of ion structure can make Fe_2O_3 react with Hg^0 to generate a polymer, which is important during the process of Hg^0 catalytic oxidation [28]. Therefore, the certain amount of Fe_2O_3 loading could improve mercury removal efficiency significantly.

3.2. Effects of Fe_2O_3 content on the catalytic oxidation of Hg^0

As Fig. 3 shows, Fe_2O_3 catalysts exhibited high activities for Hg^0 oxidation. As an important process of catalyst preparation, the active component content has a great effect on the formation of the catalysts. The active component content can affect the redistribution and aggregation of products on the SCR surface. The crystallinity and oxidation states of the catalysts can be changed at different active component contents. Generally a higher loading amount would supply more active sites for reaction and enhance the chemisorbed mercury. However, Hg^0 oxidation efficiency of Fe_2O_3 /SCR increased with increasing Fe content up to 1% (wt.) and later decreased when the Fe content was over 1%. And the results indicated that the optimal Fe content was 1% for Hg^0 catalytic

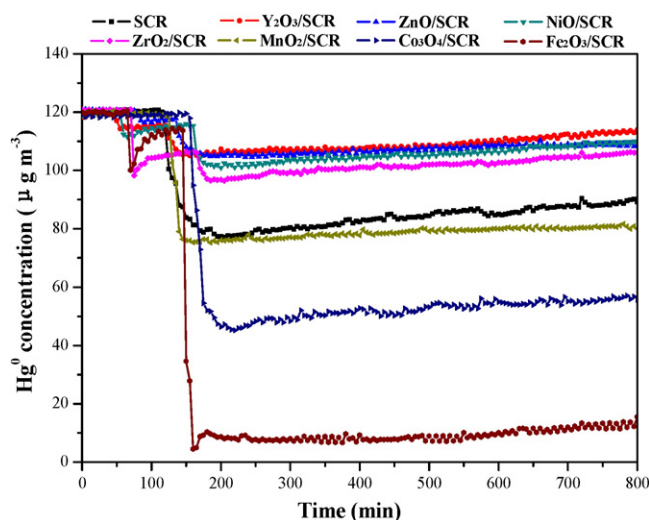


Fig. 2. Comparison of the Hg^0 catalytic oxidation efficiencies over various catalysts at 350 °C.

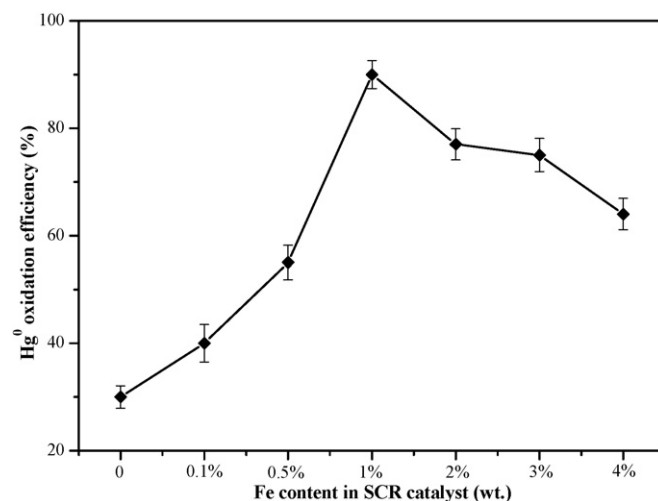


Fig. 3. Effect of Fe_2O_3 concentration on the Hg^0 oxidation efficiency.

oxidation. This may be related to structural characteristics of the modified catalysts, which will be analyzed in the latter section.

3.3. Effect of the reaction temperature and SO_2 on Hg^0 catalytic oxidation

As Fig. 4 shows, the reaction temperature was regarded as the important factor for Hg^0 oxidation. The high reaction temperature was reported to increase the Hg^0 oxidation efficiency remarkably [29,30]. The catalyst efficiency of Fe_2O_3 /SCR was improved with increasing temperature, and the mercury oxidation efficiency was highest at 350 °C, later the oxidation efficiency of Hg^0 was inhibited with increasing temperature. This indicated that the suitable reaction temperature for oxidizing Hg^0 was at 350 °C. Generally, the temperature of flue gas in SCR system is between 300 and 400 °C. Thus, the real flue gas temperature is favored for the Hg^0 oxidation by Fe_2O_3 /SCR catalyst. Meanwhile, the effect of SO_2 on the Hg^0 oxidation was also shown in Fig. 4. When HCl and O_2 were both present, the oxidation efficiency was high. While 400 ppmv SO_2 was passed, the performance of the catalyst was inhibited slightly. This was related to the structural characters of the catalysts. It was necessary to analyze the physical and chemical properties of the Fe_2O_3 /SCR catalysts and the reaction mechanism would be discussed in the following section.

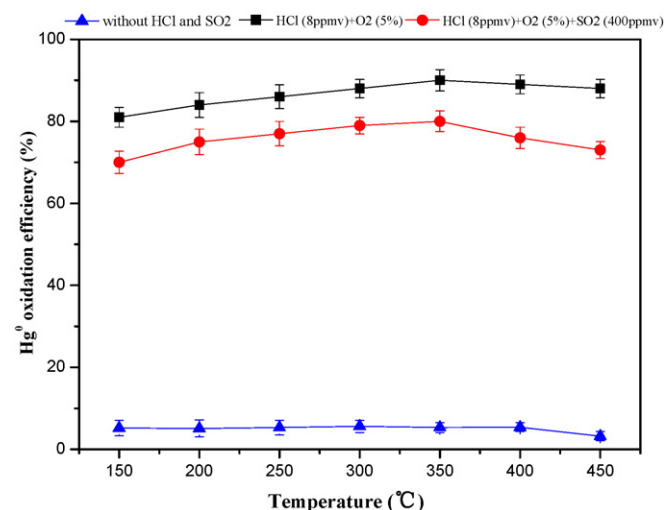


Fig. 4. Comparison of the Hg^0 oxidation efficiency over Fe_2O_3 /SCR (1%Fe) with HCl (8 ppmv) and SO_2 (400 ppmv).

3.4. Characterization of the catalysts

The XRD patterns of the Fe₂O₃/SCR series of catalysts are shown in Fig. 5. The primary crystal structure was the anatase phases of TiO₂ [16]. There were no characteristic Fe₂O₃ peaks in catalysts when the loading of Fe was lower than 4% (wt.%), which could be explained that the crystalline phases of Fe₂O₃ were too weak to be detected in the TiO₂ phase. The 10% Fe loading into SCR sample exhibited a stronger hematite Fe₂O₃ crystal phase than that of the 4% Fe loading, indicating that the pores were blocked by Fe₂O₃ due to excessive Fe₂O₃ accumulated on the SCR surface, thus resulting in a decrease of catalytic activity. In this way, a well-dispersed cluster with a small population of Fe₂O₃ may exist in the Fe₂O₃/SCR sample.

As Fig. 6 shows, the addition of Fe₂O₃ into SCR caused the slight decline of BET and pore volume of the SCR, while the BET surface areas of 3% and 4% Fe₂O₃/SCR decreased obviously from 54.6 m²·g⁻¹ to 37.9 m²·g⁻¹ and 36.4 m²·g⁻¹, respectively. The low values of the specific surface area reveal that a type of blockage was produced. According to the experiment data of Figs. 3 and 6, the results suggested that the surface areas and catalytic oxidation activity were not consistent patterns, and the diameter of the mercury atom (approximately 0.35 nm) was much smaller than the pore diameter of the Fe₂O₃/SCR catalysts. The surface area of catalyst is in favor of mercury captured. Therefore, well dispersion of Fe₂O₃ on SCR may be the main factor which affects the catalytic activity.

As Fig. 7 shows, the Fe peak located at 710.5 eV was attributed to Fe³⁺ in hematite structure, and the binding energy centered at about 712.1 eV may be ascribed to Fe³⁺ bonded with hydroxyl groups [28]. This assignment was supported by the satellite component observed at about 719.6 eV, which is the fingerprint of Fe³⁺ species. Thus, the Fe³⁺ plays an important role in Hg⁰ oxidation. This result indicated that the high valence amount of iron was beneficial for the catalyst oxidation ability. After the test under air at 350 °C, the characteristic peaks slightly shifted to the high binding energy, which indicated that Fe³⁺ might participate in the reaction.

The O 1s peak (shown in Fig. 7) mainly centered at about 529.9 eV, as expected for the iron oxides. The binding energy centered at about 530.1 eV was assigned to transition metal oxides. The oxygen species centered at about 531.1 eV was also observed, which was assigned to -OH. The O 1s peaks at about 529.5 eV and 531.4 eV correspond to the lattice oxygen and chemisorbed oxygen, respectively. After test, the amount of chemisorbed oxygen quantity decreased, suggesting that chemisorbed oxygen participated in the reaction.

The Hg 4f peaks at 101.3 eV and 105.0 eV were assigned to -O and -Cl, respectively. It suggested that Cl participated in the reaction after

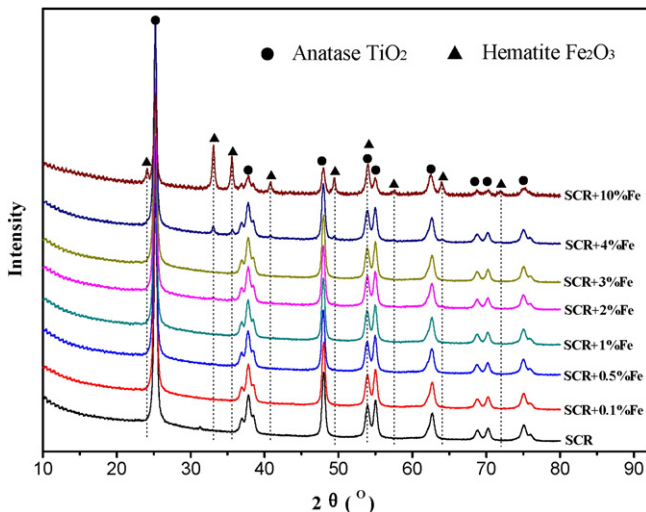


Fig. 5. XRD patterns of the Fe₂O₃/SCR catalysts.

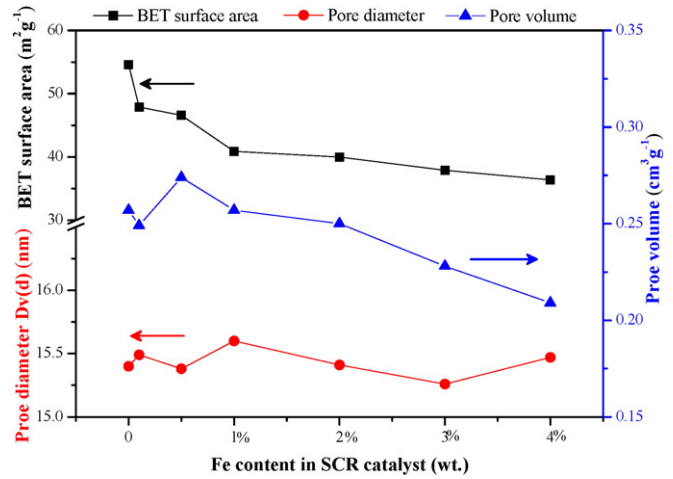
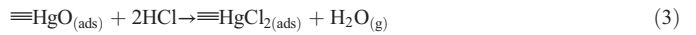
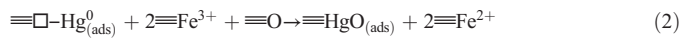


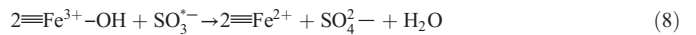
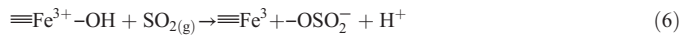
Fig. 6. Physical characteristics of the Fe₂O₃/SCR catalysts.

the test with HCl. Therefore, the Hg⁰ catalytic oxidation reaction over Fe₂O₃/SCR through the Langmuir-Hinshelwood mechanism could be approximately described as follows [31,32]:



where the $\equiv\text{O}$ was the action vacancies on the surface of the Fe₂O₃/SCR.

After the test with HCl (8 ppmv) and SO₂ (400 ppmv) at 350 °C, the Fe 2p peak at 713.6 eV was assigned to Fe₂(SO₄)₃. And the Fe 2p peak at 712.1 eV assigned to Fe³⁺-OH shifted to higher binding energy after addition of SO₂. This indicated that SO₂ reacted with Fe³⁺-OH. The higher temperature could degrade this component's performance in Hg⁰ oxidation when SO₂ was present. SO₂ may compete with gaseous Hg⁰ for the activity sites. Thus, the sorbents were poisoned by SO₂ during the oxidation process. Effect mechanism of SO₂ on Hg⁰ catalytic oxidation could be approximately described as follows:



As shown in Reactions (6)–(8), the uptake of SO₂ on Fe₂O₃/SCR may involve hydroxyl groups on the surface. In the absence of hydroxyl groups, the uptake of SO₂ on iron oxides can be neglected [33]. Reactions (6)–(8) may happen during Hg⁰ oxidation by Fe₂O₃/SCR in the presence of SO₂, resulting in an interference with Hg⁰ oxidation.

3.5. The Hg⁰ oxidation mechanism analysis

Based on the above results, the main reaction process for Hg⁰ catalytic oxidation over Fe₂O₃/SCR is discussed in this section. The mercury (Hg⁰, Hg⁺ and Hg²⁺) concentration in the outlet of Hg/HCl-O₂-NH₃ was at 350 °C, when HCl and NH₃ were added in succession, as shown in Fig. 8. Firstly, the Hg⁰ adsorption over the catalyst was saturated, and HCl was subsequently introduced. The Hg⁺ concentration decreased initially, then it returned to the original level. Meanwhile, the Hg⁰ concentration decreased immediately to stable value, which meant that Hg⁰

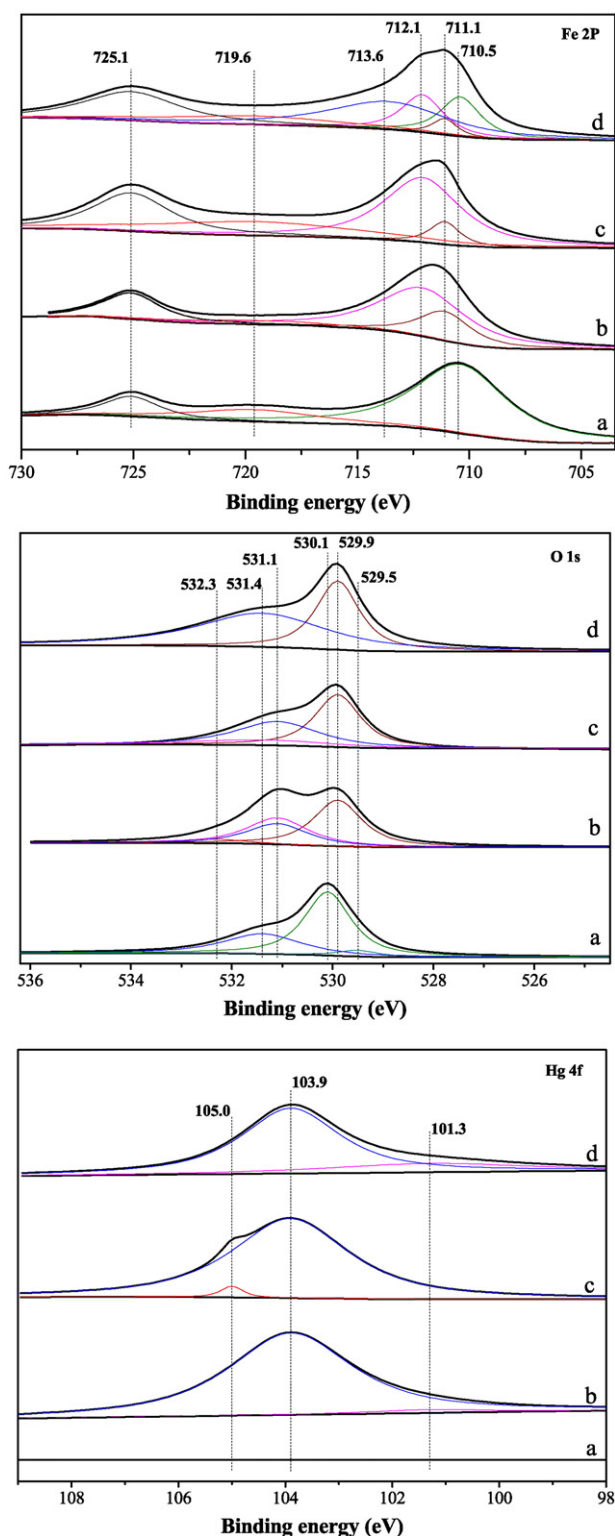


Fig. 7. XPS diagram of Fe added SCR carriers on different composition of simulated flue gas: (a) $\text{Fe}_2\text{O}_3/\text{SCR}$ (1%Fe, wt.), (b) $\text{Fe}_2\text{O}_3/\text{SCR}$ (1%Fe, wt.) after the test under air at 350 °C, (c) $\text{Fe}_2\text{O}_3/\text{SCR}$ (1%Fe, wt.) after the test with HCl at 350 °C, (d) $\text{Fe}_2\text{O}_3/\text{SCR}$ (1%Fe, wt.) after the test with HCl and SO_2 at 350 °C.

was oxidized after the addition of HCl over the surface of the catalyst. When NH_3 was added, the Hg^0 and Hg^{T} concentrations significantly increased, however Hg^{2+} decreased. This indicated that most part of the Hg^0 adsorbed on the surface of $\text{Fe}_2\text{O}_3/\text{SCR}$ was desorbed due to NH_3 added.

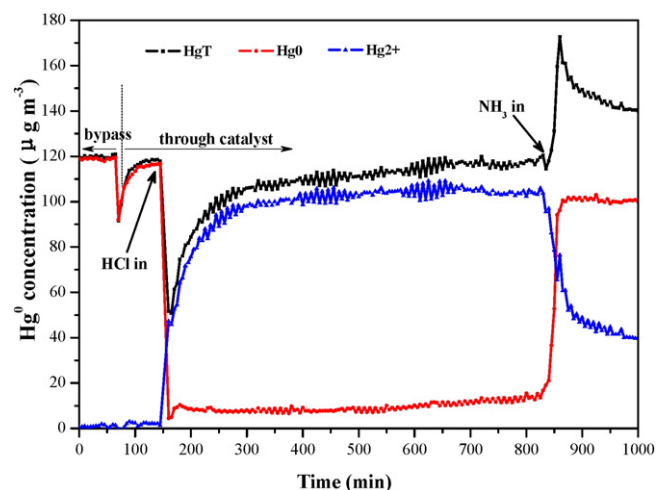


Fig. 8. Hg^0 and Hg^{T} curves over $\text{Fe}_2\text{O}_3/\text{SCR}$ carriers on different composition of simulated flue gas.

Based on the above phenomenon and Eqs. (1)–(8), the Hg^0 oxidation mechanism may be as shown in Fig. 9. Firstly, Hg^0 reacts with Fe_2O_3 on the surface to form HgO , when the HCl is added, Hg^0 is stripped. And the intermediate product (Hg-OH-Fe-Cl) is formed. Then Fe^{3+} and chemisorbed oxygen participate in the oxidation reaction by the Mars-Maessen mechanism, which oxidizes HCl into active Cl. The presence of gas-phase O_2 regenerated the lattice oxygen and chemisorbed oxygen. The active chlorine species reacted with Hg^0 adsorbed on the catalyst following the Langmuir-Hinshelwood mechanism to generate HgCl_2 .

4. Conclusions

A SCR catalyst prepared through an impregnation method, and the catalytic oxidation of Hg^0 were investigated. The $\text{Fe}_2\text{O}_3/\text{SCR}$ catalyst was determined to be highly active for Hg^0 oxidation over the temperature range of 150–450 °C. In addition, $\text{Fe}_2\text{O}_3/\text{SCR}$ (1%Fe, wt.%) exhibited the highest activity with an Hg^0 oxidation efficiency of above 90% with a HCl (8 ppmv)– O_2 (5%)– N_2 atmosphere. The results of the XRD, BET and XPS measurements indicated, hematite Fe_2O_3 was dispersed on the SCR surface. The gas component effect analysis showed that HCl was the primary catalytic component, and the SO_2 had a slightly inhibition

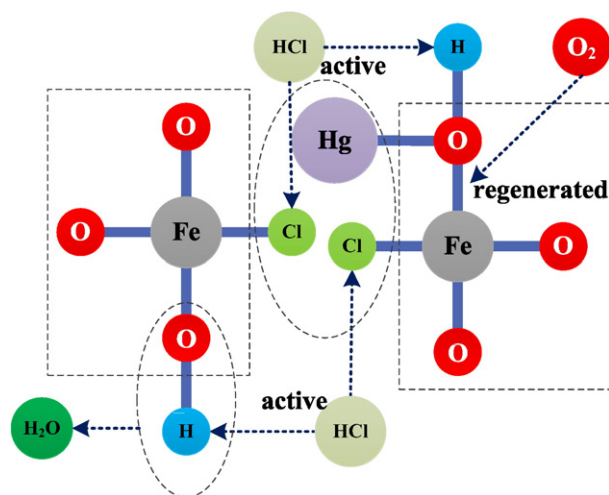


Fig. 9. Schematic of the proposed mechanism for Hg^0 oxidation in HCl– O_2 on over the $\text{Fe}_2\text{O}_3/\text{SCR}$ catalyst.

on Hg⁰ oxidation. Fe₂O₃ modified SCR catalyst had an effective catalytic oxidation ability for Hg⁰ in flue gas.

Nomenclature

SCR	selective catalytic reduction
XRD	X-ray diffraction
BET	Brunauer Emmet Teller
XPS	X-ray photoelectron spectroscopy
APCDs	air pollution control devices
ESP/FF	electrostatic precipitators/fabric filter
FGD	flue gas desulfurization
ACI	activated carbon injection
CVAFS	cold vapor atomic fluorescence spectrometry
SV	space velocity
BJH	Barrett-Jioner-Halenda

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