

Catalytic performance of CuCl₂-modified V₂O₅-WO₃/TiO₂ catalyst for Hg⁰ oxidation in simulated flue gas

Chuanmin Chen[†], Wenbo Jia, Songtao Liu, Yue Cao, Bing Zhao, and Jianqiao Wang

School of Environmental Science & Engineering, North China Electric Power University, Baoding, 071003, Hebei, China

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Abstract—CuCl₂-SCR catalysts prepared by an improved impregnation method were studied to evaluate the catalytic performance for gaseous elemental mercury (Hg⁰) oxidation in simulated flue gas. Hg⁰ oxidation activity of commercial SCR catalyst was significantly improved by the introduction of CuCl₂. Nitrogen adsorption, XRD, XRF and XPS were used to characterize the catalysts. The results indicated that CuCl₂ was well loaded and highly dispersed on the catalyst surface, and that CuCl₂ played an important role for Hg⁰ catalytic oxidation. The effects of individual flue gas components on Hg⁰ oxidation were also investigated over CuCl₂-SCR catalyst at 350 °C. The co-presence of NO and NH₃ remarkably inhibited Hg⁰ oxidation, while this inhibiting effect was gradually scavenged with the decrease of GHSV. Further study revealed the possibility of simultaneous removal of Hg⁰ and NO over CuCl₂-SCR catalyst in simulated flue gas. The mechanism of Hg⁰ oxidation was also investigated.

Keywords: CuCl₂-SCR Catalyst, Hg⁰ Oxidation, Simultaneous Removal, Coal-fired Flue Gas, Mechanism

INTRODUCTION

Mercury (Hg) emission during coal combustion is one of the most important environmental contaminants that has attracted public attention in recent years. Mercury is a volatile, toxic and persistent pollutant that accumulates in the food chain and is a threat to both human health and environment [1,2]. Consequently, various laws and/or regulations have been enacted for mercury control. In 2011, the U. S. Environmental Protection Agency (EPA) developed a federal air toxics emission standard for coal-fired power plants, including mercury emission limits [3,4]. The Minamata Convention on Mercury was signed by most countries in response to global mercury pollution in October 2013 [5]. The new Emission Standard of Air Pollutants for Thermal Power Plants (GB13223-2011) set by China was already executed in January 1, 2015, in which mercury emission was limited to be lower than 0.03 mg/m³ in coal-fired power plants [6]. Therefore, it is an urgent task to develop effective and economical technologies to reduce mercury emission from coal-fired power plants.

Mercury in coal-fired flue gas exists in three chemical forms: gaseous oxidized mercury (Hg²⁺), particulate-bound mercury (Hg^p) and gaseous elemental mercury (Hg⁰) [7]. The physical and chemical properties of mercury are different with the existing forms. Hg²⁺ has a high chemical activity and solubility in water, so it can be removed by the wet flue gas desulfurization (WFGD) system. It was revealed that 80%-95% of Hg²⁺ in flue gas can be captured during the WFGD process [8]. Hg^p, adsorbed on the surface of fly ash, can be easily removed by the dust removal devices, such as electro-static precipitator (ESP) and fabric filter (FF) [9]. In contrast,

it is hard to remove Hg⁰ from coal-fired flue gas by traditional air pollution control devices (APCDs) because of its volatility, insolubility and chemical stability [8,10,11]. Unfortunately, Hg⁰ is the dominant mercury species emitted from coal-fired power plants [12]. Therefore, increasing the conversion of Hg⁰ to Hg²⁺ is the major research issue on mercury removal by the APCDs from coal-fired power plant.

In recent years, the selective catalytic reduction (SCR) for NO_x removal has been widely applied in coal-fired power plants in China [13]. The catalysts employed in the SCR process exhibited a synergistic catalytic conversion of Hg⁰ to its oxidized form [4]. It was found that the active component of V₂O₅ played an important role for Hg⁰ oxidation on the surface of commercial SCR catalyst [14,15]. However, Hg⁰ oxidation activity of commercial SCR catalyst was limited by the flue gas components, especially HCl in flue gas [16,17]. A pilot test, performed by the U. S. Energy and Environmental Research Center (EERC), revealed that SCR catalyst exhibited notable Hg⁰ oxidation activity in coal-fired flue gas with high HCl concentration, and the impact of SCR catalyst on mercury speciation was very coal dependent [18]. Lee et al. [19] found that Hg⁰ oxidation over commercial SCR catalyst was higher than 90% when more than 100 ppm HCl was present. However, about 20% of Hg⁰ oxidation efficiency was obtained when HCl was less than 10 ppm. Shao et al. [20] found that weakly bonded mercury species (Hg₂O) could convert to more stable HgCl and HgCl₂, which substantially improved Hg⁰ oxidation activity of the catalysts. However, it is difficult for commercial SCR catalyst to achieve high Hg⁰ oxidation activity in coal-fired flue gas due to the diversity of chlorine content in coal. Besides, SO₂ and H₂O could compete for the active sites to inhibit the reaction of Hg⁰ and Cl, lowering the Hg⁰ oxidation activity [20]. In addition, NH₃ exhibits a remarkable inhibiting effect on Hg⁰ oxidation, because NH₃ competes with Hg⁰ and HCl for surface active sites of the catalysts [21-24]. Chang et al. [25]

[†]To whom correspondence should be addressed.

E-mail: hdccm@126.com

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found that the acidic sites were also important for Hg^0 adsorption. When both Hg^0 and NH_3 exist in flue gas, the acidic sites tend to be occupied by NH_3 , inhibiting the Hg^0 adsorption. This is an important reason for the inhibiting effect of NH_3 on Hg^0 oxidation. Researchers also found that NH_3 consumed the surface oxygen, which was responsible for Hg^0 oxidation [26,27]. Madsen et al. [28] found that NH_3 could result in a reduction of Hg^{2+} to Hg^0 over SCR catalyst when the reaction temperature was higher than 325°C , indicating that a reducing reaction was taking place concurrently to the Hg^0 oxidation, thus lowering the overall Hg^0 oxidation activity over the SCR catalyst. Accordingly, the appropriate active sites for the adsorption of HCl , NH_3 and Hg^0 are important to improve the Hg^0 oxidation activity of commercial SCR catalyst. To achieve high catalytic activity for Hg^0 oxidation at low HCl concentration, many researchers have synthesized a series of novel catalysts to evaluate the Hg^0 oxidation performance, such as $\text{MnO}_x\text{-CeO}_2/\text{TiO}_2$ [16], $\text{CeO}_2(\text{ZrO}_2)/\text{TiO}_2$ [29], $\text{CuO-MnO}_2\text{-Fe}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3$ [30], $\text{CuO-CeO}_2/\text{TiO}_2$ [27,31], $\text{CeO}_2\text{-V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ [32], and Cu/TiO_2 [33]. However, these novel catalysts are different from commercial SCR catalysts in components. The commercial $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ catalyst has been widely used in coal-fired power plants because of its high catalytic activity, thermal stability and economic viability. It is a co-benefit option for Hg^0 oxidation in coal-fired power plants by improving the Hg^0 oxidation activity of commercial $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ catalyst. In recent years, CuCl_2 doped catalysts were synthesized to oxidize Hg^0 at low HCl concentration. $\text{CuCl}_2/\text{TiO}_2$ catalysts were prepared by Kim et al. [34] to investigate the role of CuCl_2 for Hg^0 oxidation. It was found that the active Cl species released by CuCl_2 acted as chlorine source to oxidize Hg^0 to Hg^{2+} , thus significantly enhancing Hg^0 oxidation activity. It was also reported that the pre-chlorinated sites of CuCl_2 had a propensity for surface chlorination derived from HCl [35]. Moreover, as found by Zhou [36], the atomic Cl in CuCl_2 had an obvious positive effect on Hg^0 oxidation, and the $\text{CuCl}_2/\text{TiO}_2$ catalyst exhibited superior Hg^0 oxidation activity even in the absence of HCl . Nonetheless, there was no report related to the CuCl_2 modified $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ based commercial SCR (denoted as $\text{CuCl}_2\text{-SCR}$) catalyst for Hg^0 oxidation in simulated flue gas.

Based on the above discussion, $\text{CuCl}_2\text{-SCR}$ catalysts, which were prepared by adding CuCl_2 as the second assistant on the basis of the commercial SCR catalyst, were employed to oxidize Hg^0 in simulated flue gas in this study. The physical and chemical properties of the catalysts, as well as the Hg^0 oxidation performance were investigated. Additionally, the effects of flue gas components on Hg^0 catalytic oxidation were evaluated. The catalytic mechanism was discussed based on the experiment and characterization results. This study intended to reveal the possibility of simultaneous removal of Hg^0 and NO over $\text{CuCl}_2\text{-SCR}$ catalyst.

EXPERIMENTAL

1. Catalysts Preparation and Characterization

The $\text{CuCl}_2\text{-SCR}$ catalysts were synthesized using fresh commercial SCR catalyst (V_2O_5 : 0.6%, WO_3 : 8%, TiO_2 supported) and $\text{CuCl}_2\cdot 2\text{H}_2\text{O}$ by an improved impregnation method. The specific preparation method was as follows: First, a certain amount of $\text{CuCl}_2\cdot$

$2\text{H}_2\text{O}$ was dissolved in deionized water to form the solution. Then, the powdered commercial SCR catalyst (milled through 80 mesh) was added to the solution, and stirred in 60°C thermostatic water-bath for 2 h. Third, the excess water was evaporated, and then, the obtained solids were dried at 105°C overnight and calcined at 350°C in N_2 for 4 h. Finally, the obtained samples were ground and sieved to 60-80 mesh for Hg^0 oxidation test.

Nitrogen adsorption was carried out by an ASAP 2020 analyzer (Micromeritics, USA). The specific surface area was determined by the Brunauer-Emmett-Teller (BET) method, and the pore volume and average pore diameter were evaluated by the Barrett-Joiner-Halenda (BJH) method. X-ray diffraction (XRD) patterns for the catalysts were collected on a Rigaku X-ray diffractometer, and $\text{Cu K}\alpha$ radiation (35 kV and 20 mA) was used as the X-ray source. The samples were scanned in the range of 10° to 70° at a scanning rate of 10° min^{-1} . The compositions of the catalysts were determined by a sequential X-ray fluorescence (XRF) spectrometer (EDX3600K). To investigate the elemental states of the catalysts, X-ray photoelectron spectroscopy (XPS) method was carried out on X-ray photoelectron spectrometer (ESCALAB 250Xi, UK) with $\text{Al K}\alpha$ radiation. The observed spectra were calibrated by the C1s peak at 284.6 eV. The Hg^0 temperature-programmed desorption ($\text{Hg}^0\text{-TPD}$) method was used to investigate the mercury heterogeneous oxidation processes over $\text{CuCl}_2\text{-SCR}$ catalysts. The pretreated samples were heated linearly from room temperature to 600°C at a rate of $10^\circ\text{C}/\text{min}$.

2. Catalytic Reactor System

The catalytic activity for Hg^0 oxidation over $\text{CuCl}_2\text{-SCR}$ catalyst in simulated flue gas was tested in a fixed bed flow reactor under atmospheric pressure. A schematic diagram of the experimental setup is shown in Fig. 1. The feed gases were precisely controlled by the mass flow controllers (D08-3E, Seven Star, Beijing, China) with a total flow rate of 1 L/min. A constant quantity of Hg^0 ($72.0\ \mu\text{g}/\text{m}^3$) vapor was supplied into the gas flow by an Hg^0 permeation tube (VICI Metronics, USA) which was immersed in a water bath. The relatively high Hg^0 concentration was used to reduce the experimental errors caused by the reaction system and to ensure the experiments completed in a reasonable time scale [4]. A quartz tube with inner diameter of 10 mm was used as the reactor to avoid the adsorption and reaction of mercury species on reactor surface. The Hg^0 and NO concentrations at the inlet ($\text{Hg}_{in}^0/\text{NO}_{in}$) and outlet ($\text{Hg}_{out}^0/\text{NO}_{out}$) of the reactor were measured, respectively, by an online RA-915+ mercury analyzer (Lumex, Russia) and a flue gas

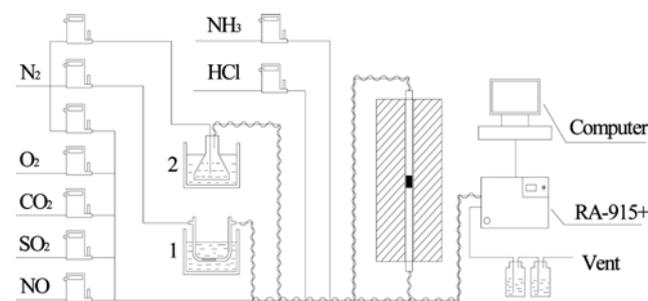


Fig. 1. Schematic diagram of the experimental system.

1. Hg^0 vapor generator 2. Water vapor generator

analyzer (ECOM-J2KN). After the analyses, the exhaust gas was introduced into the acidic potassium permanganate solution trap before discharging into the atmosphere. All Teflon lines that mercury and water vapor passed through were heated to 120 °C to prevent the deposition of Hg⁰ and H₂O on the inner surface [32,37].

3. Experimental Method

At the beginning of each test, 0.2 g catalyst sample was packed in the center of the quartz tube, and the inlet flue gas was sampled through the by-pass to ensure a stable Hg⁰ feed concentration. Hg⁰_{out} was recorded after the process reached equilibrium, which was defined as having fluctuation of Hg⁰ concentration less than 5% for more than 30 min [4]. Therefore, the loss of Hg⁰ can be considered to be the oxidized mercury [16]. At the end of each test, the mercury analyzer was switched to the reactor inlet to verify the feed Hg⁰ concentration. The Hg⁰ oxidation efficiency (E_{oxi}) and NO removal efficiency (E_{NO}) were, respectively, defined in Eqs. (1) and (2). In addition, a necessary blank experiment was conducted to identify the test error. The result showed that the flue gas components and the reactor system would not affect the test result of the instrument.

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

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

RESULTS AND DISCUSSION

1. Hg⁰ Oxidation Activity on CuCl₂-SCR Catalysts

The Hg⁰ oxidation activity on CuCl₂-SCR catalysts with different CuCl₂ loadings was investigated in simulated flue gas (SFG) as shown in Fig. 2. E_{oxi} of commercial SCR catalyst increased with the increase of reaction temperature from 250 °C to 350 °C, then decreased as the temperature further increased to 450 °C. The maximum efficiency of Hg⁰ oxidation was only 24.3%. Note that vanadia-based catalysts were not active at low temperature [32], which inhibited the Hg⁰ oxidation. However, higher temperature was unsuitable for Hg⁰ adsorption on the surface of catalysts, which also

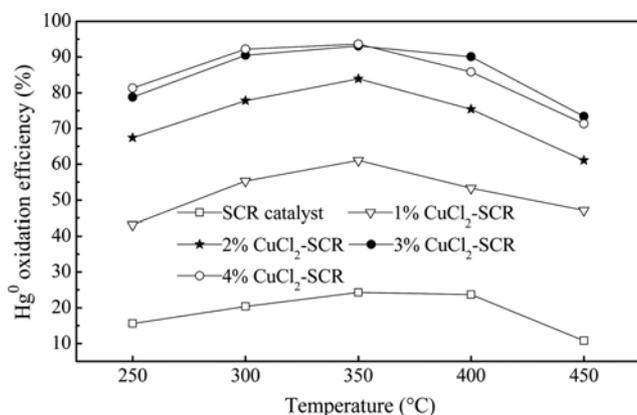


Fig. 2. Influence of CuCl₂ addition and temperature on Hg⁰ catalytic oxidation (SFG: 12% CO₂, 5% O₂, 8% H₂O, 600 ppm SO₂, 300 ppm NO, 20 ppm HCl and N₂ balanced, GHSV=120,000 h⁻¹).

inhibited the Hg⁰ oxidation. The Hg⁰ oxidation activity on CuCl₂-SCR catalysts showed similar trends to that of commercial SCR catalyst. The catalysts containing CuCl₂ exhibited superior Hg⁰ oxidation activity. E_{oxi} of CuCl₂-SCR catalysts increased dramatically with the CuCl₂ content increased from 1% to 3%, which indicated that the addition of CuCl₂ enhanced the Hg⁰ oxidation activity of the commercial SCR catalyst. E_{oxi} increased by nearly 40% when 1% CuCl₂ was added in commercial SCR catalyst. According to the literature [38], the chlorine-enriched coordination acted as the active adsorption sites for Hg⁰, which could enhance Hg⁰ removal activity of the catalysts. Besides, the activated Cl species released by CuCl₂ facilitated Hg⁰ oxidation efficiently in the presence of O₂ [34,36]. The reduced CuCl could be reoxidized by O₂ to form an intermediate copper oxychloride species, and then restored to CuCl₂ in the presence of HCl [39,40]. Thus, Hg⁰ oxidation activity was significantly enhanced by the addition of CuCl₂ in the copresence of HCl and O₂. When the CuCl₂ addition increased to 3%, the maximum E_{oxi} could reach 92.1%. Similarly, Kim et al. [34] reported that more than 90% of E_{oxi} was obtained over CuCl₂/TiO₂ catalyst containing copper content of 3%. Zhou et al. [36] also found that nearly 100% of E_{oxi} was observed over CuCl₂/TiO₂ catalyst in the copresence of O₂ and HCl. However, no obvious increase of E_{oxi} was detected when 4% CuCl₂ was added. This result indicated that the optimal addition of CuCl₂ was 3% for Hg⁰ catalytic oxidation considering both Hg⁰ oxidation activity and preparation cost for CuCl₂-SCR catalysts. Therefore, 3% CuCl₂-SCR catalyst was used in subsequent studies to explore the effects of flue gas components on Hg⁰ oxidation activity.

2. Breakthrough Curves of Hg⁰ over 3% CuCl₂-SCR Catalyst

To confirm that the CuCl₂ indeed acted as a catalyst rather than as a sorbent, the breakthrough curves of Hg⁰ over 3% CuCl₂-SCR catalyst were investigated as shown in Fig. 3. In pure N₂ gas flow, Hg⁰ concentration swiftly dropped to about 0 μg/m³ after passing through the catalyst at 20 °C, and remained at 0 μg/m³ during the entire 300 min test. As a general rule, V-W-Ti based catalysts are not active at low temperature [32]. So this huge loss of Hg⁰ could be ascribed to physical adsorption. However, faster breakthrough was observed at 350 °C in pure N₂ flow gas. Hg⁰ concentration decreased to about 40 μg/m³ after passing through the catalyst, then slowly increased to about 65 μg/m³, and remained at 65 μg/m³

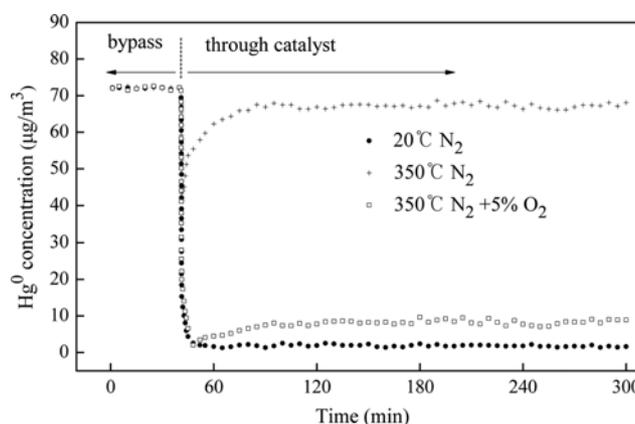


Fig. 3. Hg⁰ breakthrough curves on 3% CuCl₂-SCR catalyst.

Table 1. Textural properties of the catalysts

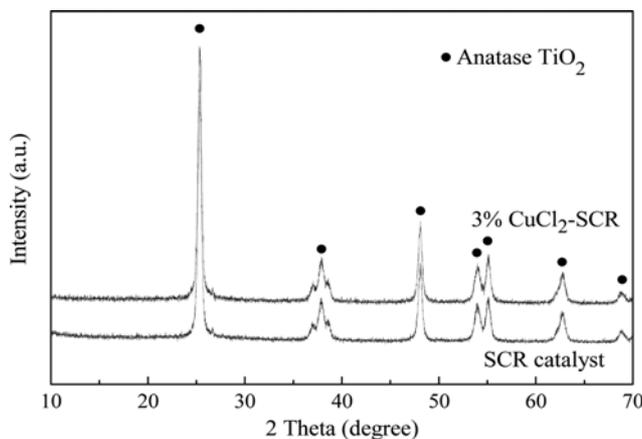
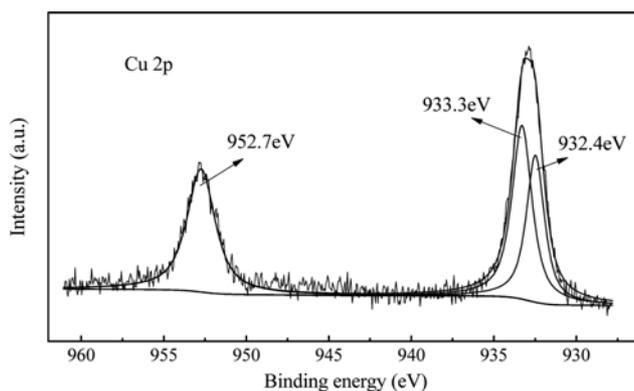
Samples	S_{BET} (m ² /g)	V_{pore} (cm ³ /g)	D_{pore} (nm)
SCR catalyst	43.51	0.233	22.29
3%CuCl ₂ -SCR	41.01	0.237	21.78

during the entire test. This result indicated that no evident adsorption of Hg⁰ was observed at 350 °C. The physical adsorption of Hg⁰ decreased as the temperature increased, and it was negligible at SCR operating temperature [4,41]. So this minor loss of Hg⁰ (about 7 μg/m³) could be explained by the catalytic oxidation effect of catalyst where gas-phase or weakly adsorbed Hg⁰ reacted with surface oxygen to form mercuric oxide [4]. Low Hg⁰ concentration (about 6 μg/m³) was observed at the outlet of the reactor in the presence of 5% O₂ with N₂ atmosphere at 350 °C. It could be explained that gas-phase O₂ regenerated the lattice oxygen or replenished chemisorbed oxygen on the catalyst surface, which served as the Hg⁰ oxidant [42,43]. In addition, activated Cl species released by CuCl₂ could react with adsorbed Hg⁰ to generate a stable mercuric chloride (HgCl₂) in the presence of O₂ [34,36], which significantly enhanced Hg⁰ oxidation activity. Consequently, the physical adsorption of Hg⁰ over CuCl₂-SCR catalyst was negligible at 350 °C. So it was reasonable that Hg_{out}⁰ was recorded after the process reaching equilibrium, and the loss of Hg⁰ could be ascribed to the oxidized mercury.

3. Characterization of Catalysts

The BET surface area, BJH pore volume and average pore diameter of commercial SCR catalyst and 3% CuCl₂-SCR catalyst are summarized in Table 1. The addition of 3% CuCl₂ caused slight decrease in specific surface area and average pore diameter of the commercial catalyst. However, 3% CuCl₂-SCR catalyst exhibited superior activity for Hg⁰ oxidation, indicating that the influence of surface area on catalytic activity was not very significant. Moreover, the radius of the mercury atom is considerably smaller than the pore radius of the CuCl₂-SCR catalyst [33]. So it could be speculated that the CuCl₂ dispersion degree on the catalyst might be the main factor affecting the Hg⁰ oxidation activity.

The XRD method was performed to investigate the crystal phases of the catalysts, and the results were displayed in Fig. 4. For both commercial SCR catalyst and 3% CuCl₂-SCR catalyst, anatase TiO₂ was observed. The characteristic peaks of V₂O₅ and WO₃ could be hardly detected in both patterns, which were due to the wide dispersion and poorer crystalline on the surface [32]. In addition, the XRD pattern of 3% CuCl₂-SCR catalyst displayed no visible crystalline phase of CuCl₂. The reason for this result might be that the CuCl₂ content was too small to be detected and/or the CuCl₂ was highly dispersed on the catalyst. Researchers found that well dispersed active elements in the catalyst can enhance the catalytic activity [30,44]. Accordingly, the highly dispersed CuCl₂ was beneficial for the dispersion of active sites over the CuCl₂-SCR catalyst,

**Fig. 4. XRD patterns of the catalysts.****Fig. 5. XPS spectra of Cu 2p on 3% CuCl₂-SCR catalyst.**

and this should be a rational reason for the superior activity of Hg⁰ oxidation.

XRF analyses were performed to investigate the concentration of the elements in the catalysts. As shown in Table 2, the mass fraction of main components (V₂O₅, WO₃, TiO₂) showed a slight decrease when CuCl₂ was added into commercial SCR catalyst, which could be explained that the addition of CuCl₂ reduced the proportion of each composition. The content of CuO and Cl on 3% CuCl₂-SCR catalyst was 1.843% and 1.219%, respectively, from which it could be concluded that the molar ratio of Cu/Cl was 0.67. Considering that primary Cu species existed in the form of Cu²⁺ (identified by XPS), it could be speculated that the main copper compound on 3% CuCl₂-SCR catalyst was CuCl₂. This result indicated that CuCl₂ was well-loaded on the catalyst surface by the improved impregnation method.

To identify the chemical state of copper on the catalyst surface, XPS analysis was performed on 3% CuCl₂-SCR catalyst, and the Cu 2p XPS spectrum is shown in Fig. 5. A higher Cu 2p_{3/2} peak

Table 2. XRF results of the catalysts

Samples	V ₂ O ₅ (wt%)	WO ₃ (wt%)	TiO ₂ (wt%)	CuO (wt%)	Cl (wt%)	Others (wt%)
SCR catalyst	0.626	7.998	84.828	0	0	6.548
3%CuCl ₂ -SCR	0.579	7.127	82.237	1.843	1.219	6.995

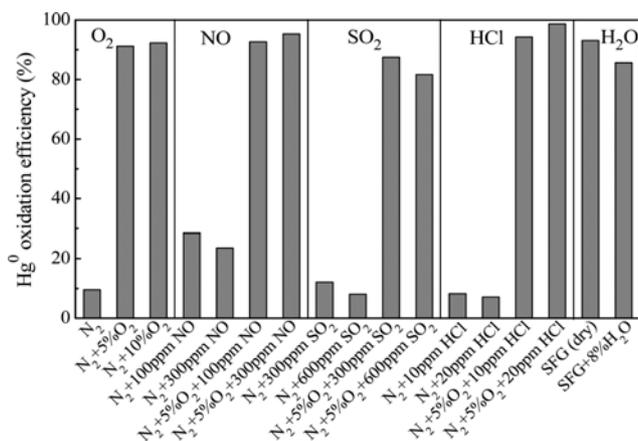


Fig. 6. Effect of individual flue gas components on Hg⁰ oxidation (SFG: 12% CO₂, 5% O₂, 8% H₂O, 600 ppm SO₂, 300 ppm NO and N₂ balanced, T=350 °C, GHSV=120,000 h⁻¹).

located at the binding energy of 933.3 eV, and the separated Cu 2p_{1/2} peak at 952.7 eV were the primary characteristic of Cu²⁺ [45]. Meanwhile, the characteristic peak at 932.4 eV was ascribed to the existence of Cu⁺ species on the catalyst [12,46]. The Cu²⁺/Cu⁺ ratio on 3% CuCl₂-SCR catalyst was 2.65, indicating that the primary Cu species existed in the form of Cu²⁺. This result also suggested that the dominant copper species on CuCl₂-SCR catalyst was CuCl₂, just as identified by XRF.

4. Effect of Individual Flue Gas Components

To better evaluate the Hg⁰ oxidation activity of CuCl₂-SCR catalyst, the effects of individual flue gas components were investigated over 3% CuCl₂-SCR catalyst at 350 °C, and the results are illustrated in Fig. 6.

4-1. Effect of O₂

O-species is considered to be important in SCR catalysts, especially in the metal oxides catalysts [33,43]. The effect of O₂ on Hg⁰ catalytic oxidation over CuCl₂-SCR catalyst was investigated as shown in Fig. 6. In pure N₂ gas flow, E_{oxi} of CuCl₂-SCR catalyst was only 9.5%. This minor Hg⁰ oxidation effect could be explained by the Mars-Maessen mechanism, by which weakly adsorbed Hg⁰ reacted with lattice oxygen and/or chemisorbed oxygen to form mercuric oxide on the catalyst surface [47]. However, E_{oxi} increased dramatically when O₂ was added into pure N₂. As shown, when 5% O₂ was added, 92.1% of E_{oxi} was obtained over CuCl₂-SCR catalyst. This significant promoting effect on Hg⁰ oxidation was explained in 3.2. The coexistence of CuCl₂ and O₂ obviously enhanced Hg⁰ oxidation activity. However, no obvious increase of E_{oxi} was detected when O₂ content was increased to 10%. This result indicates that 5% O₂ was sufficient to react with Hg⁰ on the catalyst surface. Noting that O₂ concentration in actual coal-fired flue gas is in a range of 5-8%, Hg⁰ can be oxidized with sufficient O₂ on the catalyst surface.

4-2. Effect of NO

As shown in Fig. 6, addition of 100 ppm NO in pure N₂ atmosphere exerted an enhancing effect on Hg⁰ oxidation over CuCl₂-SCR catalyst, while further increased NO to 300 ppm led to a slight decrease on Hg⁰ oxidation activity. Researchers found that a fraction of NO can react with surface oxygen on the catalyst surface to form NO_x, which can enhance Hg⁰ oxidation activity [32,47]. In

the absence of O₂, Hg⁰ oxidation activity was inhibited with the increase of NO from 100 ppm to 300 ppm because the surface oxygen was consumed by NO oxidation. When 5% O₂ was added into the flue gas, the increase of NO enhanced the Hg⁰ oxidation activity. It could be explained that the oxidation of adsorbed NO produced ample active species and the consumed surface oxygen was replenished from the gas-phase O₂ [27,37]. Therefore, the copresence of NO and O₂ could promote Hg⁰ oxidation.

4-3. Effect of SO₂

Compared to that in pure N₂ atmosphere, E_{oxi} of CuCl₂-SCR catalyst was promoted by the addition of 300 ppm SO₂. However, the addition of 600 ppm SO₂ led to a slight decrease on Hg⁰ oxidation. It was found that SO₂ could react with surface oxygen to form SO₃, which could facilitate Hg⁰ oxidation [48]. However, with the increase of SO₂ to 600 ppm, surface oxygen was consumed in the reaction of SO₂ oxidation, which inhibited the Hg⁰ oxidation. Moreover, SO₂ was found to compete for active sites with Hg⁰ on the catalyst surface, in which way it could deactivate the catalyst's capability in oxidizing Hg⁰ [43]. In the presence of 5% O₂, E_{oxi} was decreased as SO₂ increased from 300 ppm to 600 ppm, which was due to the competitive relationship between SO₂ and Hg⁰. Conclusively, SO₂ showed an inhibitive effect on Hg⁰ oxidation in the presence of O₂ over CuCl₂-SCR catalyst because of the competition effect for active sites between SO₂ and Hg⁰ on the catalyst surface.

4-4. Effect of HCl

It is well-known that HCl is the most important flue gas component for Hg⁰ oxidation over SCR catalyst, since the main oxidized mercury species in coal-fired flue gas is HgCl₂ [49-51]. In our test, E_{oxi} was inhibited by HCl in the absence of O₂. As shown in Fig. 6, the increase of HCl from 10 ppm to 20 ppm resulted in a slight decrease on Hg⁰ oxidation. However, in the presence of 5% O₂, 94.3% of E_{oxi} was obtained when 10 ppm HCl was added, and further increased HCl to 20 ppm, E_{oxi} could reach 98.7%. It was reported that HCl competed with Hg⁰ for active sites on the catalyst and that the affinity of V₂O₅-WO₃/TiO₂ for HCl was stronger than for Hg⁰. Meanwhile, gaseous HCl cannot react with Hg⁰ directly [9]. Therefore, Hg⁰ oxidation activity was inhibited by HCl in the absence of O₂. However, in the presence of O₂, gas-phase O₂ provided abundant reactive oxygen for reacting with HCl to form enough activated Cl species, which enhanced Hg⁰ oxidation activity [52]. In addition, CuCl₂ was decomposed, releasing Cl species at high temperature and restored to its original form by being exposed to gas-phase HCl, reversibly [34]. The released Cl species acted as the chlorine source to oxidize Hg⁰ to Hg²⁺. Accordingly, Hg⁰ oxidation activity was promoted by HCl in the presence of O₂.

4-5. Effect of H₂O

At SCR condition, H₂O unavoidably exists in actual flue gas and has significant impact on catalytic activity. As a general rule, moisture physisorbed or chemisorbed on SCR catalyst can occupy the active sites, which leads to an apparent reduction of the catalytic activity. The competitive adsorption of H₂O and Hg⁰ on active sites also inhibits the Hg⁰ oxidation activity at a typical SCR condition. So it is important to evaluate the H₂O resistance of CuCl₂-SCR catalyst for possible industrial application. As shown in Fig. 6, when 8% H₂O was added into simulated flue gas, E_{oxi} of CuCl₂-SCR catalyst decreased from 93.1% to 85.6%, indicating that H₂O inhib-

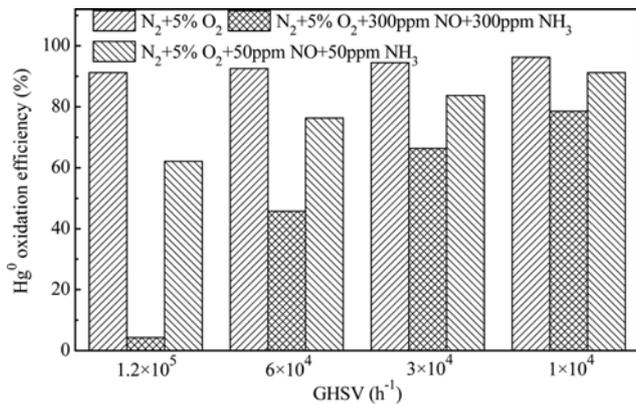


Fig. 7. Hg⁰ oxidation activity under SCR condition (T=350 °C).

ited the Hg⁰ oxidation. This mechanism could be attributed to the competition between H₂O and Hg⁰ for adsorption at the active sites on the catalyst surface. Though the addition of H₂O restrained the Hg⁰ oxidation, CuCl₂-SCR catalyst exhibited superior ability for Hg⁰ oxidation. This implies that the catalyst exhibited good H₂O-resistance.

5. Hg⁰ Oxidation Activity under SCR Condition

As an SCR catalyst, CuCl₂-SCR catalyst would probably be used in the SCR process where NO and NH₃ are simultaneously present. So it is necessary to evaluate the catalytic activity of the catalyst under SCR conditions for possible practical application. GHSV is also a crucial parameter for practical application. Hence, Hg⁰ oxidation activity of CuCl₂-SCR catalyst was investigated under SCR condition with respect to different GHSV at 350 °C, and the results are in Fig. 7. 300 ppm NO and 300 ppm NH₃ were introduced into the flue gas to simulate the SCR atmosphere at the initial stage of SCR reaction where NO and NH₃ concentrations were relatively high. Similarly, 50 ppm NO and 50 ppm NH₃ were introduced to the flue gas to simulate the SCR atmosphere at the end stage of SCR reaction where NO and NH₃ concentrations were relatively low. At high GHSV of 1.2×10⁵ h⁻¹, 4.3% and 62.1% of Hg⁰ oxidation efficiencies were obtained at the initial stage and the end stage of SCR reaction, respectively. The result suggested that the copresence of NO and NH₃ remarkably inhibited Hg⁰ oxidation, especially at the initial stage of SCR reaction. It was reported that the Hg⁰ oxidation activity was suppressed by NH₃ due to the competitive adsorption between NH₃ and Hg⁰ [34]. Many researchers also found that NH₃ consumed the surface oxygen which was responsible for Hg⁰ oxidation [26,27]. Madsen [28] found that NH₃ could result in a reduction of Hg²⁺ to Hg⁰ over SCR catalyst when the reaction temperature was higher than 325 °C, indicating that a reducing reaction was taking place concurrently to the Hg⁰ oxidation, thus lowering the overall oxidation of Hg⁰ achieved over the catalyst. So it could be concluded that the competitive adsorption and the reduction effect of NH₃ inhibited the Hg⁰ oxidation. Fortunately, this inhibitive effect of NH₃ was weakened as the GHSV decreased. At low GHSV of 1×10⁴ h⁻¹, E_{oxi} increased to 78.6% at the initial stage and 91.2% at the end stage, respectively. According to the literature [53], the low GHSV extended the residence time of Hg⁰ on the catalyst. NH₃ could be absorbed at the upstream part

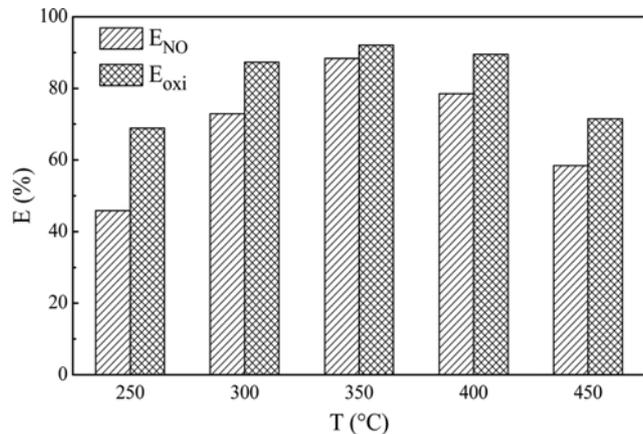


Fig. 8. Simultaneous removal of NO and Hg⁰ over 3% CuCl₂-SCR catalyst (SFG: 12% CO₂, 5% O₂, 8% H₂O, 600 ppm SO₂, 300 ppm NO, 300 ppm NH₃, 20 ppm HCl, 72 μg/m³ Hg⁰, N₂ balanced).

of the catalyst and then consumed in the SCR reaction, while Hg⁰ could be oxidized by the downstream part of the catalyst in this condition. But high GHSV supplied little time for Hg⁰ oxidation after NH₃ had adsorbed on the catalyst. Thus the inhibiting effect of NH₃ on Hg⁰ oxidation diminished as GHSV slowed down. This result also had a significant guidance for possible industrial application of CuCl₂-SCR catalyst.

Since CuCl₂-SCR catalyst was developed for simultaneous removal of NO and Hg⁰ in SCR process, the activity of simultaneous removal of NO and Hg⁰ over 3% CuCl₂-SCR catalyst was investigated under SCR condition at low HCl concentration. As shown in Fig. 8, both E_{NO} and E_{oxi} increased with the increase of reaction temperature from 250 °C to 350 °C, and then decreased as the temperature further increased to 450 °C. This result is similar to other research that the catalytic activity showed a general trend of improving first and then decreasing [53]. The maximum E_{NO} and E_{oxi} were obtained at 350 °C, which could reach 88.4% and 92.1%, respectively. It could be concluded that CuCl₂-SCR catalyst exhibited superior activity for simultaneous NO removal and Hg⁰ oxidation under low HCl concentration, indicating that the presence of Hg⁰ had no obvious impact on NO removal. This might be ascribed to the fact that the Hg⁰ concentration (72 μg/m³) was extremely small in the gas flow compared to NO concentration (300 ppm), and the impact of Hg⁰ on NO removal was almost negligible [54]. This result also revealed the possibility of simultaneous removal of Hg⁰ and NO over CuCl₂-SCR catalyst in simulated flue gas.

6. Mechanism Analysis

To investigate the mercury heterogeneous oxidation processes over CuCl₂-SCR catalyst, the Hg⁰ temperature-programmed desorption (Hg⁰-TPD) method was performed over commercial SCR catalyst and CuCl₂-SCR catalysts pretreated under N₂+5% O₂ atmosphere for 8 h. The samples were heated linearly from room temperature to 600 °C at a rate of 10 °C/min, and the results shown in Fig. 9. For commercial SCR catalyst, only one peak of mercury desorption occurred at around 453 °C. However, two desorption peaks were observed at around 135 °C and 450 °C over 1% CuCl₂-SCR catalyst. Researchers have found that the desorption peak of HgCl₂

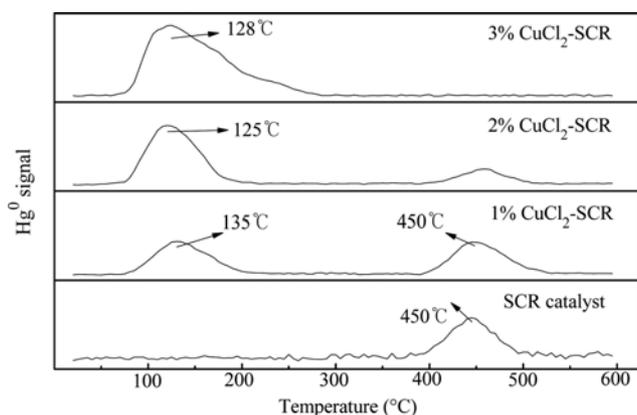


Fig. 9. Hg⁰-TPD patterns of the catalysts.

occurs at around 120-140 °C, and the desorption peak of HgO occurs at around 445-510 °C [55,56]. So it could be concluded that HgO should be the main mercury compound present on the commercial SCR catalyst surface, while both HgO and HgCl₂ were formed on the 1% CuCl₂-SCR catalyst surface. Besides, no obvious peak was identified between 150-350 °C during the TPD experiments, which could be explained that some of oxidized mercury might be released from the catalysts during the pretreated process at 350 °C. The peak area of HgO decreased with the increase of CuCl₂ content. For 3% CuCl₂-SCR catalyst, only a sharp desorption peak occurred at around 140 °C. This result indicates that only HgCl₂ was formed on the 3% CuCl₂-SCR catalyst. According to literature [57], Cu²⁺ species is effective in oxidizing Hg⁰ to HgO in an actual coal-fired flue gas. However, no HgO was formed over 3% CuCl₂-SCR catalyst in this study. It could be concluded that Cl species in CuCl₂ played a dominant role for Hg⁰ oxidation over 3% CuCl₂-SCR catalyst.

Based on our results, the addition of CuCl₂ significantly enhanced Hg⁰ oxidation over V₂O₅-WO₃/TiO₂ based SCR catalyst. It was confirmed that Hg⁰ reacted with Cl species supplied by CuCl₂ to form HgCl₂; thus, the 3% CuCl₂-SCR catalyst exhibited superior Hg⁰ oxidation activity. So it could be speculated that Hg⁰ oxidation over 3% CuCl₂-SCR catalyst follows the Mars-Maessen mechanism [32,34,36,43,52]. The detailed procedure of Hg⁰ oxidation over CuCl₂-SCR catalyst is shown in Fig. 10. In the first step, gas-phase Hg⁰ in gas flow collides with the catalyst and is adsorbed on the catalyst surface to form an adsorbed state (Hg⁰_{ad}) [36]. Then, the Hg⁰_{ad} reacts with active Cl species released by CuCl₂ to form HgCl_{2(ad)}, and CuCl₂ is reduced to CuCl [34]. When O₂ is added, the

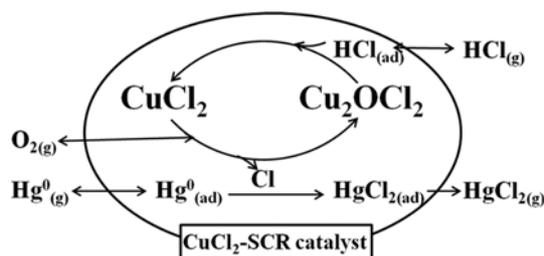


Fig. 10. Schematic diagram of Hg⁰ oxidation over CuCl₂-SCR catalyst.

reduced CuCl could react with O₂ to form the intermediate copper oxychloride (Cu₂OCl₂) [35]. Finally, when HCl is added, the Cu₂OCl₂ is re-chlorinated to CuCl₂ by reacting with adsorbed HCl. Thus, CuCl₂ is regenerated, and the first step of the reaction continues, which significantly enhances the Hg⁰ oxidation activity of CuCl₂-SCR catalyst.

CONCLUSIONS

The CuCl₂-SCR catalysts exhibited excellent performance on Hg⁰ catalytic oxidation. Hg⁰ oxidation activity was significantly enhanced by the introduction of CuCl₂. The optimal Hg⁰ oxidation activity was obtained over 3% CuCl₂-SCR catalyst at 350 °C. Hg⁰ oxidation activity was significantly strengthened in the presence of O₂. 92.1% of E_{oxi} was obtained when 5% O₂ was added in pure N₂ atmosphere. In the presence of O₂, NO had a promoting effect on Hg⁰ oxidation, while SO₂ showed an inhibiting effect. HCl exhibited facilitating effect on Hg⁰ oxidation once O₂ was added into the flue gas. In addition, CuCl₂-SCR catalyst exhibited a good H₂O resistance. Moreover, the copresence of NO and NH₃ remarkably inhibited Hg⁰ oxidation, which was due to the competitive adsorption and oxidized mercury could be reduced by NH₃ at SCR condition. Fortunately, this inhibitive effect was gradually scavenged with the decrease of GHSV. Further study revealed the possibility of simultaneous removal of Hg⁰ and NO over 3% CuCl₂-SCR catalyst in simulated flue gas. The high activity of CuCl₂-SCR catalyst could be ascribed to the CuCl₂, which acted as a redox catalyst that oxidized Hg⁰ to HgCl₂ in the presence of O₂.

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