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Mechanism of Hg^0 oxidation in the presence of HCl over a commercial $\text{V}_2\text{O}_5\text{--WO}_3/\text{TiO}_2$ SCR catalyst

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ABSTRACT

Experiments were conducted in a fixed-bed reactor containing a commercial $\text{V}_2\text{O}_5/\text{WO}_3/\text{TiO}_2$ catalyst to investigate mercury oxidation in the presence of HCl and O_2 . Mercury oxidation was improved significantly in the presence of HCl and O_2 , and the Hg^0 oxidation efficiencies decreased slowly as the temperature increased from 200 to 400°C. Upon pretreatment with HCl and O_2 at 350°C, the catalyst demonstrated higher catalytic activity for Hg^0 oxidation. Notably, the effect of pretreatment with HCl alone was not obvious. For the catalyst treated with HCl and O_2 , better performance was observed with lower reaction temperatures. The results showed that both HCl and Hg^0 were first adsorbed onto the catalyst and then reacted with O_2 following its adsorption, which indicates that the oxidation of Hg^0 over the commercial catalyst followed the Langmuir–Hinshelwood mechanism. Several characterization techniques, including Hg^0 temperature-programmed desorption (Hg-TPD) and X-ray photoelectron spectroscopy (XPS), were employed in this work. Hg-TPD profiles showed that weakly adsorbed mercury species were converted to strongly bound species in the presence of HCl and O_2 . XPS patterns indicated that new chemisorbed oxygen species were formed by the adsorption of HCl, which consequently facilitated the oxidation of mercury.

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Introduction

Mercury, which is a volatile, toxic, bio-accumulated, and persistent heavy metal, poses a significant threat to human health. Coal-fired utilities have been identified as the largest single anthropogenic emission source of mercury around the world, especially in China, India and the USA (Li et al., 2003). Mercury usually exists in three forms: Hg^{2+} , Hg^0 and Hg^{p} (particulate mercury). Among these three forms, Hg^0 is the most difficult to be remediated because of its high equilibrium vapor pressure and low solubility in water (Galbreath and Zygarlick, 2000). By contrast, Hg^{2+} can be captured in wet flue gas desulfurization (WFGD) systems (Senior et al., 2000), and

Hg^{p} can be removed using particulate control devices (Uddin et al., 2008).

The removal or conversion of Hg^0 has attracted growing interest in recent years (Presto and Granite, 2006; Schofield, 2008; Xu et al., 2013), and many technologies have been developed for this purpose. Some of the common sorbents/catalysts developed include carbon-based materials (Hutson et al., 2007; Qu et al., 2009), supported noble metals (Lee et al., 2012; Li et al., 2014; Sabri et al., 2013) and metal oxide catalysts (Ji et al., 2008; Kong et al., 2011; Li et al., 2010). Among the materials mentioned above, carbon-based materials tend to perform best for mercury abatement (Ghorishi et al., 2002; Wu et al., 2008). However, the mercury usually ends up in fly ash

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and is difficult to separate, which prevents the fly ash from being used as a concrete extender (Mei et al., 2008). Moreover, the substantial cost of carbon-based materials hinders their wide applicability, and cost is also the main drawback for supported noble metals (Reddy et al., 2012). Metal oxide catalysts have been reported to convert Hg^0 to Hg^{2+} effectively (Granite et al., 2000; Yang et al., 2011). In particular, selective catalytic reduction (SCR) catalysts were shown to convert both Hg^0 and NO_x in one system, which suggests that these materials may be more promising than other metal oxide catalysts. Furthermore, many coal-fired power plants have installed SCR systems for controlling NO_x emissions, so the future application of SCR catalysts for mercury removal will be much more convenient.

Catalysts employed in SCR systems are typically composed of vanadium and tungsten oxide supported on titania. Several catalytic mechanisms have been proposed for the oxidation of mercury over vanadia-based catalysts (Li et al., 2012; Yang and Pan, 2007). Although the precise mechanism for mercury oxidation involving HCl and SCR catalysts remains unclear, some (even controversial) possibilities have been proposed. Some researchers have suggested that the oxidation of Hg^0 over the SCR catalyst occurs via adsorbed HCl on the V_2O_5 active sites, followed by reaction of the adsorbed HCl with gaseous Hg^0 . This scenario would confirm that the reaction follows the Eley–Rideal mechanism (Niksa and Fujiwara, 2005; Senior, 2006). However, some researchers have suggested that the oxidation of mercury on the SCR catalyst follows the Langmuir–Hinshelwood mechanism. In this case, both HCl and Hg^0 first adsorb onto the vanadium sites. Then, the adsorbed HCl and Hg^0 react with each other to form an intermediate complex, which then generates HgCl_2 and H_2O (He et al., 2009). There are many factors that could affect these reaction mechanisms, such as the temperature, space velocity and the concentration of individual gases.

Among the gas components investigated in coal-fired flue gas, HCl plays a critical role for Hg^0 oxidation (Hou et al., 2014; Norton et al., 2003; Smith et al., 2011). Lee et al. (2003) reported that the HCl content in flue gas affected the adsorption and oxidation of Hg^0 over a commercial SCR catalyst. For example, 8% ppm HCl in flue gas led to 95% of Hg^0 being oxidized, whereas oxidation did not occur in flue gas without HCl . Hocquel (2004) found that Hg^0 oxidation increased as the HCl content increased using a commercial SCR catalyst, and HgCl_2 became reduced to Hg^0 at low HCl concentrations using various metal oxides.

Although studies have reported Hg^0 oxidation over a SCR catalyst in the presence of HCl , there is no general agreement on a mechanism that can explain such different results with different reaction conditions. Therefore, additional studies are required to obtain further information about the role of HCl in Hg^0 oxidation so that we might rationalize the different phenomena reported in the literature. Moreover, an understanding of mercury oxidation assisted by HCl over $\text{V}_2\text{O}_5\text{--WO}_3/\text{TiO}_2$ catalysts, which is extensively applied in power plants, may help to optimize the operation of an SCR system to maximize mercury oxidation and capture industrial applications. For these reasons, the aim of this work was to understand the fundamental mechanism governing Hg^0 oxidation over a commercial $\text{V}_2\text{O}_5\text{--WO}_3/\text{TiO}_2$ catalyst and to clarify the effect of

chlorine and oxygen on the reaction. The Hg^0 adsorption and oxidation over the $\text{V}_2\text{O}_5\text{--WO}_3/\text{TiO}_2$ catalyst were investigated using a bench-scale testing system. The roles of the specific oxidants HCl and O_2 were examined, and several characterization techniques were employed to understand the detailed mercury reaction pathways.

1. Experimental

1.1. Experimental set-up

A schematic representation of the experimental set-up is shown in Fig. 1. All individual flue gas components were from cylinder gases and were precisely controlled by mass flow controllers (D07-19B, Seven Star, Beijing, China), with a total flow rate of 150 mL/min. The gas mixture in N_2 balance contained 6% O_2 and 1 ppm HCl . The Hg^0 permeation tube was placed in a U-shaped container that was in a water bath. This device was used to provide a constant concentration of Hg^0 using N_2 as the carrier gas. The concentration of Hg^0 was controlled by adjusting the water bath temperature, and the carrier gas flow rate was fixed at 50 mL/min. Mercury vapor in the N_2 carrier gas was mixed with the reactant gas mixture immediately before the sample reached the catalyst bed. The mercury concentration in the gas mixture was varied from 30 to 50 $\mu\text{g}/\text{m}^3$ for all experiments. The concentration of mercury was analyzed by a mercury analyzer (RA 915M, Lumex, St. Petersburg, Russia; MD-254, Lab-tech, Boston, Massachusetts, USA) with a minimum limit of detection of approximately 0.1 $\mu\text{g}/\text{m}^3$.

The operation parameters used in the experiments, such as the type and concentration of individual gases and the reaction temperature, were chosen to simulate the conditions in coal-fired flue gas in a SCR reactor. Other parameters, such as particle size and space velocity, were obtained from the literature and optimized in preliminary experiments to minimize or eliminate mass transfer limitations.

1.2. Experimental procedure

The catalyst employed in this study was a $\text{V}_2\text{O}_5\text{--WO}_3/\text{TiO}_2$ commercial honeycomb SCR catalyst used in coal-fired power plants. The monolithic catalyst was crushed and sieved through 80–100 mesh and dried for 2 hr at 110°C. The catalysts were then stored in a desiccator before testing.

Catalytic activity measurements were performed in a quartz tube fixed-bed reactor with an inner diameter of 4 mm. For each test, 50 mg of catalyst was loaded in the reactor, which was placed in a temperature-controlled tubular furnace to maintain thermal stability. The reaction temperature ranged from 150 to 400°C. At each designated temperature, the Hg^0 concentration before and after the fixed-bed reactor was recorded once the process had reached the steady state, which is defined as when the fluctuations in the Hg^0 concentration were no more than 5% for more than 0.5 hr. The mean values of these two Hg^0 concentrations were used to calculate Hg^0 removal efficiencies by the following equation:

$$E_{\text{removal}} = (\text{Hg}_{\text{in}}^0 - \text{Hg}_{\text{out}}^0) / \text{Hg}_{\text{in}}^0 \times 100\%$$

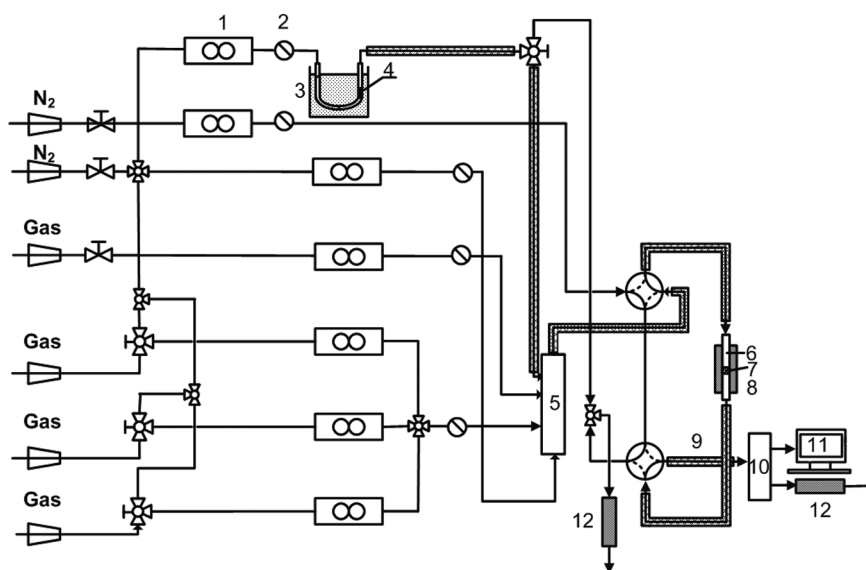


Fig. 1 – Schematic flow chart of Hg^0 removal system: (1) mass flow controller, (2) check valve, (3) water bath, (4) Hg^0 permeation tube, (5) gas mixing chamber, (6) quartz reactor, (7) samples, (8) furnace, (9) heating tape, (10) Hg^0 mercury analyzer, (11) computer and (12) tail gas cleaner.

where, E_{removal} is the Hg^0 removal efficiency and Hg_{in}^0 and Hg_{out}^0 are the Hg^0 concentrations of the inflow and outflow to the reactor, respectively.

1.3. Characterization of catalysts

Hg-TPD (Hg Temperature-programmed desorption) was conducted using 50 mg of the catalyst in a quartz reactor. The adsorption was performed by passing a gas mixture containing $40 \mu\text{g}/\text{m}^3$ Hg^0 with N_2 as the balance gas through the sample bed at 25°C and at a total flow rate of 150 mL/min. The experiment consisted of three stages: (1) sweep of the sample in N_2 at 350°C for 2 hr; (2) adsorption of Hg^0 for approximately 5 hr in an O_2/N_2 , HCl/N_2 or $\text{O}_2/\text{HCl}/\text{N}_2$ atmosphere, and purge by N_2 for 2 hr; and (3) TPD measurements were performed up to 500°C at a heating rate of $10^\circ\text{C}/\text{min}$, with the total N_2 flow rate of 150 mL/min. An on-line mercury analyzer (RA 915M, Lumex, Russia; or MD-254, Lab-tech, USA) continuously recorded the concentration of Hg^0 .

The chemical states and elemental speciation of the samples were analyzed using X-ray photoelectron spectroscopy (ESCALAB 250, Thermo, Waltham, Massachusetts, USA) with a monochromated Al $K\alpha$ X-ray source ($h\nu = 1486.6 \text{ eV}$). The spectrometer operated in a vacuum of less than 10^{-9} mbar and at a power of 150 W. The binding energy was calibrated using adventitious carbon (284.6 eV).

2. Results and discussion

2.1. Effect of HCl on Hg^0 oxidation under different conditions

Temperature is an important parameter for Hg^0 removal on $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ catalysts. Fig. 2 shows the oxidation efficiencies of Hg^0 oxidation at different temperatures and in different atmospheres. In the O_2/N_2 atmosphere, the efficiency of Hg^0 oxidation increased as the temperature increased, which is

similar to observations made previously (Kim et al., 2010; Kamata et al., 2009). In contrast, the efficiency of Hg^0 oxidation decreased as the temperature rose in the HCl/N_2 atmosphere. Generally, chemical reaction rates are positively correlated with temperature. Therefore, Hg^0 oxidation is expected to increase as the temperature rises, as was found for reaction in the O_2/N_2 atmosphere. The probable reason for the unexpected result in the HCl/N_2 atmosphere was that the increased temperature decreased the adsorption of HCl or Hg^0 onto the $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ catalyst, which consequently decreased the efficiency of Hg^0 oxidation. In other words, it is the adsorbed rather than gaseous HCl or Hg^0 that participates in the Hg^0 oxidation reaction. When both HCl and O_2 were present, the $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ catalyst demonstrated much higher Hg^0 oxidation efficiencies than in the O_2/N_2 or HCl/N_2 atmospheres. Further, the Hg^0 oxidation

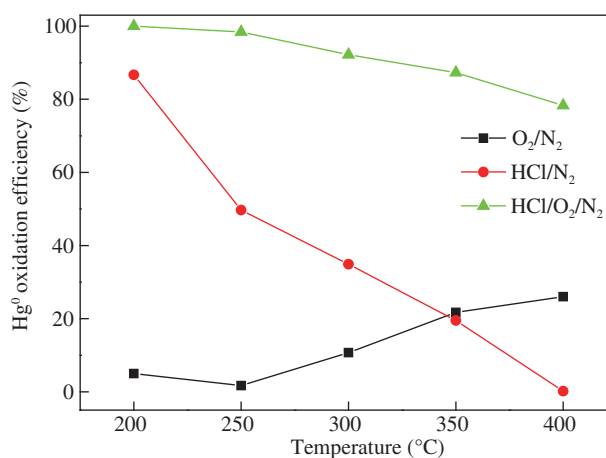


Fig. 2 – Hg^0 oxidation over $\text{V}_2\text{O}_5/\text{WO}_3/\text{TiO}_2$ catalysts at different temperatures. Reaction conditions: $32 \mu\text{g}/\text{m}^3$ Hg^0 , 6% O_2 , 1 ppm HCl and WHSV (weight hourly space velocity) = $1.8 \times 10^5 \text{ mL}/(\text{g}\cdot\text{hr})$.

efficiencies decreased slowly as the temperature increased, indicating that the adsorption of HCl dominated the Hg^0 oxidation reaction.

Clearly, the oxidation of Hg^0 was enhanced by the combined action of O_2 and HCl. However, the concentration of O_2 was two orders of magnitude higher than the concentration of HCl. Therefore, it is logical to assume that HCl reacted with the $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ catalyst with the aid of O_2 to form active Cl species that were responsible for the enhancement of Hg^0 oxidation. The $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ catalyst was pretreated with HCl to verify that the hypothesized mechanism for the oxidation of Hg^0 is improved with HCl. As shown in Fig. 3a, pretreatment by HCl and O_2 facilitated Hg^0 oxidation at 350°C . After passing through the HCl- and O_2 -pretreated catalyst for 14 hr, the outlet Hg^0 concentration was approximately $26.1 \mu\text{g}/\text{m}^3$, which is clearly lower than that observed for the catalyst without pretreatment. This result indicates that some active Cl species were formed and remained on the catalyst surface during the pretreatment process. Because the catalyst pretreated with HCl or pure O_2 showed similar catalytic activity to that of the sample without pretreatment, it is clear that the active Cl species are not generated by the presence of HCl or O_2 alone; instead, it appears as though they can only be formed by the combined action of both O_2 and HCl.

To more fully investigate the HCl- and O_2 -pretreated catalyst, it was tested at different temperatures. Fig. 3b shows that the catalyst performed much better as the reaction temperature decreased. Notably, the mercury was almost completely removed after 14 hr when the catalyst was tested at 150°C . For comparison, the outlet Hg^0 concentrations after 14 hr at 250 and 350°C were approximately 15.6 and $26.1 \mu\text{g}/\text{m}^3$, respectively. Clearly, this result indicates that lower temperatures benefit mercury oxidation. The most probable reason for this behavior is that lower temperatures facilitate the adsorption of Hg^0 and hence promote its oxidation. It also can be inferred that it is the adsorbed Hg^0 rather than the mercury vapor that participates in and dominates the reaction. This inference was in accordance to the one reached in the discussion of Fig. 2.

The catalysts were treated by HCl and O_2 at three different temperatures. As shown in Fig. 3c, the catalyst treated at 100°C demonstrated the worst performance, as indicated by

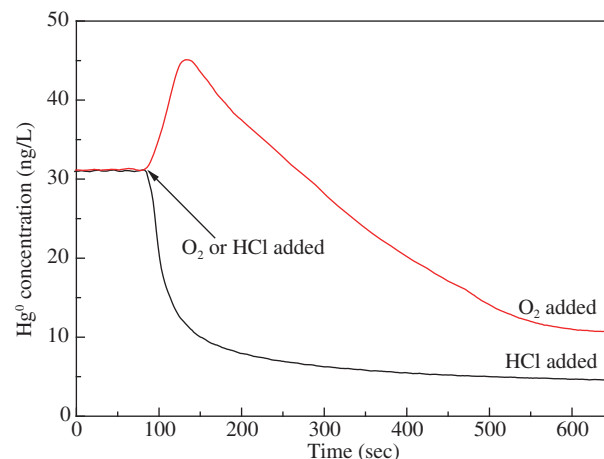


Fig. 4 – Measured concentrations of Hg^0 following the injection of O_2 or HCl into the reactor. Original Hg^0 concentration = 31 ng/L , WHSV (weight hourly space velocity) = $1.8 \times 10^5 \text{ mL}/(\text{g}\cdot\text{hr})$, reacted at 350°C .

the return of the Hg^0 concentration to its original value after passing through the catalyst for approximately 7 hr. The catalyst treated at 200°C demonstrated slightly better performance than the one treated at 100°C , indicating that a small amount of active chlorine species was formed at this higher temperature. Clearly, the $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ catalyst pretreated at 350°C demonstrated the best performance compared to the catalysts pretreated at lower temperatures. Notably, the Hg^0 concentration was only $26.1 \mu\text{g}/\text{m}^3$ after passing through the catalyst for approximately 14 hr, implying that $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ catalysts are more reactive with HCl at higher temperatures. This result also indicates that the chlorine species on the catalyst are stable at 350°C , and not decomposed in the pretreatment process, or the significant loss of elemental mercury would not be observed.

In a N_2 atmosphere, Hg^0 was passed into the catalyst until equilibrium was achieved. Then, HCl or O_2 was added into the Hg/N_2 system and the result was recorded. As shown in Fig. 4, a significant increase of the Hg^0 concentration was observed

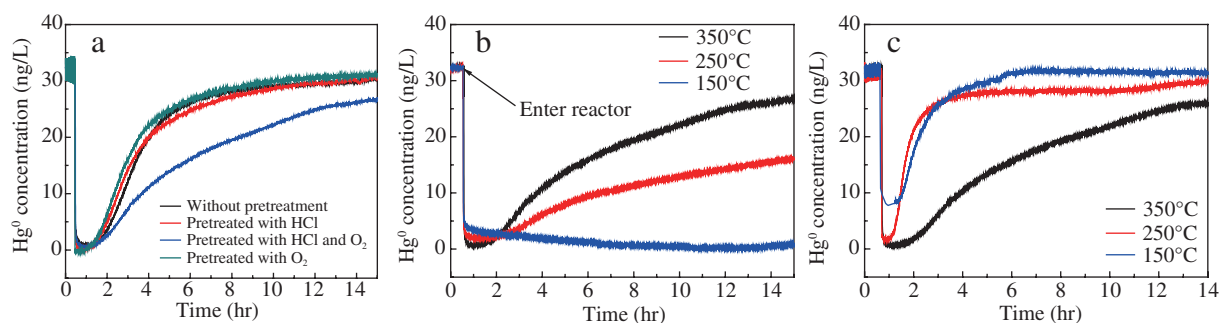


Fig. 3 – Hg^0 breakthrough curves for $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ catalysts. (a) Catalyst pretreated in different atmospheres at 350°C for 2 hr and reacted at 350°C , (b) catalyst pretreated in $\text{HCl}/\text{O}_2/\text{N}_2$ at 350°C for 2 hr and reacted at different temperatures; and (c) catalyst pretreated in $\text{HCl}/\text{O}_2/\text{N}_2$ at different temperatures for 2 hr and reacted at 350°C . Reaction conditions: 32 ng/L Hg^0 , 6% O_2 , WHSV (weight hourly space velocity) = $1.8 \times 10^5 \text{ mL}/(\text{g}\cdot\text{hr})$, N_2 purge for 0.5 hr after the pretreatment of the catalysts, and then tested in O_2/N_2 .

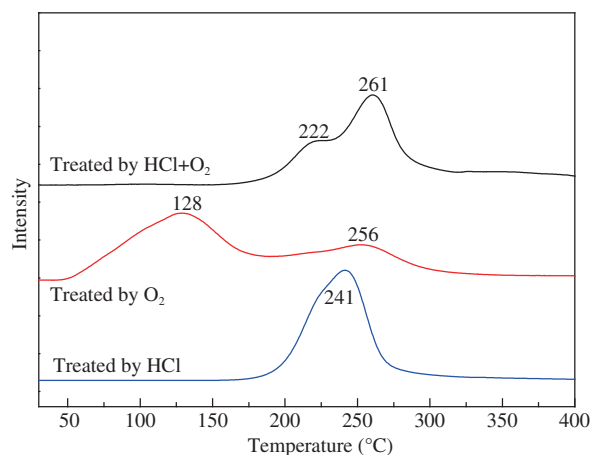


Fig. 5 – Hg-TPD profiles following adsorption in HCl/N₂, O₂/N₂ and HCl/O₂/N₂ at a heating rate of 10°C/min.

following the addition of HCl. Then, the concentration decreased gradually until another equilibrium state was reached. This result indicates that HCl competes with Hg⁰ for active sites on the catalyst and that the affinity of V₂O₅-WO₃/TiO₂ for HCl is stronger than for Hg⁰. It also suggested that HCl was adsorbed onto the catalyst before the reaction with Hg⁰ occurred, and that gaseous HCl could not react directly with Hg⁰. In contrast, the Hg⁰ concentration decreased rapidly when O₂ was added. On the basis of this result it can be inferred that gaseous O₂ can react directly with Hg⁰, or that the active sites onto which O₂ is adsorbed are different than those for Hg⁰. As discussed before, it is the adsorbed Hg⁰ that participates in the mercury oxidation reaction. Therefore, it can be concluded that Hg⁰ oxidation in the presence of HCl over the commercial catalyst primarily follows the Langmuir–Hinshelwood mechanism. This conclusion is in accordance with reports by Eom and He, who also proposed the Langmuir–Hinshelwood mechanism to rationalize mercury oxidation on a V₂O₅/TiO₂ catalyst (Eom et al., 2008; He et al., 2009). The oxidation mechanism on a V₂O₅-WO₃/TiO₂ catalyst has also been investigated (Gao et al., 2013), however, in this case an Eley–Rideal mechanism was postulated to occur. These different conclusions are likely to be the result of different catalysts and/or operational parameters.

2.2. Characterization of catalysts

The Hg-TPD technique was applied following the mercury removal experiments to identify the captured mercury on the catalysts. The results are shown in Fig. 5. For the catalyst adsorbing Hg in an O₂/N₂ atmosphere, two desorption peaks are observed at approximately 128 and 256°C. The low-temperature peak is caused by the decomposition of weakly adsorbed species, whereas the high-temperature peak is ascribed to strongly bound species (Wan et al., 2011). Clearly, the peak area at 128°C is higher than the peak at 256°C, and the quantity of the desorbed Hg⁰ was 60.5 and 30.6 ng for the two peaks respectively, indicating that the majority of the mercury content existed as weakly adsorbed species. However, for the catalyst adsorbing Hg⁰ in a HCl/O₂/N₂ atmosphere, a desorption peak at 261°C desorbing 14.5 ng Hg⁰ and a shoulder at 222°C desorbing 53.1 ng Hg⁰ were observed, which indicates that the majority of the mercury existed as strongly bound species. The Hg-TPD profile for the HCl/N₂ atmosphere shows a peak at 241°C, which is similar to the findings of Ozaki et al. (2008). In conclusion, the mercury species captured on the catalyst appear to be altered by the presence of HCl. Further, weakly adsorbed mercury species were converted to strongly bound species with the assistance of O₂. Because the adsorbed mercury species on the catalyst surface are known to play an important role in these reactions, the present results show good Hg adsorption on the catalyst's surface in an HCl/O₂/N₂ atmosphere, which consequently facilitates the oxidation of Hg⁰.

To further identify the Hg⁰ removal mechanism, the catalysts were analyzed by XPS. First, samples were subjected to a HCl/N₂ or HCl/O₂/N₂ atmosphere for 120 min at 350°C. Subsequently, pure N₂ was passed through the samples for 30 min to remove the weakly adsorbed HCl. As shown in Fig. 6, peaks were observed at 530.0 (Peak A), 532.2 (Peak B) and 534.0 eV (Peak C). The peak at 530.0 eV can be attributed to lattice oxygen atoms (He et al., 2009). The other two peaks with higher binding energies can be assigned to chemisorbed oxygen and hydroxyl species (Hou et al., 2014). Following the pretreatment with HCl/N₂ or HCl/O₂/N₂, the peak at 532.2 eV increased from 13.9% to 14.5% and 16.6% for HCl/N₂ and HCl/O₂/N₂, respectively (shown in Fig. 7), indicating that new chemisorbed oxygen species were formed. The formation of these new species could be caused by the adsorption of HCl. According to

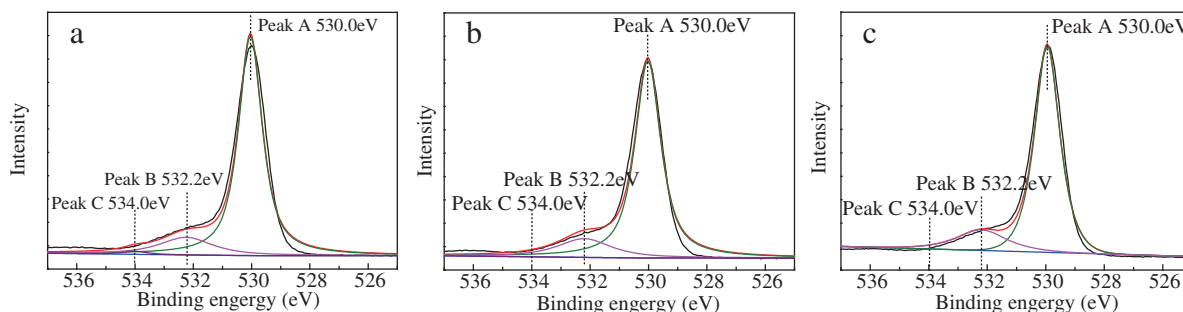


Fig. 6 – XPS spectra of the O1s peaks of (a) fresh V₂O₅-WO₃/TiO₂ catalyst, (b) V₂O₅-WO₃/TiO₂ catalyst pretreated with HCl and (c) V₂O₅-WO₃/TiO₂ catalyst pretreated with HCl and O₂.

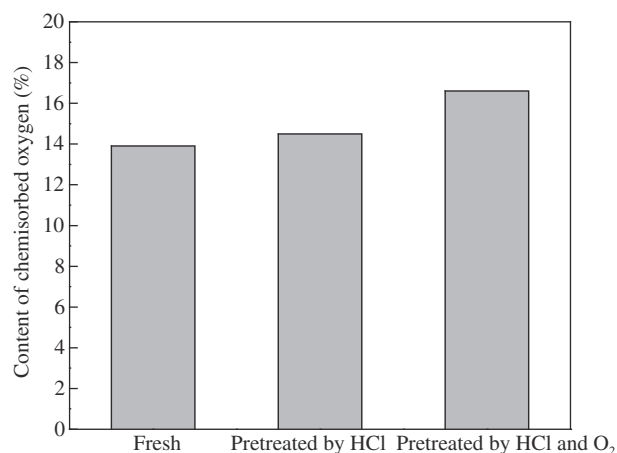
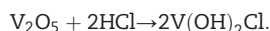
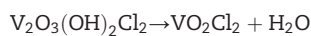
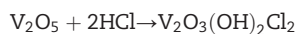
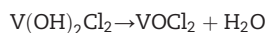
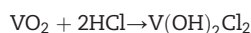


Fig. 7 – The content of chemisorbed oxygen in different samples.

the literature (He et al., 2009; Machalek et al., 2003), the vanadium oxides supported on TiO₂ react with HCl as follows:



Chemisorbed oxygen has been reported to be very active and may be responsible for mercury removal (Li et al., 2011). Furthermore, compared to the catalyst treated by HCl/N₂, peaks A and B were larger for the sample treated by HCl/O₂/N₂. We suggest that the presence of gaseous O₂ replenishes the

consumed chemisorbed oxygen, which regenerates the lattice oxygen and hence maintains a high surface oxygen concentration. Therefore, more HCl can be oxidized to form active chlorine species in the presence of gaseous O₂.

On the basis of the experimental data obtained in this study, the mechanism of the mercury oxidation on the V₂O₅-WO₃/TiO₂ SCR catalyst is proposed and illustrated in Fig. 8. In the first step, one molecule of Hg⁰ adsorbs on the sample surface to form an adsorbed species (Hg⁰_{ads}) (Fan et al., 2010). At the same time, two molecules of HCl also become adsorbed on the catalyst to form an adsorbed state (HCl_{ads}). The active sites are similar for HCl and Hg⁰ adsorption, though their affinity for HCl is stronger. Thus, when HCl is added after the addition of Hg⁰, the latter species is displaced from the active sites, as shown in Fig. 4. Following the adsorption of Hg⁰ and HCl, Hg⁰_{ads} reacts with HCl_{ads} to form an intermediate complex, which decomposes to V₂O₅, HgCl₂ and water, completing the reaction cycle. Additionally, the adsorbed HCl on the catalyst will be converted to atomic chlorine with the addition of O₂ (Xu et al., 2014; Zhou et al., 2014), which enhances Hg⁰ oxidation and consequently accelerates the oxidation reaction.

The mechanism deduced in this study is different from those suggested previously. For example, Gao et al. (2013) investigated the oxidation of Hg⁰ using the V₂O₅-WO₃/TiO₂ SCR catalyst and concluded that the reaction followed the Eley–Rideal mechanism in the presence of HCl. In addition, others have reported that the oxidation of Hg⁰ follows the Langmuir–Hinshelwood mechanism by the assistance of HCl when the SCR catalyst V₂O₅/TiO₂ is used (He et al., 2009). The present study seeks to enrich the discussion of Hg⁰ oxidation with SCR catalysts and has shown that different reaction conditions may affect the type of mechanism that is operative.

3. Conclusions

This study investigated a commercial V₂O₅-WO₃/TiO₂ catalyst for its ability to oxidize Hg⁰ in the presence of HCl and O₂. Mercury oxidation was enhanced remarkably by adding HCl and O₂ to the atmosphere. The catalytic activity could also be improved by pretreatment of the catalyst with HCl and O₂. It is the adsorbed HCl and Hg⁰ rather than their gaseous counterparts that participate in the reaction, which suggests that the oxidation of Hg⁰ over the V₂O₅-WO₃/TiO₂ catalyst in the presence of both HCl and O₂ primarily follows the Langmuir–Hinshelwood mechanism. In the presence of HCl and O₂, weakly adsorbed mercury species were converted to strongly bound species, and new chemisorbed oxygen species were formed on the surface of the catalyst, which consequently facilitated mercury oxidation.

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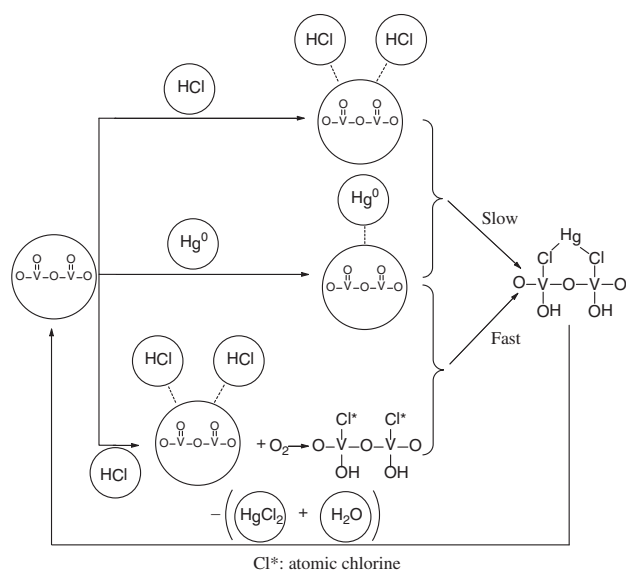


Fig. 8 – Schematic of the proposed mechanism of Hg⁰ oxidation in a HCl/O₂/N₂ atmosphere over the V₂O₅-WO₃/TiO₂ catalyst.

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