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Mechanism of Hg^0 oxidation in the presence of HCl over a commercial V_2O_5–WO_3/TiO_2 SCR catalyst

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ABSTRACT

Experiments were conducted in a fixed-bed reactor containing a commercial V_2O_5/WO_3/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.

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 Zygarlicke, 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 NOx 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 NOx 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 V_2O_5–WO_3/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 V_2O_5–WO_3/TiO_2 catalyst and to clarify the effect of chlorine and oxygen on the reaction. The Hg^0 adsorption and oxidation over the V_2O_5–WO_3/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 $\mu g/m^3$ 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 $\mu g/m^3$.

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 V_2O_5–WO_3/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:

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