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Synergistic effect of HCl and NO in elemental mercury catalytic oxidation over La_2O_3-TiO_2 catalyst

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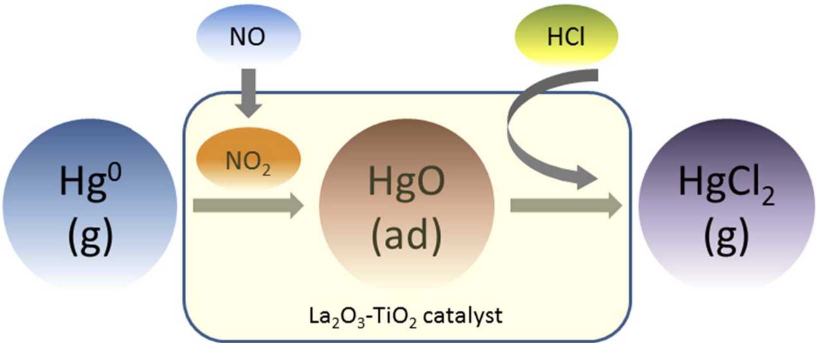
GRAPHICAL ABSTRACT



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ABSTRACT

Elemental mercury (Hg^0) oxidation over a low-temperature La_2O_3-TiO_2 (LaTi) catalyst through a fixed-bed reactor system is reported here. Despite the presence of oxygen (O_2), Hg^0 was not effectively oxidized by either hydrogen chloride (HCl) or nitrogen oxide (NO). However, Hg^0 oxidation over the LaTi catalyst was greatly improved when both HCl and NO were present in the simulated flue gas. Several methods, including X-ray photoelectron spectroscopy (XPS), diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy, and temperature-programmed decomposition (TPD), were used to study the inherent mechanisms involved in the Hg^0 oxidation by HCl and NO. The results indicated that the combined presence of HCl and NO exhibited great synergy for Hg^0 catalytic oxidation over the LaTi catalyst. The reaction mechanism is proposed as follows: 1) NO was adsorbed and oxidized on the catalyst surface, forming NO_2; 2) the reactive NO_2 then oxidized gas phase Hg^0 to mostly HgO, and; 3) HgO reacted with gas phase HCl to produce $HgCl_2$, which escaped from the catalyst's surface. Differing from previously proposed mechanisms, La_2O_3 was first studied as an active substance in Hg^0 oxidation. These findings are beneficial for those seeking economical and efficient Hg^0 oxidation catalysts for coal-fired power plants.

1. Introduction

Mercury (Hg) is a trace element of special environmental and health concern due to its persistence, volatility, bioaccumulation, and toxic effects on the human nervous system [1]. Coal-fired power plants, especially those equipped with utility boilers, are often regarded as the

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largest emission source of anthropogenic mercury worldwide [2]. By December 2011, both China and the United States had adopted strict standards for limiting mercury discharge from the power plants with coal as their main energy source. Furthermore, the 50-ratification milestone for the Minamata Convention on Mercury was reached on May 18th, 2017. As a result, the Minamata Convention, aiming at the protection of human health and the environment from anthropogenic mercury emissions, will go into effect on August 16th, 2017. To meet these global and national mercury emission standards, efficient mercury control technologies for coal-fired power plants are urgently needed.

Control methods, such as activated carbon injection (ACI) and catalytic oxidation followed by wet flue gas desulfurization (WFGD) [3–5], have been adopted by power plants to prevent gas-phase mercury from emitting from the stack into the atmosphere. Generally, the efficiency of a mercury control technology is highly dependent on the mercury species [6]. In addition to oxidized mercury (Hg^{2+}), particulate-bound mercury (Hg^p) and elemental mercury (Hg^0) are present in coal combustion flue gas [6]. Among these three different forms, Hg^p can be effectively removed by existing particulate matter (PM) control devices, such as fabric filters (FF) and electrostatic precipitators (ESP), while the water-soluble Hg^{2+} is easily captured in WFGD systems or adsorbed by fly ash and then collected by PM control devices [7,8].

In contrast, it is challenging to capture Hg^0 vapor with conventional air pollution control devices (APCDs) [9], due to its high degree of volatility and insolubility in water [10]. As the popular commercial technology for the removal of Hg^0 from coal-fired flue gas, ACI technology employs activated carbon to adsorb Hg^0, and then removes the adsorbed mercury and activated carbon together, using PM control devices. However, the application of ACI is limited by its high cost and dependence on coal type, reaction temperature, and inlet mercury concentration [11]. Another promising method is to catalytically oxidize Hg^0 to Hg^{2+}, which can be collected easily by WFGD systems. Even though Hg^0 could re-emit from the WFGD systems [12], several methods such as adding solid porous materials could avoid or alleviate the Hg^0 re-emission process [13].

In recent years, several potential Hg^0 oxidation catalysts, including noble metals, metal oxides, such as vanadium (V) oxide (V_2O_5), manganese (III) oxide (Mn_2O_3), cerium (IV) oxide (CeO_2), iron (III) oxide (Fe_2O_3), chromium (III) oxide (Cr_2O_3) and copper (II) oxide (CuO), and lanthanum manganite ($LaMnO_3$)-based perovskites were extensively investigated [14–21]. Among these catalysts, V_2O_5, which was originally designed for selective catalytic reduction (SCR) of nitrogen oxides (NO_x), was demonstrated to be effective for Hg^0 oxidation [22]. However, Hg^0 oxidation efficiency over V_2O_5-based SCR catalyst highly depends on the hydrogen chloride (HCl) concentration in coal combustion flue gas [17]. Less than 30% Hg^0 oxidation was achieved for sub-bituminous coal combustion flue gas with a small amount of HCl [23]. Therefore, it is necessary to develop a catalyst that is reactive for Hg^0 oxidation in flue gas with a low HCl concentration. In addition, the operating temperature (typically 300–400 °C) for a V_2O_5-based SCR catalyst requires the SCR reactor to be located upstream of the FF/ESP and WFGD, which might accelerate the deactivation of catalyst through exposure to high concentrations of PM [24]. Therefore, it is critical to develop an SCR catalyst with high Hg^0 oxidation activity at low temperatures (100–250 °C), which allows the SCR reactor to be placed downstream of PM control devices to slow down the deactivation of the catalysts.

La_2O_3 was demonstrated to be an effective low-temperature catalyst for NO_x SCR because of its near 100% selectivity to nitrogen [25–27]. It should be noted that La_2O_3 significantly promoted the oxidation of NO to NO_2 at low temperatures [28], which was reported to be capable of oxidizing Hg^0 into mercury oxide (HgO) [29,30]. Compared with the high energy barrier between HCl and Hg^0 [31], HCl is more likely to react with HgO to generate mercury chloride ($HgCl_2$), which can then escape from the catalyst surface and be subsequently removed by WFGD [14]. Based on the above assumptions, we hypothesize that the synergistic effect of HCl and NO in elemental mercury catalytic oxidation over a La_2O_3-TiO_2 (LaTi) catalyst could potentially work with low flue gas temperatures. If demonstrated, the LaTi catalyst could be a promising candidate for Hg^0 catalytic oxidation at low temperatures, since HCl and NOx generally coexist in coal combustion flue gases. However, no related study has yet been reported.

In the present study, LaTi catalyst prepared through a sol-gel method was applied for Hg^0 oxidation at a relatively low flue gas temperature. HCl exhibited negligible impact in Hg^0 oxidation over the LaTi catalyst, even in the presence of O_2. NO partially facilitated Hg^0 oxidation on the LaTi catalyst, but the Hg^0 oxidation efficiency was still low. However, the Hg^0 oxidation was significantly improved with the co-presence of HCl and NO. The goal of the present study was to identify the mechanisms that were responsible for the synergistic effect of HCl and NO in Hg^0 oxidation over the LaTi catalyst.

2. Experimental section

2.1. Materials preparation

The sol-gel method was used for the preparation of LaTi catalyst. A stoichiometric amount of lanthanum nitrate (Aladdin, AR, 99%) was dissolved in a solution consisting of nitric acid (Sinopharm, AR, 66.5%), anhydrous ethanol (Sinopharm, AR, 66.5%), and deionized water with volume ratio of 1:5:5. Then 50 ml Anhydrous ethanol and butyl titanate (Sinopharm, CP, 98%) mixed solution with volume ratio of 1:9 was dropwise added to 22 ml lanthanum nitrate solution with vigorous stirring to promote hydrolysis at 25 °C. The stirring continued for 3 h (h) after the titration finished to form a sol. The sol was dried at 80 °C for 24 h to obtain a gel. The resulting gel was subsequently calcined in air at 300 °C for 1 h, followed by raising the temperature to 750 °C at a rate of 10 °C/min, and then calcined at 750 °C for another 5 h to generate the final LaTi catalyst. The catalyst was grounded and sieved to 80–100 meshes. The mass ratio of La_2O_3 and TiO_2 was 0.4 (corresponding to mole ratio of 0.1), of which the LaTi catalyst exhibited the best Hg^0 oxidation performance in our preliminary studies.

2.2. Catalytic activity measurement

The catalytic activity of LaTi catalyst was evaluated by using a laboratory-scale experimental system, shown in Fig. 1. The simulated flue gas components, including N_2, O_2, NO, and HCl, were from compressed cylinder gases, and the flow of each gas was precisely controlled by mass flow controllers (MFC), with a total flow rate of 1 liter per minute (L/min). A sustained feed of Hg^0 vapor (about $75\,\mu g\cdot m^{-3}$) was generated from a Dynacal mercury permeation device (VICI Metronics) mounted in a sealed U-shaped glass tube loaded in a thermostat water bath. The vapor-phase Hg^0 with high purity N_2 as the carrier gas was introduced into a chamber to mix with other flue gases. Downstream of the mixing chamber, a borosilicate glass reactor with 10-mm inner diameter was placed in a temperature-controlled tube furnace. The reaction temperature was kept at 200 °C with fluctuation less than 1 °C, at which the LaTi catalyst exhibited the best Hg^0 oxidation performance in the preliminary study. 0.40 g LaTi catalyst was loaded in the middle of borosilicate glass reactor during each test, which corresponded to a gas space hourly velocity (GHSV) of $160000\,h^{-1}$. Hg^0 concentrations were continuously monitored by a mercury analyzer (VM3000 Mercury Instruments) at the inlet and outlet of the borosilicate glass reactor. To improve the experimental accuracy, a sodium hydroxide (NaOH) solution and a condenser were employed to remove acid gases and water vapor in simulated flue gas before proceeding to the mercury analyzer, respectively. A sodium borohydride ($NaBH_4$) solution was used to reduce Hg^{2+} to Hg^0 at the outlet of the reactor, which would therefore be measured as total mercury (Hg^T).

Prior to each test, the gas stream bypassed the reactor and the inlet