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CuO/TiO$_2$ catalysts for gas-phase Hg^0 catalytic oxidation

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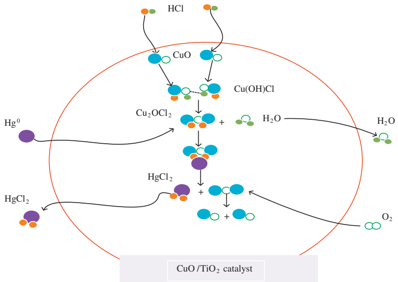
HIGHLIGHTS

- CuO/TiO$_2$ catalyst is highly active for Hg^0 oxidation over the temperature range of 50–300 °C.
- HCl was adsorbed on the CuO sites to form the key intermediate product (Cl–Cu–OH).
- The partial Deacon Mechanism may be one of the pathways for Hg^0 oxidation in HCl/N$_2$–O$_2$ over CuO/TiO$_2$.
- The dominant pathway may be the direct reaction between gas-phase Hg^0 with the intermediate Cl–Cu–OH.

GRAPHICAL ABSTRACT



The process of Hg^0 oxidation in HCl/N$_2$-O$_2$ over CuO/TiO$_2$ catalyst.

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ABSTRACT

CuO/TiO$_2$ catalysts prepared by an impregnation method were studied to determine their efficiencies of mercury oxidation in the simulated flue gas. In this study, 7% CuO/TiO$_2$ was found to be an optimal catalyst with an oxidation efficiency of over 98% at temperatures in the range of 50–300 °C. X-ray diffractograms (XRD), Brunauer–Emmet–Teller (BET) measurements, transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS) were used to characterize the catalysts; the results indicated the CuO was well-dispersed on the surface of TiO$_2$ and that Cu^{2+} was the primary Cu species contributing to Hg^0 oxidation. HCl was the most effective flue gas component responsible for the Hg^0 oxidation. Also, 5-ppm HCl resulted in 100% Hg^0 oxidation under the experimental conditions. The mechanism of Hg^0 oxidation was also investigated.

1. Introduction

Mercury, being a highly toxic heavy element, has received considerable attention from environmental researchers due to its high volatility, environmental persistence, and robust bioaccumulation properties. Coal combustion is the largest anthropogenic source of mercury emissions in the world [1–3]. Mercury in the flue gas of coal combustion is present in three forms: elemental mercury (Hg^0), oxidized mercury (Hg^{2+}), and particulate-bound mercury (Hg$_p$). Hg^{2+} is water-soluble and may therefore be effectively captured by wet flue gas desulfurization systems as a co-benefit. Most Hg$_p$ can be collected by electrostatic precipitators or fabric filters. However, Hg^0 is the most difficult species to remove because of its high volatility and low aqueous solubility [4]. Due to the intractability of Hg^0, the study on Hg^0 removal from flue gas is becoming increasingly important.

The particulate adsorption method and oxidation method have been considered to be the most effective methods for control of Hg^0 emissions. As a representative adsorbent for Hg^0, activated carbon has been frequently used in an injection chamber [5], but has not been widely used commercially because of its high price and its negative effect on fly ash quality [6]. The drawbacks associated with the use of particulate adsorbents make the oxidation method be potentially attractive. Currently, certain transition metal catalysts, such as V$_2$O$_5$, MnO$_2$, Co$_3$O$_4$, and CeO$_2$, and noble metal

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catalysts, such as Rh, Au, and Pd, had been observed to be effective for the oxidation of Hg^0 to Hg^{2+} [7–12]. Compared with noble metal catalysts, the lower-cost transition metal catalysts also exhibit high catalytic oxidation activity, but the activation is affected by different flue gases. To prevent the deactivation of these catalysts due to exposure to high concentrations of fly ash, catalysts are better placed downstream of the electrostatic precipitators or fabric filters, where the flue gas temperature (below 250 °C) is relatively low, and thermal decomposition of formed mercuric compounds can be avoided [13]. The operating temperature of a V_2O_5-based catalyst is 300–350 °C, which is higher than 250 °C [7]. As a result, we focus on catalysts with high Hg^0 catalytic oxidation efficiency at low temperatures.

HCl is known to be able to efficiently oxidize Hg^0. However, such oxidation is difficult to realize at low HCl concentrations using the traditional V/TiO_2 catalyst [7]. Consequently, we examined Hg^0 oxidation at low HCl concentrations. Several mechanisms, including the Deacon process (HCl can be oxidized to Cl_2 or Cl by oxygen), the Langmuir–Hinshelwood mechanism, the Eley–Rideal mechanism and the Mars–Maessen mechanism, have been proposed to explain the heterogeneous Hg^0 oxidation in the presence of HCl [4]. CuO has been regarded as a good active component for HCl oxidation through the Deacon process [14]. In addition, CuO has demonstrated to be high oxidation activity for NO_x and SO_x and CO removal at low temperatures [15,16]. CuO has also exhibited good oxidation efficiency for Hg^0 oxidation at low HCl concentration; however, its oxidation activity decreased as the CuO particle size increased [17]. Furthermore, pure CuO is thermo-unstable. It has been reported that TiO_2 is a good carrier for many catalysts, supporting such reactions as the SCR reaction [18] and Hg^0 oxidation [19]. However, there have been few studies reporting the use of a CuO catalyst supported on TiO_2 as a system for Hg^0 oxidation. Furthermore, no single process has been verified as the dominant mechanism for Hg^0 oxidation. Therefore, the mechanism dominating Hg^0 oxidation over CuO/TiO_2 catalysts needs to be defined.

Based on the above discussion, the aim of this study was to investigate the Hg^0 oxidation efficiencies of the metal oxide catalysts loaded onto TiO_2. The effect of HCl concentration was examined. Furthermore, XRD, BET, TEM, and XPS were used to characterize the catalysts, and the reaction mechanism was discussed based on the experimental and characterization results. This study provides information regarding the industrial applications of CuO/TiO_2 catalysts.

2. Experimental

2.1. Catalyst preparation

The catalysts were prepared by incipient wetness impregnation method as follows: first, the aqueous solutions of metal nitrates were dissolved in de-ionized water to form the solution. Then, TiO_2 was added to the solution with stirring in a proportion. Third, excess water was evaporated while stirring, and the solid obtained was dried at 110 °C and calcined at 500 °C for 4 h in air. Finally, all the catalysts above were sized to 40–60 mesh for testing. The catalysts were denoted as $x\%$ MOx/TiO_2, where x represented the weight ratio of M to TiO_2.

2.2. Catalyst activity test

The catalytic activity was evaluated in a fixed-bed reactor (Fig. 1) containing 0.05 mL of catalyst (25 mg). The flow rate of gas was 700 mL/min, which provided for a gas hourly space velocity (GHSV) of 840,000 h^{-1}. Hg^0 vapor was generated from an Hg^0 permeation tube, and the flue gas consisted of 150 $\mu g\, m^{-3}$ Hg^0, 5-ppm HCl and 5% O_2, with the balance being N_2. As needed, 500-ppm SO_2 was added. The Hg^0 and Hg^T (Hg^{2+} was reduced to Hg^0 by $SnCl_2$) concentration was continuously monitored using a Lumex RA-915M Zeeman mercury analyzer (Lumex-Marketing JSC, Russia). All lines that mercury passed through were heated to a temperature of 90 °C to prevent mercury deposition, especially oxidized mercury, on the inner surface. A mercury concentration mass balance was conducted before each test. The SO_2 and SO_3 concentrations were measured using an on-line Nicolet 6700-FTIR spectrophotometer equipped with a gas cell of volume 0.2 dm^3. The HCl and Cl_2 concentrations were determined using specific detecting tubes (Gastec). The Hg^0 oxidation efficiency (η) was quantified by the following formula:

$$\eta = \frac{\Delta Hg^0}{Hg^0_{inlet}} = \frac{Hg^0_{inlet} - Hg^0_{out}}{Hg^0_{inlet}} \times 100\%,$$

where Hg^0_{inlet} ($\mu g\, m^{-3}$) and Hg^0_{out} ($\mu g\, m^{-3}$) are the concentrations of Hg^0 measured at the inlet and outlet of the reactor, respectively.

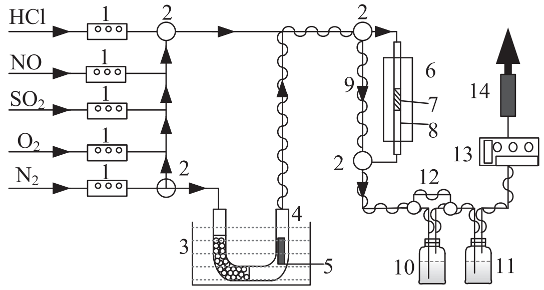

Fig. 1. Flow diagram of the experimental setup for Hg^0 removal: (1) mass flow controller, (2) three-way valve, (3) water bath, (4) U-type pipe, (5) Hg^0 permeation tube, (6) fixed-bed reactor, (7) catalyst, (8) reaction tube, (9) by-pass for Hg^0 detection, (10) $SnCl_2$–H_2SO_4, (11) NaOH, (12) by-pass, (13) Hg analyzer, and (14) exhaust gas collector.

2.3. Characterization of the catalysts

Nitrogen adsorption–desorption isotherms were obtained using a nitrogen adsorption apparatus (ASAP 2020). The specific surface area of the catalyst was determined using the BET method, and the pore volume and pore sizes were calculated by the Barrett–Jioner–Halenda (BJH) method. TEM imaging was performed on a JEOL JEM-2100 transmission electron microscope operated at 200 kV using the software package for automated electron tomography. XRD data were obtained using a Rigaku D/Max-RA powder diffractometer using a Cu Kα radiation source (40 kV and 150 mA). XPS measurements were performed with an ESCALAB 250Xi spectrometer (vacuum generators, UK) using Al Kα radiation ($h\nu$ = 1486.6 eV). The binding energy was corrected for the effect of contaminated carbon (284.8 eV).

3. Results and discussion

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

The catalytic oxidation performance of a series of different metal oxide additives for the catalytic oxidation of Hg^0 was investigated at different temperatures. The concentrations of all the metal oxides in the study were 1%. From Fig. 2, a significant difference of activity was observed among the catalysts. The Hg^0 oxidation of CuO-, Fe_3O_4-, MnO_2-, CeO_2-, and Co_3O_4-supported TiO_2 catalysts were higher than that of blank TiO_2, and the following order of activity was observed at low temperature: CuO > Fe_3O_4 > -