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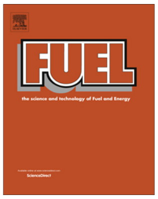

Full Length Article

Study on the preparation of bimetallic oxide sorbent for mercury removal

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ABSTRACT

Series of adsorbents based on Al_2O_3 supported Cu and Mn have been prepared and tested for mercury removal from gas streams under various conditions. The metal content, impregnating sequence and the gas composition have significant effect on the performance of the adsorbents. Co-impregnation of Cu and Mn solutions is simple but also of help to improve the Hg pickup capacity, due to the synergic effect of the CuMn oxide, the sorbent prepared using incipient wetness method containing 20% CuO and 20% wt MnO_2 has Hg pick capacity of 12.0% wt. It is showed that the oxide form the adsorbent can reduce Hg from more than 11,600 ppb to 0.1 ppb in a single pass. The presence of H_2S in the gas stream changes the Hg sorption mechanism and increase Hg pickup capacity. XRD and electron microscope characterization results of the fresh and spent sorbent show that the active phases of the sorbent are $CuMn(OH)_3Cl$ and the presence of Mn_2O_3 catalyses the metallic Hg to convert into $HgCl_2$ or HgCl. There are no elemental Hg present in the spent sorbent, but in the chemical states.

1. Background

Mercury is naturally present in most fossil fuels such as coal, crude oil and natural gas streams to varying levels [1]. The mercury compounds fossil fuels can exist in different forms: inorganic (such as $HgCl_2$), organic (such as CH_3HgCH_3, $C_2H_5HgC_2H_5$) and organo-ionic (such as $ClHgCH_3$) compounds [2]. There have been lots of studies on the Hg removal from flue gas of coal fired power station [3], which are based on nobel metal such as gold [4] or Pd [5] or active carbon injection [6]. However, mercury exists predominantly as elemental mercury in nature gas, which at a range from ppt to hundreds of ppb level, and must be removed in processing nature gas, as the accumulation of mercury would erode aluminium heat exchangers and cause potential safety issues [7]. In recent years, elemental mercury in natural gas has caused numerous aluminium exchanger failures. Also in the industrial process, mercury free product stream are needed, which requires deep removal of Hg [8]. In fact, the mostly extensive requirement for mercury removal is for environmental reasons, as mercury emission from the combustion of fossil fuel is one of the most serious environmental problems and threat to human health because of its bio-accumulation and persistence. Mercury metal vapour can travel long distances and may settle into oceans and waterways, where it builds up in fish [9]. A large number of methods have been studied in order to solve the problem of mercury release. Adsorption is the simplest and most often used method for removal of mercury. Activated carbon, a well-known adsorbent, has shown to have a good capacity for the capture of both elemental and oxidized mercury [8d,10]. Bisson, T even studied the potential hazards of brominated carbon sorbents for mercury emission control [11]. However, the low density and slow absorption rate of elemental mercury means it is not suitable for natural gas purification, although activated carbon based mercury removal adsorbent has been sprayed into power plant exhausted gas to remove Hg to be removed with dust.

In mercury removal material development, it is generally found that high adsorption capability and proper oxidation ability are two essential properties. Therefore manganese oxides as well as ceria have been studied extensively and proven to be good catalysts for Hg^0 catalytic oxidation [12]. For example, Cimino, S. studied the removal of elemental mercury by MnOx catalysts supported on TiO_2 or Al_2O_3 [13]. Reddy et al. developed a sulfur-tolerant Mn-Ce-Ti sorbents for elemental mercury removal from flue gas and studied the mechanistic using XPS [12b].

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Recently, Cu based sorbents have attracted attention, Yang et al. studied the removal of elemental mercury from flue gas by recyclable $CuCl_2$ modified magnetospheres catalyst from fly ash [14]. Du et al. prepared neutral Al_2O_3 supported CuOx based sorbents and studied their performance for on mercury removal from simulated coal combustion flue gas [15].

It is observed that little research on Cu–Mn binary metal oxides for mercury adsorption has yet been reported. In this work, we have developed an alumina supported copper and manganese oxide sorbent which shows superior performance for Hg pickup and can decrease mercury from thousands of ppb to ppt level, the Hg pickup capacity is more than 10% wt and the preparation parameters have significant effect on the sorbent performance.

2. Experimental

Preparation of CuOx/Al_2O_3, MnOx/ Al_2O_3 and CuMnOx/Al_2O_3 sorbents.

The γ-Al_2O_3 supported Cu, Mn and CuMn mercury sorbents were prepared using incipient wetness impregnation method. The Al_2O_3 support (surface area, 266 m^2/g, was supplied by Qingdao Lianxin Chemical Co Ltd, China, particle size, 150–250 μm, strength, 120 N/granule) which was dried at 120 °C for 4 h, cooled down to room temperature in a sealed saturator, and then measured its water pick-up capacity. The dried γ-Al_2O_3 support is impregnated with various Copper and/or Mn water solutions to get the supported metal oxide sorbent. For example, to prepare 20.0% wt of CuO and 20.0% wt of MnO_2, (as $MnCl_2$ can be converted into various Mn oxides, in this paper, the Mn content is expressed as MnO_2 and also its oxide will be generally remarked as MnO_2 in the prepared adsorbent) first 10.0 grams of Al_2O_3 is impregnated with 7.0 ml of 3.1 M $CuCl_2{\cdot}2H_2O$ solution, placed in static air for 24 h, then dried at 120 °C for 24 h, and calcined at 400 °C for 4 h. Then the copper oxide containing Al_2O_3 is impregnated with 2.7 M $MnCl_2$ solution, and dried, calcined under the similar conditions as above to get an Al_2O_3 supported CuMnOx sorbent, the obtained sorbent has a strength of 80–100 N/granule, which is often very strong under pressure conditions.

The effect of metal contents on the sorption capacity was examined by changing the copper precursor or manganese precursor content in the solution, with the other preparation conditions left unchanged.

The metal loading over the sorbent was determined using atomic absorption spectrometer (Hitachi Z-2000) of the various metals and also validated with the weight change of each step. In addition, the co-impregnation method, e.g., a solution containing both Cu and Mn compounds were impregnated with the dried support, and then dried and calcined under the similar conditions.

2.1. Hg removal performance test

The mercury removal test system consists of four parts: gas supply system, reaction unit for removal of mercury, on-line monitoring instrument and tail gas disposal unit. The schematic diagram of the setup is shown in Fig. 1. In this work, we use N_2 to replace natural as as the gas stream to avoid greenhouse gas emission, the nitrogen gas (or H_2S containing nitrogen gas) goes through the flowmeter, to Hg saturator (controlled by the temperature of the water bath), then upflows through the sorbent (loaded in the tubular reactor, black part), and then vents or goes for absorption, then analysis.

The cold vapour atomic fluorescence spectrometry mercury vapour meter MODEL made by Brooks Rand was used to measure the elemental mercury content in the gas stream. During the experiment, setting and keeping the water bath temperature at 25 °C, the exhaust gas was treated with Ontario-Hydro solution as recommend by US EPA. Meanwhile, the level of elemental mercury was regularly checked at the inlet and outlet of the saturator simultaneously. In our experimental system, the inner tube of the whole pipe and its joint connection which is contacting directly to mercury are lined using PTFE.

2.2. Methods and calculations

A quartz reactor (φ 6.0 mm) was used for the adsorbent loading, which was washed completely before the experiment, each time 1.0 ml samples (diameter of 0.28 mm–0.45 mm) was loaded in the middle of the quartz tube with the two ends held with the quartz fibre. The flow rate of the gas is adjusted based on the GHSV of 4000 h^{-1} and the desired mercury concentration for blank test, until the outlet Hg concentration becomes steady and constant. In the experiment at ambient temperature, the gas pressure for mercury adsorption experiments is 0.1 MPa. During the experiment, a MODEL mercury analyzer was used to measure the Hg concentration of inlet and outlet of reactor bed. The experiment is stopped when the outlet mercury content is 0.1 μg/m^3 or above.

The catalyst mercury capacity and mercury removal ratio were calculated according to the Eqs. (1) and (2) as below:

$$\text{Hg capacity}/\% = \text{mHg}/\text{Mcat} \times 100\% \tag{1}$$

where mHg is the total weight of Hg adsorbed by the catalyst, which is obtained by the total weight of spent sorbent deducted by the catalyst amount loaded in the reactor

M cat is the weight of the catalyst used, g.

$$\eta/\% = \text{C(Hg adsorbed)}/\text{C(Hg total)} \times 100\% \tag{2}$$

where C(Hg adsorbed) is for the concentration of Hg adsorbed, μg/m^3, C(Hg total) is for the inlet consistence of Hg before adsorption, μg/m^3.

As the Hg vapour is brought into the reactor by flowing N_2 or natural gas saturated with Hg bath at 20 °C and ambient pressure, the gives Hg content at 11,600 μg/m^3. It is determined that when the outlet Hg is 0.1 μm/m^3 or above, the test is stopped.

2.3. Characterization of the sorbent

The physical properties i.e. surface area, pore volume and pore distribution of the sorbent before and after Hg sorption were measured using nitrogen physi-sorption at the nitrogen liquid temperature (−196 °C). The sample (about 100 mg) was initially degassed at 180 °C under vacuum conditions of 1×10^{-3} bar for 2 h, the adsorbed volume of nitrogen at different relative pressure (P/Po) was measured in order to obtain an isotherm curve. The specific surface area was obtained using the Brunauer, Emmett, Teller (BET) method where pore volume and pore distribution are determined with the Barret-Joyner-Halenda (BJH) method.

The crystalline structure of the sorbents were measured at various stages using X-ray diffraction (XRD) with a Philips PW1710 diffractometer equipped with an X-ray tube (Cu Kα radiation λ = 1.5406 Å; 40 kV, 30 mA). The samples were ground into fine powder and then loaded into a flat glass sample holder. The data were collected in θ/2θ reflection mode, from 10 to 70° in 2θ, using steps of 0.05°. The morphologies of the sorbent samples before and after Hg pickup were observed with a JEOL JEM-2100 instrument operating at an accelerating voltage of 200 kV. Before the experiments, each sample was grinded into fine powder and then ultrasonically dispersed in ethanol solvent, and a couple of drops of the suspension were deposited on a standard 3 mm copper grid covered with a holey carbon film.