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Enhancement of elemental mercury adsorption by silver supported material

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ABSTRACT

Mercury, generally found in natural gas, is extremely hazardous. Although average mercury levels are relatively low, they are further reduced to comply with future mercury regulations, which are stringent in order to avoid releasing to the environment. Herein, vapor mercury adsorption was therefore investigated using two kinds of supports, granular activated carbon (GAC) and titanium dioxide (TiO₂). Both supports were impregnated by silver (5 and 15 wt.%), before testing against a commercial adsorbent (sulfur-impregnated activated carbon, SAC). The adsorption isotherm, kinetics, and its thermodynamics of mercury adsorption were reported. The results revealed that Langmuir isotherm provided a better fit to the experimental data. Pseudo second-order was applicable to describe adsorption kinetics. The higher uniform Ag dispersion was a key factor for the higher mercury uptake. TiO₂ supported silver adsorbent showed higher mercury adsorption than the commercial one by approximately 2 times. Chemisorption of mercury onto silver active sites was confirmed by an amalgam formation found in the spent adsorbents.

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Introduction

In natural gas production, several undesirable compounds may contaminate in natural gas as received. One of the major concerns is a contamination of heavy metals such as Hg, Cr, Cd, etc. Among those, mercury (Hg) compounds are heavily regulated. Mercury could exist in three oxidation states (Hg(II), Hg(I), and Hg⁰) and is predominantly found as Hg⁰ in the gas phase. Mercury is considered to be a toxic element to human health. The Environmental Protection Agency (EPA)

has disclosed the associated mercury, with possible health effects and threshold amount of Hg, and should be below a level of whole blood 5.8 ppb (for human being) (Slotnick, 2012).

Elemental Hg in natural gas received from the Southeast Asia region is found in high levels of concentration up to 2000 μg/Nm³ (ca. 2400 ppbw) (Eckersley, 2010). Not only elemental Hg, but also mercury compounds such as, mercuric chloride (HgCl₂), methyl mercuric chloride (CH₃HgCl), dimethyl mercury (CH₃HgCH₃) and diethyl mercury (C₂H₅HgC₂H₅) were found (Wilhelm and Bloom,

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2000). Therefore, several treatments have been incorporated to reduce the Hg concentration contaminated in natural gas to the threshold level. To reduce the vapor Hg dispersed in the air after combustion, the USEPA sets a standard Hg level in air to be less than 0.1 ppb. Consequently, refineries and gas separation plants generally reduce the levels of Hg in gas processing down to 0.001 ppb (Mokhatab and Poe, 2012).

Treatments of mercury in liquid state have been extensively investigated (Ghassabzadeh et al., 2010; Ma et al., 2009; Idris et al., 2011). The removal of Hg from aqueous phase is performed using the Outokumpu process, the Bolkem process, selenium filter process, the Boliden–Norzink process and sulfide precipitation (Louie, 2008). They have been applied to commercial scales. The processes are carried out in scrubbers using acid solution (H_2SO_4 and H_2SeO_3) to scrub elemental mercury (Hg^0) in the gas into a sulfate and mercury selenide for further removal. These methods require chemicals and chemical treatments, in which, a large amount of chemical waste is produced.

Unlike mercury treatment in liquid phase, the treatment in vapor phase has not been widely studied. The removal of mercury in vapor phase is mainly performed by adsorption technique. The process has been investigated by various adsorbents, including calcium-based one (Ghorishi and Sedman, 1998), coal (Díaz-Somoano et al., 2007), zeolites (Morency, 2002), iodine-modified rice husk ash (Zhao et al., 2010), activated carbon (Sasmaz et al., 2012; Padak and Wilcox, 2009) and carbonaceous material derived from sewage sludge (Fang et al., 2010). However, the uptake of mercury onto adsorbents was extremely inefficient.

Based on the property of mercury, the physical adsorption between Hg^0 and active adsorbents may not be attractive. Active sites on the adsorbent surface should be modified for chemical attraction. It has been noted that metals, such as palladium, platinum, rhodium, gold, zinc, aluminum, copper and silver, are ready to form amalgam with Hg^0 (Granite et al., 2006; Wilcox et al., 2012). Besides, the solubility of these metal mercury amalgams is relatively low, and consequently very little mercury releases after the uptake (Henderson et al., 2001). Among those chemicals, silver was reported for having lower solubility, therefore, it was selected to modify adsorbent support and create more active sites.

In this research, the suitable loading of Ag on two kinds of adsorbent supports, TiO_2 and granular activated carbon (GAC), was investigated. Selected adsorbents, based on high adsorption performance, were reported adsorption isotherms, temperature effect on the adsorption and adsorption kinetics.

1. Materials and methods

1.1. Preparation

Two types of materials, TiO_2 (P25) and GAC, were used as adsorbent supports. Silver was loaded onto the materials via an impregnation technique. AgNO_3 corresponding to 5% and 15% by weight of Ag over the supports, was dissolved in deionized (DI) water under a vigorous stirring condition until the solution was homogeneous. The solutions were gradually dropped onto the supports, TiO_2 or GAC particles. The samples were sonicated and kept for 3 hr, then dried at 80°C

for 6 hr and ground with an agate mortar. The obtained adsorbents in powder form were calcined in air at 480°C with the heating rate of 10°C/min and kept for 3 hr. Adsorbent powder was pelletized to cylindrical form and sieved to 2 mm in diameter before testing.

Commercial adsorbent used in this study was sulfur-impregnated activated carbon (SAC) supplied by Carbokarn, Thailand.

1.2. Characterization

The physico-chemical properties of adsorbents were examined by various techniques such as X-ray diffraction (XRD), nitrogen adsorption isotherms, and field emission scanning electron microscopy (FESEM).

The XRD patterns were obtained using $\text{CuK}\alpha$ radiation on Bruker AXS diffractometer (Bruker-AXS D8-A25 Advance, Karlsruhe, Germany). The samples were scanned from 10 to 80° (2 θ) in steps of 0.02° per second. Nitrogen adsorption isotherms of samples were measured using an Autosorb-1 analyzer (Quantachrome Instruments, Boynton Beach, FL, USA) for calculating the Brunauer–Emmett–Teller (BET) surface area. Sample micrograph was observed under field emission scanning electron microscope (FESEM, JSM-6301F, JEOL, Ltd., Tokyo, Japan). Powder sample was scattered on an adhesive tape on a brass bar. The sample was then coated with carbon and transferred into the sample chamber. The microscope was equipped with energy dispersive X-ray spectrometry (EDS, INCA 350, Oxford Instruments, High Wycombe, UK), for elemental mapping images.

1.3. Mercury adsorption

The adsorption vessel for static test was made of three parts: holder, Pyrex glass-stand and cap. Hg^0 was dropped into the holder. A Pyrex glass-stand was placed over 0.5 g of Hg^0 . Before the study, a blank test was carried out for the adsorption baseline. In the test, a certain amount of prepared adsorbent was placed on the Pyrex glass-stand (Fig. 1). The holder was closed tightly with a cap and wrapped with parafilm. The vessel was placed inside the heating bath throughout the test. Temperatures were set at 40 and 60°C for the tests, which could minimize mercury stick on the surface of experimental vessel. The adsorption was carried out for 40–60 days. Mercury was determined by a mercury analyzer (Lumex-RA915+, Ohio Lumex, Twinsburg, OH, USA). The mercury amount in spent adsorbent (after mercury uptake) was measured by the mercury amount according to US EPA 7473. The adsorbent was thermally decomposed and amalgamation with gold and detected by cold vapor atomic fluorescent spectrometry (CV-AFS). The detection limit was 0.5 $\mu\text{g}/\text{kg}$. To prevent erroneous interpretation of instrument readings, sample was diluted with the same support material. Mercury vapor concentration inside the vessel was also analyzed in the same instrument with a frequency of 1 Hz at concentrations ranging from 0.01 to 22 $\mu\text{g}/\text{m}^3$ using a long-path analytical cell.

To investigate the effect of temperature on the adsorption, the experiment was conducted at four different temperatures of 30, 40, 50 and 60°C. In order to prevent the multilayer adsorption, a certain amount of 0.2 g of Hg^0 was used.

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