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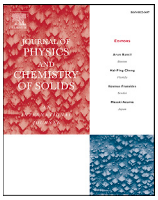

Influence of crystal/particle size and gold content of a structured Au/C based sorbent on mercury capture

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ABSTRACT

A sorbent based on gold nanoparticles deposited by direct reduction of a gold salt on a structured carbon surface has been prepared to be used in the mercury capture at low concentrations. A total of 13 samples have been obtained varying preparation conditions (stirring rate, gold salt concentration and contact time). A kinetic study of the gold reduction on the carbon surface has been carried out, indicating that the calculated reaction rate constant corresponds to the diffusion rate equation. The study of the influence of gold salt concentration on the reduction potential of the gold showed that the use of a high concentration gold salt solution shifts the reduction reaction to gold reduction. Mercury capture capacity cannot be directly related with either gold content or average particle size or average crystal size, but the study of the grain size distribution can explain the mercury capture performance of the samples.

1. Introduction

Mercury related legislation has forced some countries to install mercury-specific emission control equipment [1]. In particular, the need to control mercury emissions from power plants burning coal has forced to the development of new technologies to meet the emission requirements, such as the ACI (Activated Carbon Injection) technology [2]. It has been proven through numerous full-scale demonstrations as effective way to reduce mercury emissions when burning low sulfur coals. However, main drawback associated to ACI technology is the high carbon to mercury ratio needed to achieve high retention efficiency, being this activated carbon captured with fly ashes in the particulate matter control devices. This fact leads to a loss of fly ash marketability and, depending on mercury content, to its disposal as toxic residue.

Regenerable sorbents can accomplish high mercury retention, which can be recovered, as well as balance cost because of its regenerability; some of these sorbents have been reported in Refs. [1,3]. Recognizing reversible characteristics of mercury amalgam with gold, this sorption has been used to pre-concentrate low concentration of elemental mercury for its detection [4], because Hg-Au amalgams are stable at room temperatures, decomposing at higher temperatures to release mercury and leaving gold surface ready for further sorption and amalgam formation. The use of Au films is effective for mercury capture [5] but several cycles of exposure to gas and heating makes the gold to aggregate into islands, which lead to inefficient amalgam formation [6]. Au monolayers have been used by others [7] to detect mercury through amalgamation process showing higher affinity to Hg than thin films. Carbon-Au based materials have also been used for sensing for their high affinity toward Hg [8].

In the last decades gold has been found to become active for many reactions when it is stabilized in the form of nanoparticles, increasing the use of supported gold nanoparticles (GNPs) for a wide variety of reactions. The activity of these materials depends greatly on the method of preparation. Traditional way to prepare GNPs is the colloidal gold method [9], which consist mainly of the use of a reducing agent for the gold salt and a protector to prevent the agglomeration of the GNPs formed [10]. Different variations of this method include the pre-adsorption of the reducing agent [11] or the use of microwave assisted deposition [12], among others. Some of these reducing and protective agents are harmful to the environment, so a new method of GNPs preparation based on the reducing ability of carbons can be found in the literature [13,14], where the use of these reagents are avoided.

This method, based on the direct reduction of a gold precursor over carbon structures, is described by the following reactions:

$$AuCl_4^-(aq) + 3e^- \leftrightarrow Au(0) + 4Cl^- \quad (1)$$

$$C(s) + 2H_2O(aq) \leftrightarrow CO_2(g) + 4H^+ + 4e^- \quad (2)$$

with the global reaction of the process:

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List of symbols

$C_{AuCl_4^-}$	gold salt solution concentration
$C^i_{AuCl_4^-}$	gold salt solution concentration at the interphase
K	reaction rate constant
K_c	the mass transfer coefficient
$N_{AuCl_4^-}$	mol of ions
S	carbon surface area
t	time

$$4AuCl_4^-(aq) + 3C(s) + 6H_2O(aq) \leftrightarrow 4Au(0)(s) + 16Cl^- + 12H^+ + 3CO_2(g) \quad (3)$$

The reduction potential of $AuCl_4^-$ to Au(0) is 1.002 V and the oxidation potential of C(s) to CO_2(g) is 0.206 V, with the global standard potential of 0.796 V and an equilibrium constant $K = 2.96 \times 10^{161}$ [15]. This high value means that gold ions are easily reduced by the carbon. However, this is a heterogeneous reaction involving solid and liquid phase and there is a diffusion process of $AuCl_4^-$ ions to the carbon surface before the reduction process itself. It has been demonstrated that the limiting step of the overall process is the diffusion with a potential higher than 0.3 V [16]. Other variables, such as salt concentration, stirring rate, affecting the reduction process have been studied [15,17].

In this work, different sorbents based on GNPs have been prepared by direct reduction of a gold precursor over a structured carbon support varying the concentration of the gold precursor, the stirring rate and the contact time to obtain sorbents with different particle size, crystal size and gold content in order to stablish the most suitable characteristics enhancing mercury capture.

2. Experimental

2.1. Sorbent preparation

Cordierite honeycomb structure (from Corning Inc.) in pieces of 0.7 × 0.7 × 1.5 cm was impregnated with a phenolic resin (Novolak type delivered by Ilarduya, from Hüttenes Albertus group) by immersion and further centrifugation of the excess of resin. The impregnated resin was thermally cured at 150 °C in air during 1 h and further carbonized at 700 °C during 1 h under inert flow. This carbon support had square channels with a density of 33 cells/cm^2.

The method for gold deposition involved the direct reduction of the gold salt ($HAuCl_4 \cdot 3H_2O$) by the own carbon support surface without the addition of reducing or protective chemicals. The system consists of a pot, a stirring device and support for the monoliths, all of these parts made of Teflon in order to avoid gold salt reduction except over the monolith.

After gold deposition, sorbents were undergone to a Reducing Thermal Treatment (RTT) at 300 °C during 1 h in a flow containing 4% H_2 in N_2.

2.2. Sorbent characterization

The bulk gold content of the sorbents was determined by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) with a Jobin Ybon 2000 equipment. Gold nanoparticle size distribution was obtained by Scanning Electron Microscopy with Field Emission (FE-SEM) with a Carl Zeiss MERLIN microscope equipped with an In-Lens detector. The established method to analyze the sorbents was based on taking four images per channel and two channels per monolith. The images were analyzed by Image J software and GNPs size distribution and Feret diameter (FD) were obtained. FD is defined as the longest distance between any two points along the selection boundary for each particle. More details of this procedure can be found in Refs. [13,18]. High resolution TEM (HRTEM) was performed with a Tecnai G2-F30 field emission gun microscope working at 300 kV with super-twin lenses and 0.2 nm point-to-point resolution and 0.1 nm line resolution. Samples for TEM observations were prepared by releasing GNPs from the support by sonication or through surface scrapes of the channels with a fine needle and dispersing the nanoparticles in ethanol or methanol, then evaporating the suspension drops on carbon-coated copper grids. X-ray diffraction (XRD) was used to obtain information about the crystalline structure of gold. XRD diffractograms were collected by a Bruker D8 Advance X-ray powder diffractometer equipped with X-ray source with Cu anode working at 40 kV and 40 mA, a Göbel mirror and a scintillation detector. Diffraction pattern was obtained over the 2θ° range of 35°-80°, with a step-size of 0.05° and at grazing incidence. Whole pattern decomposition of the diffractograms was performed using Pawley method with pseudo-Voigt approach in order to obtain crystallite size. The volume weighted column height (LVol-IB) was taken to obtain the average crystallite size. The oxidation state of deposited gold was studied by XPS an ESCAPlus Omicron spectrometer equipped with a non-monochromatized MgKα radiation (1253.6 eV). The samples were introduced into the analysis chamber where the vacuum was lower than $5 \cdot 10^{-9}$ torr. The hemispherical electron energy analyzer was operated at pass energy of 50 eV for surveys, and 20 eV for high-resolution spectra. The energy scale was calibrated by referencing the C1s peak to 284.5 eV. CASA software was used to process the XPS data.

2.3. Mercury capture tests

A bench-scale plant was designed and built specifically to test the sorbents. A certified Dynacal Hg^0 permeation device was used to generate a constant feed of Hg^0. The resulting gas mixture is sent to the quartz reactor tube, with an internal diameter of 16 mm, where the sorbent is fitted between two ceramic pieces. A furnace surrounding the reactor was used to control the temperature. An on-line elemental mercury analyzer (VM3000) continuously monitors Hg^0 evolution downstream of the sorbent. More details of the experimental installation can be found elsewhere [19].

The Hg breakthrough curves were obtained at a flow of 15 l h^{-1}, 50 °C of temperature and Hg inlet concentration of 100 μg/m^3 and inert gas as balance. Some experiments were performed two or three times under the same operational conditions in order to test reproducibility. The amount of Hg captured was calculated by integration of the breakthrough curve. A baseline test on the support (no Au) was also carried out.

After some experiments, exhausted sorbents were analyzed by an Advanced Mercury Analyzer (AMA from LECO) to directly determine mercury captured on sorbents. The total amount of sample used for the mercury capture experiment was crushed and aliquots of it were analyzed in the AMA. These results were compared with those obtained from integration of the mercury breakthrough curves.

2.4. Gold salt reduction kinetics

The kinetic study of gold reduction over carbon monoliths was carried out at fixed stirring rate of 150 rpm, at two concentrations of gold salt, 0.5 mM y 0.7 mM, at room temperature varying contact time in the interval 0–240 min. The variation of gold salt concentration with contact time has been followed by a Shimadzu UV-2401 PC UV–Vis spectrometer at wavelength of 315 nm, taking an aliquot of the gold salt each time. In some experiments, the reduction process was stopped at a defined time and FE-SEM images were obtained in order to follow the particle size distribution with time.

The surface of the support can be considered hydrophobic and accordingly the existing interphase gold salt solution and support could reduce the $AuCl_4^-$ ions diffusion.

Considering the rate of reaction $(-r_{AuCl_4^-})$ as a function of the diffusion, it can be written as: