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Mercury capture by regenerable sorbents under oxycoal combustion conditions

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1. Introduction

The largest source of mercury to the atmosphere in the world is the burning of fossil fuels, primarily coal. Electrical power plants are estimated to account for about 25% of the global anthropogenic mercury emissions to the atmosphere and industrial and residential heating for another 20% [1]. According to the European Environmental Agency (EEA), Spain is the third country among EU27 in mercury emissions, mainly due to coal-fired plants [4]. Mercury is found in coal in the form of sulphides or associated to them, interchanged on clays and associated to the organic matter in low rank coals. During the combustion processes, these forms evaporate, giving rise to Hg(0), HgO and HgCl₂, which proportions in gas phase depend on the concentration and mode of occurrence in the coal and on the compounds present in the gaseous stream, especially particulates and HCl.

The environmental implications of mercury do not correspond only to the emissions to the atmosphere; the quality of CO₂ to be transported and sequestered has been subject of research, concerning trace quantities of heavy metals participating in mineralization and precipitation reactions in sequestration conditions. However, for coal oxy-combustion mercury is not an environmental issue alone but also an operational issue, particularly about where mercury could accumulate within the CO₂ processing unit. The removal of Hg is necessary to prevent Hg attack on the aluminum heat exchangers. Because of this, an activated carbon bed guard is placed downstream the dryers. Once exhausted, this activated carbon must be treated as a toxic residue.

Regenerable sorbents can accomplish high mercury retention that can be recovered as well as balance cost because of its regenerability. Recognizing reversible characteristics of mercury amalgamate with gold have been widely used to pre-concentrate low concentration of elemental mercury for its detection. The gold-mercury amalgam is extremely stable at room temperature. However, the amalgam decomposes to release mercury to a gas phase at
higher temperatures, leaving clean gold surfaces ready for further mercury capture. To effectively collect trace amounts of mercury, it is necessary to have the gold in a form of large surface areas, as gold nanoparticles deposited onto a support.

In this work, a preliminary study of Hg capture and regeneration on Au/C based sorbents has been carried out under oxyfuel combustion conditions.

2. Experimental

Mercury capture test were carried out in an experimental facility (Figure 1) built up at the Instituto de Carboquímica (ICB). It consists of a permeation tube for mercury to give the desired Hg(0) concentration, gas cylinders to simulate flue gas under oxyfuel conditions (CO₂, O₂, SO₂, NO, HCl) and a system for H₂O feeding. The Hg(0) is analyzed on-line with an elemental mercury analyzer (VM3000). Moreover, the installation is provided with a tail-end train of flasks to allow the capture the mercury as well as its speciation (in the case of evidences of oxidation under the experimental conditions). The installation is built up with Teflon pipes and pieces (in the part of the installation where Hg is present) to prevent possible mercury attack to steel. CO₂, O₂, SO₂ and H₂O concentrations are determined by a GC on-line. Inlet Hg concentration was 100 µg/m³ and space velocity 7x10⁸ h⁻¹ (referred to the active phase, Au). The amount of Hg captured as well as the capture efficiency was calculated from the integration of the breakthrough curve. Some experiments were repeated to test reproducibility. Some of the exhausted sorbents after Hg capture were analyzed for Hg content in an automated mercury analyzer (AMA) from Leco, and the results were compared with those obtained by breakthrough curve integration. Regeneration of exhausted sorbents was carried out at 220°C during 2h before reuse.

Gold nanoparticles were deposited onto a carbonaceous honeycomb structured support through a novel procedure which does not involve the use neither of reducing nor protective agents, using the carbon reducing capacity. A solution of HAuCl₄•3H₂O was forced to pass through the channels of the carbon monolith to achieve a homogeneous deposition of gold along the channels of the monolithic supports. After deposition were treated at 300°C in a flow containing 4%H₂ during 1 h. Bulk gold content of sorbent was 0.11%.

More details of the sorbent preparation are given elsewhere [3].

3. Results

Figure 2 depicts the Hg(0) retention efficiency for 20% breakthrough at different temperatures under air or oxyfuel conditions, maintaining fixed the Hg(0) concentration and the space velocity, in order to test the possibility to use the sorbent at different positions on the power plants (cold side ESP, after WFGD, downstream dryers).

Hg(0) retention efficiency at 150°C is slightly lower than that for lower temperatures. This fact can be explained in terms of this temperature coming near regeneration temperature of the sorbent. A mercury capture capacity as high as 0.8 mg/g sorbent (15 mg/g Au) for 80% mercury capture was obtained at 150 °C, higher than the mercury capacity of activated carbon at similar temperature (135°C) under Ar atmosphere [4]. At lower temperatures, Hg capture can be as high as 20 mg/g Au.

After sorbent saturation, it is regenerated at 220°C during 2 h. Then, the sorbent is ready for reuse. Several capture-regeneration cycles have been performed and the efficiency is maintained along cycles.

The impacts of HCl, SO₂ and NO existing in simulated flue gas on Hg(0) capture of the sorbents was evaluated compared to baseline components (CO₂ and O₂). It seems that Hg(0) capture capacity as well as efficiency is negligibly impacted by HCl, SO₂ and NO at low concentrations. This should mean that at the temperatures used neither Hg nor Au are oxidized. The oxidation of mercury was tested by capturing the possible formation of Hg(II) in KCl impingers and measuring concentration. The Au oxidation was tested by XPS, compared to the Au oxidation state of as prepared sorbent. However, high concentration of SO₂ seems to oxidize Au surface, which lead to less Au at elemental state available for the Hg capture.

On the other hand, after regeneration a slight loss in Hg(0) capture capacity as well as efficiency is observed, probably due to the increase of Au particle size.
4. Acknowledgements

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5. References


