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.

Keywords: gold nanoparticles; direct reduction; regenerable sorbent; mercury capture
List of symbols

\( C_{\text{AuCl}_4} \) gold salt solution concentration

\( C_{\text{AuCl}_4}^i \) gold salt solution concentration at the interphase

\( K \) reaction rate constant

\( K_c \) the mass transfer coefficient

\( N_{\text{AuCl}_4} \) mol of ions

\( S \) carbon surface area

\( t \) time
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 [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 preadsorption 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:

\[
\text{AuCl}_4^-(aq) + 3e^- \leftrightarrow \text{Au}(0) + 4\text{Cl}^- \quad (1)
\]

\[
\text{C}(s) + 2\text{H}_2\text{O}(aq) \leftrightarrow \text{CO}_2(g) + 4\text{H}^+ +4e^- \quad (2)
\]

with the global reaction of the process:

\[
4\text{AuCl}_4^-(aq) + 3\text{C}(s) + 6\text{H}_2\text{O}(aq) \leftrightarrow 4\text{Au}(0)(s) + 16\text{Cl}^- + 12\text{H}^+ +3\text{CO}_2(g) \quad (3)
\]

The reduction potential of \(\text{AuCl}_4^-\) to \(\text{Au}(0)\) is 1.002 V and the oxidation potential of \(\text{C}(s)\) to \(\text{CO}_2(g)\) is 0.206 V, with the global standard potential of 0.796 V and an equilibrium constant \(K= 2.96\times10^{161}\) [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 \(\text{AuCl}_4^-\) 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 establish the most suitable characteristics enhancing mercury capture.

2. EXPERIMENTAL

2.1. Sorbent preparation

Cordierite honeycomb structure (from Corning Inc.) in pieces of 0.7x0.7x1.5 cm was impregnated with a phenolic resin (Novolak type delivered by Ilarduya, from Hütttenes Albertus group) by immersion and further centrifugation of the excess of resin. The impregnated resin was thermally cured at 150 °C in air during 1h and further carbonized at 700 °C during 1h under inert flow. This carbon support had square channels with a density of 33 cells/cm². The method for gold deposition involved the direct reduction of the gold salt (HAuCl₄·3H₂O) 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 ºC during 1 hour in a flow containing 4 % H\textsubscript{2} in N\textsubscript{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 Yvon 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 [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 5·10⁻⁹ 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 Hg⁰ permeation device was used to generate a constant feed of Hg⁰. 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 Hg⁰ 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/m³ 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 \((- r_{\text{AuCl}_4^-})\) as a function of the diffusion, it can
be written as:

\[
(r_{AuCl_4^-})_{\text{difusión}} = -\frac{1}{S} \frac{dN_{AuCl_4^-}}{dt} = K_c (C_{AuCl_4^-} - C_{i_{AuCl_4^-}})
\] (4)

Considering the order of the reaction 1, the rate of the reduction reaction is:

\[
(r_{AuCl_4^-})_{\text{reacción}} = KC_{i_{AuCl_4^-}}
\] (5)

At equilibrium both (4) and (5) are equals:

\[
K_c(C_{AuCl_4^-} - C_{i_{AuCl_4^-}}) = KC_{i_{AuCl_4^-}}
\] (6)

And the ions concentration at the interphase can be obtained:

\[
C_{i_{AuCl_4^-}} = \frac{K_c}{K_c + K} C_{AuCl_4^-}
\] (7)

As this concentration is unknown, the global reaction rate can be obtained as a function of the gold salt concentration in the liquid phase, substituting (7) in (6):

\[
(r_{AuCl_4^-})_{\text{global}} = \frac{KK_c}{K_c + K} C_{AuCl_4^-} = \frac{1}{K_c + K} C_{AuCl_4^-}
\] (8)

It has been demonstrated that the limiting step of the overall process is the diffusion with a potential higher than 0.3 V [16]. So, the limiting step is the diffusion from liquid phase to the surface of the carbon material and reaction rate constant K is higher than that the mass transfer coefficient K_c. Accordingly, the rate for the overall process can be written as:

\[
(r_{AuCl_4^-})_{\text{global}} \approx K_c C_{AuCl_4^-}
\] (9)

The reduction potential depending on gold salt concentration was studied according to Nernst equation:

\[
E = E^0 - \frac{0.059}{n} \ln \left( \frac{Au^0}{AuCl_4^-} \right)
\] (10)

where Au^0 is a solid and takes value 1, n is the number of electrons, in present
case 3 electrons in reaction (1).

3. RESULTS AND DISCUSSION

The kinetic of gold reduction over carbon monoliths can influence the particle formation. According to bibliography the order of the reduction reaction of \( \text{AuCl}_4^- \) by a carbon materials in reaction (3) is 1 [15, 17]. However, in those studies carbon materials were in powder form, which were stirred; in present study, the monoliths are fixed and only the solution is stirred. Under these conditions and the experimental conditions described in section 2.4, the values of gold salt concentration-time were adjusted and the order of reaction obtained was 1 and the reaction rate constant was \( 1.34 \times 10^{-2} \) s\(^{-1} \) when using 0.5 mM salt concentration and \( 1.22 \times 10^{-2} \) s\(^{-1} \) when using 0.7 mM salt concentration. According to equations (4) to (9), the calculated reaction rate constants correspond to the diffusion rate equation.

So, it was expected that the increase of salt concentration could enhance ions diffusion. However, some studies suggest that gold particles can be sintered in the early stages by surface diffusion [20] and by grain boundary diffusion [21] and previous research of GNPs deposition on honeycomb carbons structures following similar deposition procedure confirms this trend [13, 18]. The evolution of particle size with time can be follow from Figure 1, starting from a gold salt solution of 0.7 mM. As can be seen, particle size increases with contact time despite the low concentration of the gold salt solution used.
In order to study the influence of the gold salt concentration on the reduction potential of reaction (3), 0.795 V, two more diluted gold salt dissolutions were used: 0.01 mM and 0.005 mM. It can be supposed that the carbon surface exhibits a heterogeneous reduction potential. This fact means that oxidation potential of 0.206 V, according to bibliography [15], could vary for different reduction points on the heterogeneous carbon surface. For a more favored reduction point on the carbon surface, reduction potential would be lower than that value.

According to equation (10), the reduction potential for gold salt concentration 0.01 mM is 0.904 V and for gold salt concentration 0.005 mM is 0.917 V.

From the bibliographic value of reduction point on the carbon surface (oxidation potential in reaction (2)), the global potential of the reaction (3) would be 0.698 V for the more diluted solution and 0.711 V for the more concentrated solution.

Considering a more favored reduction point on the carbon surface, with for example a oxidation potential 0.051 V for reaction (2) (one third of the bibliographic value), the global potential of the reaction (3) would be 0.853 V for the more diluted solution and 0.866 V for the more concentrated solution.
can be deduced, the difference for the same dilution and two reduction points is the same for the both gold salt concentrations used, 0.155 V.

The effect of using a more diluted gold solution is that the global potential of the reaction (3) is higher and, accordingly, the equilibrium constant is lower, indicating that is not as shifted to the gold reduction as in the case of using a more concentrated gold solution.

Under this experience, the parameters to prepare GNPs based sorbents were changed according to Table 1. Gold salt concentration, agitation rate and contact time were varied. First column is the label of the sample. Second column is the stirring rate; when two values appear it means a two steps procedure: first stirring rate corresponds to stirring rate for low gold salt concentration and second one to the high salt concentration. Third column is the salt concentration; when two concentrations appear it means that the process starts with the lowest concentration and after a specified time a small volume of high concentration salt solution is added. Fourth column is the contact time. For samples P9 and P21, contact time is 20 minutes, 10 minutes in each stirring flow direction. To achieve this goal, sorbent is rotated 180 degrees around its vertical axis twice without being removed from the solution. For the rest of the samples, the experiment has two well-differentiated parts. Between them, there is a break time where sorbent is removed from the solution. This break is indicated in the table by a forward slash (gold salt concentration column) and by a plus (contact time column). The first contact time indicates time immersion in the less concentrated solution and the second one indicates time immersion in the more concentrated solution. In both periods of time sorbent is rotated 180 degrees around its vertical axis twice without,
being removed from the solution.

Table 1. Conditions to prepare sorbent samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Stirring velocity rpm</th>
<th>Gold salt concentration mM</th>
<th>Contact time min</th>
</tr>
</thead>
<tbody>
<tr>
<td>P9</td>
<td>80</td>
<td>0.0075</td>
<td>20</td>
</tr>
<tr>
<td>P21</td>
<td>80</td>
<td>0.0016</td>
<td>20</td>
</tr>
<tr>
<td>P25</td>
<td>130/90</td>
<td>0.0064/0.0629</td>
<td>10+5</td>
</tr>
<tr>
<td>P26R</td>
<td>130/90</td>
<td>0.0081/0.0612</td>
<td>10+8</td>
</tr>
<tr>
<td>P27</td>
<td>80/100</td>
<td>0.0081/0.0943</td>
<td>10+8</td>
</tr>
<tr>
<td>P28</td>
<td>80/100</td>
<td>0.0081/0.0943</td>
<td>10+15</td>
</tr>
<tr>
<td>P29R</td>
<td>80/135</td>
<td>0.0081/0.0791</td>
<td>10+5</td>
</tr>
<tr>
<td>P30</td>
<td>80/135</td>
<td>0.0081/0.0791</td>
<td>10+8</td>
</tr>
<tr>
<td>P33</td>
<td>90/120</td>
<td>0.0087/0.0870</td>
<td>10+5</td>
</tr>
<tr>
<td>P34</td>
<td>90/120</td>
<td>0.0087/0.0870</td>
<td>10+8</td>
</tr>
<tr>
<td>P35</td>
<td>80/100</td>
<td>0.0082/0.0867</td>
<td>10+12</td>
</tr>
<tr>
<td>P36</td>
<td>80/120</td>
<td>0.0081/0.1130</td>
<td>10+5</td>
</tr>
<tr>
<td>P37</td>
<td>80/120</td>
<td>0.0081/0.1130</td>
<td>10+8</td>
</tr>
</tbody>
</table>

The bulk gold content of the samples determined by ICP-OES is given in Table 2. According to XPS results, most of the deposited Au was in its elemental state. Before the RTT, about 23% of the deposited gold was in the oxidized form, mainly in the form of ionic species (Au$^{5+}$) and only 2% of the deposited gold as Au$^{3+}$. After the RTT, Au$^{3+}$ contribution disappear and the ionic species represent in all cases less than 9% of the deposited gold.

As can be deduced from Table 2, the preparation conditions influences Au crystal size and particle size.

Low salt concentration was used in order to avoid GNPs sintering. However, the amount of gold deposited was too low for samples P9 and P21 on which lower particle size can be found, as can be seen in Table 2. For this reason, the supports were put in contact with low amount of gold salt to create centers for further nucleation increasing the amount of gold salt in the solution.

Table 2. Characteristics of the sorbent samples.
Since Table 2, it can be seen that there is not a relationship between particle size and crystal size, indicating that nucleation and growing processes follow different evolution depending on preparation procedure.

In the literature it is reported a relationship between crystal size and the surface defects, where an incomplete set of nearest neighbors can be found [22]. These defects can be active sites for sorption processes or catalytic reactions rather than the number of surface atoms. Different defects are considered: on corners, edges or faces of the crystal; the relative occurrence of these defects depends on crystal size [22]. These authors establish 5 nm as the crystal size above gold activity would be rather insensitive. Those studies have been used to explain the catalytic activity of gold nanoparticles in further research by other authors [23] and [24]. However, these two studies represent the dependence of relative amounts of surface sites on particle diameter of gold particles instead on crystals size, based on cuboctahedron model for crystals by [22]. Those results relating catalytic activity and gold particle size [23, 24] can only be understood

<table>
<thead>
<tr>
<th>Sample</th>
<th>XRD crystal size</th>
<th>FE-SEM FD</th>
<th>ICP-OES Au content</th>
</tr>
</thead>
<tbody>
<tr>
<td>P9</td>
<td>20 nm</td>
<td>50 nm</td>
<td>0.085 mg Au/g sorbent</td>
</tr>
<tr>
<td>P21</td>
<td>28 nm</td>
<td>54 nm</td>
<td>0.239 mg Au/g sorbent</td>
</tr>
<tr>
<td>P25</td>
<td>26 nm</td>
<td>62 nm</td>
<td>0.032 mg Au/g sorbent</td>
</tr>
<tr>
<td>P26R</td>
<td>40 nm</td>
<td>61 nm</td>
<td>0.815 mg Au/g sorbent</td>
</tr>
<tr>
<td>P27</td>
<td>51 nm</td>
<td>94 nm</td>
<td>0.915 mg Au/g sorbent</td>
</tr>
<tr>
<td>P28</td>
<td>72 nm</td>
<td>105 nm</td>
<td>1.998 mg Au/g sorbent</td>
</tr>
<tr>
<td>P29R</td>
<td>32 nm</td>
<td>80 nm</td>
<td>0.699 mg Au/g sorbent</td>
</tr>
<tr>
<td>P30</td>
<td>73 nm</td>
<td>81 nm</td>
<td>1.044 mg Au/g sorbent</td>
</tr>
<tr>
<td>P33</td>
<td>50 nm</td>
<td>82 nm</td>
<td>0.708 mg Au/g sorbent</td>
</tr>
<tr>
<td>P34</td>
<td>53 nm</td>
<td>100 nm</td>
<td>1.410 mg Au/g sorbent</td>
</tr>
<tr>
<td>P35</td>
<td>38 nm</td>
<td>88 nm</td>
<td>1.653 mg Au/g sorbent</td>
</tr>
<tr>
<td>P36</td>
<td>75 nm</td>
<td>87 nm</td>
<td>0.910 mg Au/g sorbent</td>
</tr>
<tr>
<td>P37</td>
<td>65 nm</td>
<td>110 nm</td>
<td>1.708 mg Au/g sorbent</td>
</tr>
</tbody>
</table>
in terms of gold particles consisting of one single crystal. However, depending on nanoparticles preparation, particles may consist of various crystals. Figure 2 shows TEM and HRTEM images of selected particles. Most of those particles can be considered as multi-twinned particles as evidenced by the presence of twin planes, and only a few particles (the smallest ones) seem to be monocristalline or formed by twinned crystals (Figure 2c).

Figure 2. TEM (a, b) and HRTEM (c, d) images of Au particles of the sorbent.
According to this fact, the interpretation of the results in [23] and [24] respect to [22] could lead to a misunderstanding about the influence of preparation conditions on characteristics of the sorbent and, in present case, on the mercury retention performance on the different samples prepared. However, particle size can be an important parameter despite the crystal size is small enough: the influence of heat and mass transport cannot be neglected during mercury capture application.

As can be seen in Table 2, particle sizes are higher than crystallite size in all the samples prepared, indicating that particles are composed mainly of more than one crystal. However, the largest particle size does not imply the largest crystallite size. However, the crystal size is rarely and is usually broadly distributed; the usual methods applied to XRD patterns give an average value of the distribution of the crystal size. Accordingly, the study of the grain size distribution (GSD) could give a more comprehensive view of the characteristics of the Au deposited. GSD was obtained for all the samples according the methodology described in [25], based on FW_{1/5/4/5}M procedure using as fitting function Pearson7. As can be seen in Figure 3 average crystal size does not coincide with GSD, in which maximum crystal size is the mode of the crystal size distribution. In addition, the resulting GSD shows anisotropy of average shape for all the samples. Figure 3b depicts this anisotropy for samples P25 and P26R as example.

Moreover, values of crystal size obtained from GSD give a more homogeneous picture compared to that of average crystal size, as can be seen in Figure 4.
Figure 3. a) GSD of some samples (lines); ■ average crystal size. b) Anisotropy of average crystal size calculated: solid lines sample P26R; dashed lines sample P25.

Figure 4. Relationship between FD and crystal size.

The gold particle size (FD) as well as crystal size of samples prepared without seeding step are lower than those obtained with seeding step as can be seen in Figure 5. The effect of gold salt concentration and contact time on growing step is studied for samples prepared with seeding step. The general trend is that FD of GNPs increases at increasing gold salt concentration maintaining the total contact time, despite the distribution of this time is different, according to Table 1. Contact time between sorbent and gold solution enhances nanoparticles growth and GNPs size increases with total contact time. However, the relationship between gold salt concentration and GNPs crystal size is not
maintained, indicating that other factors such as stirring rate or gold salt concentration during seeding could have some influence on growing rate of the crystals.

Figure 5. Feret diameter of Au particles and Au crystal size with gold salt concentration used after seeding during preparation according to conditions reported in Table 1.

Mercury breakthrough curves of the samples are depicted in Figure 6. The amount of mercury captured calculated from the breakthrough curves and, for some samples, the amount of mercury captured measured directly on the samples by AMA are reported in Table 3. The characteristics of the samples have an important effect on their performance in mercury capture, as can be seen in Table 3. However, there is not a direct relationship between either Au content or particle or crystal size and mercury capture capacity of the samples. Figure 7 depicts the amount of mercury captured by the samples (after 500 min of experiment), normalized to the gold content of each sample. There is a general trend indicating that at lower particle or crystal size the higher is the amount of mercury captured. However, it can be found similar mercury capture performance for quite different particle size. On the contrary, for example, sorbent with Au particles of similar size, i.e. 80 nm, have different performances, one adsorbing near the double
mercury than the other. This is a surprising result because the functionality of nanoparticles comes mainly from their size-dependent properties with large fraction of atoms having different coordination than in bulk. In general, these size dependencies are steep, having often times form of $1/R$, where $R$ is the grain size, for catalysis [26, 27] and for adsorption [27, 28].

Figure 6. Mercury breakthrough curves for samples with: a) low Au content (<0.9 mg Au/g sorbent) and b) high Au content (>0.9 mg Au/g sorbent).

Table 3. Amount of mercury captured.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Amount captured* $\mu$g Hg/g sorbent</th>
<th>Amount captured** $\mu$g Hg/g sorbent</th>
</tr>
</thead>
<tbody>
<tr>
<td>P9</td>
<td>3.8</td>
<td>-</td>
</tr>
<tr>
<td>P21</td>
<td>8.9</td>
<td>9.1</td>
</tr>
<tr>
<td>P25</td>
<td>13.4</td>
<td>-</td>
</tr>
<tr>
<td>P26R</td>
<td>20.0</td>
<td>-</td>
</tr>
<tr>
<td>P27</td>
<td>15.7</td>
<td>-</td>
</tr>
<tr>
<td>P28</td>
<td>23.9</td>
<td>24.4</td>
</tr>
<tr>
<td>P29R</td>
<td>24.0</td>
<td>-</td>
</tr>
<tr>
<td>P30</td>
<td>19.5</td>
<td>-</td>
</tr>
<tr>
<td>P33</td>
<td>16.8</td>
<td>-</td>
</tr>
<tr>
<td>P34</td>
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<tr>
<td>P35</td>
<td>34.0</td>
<td>-</td>
</tr>
<tr>
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<tr>
<td>P37</td>
<td>21.9</td>
<td>22.4</td>
</tr>
</tbody>
</table>

*from breakthrough curves, after 500 min  
**directly on used exhausted sorbent
When representing the inverse of the particle size against the amount of mercury captured (normalized to the gold content of the sample) it can be found the similar than that found in Figure 7: the lower particle size the higher mercury capture capacity. However, FD differences near 30 nm lead to similar values of mercury captured. When the inverse of the average crystal size against the amount of mercury captured is depicted (Figure 8) the same trend is again observed. It fails to explain that similar crystal size exhibits large differences in mercury captured.

Regarding the results depicted in Figure 3, it seems clear that the value of average crystal size is far from the value of the mode of crystal size obtained from GSD. Mercury is most likely to be in contact with gold crystals with size represented by the maximum of the GSD curve than that with gold crystal with the average size obtained by Pawley method.

Accordingly, the values that were depicted in Figure 4 have been used in Figure 8 to represent the size-dependence of mercury captured with the inverse of the value of the mode crystal size. As can be seen, there is a direct correlation between mercury capture capacity (normalized to the gold content of each
sample) and the inverse of the mode crystal size, with a correlation coefficient \( R^2 = 0.988 \). This size dependency has been previously observed for catalysis [26, 27] and for adsorption [27, 28].

Figure 8. Relationship between mercury capture capacity of samples (normalized to the Au content) and \( 1/R \), being \( R \) average crystal size or mode crystal size.

4. CONCLUSIONS

Gold nanoparticles have been deposited on a structured carbon by direct reduction of a gold salt by the carbon surface in the absence of reducing agents for the gold salt or a protector of the formed particles. The preparation conditions (stirring rate, gold salt concentration and contact time) were varied to obtain a total of 13 samples with different Au content, Au particle size and Au crystal size. The kinetic study of the gold reduction on the carbon surface has allowed to obtain 1 as the order of the reaction and to establish that the reaction rate constant corresponds to the diffusion rate. The use of a high concentration gold salt solution leads to a shift of the reduction reaction to gold reduction. The increase of the contact time between
the carbon surface and the gold salt solution leads to an increase of the particle size and it seems that gold particles can be sintered in the early stages of the reaction.

Gold particles are composed by several crystals with an average value far from the maximum obtained from the calculated grain size distribution (GSD) curve obtained from XRD patterns, indicating anisotropy of the crystals.

The samples have been used for mercury capture at low concentrations (100 μg/m³). The amount of mercury captured is not size-dependent with either gold content, average particle size or average crystal size as well as is not size-dependent with the inverse of those characteristics. However, the study of the grain size distribution can explain the mercury capture performance of the studied samples, obtaining a good correlation between the inverse of the mode of the crystal size obtained from GSD and the amount of mercury captured by the different samples.

5. ACKNOWLEDGEMENTS

The financial support from Spanish Ministry of Science and Innovation and European Regional Developments Funds (ref: ENE2011-23412) is duly recognized. C. Gomez-Giménez thanks CSIC and European Regional Developments Funds for JAE grant.

6. REFERENCES


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