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Pt, PtBi, PtCu and PtCuBi clusters grown in a plasma based gas aggregation source for glycerol electrocatalytic oxidation

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Abstract: Metallic Pt, PtBi, PtCu and PtCuBi clusters were grown in a plasma magnetron based gas aggregation source. The results show how the addition of Cu or Bi to the Pt clusters leads to the decrease of cluster mass. X-ray diffraction results show that Pt-based clusters have different lattice parameter values depending on the formation of alloys or the presence of other phases. Electrochemical measurements show that the addition of Bi or Cu to the Pt clusters enhances the catalytic activity for glycerol oxidation (decrease of the onset potential).

Keywords: Metallic clusters, Gas Aggregation Source, Electrocatalysis, Sputtering.

1. Introduction

There is a growing interest on the catalytic conversion of renewable raw materials for the production of fine chemicals or biofuel due to the depletion of fossil reserves and to the release of greenhouse gases. In biofuel industry, glycerol is one of the main by-products generated during the production of bioethanol and biodiesel. The transformation of glycerol into value added compounds would help to reduce the biofuel production costs¹. This conversion may lead to monoglycerides, glycerol carbonates (useful for colors, varnishes, glues, cosmetics and pharmaceuticals), to ethers (useful in cosmetics, foodadditives or lubricants) or to acetals and ketals (flavoring agents). Glycerol oxidation is mainly carried out using strong oxidants that are not selective, leading to the production of undesired molecules. Heterogeneous catalysts have been already explored (Au, Pd, Pt) but the control of the reaction selectivity still remains difficult. Electrocatalytic processes are surface reactions, therefore, the use of metallic clusters (< 5 nm) dispersed on high surface carbon support can increase its specific surface area and further help to drastically decrease the noble metal amount in electrodes. Our aim is to grow multimetallic catalysts based on Pt with admixture of Bi and Cu in a plasma magnetron based gas aggregation source (GAS) and to study the electrochemical conversion of glycerol, mainly the current density and the oxidation onset potential. This work gives an insight about the relationship between composition, nanostructure and catalytic activity of the Pt-based clusters and their influence during glycerol oxidation.

2. Experimental setup

The Pt-based catalysts are synthesized either by wet chemistry (water-in-oil microemulsion method, not shown in this poster) and by a plasma magnetron based Gas Aggregation Source (GAS) allowing the gas phase production of clusters with an optimum size control².

The GAS setup is based on a commercial Nanogen 50 from Mantis Deposition Ltd and has been modified in order to include three magnetrons (ONYX 1" from Angstrom Sciences). A Pt, Cu or Bi target is mounted on each magnetron. The distance between these magnetrons and the 5 mm outlet orifice of the GAS (30 cm long, 13 cm in diameter) is fixed to 70 mm while the pressure is fixed to 42 Pa allowing the gas-phase growth of clusters. By using such device, alloyed, core-shell and Janus nanclusters could be obtained depending of the experimental conditions and the nature of the materials^{3,4}. The GAS is placed inside a HV deposition chamber and the generated cluster beam pass through a quadrupole mass spectrometer (QMS) collecting only the negatively charged clusters and allowing to follow in-situ the cluster mass distribution. A mobile substrate is placed in the HV deposition chamber between the GAS and the QMS. The deposition rate could be estimated with a Quartz crystal microbalance replacing the substrate. Fig. 1 gives an overview of the experimental setup based on plasma magnetron sputtering. In this study, four types of clusters are produced: pure Pt clusters (denoted PtXW), bimetallic PtCu (PtXWCuYW) and PtBi clusters (PtXWBiZW) and trimetallic PtCuBi clusters (PtXWCuYWBiZW). To vary the cluster composition, the power applied on each magnetron (P_{Pt} , P_{Cu} and P_{Bi}) is varied: between 20 and 30 W for Pt, between 8 and 12 W for Bi and between 20 and 30 W for Cu. X, Y and Z correspond to the power applied to the respective target Pt, Cu and Bi. Before each deposition, the targets are cleaned by sputtering during at least 5 min in order to obtain a stable voltage.



Fig. 1. Schematic of the experimental setup used for the multimetallic clusters synthesis.

Clusters are deposited during 3 min onto N-type doped Si (100, P-doped) and carbon-coated Cu TEM grids (300 mesh, SPI) for physical characterization. Physical characterization includes Grazing Incidence X-ray diffraction (GIXD) performed with a Bruker diffractometer with a Cu X-ray source (1.5418 Å) and

Energy-dispersive X-ray spectroscopy (EDX) with a Bruker QUANTAX X-ray detector mounted in a Zeiss Supra 40 scanning electron microscope. To evaluate the electrochemical properties of the deposit, catalytic clusters are deposited onto gold electrodes during 2 s. The electrochemical measurements are performed in a classical three-electrode cell, using a reversible hydrogen electrode (RHE), the Pt-based clusters deposited on a gold disk as working electrode and a glassy carbon plate as counter electrode. Cyclic voltammetry (CV) measurements were performed using a VersaSTAT 4 potentiostat in a N2purged 0.1 M NaOH electrolyte between 0.05 and 1.2 V vs RHE with a scan rate of 50 mV s⁻¹. The electrocatalytic activity toward the glycerol oxidation is evaluated in the presence of glycerol in the electrolyte (0.1 M NaOH + 0.1 m)M glycerol).

3. Results and discussion

The deposition rate is estimated for each pure materials. When only the Pt target is sputtered, this rate linearly varies between 0.7 and 1.1 mg h⁻¹ cm⁻² in the range of power (20-30 W). For Cu the deposition rates is between 0.1 and 0.6 mg h⁻¹ cm⁻² and for Bi it not measureable. Unfortunately, for bimetallic and trimetallic clusters, the deposition rate cannot be measured using the microbalance, however the quadrupole filter allows to estimate the variation of the clusters mass by integrating the mass distribution curves. Figure 2 gives the mass distribution of the clusters for different powers applied to the magnetron. For Pt-Bi clusters (red curves in Fig. 2a), the mass distribution curves are narrower than the one for pure Pt (black) and the position of the maximum is shifted to lower mass values, indicating that addition of Bi in Pt decreases their mass (lighter clusters). For 10 W applied on the Bi target, the clusters mass decreases by a factor of 2. For Pt-Cu clusters (blue curves in Fig. 2b), the mass distribution curves have a different behaviour. The addition of Cu in the Pt cluster induces a decrease of the maximum intensity, a broadening of the mass distribution curve and an increase of the clusters mass for all the experimental conditions. For Pt-Cu clusters the deposited mass change is less important than for the Pt-Bi system (4% decrease instead of 50%). For the trimetallic clusters (green curve on Fig.2c), the position of the maximum and the overall deposited mass remain almost unchanged compared to Pt clusters. The clusters deposited onto Si substrates are analysed with EDX to confirm the presence of each metal as observed in Fig. 3. EDX spectra show no contamination of Bi for the PtCu clusters and no contamination of Cu for the PtBi clusters. Oxygen is detected for all co-sputtered clusters but more strongly with those containing Cu and/or Bi showing that these two metals are more reactive to the residual oxygen in the aggregation chamber that can be easily explained by the oxidation Gibbs energy for Pt, Bi and Cu⁵. The presence of oxygen was confirmed by Rutherford Backscattering Spectroscopy (not shown here) and its amount is about 30%. RBS measurements allow us to estimate the stoichiometry of the PtCu clusters. By applying 30 W on the Cu target, the Cu atomic percentage inside the cluster reaches around 20%.



Figure 2. Mass distribution curves obtained from the QMS for clusters grown at different conditions. (a) Pt-Bi clusters, (b) Pt-Cu clusters, (c) Pt-Cu-Bi clusters. The experimental conditions are described in each graphic.

The presence of Bi and Cu in the Pt-based clusters can affect their crystal structure. To obtain information about these changes, grazing incident X-ray diffraction measurements were performed for Pt, PtBi, PtCu and PtCuBi clusters deposited onto Si. The Pt clusters diffractogram (Fig. 4, black curve) shows two signals that peak close to 40° and 46°, two other signals (not shown here) appear at 67° and 81°. These signals correspond respectively to the (111), (200), (220) and (311) diffraction planes of the face-centered cubic (fcc) phase of Pt. For clusters containing bismuth (Fig. 4, red curve), a broad signal centred at 29 ° is observed. In this region are present different diffraction peaks of phases of Bi, PtBi and BixOy, therefore is not clear to have a correct indexation. This broad signal could be due to a short coherence length domain, present in small size clusters (<1 nm) or with a poor crystallinity.



Figure 3. Energy-dispersive X-ray spectra of Pt-based clusters deposited onto a Si substrate. For more clarity, the figure shows the square root of the measured intensity. For more clarity, the Si substrate signal is not shown.



Figure 4. Grazing incident X-ray diffractograms of Pt, Pt-Bi, Pt-Cu and Pt-Cu-Bi clusters.

Co-sputtering of Pt and Cu lead to a similar diffractogram (blue curve) than for Pt clusters (black) and there are no additional peaks. For trimetallic clusters, the main peak corresponds to Pt (111) diffraction plane and a weak signal corresponding to the presence of Bi is detected. Figure 5 shows in detail the peak position of the Pt (111) diffraction plane and the calculated lattice parameter a for different powers applied on the magnetron. The peak position for the Pt (39.765°). When adding and increasing the Bi content ratio (lower Pt power, higher Bi power), the peak position has a slight shift to lower values. The opposite behaviour is observed in PtCu clusters showing a shifting to higher degree values.



Figure 5. (Left axis) X-ray diffraction peak position of the (111) plane of the Pt fcc crystal lattice and (right axis) *a* lattice parameter for (a) Pt clusters (square), PtBi clusters (circles), (b) PtCu clusters (triangles) and (c) PtCuBi clusters (diamonds). Each figure is shown as a function of the ratio of the applied power of Bi and/or Cu magnetrons compared to that on the Pt magnetron (P_x/P_{Pt}).

We can conclude that Bi addition leads to a Pt crystal lattice expansion while Cu addition leads to a decrease in the interatomic distances (shrinkage of the crystal lattice). For the slight expansion of the lattice parameter when adding Bi, it could be to the insertion of interstitial Bi or O in the Pt crystal lattice but further studies should be performed. For the PtCu clusters, as Cu also has a fcc crystal cell, it is possibly to assume that the shifting is due to the formation of a PtCu alloy. Assuming that it follows the Vegard law it would correspond to a composition between 1 and 10 %. Semiquantitative analysis of the EDX measurements have shown that the Cu content is around 20

and 32 at. % (similar to RBS results). This underestimation of the composition by the Vegard law could be due to a nano-size effect or because of the formation of core-shell where the Vegard law is not valid⁶.

Evaluating the Pt-based clusters by cyclic voltammetry shows how the electrochemical response can be influenced by the addition of Cu or Bi to the Pt clusters. Figure 6a shows a typical CV curve of Pt clusters in NaOH with the H desorption peak at ca. 0.3 V while for PtBi clusters this peak signal is supressed but remains present for PtCu clusters⁷. When performing electrochemical measurements in presence of glycerol (Fig. 6b), we observe that, compared to Pt clusters, there is a weak shift of the oxidation potential to lower values both for PtBi and for Pt-Cu clusters but further analysis at different composition should be performed. Because we do not have access to the effective load (expressed in mg cm⁻²) of each catalyst, the three CV curves are normalized to the maximum of the oxidation peak.

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Figure 6. Cyclic voltammetry of (a) Pt-based clusters deposited onto Au electrodes in NaOH 0.1 and of (b) Pt-based clusters deposited onto an Au electrode in NaOH 0.1 M, glycerol 0.1 M. The measurements were performed with a scan rate of 50 mV/s.

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