Morphology and Structure by Fractal Analysis of Pt-Cu Nanoparticles

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Abstract: - A procedure to determine the fractal dimension of the Pt-Cu bimetallic nanoparticles stabilized by PVP (polyvinyl pyrrolidone) from Transmission Electron Microscopy (TEM) micrographs is described. The analysis indicates a bimodal fractal behavior characterized by a small fractal dimension (2.39) at low scales (0.18nm-1.24nm) and a higher fractal dimension (2.81) for a self-similarity domain of 1.24nm-4.50nm. The inflexion point situated at 1.24 nm (the length for which the fractal dimension changes) indicates the mean particle size. This behavior is probably due to a mixed-fractal structure, rather than a lack in instrument resolution.

Key-Words: computational fractal theory, TEM, nanoparticle, Pt-Cu bimetallic nanoparticle.

1 Introduction

The fractal theory is an important tool in understanding and describing surfaces and structures with irregular geometries. It provides a method to compute a number – the fractal dimension – that describes how irregular, porous, agglomerate is the surface or the structure, and also, shows if the object is self-similar or not. Self-similarity is the property of an object to look the same at different magnifiers. For objects found in nature, self-similarity is obeyed only at finite scale range, named cut-off limits. At molecular-size range, surfaces of most materials are fractals, in other words, geometric irregularities and defects are self-similar at different scales.

Bimetallic nanoparticle catalysts consisting of noble (i.e. Pt or Pd) and d-metals are of great practical interest for due to their interesting application in catalytic field. Significant examples for catalytic applications are oxidative conversion of methane [1], CO oxidation [2], nitrate reduction [3], methanol oxidation in fuel cells [4], hydrogenation of acrolein [5], dehydrogenation of isopropyl alcohol [6] and oxidation of alcohols [7]. When the metal nanoparticles are very small, at the limit of TEM resolution, the fractal analysis of TEM micrographs may prove to be an essential characterization tool. The bimetallic colloidal Pt-Cu nanoparticles, selected to be analyzed by fractal theory in this study, were prepared by two-step reduction procedure using polyol method. To control the particles growth, to avoid the particle agglomeration as well as to obtain narrow size distribution, PVP (polyvinyl pyrrolidone) was used as protective polymer.

The aim of this study was to characterize the morphology (size and shape) of Pt-Cu nanoparticles by fractal analysis.

2. Experimental

2.1 Synthesis of Pt-Cu nanoparticles

The bimetallic Pt-Cu nanoparticles were synthesized by polyol method [8]. H2PtCl6 (Alfa Aesar) and Cu(Ac)2-H2O (Merck) were used as metal precursors. The first step consisted in the preparation of stock solutions of metals in ethylene glycol (3.8×10⁻² M) and PVP. The molar ratio between the protective polymer (calculated on basis of monomer units) and metals was 1:5. The experimental procedure was the following. 10 mL solution of Pt²⁺/EG (3.8×10⁻² M Pt²⁺) were mixed at room temperature with 10 mL solution of NaOH (0.25 M)/ PVP (0.38 M)/EG solution under Ar bubbling to keep inert atmosphere. The obtained solution was deaerated by Ar bubbling for 30 minutes and then rapidly heated to 120 °C under stirring. The initial transparent color of the solution turned suddenly to dark gray color at around 90°C, indicative of Pt²⁺ reduction to Pt⁰ by EG. The process of nucleation and growth of Pt particles at 120 °C lasted for 90 min. The solutions were then
cooled at room temperature under Ar atmosphere. The second stage of the synthesis consisted in the addition of 10 ml solution of copper acetate in EG (3.8×10^{-2} M Cu^{2+}) to the colloidal suspension of reduced platinum at room temperature under inert atmosphere. The rapid heating of colloidal suspension to 140 °C for 60 minutes allowed the reduction of Cu^{2+} to Cu^0. Finally, a stable, black colored, colloidal suspension of bimetallic Pt-Cu in EG nanoparticles was obtained. The separation of the extremely stable colloidal bimetal particles was only possible by adding an equal amount of acetone (≈ 30 mL) and then cooling the resulted mixture to -16 °C for 24 h. The ultracentrifugation proved to be completely inefficient for the separation of bimetallic nanoparticles. The metallic phase, precipitated at the bottom of the flask, was separated by decantation and then washed several times with acetone to remove the viscous EG. The great advantage of this procedure is that the black metal powder, consisting of Pt-Cu nanoparticles functionalized with PVP, can be stored indefinitely and at need they can be redispersed easily in aqueous or alcoholic media by ultrasonification.

2.2 Characterization of bimetallic Pt-Cu nanoparticles

The as prepared bimetallic nanoparticles were characterized by transmission electron microscopy (TEM - Philips CM20). Fractal analysis was carried out on a squared window of a TEM micrograph.

The bimetallic Pt-Cu nanoparticles obtained by alkaline polyol method were fine well dispersed (Fig. 1 A and B). The TEM diameter of around 1.5 nm was calculated by counting more than 200 nanoparticles. The mean size of Pt-Cu nanoparticles are smaller than those prepared by Weihua et al. [9] using water in oil microemulsion. Two distinct morphologies can be distinguished from TEM photos. One predominant shape is spherical one. Other shapes are vermicular or even branched (tripod).

The determination of the average size from the TEM micrographs presented in Fig. 1 can be subjected to errors as the particles are very fine and in addition there are at least two dominant morphologies (spherical and branched). Thus the fractal analysis of the TEM image was selected to give additional information on the Pt-Cu morphology. The fractal analysis was carried out on image 1B, which is a squared window 1530 pixels x 1530 pixels of the TEM image of Fig 1 A.

Eliminating the background electronic noise, the micrograph quality was improved. It is known that the presence of electronic noise in the image can increase the fractal dimension [10]. Using the image histogram the noise peaks in the 168-255 grey levels domain was removed. The grey level of each image pixel was converted in height and the fractal dimension of the equivalent surface was computed using two methods: the height correlation function method and the variable length scale method.

Both methods use the self-similarity property of the fractal object. Self-similarity has a mathematical description [11],[12]:

\[ N(r / R) \sim (r / R)^{-D} \]  

where \( D \) is the fractal dimension and \( N(r,R) \) is the number of boxes of size \( r \) which cover the object of linear size \( R \), in other words, self-similarity is the property of an object to look the same when zooming it.

Fractal dimension of a rough surface can be computed from the height correlation function [13]:

\[ G(r) \equiv < C(\tilde{x},r) >_x \]  

where the symbol \(<...>\) denotes an average over \( x \), and \( C(x,r) \) is defined as:

\[ C(\tilde{x},r) = [h(\tilde{x}) - h(\tilde{x} + \tilde{r})]^2 \]  

and surface is described by the function \( h(x) \) which gives the maximum height of the interface at a position given by \( x \). Thus the height correlation function \( G(r) \) obeys the following scaling relation [14]:

\[ G(r) \sim r^{2\alpha}, r \ll L, \]  

where, for a surface embedded in a 3-dimensional Euclidean space:

\[ \alpha = 3 - D, \]  

with \( D \) - the fractal dimension. (5)

The scaling range in which equation (4) is obeyed is called the “cut-off” limits and it indicate the range of self-affinity, in other words, the range where there
are correlations between surface points. The first method [13],[14] uses equations (2)-(5) to compute fractal dimension. The second method was proposed by Chauvy et al [15] and consists in computing the rms deviation of the surface. The algorithm is the following:

(i) an interval of length $\varepsilon$, in case of a profile, (or a box of size $\varepsilon \times \varepsilon$, in case of a surface) is defined;
(ii) a linear (or planar) least square fit on the data within the interval is performed and the roughness is calculated;
(iii) the interval (box) is moved along the profile (surface) and step (ii) is repeated;
(iv) the rms deviation for multiple intervals is computed, and (v) steps (ii)-(iv) are repeated for increasing lengths (box sizes).

Rms deviation $R_{q\varepsilon}$, averaged over $n_\varepsilon$, the number of intervals of length $\varepsilon$, is defined by:

$$R_{q\varepsilon} = \frac{1}{n_\varepsilon} \sum_{i=1}^{n_\varepsilon} \left( \frac{1}{p_\varepsilon} \sum_{j=1}^{p_\varepsilon} z_j^q \right)$$

where $z_j$ is the jth height variation from the best fit line within the interval i, and $p_\varepsilon$ is the number of points in the interval $\varepsilon$.

For a self-similar structure, the rms deviation depends on the interval length $\varepsilon$ as a power function. Thus, the log-log plot of $R_{q\varepsilon}$ versus $\varepsilon$ gives the Hurst or roughening exponent $H$, and the fractal dimension $D$, can be calculated as:

$$D = D_T - H$$

where $D_T$ is the topological dimension of the embedding Euclidean space ($D_T=2$ for profiles and $D_T=3$ for surfaces).

The variable length scale method is more suitable for higher scaling range than the correlation function method because of the necessity to have enough points in an interval $\varepsilon \times \varepsilon$ to compute rms deviation $R_{q\varepsilon}$, averaged over $n_\varepsilon$, meaning that $\varepsilon$ must be high enough for a good statistic. Results are presented in the following table:

**Table 1 Fractal dimensions obtained using the correlation function method**

<table>
<thead>
<tr>
<th>Fractal dimension</th>
<th>Linear correlation coefficient</th>
<th>Self-similarity domain (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.39±0.01</td>
<td>0.996</td>
<td>0.18-1.24</td>
</tr>
<tr>
<td>2.81±0.01</td>
<td>0.975</td>
<td>1.24-4.50</td>
</tr>
</tbody>
</table>

The analysis indicates a bimodal fractal behavior characterized by a small fractal dimension (2.39) at low scales (0.18nm-1.24nm) and a higher fractal dimension (2.81) for a self-similarity domain of 1.24nm-4.50nm. The inflexion point situated at 1.24 nm (the length for which the fractal dimension changes) indicates the mean particle radius. This behavior is probably due to a mixed-fractal structure, rather than a lack in instrument resolution. The fractal dimension of 2.81 indicates a compact, agglomerated structure composed by low-range correlated particles. The higher fractal dimension characterizes the spherical predominant shape and the lower one is related to the worm-like-shape.

For the variable length scale method no linear domain can be observed so, for higher length scale (>4.5 nm) there is no fractal behavior (fig. 4).
The most important result is that the structure obtained exhibits fractal properties as presented in Table 1. This behavior means that bimetallic Pt-Cu particles are self-similar structures over a significant range and these structures can be characterized by a non-integer exponent, the fractal dimension. All these fractal dimensions obey Pfeifer’s self-similarity condition: \( r_{\text{max}} / r_{\text{min}} > 2^{1/D} \), where \( r_{\text{max}} \) and \( r_{\text{min}} \) are the cut-off limits, meaning that for the indicated range the sample shows fractal behavior.

4 Conclusions
The fractal analysis proved to be a versatile tool for morphological characterization of nanoparticles. The average size as well as the shape of model Pt-Cu bimetal nanoparticles were successfully determined from TEM micrographs using fractal analysis. The sample reveal fractal behavior, meaning that it is self-similar over the cut-off domain.

References: