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Selective deactivation of gold catalyst

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ABSTRACT

The progressive poisoning effect of different molecules on carbon supported gold catalysts has been evaluated during the aerobic oxidation of glucose. A geometrical model has been derived for describing the morphological properties of two catalysts made of carbon supported gold particles having a known size distribution centered at 3.30 and 7.89 nm respectively. The observed deactivation trend follows the order thiocyanate > cyanide ≈ cysteine > thiourea and it obeys an exponential law. The kinetics of catalyst deactivation has been interpreted by considering the important contribute of electronic factors which overlap the space shielding of active sites, due to long range poison–catalyst interaction influencing the entire metal particle. Considering the nature of the molecules showing a high poisoning effect and the promoting effect of OH^-, a molecular model for electronic interactions in gold nanoparticles during the aerobic oxidation of glucose has been proposed where the dioxygen reduction step is differently influenced by soft and hard-nucleophiles.

1. Introduction

Correlation between surface structure and catalytic behavior in solid materials is of strategic importance for producing quick and clean industrial reactions, whereas speculations on the nature of active sites are a matter of scientific relevance for the progress in catalysis [1].

In recent years gold catalysis has received a growing interest [2] due to exciting applications in dihydrogen activation [3], carbon monoxide oxidation [4], synthesis of hydrogen peroxide [5] and selective liquid phase oxidation [6]. Among studies on the mechanistic aspects of gold catalysis [7,8] only a few papers concern morphological aspects of the active sites. In this context, two recent reports are of great relevance because they seem to demonstrate that unsupported gold promotes the low temperature CO oxidation [9] as well as carbohydrates oxidation [10] with an efficiency similar to the supported gold particles. This observation is helpful for simplifying the design of models taking into account only gold species as the active sites.

Considering the liquid phase oxidation of glucose catalyzed by colloidal gold nanoparticles, we observed a very strong dependence of the activity, expressed as *initial rate/total Au concentration*, from the particle size; we call this ratio, represented by T, *turnover number* since it is different from the canonical TOF (*turnover frequency*), *expressed as initial rate/active sites*. In a series of experiments, carried out under the same conditions of temperature, pressure and amount of gold, the turnover number T rapidly decreased during glucose oxidation from a value of 23,000 h^{-1}, for particles having a mean diameter of 3 nm, to zero for particles of about 10 nm [10] (Table 1).

The experimental turnover numbers correlate very well with the diameter d of the particles, expressed in nm, according to the equation:

$$T\ (h^{-1}) = (9{,}22 \cdot d^{-0{,}335} - 4{,}21) \times 10^4. \qquad (1)$$

This equation, as all the successive others showing the dependence of some experimental variable from another one (in this case T vs d) was obtained by non-linear correlation analysis starting from some arbitrary functions (in this case $T = a \cdot d^b + c$) and searching the values of the constants (a, b, c) with the aid of well known programs, like "Mathematica" or "MathCad." For each correlation we tried several arbitrary functions, in order to optimize the best fit (all the equations so obtained show a correlation coefficient >0.98).

Assuming a simple model of gold nanospheres having the same diameter d, for a constant total amount of gold the external surface S results in inverse proportion to the diameter, $S = k_1/d$, and then if a given reaction rate was simply proportional to the amount of surface atoms we should expect the linear correlation rate $\cdot\, d = k_2$. On the contrary, in the case of glucose oxidation, a strong deviation from the linear dependence of the activity on total surface metal atoms is observed by plotting $T \cdot d$ vs d, where d is the mean diameter of the different catalyst samples (Fig. 1, where the continuous

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Table 1

d (nm)	T (h^{-1})
2.96	22,836
3.17	19,370
4.33	14,000
4.87	12,065
6.25	9750
7.02	4560
9.92	400

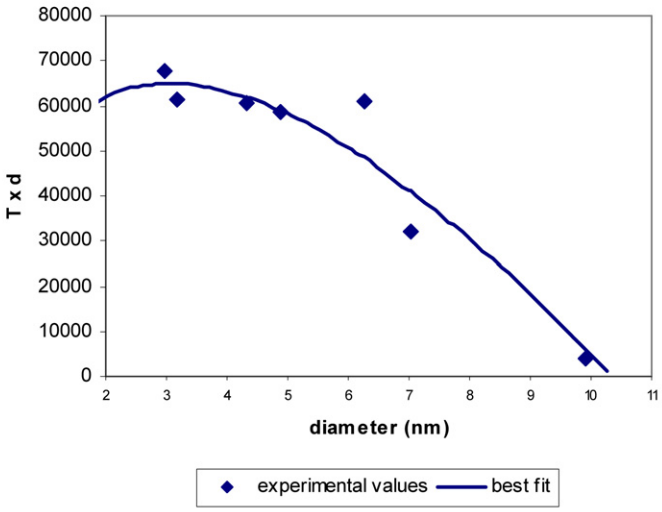

Fig. 1. Deviation from a linear dependence of activity on total surface.

line represents the values of T, obtained from Eq. (1), multiplied by the corresponding values of d).

The high degree of reactivity for gold particles below 5 nm and its rapid decreasing for higher values of the particles size, shown in Fig. 1, have been observed in many experiments of gold catalysis [11–13] and it was interpreted as a coordination effect on the Fermi energy levels, with the subsequent variation of the d-band contribution to the total chemisorption energy of the gold particles [14].

The complexity of heterogeneous catalytic systems is very high because each sample contains a vast number of individual particles characterized by their own peculiar but unknown geometric properties (diameter, structure, conformation of the surface atoms). Moreover, the activity of each site is related both to the dimension of the single particle and the atomic structure of its immediate surroundings, varying from one to another site of the same particle. As a consequence, models are needed for deriving separate information on the contribute of geometrical and electronic factors on the catalytic activity of gold particles having different size. In this work we have investigated a new experimental approach for characterizing the nature of the active sites in differently sized gold particles, which is based on catalyst perturbation induced by poisoning molecules during glucose oxidation.

2. Models

The morphology of gold nanoparticles has been the object of several investigations outlining the appearance of several geometries deriving from different particle dimension and preparation method, which include cubeoctahedra, truncated octahedra, icosahedra, decahedra and amorphous particles [15].

The geometry of "naked" gold particles of diameter larger than 2 nm, formed by nucleation and growth processes in the absence of any support, usually presents structures not too much dissimilar from those of regular polyhedra (mostly cubehoctahedron or truncated octahedron [15–17]), but there are experimental evidences that for the smallest clusters (1–3 nm), Marks decahedron- and icosahedron-structures are quite common [18–20].

In order to derive the geometrical properties of the gold catalyst prepared as colloidal particles, in the absence of experimental high quality HR-TEM images, we have applied either the spherical model or the regular cubeoctahedra/truncated octahedral model.

For the first model the total atoms were calculated from the diameter assuming a close packed fcc structure whereas the surface atoms were calculated assuming a surface packing density intermediate between that of (1 0 0) and (1 1 1) faces. For the polyhedral clusters the diameter and the distribution of atoms (total and surface atoms) could be calculated from the number of atoms on the polyhedron edges [17], but, since we are concerned only with regular polyhedra, we used our simpler equations shown in Appendix A.

In the case of supported particles, the molar fraction of surface atoms available for catalysis was calculated for gold polyhedra laying on an inactive support, like graphite or carbon, with a (111) type face.

Although the particles present in real systems show irregular structures different from perfect spheres or polyhedra, we assume in these models that both the total number of atoms and the related fraction of surface atoms, in a given particle, can be expressed as a continuous function of their diameter (Figs. 2 and 3). It should be outlined that both regular cubeoctahedra and truncated octahedra show a quite similar dependence of the total number of atoms on the diameter. Then the dependence on the particle diameter of the number of the various types of atoms is given by the best fit of the calculated values, as shown by Eqs. (2) and (3), valid in the interval $2 \leqslant d \leqslant 10$ (nm).

$$\begin{aligned} &N_{\text{sphere}} = 30.87 \cdot d^3, \\ &N_{\text{polyhedra}} = 13.5 \cdot d^{3.163} - 29, \quad \text{for } 1 \leqslant d \leqslant 7, \\ &N_{\text{polyhedra}} = 20.64 \cdot d^{2{,}99} - 550{,}5, \quad \text{for } 6 \leqslant d \leqslant 12, \end{aligned} \tag{2}$$

$$\alpha_{\text{sphere}} = \frac{1.31}{d}, \qquad \alpha_{\text{sup ported\_polyhedra}} = 1.107 d^{-0{,}523} - 0.187, \tag{3}$$

where N represents the total number of gold atom in a particle of diameter d nm, and α represents the ratio [number (or mol) of surface atoms/number (or mol) of gold atoms] in the particle of diameter d nm.

The surface atoms fraction calculated from the mean diameter cannot represent a good measure of the real surface fraction present in the catalytic sample, constituted of a more or less wide particle size distribution. More exactly, in a mixture of particles distributed in i groups according to their diameter, the surface atoms fraction σ_i (included, for each group, in a given interval) can be expressed by Eq. (4):

$$\sigma_i = \frac{\alpha_i \cdot N_i \cdot f_i}{\sum_i (f_i \cdot N_i)}, \tag{4}$$

where f_i is the frequency of the i-group particles, N_i and α_i are respectively the number of atoms and the mean surface atoms fraction of that group of particle. The mean molar ratio (surface atoms/Au) of the catalytic sample is then given by:

$$\sigma = \sum \sigma_i \quad \text{(mol surface atoms/mol Au)}. \tag{5}$$

The meaning of σ must not be confused with that of α: both are expressed as molar ratio, but σ represents the ratio between *all the surface atoms and all the Au atoms present in the sample*, whereas a represents the ratio between *the surface atoms and the Au atoms present in a single particle of a specified diameter*. The value of σ,