Heterogeneous Catalysis

The Catalytic Activity of “Naked” Gold Particles**

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The metal–support interaction in catalysis is of relevance both for academic studies and for industrial applications, and theoretical concepts have contributed to understanding the basic principles behind this interaction.[1] In most cases, however, the metal–support interaction is only described in terms of catalytic behavior and its nature often remains debatable. In recent years interest in gold catalysts for various applications in organic and inorganic chemistry[2] has increased and, our and other research groups have investigated the liquid-phase oxidation of polyol,[3–7] aminoalcohols,[8] and glucose[9] to carboxylates, and the gas-phase oxidation of alcohols to the corresponding carbonyl derivatives[10] using metal particles supported on different materials.

In liquid-phase applications, carbon was found to be the support of choice, and in the case of ethane-1,2-diol oxidation, by comparing different commercial carbons, a tentative hypothesis of metal–support interactions, connected to the density of phenolic groups at the carbon surface, was formulated.[11] However, the synergism between gold particles and carbon was not demonstrated and this point remained unresolved.

Although gold colloids have widely been employed to prepare supported gold catalysts, no report of particles derived from colloidal dispersion being used as catalysts has appeared. We have now found that, under controlled conditions, water-dispersed gold sol exhibits a surprising activity when used as “naked particles”, that is, in the absence of common protectors as polyvinylalcohol (PVA), polyvinylpyrrolidone (PVP), tetrahydroxymethylphosphonium chloride (THPC). As a model reaction, we have investigated the aerobic oxidation of glucose to gluconate which occurs under mild conditions.

As shown in the conversion–time plot (Figure 1), naked gold particles having a mean diameter of 3.6 nm behave as an active catalyst allowing 21 % glucose conversion in the first 200 s.

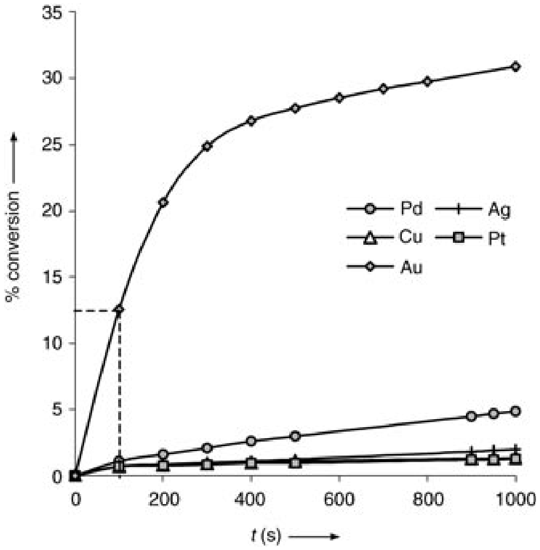

Figure 1. The activity of different metal particles in glucose oxidation. [Metal] = 10^{-4} M, [glucose] = 0.4 M, T = 303 K.

These particles are produced as a colloidal sol by reducing $HAuCl_4$ in the presence of a large excess of glucose acting either as reagent or protector. From the initial rate, a specific molar activity of 18043 mol gluconate [mol Au]$^{-1}$ h^{-1} (calculated with respect to the total gold) can be derived. Under similar conditions, Cu, Ag, Pd, and Pt colloidal particles of similar dimension (3–5 nm) were scarcely active. During the catalytic test, gold coagulated into larger particles owing to the formation of sodium gluconate that, as is common with other electrolytes, promoted sol coagulation leaving a colorless, inactive solution after about 400 s. The growth of gold crystallites during the reaction has been followed by X-ray diffraction (XRD) analysis at various time intervals, after sol immobilization on carbon (Figure 2).

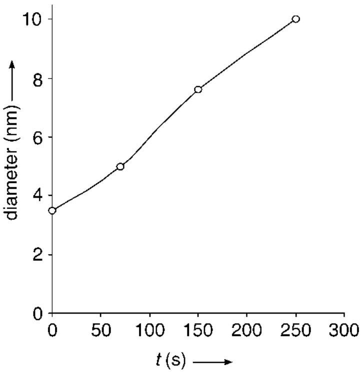

Figure 2. Growth of gold particles during glucose oxidation.

Gold particles are also poisoned by sulfur compounds, such as sulfides and sulfites, and inhibited by protecting molecules, such as polyvinyl alcohol. Although the short life of the gold sol does not allow its use as a practical catalyst, its activity is of relevance both for assigning the catalytic role in the oxidation reaction and for evaluating metal–support interactions. For the latter purpose, a 0.5 % w/w gold-on-carbon catalyst **II** was prepared by contacting the gold sol **I** with carbon powder. The size of gold particles remained unchanged after immobilization on carbon, as derived by

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XRD. Under kinetic control, and using the same amount of gold, the curve of glucose oxidation with supported particles is quite similar to that of unsupported particles during the first 100 s (Figure 3 a). This result means that both catalytic systems are similarly efficient and, therefore, metal–support interactions, if present, are negligible in terms of enhancing gold activity. However, a benefit was obtained by using the supported gold particles as their morphology and activity were preserved for long time allowing the total conversion of glucose (Figure 3 b). In particular, the gold dimension resulted unchanged at the end of the first catalytic cycle.

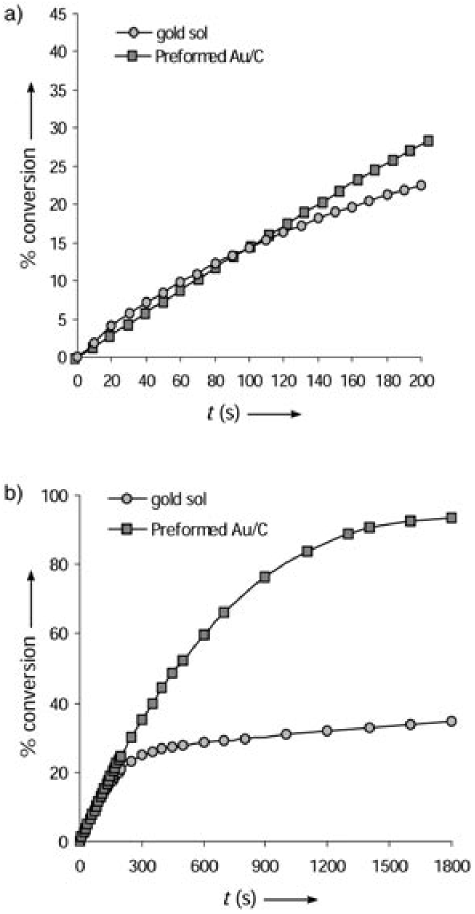

Figure 3. a) Initial rate of glucose oxidation with naked (gold sol) and supported gold particles (preformed Au/C). [Au] = 10^{-4} M, [glucose] = 0.4 M, T = 303 K. b) Rate of glucose oxidation with naked (gold sol) and supported gold particles (preformed Au/C). [Metal] = 10^{-4} M, [glucose] = 0.4 M. T = 303 K.

In principle, the knowledge of particle size in the sol allows the calculation of the turnover frequency (TOF) of gold. For this purpose, a series of experiments were undertaken to better characterize the kinetics of glucose oxidation with gold sol. Using colloidal particles having a mean diameter of 3.6 nm, a linear correlation between gold concentration (10^{-5}–10^{-6} M) and catalytic activity was found (Figure 4), which indicates that the rate is not limited by mass-transport phenomena.

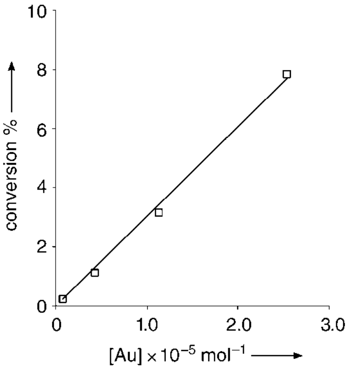

Figure 4. Conversion versus [Au]; t = 100 s, [glucose] = 0.1 M. T = 303 K.

Furthermore, colloidal particles of different size have been produced by changing the chloroauric concentration from 50 to 600 mg L^{-1}, and the mean dimension of coherent scattering crystallites was determined by XRD (using the Scherrer equation[11]) after immobilization on carbon. For comparing activity with size, this technique allows a better correlation than that obtained by TEM where a broad distribution is observed in the case of larger particles (5–10 nm) owing to the formation of aggregates after deposition on carbon. These aggregates, however, retain their XRD identity. The chemical nature of gold particles under reaction conditions has been investigated by X-ray photoemission spectroscopy (XPS) after deposition on carbon. The presence of a sharp peak centered at 83.9 ± 0.2 eV, relative to the Au 4f7/2 signal, suggests the existence of the metallic state only.[12] By using gold particles of different size in the range 3–6 nm, we observed a catalytic activity inversely proportional to the diameter at the total gold concentration of 3.2×10^{-5} M (Figure 5). Particles larger than 6 nm deviate from linearity and a sharp cut off is observed at approximately 10 nm. We have no arguments that give a satisfactory interpretation for the sudden loss of activity. However, discontinuity at the nanometric scale has been observed in the case of other physicochemical properties of gold, for example, the sharp

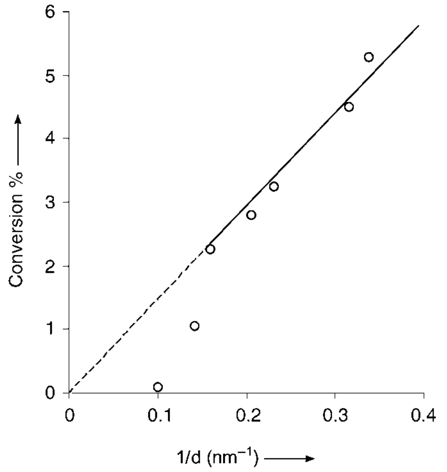

Figure 5. Conversion versus particle dimension; t = 100 s, [glucose] = 0.38 M; glucose:Au = 12 000.

decrease of the melting point, related to the transition from nonmetallic to metallic bonding, which occurs at a lower sizes, approximately 1–2 nm.[2] For particles smaller than 6 nm the observed correlation between activity and diameter agrees with the concept that only exposed atoms are catalytically active. By using the simple model of spherical particles, the total surface area, and therefore the number of exposed atoms, at a given metal amount, is in inverse proportion with particle diameter. By assuming in the first instance uniform particles of 3.6 nm present in the gold sol, 0.288 nm being the atomic diameter, the fraction of atoms lying at the surface should be approximately 36 %.[2,13] Therefore, considering the initial specific activity of 18043 mol of gluconate formed per mol of total gold per hour, the initial TOF calculated for gold in the glucose oxidation is 50120 h^{-1}. Further investigation, based on a more appropriate model and using detailed particle size distribution in the liquid matrix, would give a more accurate result. A high activity can be preserved for a long time during the oxidation of glucose with the supported particles (Figure 3b). The estimated TOF value for carbon-supported particles should be similar to the unsupported particles, considering the similar catalytic efficiency (Figure 3a), and observing that dimension and form are in both cases identical (as derived by TEM), whereas diffusion in the carbon-supported catalyst is not a rate-limiting factor. This latter point has been experimentally verified by observing a linear increase of the reaction rate either on increasing the amount of catalyst (0.5 % Au on C) or on increasing the loading of gold (0.1–1 %) on the carbon.

The catalytic behavior of unsupported gold nanoparticles which interact with dissolved oxygen and glucose under conditions which are at the boundary between homogeneous and heterogeneous conditions, is also of interest for making comparisons with homogeneous catalysis. In fact, homogeneous enzymatic systems, containing the oxidase-catalase proteins derived from *Aspergillus Niger* mould, are the basis of the industrial process for the production of gluconate.[14] Catalytic tests were carried out, in the same apparatus as for the gold reactions, using a commercial enzymatic system (hyderase, Amano) containing 1.3×10^{-6} mol g^{-1} (hydrase) of flavine-adenine dinucleotide (FAD) as the rate-limiting factor. Operating at 303 K and 101.3 kPa, the pH value was fixed at 7 and a glucose/FAD molar ratio of 6.7×10^5 was used for optimizing the activity.

Under these conditions, the enzymatic system was about one order of magnitude more active than gold, its initial TOF value being 7.0×10^5 h^{-1} referenced to FAD (Figure 6) compared to 5.0×10^4 h^{-1} for the inorganic catalysis referenced to the exposed gold.

Despite the higher molecular efficiency of the enzymatic catalysis, for practical application gold seems to be a competitive alternative for glucose oxidation owing to the simplicity of catalyst manufacturing, nontoxicity of the metal and possibility of recycling.

In conclusion, the catalytic role and the properties of unsupported gold nanoparticles towards glucose oxidation have been investigated, allowing the evaluation of the specific activity of the metal which resulted comparable to that of enzymatic systems.

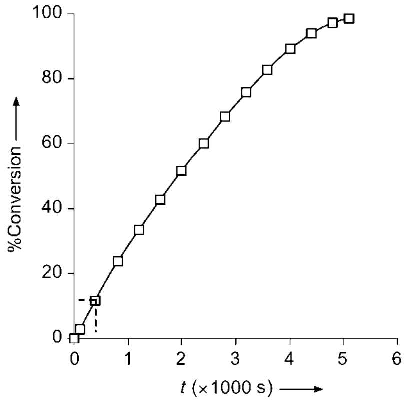

Figure 6. Rate of glucose oxidation with hyderase. [Glucose] = 1 M, [FAD] = 1.5×10^{-6} M, T = 303 K.

Experimental Section

A colloidal dispersion of gold **I**, was prepared by treating a 1.25×10^{-4} M aqueous solution of gold (as $HAuCl_4$) with $NaBH_4$ ($NaBH_4$:Au = 5:1) under N_2 atmosphere, in the presence of a large excess of glucose (0.35 M). The resultant brown sol contained metal particles, stable for several hours in the absence of dioxygen, having a mean diameter of 3.6 nm, as determined by TEM performed on a drop of dispersion evaporated on copper grid. In a similar manner Cu, Ag, Pd, and Pt colloidal particles (3–5.5 nm) were prepared. Supported 0.5 % (w/w) gold on carbon catalyst, **II**, was prepared by contacting 2 g of carbon powder (X40S, Camel, 1200 $m^2 g^{-1}$) with sol **I** containing the appropriate amount of Au. Inductively coupled plasma (ICP) analysis showed total depletion of gold from the solution in a few minutes, and the residue material collected by filtration was used for the catalytic test without washing.

Hyderase: a glucose oxidase preparation produced by *Aspergillus Niger* fermentation (Amano Enzyme Co.) contained 1 mg g^{-1} of FAD. The oxidation of glucose was carried out in a thermostatted, magnetically stirred reactor (80 mL) purged with dioxygen at atmospheric pressure. The reaction was started by adding the catalyst to the O_2 saturated solution. Gluconic acid was continuously titrated at fixed pH value (9.5 for gold and 7 for hyderase) with NaOH, using a GPD 751 Titrino apparatus (Metrohm). Catalyst amount, stirring speed (1600 rpm), gas flow (60 L h^{-1}), and temperature (303 K) were chosen to carry out the test under catalyst-controlled kinetics. As the reaction product only gluconate was detected by HPLC as previously reported.[8]

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