

CATALYSIS AND CAPACITANCE OF NANOSTRUCTURED GOLD SPONGES

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In the present paper we describe the catalytic properties and electrolytic double-layer capacitance of nano-structured, mesoporous gold sponges. These materials are effective catalysts for CO oxidation, and for the selective catalytic conversion of NO_x. The possible application of mesoporous gold in electric double layer capacitors is premised on its high surface area, corrosion resistance and excellent electrical conductivity. The niche, if any exists, would be in high-efficiency, and high-power density ultra-capacitors for top-end consumer appliances.

1. Introduction

The properties of metals in nano-particulate form are currently receiving much attention. However, the inverse situation, that of a mesoporous metal skeleton containing nano-scale cavities, has scarcely been investigated. Nevertheless, such mesoporous materials have been known since at least 1927, when Raney patented his famous nickel hydrogenation catalyst produced by de-alloying Ni_xAl_y with NaOH¹. ‘Raney copper’ and ‘Raney platinum’ may be produced by an analogous process². Generally the resulting nanoscale sponge is pyrophoric and must be handled with care. However, mesoporous gold is a rare exception to this rule, and it has recently been shown that non-combustible, mesoporous sponges may be produced by de-alloying an AuAl₂ intermetallic precursor^{3,4}. The result is a skeletal gold network, characterized by a continuous network of channels of nanoscale dimensions. In this paper we will describe the properties and possible uses of this mesoporous gold sponge.

2. Anomalous properties of mesoporous gold

Bulk gold is yellow and melts at 1064°C. However, these ‘facts’ do not apply to the sponge. For example, the melting point of nano-structured gold protrusions or particles of 5 nm radius is reduced by up to 400°C⁵. In combination with the well-known high mobility of Au surface atoms (due to their reluctance to bond with atmospheric gases), the net effect is that mesoporous gold sponges are relatively unstable with regard to sintering. When freshly prepared mesoporous gold is black, and in this state is one of the best absorbers known of infra red

radiation⁶. However, unless the mesoporous state is stabilized by some coating substance, such as sodium citrate, aluminum oxide or copper oxide, the black gold has a tendency to sinter to the denser yellow form.

The size distribution of the channels in a sample with a BET surface area of $20 \text{ m}^2/\text{g}$ is shown in Figure 1. It is evident that this material consists of a large number of nominally 13 nm diameter cavities embedded in a matrix of gold.

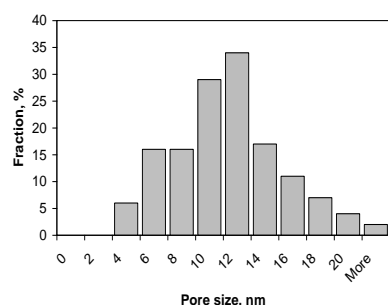


FIGURE 1. Channel sizes in meso-porous gold surface prepared by de-alloying of AuAl_2 in 1M NaOH. Sample has been dried out for SEM examination but has been ostensibly stabilized by about 5 wt% Al_2O_3 .

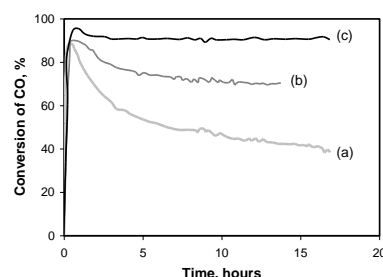


Figure 2. Oxidation of 1% carbon monoxide in air at 60°C . The space velocity is $9 \text{ l.g}^{-1}.\text{h}^{-1}$; (a) commercial hopcalite, (b) hopcalite on which gold nanoparticles have been deposited, (c) mechanically alloyed composite of hopcalite and mesoporous gold

3. Catalysis

It was only discovered in the 1980s that gold nano-particles can be active heterogeneous catalysts^{7,8}. On the face of it, the nobility of metallic gold makes it an unlikely candidate for heterogeneous catalysis. However, gold particles of less than 10 nm diameter have now been shown to be active catalysts for diverse chemical reactions⁹, of which the oxidation of carbon monoxide at low temperatures has been especially well studied¹⁰. The mechanism is still controversial⁵ although the majority of opinion opts for the effect requiring a discrete gold nano-particle, an oxide support, and a special nanoscale electronic state. However, in contradiction to this we show that mesoporous gold networks are active catalysts too, especially if combined into a nano-composite with oxides such as Al_2O_3 , Fe_2O_3 , TiO_2 and Co_2O_3 .

Pure mesoporous gold is not particularly active for CO oxidation, but the prior alloying of Fe into the AuAl_2 precursor produces a very active catalyst⁴. In this case the alloyed Fe^0 is converted to Fe_2O_3 during the catalysis of CO oxidation, producing an *in situ* oxide support. Alternatively, the AuAl_2 can be mechanically alloyed with a catalytic support material. Hopcalite ($\text{Mn}_x\text{Cu}_y\text{O}_z$), for example, has long been known as a capable of oxidizing CO at room temperature. However, it deactivates within a few hours. Composite gold-

hopcalite catalysts prepared by mechanical alloying followed by leaching retain their activity with regard to CO oxidation for very long times (Figure 2).

Another application for mesoporous gold is in the conversion of NO_x to nitrogen. There is no place here to discuss the intricacies of this process, save to note that it is a tough task to reduce NO_x to nitrogen in a gas stream that is super-stoichiometric in oxygen. In contrast to the situation with CO oxidation, the selective catalytic reduction of NO_x with propene occurs most readily on the unalloyed sponge¹¹ (Figure 3). The oxidation of NO to NO_2 can also be catalyzed, although in this case a gold- Co_2O_3 composite has proven to be the more active¹¹ (Figure 3).

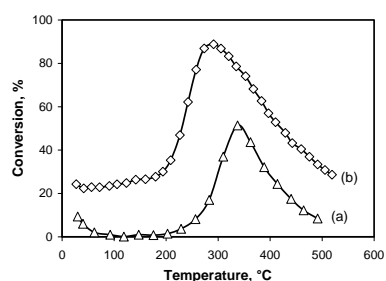


Fig. 3. (a) Selective catalytic reduction of NO to N_2 over mesoporous Au with propene, (b) catalytic oxidation of NO to NO_2 over mesoporous Au/ CoO_x composite. The space velocity in both instances is $60\text{l.g}^{-1}\text{.h}^{-1}$.

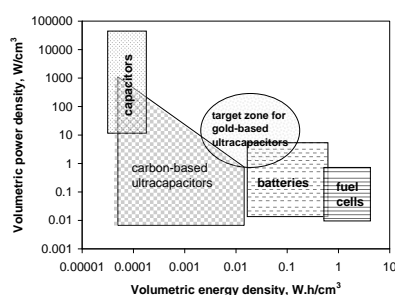


Fig. 4. Volumetric 'Ragone plot' showing the energy/power performance of various storage devices, and the anticipated niche for gold-based ultracapacitors. Based on use of an organic electrolyte with 2.5 V cell voltage.

4. Capacitance

The surface of a charged conductor placed into an liquid containing ions becomes coated with a double-layer of charged ions. If the surface area is very large, as for example for activated carbon at $\sim 1000\text{ m}^2/\text{g}$, then the capacitance can be very large. This effect has recently been exploited by some companies to produce 'ultra-capacitors'. Ultra-capacitors have considerably better power buffering capacities than batteries or ordinary capacitors but are not as good as batteries for storing energy. After accounting for energy lost to internal heating, the peak power P that can be drawn from an ultra-capacitor while discharging it from voltage V_0 to $\frac{1}{2}V_0$ is given by¹²:

$$P = \frac{9}{16} (1 - E_f) \frac{V_0^2}{R} \quad (1)$$

where E_f is the discharge efficiency, and R is the internal resistance. The effect of this is that the power that can be supplied at a given efficiency is inversely proportional to the internal resistance. Since devices based on mesoporous gold should have very much lower resistances than carbon-based ultra-capacitors,

they should deliver much higher volumetric power density. The maximum energy storage possible in a gold-based ultra-capacitor is not yet known. However, a electrolytic capacitance of 20 to 40 $\mu\text{F}/\text{cm}^2$ in combination with a surface area of 20 m^2/g , a density of $\sim 7 \text{ g}/\text{cm}^3$ and a rapid discharge of 3 to 5 seconds implies that possible power densities of between 1 and 9 W/cm^3 are feasible, in comparison to the 3 W/cm^3 currently available from large carbon based ultra-caps¹³. The possible position of gold-based ultra-capacitors in terms of volumetric power density and energy storage is shown in Figure 4.

5. Conclusions

Mesoporous gold can be produced with a surface area of as high as 20 m^2/g but is susceptible to sintering unless stabilized by an admixture of oxide or other substance. It is an active catalyst for the selective catalytic reduction of NO_x , and, when combined with Fe, an active catalyst for the oxidation of CO. Its high surface area, electrical conductivity and corrosion resistance also suggest its use in ultra-capacitor technology, with volumetric power densities of between 1 and 9 W/cm^3 appearing to be achievable.

Acknowledgement

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6. References

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