Gold Nanoparticles Supported on Carbon Materials for Cyclohexane Oxidation

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Hydrocarbons, particularly alkanes, are interesting compounds as main constituents of natural oil and gas and their C-H bond(s) can be converted to C-OH or C=O functional groups leading to the production of more valuable products for fine chemical synthesis. However, activation of the former bonds in such stable compounds is difficult, which still prevents their generalised use in the direct synthesis of added value chemical products [1].

An example with high industrial significance concerns the oxidation of cyclohexane to cyclohexanol and cyclohexanone (Scheme 1) that are important reagents for the production of adipic acid and caprolactam, used for the manufacture of nylon. The industrial process uses a homogeneous cobalt species as catalyst and dioxygen as oxidant at a considerably high temperature (150 ºC). However, the oxidation products are formed in low yields (5-12%) to achieve a good selectivity (ca. 80-85 %) [1], and thus the need for more effective systems under milder reaction conditions has been recognised [1].
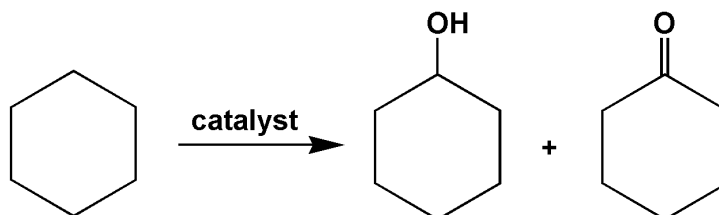
Scheme 1 – Oxidation of cyclohexane to cyclohexanol and cyclohexanone.

Gold catalysts are currently a ''hot topic'' of research, as they show application in many reactions of industrial and environmental importance [2]. Several variables have been considered as important factors influencing the chemistry, structure and catalytic activity. Among them are the method of preparation, the nature of the support and, particularly, the gold nanoparticle size [2].

Gold (1 wt.%) was loaded on several types of carbon materials: activated carbon (AC), polymer based carbon xerogels (CX with smaller mesopore width and CXL with larger width), multi-walled carbon nanotubes (CNT), nanodiamonds in liquid (NDLIQ) and powder (NDPW), microdiamonds (MD), graphite (GR) and silicon carbide (SC) using two different methods (sol immobilization, COL, and double impregnation, DIM).

The obtained Au/carbon materials were used as catalysts for the oxidation of cyclohexane to cyclohexanol and cyclohexanone, with aqueous H_2O_2, under mild conditions. The most active catalyst was prepared by supporting gold nanoparticles on carbon nanotubes by the sol method, achieving an overall turnover number of ca. 171 and an overall yield of 3.6 % after 6 h reaction time (Figure 1). These values are comparable to the industrial process (that uses Co catalysts and high temperature), but were obtained at ambient temperature with considerable low loads of catalyst (Au catalyst to substrate molar ratio always lower than 1×10^{-3}), which is of relevance for establishing a greener catalytic process for cyclohexane oxidation. Moreover, a very high selectivity towards the formation of cyclohexanol and cyclohexanone was achieved, since no traces of by-products were detected.

Catalyst recycling was tested up to six consecutive cycles for the most active catalytic system (gold deposited on carbon nanotubes by sol immobilisation), and it was found that the catalyst maintains almost the original level of activity after several reaction cycles (there was only a 6% drop in activity after the sixth cycle) with a rather high selectivity to cyclohexanol and cyclohexanone and with no catalyst leaching.

The differences in catalytic performance of the studied Au/carbon catalysts can be explained in terms of gold nanoparticle size (Figure 2), the lower sizes generally showed improved activity, as expected [1,2].
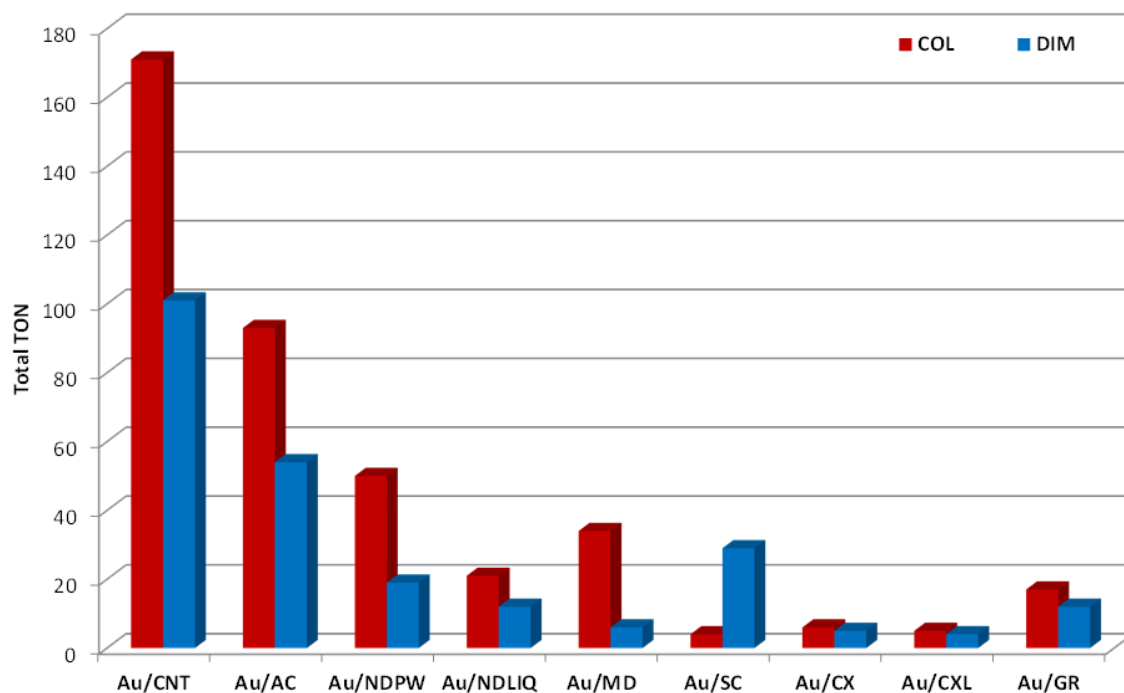

Figure 1 – Dependence of the overall turnover number (moles of cyclohexanol + cyclohexanone per mole of Au nanoparticles loaded on the carbon material) of the products on the type of support and impregnation method (COL (■) and DIM (■)). Reaction conditions: CH_3CN (3.0 mL), cyclohexane (5.0 mmol), n(Hpca)/n(catalyst) (50), room temperature, 6 h.
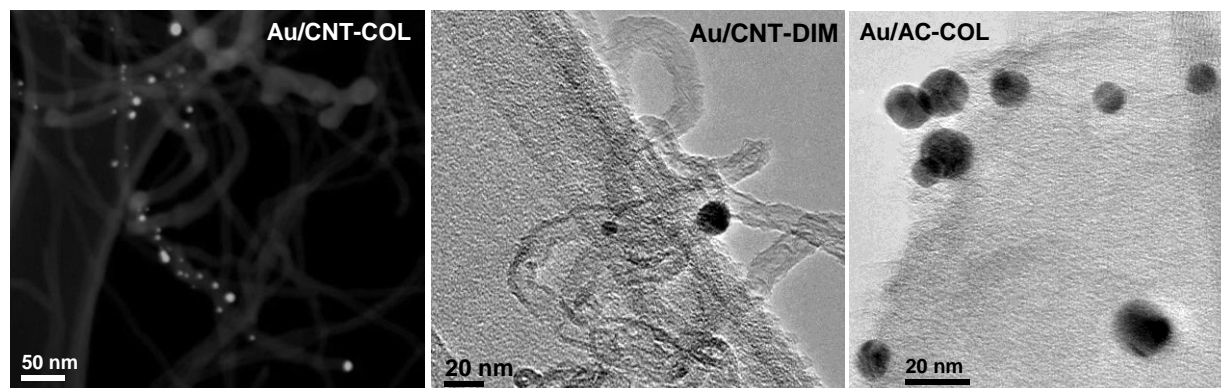
Figure 2 –HAADF micrograph of Au/CNT-COL (left). HRTEM images of Au/CNT-DIM (middle), Au/AC-COL (right) Gold nanoparticles are seen as darker spots on HRTEM images and as bright spots on HAADF micrograph.

References
[1] S.A.C. Carabineiro, L.M.D.R.S. Martins, J.G. Buijnsters, M. Avalos-Borja, A.J.L. Pombeiro, J.L. Figueiredo, Applied Catalysis A: General, 467 (2013) 279–290.
[2] S.A.C. Carabineiro, D.T. Thompson (2010), In: Gold: Science and Applications, Eds. C. Corti, R. Holliday, CRC Press, Taylor and Francis Group, New York, pp.89-122 (ISBN-978-1-4200-6523-7).