

## Gold nanoparticles supported on magnesium oxide for CO oxidation

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It is well known from the literature that for gold to be active as a catalyst, a careful preparation is needed in order to obtain nanoparticles well dispersed on the support [1-4]. Many supports have been used so far, including MgO [2-4]. However, when compared with other supports, MgO is considered “inactive” [5-8] since it is basically an irreducible oxide, such as Al<sub>2</sub>O<sub>3</sub>. These materials have a low ability to adsorb or store oxygen at low temperatures [5].

However, several authors like Margitfalvi et al. [9] and Gates and co-workers [10-11] managed to prepare Au/MgO catalysts that had high activity for low temperature CO oxidation. Also Grisel et al. found that gold on magnesium oxide catalysts supported on alumina were also extremely active for this reaction [12].

As Co-Precipitation (CP) [1-5] and Deposition-Precipitation (DP) [1-4, 12] are the most common ways to prepare oxide supported gold catalysts, in the present work, we wanted to use less usual Au loading methods (1% wt.), such as double impregnation (DIM) [13], liquid phase reductive deposition (LPRD) [14] and sonication (US) [15], in order to prepare Au nanoparticles. To the best of our knowledge, the only reports on the use of DIM is the work of Bowker et al. dealing with TiO<sub>2</sub> samples [13] and our previous works with CeO<sub>2</sub> [16-17] and ZnO [15] catalysts. This method represents an environmentally and economically more favorable route to the production of high activity gold catalyst, when compared with the traditional DP method [13]. As far as we know, LPRD has only been used by Sunagawa et al. to prepare Pt and Au catalysts on Fe<sub>2</sub>O<sub>3</sub>, FeOOH, ZrO<sub>2</sub> and TiO<sub>2</sub> supports [14], and also by us for CeO<sub>2</sub> [18] and TiO<sub>2</sub> [19] catalysts. US method was only used by our group to prepare Au/ZnO materials [15]. These methods include a washing procedure, in order to eliminate residual chloride that causes sintering of Au nanoparticles, thus turning them inactive [1-4].

Figure 1 shows the XRD micrographs obtained for the MgO support alone (commercial sample obtained from Merck, with a BET surface area of 32 m<sup>2</sup>/g), and loaded with Au by DIM. The identified phase for the unloaded material is the respective oxide (cubic, Fm-3m, 01-078-0430); however, when gold is loaded, a new Mg(OH)<sub>2</sub> phase (hexagonal, P-3m1, 01-076-0667) was formed (Figure 1). 99% of this hydroxide phase was detected along with 1% MgO. Gold was not detected, most likely due to the low loading and small particle size. The hydroxide is most likely formed by reaction with water, in which the gold precursor is dissolved (MgO + H<sub>2</sub>O → Mg(OH)<sub>2</sub>). Similar results were obtained for the other loading methods. Figure 2 shows a HRTEM image of the MgO support which is quite different from what is observed in Figure 3 (MgO with Au loaded by DIM), as the support structure changes from large crystals (Figure 2) into a fiber appearance (Figure 3). Gold particles are also observed with sizes ranging from 2-12 nm. Other methods showed larger gold nanoparticle sizes between 3 to 15 nm. Also the average size of gold particles is 5.4 nm for DIM, while it is above 6.7 nm for LPRD and US.

All samples prepared were tested for the oxidation of CO (Figure 4), which is a simple established model reaction to evaluate gold catalysts that has many potential applications, namely in CO removal from H<sub>2</sub> streams for fuel cells and gas sensing [1-4, 15-18]. Loading MgO with Au leads to the total conversion of CO at much lower temperatures than with MgO alone, as expected. The best results were obtained with DIM. This can be explained in terms of the nanoparticle size, well known to be related with catalytic activity of gold catalysts [1-4].

**Acknowledgements:** Authors thank Fundação para a Ciência e a Tecnologia (FCT), Portugal, for financial support (CIENCIA 2007 program for SAC), and project PTDC/EQU-ERQ/101456/2008, financed by FCT and FEDER in the context of Programme COMPETE.

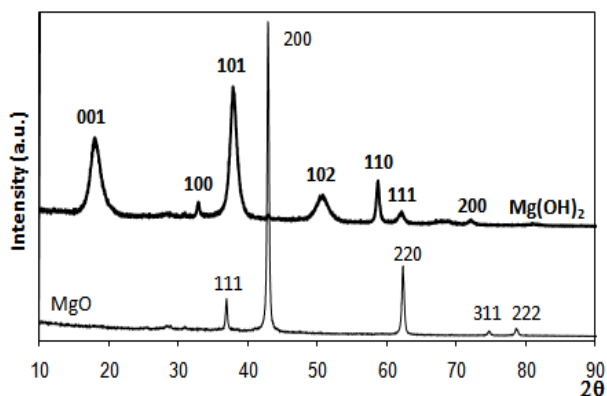


Figure 1 - X-ray diffraction spectra of MgO (thin line) and loaded with Au (thicker line), with phases and crystal planes (Miller indexes) identified. Gold was not detected by XRD.

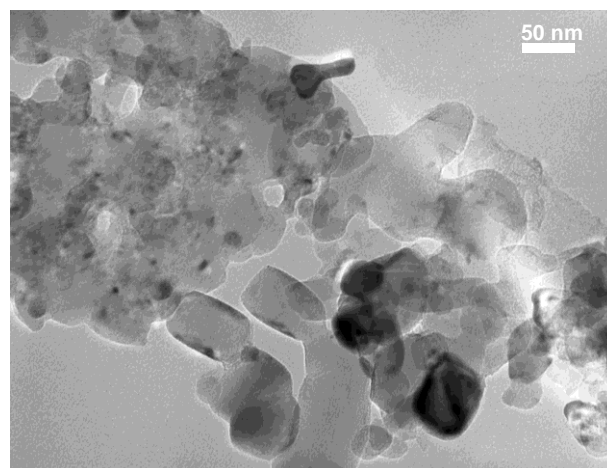


Figure 2 – HRTEM image of the MgO support.

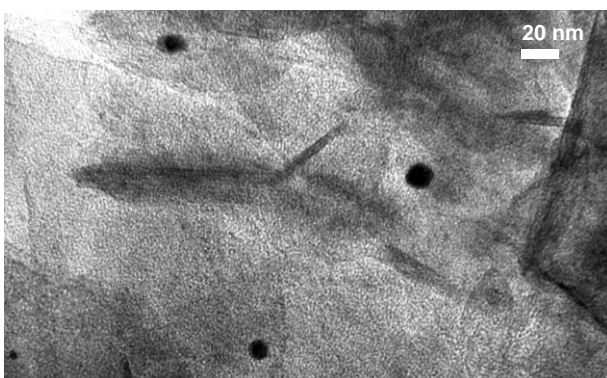


Figure 3 – HRTEM image of the MgO with Au loaded by DIM.

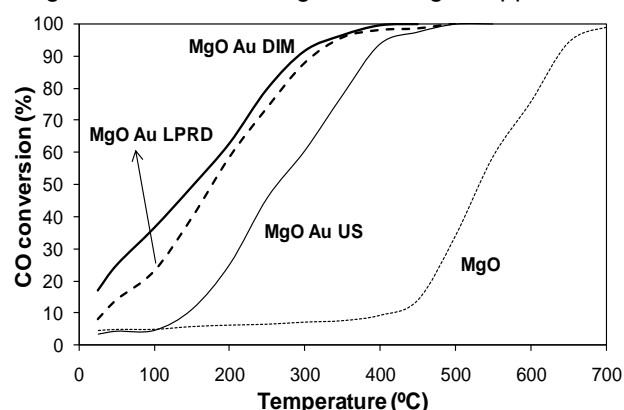


Figure 4 – CO conversion (%) versus temperature for the MgO support alone and with Au loaded by different methods.

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