

XAS study on the gold particle size of Au catalysts

Alvarez, M.¹ and Campo, B. C.¹

¹Universidad Nacional del Sur - Bahía Blanca Bueno Argentina

INTRODUCTION

In the last few years, gold catalysts have generated a great amount of interest [1]. This has been the result of two main findings: gold is the most active catalyst for ethyne hydrochlorination [2], and it is also effective for CO oxidation at low temperatures [3]. Because of these findings and their industrial importance, the potential of gold catalysts for CO oxidation and selective oxidation reactions is now the subject of intensive research. Consequently, progress has been made in the understanding of the effect of the many variables that govern catalytic activity in oxidation reactions, such as gold particle morphology and catalyst preparation method [1]. The support is also reported to play an important role in hydrogenation reactions although this role might be dependent on the reagent, being for some reactions practically negligible. This role can be the one providing a source of hydrogen to the metal sites, or interacting with gold to produce more selective electron-rich gold particles. The origins of the high activities of supported Au catalysts are discussed in the literature [1]. Among various supports, reducible oxides such as TiO₂ are more popular because they produce Au catalysts with high activities and are expected to follow the synergistic Au-oxide interfacial site model. However, refractory oxides are also efficient enough to prepare good Au catalysts, but the origin of the synergistic Au-oxide interfacial site is not as obvious as that of the Au supported on reducible oxides. So, a careful study of the active Au supported on different supports could help to explain the active morphology of Au catalysts. Therefore, this work proposes the study of gold catalysts prepared using pure and modified γ -Al₂O₃ as the supports. EXAFS spectroscopy could be used to examine the Au morphology following the direct anionic exchange (DAE) method [4] of preparation of the catalysts.

EXPERIMENT

γ -Al₂O₃ (Rhone Poulenc, 77 m²/g) was impregnated with a Fe(AcAc)₃ solution in toluene, with concentration corresponding to a target ion load of the solid of 5 wt%. After 48 h, the solid was filtered and washed with fresh solvent. The solid was calcined for 4 h at 450 °C to form superficial species (named as Fe_xO_y). Gold was fixed to the support by the DAE method [4]. A solution of HAuCl₄ (1 × 10⁻³ M) was added to the solid at 60 °C (target gold concentration: 2%). Suspension was stirred for 2 h at pH 4. Afterwards, a dilute ammonia solution was added to eliminate the chlorine species. Solid was filtered and washed several times with distilled water. Then,

the sample was calcined at 300 °C for 3 h in chromatographic air, and reduced at 120 °C. Iron and gold contents were determined by ICP-AES, and the specific surface area was measured from BET method.

XAS beam line: experimental conditions

Transmission mode.

Monochromator: XAS: Si(111) channel cut.

Fe K-edge & Au L_{III}-edge (7112 & 11919 eV).

Step and counting times at both edges: XANES: step 0,5 and 1 eV, ct: 3 s; EXAFS: step 0,5 and 3 eV, ct: 5 s.

Analysis: IFEFFIT library (ATHENA and ARTEMIS).

RESULTS AND DISCUSSION

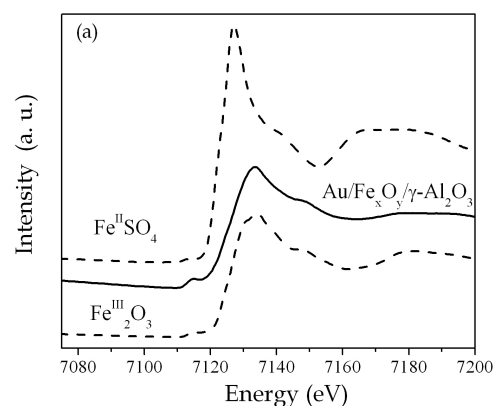
Table 1 shows the results of the chemical analyses:

Table 1.

Sample	Surface area (m ² /g)	%Fe	%Au
γ -Al ₂ O ₃	77	0	0
Fe _x O _y / γ -Al ₂ O ₃	76	4.8	0
Au/Fe _x O _y / γ -Al ₂ O ₃	77	4.7	1.1

The iron-modified γ -Al₂O₃ retains only 50% of Au referred to the nominal content. So, only a low fraction of OH of this support is active for the anchoring of gold complexes, in spite of its large specific surface area.

XANES Analyses - The first Fe K- prominent signal of the catalyst appears at 7133.5 eV, this value coincides with the value for α -Fe₂O₃, and indicates the presence of Fe⁺³. At the Au L_{III}-edge, the first signal appears at 11923 eV, coincident with the Au⁰ profile.



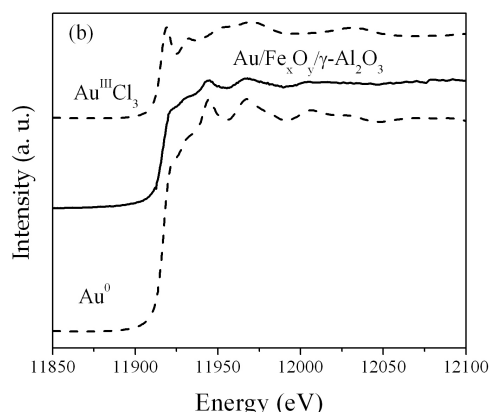


FIG. 1: XANES at the (a) Fe K- and (c) Au L_{III} -edges for the $\text{Au/Fe}_x\text{O}_y/\gamma\text{-Al}_2\text{O}_3$ catalyst. Reference compounds spectra are also presented

EXAFS Analyses - Figure 2 shows the FT for the prepared sample at the Fe K- and Au L_{III} -edges, and the fit parameters are summarised in Table 2. The traces confirm the difference between both coordination environments.

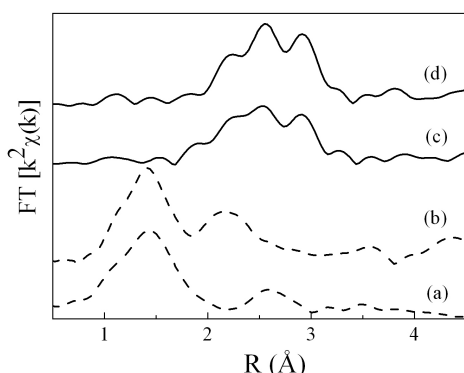


FIG. 2: FT for samples at the Fe K-edge: (a) $\text{Fe}_x\text{O}_y/\gamma\text{-Al}_2\text{O}_3$, (b) $\text{Au/Fe}_x\text{O}_y/\gamma\text{-Al}_2\text{O}_3$; and at the Au L_{III} -edge: (c) $\text{Fe}_x\text{O}_y/\gamma\text{-Al}_2\text{O}_3$ and (d) Au metal.

The RDF for the reference Au foil is typical for the fcc structure (Figure 2-d); the main peak on this curve corresponds to the shortest Au-Au distance ($R_{\text{Au-Au}} = 2.88 \text{ \AA}$, CN = 12) [5]. The shape of the RDFs of our sample is similar to that

for an Au foil with an fcc structure; however, the amplitude of the first Au-Au peak (shortest Au-Au distance $\sim 2.84 \text{ \AA}$) is slightly decreased as compared to the reference one (Figure 2-c). A similar trend is observed for the next Au-Au distances. No features that would point out the presence of Au-O species were found for the samples.

Table 2. Parameters obtained for Au-catalyst and the oxidic support from first neighbour single scattering EXAFS

Parameter	$\text{Au/Fe}_x\text{O}_y/\gamma\text{-Al}_2\text{O}_3$ (Au L_{III}) ^a	$\text{Fe}_x\text{O}_y/\gamma\text{-Al}_2\text{O}_3$ (Fe K-) ^b
E_0 (eV)	4.20	-1.15
R (1 st shell)	2.84	1.90
N	12	3
σ^2	0.009	0.001

^aIndependent points 19; number of variables in fit: 4; R-factor: 0.024; χ^2 : 64; reduced χ^2 : 4, k-space interval: 2.5 - 13.9, R-space interval: 1.3 - 4.1

^bIndependent points 15; number of variables in fit: 4; R-factor: 0.040; χ^2 : 915; reduced χ^2 : 82, k-space interval: 2.6 - 13.7, R-space interval: 0.8 - 3

CONCLUSION

A EXAFS study at the Au and Fe edges was carried out in order to elucidate the nature of the active gold species and to determine the Au-Au interactions in a catalyst prepared from a reducible support. XANES spectra confirm the presence of iron in its trivalent state, and metallic gold. This is coincident with the the similarity of the FT magnitude profiles of the catalyst and the reference metallic gold, although the first Au-Au distance is slightly modified.

ACKNOWLEDGEMENTS

This work has been supported by the Brazilian Synchrotron Light Laboratory (LNLS) / Brazilian Biosciences National Laboratory (LNBio) under proposal D04B - XAFS1 7287, and by Grant PICT 1353 (APCyT).

- [1] Bond and Thompson, *Cat. Rev. Sci. Eng.* 41, 319 (1999)
- [2] Hutchings, *J.Catal.* 96, 292 (1985)
- [3] Haruta et al., *Chem. Lett.* 2, 405 (1987)
- [4] Ivanova et al., *Appl. Catal. A* 267, 191 (2004)
- [5] ICSD Database Code 64701-Au⁰