

New insight on the nature of catalytically active gold sites: analysis of FTIR CO spectra and of quantitative CO chemisorption data

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Gold catalysts are very active in CO oxidation, in PROX and WGS reactions¹. However, up to now key questions concerning the reaction mechanisms and the nature of the active sites are still without shared answers, possibly because the real catalysts have many of potential active centres. When studying real gold catalysts, it is useful to utilize different combined experimental methods, to distinguish and qualitatively determine the different gold sites exposed at the surface, together with their quantitative estimation.

The analysis of the FTIR spectra of samples differently pretreated after adsorption at different temperatures of i) CO, ii) CO isotopic mixtures and iii) CO in interaction with ¹⁸O₂ can be very useful to get qualitative information on the nature and on the structure of the gold active species in the CO oxidation². In addition, the relation between a defined amount of sites and the catalytic activity can be achieved by the volumetric measurement analysis of CO quantitative adsorption³ in specific experimental conditions, chosen on the basis of the spectroscopic experiments.

FTIR absorption spectra of CO, of ¹²CO–¹³CO isotopic mixtures and CO – ¹⁸O₂ on gold catalysts supported on the IV group oxides will be reported and analyzed together with CO quantitative chemisorption data. On Au/TiO₂ two kinds of metallic gold surface sites have been found to adsorb CO, 6-coordinated corners and 7-coordinated edges, mutually interacting in spite of the low CO/Au ratio (0.03) determined volumetrically, as reported in Table 1. On Au/ZrO₂, where a CO/Au ratio of 0.30 has been determined, mutually interacting corner sites exposed at the surface of non metallic gold nanoclusters are the adsorbing sites. Finally, almost isolated and negatively charged gold nanoclusters have been evidenced on the CeO₂ supported sample. Differences in the absorption coefficients have been found, as a consequence of the different nature of the adsorption sites.

Table 1. Quantitative CO chemisorptions and FTIR integrated intensities at 157 K.

Sample	Au wt%	mol _{CO} /mol _{Au}	Integrated Area, cm ⁻¹ /mol _{Au} (x 10 ³)	Absorption coefficient, cm ⁻¹ ·mol ⁻¹ (x 10 ⁴)
Au/TiO ₂	1.51	0.033	1.05	3.2
Au/ZrO ₂	1.94	0.301	5.41	1.8
Au/CeO ₂	3.0	0.081	1.07	1.3

On all samples, by contacting CO–¹⁸O₂ at 90 K, only C¹⁶O¹⁸O is produced: gold sites are involved in the activation of both molecules, without participation of the support. The largest amount of C¹⁶O¹⁸O is produced on the CeO₂ supported sample, as a consequence of an easier activation of the oxygen on the anionic gold clusters.

References

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