

FARADAY DIVISION

# Gold

## Faraday Discussion 152

4-6 July 2011  
Cardiff, UK



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## Role of the size of gold particles for selective oxidations with molecular O<sub>2</sub>

Flora Boccuzzi\*<sup>a</sup>, Anna Chiorino<sup>a</sup>, Maela Manzoli<sup>a</sup>, Federica Menegazzo<sup>b</sup>, Francesco Pinna<sup>b</sup>, Michela Signoretto<sup>b</sup>, Valentina Trevisan<sup>b</sup> Floriana Vindigni<sup>a</sup>.

<sup>a</sup>Department of Chemistry IFM and NIS Centre of Excellence, University of Torino (Italy)

<sup>b</sup>Department of Chemistry, Cà Foscari University and "Consorzio INSTM", Venice (Italy)

Nanodispersed Au has been recognized as a very good catalyst for selective oxidations with molecular O<sub>2</sub><sup>1</sup>. "Inert" and "active" support materials were initially postulated<sup>2</sup>. More recently it has been shown that Au clusters, supported on chemically and electronically inert materials, can adsorb and dissociate O<sub>2</sub><sup>3</sup>. The dissociation appears to be sensitive to the presence of other adsorbates, including the reactant molecule itself. Some recent experimental data, obtained for both propylene and styrene epoxidation<sup>4</sup>, indicate that there is a limiting size of gold particles (1.5-2nm), dividing active from inactive catalysts. Finally, it has been shown that furfural, coming from xylose, can be quite easily converted into methyl furoate by an oxidative esterification with a NaCH<sub>3</sub>O solution in CH<sub>3</sub>OH with O<sub>2</sub> at 22 °C on a Au/TiO<sub>2</sub> reference catalyst<sup>5</sup>.

Recently, we have tested different Au samples dispersed on different supports by CO quantitative chemisorption experiments and by FTIR CO adsorption at 90 K<sup>6</sup> after a preliminary activation by outgassing and oxidation at 180 °C and successive reduction and outgassing at 150 °C. By the combined use of these data, informations on the amount of surface uncoordinated gold sites and on the nature of these sites (metallic or non metallic) have been deduced. The effect of the addition of various amounts of sulfates to a zirconia support and their role during the Au deposition–precipitation step was also examined<sup>7</sup>. In particular, a positive role of SO<sub>4</sub><sup>2-</sup> groups, that determine the deposition of Au in the form of highly dispersed non-metallic gold clusters in close contact with the support, has been put in evidence.

Here catalytic and spectroscopic results on the furfural conversion into methyl furoate by oxidative esterification with oxygen and methanol, without NaCH<sub>3</sub>O, on some different Au/ZrO<sub>2</sub> samples, in comparison with Au/TiO<sub>2</sub> will be presented. Interestingly the Au/ZrO<sub>2</sub> samples (where highly dispersed non-metallic gold clusters are present) are more active and in particular more selective than the Au/TiO<sub>2</sub> (where mainly particles of 3.2 nm are present).

By FTIR the interaction and chemisorption of furfural, furfural-oxygen and furfural-oxygen-methanol mixtures at room temperature and after reaction at 120 °C have been examined, looking at the nature of the adsorbed species, at the reversibility by outgassing and at their dependence on the support, by the analysis of the FTIR spectra. The amount of gold uncoordinated sites has been also tested by CO adsorption before and after all interactions. After outgassing of the reaction mixture at room temperature the amount of gold uncoordinated sites is lower than before reaction, while intensity of the absorption band is larger after reaction at 120 °C and reoxidation at 250 °C. An analysis and discussion of these data will be presented, on the basis, also, of HRTEM data of fresh and used catalysts.

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