On the regeneration of gold nanoparticles for the selective oxidation of furfural

Laura Contessotto[1], Michela Signoretto[1*], Federica Menegazzo[1], Francesco Pinna[1], Maela Manzoli[2], Flora Boccuzzi[2]

[1]Department of Molecular Sciences and Nanosystems, Cà Foscari University, Dorsoduro 2137, 30123 Venezia, and INSTM-UdR Venezia (Italy)
[2]Department of Chemistry IFM and NIS Centre of Excellence, University of Torino (Italy)

**Email address: miky@unive.it*

Innovative transformations of furfural are highly desired: among these, the synthesis of alkyl furoates can open very interesting perspectives for the use of xyloses, because they can be used either as solvent or extracting agents in many different industrial plants if produced in larger amounts and at low price. Currently we are studying the oxidative esterification of furfural on Au/ZrO_2 samples without the addition of $NaCH_3O$, a base that would make the process less green and more expensive. The goal of the work herein presented is to investigate the stability and the reusability of our best Au/ZrO_2 samples.
Catalysts were prepared by deposition-precipitation (dp) on calcined support. The oxidative esterification of furfural with oxygen and methanol, without $NaCH_3O$ addition, was investigated at 120°C and 12 bar. After the first catalytic run the sample was filtered off, washed with methanol, dried and used again, obtaining very low selectivity in the subsequent runs. As the reason for catalysts deactivation we have excluded gold leaching in the discharged samples. In order to investigate catalyst poisoning, by TPO analyses we have verified on exhausted catalysts the presence of an organic residue. According to TPO profiles, we have decided to heat the catalyst until 450°C in oxygen atmosphere, in order to eliminate organic poisons. The deactivation in this case is reversible and by thermal calcination at a proper temperature it is possible to restore almost fully the initial selectivity. In fact, by pulse-flow CO chemisorption [1] we have found for the regenerated samples a mol_{CO}/mol_{Au} ratio comparable to the value of the fresh samples, meaning the absence of gold sintering during the catalytic reaction.
FTIR spectroscopy demonstrated that the organic residue can be removed starting from 350°C in O_2. At the same time, CO adsorption reveals that the Au phase is quite stable, even after repeated thermal treatments in O_2 at increasing temperature up to 6 hours.

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[1] F. Menegazzo, M. Manzoli, A. Chiorino, F. Boccuzzi, T. Tabakova, M. Signoretto, F. Pinna, N. Pernicone, *J. Catal.* 237, **2006**, 431-434.