

The effects of gold nanosize for the exploitation of furfural by selective oxidation

Francesco Pinna^{*1}, Alberto Olivo¹, Valentina Trevisan¹, Federica Menegazzo¹, Michela Signoretto¹, Maela Manzoli², Flora Boccuzzi²

¹Department of Molecular Sciences and Nanosystems, Cà Foscari University and "Consorzio INSTM", Venezia, 30123, Italy

²Department of Chemistry IFM and NIS Centre of Excellence, University of Torino, 10125, Italy
*pinna@unive.it

Introduction

A huge challenge for scientists today is to provide the chemical industry with new tools to convert renewables into useful chemicals in an economically viable fashion. For the C5 fraction (xylose) there are no well developed process yet. Furfural can be obtained from xyloses by dehydration in acidic media and it can be used in soil chemistry and as a building block in the production of Lycra®, etc. However, additional transformations of furfural are highly desired: among these, the synthesis of alkyl furoates can open very interesting perspectives for the use of xyloses. Recently it has been shown that furfural can be quite easily converted in methyl furoate by an oxidative esterification with a NaCH₃O solution in CH₃OH with O₂ at 22 °C on a Au/TiO₂ reference catalyst purchased by the World Gold Council [1], while in the absence of the base experimental conditions must be strongly raised up [2]. Gold nanoparticles have been recognized as a very good catalyst for selective oxidation with molecular O₂ but it's known that there is a limiting size dividing active from inactive catalysts.

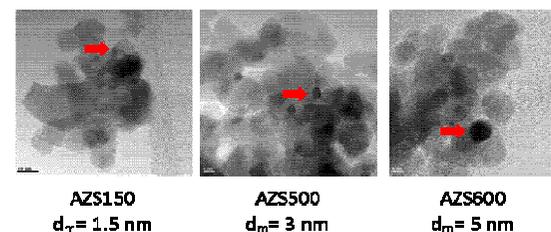
The goal of the present work is to verify the role of the size of gold nanoparticles for Au/ZrO₂ samples in the oxidative esterification of furfural, even without the addition of NaCH₃O that would make the process less green and more expensive.

Experimental

Au(1.5 wt%)/ZrO₂ catalyst was prepared [3] by deposition-precipitation on the calcined support and then treated in air at different temperatures (150°C, 300°C, 500°C, 600°C, 650°C). The oxidative esterification of furfural with oxygen and methanol, without NaCH₃O addition, was investigated at 120°C and 12 bar. Fresh and used samples were characterized by N₂ adsorption analysis, metal content analysis, HRTEM, FTIR spectroscopy and pulse-flow CO chemisorption.

Results/Discussion

The Au/ZrO₂ catalyst has been calcined at different temperatures in order to modulate gold nanosize and investigate its role in the oxidative esterification of furfural. A detailed characterization has been carried out in order to verify if micro structural changes occurred. On samples treated at lower temperatures gold clusters have been evidenced by quantitative CO chemisorption and by HRTEM. On the contrary, a thermal treatment at higher temperatures results in the presence of nanoparticles larger than 4nm.



Au/ZrO₂ catalysts calcined at temperatures lower than 500°C are very active and selective in the oxidative esterification of furfural, while a drastic decrease in the catalytic performances occurs for samples calcined at higher temperatures, as reported in the table.

	AZS150	AZS300	AZS500	AZS600	AZS650
conversion (%)	90	90	86	40	24
methyl furoate selectivity (%)	90	90	88	70	60

The limiting size appears related to an intrinsic modification of the electronic structure of Au clusters with respect to nanoparticles. Au clusters, supported on chemically and electronically inert materials, can adsorb and activate O₂, presumably by dissociating O₂ to yield O adatoms that initiate the partial oxidation. FTIR results on O₂-methanol-furfural interaction at room temperature and at 120°C will be showed. Additionally, CO was used to probe the Au sites before and after reaction.

Catalysts stability and reusability has been investigated and will be discussed.

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References.

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