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

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ABSTRACT

An Au/ZrO_2 catalyst was prepared and characterized in order to study the role of gold nanosize in the conversion of furfural into methyl furoate by oxidative esterification with O_2 and methanol, without $NaCH_3O$. The comparison with the Au/TiO_2 reference catalyst provided by the World Gold Council and with an Au/ZrO_2 catalyst treated at 600 °C in oxygen emphasized very good catalytic performances. Highly dispersed Au was evidenced on Au/ZrO_2 by quantitative CO chemisorption, HRTEM analysis and FTIR spectroscopy of adsorbed CO. On the contrary, the thermal treatment at 600 °C results in the presence of nanoparticles larger than 4 nm that make the catalyst poorly active and selective. The Au clusters and their ability in the activation of the O_2 molecule play a key role in the reaction.

1. Introduction

The challenge for scientists today is to provide the chemical industry with new tools to convert biomass into useful chemicals in an economically viable fashion. For the C5 fraction (xylose) for example there is 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, 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.

Suitable catalysts for the selective oxidation are mainly supported metal samples. In particular, nanodispersed Au has been recognized as a very good catalyst for selective oxidations with molecular O_2 [1]. It has been shown [2] that furfural can be converted to methyl furoate by an oxidative esterification with $NaCH_3O$ and CH_3OH under mild conditions on an Au/TiO_2 reference catalyst purchased by the World Gold Council (WGC). However, in order to be applied in a large scale production, the composition and the microstructure of the catalyst have to be optimized. Recently Corma and coworkers [3] have reported a base-free synthesis of methyl furoate on an Au/CeO_2 catalyst, but using temperature and pressure higher than those employed in the activity test of Christensen et al. [2].

Catalysis by gold nanoparticles is a topic of current interest, as proved by the exponential growth of the papers on this subject [4]. In fact, gold supported on oxides or carbon, once considered catalytically inert, is now firmly established as an effective catalyst and the catalogue of reactions that it can catalyze is really wide [5]. However, the relationship between activity, microstructure and nature of the catalytically active gold sites is, up to now, not fully understood.

We have recently focused our attention on Au/ZrO_2 catalysts [6,7]. The choice of zirconia as support is due to its intrinsic chemical and physical characteristics that can be adjusted by choosing different precursors and synthesis conditions. Moreover, the addition of dopants, in particular sulfates, increases surface acidity, retards crystallization and enhances the surface area [8]. We have recently demonstrated [9] that sulfate addition to zirconia means a twofold advantage: (i) higher gold dispersion due to higher surface area; (ii) higher gold dispersion due to the positive role of SO_4^{2-} groups that address the deposition of Au in the form of highly dispersed non metallic gold clusters in close contact with the support. However, no sulfates are present in the final catalysts anymore, due to the detachment of sulfate groups during the deposition–precipitation. So, as already discussed in depth [6,7], sulfates do not behave as promoters of the gold active phase in the final samples, but they act as structural promoters of the support and as nucleation centers for small gold clusters. For this reason we have named the catalyst object of the paper only as Au/ZrO_2 samples.

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The goal of the present work is to verify the role of gold nanosize for Au/ZrO_2 and Au/TiO_2 samples in the oxidative esterification of furfural, without the addition of $NaCH_3O$, that would make the process less green and more expensive [3].

2. Experimental

2.1. Catalyst preparation

Au/ZrO_2 was prepared by a two-step synthesis technique. $Zr(OH)_4$ was prepared by precipitation from $ZrOCl_2{\cdot}8H_2O$ at constant pH (pH 8.6) and then aged for 20 h at 90 °C, washed free from chloride ($AgNO_3$ test) and dried at 110 °C for 15 h. The hydroxide was then sulfated with $(NH_4)_2SO_4$ (Merck) by incipient wetness impregnation in order to obtain a 2 wt% amount of sulfates.

Sulfated zirconium hydroxide was calcined in air (30 mL/min) at 650 °C for 3 h. Gold was added by deposition–precipitation (DP) at pH 8.6: the oxide support was suspended in an aqueous solution of $HAuCl_4{\cdot}3H_2O$ for 3 h and the pH was controlled by the addition of NaOH (0.5 M). After filtration the sample was dried at 35 °C and finally calcined in air at either 180 °C or 600 °C for 1 h. Since no sulfates are anymore present in the final catalysts, due to the detachment of sulfate groups during the deposition–precipitation [9], we refer to the catalysts as Au/ZrO_2 samples.

A comparison with the Au/TiO_2 reference sample provided by the World Gold Council [10] has been carried out. The samples are listed in Table 1, where preparation method, Au loadings, CO chemisorption results and gold average size (d_m) obtained by HRTEM are summarized.

2.2. Catalytic activity measurements

Furfural oxidative esterification with oxygen and methanol was investigated at 120 °C, without $NaCH_3O$ addition, using a mechanical stirred autoclave fitted with an external jacket. Catalyst (100 mg), furfural (300 μL) and n-octane (150 μL), used as internal standard, were added to the solvent (150 mL of methanol). The reactor was charged with oxygen (6 bar) and stirred at 1000 rpm. The progress of the reaction was followed by gas-chromatographic analysis of the samples withdrawn from the reaction mixture.

2.3. Characterization methods

The gold amount was determined by atomic adsorption spectroscopy after disgregation of the catalysts. In particular, dried samples (100 mg) were disgregated in *aqua regia* and HF by microwaves (Milestone Ethos 1600). The solutions were then analyzed by atomic adsorption spectroscopy (Perkin-Elmer Analyst 100).

HRTEM analysis of AuZ and AuZ600 was performed using a Jeol 3010 EX electron microscope (300 kV) equipped with a side entry stage and a LaB_6 filament. The powdered samples were deposited on a copper grid, coated with a porous carbon film. The mean gold particle diameters and size distribution measurements were performed by counting a statistically meaningful number of particles.

CO pulse chemisorption measurements were performed at −116 °C in a lab-made equipment. Before the analysis the following pretreatment was applied: the sample (200 mg) was reduced in a H_2 flow (40 mL/min) at 150 °C for 60 min, cooled in H_2 to room temperature, purged in He flow and finally hydrated at room temperature. The hydration treatment was performed by contacting the sample with a He flow (10 mL/min) saturated with a proper amount of water. The sample was then cooled in He flow to the temperature chosen for CO chemisorption (−116 °C) [7].

The FTIR spectra were collected on a Perkin-Elmer 1760 spectrometer (equipped with a MCT detector) with the samples in self-supporting pellets introduced in a cell allowing thermal treatment in controlled atmospheres and spectrum scanning at controlled temperature. The curves reported in the figures are the spectral differences between the spectrum related to the bare sample and the spectrum of the sample after the inlet of CO. The spectra are normalized in respect to the gold content in each pellet. The samples have been submitted to an activation procedure consisting of an oxidative pretreatment and a reductive one before the spectroscopic experiments. More in detail, the oxidative treatment included heating from room temperature (r.t.) to 150 °C (Au/ZrO_2, hereafter denoted as AuZ) or 200 °C (Au/TiO_2, hereafter denoted as AuWGC) under outgassing; followed by an inlet of O_2 (20 mbar) and heating up to 180 °C (AuZ) or 400 °C (AuWGC); at 180 °C (AuZ) or 400 °C (AuWGC) the oxygen was changed three times (20 mbar for 10 min each one). After that, the sample was cooled down to r.t. in oxygen and finally outgassed at the same temperature. The reductive treatment was carried out (after oxidation) by heating from r.t. up to 150 °C (AuZ) or 250 °C (AuWGC) in H_2 (10 mbar), keeping that temperature for 10 min. Then the sample was cooled to r.t. under outgassing. The reason for which contrasting activation temperatures have been used for the two catalyst has to be ascribed to the different nature of the samples, either in terms of dispersion of the gold phase and nature of the support or in terms of preparation, since they underwent a final calcination at different temperature (180 °C for AuZ and 400 °C for AuWGC).

3. Results and discussion

3.1. Catalytic activity results

The oxidative esterification of furfural has been carried out in methanol without the addition of $NaCH_3O$, that would make the process less green and more expensive [3]. Moreover, mild reaction conditions were employed (120 °C and 6 bar), comparable to those reported in the literature [3].

Apart from the methyl furoate, the only by-product found was the acetal derivate, as detected by mass spectroscopy.

In Fig. 1, section a, the conversion and selectivity to methyl furoate for AuZ are shown. The sample shows very good catalytic performances, in particular, after 90 min both conversion and selectivity are complete. On the contrary, catalytic performances obtained for the AuZ600 sample are noticeably lower (at 180 min conversion 40%, selectivity 70%, 30% of acetal). The results obtained for the Au/TiO_2 reference catalyst are displayed in section b. The AuWGC reaches an almost complete conversion only after 180 min of reaction. For this sample selectivity is about 80% after 30 min and smoothly decreases to 65% at increasing time.

In order to explain the differences observed among the catalysts, a detailed characterization has been performed to highlight the parameters that control the catalytic activity in the oxidative esterification of furfural.

3.2. Catalyst characterization

3.2.1. Morphology and gold site quantification

HRTEM analysis has been performed on both AuZ and AuZ600 samples and the results are shown in Fig. 2, sections a and c, respectively. More in detail, the AuZ sample contains highly dispersed gold particles, that appear as darker dots on zirconia particles, due to the contrast phase between gold and zirconium oxide. The particle size distribution, that is reported in section b of Fig. 2, is quite narrow and it well evidences that most of the gold has size below 2 nm. Moreover, the Au particles have homogenous size, having an average diameter $d_m = 1.68 \pm 0.38$ nm.