

Effect of acid-base properties of highly dispersed gold catalysts in the oxidative esterification of renewable furfural

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Introduction

Upgrading of lignocellulosic biomass wastes into fuels and higher added-value chemicals is one of the most investigated topics in the forthcoming concept of biorefinery. Among the C-5 fraction products, additional transformations of furfural are highly desired: alkyl furoates can find applications as flavour and fragrance component in the fine chemicals industry and also as solvent or extracting agents in many different industrial plants if produced in larger amounts and at low price.

Up to now, the upgrade of furfural has been little investigated [1,2]. Firstly, it can be converted to methyl furoate by an oxidative esterification with NaCH_3O and CH_3OH under mild conditions on a Au/TiO_2 reference catalyst purchased by the World Gold Council (WGC) [1]. Very recently, we examined Au/ZrO_2 catalysts for a base free esterification of furfural [3,4], finding excellent catalytic performances of Au/ZrO_2 in comparison to the WGC Au/TiO_2 catalyst [3]. Afterwards, we investigated Au/ZrO_2 catalysts with different Au dispersion and demonstrated that it is possible to completely recover the catalytic performances only if the organic residue of the exhausted sample is removed from both Au active sites and zirconia [4]. Such results suggested that, beside the size of gold, also the support plays an important role in the reaction. Therefore, we examined a series of Au containing catalysts with different supports: firstly zirconia, due to its intrinsic chemical and physical characteristics that can be adjusted by choosing different precursors and synthesis conditions. In particular, the addition of sulfates increases surface acidity, retards crystallization and enhances the surface area [5]. Moreover, TiO_2 , that is a widely used material because of its high photocatalytic activity, non-toxicity, good availability, low cost and stability. Its main characteristics strongly depend on surface area, crystal structure, crystallite size and surface hydroxyl groups [6]. Finally, ceria which is characterized by a high oxygen storage capacity (OSC) and reducibility [7], because of the leading role in the process of atomic O produced by reaction with the oxygen molecule.

The goal of the present work is to optimize gold dispersion and to verify the role of different supports such as ZrO_2 , sulfated ZrO_2 , TiO_2 and CeO_2 on Au-based catalysts in the oxidative esterification of furfural, without the addition of NaCH_3O .

Experimental

Gold supported catalysts were prepared by deposition-precipitation of HAuCl_4 on various supports: zirconia (Z), sulphated zirconia (SZ), ceria (Ce) and titania (Ti) and then submitted to calcination at different temperatures. In addition, Au/TiO_2 provided by the World Gold Council (WGC) was examined as reference catalyst. The oxidative esterification of furfural with 6 bar of O_2 and methanol, without NaCH_3O addition, was investigated at 120 °C. Fresh and used samples were characterized by N_2 adsorption analysis, metal content analysis, HRTEM, FTIR spectroscopy, pulse-flow CO chemisorption and TPO.

Results and discussion

The effect of the calcination temperature on the dispersion of gold was examined. The amount of highly uncoordinated Au sites exposed at the surface of the different samples was measured by CO pulse chemisorption measurements. These experiments indicated that the molar ratio between adsorbed CO and gold is quite high on ZrO₂ supported samples calcined at a proper temperature, revealing the presence of Au clusters undetectable by HRTEM. Such clusters can be able to activate molecular oxygen producing basic atomic O species, that render the catalyst more active for furfural esterification reaction. In fact, zirconia supported catalysts exhibit the best catalytic performance both for activity and selectivity. On the contrary, the sample supported on titania presents the lowest mol_{CO}/mol_{Au} value, meaning that it contains large gold particles, whilst an intermediate ratio is obtained for AuCe and AuWGC.

In addition, a comparison among samples with very similar mol_{CO}/mol_{Au} ratios indicates that also the choice of the support is an essential step. In fact, the catalytic performances follow the trend: AuSZ>AuZ>AuCe~AuWGC>>AuTi. FTIR measurements of adsorbed CO₂ were performed at room temperature in order to shed some light on the acidic-basic properties of the various materials.

Zirconia supported catalysts, if compared to the other systems, exhibit very good and comparable catalytic performances both for activity and selectivity. This feature can be ascribed to the high gold dispersion combined with the presence of Lewis acid sites on zirconia. Ceria-based catalyst exhibits a lower performance than the zirconia-based ones, possibly due to the small amount of Lewis acid sites. Moreover, ceria displays a redox behaviour, that seems to have no role in the reaction. The AuTi sample exhibits the lowest conversion degree, that can be due to the worst Au dispersion. On the contrary, the AuTi catalyst presents a very high selectivity; CO₂ adsorption on this sample revealed the poor formation of carbonates/hydrogen-carbonates species, with a parallel presence of a high amount of Lewis acid sites.

Conclusions

Au-based catalysts were investigated in the oxidative esterification of furfural and the catalytic performances follow the trend: AuSZ>AuZ>AuCe~AuWGC>>AuTi. The chemical and morphological properties observed for zirconia samples seem to fulfill a compromise between the presence of gold clusters and the need of proper acid-base properties for good selectivity.

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