GOLD BASED CATALYSTS FOR THE OXIDATIVE ESTERIFICATION OF RENEWABLE FURFURAL

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The upgrading of lignocellulosic biomass wastes into higher added-value chemicals is one the most researched topics in the forthcoming concept of bio-refinery. In particular, additional transformations of furfural are highly desired, and the synthesis of alkyl furoates could open very interesting perspectives for the use of xyloses [1]. Currently, we are studying the oxidative esterification of furfural to either methyl or ethyl furoate on gold based catalysts [2, 3]. The goal of the present work is to verify the role of different supports for Au samples; in particular, zirconia (Z), sulphated zirconia (SZ), titania (T) and ceria (Ce) oxides were investigated.

The oxidative esterification of furfural with methanol was tested without the addition of $NaCH_3O$, a base that would make the process less green and more expensive [4]. Both molecular oxygen and air were charged in the 1-6 bar pressure range, while temperature was investigated in the 60 – 120 °C range. The comparison among Au samples over different supports was performed under identical experimental conditions, showing that the catalytic performances follow the trend: AuSZ≥AuZ>AuCe> >AuT.

Fresh and used samples were characterized by metal content analysis, ionic chromatography (IC), N_2 adsorption, HRTEM, FTIR spectroscopy, pulse-flow CO chemisorption, TPO analyses. In order to obtain the best performing catalyst, both gold dispersion (for good conversion) and acid/base properties of the support (for good selectivity) must be taken into account: these were achieved only for the zirconia-supported catalysts. This feature can be ascribed to the high gold dispersion combined with the presence of the proper uncoordinated basic sites (i.e., O^{2-}) on zirconia. AuCe catalyst exhibited a lower performance than the zirconia-based ones, due to a very low amount of free basic sites, as the surface is covered almost totally by anionic species. Moreover, ceria displayed an enhanced redox behaviour, that seems to have no role in the reaction. The AuT sample exhibited a low conversion degree, which can be due to the worst Au dispersion, even if it was extremely selective due to the proper amount of O^{2-} sites. Catalysts stability and recycling were investigated too, and the opportunity of reusability by thermal oxidation at a proper temperature was successfully proved.

In conclusion, Au-based catalysts were investigated in the oxidative esterification of furfural by an efficient and sustainable process. The chemical and morphological properties observed for zirconia samples seem to fulfil the best compromise between high dispersion and the proper acid-base properties for good selectivity. AuSZ catalyst is therefore active, selective, recyclable and proper for a chemistry based on renewable resources.

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