Au/ZrO_2: an efficient catalyst for an industrial chemistry based on renewable resources

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Highly dispersed Au/ZrO_2 catalysts were successfully employed in the oxidative esterification of furfural by an efficient and sustainable process. Catalysts stability and recycling were investigated, and the reusability by thermal oxidation at a proper temperature was successfully proved.

Introduction

The sustainability of biorefineries derives from their ability of exploiting every product, as actually occurs in the oil refineries. The upgrad and valorization of C5 fraction represents a specific relevant issue. In particular, additional transformation of furfural are highly desired. Currently we are studying the oxidative esterification of furfural on Au/ZrO_2 samples. The goal of the work herein presented is the optimization of the process and the catalyst by deeply investigating the sample recycle.

Experimental

Catalysts were prepared by deposition-precipitation of $HAuCl_4$ on ZrO_2[1]. The oxidative esterification of furfural with oxygen and methanol was investigated in the temperatures range 80 – 120 °C with 6 bar of O_2. Fresh and used samples were characterized by metal content analysis, N_2 adsorption, HRTEM, FTIR spectroscopy, pulse-flow CO chemisorption[2], TPO.

Results and discussion

The oxidative esterification of furfural was studied on Au/ZrO_2 samples without the addition of $NaCH_3O$, a base that would make the process less green and more expensive[3].

The calcination temperature of the Au/ZrO_2 samples was investigated: it turned out that the optimal range for gold nanosizes in this reaction was between 2 and 3 nm. In order to optimize the reaction conditions the variation of conversion with temperature and time was examined.

After the first catalytic run the samples were filtered off, washed with methanol, dried and used again: the obtained conversions and in particular the selectivities were very low. Therefore catalysts deactivation was investigated: both gold leaching and gold sintering in the discharged samples were ruled out.

By FTIR spectroscopy it was pointed out the presence of organic residues both on gold active sites and on the support. On the bases of the TPO profiles the exhausted catalysts were heated up to 250 ℃ in oxygen atmosphere in order to eliminate these organic poisons. Unfortunately this treatment was able to restore only partially the activity obtained with the fresh catalysts. FTIR measurements on this sample show that the organic residues are still present on the support. After thermal treatment at 450 ℃ it is possible to remove all the organic residue and restore almost completely the initial activity.

HRTEM measurements and pulse-flow CO chemisorption on the sample regenerated at 450 ℃ point out the absence of gold sintering during the calcination treatment. Moreover FTIR data revealed that the Au phase is quite stable, even after repeated thermal treatments in O_2.

These results support with the idea that the reaction occurs within a zone at the perimeter of Au particles surrounded by the surface sites of the support, which form dual sites for the reaction[4].

Conclusions

The catalyst Au/ZrO_2 calcined at 500 ℃ is active, selective, recyclable and proper for an industrial chemistry based on renewable resources. The furoate ester can be obtained with optimal yields by a process greener than the actual one.

References

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