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Aerobic Oxidation of Alcohols Catalyzed by Gold Nanoparticles Incarcerated in Nanoporous Syndiotactic Polystyrene: an insight into the reaction mechanism

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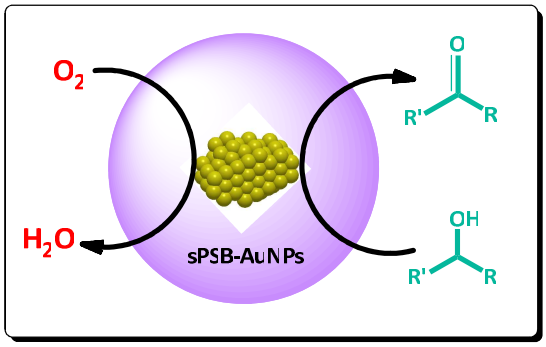
Oxidation of alcohols catalyzed by gold nanoparticles (AuNPs) is one of the most interesting reactions in green chemistry [1]. To properly address the substrates to be oxidized, an important aspect is the elucidation of the reaction mechanism. Corma *et al*. investigated oxidation of alcohols by AuNPs supported on metal oxides [2] whereas Tsukuda *et al*. reported some preliminary studies on the oxidation of benzyl alcohol by gold nanoclusters supported on poly(*N*-vinyl-2-pyrrolidone) (PVP) [3].

We studied oxidation of alcohols catalyzed by AuNPs incarcerated in a polymer matrix consisting of a crystalline nanoporous block copolymer of syndiotactic polystyrene with cis-1,4polybutadiene (sPSB). This catalyst was successfully tested in the selective oxidation of a variety of primary and secondary alcohols using dioxygen as oxidant under mild conditions [4]. 1-Phenylethanol and benzyl alcohol were quantitatively oxidized to acetophenone and benzaldehyde in 60 min and 6h, respectively, with high selectivity.



The investigation at room temperature of the kinetic profiles of 1-phenylethanol oxidation under different concentration of KOH, showed that the KOH/alcohol molar ratio of 1:1 is optimal and that after a partial induction time of about 30 min the reaction follows a pseudo first order kinetics with a $k = 1.10 \pm 0.10\ h^{-1}$. Under these conditions activation Energy (E_a) of about 20 kJ/mol was determined for benzyl alcohol. This value is in agreement with the one determined by Tsukuda [3] for polymer incarcerated AuNPs but different for that one determined by Corma [5] (59 KJ/mol) for AuNPs supported on nanoparticulate ceria suggesting that likely different reaction mechanisms are operative in these two classes of catalysts.

To elucidate if the oxidation reaction catalyzed by AuNPs-sPSB proceeds through a radical pathway, oxidation of benzyl alcohol was carried out in the presence of 4-methoxyphenol as radical trap at increasing 4-methoxyphenol/benzyl alcohol molar ratios. Increasing deactivation was observed as the molar ratios were increased and the complete inhibition of the oxidation reaction was observed at 1:1 molar ratio. These preliminary results support a radical mechanism under the conditions we explored. Further details dealing with the alcohol oxidation catalyzed by AuNPs –sPSB will be discussed in this communication.

References

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