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Application of gold and palladium nanoparticles supported on polymelamine microspheres in the oxidation of 1-phenylethanol and some other phenyl substituted alcohols

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ABSTRACT

Melamine formaldehyde and melamine resorcinol formaldehyde microspheres were decorated with Au and Pd nanoparticles and applied as heterogeneous catalysts in the oxidation of 1-phenylethanol. The catalysts showed similar activities irrespective of the support employed. Moderate conversion activities of 48–50% were achieved when using acetonitrile as solvent; however, when employing water as solvent, the supported catalysts formed a three-phase, emulsion system which facilitated the catalytic conversion of 1-phenylethanol to acetophenone at much higher conversions of around 83%. The oxidant, TBHP, decomposed rapidly in acetonitrile, whilst it remained stable in aqueous solution, leading to the enhanced activities observed when using water as solvent. These systems also proved to be recyclable for up to five cycles, with only slight loss of activity observed; this can be attributed to the physical loss of catalyst during the workup procedure conducted between each cycle.

1. Introduction

The use of supported Au and Pd nanoparticles as oxidation catalysts is well known [1–3]. It has been established that the type of support material used could have a significant influence on the nature of the catalyst. This, in turn, influences the activity and selectivity of the catalytic system [4]. Different types of support materials have previously been applied to stabilize metal nanoparticles; these include inorganic [5,6], organic [7–9], and hybrid support materials [10–12].

Melamine formaldehyde polymers are thermally stable [13] materials which have a range of applications, including use as adsorbents [14–16] or as flame-retardant [17] enhancers in other materials. Melamine formaldehyde polymers can also be prepared as microspheres, with enhanced surface areas [18]. Its thermal stability in organic solvents, as well as its water resistance and high nitrogen content make it ideal as a potential support for metal nanoparticles. Stabilization of the nanoparticles can be achieved through an interaction between the nitrogen atoms in the melamine formaldehyde scaffold and the metal centres. Using such polymeric supports allow for the recovery and re-use of metal nanoparticle-containing catalysts. This is crucial when employing noble metal-based catalysts owing to their high cost.

Supported nanoparticles have found application in a range of organic transformations, amongst which the synthesis of compounds with carbonyl functionalities is common. Carbonyl containing products are widely used to produce pharmaceuticals and fine chemicals [19,20]. Often, these types of products are synthesized through stoichiometric processes utilizing environmentally harmful reagents [21,22]. One such process is the oxidation of alcohols to carbonyl-containing compounds, for example 1-phenylethanol to acetophenone. The catalytic oxidation of alcohols is a more environmentally friendly process compared to the stochiometric oxidation of alcohols to produce these value-added chemicals. This allows for a reduction in toxic waste formation and the utilisation of more energy-efficient reaction conditions. A variety of Au and Pd nanoparticle-based catalysts have been applied in the oxidation of 1-phenylethanol to acetophenone. Antonetti et al. [23](a) reported the use of a polyketone-silica (PK-SiO_2) organic-inorganic hybrid support for Pd nanoparticles. The 1.0 wt% Pd/60%PK-SiO_2 achieved 100 % selectivity towards acetophenone under O_2 (1 MPa) at 100 °C over 12 h. Mori et al. [23](b) used hydroxyapatite-supported Pd nanoparticles in the oxidation of alcohols. One of the hydroxyapatite-supported systems PdHAP-0, gave conversions around 99% with 99% yield. However another example of a

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