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Editorial

Advance in Selective Alcohol and Polyol Oxidation Catalysis

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The aerobic oxidation of organic molecules and in particular alcohols and bio-derived poly alcohols to value-added commodity molecules is under continuous investigation, due to the importance of oxidation products (aldehydes, ketones carboxylic acids and esters) and the challenging nature of this chemical transformation, since rather harsh reaction conditions (T > 100 °C) are needed to gain a significant substrate conversion [1–3]. The development of mainly robust heterogeneous catalysts, which are recyclable without the need of a regeneration step, is of utmost importance. In addition, the study of the synergistic effects between the catalytic metal-based reaction sites and the support is of utmost importance, since it paves the way for a tailored architecture of new catalysts with improved activity, selectivity and stability over time [4].

In the present Special Issue are collected six research articles focused mainly on the preparation and optimization of heterogeneous Au and Pt nanoparticle-based catalysts employed for aerobic alcohol oxidation. The main outcomes of the research articles included in this Special Issue are summarized as follows:

(i) The synthesis of colloidal Au nanoparticles employed in the aerobic oxidation of 1,6-hexandiol to give the industrially important adipic acid is reported [5]. The efficiency of the heterogeneous catalyst has been optimized by varying the type of polymeric stabilizer (polyvinylalcohol (PVA) vs. polyvinylpyrrolidone (PVP)) and the stabilizer to Au weight ratio. The highest yield of adipic acid (40%) was obtained using an Au-PVA catalyst in the absence of a base.

(ii) Palladium-phosphorus alloy nanoparticles anchored to amoniopropyl-fuctionalized mesoporous silica were successfully applied in the selective aerobic oxidation of benzyl alcohol to benzaldehyde carried out in toluene, outperforming pure palladium-based nanoparticles localized onto the same support material [6]. A combination of a smaller nanoparticle size encountered in Pd-P compared to Pd nanoparticles and the lower electron density at Pd in Pd-P has been suggested to account for the higher catalytic activity of the latter catalyst.

(iii) The biggest challenge to be faced in aerobic cyclohexanol oxidation to cyclohexanone, an industrially important intermediate in the synthesis of caprolactam and adipic acid (i.e., nylon 6,6 synthesis), consists of decreasing the strong interaction of the oxidation product with the catalysts' (Pt-nanoparticle) surface, thus slowing down the cyclohexanol conversion. The interaction of Pt nanoparticles with a Bi_2O_3-modified support showed a beneficial effect in the latter cyclohexanol conversion [7]. A suitable modification of the electronic property of the Pt-surface atoms by Bi atoms significantly decreased the adsorption energy for cyclohexanone, favoring the oxidation of cyclohexanol.

(iv) The acceptorless oxidation of biomass has been found to be a suitable source for hydrogen [8]. Hence, many catalytic systems that produce hydrogen gas along with carbon monoxide, carbon dioxide or methane are known, while catalysts which lead to highly pure hydrogen are rare. Generally, water soluble Ir(III)-complexes, bearing either 2,2′-bipyridine modified ligands [9] or N-heterocyclic carbenes (NHCs) [10], are among the most efficient catalysts for this type of chemistry. New cationic iridium(III)-based catalysts were developed which produce hydrogen in 95% purity, using various

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monosaccharides, mainly glucose, as a substrate in refluxing water without the need for further additives such as acids or bases [11]. A clear ligand effect emerged from the catalyst screening.

(v) Gold nanoparticles supported by ceria are highly efficient catalysts in aerobic oxidation reactions [12,13]. Their synthesis can be achieved by co-precipitation of a gold precursor with a cerium(III) salt in the presence of a co-precipitation agent. The effect of the co-precipitation agent on the Au nanoparticle size and its catalytic activity as well as selectivity in aerobic benzyl alcohol oxidation has been studied [14]. From this study, it clearly emerged that NaOH is much more suitable as a co-precipitation agent compared to urea and hexamethylene tetramine.

(vi) Small Au nanoparticles with diameter <5.0 nm supported onto hydrotalcite (HT) are known to be active catalysts for acceptorless benzyl alcohol dehydrogenation reaction. The Brønsted basic sites of HT (i.e., Mg-OH) activate the alcohol as alcoholate, which successively undergoes, in the presence of Au nanoparticles, a hydride shift, which is the rate-determining step in the oxidation reaction, releasing the aldehyde [15]. The Au-hydride is regenerated upon the reaction with the Brønsted acid site (AlO-H) to give hydrogen. The same-sized Au nanoparticles located on Zn-Al-HT have been successfully applied to generate methyl methacrylate and other esters in the presence of oxygen using a fixed-bed reactor [16]. The strong basic sites of the HT support, revealed by CO_2- temperature programmed desorption, accounted for the facile formation of the hemiacetal intermediate, which contributed to the formation of the final ester product.

In summary, the contribution of the research articles collected in this Special Issue will be stimulating for those authors working in the field of aerobic alcohol oxidation, and will provide a valuable guide to develop new innovative catalysts for aerobic alcohol oxidation reactions used under batch or flow catalytic conditions.

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