

# Highlights of the Nanocatalysis in Organic Chemistry

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Nanocatalysts with superior characteristics regarding activity, selectivity, durability, and recoverability, are envisaged playing a pivotal role to enable a wealth of future applications and contribute to solve current environmental, social, and industrial problems.

In fact, nanocatalysis closes the gap between both conventional homogenous and heterogeneous catalysis, while concomitantly requiring totally new synthetic approaches and displaying unique characteristics. Selective reactions, high activity, and excellent yield (typically related to homogeneous catalysis), as well as enhanced products separation and catalyst recover (traditionally associated with heterogeneous catalysts), are key targets pursued by nanocatalysis combining the advantageous characteristics of homo- and heterogeneous catalysis while reducing their respective drawbacks.

Nanosized materials show additional unique properties compared to the macroscale. In addition, the nature of the nanoparticles support can have a significant influence on their catalytic performance. This aspect is addressed in several papers of this section [1,2].

Chen et al. [1], successfully fabricated highly ordered mesoporous  $\text{Fe}_2\text{O}_3$  supported gold nanoparticles with a desired specific surface area and porous structure ( $\text{Au}/\text{meso-Fe}_2\text{O}_3$ ) a hard templating method by using KIT-6 as the template. The catalytic performance of the synthesized catalyst was studied for the aerobic (by molecular oxygen) of oxidation benzylic alcohols in  $\beta$ -O-4 linked lignin model dimers to the corresponding carbonyl products under atmosphere pressure.  $\text{Au}/\text{meso-Fe}_2\text{O}_3$  shows an enhanced activity for the aerobic oxidation of 1-phenylethanol in comparison with that of  $\text{Au}/\text{bulk-Fe}_2\text{O}_3$ . The promoted catalytic activity is related to the confined porous structure of mesoporous  $\text{Fe}_2\text{O}_3$  and more boundaries contact between gold and meso- $\text{Fe}_2\text{O}_3$ , which shows that the porous structure of the support has a significant influence on the activity of gold catalysts. In addition, the  $\text{Au}/\text{meso-Fe}_2\text{O}_3$  shows a good catalytic reusability. The structural framework of the as-prepared catalyst was not changed during 3 cyclic runs and shows an excellent catalytic performance. These results indicated that the heterogeneous catalyst  $\text{Au}/\text{meso-Fe}_2\text{O}_3$  could be used as a highly efficient catalytic system for the degradation of lignin, which shows a great significance for lignin valorization to added-value low molecular weight aromatics.

The challenging selective oxidation of alcohols to the corresponding carbonyl compounds through sustainable catalytic procedures was addressed by Liu et al. [2] focusing on selective oxidation of benzyl alcohol to benzaldehyde, using molecular oxygen as the oxidizing agent. In total, three bimetallic Cu–Ni nanoparticle-supported catalysts were synthesized by co-immobilization followed by  $\text{H}_2$  reduction. A chromium(III) terephthalate metal organic framework (MIL-101), titanium dioxide ( $\text{TiO}_2$ ), and carbon (C) with different properties (acidity and Brunauer–Emmett–Teller surface area) were selected as supports for studying the effect of the support nature on the catalytic activity and selectivity in the oxidation of benzyl alcohol. The highest benzaldehyde yields were achieved with  $\text{CuNi}/\text{TiO}_2$ ,  $\text{CuNi}/\text{MIL-101}$ , and  $\text{CuNi}/\text{C}$  catalysts, with an Cu:Ni mole ratio of 1:1, at 100 °C within 4 h under 5, 3, and 3 bar of  $\text{O}_2$ , respectively. Importantly, the catalysts exhibited a high functional group (electron-donating and electron-withdrawing groups) tolerance. Reusability and leaching experiment results exhibited that  $\text{CuNi}/\text{MIL-101}$  showed better stability than  $\text{CuNi}/\text{TiO}_2$  and  $\text{CuNi}/\text{C}$  catalysts due to the large porous cavities of



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MIL-101 support; these cavities can be used to trap bimetallic Cu–Ni nanoparticles and inhibit nanoparticle leaching. These findings emphasize the potential of developing new heterogeneous catalytic systems for the oxidation of benzyl alcohol under mild conditions.

Another extremely important industrial catalytic reaction is the carbonylative Suzuki–Miyaura coupling, providing relevant diarylketones. Trzeciak and co-workers [3] prepared and characterized three nanosize palladium catalysts supported on graphene oxide (GO) and on its composite with TiO<sub>2</sub> (GO–TiO<sub>2</sub>) from PdCl<sub>2</sub>(MeCN)<sub>2</sub> and Pd(OAc)<sub>2</sub>. The presence of palladium nano particles, Pd NPs, of different diameters (4–89 nm) and size distributions was evidenced by transmission electron microscopy (TEM) measurements. An effect of the palladium precursor and the synthetic method on the structure of the catalyst was confirmed by physicochemical methods. The introduction of Pd to the GO matrix resulted in an increase in photoemission due to an increase in the number of sp<sup>2</sup> centers. GO-supported palladium efficiently catalyzed the carbonylative coupling of iodobenzenes with aryl boronic acids forming relevant diarylketones at 1 atm CO and a low amount of the catalyst (0.2 mol%). The highest activity and recyclability were obtained for Pd/GO–TiO<sub>2</sub>. The emission behavior of Pd/GO and Pd/GO–TiO<sub>2</sub> catalysts indicated structural changes occurring during the catalytic reaction and showed that emission spectra can provide useful information about these catalytic systems.

The above examples show that nanocatalysts could potentially make an important contribution to render chemistry greener.

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