Selective hydrogenation of alkynols in ethanol medium in a batch mode using polyamine-supported Pd catalysts

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Abstract

Selective hydrogenation of acetylene alcohols is widely used in fine organic synthesis in production of fragrances, biologically active compounds and fat-soluble vitamins. Palladium is well known to be the most selective catalyst for hydrogenation of triple -C≡C- bond of alkynols. Historically, Lindlar suggested Pd/CaCO₃ catalyst modified with lead acetate and quinoline, which allows up to 95% selectivity at nearly 100% conversion in triple bond hydrogenation. However, the application of these modifiers leads to pollution of target products. The use of polymeric matrices as supports allows achieving high activity and selectivity without the necessity of the use of toxic modifiers as well as providing the possibility of stabilization of Pd-containing species inside polymer nanostructures.

Functionalized polymers, especially nitrogen-containing ones, were shown to be the most promising ones from the point of view of provision of high metal dispersion, improvement of reactant diffusion into the pores and facilitation of interaction between polymer and metal nanoparticles (NPs). It is noteworthy that free electron doublet of nitrogen in the amino groups can be involved in binding of Pd²⁺ ions from the precursor solution that likely results in more uniform distribution of Pd precursor inside the polymer along with prevention of Pd leaching. Besides, more rapid reduction of Pd²⁺ ions to Pd⁰ with formation of Pd NPs can be found.

In the framework of this study the series of Pd-containing catalysts based on polyamines (1%-Pd/PA) was synthesized via conventional wet-impregnation method at variation of PA type (molecular weight, existence of additional functional groups (-OH, -COOH, -PO(OH)₂, etc.), cross-linking degree hydrophobicity/hydrophilicity) while using Pd acetate as a precursor. All the synthesized catalysts were tested in hydrogenation of...
2-methyl-3-butyn-2-ol (intermediate product in the synthesis of fragrant compounds (such as linalool, linalyl acetate, citral, citronellol etc.) and vitamins A, E and K) in ethanol medium in a batch mode at ambient hydrogen pressure.

It was shown that the use PA as supports led to noticeable increase in selectivity (more than 99% at 98% of 2-methyl-3-butyn-2-ol conversion was achieved) at reasonable activity, which was comparable to industrial Lindlar catalyst, at lower metal loading. It is noteworthy that the variation of PA nature had strong influence on the catalytic behavior: best results were found for hydrophilic polymer having highest degree of cross-linking.

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