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Pd-functionalized polydopamine-coated polyurethane foams as highly reusable structured catalyst for selective alkyne semi-hydrogenation

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PURPOSE OF THE ABSTRACT

Structured Catalyst Supports (SCS) are widely used in continuous process applications due to their efficient mass transfer, low pressure drop, intimate mixing of the reagents, and easy separation of the catalyst from the products [1]. Among the variety of SCS, open cell foams are prime candidates. However, foams with ceramic and metallic structures have many disadvantages, including high cost, high brittleness, and a large number of closed cells, which render the reproducibility of reactions uncertain. Our group has recently proposed an alternative based on the use of flexible, mechanically resistant and inexpensive polyurethane foams (PUF). These foams can be readily coated in buffered (pH 8.5) water with a thin layer of polydopamine (PDA) - inspired by the mussels' adhesion principle [2] - which then allows the grafting of both inorganic particles [3] and molecular compounds that bear alkoxysilyl arms [4].

The selective hydrogenation of alkynes to alkenes covers an important area of industrial production. However, olefins production from alkynes requires catalysts able to both hydrogenate the triple bond and hamper over-hydrogenation toward alkanes. In addition, these catalysts should limit the undesired double-bond chain-walking phenomena [4]. Supported catalysts containing Pd nanoparticles (NPs) are among the best candidates in terms of activity, but they often suffer from moderate selectivity. Typical approaches to improve their chemoselectivity rely on the modification of the NPs by the addition of N-, P-, or S-containing ligands or on the codoping with a less active metal. A typical example in this domain is the Lindlar catalyst, where Pd/CaCO3 is partially ?poisoned? by the addition of Pb and quinoline. However, the presence of Pb represents a serious limit for its eco-sustainable use. Another effective approach relies on the ?active site isolation? strategy, dealing with the development of single atom-based catalysts. These strategies however require complex and costly synthetic solutions that compromise the process sustainability and its large-scale implementation. Therefore, the quest for easy-to-make, highly efficient and selective catalysts working at moderate H2 pressure without extra ligands or co-catalysts is a matter of intense research activity worldwide.

In this context, we will present a straightforward and fully reproducible catalyst preparation methodology based on the simple immersion of the non-innocent structured support, PDA@PUF, in a hydro-alcoholic solution of a commercial Pd(II) salt (Figure 1). The as-prepared flexible structured-supported catalyst, Pd@PDA@PUF, is able to hydrogenate various alkynes to the corresponding alkene under H2 flow (5-13 mL H2 / min) at room temperature with high selectivity. In particular, with internal alkynes almost no over hydrogenation or alkene isomerization is observed, even several hours after all the alkyne has been consumed (Figure 2). At odds with more conventional preparation methods, this protocol does not require any calcination/reduction treatment to get a highly performing and robust hydrogenation system. Thus, the applied procedure shows a significant reduction of many energy and reagent wastes typically encountered in classical synthetic approaches towards the preparation of shape- and size-controlled metal particles to be engaged as selective hydrogenation catalysts. Furthermore, no Pd leaching is observed, and Pd@PDA@PUF can be reused up to 15 times without any observable decrease in activity. In addition, it can also be used for Suzuki cross-couplings, thus demonstrating versatility in addition to its excellent reusability. Analyses by ICP/AES, SEM, TEM and XPS, carried out before and after catalysis, will provide some insight into the material structure, and the mode of reduction of the Pd(II) salt to Pd(0), as well as the possible role of the PDA layer in this event.

FIGURES

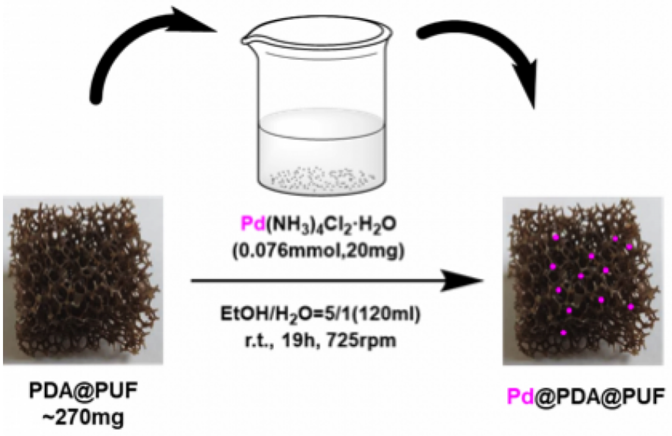

FIGURE 1

Figure 1

One-step immobilization of a Pd(II) salt on PDA@PUF

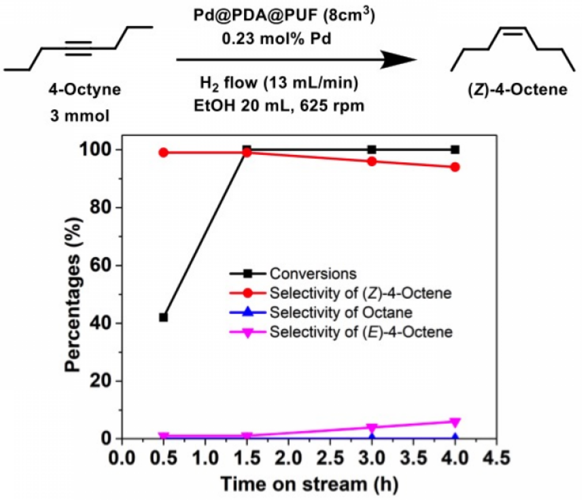

FIGURE 2

Figure 2

Pd@PDA@PUF-catalyzed semi-hydrogenation of 4-octyne

KEYWORDS

Semi-hydrogenation | alkyne | polyurethane foam | polydopamine

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