

N°696 / OC

TOPIC(s) : Homogenous, heterogenous and biocatalysis / Industrial chemistry

Cyclodextrin-assisted low-metal Ni-Pd/Al₂O₃ bimetallic catalysts for the direct amination of aliphatic alcohols

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PURPOSE OF THE ABSTRACT

Amines are N-containing intermediates with a broad variety of applications in the chemical industry as solvents, agrochemicals, pharmaceuticals, detergents and fabric softeners [1]. The direct amination of alcohols via the hydrogen borrowing mechanism is a promising strategy for preparing amines, since no external hydrogen supply is required and water is generated as main by-product [2]. The present catalytic systems (Ni & Cu) [3] suffer from poor selectivity, high metal loading (>10 wt%) and heterogeneous distribution of metal particles. In our quest for low-metal-based stable catalysts, we report here a series of low-Ni based bimetallic Ni-Pd catalysts synthesized by six different methods using β -CD as pre-shaping agent and their characterization in their aqueous solution, dried, calcined, and reduced states. The catalytic performance of the as-prepared formulations was assessed in the amination of 1-octanol (OL) with NH₃ (7 bar) and 55 mg catalyst at 160 °C for 4 h.

The primary Ni-Pd- β -CD interaction was inspected by marrying ESI-MS experiments with DFT calculations. The results revealed a higher affinity of the Ni(II) nitrate precursor for β -CD to form a molecular complex compared to the Pd(II) precursor. This complex conditioned to an important extent the catalyst architecture in the further thermal treatment steps (drying, calcination, reduction), as inferred by combining H₂-TPR, XPS, CO-pulse chemisorption and STEM-EDX-SDD. By optimizing the preparation protocol, 90% OL conversion and 79% selectivity (71% yield) to the primary amine (i.e. 1-octylamine) (TON = 93) could be achieved on a formulation based on 5 wt%Ni and 0.5 wt%Pd prepared by pre-adsorbing β -CD on Al₂O₃ before impregnating the Ni(II) and Pd(II) salts. This results places this catalyst among the most active and selective Ni catalysts reported in the literature for the synthesis of primary amines from aliphatic alcohols [4].

FIGURES

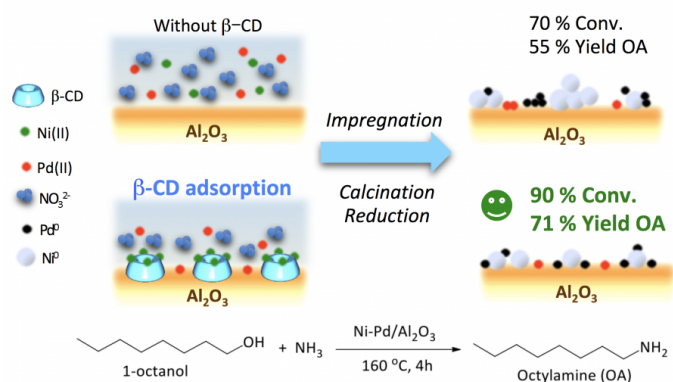


FIGURE 1

Figure 1

CD-assisted preparation of NiPd catalysts for the selective synthesis of 1-octylamine from the direct amination reaction of 1-octanol with ammonia.

FIGURE 2

KEYWORDS

Direct amination | 1-octanol | Nickel-palladium | Cyclodextrin

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