



Ni–Co–Cu supported on pseudoboehmite-derived Al₂O₃: Highly efficient catalysts for the hydrogenation of organic functional groups

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ARTICLE INFO

Article history:

Received 18 August 2011

Received in revised form 26 February 2012

Accepted 1 March 2012

Available online 9 March 2012

Keywords:

Hydrogenation

Nitro, nitrile and alkynyl groups

Dispersed Ni–Cu–Co catalyst

ABSTRACT

Ni–Co–Cu catalysts supported on pseudoboehmite-derived Al₂O₃ were developed for efficient hydrogenation of organic functional groups: CN and NO₂ associated with benzene as well as $\text{—C}\equiv\text{C—}$ in butynediol. Factors such as thermo-treatment of pseudoboehmite, Ni loading, Cu and Co content, and catalyst operating parameters were systematically studied. Among the catalysts, 20%Ni–3%Cu–5%Co/Al₂O₃ performed the best, showing 100% feed conversion and 84–99.8% selectivity of target products. Techniques such as N₂ sorption measurement, scanning electron microscope, hydrogen temperature-programmed reduction and desorption, X-ray photoelectron spectroscopy, and in situ X-ray diffraction were used to characterize the catalysts. The superior performance of the catalyst can be attributed to synergetic interaction among the Ni–Cu–Co constituents as well as enhancement of Ni²⁺ reduction and Ni⁰ dispersion that are resulted due to the co-presence of Cu and Co.

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1. Introduction

Meta-xylylenediamine (*m*-XDA) is widely used as an important intermediate of fine-chemicals and a curing agent of epoxy. It is mainly produced by the hydrogenation of isophthalonitrile (IPN). In the presence of catalysts, successive hydrogenation of IPN occurs to produce single- (with one $\text{—CH}_2\text{NH}_2$ group) and di-amine (with meta- CH_2NH_2 groups in benzene ring); under severe conditions, there is condensation of *m*-XDA product via —NH_2 groups to generate the condensed by-products. The reaction can be catalyzed by a variety of catalysts such as Raney Ni [1], Raney Co [2], Fe- or Cr-doped Raney Ni [3,4], Pt–Ni/Al₂O₃ [5], Co–Ti/diatomite or Ni–Ti/diatomite [6], Co–Rh/diatomite [7], and Rh/Al₂O₃ [8]. In these supported Ni or Co catalysts, high loading (up to 60 wt%) is usually adopted. The reported maximum *m*-XDA yields over Raney Ni, modified Raney Ni, and dispersed Ni catalysts were approximately 85%, 95%, and 95%, respectively. The *m*-XDA yield, however, was strongly dependent on reaction parameters such as IPN concentration, catalyst amount, reaction temperature and pressure. Generally speaking, Co is more selective than Ni for nitrile formation, but also more costly than Ni. Also, the skeletal-type Ni catalyst is more expensive than the supported Ni counterpart and deactivates in the reaction.

In the cases of Pt–Ni/Al₂O₃ and Co/Ni–Ti/diatomite catalysts, the reactions were operated under rather severe conditions (temperature up to 180 °C and pressure to 22 MPa). It is known that both Ni and Co are elements active for catalyzing nitriles hydrogenation. For nitrile compounds, the adsorption strength is weak on Pt and Pd, medium on Cu and Rh, and strong on Co and Ni. The adding of certain amount of Cu to Ni can purposely modify the electronic property of Ni; meanwhile the electronic property of Ni–Co metals can be tuned through the control of Ni/Co ratio. The change in electronic property of metal constitutes can in turn bring about alteration in adsorption and reaction behavior of reactant. Besides the hydrogenation of IPN to *m*-XDA, the hydrogenation of nitrobenzene (NB) to aniline, butynediol (BD) to 2-butane-1,4-diol (BDO), and 4-nitrophenol (4-NP) to 4-aminophenol are also important processes in chemical industry. The corresponding products are essential chemicals or fine chemical intermediates widely used in the fields of medicine, pesticides, dye, and perfume; the demand for them is getting higher and higher in recent years.

The current industrial processes for these products, however, are either environment-unfriendly (for instance, the hydrogenation of NB by Fe powder with acid [9]) or energy-demanding (high temperature and pressure adopted in the Reppe process for BD hydrogenation [10–13]). The motivation of this study is to develop hydrogenation catalysts that are efficient yet less costly, and can be applied to organic molecules with different functional groups. The strategy of catalyst design is: (1) to develop a kind of supported Ni-based catalyst using comparatively lower Ni loading; (2) to select pseudoboehmite-derived Al₂O₃ as support and to tune its property

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