



Reductive amination of 2-propanol to monoisopropylamine over Co/ γ -Al₂O₃ catalysts

Jun Hee Cho^a, Jung Hyun Park^a, Tae-Sun Chang^b, Gon Seo^c, Chae-Ho Shin^{a,*}

^a Department of Chemical Engineering, Chungbuk National University, Chungbuk 361-763, Republic of Korea

^b Environment & Resources Research Center, Korea Research Institute of Chemical Technology, Daejeon 305-353, Republic of Korea

^c School of Applied Chemical Engineering and the Institute for Catalysis Research, Chonnam National University, Gwangju 500-757, Republic of Korea

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ABSTRACT

Co/ γ -Al₂O₃ catalysts with 4–27 wt% cobalt loadings were prepared by incipient-wetness impregnation and used to catalyze the synthesis of monoisopropylamine by the reductive amination of 2-propanol in the presence of hydrogen and ammonia. The catalysts were characterized by X-ray diffraction, H₂-temperature programmed reduction, N₂-sorption, and H₂-chemisorption. 23 wt% Co loading resulted in the highest catalytic activity and a long-term stability of up to 100 h on stream. 2-Propanol conversion was related to the exposed metal surface area and the number of exposed cobalt atoms. In the absence of hydrogen, the catalyst was progressively deactivated; its initial activity and selectivity were completely recovered upon re-exposure to hydrogen. The deactivation was due to the formation of metal nitride caused by the strong adsorption of ammonia on the surface of the metal phase. Excess hydrogen hindered the phase transition to metal nitride, preventing deactivation.

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1. Introduction

The reductive amination of aliphatic alcohols is used to produce alkylamines that can be used as intermediates for the synthesis of herbicides, insecticides, pharmaceutical chemicals, corrosion inhibitors, plastics, and rubber chemicals [1–5]. The process can proceed by hydrogenation–dehydrogenation over nickel, cobalt, copper, and solid acid catalysts; it is metal-catalyzed, with alcohol conversion being proportional to the exposed metal surface area [6–10].

Monoisopropylamine (MIPA) is generally synthesized by contacting 2-propanol and ammonia at high pressure (≈ 20 bar) [11,12]. The reductive amination of 2-propanol over supported metal catalysts is complex and involves dehydrogenation, condensation, and hydrogenation steps (Scheme 1), with the dehydrogenation of 2-propanol to acetone being the rate determining step. The first and last redox processes are catalyzed by the metal; the reaction of the intermediate carbonyl compound with NH₃ to form an imine can be accelerated by acid/base catalysis [13–16].

Cobalt-based catalysts are industrially important in a variety of reactions. The redox properties of cobalt species allow their use in either the reduced state for Fischer–Tropsch synthesis and

hydrogenation and dehydrogenation reactions or the oxidized state for oxidation [17–21]. Gardner et al. [22] reported cobalt catalysts with higher activity than supported nickel catalysts for reductive amination with high metal loadings and high space velocity at relatively low temperature. However, conversion and yield are usually low in the synthesis of alkylamines from alcohols and ammonia at atmospheric pressure.

In batch-type reductive amination, industrial separation and recycling of catalyst and by-product are difficult. The reductive amination of alcohols has been widely investigated. Dobson et al. [23] reported the reductive amination of 2-propanol over supported nickel–palladium–ruthenium catalysts at high pressures (≈ 50 bar) in an autoclave. However, most studies were focused on methanol, ethanol and cyclohexanol [5,24–26]. There are few reports regarding the influence of reaction parameters on the reductive amination of 2-propanol over supported metal catalysts.

This work reports the catalytic properties of Co/ γ -Al₂O₃ catalysts for the reductive amination of 2-propanol in the presence of ammonia and hydrogen at atmospheric pressure. 2-Propanol conversion and selectivities to MIPA, acetone, diisopropylamine (DIPA), and diisopropylether (DIPE) were evaluated on Co/ γ -Al₂O₃ catalysts with various Co loadings. Various hydrogen and ammonia feed compositions and reaction temperatures were tested. Calcined and reduced catalysts were characterized by X-ray diffraction (XRD), H₂-temperature programmed reduction (H₂-TPR), NH₃-temperature programmed desorption (NH₃-TPD), N₂-sorption, and H₂-chemisorption.

* Corresponding author. Tel.: +82 43 261 2376; fax: +82 43 269 2370.

E-mail address: chshin@chungbuk.ac.kr (C.-H. Shin).