



Direct Au-Ni/Al₂O₃ catalysed cross-condensation of ethanol with isopropanol into pentanol-2



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ARTICLE INFO

Article history:

Received 30 December 2015

Received in revised form 6 June 2016

Accepted 7 June 2016

Available online 20 June 2016

Keywords:

Cross-condensation

Au-Ni synergism

β-alkylation

Ethanol

Isopropanol

Guerbet reaction

ABSTRACT

Ethanol and isopropanol cross-condensation 0.2Au-0.06Ni/γ-Al₂O₃ catalyst have been developed based on the synergetic effect of gold and nickel in many reactions. A cross-condensation reaction results in the formation of pentanol-2 and pentanon-2 in high yields in the absence of any alkali or sacrificial agents (e.g., hydrogen acceptors or hydrogen donors). In this study, heterogeneous Au-Ni/Al₂O₃ catalysts were used in this type of reaction for the first time. The catalyst developed in this study is also effective for the self-condensation of ethanol, providing 85% selectivity of linear α-alcohols at 63.5% ethanol conversion. Structural investigations show that the morphological peculiarities and charge state of gold may produce the different activities of mono- and bimetallic Au- and Ni-containing catalysts.

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1. Introduction

Alcohols are an important class of organic compounds due to their wide variety of uses in industrial and laboratory chemistry. Due to the increasing availability of bio-based alcohol feedstocks, we propose a chemical route to convert fermentation products (e.g., ethanol and isopropanol) into pentanol-2 in this study. Ethanol can be produced via the fermentation of sugar-containing or lingo-cellulose feedstock [1]. Isopropanol may be efficiently produced from lignocellulosic biomass via cellobiose degradation [2] or the isopropanol–butanol–ethanol (IBE) process [3].

The synthesis of higher alcohols from lower alcohols is generally known as the Guerbet reaction, in which basic catalysts are typically used [4,5]. The Guerbet reaction is an important method when constructing complex molecules from simple substrates and has thus attracted marked interest in recent years [6]. Both alcohol self-condensation and cross-condensation includes four general reaction steps: the alcohol is first dehydrogenated, after which the carbonyl compounds are coupled via aldol addition and subsequent dehydration; finally, the compounds are hydrogenated into saturated alcohols [5]. Depending on the types of alcohols used in the

reaction (e.g., primary versus secondary, long chain versus short chain), branched or unbranched products can be formed. Additionally, when different alcohols are present in the reaction, both self-coupling and cross-coupling reactions can occur [7].

Many examples of alcohol self-condensation can be found in the literature that can be categorized into three primary catalytic composition types: (1) homogeneous base combined with homogeneous transition metals; (2) homogeneous base combined with heterogeneous transition metals; and (3) heterogeneous systems with or without transition metals [7]. The use of alkali compounds creates certain implications for use in industry, such as the stability of the dehydrogenation catalyst, reactor vessel corrosion and intensive product purification. The application of heterogeneous catalytic systems provides easy separation from the reaction mixture, does not cause corrosion and metal leaching, and can ideally be reused multiple times without extensive regeneration. To develop cost efficient Guerbet processes, the use of solid acid-base catalysts is required.

The conversion of ethanol into *n*-butanol over purely heterogeneous catalysts has been reported in several publications and patents [8–18]. Generally, the reaction temperature varies from 200 up to 450 °C with a relatively low conversion (e.g., 10%–20%) and a selectivity approaching 70%. Hydroxyapatites have been shown to be the most active and selective catalytic systems for higher alcohols production [10,11]. In a plug flow reactor, the highest *n*-

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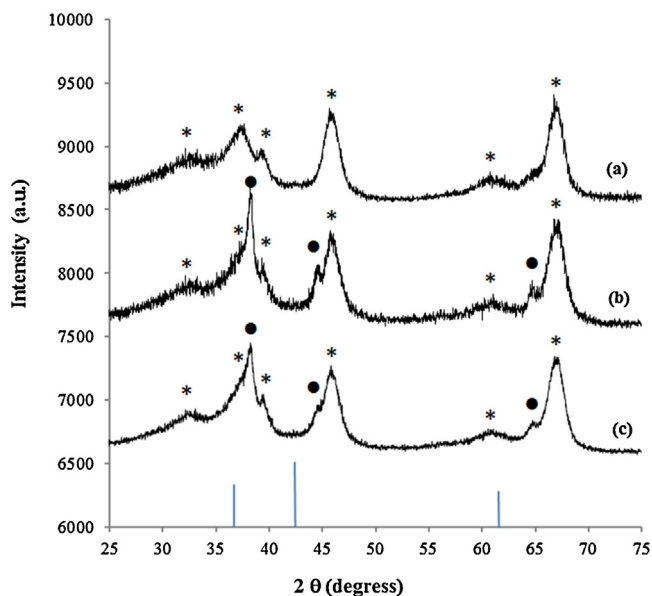


Fig. 1. XRD pattern of catalysts: (a) Ni/Al₂O₃, (b) Au/Al₂O₃ and (c) Au-Ni/Al₂O₃. The symbol (*) indicates reflections of gamma alumina (JCPDS card, No. 29-0063). The symbol (●) indicates reflections of gold crystallites (JCPDS card, No. 04-0784). The vertical lines indicated the position of the most intense reflections of nickel oxide (JCPDS card, No. 78-0643).

butanol selectivity was found to be 76.3% at 14.7% conversion of ethanol [11] and 81.2% at 7.6% conversion of ethanol [10]. The study of a batch reactor process showed that a 20% Ni/Al₂O₃ catalyst manufactured by Crossfield produces the highest selectivity of 80% at a conversion of approximately 25% after 72 h [12].

Isopropanol condensation generally leads to ketones formation due to its higher rate of acetone alkylation compared to Guerbet condensation. Over hydrotalcite-derived mixed oxide (Mg₃AlO_x), the primary products are diacetone alcohol, phorone and isophorone [19]. The Guerbet reaction of supercritical isopropanol into a small amount of 3,3,5-trimethylcyclohexanol was observed in a study of the decomposition of epoxy resin with KOH [20]. The self-coupling of 2-propanol occurred with a heterogeneous Ni/CeO₂ catalyst [21] (>200 °C) and various coupling products, including methyl isobutyl ketone (21%), 4-methyl-2-pentanol (19%), diisobutyl ketone (21%) and 2,6-dimethyl-4-hexanol (9%), were obtained in comparable yields to previous studies [22–24].

Several examples are shown to describe acetone-butanol-ethanol (ABE) fermentation products conversion in comparison to Guerbet type catalysts [25,26]. In both catalytic systems studied in these works, the formation of ketones C₇–C₁₉ was observed, which indicates that no interaction between the ethanol and acetone occurred. The formation of 2-pentanone occurred only in the presence of Pd-hydrotalcite catalyst, and its yield did not exceed 10% from other C₇–C₁₁ ketones [26]. The fermentation mixture of the IBE conversion also did not lead to C₅ product formation. The condensation of secondary alcohols with primary alcohols thus effectively catalysed by homogeneous base and homogeneous/heterogeneous transition metal systems [9,27,28] but never a pure heterogeneous catalytic system.

Gold had long been considered to be a catalytically inert metal until Haruta et al. found the surprisingly high activity of gold nanoparticles during low-temperature CO oxidation [29]. The recent progress in heterogeneous catalysis resulted in remarkable investigations that showed the high catalytic activity of gold nanocomposites in the water-gas shift reaction [30,31], hydrogenation [32,33], isomerization [34,35], hydrodechlorination [36,37]

and other reactions [38]. It was reported in references [39,40] that the modification of gold with a small amount of transition metals might result in synergistic interactions between the Au and M phases that markedly enhance the catalytic performance of poly-metallic Au-M catalysts. Although it is generally accepted that the high activity of monometallic Au catalysts can be attributed to the presence of small gold crystallites (i.e., <4 nm) [41], the nature of the most active sites in poly-metallic gold-contained catalysts remains under discussion. Certain authors report that ionic gold is formed on the surface of Au-M catalysts and provides a high synergistic activity [42,43], while others claim that metallic nano-sized gold contains the most active sites [44]. Additionally, a third group of authors reports that the rough shape of particles [45], the atoms on the interface between gold and the second metal [41], the specific surface chemistry of bimetallic alloys [38,39] are most important for synergistic activity.

Gold-nickel catalysts possess high synergistic activities and long lifetimes when converting a variety of hydrocarbons, such as *n*-butane [46], allylbenzene [47], ethyne [48], and dichlorophenols [49]. The results of these studies and other recent findings [50] on the γ-Al₂O₃ supported Au-Ni catalysed ethanol conversion into hydrocarbons C₃–C₉ indicate that gold-nickel nanocomposites are promising for the cross-condensation of ethanol with isopropanol into other valuable chemicals.

This study compares the direct cross-condensation of ethanol with isopropanol in the presence of synergistic Au-Ni/Al₂O₃ catalyst and its monometallic analogues (Au/Al₂O₃ and Ni/Al₂O₃). This study is the first to investigate the catalytic performance of Au-Ni catalysts in this reaction. To describe the differences between the structure of supported metals in catalysts, X-ray diffraction (XRD) analysis, energy dispersive X-ray (EDX) analysis and transmission electron microscopy (TEM) analysis were performed. Structural investigations of Au-Ni/Al₂O₃, Au/Al₂O₃ and Ni/Al₂O₃ catalysts were conducted via X-ray photoelectron spectroscopy (XPS), infrared spectroscopy (IR) of adsorbed CO; X-ray absorption spectroscopy (XAS) was also performed and published earlier in reference [47]. The relationships between a compound's structure, activity and mechanistic aspects are discussed to clarify the factors that may affect the synergetic effect in the presence of the Au-Ni catalyst.

2. Experimental

2.1. Catalysts preparation

Gamma alumina (Catalyst LLC, grains ϕ = 0.5 mm, S = 160 m²/g) was used as a support for the catalysts. Aqueous solutions of Ni(NO₃)₂ and HAuCl₄ (Sigma-Aldrich, 98–99% pure) were used as metal precursors.

Ni/Al₂O₃ (Ni = 0.06 wt.%) catalyst was produced via impregnation, as described in reference [47]. Al₂O₃ (5 g, calcined at 400 °C for 3 h) was first impregnated with 5.5 mL of an aqueous solution containing the desired amount of nickel. Then, the wet solid was dried at 24 °C for 24 h and calcined at 400 °C for 6 h.

Monometallic Au/Al₂O₃ (Au = 0.2 wt.%) catalysts with a metal content similar to Ni/Al₂O₃ was produced via deposition-precipitation, as described in references [47,51]. An aqueous solution of HAuCl₄ with the desired concentration of gold was adjusted to pH = 7.0 by adding NaOH (0.1 M). Then, Al₂O₃ (10 g, calcined at 400 °C for 3 h) was dispersed in this solution while being stirred at 50 °C for 1 h. The solid was washed with water to remove Cl⁻, dried at 24 °C for 24 h, and calcined at 400 °C for 3 h. The obtained precursor was then separated into two parts: the first part (5 g) was calcined at 400 °C for 3 h to fabricate Au/Al₂O₃ (Au = 0.2 wt.%); the second part (5 g) was impregnated with an

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