



Mixed oxides supported low-nickel formulations for the direct amination of aliphatic alcohols with ammonia



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ABSTRACT

The present study focuses on the selective synthesis of primary amines from aliphatic alcohols and ammonia using alumina-ceria supported nickel formulations based on very low nickel loading (≤ 2 wt%) and without any additive or external H₂ supply. The effect of the catalyst preparation methods and modes of nickel impregnation were studied in detail and comprehensively characterized. The best formulation afforded 80% *n*-octanol conversion with 78% selectivity to *n*-octylamine at optimized reaction conditions, which were far better than control catalysts and benchmark Ni-alumina formulations relying on high Ni loadings. The enhanced activities of the alumina-ceria supported nickel catalysts was attributed to three combined effects: (1) a higher reducibility of surface nickel oxide species, (2) the genesis of very small and homogeneously distributed nickel nanoparticles (2–3 nm), and (3) a strong decline in the formation of nickel aluminates. Furthermore, unlike benchmark Ni catalysts, these formulations afforded a higher resistance to leaching.

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1. Introduction

Synthetic amines are extensively used as intermediates for the production of pharmaceuticals, agrochemicals, detergents, polymers, varnishes and dyes [1,2]. Alkylamines constitute a particular family of amines derived from fatty acids, olefins or alcohols issued either from natural sources (fats, oils) or from petrochemical raw materials. The global fatty amines market was valued at US\$ 1.7 Mn in 2014 and is estimated to grow to US\$ 2.2 Mn by 2020 mainly driven by the Asia-Pacific region excluding Japan (APEJ), accounting for more than 25% of the revenue share in 2014 [3]. The world market of alkylamines is segmented in 6 sectors: (1) water treatment, (2) agrochemistry, (3) oilfield, (4) asphalt additives, (5) anti-caking, and (6) others (personal care, mining, fabric softening, paints and coatings) [4,5]. Water treatment constitutes the largest market with more than 29% of the global revenue (2014), and it is anticipated to grow by 4.7% until 2020 [3].

Various methods are available for synthesizing alkylamines, including alkyl halide amination, reductive amination of ketones or aldehydes, hydroamination of olefins, hydroaminomethylation, and nitrile hydrogenation [6–11]. However, most of these methods suffer from poor selectivity to the desired amines, use toxic or

hazardous reagents, consume H₂ stoichiometrically, and/or produce significant amount of waste (e.g., salts). As an alternative, the alkylation of amines with (bio)alcohols appears as an eco-efficient method for amine production as water is generated as the main byproduct [12].

The most extended catalysts for the direct synthesis of amines from alcohols rely on homogeneous Ru and Ir complexes operating via the borrowing H₂ or H₂ auto-transfer mechanism without external H₂ supply [13–18]. In parallel, heterogeneous catalysts based on Raney Ni [19,20], and Ni [21–25], Cu [26–29], NiCu [30–32], NiCuFeO_x [33] and NiCuZn [34] nanoparticles supported over alkaline or amphoteric oxides have shown high versatility for the additive-free alkylation of amines and ammonia with aromatic and aliphatic alcohols. In particular, Shimizu and co-workers recently showed that 10 wt%Ni/θ-Al₂O₃ could afford high yields (70–96%) in the reaction of primary and secondary alcohols with excess ammonia at 160 °C for 13–72 h [23]. The major shortcoming of non-noble based catalysts is often ascribed to the use of large metal contents (most often >15 wt%), as well as to their heterogeneous particle size distributions and low metal dispersion, which impacts their activity for amination. High-Ni loaded formulations may result in the formation of a NiO crystalline phase on the support, resulting into large Ni particles and accordingly low Ni dispersion during the reduction process. Furthermore, high-Ni loaded catalysts are prone to Ni leaching upon exposure to

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ammonia and polar solvents, thereby affecting not only the catalytic activity, but also favoring the contamination of the amine product by Ni. In this context, the development of eco-efficient processes with stable and selective heterogeneous catalysts minimizing the Ni content for the direct amination of alcohols is hour of need.

Ceria is a well-known promoter that can modify the structural or electronic properties of catalysts in many industrial reactions such as automotive exhaust gas conversion (i.e. 3-way catalysts) [35–37], methane reforming with CO₂ and/or with steam, and water-gas shift reactions [38–42]. In particular, ceria is well known to enhance the thermal stability of alumina [43,44], reduce the Ni particle size and mitigate coke formation and metal sintering in Ni/ γ -Al₂O₃ catalysts, especially for CO methanation and steam-reforming reactions [39,40,42,45,46]. In parallel, several patents have reported the amination of aliphatic and ethoxylated alcohols relying mostly on Ni, Cu or Co, either in bulk form or supported over single and mixed oxides containing rare-earth oxides [47–52]. In particular, a process patented by Imperial Chemical Industries (UK) describes the amination of ethanol in the presence of a catalyst comprising NiO-CoO-Al₂O₃-CeO₂ prepared by co-precipitation in the presence of sodium carbonate [48]. The catalyst afforded 98% ethanol conversion to ethylamine, diethylamine and triethylamine with 43%, 44% and 13% yields, respectively, with the simultaneous formation of high boiling byproducts. A patent by BASF SE disclosed the use of a catalyst based on Cu supported over La₂O₃-Al₂O₃ support for the liquid-phase synthesis of secondary amines from primary and secondary alcohols such as ethanol, isopropanol and cyclohexanol and primary amines [52].

To the best of our knowledge, no report is available in neither the open nor the patent literature on low-Ni formulations (≤ 2 wt % Ni) for the direct amination of alcohols, especially over alumina. This is probably due to the fact that low-Ni formulations are poorly active for amination due to the formation of inactive surface Ni aluminates even when subjected to low calcination temperatures [53,54]. Ni-aluminates are also favored at higher Ni loadings (2–5 wt% Ni) at a calcination temperature >550 °C by promoting solid-state diffusion of Ni²⁺ cations into the alumina lattice [55–58]. Here we report for the first time a cooperative effect between alumina and ceria in 2 wt.%Ni/CeO₂-Al₂O₃ catalysts affording high activity and selectivity to primary amines in the liquid-phase direct amination reaction of *n*-octanol with ammonia.

2. Experimental

2.1. Materials

γ -Al₂O₃ (Puralox Sasol Scca-5/170, 154 m²/g), CeO₂ (Solvay HSA5, 250 m²/g), were used as supports for catalyst synthesis. Cerium nitrate hexahydrate (Ce(NO₃)₂·6H₂O, >99 wt%) and nickel nitrate hexahydrate (Ni(NO₃)₂·6H₂O, >99 wt%), both supplied by Sigma-Aldrich, were used as precursors for the synthesis of mixed oxides and for Ni impregnation, respectively. NaOH (>98 wt%) and citric acid monohydrate (>99 wt%) were procured from J&K. Aniline, benzyl alcohol, *n*-octanol and ammonia, all supplied by J&K (99.5% purity), were used in the catalytic tests. *o*-xylene (J&K, purity 99.5%) was used as solvent in the *n*-octanol/ammonia amination tests. *N*-benzylideneaniline, *N*-benzylaniline, *N,N*-dibenzylaniline, benzonitrile, toluene, benzene, *n*-octylamine, di-*n*-octylamine, trioctylamine and octanenitrile standards for GC calibration were all purchased from J&K (purity 99.5%). All the reactants were used as received without further purification.

2.2. Catalyst synthesis

The preparation of Ni-supported mixed oxides was divided into two steps. The first step focused on the synthesis of cerium-

aluminum mixed oxides (Ce-Al) (used as supports) using two different methods, whereas the second step encompassed Ni impregnation (2 wt%) over the mixed oxides either in the dried or calcined forms.

2.2.1. Ce-Al mixed oxides prepared by wet impregnation (WI)

In a typical preparation, 5 g of γ -Al₂O₃ suspended in 70 mL of deionized water in a two-neck round bottom flask were thermally treated at 145 °C for 1 h. Subsequently, 20 mL of an aqueous solution of cerium nitrate (2.65 g) were added for 20 min at a constant stirring speed of 600 rpm using a dropping funnel. The mixture was aged for 2 h, cooled down to room temperature and the excess water was slowly removed at 60 °C using a rotary evaporator. The final solid (yellowish) was dried in an oven overnight at 120 °C and further calcined at 500 °C for 6 h using a heating rate of 3 °C min⁻¹ in a muffle furnace under static air. The solid prepared by wet impregnation is hereinafter denoted as Ce-Al_WI.

2.2.2. Ce-Al mixed oxides by the co-precipitation (PPT)

A series of Ce-Al oxides were also synthesized by a co-precipitation method as described elsewhere [59]. In a typical preparation, 5 g of γ -Al₂O₃ suspended in 50 mL of deionized water in a two-neck round bottom flask were thermally treated at 80 °C for 1 h. A 20-mL solution of cerium nitrate was added to the above solution and stirred for 5 min. Subsequently, a 25-mL solution of NaOH and citric acid (NaOH/citric acid molar ratio = 1) was added during 20 min using a dropping funnel and the solution was further aged for 2.5 h. Finally, the solid mixture was cooled down to room temperature, vacuum filtered and thoroughly washed until neutral pH using ca. 2 L deionized water. The as-obtained solid (yellowish) was dried overnight at 120 °C and further calcined at 500 °C for 6 h in a muffle furnace using a heating rate of 3 °C min⁻¹ under static air. The solid prepared by co-precipitation is hereinafter denoted as Ce-Al_PPT.

2.2.3. Ni impregnation over mixed oxides by the IWI method

Nickel (2 wt% nominal loading) was impregnated by Incipient Wetness Impregnation (IWI) over the prepared mixed oxides (Ce-Al_WI and Ce-Al_PPT). Before impregnating the nickel nitrate solution, the dried mixed oxides were divided into two halves. On the one hand, one half of the dried mixed oxide was directly impregnated with the nickel nitrate solution and then calcined at 500 °C for 6 h in a muffle furnace. On the other hand, the second half of the dried mixed oxide was subjected to a first calcination step at 500 °C for 6 h before impregnation and then calcined at similar conditions. Two routes for Ni impregnation were considered, namely after (A) and before (B) calcination. The final samples displayed different characteristic colors regardless of the support (Fig. S1).

Along with the above-mentioned catalysts, control monometallic catalysts were also prepared, namely 2Ni/Al₂O₃, 8Ni/Al₂O₃ and 2Ni/CeO₂-HS_300 (CeO₂_HS pre-calcined at 300 °C before Ni impregnation). All the catalysts were prepared by the IWI method using the nickel nitrate solution and then calcined at 400 °C for 2 h in a muffle furnace.

2.3. Catalyst characterization

The bulk metal composition of the calcined catalysts was measured using a Varian Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) available at the REALCAT platform at UCCS Lille. Before the analyses, the dried and ground sample (10 mg) was dissolved in 1.5 mL of concentrated *aqua regia* and 250 μ L of HF solution. The solutions were heated to 50 °C and stirred for 24 h.

The specific surface area and pore volume of the different catalysts was measured from N₂ adsorption/desorption isotherms at

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