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Facile preparation of Ni/Al_2O_3 catalytic formulations with the aid of cyclodextrin complexes: Towards highly active and robust catalysts for the direct amination of alcohols

Ajay Tomer [a,b], Frédéric Wyrwalski [a], Cédric Przybylski [c], Jean-François Paul [a], Eric Monflier [a], Marc Pera-Titus [b,*], Anne Ponchel [a,*]

[a] Univ. Artois, CNRS, Centrale Lille, ENSCL, Univ. Lille, UMR 8181, Unité de Catalyse et de Chimie du Solide (UCCS), F-62300 Lens, France
[b] Eco-Efficient Products and Processes Laboratory (E2P2L), UMR 3464 CNRS-Solvay, Shanghai 201108, PR China
[c] Sorbonne Universités, Université Pierre et Marie Curie, IPCM-CNRS UMR 8232, Paris, France

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ABSTRACT

A series of Ni/Al_2O_3 catalysts with variable Ni loading (2–20 wt%) were prepared by aqueous wet impregnation of a nitrate precursor using native cyclodextrins as metal complex hosts. The impact of β-CD was carefully characterized at different stages of the preparation by a set of complementary techniques including TG-MS analysis, mass spectrometry, X-ray diffraction, temperature-programmed reduction, CO pulse chemisorption, X-ray photoelectron spectroscopy and electron microscopy. It was found that the use of cyclodextrins afforded a much higher Ni dispersion and narrower distribution of Ni particle sizes, as well as a much higher availability of reduced surface Ni species. As a result, the cyclodextrin-assisted catalysts exhibited enhanced catalytic properties in the direct amination of benzyl alcohol with aniline and 1-octanol with ammonia, both operated *via* the hydrogen borrowing mechanism. Furthermore, the use of cyclodextrins allowed a significant improvement of the robustness of the catalysts by mitigating the nickel leaching during reaction.

1. Introduction

Amines are N-containing intermediates with a broad variety of applications, serving as building blocks in the manufacture of agrochemicals, pharmaceuticals, detergents, polymers, solvents and dyes [1]. The world demand of amines is expected to increase by 8% in the following years mainly driven by China and other Asian markets to reach a value of $ 20 billion US by 2020. Although the amine industry has attained a position of maturity, it still faces numerous challenges, especially when regarding the synthesis of primary alkylamines. The existing processes often lack of selectivity, producing a mixture of amines and/or encompassing hazardous reagents and waste (*e.g.*, salts) [2]. As an alternative, the direct amination with alcohols could become an eco-efficient strategy, since water is formed as sole byproduct and the process is compatible with biorefineries [3–5].

The direct amination of alcohols proceeds over metals *via* a H_2 borrowing or H_2 autotransfer mechanism. This tandem mechanism, which has been well described for organometallic cata-lysts based on Ru and Ir, [6–12] comprises three consecutive steps: (1) dehydrogenation of the alcohol to an aldehyde/ketone, (2) formation of an imine or enamine intermediate by fast condensation of the carbonyl with ammonia or an amine, and (3) hydrogenation of the imine to give the final amine. In this mechanism, H_2 is temporally borrowed by the action of the catalyst from the alcohol to the imine.

The most studied heterogeneous catalysts for the direct synthesis of amines from long-chain (fatty) alcohols *via* the H_2 borrowing mechanism rely on Ni and Cu comprising Raney Ni [13–16] as well as Ni [17–22], Cu [23–28], NiCu [29–32], $NiCuFeO_x$ [33] or NiCuZn [34] supported over alkaline or amphoteric oxides. In particular, Shimizu and co-workers recently showed that 10 wt% $Ni/\theta\text{-}Al_2O_3$ could afford high yields (70–96%) in the reaction of primary and secondary alcohols with excess ammonia at 160 °C for 13–72 h [20]. The major shortcoming of Ni and Cu catalysts is ascribed to their large metal contents (most often >15 wt%), as well to their heterogeneous particle distribution and poor dispersion, which impact negatively their activity for amination. Furthermore, high Ni/Cu loaded catalysts are prone to leaching upon exposure to ammonia and polar solvents.

* Corresponding authors.
E-mail addresses: marc.pera-titus-ext@solvay.com (M. Pera-Titus), anne.ponchel@univ-artois.fr (A. Ponchel).

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Since the size of metal clusters, their dispersion and degree of reduction largely determine the catalytic activity for direct alcohol amination, the optimization of catalyst preparation through simple and reliable protocols remains of fundamental importance. Conventional metal-supported catalysts are often prepared by aqueous impregnation of a water-soluble metal salt precursor (generally nitrate) followed by calcination and reduction under H_2. The direct introduction of organic additives in the impregnation solution has been reported as a simple method for improving the dispersion and tuning the morphology of metal nanoparticles over supports while reducing the metal-support interaction. This is the case for instance of cyclodextrins (CDs) [35–37]. Native CDs are cyclic oligosaccharides with 6 (α-CD), 7 (β-CD) or 8 (γ-CD) glucopyranose units connected through glycosidic α-1,4 bonds generating a characteristic doughnut-shaped structure [38,39]. This particular structure allows not only the formation of inclusion complexes with a wide variety of organic compounds, but also the formation of adducts with inorganic metal salts, which can find applications as capping agents or templates in the synthesis of nanoparticles and materials [40–44].

In 2011, Khodakov and Monflier reported the first application of CDs in the preparation of alumina-supported Co catalysts for Fischer-Tropsch synthesis. The addition of β-CD to the cobalt nitrate impregnation solution afforded higher metal dispersions (after calcination at 400 °C) and a higher metal reducibility, resulting in a higher hydrocarbon productivity [35]. The use of CDs was further extended to the preparation of zirconia-supported cobalt oxide catalysts (5 wt% Co) for the total oxidation of formaldehyde. Both the nature of the cobalt precursor and the β-CD/Co molar ratio played a crucial role on the catalytic performance of Co_3O_4/ZrO_2 catalysts by enhancing the dispersion and reducibility of the cobalt active species [36,37]. The most striking effects were observed with the optimized catalyst prepared from a cobalt nitrate precursor with a β-CD/Co molar ratio of 0.1, resulting in a drop by 20 °C in the light-off temperature. This optimal ratio was related to the ability of β-CD to interact with $Co(NO_3)_2$ by forming ion-molecule complexes, where Co(II) cations are coordinated between two O atoms of the hydroxyl groups at the β-CD rim (note that β-CD has 21 OH groups in total). The use of β-CD as additive for metal impregnation over supports was also applied to other catalytic transformations [45–47]. For example, He and coworkers reported the beneficial effect of native CDs on the Ni dispersion over silica supports (SBA-15, MCM-41, 5 wt% Ni), resulting in a higher activity and resistance against coke deposition for the dry reforming of methane [46,47].

Herein, we concentrate our attention on the preparation of Ni/Al_2O_3 catalysts assisted by CDs (CD/Ni = 0.1) for the synthesis of primary amines from aliphatic alcohols *via* the H_2 borrowing mechanism. In particular, we studied the effect of β-CD addition with respect to the metal content in the supported catalysts (range 2–20 wt% Ni) to assess the versatility of the preparation method. Detailed characterization of the different CD-assisted Ni/Al_2O_3 catalysts was conducted, underlying the main benefits of β-CD for achieving homogeneous particle size distributions and preferential surface Ni species while discouraging the formation of inactive Ni aluminates. Finally, the catalytic performance was assessed in the direct amination of benzyl alcohol (chosen as a model reaction), and more importantly in the direct amination of 1-octanol with NH_3, aiming at promoting the selectivity to the value-added primary 1-octylamine.

2. Experimental section

2.1. Materials

γ-Al_2O_3 (Puralox SCCA 5/170, 154 $m^2\ g^{-1}$) was purchased from SASOL and used without further pre-treatment. Nickel nitrate hexahydrate $Ni(NO_3)_2{\cdot}6H_2O$ (>99 wt%) was procured from Sigma Aldrich, China. Native β-cyclodextrin was supplied by Roquette Frères (Lestrem, France) whereas α- and γ-cyclodextrins were purchased from Wacker Chemie. The reactants aniline, benzyl alcohol, 1-octanol and ammonia, all supplied by J&K Scientific, China (99.5% purity), were used in the catalytic tests. O-xylene (J&K, 99.5% purity) was used as solvent in the 1-octanol/ammonia catalytic tests. N-benzylideneaniline, N-benzylaniline, N,N-dibenzylaniline, benzonitrile, toluene, benzene, 1-octylamine, dioctylamine, trioctylamine and octanenitrile standards for GC calibration were all purchased from J&K (purity 99.5%). All the reactants were used without further purification.

2.2. Catalyst preparation

A series of Ni oxide catalysts with Ni loading in the range 2–20 wt% were synthesized by wet impregnation using an aqueous solutions of Ni nitrate and β-CD as follows: Ni(II) nitrate hexahydrate solutions based on different concentrations was added to 250 mL of an aqueous solution containing 0.1 M equivalent of native β-CD ($C_{42}H_{47}O_{35}$, M = 1134 g mol^{-1}). This solution was kept under stirring for 2 h at room temperature. The alumina support (5 g) was then added to the solution and the as-generated solid suspension was further stirred for 2 h. After this period, water was slowly removed at 60 °C until dryness using a rotary evaporator. The recovered solid was dried overnight in an oven at 100 °C and calcined at 400 °C for 4 h using a heating ramp of 2 °C min^{-1} under air flow (2 L(STP)/h). The final catalysts were denoted as *x*Ni/Al-CD*y* where *x* corresponds to the wt% Ni loading and *y* corresponds to the β-CD/Ni molar ratio (*y* = 0.1). Some catalysts were also synthesized using α-CD and γ-CD at a CD/Ni molar ratio of 0.1. Likewise, a series of Ni-alumina catalysts were also synthesized by the wet impregnation method without CD, which are hereinafter designated as *x*Ni/Al, where *x* stands for the wt% Ni loading.

2.3. Catalyst characterization

Thermogravimetry – Mass Spectrometry (TG-MS). TG measurements were performed using a TA SDT 2960 instrument equipped with a gas flow system. The solid was treated from room temperature to 800 °C (5 °C min^{-1}) under a gas mixture composed of He (80 vol%) and O_2 (20 vol%) with a flow rate of 75 mL(STP) min^{-1}. Approximately, 10 mg of sample was heated in an open Pt crucible. The temperature-programmed decomposition products were *in-situ* analyzed using a Pfeiffer vacuum Omnistar GSD 320 mass spectrometer.

Electrospray ionization-Mass Spectrometry (ESI-MS). Electrospray-mass spectrometry (ESI-MS) experiments were performed using a LTQ-Orbitrap XL from Thermo Scientific (San Jose, CA, USA) and operated in positive ionization mode, with the spray voltage at +3.85 kV and a sheath and auxiliary gas flow at 45 and 15 a.u., respectively. α-, β- and γ-CD at 10 μM in water/methanol 1/1 (v:v) with or without a nickel nitrate were continuously infused at 5 μl min^{-1} using a 250-μL syringe. The applied voltages were +40 and +100 V (positive mode) for the ion transfer capillary and the tube lens, respectively. The ion transfer capillary was held at 275 °C. The resolution level was set to 30,000 (m/z = 400) for all the studies, while the m/z range was set to 300–2000 m/z in the profile mode and in the normal mass ranges during full scan experiments. The spectra were analyzed using the acquisition software XCalibur 2.0.7 (Thermo Scientific, San Jose, CA, USA) without smoothing and background substraction. Higher energy collision dissociation (HCD) experiments were performed with an activation time of 100 ms according to a previous study [48] and occurred in an octopole collision cell aligned to the C-trap and detection in the Orbitrap in centroid mode. This dedicated cell was supplied with