Facile preparation of Ni/Al_2O_3 catalytic formulations with the aid of cyclodextrin complexes for the direct amination of aliphatic alcohols with NH_3

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

[a]*Univ. Artois, CNRS Centrale Lille, ENSCL, Univ. Lille, UMR 8181, Unite de Catalyse et de Chimie du Solide (UCCS), F-62300 Lens, France*

[b]*Eco-Efficient Products and Process Laboratory (E2P2L), UMI 3464 CNRS-Solvay, Shanghai, 201108, PR China*

[c]*Sorbonne Universités, Université Pierre et Marie Curie, IPCM-CNRS UMR 8232, Paris, 75252, France*

**Corresponding authors: +86 (0)21 2408 9267, marc.pera-titus-ext@solvay.com; anne.ponchel@univ-artois.fr*

Abstract: A series of Ni/Al_2O_3 catalysts with variable Ni loading (3-20 wt. %) were prepared by aqueous wet impregnation of a nitrate precursor using native cyclodextrins (CDs) as metal complex hosts and the prepared catalysts were carefully characterized at different stages of the preparation by a set of complementary techniques. The use of CDs afforded a much higher Ni dispersion, a narrower size distribution of Ni nanoparticles and much higher availability of reduced surface Ni species. As a result, CD-assisted catalysts exhibited enhanced catalytic properties in the direct amination of benzyl alcohol with aniline and 1-octanol with ammonia.

Keywords: Cyclodextrin, Alcohol-amination, Nickel-alumina.

1. Introduction

Amines are N-containing intermediates with a broad variety of applications in the chemical industry as solvents, agrochemicals, pharmaceuticals, detergents and fabric softeners.[1] The direct amination of alcohols *via* the hydrogen borrowing mechanism is a promising strategy for preparing amines, since no external hydrogen is required and water is the main byproduct.[2] The most studied heterogeneous catalysts for the direct amination of alcohols rely on Ni[3] and Cu[4] nanoparticles supported over alkaline or amphoteric oxides, which are often prepared by conventional impregnation methods. A major shortcoming of these catalysts is ascribed to their large metal contents (>10 wt.%), as well as to their heterogeneous particle distribution and poor dispersion. In our quest to more active formulations, cyclodextrins (CDs) have recently emerged as potential agents assisting the preparation of metal or metal oxide materials.[5] Herein, we report the CDs-assisted synthesis of Ni/Al_2O_3 catalysts and their catalytic performance in the direct amination of alcohols along with detail characterization of their surface and morphological properties.

2. Experimental

The catalysts were prepared by a wet impregnation method in the presence of CD (CD/Ni molar ratio = 0.1) followed by drying and calcination. To understand the effect of CD on the physicochemical properties, the as-prepared catalysts were characterized in the dry state by TG-MS and ESI-MS and in the calcined state by BET, XRD and *in-situ* XRD, H_2-TPR, CO pulse chemisorption, XPS and TEM. The amination of benzyl alcohol with aniline was carried out in Biotage sealed vials at 140 °C for 1 h with 35 mg of pre-reduced catalyst under Ar atmosphere, while 1-octanol amination with ammonia was conducted in an autoclave at different temperatures (160 and 180 °C) for 4 h with 7 bar NH_3 and 55 mg of pre-reduced catalyst. Recycle tests were performed on the spent catalysts to assess the heterogeneity of the different formulations, and the metal content was measured by ICP.

3. Results and discussion

TG-MS analysis of dried catalysts revealed that the decomposition temperature of nitrate to NO was consistent with that of CD to CO_2 and H_2O indicating that both the nitrate and CD are intimately linked within the dried oxides. Among the native CDs (α, β, γ), β-CD was found to outstand in catalytic activity owing to the formation of stable binary and ternary complexes with the nickel nitrate precursor, as evidenced by ESI-MS experiments. From *in-situ* XRD, the reflection lines of NiO and Ni displayed a weak intensity, indicating a smaller crystallite size, whereas the reduction of NiO to Ni was lowered by 50 °C in the CD-assisted catalyst. Likewise, an enhanced reducibility and higher proportion of surface nickel species was obtained in the catalysts synthesized with β-CD as shown in Table-1. A higher catalytic activity and selectivity to the primary amine (octylamine) was obtained in the amination of 1-octanol with ammonia over the catalysts prepared in the presence of CD (i.e. xNi/Al-β-CD, x = 5-15 wt.%) compared to the control catalysts (Figure 1-A). These beneficial effects are associated to the higher dispersion and reducibility of nickel species over the alumina support. Furthermore, the use of β-CD during the Ni impregnation afforded catalysts with higher robustness by discouraging Ni leaching during the amination reaction(Figure 1-B).

Table 1. Reducibility and physicochemical properties of Ni/Al catalysts synthesized in this study.

Sample	T (°C) Surf Ni (β1+β2) [a]	%Red^n Ni_2O_3	%Red^n Bulk Ni (α)	%Red^n Surf Ni (β1+β2) [b]	%Red^n $NiAl_2O_4$ (γ)	Dispersion (%D)[c]	Metal surf. area ($m^2_{Ni} \cdot g_{Ni}^{-1}$) [c]	Particle size (nm) [c]
5Ni/Al	558	0	13	49	21	14.2	94.7	7.1
5Ni/Al-β-$CD_{0.1}$	502	0	6	70	23	19.8	132.6	5.1
10Ni/Al	563	9	18	67	6	13.5	90.2	7.6
10Ni/Al-β-$CD_{0.1}$	529	2	3	89	6	21.9	146.0	4.5
15Ni/Al	565	7	31	60	2	12.9	86.3	7.8
15Ni/Al-β-$CD_{0.1}$	531	3	6	87	4	19.7	131.6	5.1

[a] from H_2-TPR, [b] calculated by integration in the temperature range 450-750 °C in H_2-TPR, [c] from CO pulse chemisorption

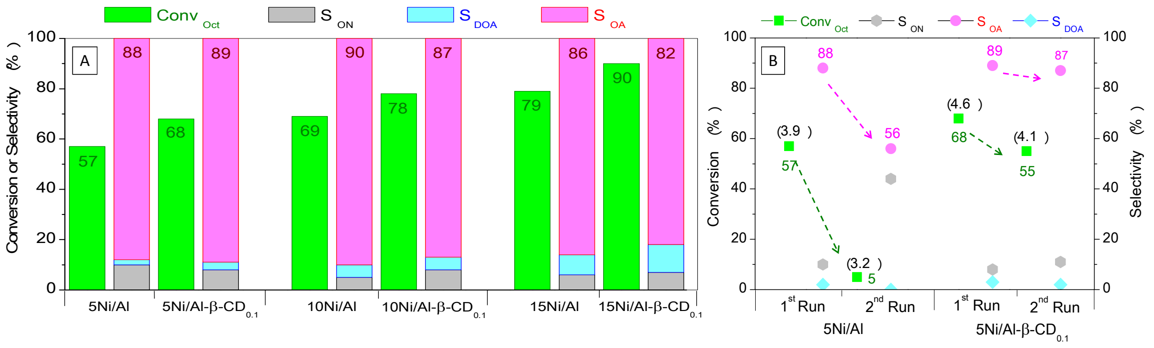

Figure 1. Amination of 1-octanol with NH_3; A) Effect of Ni loading, B) Recycling study. Reaction conditions: 1-octanol-1.3 mmol, T- 160 °C, NH_3- 7 bar, Time- 4 h, rpm- 600, Solvent- 3mL o-xylene, Cat.-55 mg.

4. Conclusions

In short, a simple preparation method of alumina-supported Ni catalysts using native cyclodextrins as water-soluble additive *via* wet impregnation was developed. The enhanced activity of β-CD-assisted catalysts was attributed to the ability of generating stable complexes with the Ni nitrate precursor, delaying its decomposition upon calcination. As a result, a higher Ni dispersion and reducibility of NiO species, as well as a more homogeneous particle size distribution could be obtained. A 70% yield to octylamine was achieved in the reaction of 1-octanol with NH_3 with a saving of 50% Ni for CD-assisted catalysts compared to the control catalysts.

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