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# Facile preparation of Ni/Al<sub>2</sub>O<sub>3</sub> catalytic formulations with the aid of cyclodextrin complexes: Towards highly active and robust catalysts for the direct amination of alcohols



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#### ABSTRACT

A series of Ni/Al<sub>2</sub>O<sub>3</sub> 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  $\beta$ -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 cyclodextrinassisted 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.

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# 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<sub>2</sub> 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<sub>2</sub> 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<sub>x</sub> [33] or NiCuZn [34] supported over alkaline or amphoteric oxides. In particular, Shimizu and co-workers recently showed that 10 wt% Ni/ $\theta$ -Al<sub>2</sub>O<sub>3</sub> 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.

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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<sub>2</sub>. 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 ( $\alpha$ -CD), 7 ( $\beta$ -CD) or 8 ( $\gamma$ -CD) glucopyranose units connected through glycosidic  $\alpha$ -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  $\beta$ -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  $\beta$ -CD/Co molar ratio played a crucial role on the catalytic performance of Co<sub>3</sub>O<sub>4</sub>/ZrO<sub>2</sub> 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  $\beta$ -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  $\beta$ -CD to interact with Co(NO<sub>3</sub>)<sub>2</sub> by forming ionmolecule complexes, where Co(II) cations are coordinated between two O atoms of the hydroxyl groups at the  $\beta$ -CD rim (note that  $\beta$ -CD has 21 OH groups in total). The use of B-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<sub>2</sub>O<sub>3</sub> catalysts assisted by CDs (CD/Ni = 0.1) for the synthesis of primary amines from aliphatic alcohols *via* the H<sub>2</sub> borrowing mechanism. In particular, we studied the effect of  $\beta$ -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<sub>2</sub>O<sub>3</sub> catalysts was conducted, underlying the main benefits of  $\beta$ -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<sub>3</sub>, aiming at promoting the selectivity to the value-added primary 1-octylamine.

#### 2. Experimental section

# 2.1. Materials

 $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (Puralox SCCA 5/170, 154 m<sup>2</sup> g<sup>-1</sup>) was purchased from SASOL and used without further pre-treatment. Nickel nitrate hex-

ahydrate Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (>99 wt%) was procured from Sigma Aldrich, China. Native  $\beta$ -cyclodextrin was supplied by Roquette Frères (Lestrem, France) whereas  $\alpha$ - and  $\gamma$ -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  $\beta$ -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<sup>-1</sup>). 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<sup>-1</sup> under air flow (2 L(STP)/h). The final catalysts were denoted as xNi/Al-CDy where x corresponds to the wt% Ni loading and y corresponds to the  $\beta$ -CD/Ni molar ratio (y = 0.1). Some catalysts were also synthesized using  $\alpha$ -CD and  $\gamma$ -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 xNi/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<sup>-1</sup>) under a gas mixture composed of He (80 vol%) and O<sub>2</sub> (20 vol%) with a flow rate of 75 mL(STP) min<sup>-1</sup>. Approximately, 10 mg of sample was heated in an open Pt crucible. The temperature-programmed decomposition products were *insitu* 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.  $\alpha$ -,  $\beta$ - and  $\gamma$ -CD at 10  $\mu$ M in water/methanol 1/1 (v:v) with or without a nickel nitrate were continuously infused at 5  $\mu$ l min<sup>-1</sup> using a 250- $\mu$ L 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 an rf voltage (2.6 MHz, 500 Vp-p), where the DC offset can be varied by 250 V and crossed with nitrogen gas at a pressure of  $5.10^3$ mbar. The endcap voltage was controlled using normalized collision energy (NCE) technology, where the collision energy was modified for each experiment and was expressed in% of NCE. The peak-to-peak voltage was scaled as Vp-p = NCE/30 × (a(m/z) + b), where a and b are the instrument variable parameters set to 0.002 and 0.4, respectively. The standard range was 0-100% corresponding to 0-500 V. During the survival yield experiments, the NCE was varied from 0 to 50%. The precursor selection window was set to m/z = 2.5 during MS/MS experiments. The automatic gain control (AGC) allowed accumulation up to 10<sup>6</sup> ions for FTMS scans, 3.10<sup>5</sup> ions for FTMSn scans and 3.10<sup>4</sup> ions for ITMSn scans. The maximum injection time was set to 500 ms for both FTMS and FTMSn scans and 100 ms for ITMSn scans. For all scan modes. 1 uscan was acquired.

*BET analysis.* N<sub>2</sub> adsorption/desorption isotherms were measured at -196 °C using an ASAP2020 Micromeritics AutoChem apparatus after degassing the samples overnight at 100 °C. The specific area was computed using the Brunauer-Emmett-Teller (BET) equation in the P/P<sub>0</sub> range 0.05–0.25, while the pore size distribution was measured from the desorption branch using the Barrett-Joyner-Halenda (BJH) method.

Room temperature and in-situ X-Ray diffraction (XRD). At normal configuration (room temperature), the XRD experiments were conducted on a Bruker D8 Advance diffractometer in Bragg Brentano geometry equipped with a copper anode ( $\lambda = 1.5418$  Å) and a 1D PSD Lynxeye detector. The scattering intensities were measured in the range  $5^{\circ} < 2\theta < 80^{\circ}$  with a step size of 0.02°. The diffraction patterns were indexed by comparison with JCPDS files. In-situ temperature controlled XRD patterns were measured to assess the structural changes that may occur during the thermal reduction of the catalyst under H<sub>2</sub>. The measurements were conducted on a Bruker D8 diffractometer equipped with a Vantec 1 PSD detector and an Anton Paar HTK 1200N chamber connected to a gas line. The powder sample was placed in its calcined form on a Pt holder and the XRD measurements ( $30^{\circ} < 2\theta < 70^{\circ}$ ) were performed under H<sub>2</sub> flow (5% vol.. 2 L(STP)  $h^{-1}$ ) from room temperature to 800 °C (5 °C·min<sup>-1</sup>) with a scan every 25 °C, hold at 800 °C for 1 h with two scans, and then decrease in temperature  $(50 \circ C \cdot min^{-1})$  with a scan every  $100 \circ C$ .

 $H_2$ -Temperature programmed reduction ( $H_2$ -TPR).  $H_2$ temperature programmed reduction was used to assess the reducibility of the different catalysts. The reduction profiles were measured using a Micromeritics AutoChem 2920 instrument equipped with a thermal conductivity detector (TCD) and a cold trap before the detector. The profiles were recorded by reducing *ca*. 75 mg of sample under 5%  $H_2$ -Ar flow (40 mL(STP) min<sup>-1</sup>) and heating the sample from 30 °C to 1000 °C using a heating rate of 10 °C min<sup>-1</sup>. The  $H_2$  consumption was used to measure the reduction level of the different nickel oxide species present in the calcined samples.

*CO pulse chemisorption.* Pulse CO chemisorption measurements were carried out on a Micrometrics AutoChem 2920 instrument. Briefly, a known amount of sample (*ca.* 100 mg) was pre-reduced under H<sub>2</sub> at 580 °C for 30 min using a heating rate of 10 °C min<sup>-1</sup>. Later on, the sample was cooled down to 50 °C and then CO chemisorption analysis was performed by introducing successive pulse doses of 5% CO-He. Most often, the chemisorption process occurred in the first few pulses and the pulse area was smaller than the sequential pulse area. The chemisorption was repeated until the pulse area peaks exhibited no longer change.

X-ray photoelectron spectroscopy (XPS). The surface composition of the synthesized catalysts was analyzed by XPS using a Kratos Axis Ultra DLD apparatus equipped with a hemi-spherical analyzer and a delay line detector. The spectra were recorded using an Al monochromated X-ray source (10 kV, 15 mA) with a pass energy of 40 eV (0.1 eV/step) for high resolution spectra, and a pass energy of 160 eV (1 eV/step) for survey spectrum in hybrid mode and slot lens mode, respectively. The adventitious C1s binding energy (285.0 eV) was used as an internal reference. Prior to the measurements, the samples were reduced in a pre-treatment chamber at 580 °C for 30 min under a H<sub>2</sub> flow (50 mL (STP)/min).

TEM & SEM-EDX. TEM/STEM was performed using a Tecnai microscope operating at an accelerating voltage of 100 kV with a resolution point of 4.5 Å. Before analysis, the solid powder was directly dispersed over the carbon coated copper grid. Several micrographs from different areas of the sample were taken. The size distribution of the nanoparticles was estimated after the measurement of 50 particles through a manual analysis of micrographs with Image J software using Origin 8 Pro to generate the particle size distributions.

## 2.4. DFT calculations

The DFT calculations were performed using the VASP package [49–51] relying on the GGA PBE [52] functional to compute energies and including an implicit solvation module [53,54]. The Kohn-Sham equations were solved until the energy was converged within  $10^{-6}$  eV and the electron ion interactions were described using PAW pseudo potential [55]. The cut off energy was set to 450 eV and due to the size of the unit cell ( $25 \times 25 \times 25 \text{ Å}^3$ ) the calculations were performed at the gamma-point. The molecules placed on the center of the unit cell were fully optimized without any constraint until the force was lower than 0.03 eV Å<sup>-1</sup>.

#### 2.5. Catalytic tests in amination reactions

The performance of the different Ni catalysts was evaluated first in the model amination reaction of benzyl alcohol with aniline (Scheme 1). In typical conditions, the reaction was performed using 2 mmol of aniline, 6 mmol of benzyl alcohol and 35 mg of catalyst at 140 °C for 1 h using Biotage microwave vials under atmospheric N<sub>2</sub> pressure and a stirring speed of 600 rpm. Likewise, the reaction of 1-octanol with ammonia was performed in a 30-mL stainless steel autoclave equipped with a pressure gauge and a safety valve (Scheme 2). In a given experiment, the reactor was charged with a known amount of 1-octanol (1.3 mmol) and a known amount of pre-reduced catalyst (55 mg). The reactor was sealed and evacuated by applying vacuum followed by ammonia charging (7 bar). The reactor was then placed on a hot plate equipped with a magnetic stirrer and the reaction was conducted at different temperatures (160 °C, 180 °C) for 4 h.

The reactants (aniline, benzyl alcohol and 1-octanol) and the expected products for both reactions, i.e. N-benzylideneaniline (BZIA), N-benzylaniline (BZA), N,N-dibenzylaniline (DBZA), octylamine (OA), dioctylamine (DOA), trioctylamine (TOA), octanenitrile (ON) and 1-octanol were analyzed and quantified using an Agilent 7890 GC equipped with a J&W Scientific HP-5 capillary column (30 m  $\times$  0.32 mm  $\times$  0.25 µm) with 5 wt% phenyl groups. In addition to the above stated main products, toluene (Tol) was formed in the model reaction as side product by dehydroxylation of benzyl alcohol. Biphenyl was used as the internal standard. Mass balances were accurate to within 5% for all the catalytic tests. The conversion of the limiting reactant (LR: aniline and 1-octanol), selectivity, normalized selectivity and yield to the N-containing products were defined as follows:

Conversion (%) = 
$$1 - \frac{n_{LR}}{n_{LR}^o} * 100$$



Scheme 1. Potential amination products in the reaction between benzyl alcohol with aniline.



Scheme 2. Potential amination products in the reaction between 1-octanol with ammonia.

$$\text{Selectivity}_i~(\%) = \frac{n_i}{n_{\text{LR}}^{\text{o}} - n_{\text{LR}}} * 100$$

Normalized selectivity (%) =  $\frac{n_i}{\sum n_i} * 100$ 

 $Yield_{i} (\%) = \frac{n_{i}}{n_{LR}^{o}} * 100$  (1)

Carbon balance =  $\frac{\text{Moles of formed product} + \text{reactants}}{\text{Moles of reactants}}$ 

where  $n_{LR}^{o}$  and  $n_{LR}$  refer to the initial and final mole number of the limiting reactant, respectively, whereas  $n_i$  corresponds to the mole number of the N-containing products formed. Each catalytic run was performed in duplicate and the reported results are the average between two runs with an uncertainty equal or less than 3%.

# 3. Results and discussion

3.1. Characterization of the dried catalysts by thermogravimetric analysis coupled to mass spectrometry (TG-MS)

The ability of  $\beta$ -CD to interact with the Ni nitrate precursor was first investigated in the dried state by TG-MS at a Ni/β-CD molar ratio of 0.1. Fig. 1 plots the thermal profiles of the alumina support wet-impregnated with Ni nitrate alone (5Ni/Al), and Ni nitrate with  $\beta$ -CD (5Ni/Al- $\beta$ -CD<sub>0.1</sub>) after drying at 100 °C (see Section 2 for further details). For comparison, the TG-MS results obtained with a Ni-free control sample prepared by  $\beta$ -CD impregnation onto the parent alumina (Al- $\beta$ -CD<sub>0.1</sub>) are also provided. The thermal profile of Al- $\beta$ -CD<sub>0.1</sub> exhibits a two-step decomposition process with a total weight loss of ca. 13% at 800 °C. The first weight loss (2%) in the temperature range 50-200 °C corresponds to the removal of physically adsorbed water, whereas the second weight loss (11%) in the range 260–370 °C with a major weight loss at ca. 277 °C is attributable to the thermal decomposition of  $\beta$ -CD (Fig. 1A) [56]. The thermal pattern of 5Ni/Al also exhibits a two-step decomposition process with a first weight loss at a temperature below 120 °C corresponding to the desorption of physically adsorbed water, and a second weight loss in the temperature range 200-500 °C corresponding to nitrate decomposition (Fig. 1B). The total weight loss for this sample is ca. 14%. This value is close to the weight loss (16%) that can be expected by assuming total conversion of fully hydrated Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O into NiO. The low intensity of the mass fragmentogram corresponding to the signal of NO release at m/z = 30 suggests that the nitrate precursor decomposed very early during Ni impregnation, most likely along the drying step. The presence of weak NO release bands decomposing at higher temperature and

at a much broader temperature range 250–400 °C suggests the presence of Ni nitrate species with a high affinity for the support.

 $5Ni/Al-\beta-CD_{0,1}$  displays a markedly different thermal pattern with three distinct weight loss regions (Fig. 1C). The total weight loss of 20.5% is in good agreement with the value of 19.5% corresponding to the theoretical weight loss for complete decomposition of Ni nitrate hexahydrate into NiO. The first weight loss below 120 °C is attributed to physically adsorbed H<sub>2</sub>O, the second and most distinct weight loss between 150 °C and 250 °C is due to the decomposition of nitrate ions, and the third weight loss above 275 °C refers to the thermal decomposition of free β-CD, as previously evidenced in the thermal pattern of  $Al-\beta-CD_{0,1}$  (Fig. 1A). This interpretation is consistent with the mass fragmentograms. The decomposition of  $\beta$ -CD in 5Ni/Al- $\beta$ -CD<sub>0.1</sub> exhibits two CO<sub>2</sub> bands (m/z = 44) centered at 212 °C and 275 °C, respectively. The first band, matching perfectly the NO release band, can therefore be attributed to the interaction between β-CD and the nickel nitrate salt. The second band can be at first sight ascribed to the decomposition of  $\beta$ -CD free from interaction with the precursor. This hypothesis can be further confirmed by comparing the bands at 275 °C for 5Ni/Al-β-CD<sub>0.1</sub> and Al-β-CD<sub>0.1</sub>. Note also that the presence of a band at 210 °C, which can be attributed to nitrate decomposition into NO (Fig. 1C, m/z = 30), is consistent with the decomposition of part of the  $\beta$ -CD into CO<sub>2</sub> and H<sub>2</sub>O, as evidenced by the bands at 212 °C and 213 °C, respectively (Fig. 1C, m/z = 44and m/z = 18). These similar temperatures strongly suggest that both β-CD and the Ni nitrate precursor are intimately linked together within the dried oxide catalyst and that their interaction significantly accelerates the decomposition of the oligosaccharide with a temperature difference of  $\sim$ 70 °C. Furthermore, it is worth mentioning that the signal accounting for Ni nitrate decomposition in the MS spectrum of  $5Ni/Al-\beta-CD_{0.1}$  is also much more intense than that observed for 5Ni/Al (compare the profiles at m/z = 30, Fig. 1C and B). The latter observation suggests that an important portion of the nitrate species coming from the Ni salt precursor is still present over 5Ni/Al- $\beta$ -CD<sub>0.1</sub> after the drying step (100 °C overnight). This behavior can be connected again to the presence of specific interactions occurring between β-CD and the Ni nitrate precursor via the immobilization onto the support of non-covalent complexes with enhanced thermal stability against transformation into nickel oxide. Very similar decomposition patterns were also observed for the dried catalysts synthesized with the two other native CDs (i.e.  $\alpha$ -CD and  $\gamma$ -CD), underlining that whatever the type, CDs behave as complexing molecules for Ni nitrate (Fig. S1).

# 3.2. Study of the metal-CD complex formation by Electrospray-Mass Spectrometry (ESI-MS)

To gain further insight into the occurrence of an interaction between CDs ( $\alpha$ ,  $\beta$  and  $\gamma$ -CD) and the Ni nitrate precursor, we con-



**Fig. 1.** TG profiles (left side) and corresponding MS spectra of CO<sub>2</sub> (*m*/*z* = 44), H<sub>2</sub>O (*m*/*z* = 18) and NO (*m*/*z* = 30) (right side) for the following dried materials: (A) Al-β-CD<sub>0.1</sub>, (B) 5Ni/Al and (C) 5Ni/Al-β-CD<sub>0.1</sub>.

ducted a series of electrospray-mass spectrometry (ESI-MS) analyses in positive mode. The experiments were carried out on Ni  $(NO_3)_2$  and CD ( $\alpha$ -CD,  $\beta$ -CD and  $\gamma$ -CD) mixtures in aqueous methanol by setting the CD/Ni molar ratio to 0.1 (see Section 2). The most intense ion in the positive MS spectrum of the β-CD/Ni nitrate system appears at m/z = 596.15, which can be unambiguously assigned to  $[\beta$ -CD + Ni]<sup>2+</sup>, supporting the direct complexation of β-CD with Ni. Further evidence of complexation can be deduced from the presence of additional ions at m/z = 624.11 and m/z =1163.33, which can be ascribed to  $[\beta$ -CD + 2Ni-2H]<sup>2+</sup> and  $[2\beta$ -CD + Ni]<sup>2+</sup>, respectively. Even if less prominent, numerous other complexes encompassing the coordination of the nitrate counterion with  $\beta$ -CD are also observed at m/z = 655.61, m/z = 687.10, m/z =747.56 and m/z = 855.83, being attributed to [ $\beta$ -CD + 2Ni + NO<sub>3</sub>-H]<sup>2+</sup>,  $[\beta$ -CD + 2Ni + 2NO<sub>3</sub>]<sup>2+</sup>,  $[\beta$ -CD + 3Ni + 3NO<sub>3</sub>-H]<sup>2+</sup> and  $[2\beta$ -CD + 3Ni + 2NO<sub>3</sub>-H]<sup>3+</sup>, respectively. Noteworthy, similar complexes were observed in the ESI-MS spectra of  $\alpha$ -CD or  $\gamma$ -CD mixed with  $Ni(NO_3)_2$  (Fig. S3).

The strength of the interaction in non-covalent complexes can be assessed from the center-of-mass energy, which is the energy required to decompose 50% of the initial ion (CE<sub>50</sub>). This value can be measured from the sigmoid survival yield curve using the higher collision-induced dissociation (HCD) mode [48,57]. The survival yield curves issued from the decomposition of some complexes formed between Ni nitrate with either  $\alpha$ -CD,  $\beta$ -CD or  $\gamma$ -CD are gathered in Fig. S4. For most of the complexes, the stability was found to follow the trend  $\beta$ -CD >  $\alpha$ -CD >  $\gamma$ -CD. Interestingly, such complex formation can be explained on the basis of the interaction between the OH groups present on the CD rims and the Ni nitrate precursor by assuming 2OH groups per 1Ni for molar ratio of CD/Ni = 0.1.

# 3.3. DFT study of the metal-CD complex formation

Periodic DFT calculations were performed on  $\beta$ -CD-Ni complexes to rationalize the interaction between the organic and the metallic part, but also to define the most favorable interaction sites for the formation of complexes. To take into account the presence of an aqueous environment, an implicit solvation model was used for  $\beta$ -CD, the aqua nickel cation [Ni(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup> and the resulting inclusion complex [53,54]. If the nickel cation is placed inside the β-CD, the inclusion reaction is endothermic ( $\Delta_r E = 0.26 \text{ eV}$ ), which confirms that the inclusion of the hexahydrated nickel ion is not favorable in the hydrophobic cavity of β-CD. Alternative reaction sites are formed by OH groups on the rims of the  $\beta$ -CD molecule, which can substitute one water molecule on the aqua-nickel complex. Due to the geometry of the secondary face, two bonds are formed between the cation and  $\beta$ -CD, and the formation of the compound is exothermic. The reaction energies are -0.59 eV or -0.38 eV when the two OH groups belong to the same or different glucose molecules, respectively. The cation can also interact with one primary OH group on the other side of  $\beta$ -CD. This reaction leads to the most stable  $\beta$ -CD-Ni complex with a reaction energy of -0.75 eV. The final geometry after optimization is given by way of illustration in Fig. 2. This type of complex formed has also been detected in the ESI-MS experiments. Taken together, our calculations provide further evidence on the fact that the hydroxyl sites (either on the primary or secondary rim) can effectively contribute to the formation of CD-Ni complexes and that various geometries are possible due to the numerous OH groups present on β-CD.

#### 3.4. Characterization of calcined catalysts

#### 3.4.1. Textural properties

Table S1 lists the textural properties of the different catalysts prepared in this study, with and without  $\beta$ -CD addition (i.e. xNi/ Al and *x*Ni/Al-CD<sub>0.1</sub>, respectively). For comparison, the textural properties of 5Ni/Al catalysts prepared with other native CDs ( $\alpha$ -CD and  $\gamma$ -CD), as well of the parent  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, are also given. The support shows a mesoporous structure with a BET specific surface area of 154 m<sup>2</sup> g<sup>-1</sup>, a pore volume of 0.52 cm<sup>3</sup> g<sup>-1</sup> and an average pore size of 11.8 nm. Very similar textural properties are observed for  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> impregnated with  $\beta$ -CD and calcined at 400 °C. It is clear from this observation that  $\beta$ -CD does not alter the support properties, and that, after thermal treatment under air at 400 °C, β-CD is completely removed without any trace of coke deposition. The surface area, pore volume and pore size decrease to 142 m<sup>2</sup> g<sup>-1</sup>, 0.46 cm<sup>3</sup> g<sup>-1</sup> and 10.7 nm, respectively, after Ni impregnation and further calcination (5Ni/Al), reflecting a partial blockage of the alumina pores [58]. The specific surface area generally decreases with the Ni loading, but this trend seems to be more moderate for the series of catalysts prepared by the assistance of CD.

# 3.4.2. X-Ray diffraction

Fig. 3 plots the XRD patterns of the xNi/Al and xNi/Al- $\beta$ -CD<sub>0.1</sub> catalysts after calcination at 400 °C under air as a function of the Ni loading (range 2–20 wt%).

In the absence of  $\beta$ -CD (Fig. 3A), a neat Ni(200) reflection line can be visualized at  $2\theta = 43.5^\circ$ , becoming more intense with the Ni loading, especially above 8 wt%. In contrast, the XRD patterns of the catalysts synthesized using β-CD exhibit weaker and broader NiO (200) lines (Fig. 3B). These observations point out a decrease in the average size of the NiO crystallites mediated by  $\beta$ -CD, suggesting a higher NiO dispersion over alumina after calcination at 400 °C irrespective of the Ni loading. For example, for the highest Ni-loaded catalyst (20 wt%), the average NiO crystallite size can be estimated at 9.4 nm for 20Ni/Al- $\beta\text{-}CD_{0.1}$  against 15.8 nm for 20Ni/Al. These results unambiguously demonstrate that the addition of B-CD during Ni impregnation can induce the formation of smaller NiO nanoparticles. We attribute this observation to the stabilization of β-CD-Ni(II) adducts after water removal, thus preserving a good distribution of Ni(II) species in the vicinity of β-CD and delaying the formation, growth and aggregation of NiO during calcination. This behavior is perfectly in line with the results presented above from TG-MS analyses (Fig. 1).

To visualize the phase transformations occurring during reduction under H<sub>2</sub>, the *in-situ* temperature-controlled XRD patterns were further measured at temperatures up to 800 °C. To this aim, we selected two highly Ni-loaded calcined catalysts synthesized without and with  $\beta$ -CD (i.e. 15Ni/Al and 15Ni/Al- $\beta$ -CD<sub>0.1</sub>), for which the NiO reflection lines were clearly visible (Fig. 4A and B). The reflections at  $2\theta = 43.5^{\circ} (200)$  and  $63^{\circ} (22)$ 0) are attributed to NiO, while the characteristic reflections belonging to reduced Ni (Ni<sup>0</sup>) can be visualized at  $2\theta = 44.3^{\circ} (111)$  and 51.8° (200). The reflection lines of NiO at  $2\theta$  = 43.5° and  $2\theta$  = 63° are relatively intense between room temperature and 400 °C for 15Ni/Al. These lines roughly disappear after 350 °C, whereas the intensity of the  $(1 \ 1 \ 1)$  and  $(2 \ 0 \ 0)$  reflections belonging to Ni<sup>0</sup> increase from 350 °C to  $\sim$ 700 °C and then stabilize, suggesting a complete reduction of NiO after 350 °C. Opposing this behavior, 15Ni/Al-β-CD<sub>0.1</sub> exhibits less intense and broader NiO reflections at lower temperature (T <250 °C), confirming the genesis of smaller NiO particles. Note also that the only visible NiO (200) reflection disappears at 300 °C as compared to 350 °C for 15Ni/Al, revealing a faster NiO reduction into Ni<sup>0</sup>. Unlike 15Ni/Al, 15Ni/Al-β-CD<sub>0.1</sub> does not show any reflection belonging to NiO or Ni<sup>0</sup> at  $2\theta = 43.5^{\circ} (200)$ and 44.3° (111), respectively, in the mid temperature region (300–450 °C, orange patterns). Overall, these results confirm the genesis of finer and better dispersed Ni nanoparticles over  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> for the  $\beta$ -CD-assisted preparations.

## 3.4.3. Catalyst reducibility

The effect of  $\beta$ -CD on the reducibility of the two series of catalysts prepared with and without  $\beta$ -CD was assessed by temperature programmed reduction (H<sub>2</sub>-TPR) as a function of the Ni loading (range 2–20 wt%) (Fig. 5 and Table 1). In all cases, the total H<sub>2</sub> consumption increases with the Ni content, matching the expected values calculated by assuming the complete reduction of NiO to Ni.

In the absence of  $\beta$ -CD, the band corresponding to Ni<sub>2</sub>O<sub>3</sub> [59– 62] shifts to lower temperatures, i.e. from 298 °C to 249 °C when increasing the Ni loading in the xNi/Al catalysts (with x = 5 to x = 20 wt% Ni) along with a slight decrease in its percent reduction from 10% for 8Ni/Al to 5% for 20Ni/Al (Fig. 5A). Ni<sub>2</sub>O<sub>3</sub> species are generally formed due to NiO disproportionation, generating two Ni species with different oxidation states (3NiO  $\rightarrow$  Ni + Ni<sub>2</sub>O<sub>3</sub>) [61,62]. It is worth noting that the H<sub>2</sub> consumption corresponding to the second band increases dramatically with the Ni loading, reflecting the presence of a larger density of bulk Ni species ( $\alpha$ -



Fig. 2. Geometry of the most stable complex: (Ni in blue, C in grey, O in red and H in white).



**Fig. 3.** XRD patterns of the calcined xNi/Al catalysts prepared in the absence (A) and presence (B) of  $\beta$ -CD ( $\beta$ -CD/Ni = 0.1) for: (a)  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, (b) 2 wt%, (c) 5 wt%, (d) 8 wt%, (e) 10 wt%, (f) 12 wt%, (g) 15 wt% and (h) 20 wt%. The numbers in the right indicate the average crystallite size of NiO (2 0 0) estimated from the Scherrer equation.



**Fig. 4.** *In-situ* XRD patterns of calcined 15Ni/Al prepared without (A) and with  $\beta$ -CD (B) heated under 5% H<sub>2</sub> atmosphere from 30 °C to 800 °C at a rate of 5 °C min<sup>-1</sup> and then cooled down to 50 °C at a rate of 50 °C min<sup>-1</sup>. The violet lines indicate the patterns recorded every 25 °C from room temperature to 775 °C, the red lines indicate the patterns recorded at 800 °C after holding for 2 h, while the aqua blue lines refer to the patterns recorded every 100 °C during cooling (800 °C to 50 °C). The orange lines indicate the temperature range where reflection lines of 20 = 43.5 (NiO) and 44.3 (Ni) are absent.

type [63–65]) generated by an uncontrolled growth of NiO species during the early stage of the impregnation process. Moreover, the band appearing in the highest temperature region ascribed to the reduction of hard-to-reduce Ni aluminate species [63,64] appears to decrease and to be shifted towards lower temperatures with the Ni loading (compare profiles a and g). This observation indicates that higher Ni loadings favor the formation of more readily reducible Ni species [64]. Also note that for the catalysts prepared by conventional Ni impregnation, the reduction level of surface Ni species ( $\beta$ 1 +  $\beta$ 2 type [66–69]) is very sensitive to the Ni content. As evidenced from Fig. 6, the highest percentage of reducible surface metal Ni is achieved for 8Ni/Al



**Fig. 5.** H<sub>2</sub>-TPR profiles of calcined *x*Ni/Al catalysts prepared without (A) and with β-CD (B); (a) 2Ni/Al, (b) 5Ni/Al, (c) 8Ni/Al, (d) 10Ni/Al, (e) 12Ni/Al, (f) 15Ni/Al and (g) 20Ni/Al.

(73%) and decreases dramatically with the Ni loading down to 37% for 20Ni/Al due to the formation of bulk Ni oxide species with larger crystallite sizes.

A significant effect of  $\beta$ -CD addition on the reduction behavior of NiO species can be observed on the H<sub>2</sub>-TPR profiles (Fig. 5B). Except for 2Ni/Al- $\beta$ -CD<sub>0.1</sub>, for which the main species are Ni aluminates (84%), the use of  $\beta$ -CD affects the reduction behavior of the Ni species. On the one hand, the area of the reduction band assigned to Ni<sub>2</sub>O<sub>3</sub> (Fig. 5B, profiles b-g) is much lower for the  $\beta$ -CD-assisted samples ( $xNi/Al-\beta-CD_{0.1}$  with x = 5–20 wt% Ni) than for the control catalysts prepared without  $\beta$ -CD (Fig. 5A, profiles b-g). Likewise, the reduction percentage of bulk NiO species ( $\alpha$  type) in the catalysts prepared with  $\beta$ -CD (Table 1, entries 4, 6, 8, 10, 12, 14) is lower than for those prepared without  $\beta$ -CD (Table 1, entries 3, 5, 7, 9, 11, 13). On the other hand, the decline in the relative proportion of bulk NiO or Ni<sub>2</sub>O<sub>3</sub> species compares well with the higher formation of surface Ni species irrespective of the Ni loading (Fig. 6). Indeed, for the  $xNi/Al-\beta-CD_{0,1}$  series (Fig. 5B, profiles dg), the area of  $\alpha$ -type species increases fast with the Ni loading in the range 10-20 wt%, encompassing an increase of the reduction level ranging from 3 to 21% (Table 1). Besides the effect of  $\beta$ -CD addition on the reducibility of NiO species, it can be noticed that  $\alpha$ -CD and  $\gamma$ -CD also show a similar reduction behavior. Overall,  $\sim$ 80% of NiO surface species can be reduced at slightly higher reduction temperatures, i.e. 522 °C and 511 °C for  $\alpha$ -CD and  $\gamma$ - CD, respectively against 502 °C for  $\beta$ -CD (Table 1, entries 15 and 16).

# 3.4.4. CO pulse chemisorption

CO pulse chemisorption was used for measuring the Ni dispersion, the average Ni particle size and the Ni surface area per gram of catalyst or per gram of Ni metal on the different catalysts (Table 1). Fig. 7 compares the CO uptake measured as a function of the Ni loading for the catalysts prepared without and with  $\beta$ -CD.

In both cases, an increase of the CO uptake is observed with the Ni loading due to a larger amount of metal Ni sites interacting with CO molecules. Whatever the Ni loading, the CO uptake is significantly higher on xNi/Al- $\beta$ -CD<sub>0.1</sub> than on xNi/Al catalysts (compare for instance the CO up-take of 252 µmol g<sup>-1</sup> for 15Ni/Al- $\beta$ -CD<sub>0.1</sub> and 165 µmol g<sup>-1</sup> for 15Ni/Al). In line with this, a relatively high Ni dispersion can be maintained with values ranging from 20% to 22% in the range 5–15 wt% Ni, while a further increase to 20 wt% Ni induces a considerable reduction of the metal dispersion to 13% (Table 1). The resulting Ni particle size estimated from the CO uptake shows lower values for xNi/Al- $\beta$ -CD<sub>0.1</sub> catalysts as compared to control xNi/Al catalysts (4.5–7.8 nm vs. 6.7–10.8 nm, respectively).

#### 3.4.5. X-ray photoelectron spectroscopy

Fig. S5 plots the Ni2p XPS spectra measured on 5Ni/Al and 5Ni/ Al-β-CD<sub>0.1</sub> after calcination and *in-situ* reduction at 600 °C. Noteworthy, no band belonging to the C1s core level is observed in the survey XPS spectrum of 5Ni/Al-β-CD<sub>0.1</sub>, confirming the complete removal of  $\beta$ -CD upon calcination. The deconvoluted spectra of the Ni2p core level for the calcined catalyst (Fig. S5-A.C) exhibit two main bands centered at 856.5 and  $\sim$ 861 eV that are indicative of the Ni<sup>2+</sup> state and shake-up satellite bands of NiO or Ni<sub>2</sub>O<sub>3</sub>, respectively [70]. An additional band at 852 eV is observed for the *in-situ* reduced catalysts (Fig. S5-B,D), which can be attributed to reduced Ni (Ni<sup>0</sup>) [71]. The surface concentrations measured from the XPS spectra indicate that a larger density of surface Ni species are present in the calcined catalyst synthesized with  $\beta$ -CD (Ni/ Al = 0.10 for 5Ni/Al vs. Ni/Al = 0.14 for 5Ni/Al- $\beta$ -CD<sub>0.1</sub>). A similar trend is observed for the reduced catalysts, showing Ni/Al ratios of 0.05 and 0.07, respectively. Interestingly, a gain of 30% surface Ni species has been estimated for reduced 5Ni/Al- $\beta$ -CD<sub>0.1</sub> as compared to reduced 5Ni/Al. This body of results unambiguously confirms that the controlled addition of  $\beta$ -CD during Ni impregnation over alumina allows a marked enhancement of the density of surface Ni species on the support.

# 3.4.6. TEM and STEM imaging

To confirm the positive effect of  $\beta$ -CD on reducing the Ni particle size, a dedicated TEM study was carried out on two selected reduced catalysts, i.e. 10Ni/Al and 10Ni/Al- $\beta$ -CD<sub>0.1</sub>, after reduction under H<sub>2</sub> flow at 580 °C. Figs. 8 and 9 show the corresponding TEM images. The Ni particles in 10Ni/Al are somewhat spherical in shape being heterogeneously dispersed over alumina (Fig. 8A and B). The Ni particles show a size in the range 3–10 nm with an average particle size centered on ~6–7 nm (Fig. 8D). Note that additional STEM imaging of 10Ni/Al clearly indicates that the smallest particles are Ni rich (Fig. S6).

In the case of  $10Ni/Al-\beta-CD_{0.1}$ , the Ni particles appear to be more homogeneously dispersed over the support with a majority of particles having a diameter of around 3–4 nm, which is significantly smaller than that estimated for the 10Ni/Al sample (Fig. 9D). Note that no particles with a size larger than 6 nm are observed. Although the number of counted particles (about 50 in each case) is relatively small, requiring careful consideration, the average particle sizes measured by TEM are in good agreement with the values

Table 1									
Reducibility	/ and j	physicochemical	propertie	s of xNi/	Al cataly	ysts synthesized	l without and	d with β-C	CD.

Entry	Sample	Total H <sub>2</sub> uptake µmol g <sup>-1a</sup>	T (°C) Surf Ni (β1 + β2)	%Red <sup>n</sup> Ni <sub>2</sub> O <sub>3</sub> <sup>b</sup>	%Red <sup>n</sup> Bulk Ni <sup>c</sup> (α)	%Red <sup>n</sup> Surf Ni <sup>d</sup> (β1 + β2)	$\operatorname{NiAl}_2O_4^e$ ( $\gamma$ )	CO uptake (µmol g <sup>-1</sup> ) <sup>f</sup>	Dispersion (%D) <sup>g</sup>	$\begin{array}{l} \text{Metal surf.} \\ \text{area, } A_m \ (m_{\text{Ni}}^2 \\ g_{\text{Ni}}^{-1})^h \end{array}$	Particle size, S <sub>m</sub> (nm) <sup>i</sup>
1	2Ni/Al	330 (106)	_		38	-	61	23.0	13.5	90.2	7.5
2	2Ni/Al-β-CD <sub>0.1</sub>	266 (89)	-	0	16	-	84	27.5	16.2	107.9	6.2
3	5Ni/Al	793(105)	558	0	13	49	21	60.5	14.2	94.7	7.1
4	5Ni/Al-β-CD <sub>0.1</sub>	674 (92)	502	0	6	70	23	84.7	19.8	132.6	5.1
5	8Ni/Al	1098	568	10	11	73	6	102.3	15.0	100.1	6.7
6	8Ni/Al-β-CD <sub>0.1</sub>	1002 (93)	538	2	4	86	8	137.9	20.3	135.0	5.0
7	10Ni/Al	1364 (94)	563	9	18	67	6	115.3	13.5	90.2	7.6
8	10Ni/Al-β-CD <sub>0.1</sub>	1373	529	2	3	89	6	186.5	21.9	146.0	4.5
9	12Ni/Al	1570	560	7	25	65	3	144.9	14.1	94.5	7.1
10	12Ni/Al-β-CD <sub>0.1</sub>	1588	545	3	11	81	4	218.5	21.4	142.5	4.7
11	15Ni/Al	1934	565	7	31	60	2	165.3	12.9	86.3	7.8
12	15Ni/Al-β-CD <sub>0.1</sub>	1995	531	3	6	87	4	252.1	19.7	131.6	5.1
13	20Ni/Al	2583	558	5	56	37	2	159.0	9.3	62.3	10.8
14	20Ni/Al-β-CD <sub>0.1</sub>	2446	540	3	21	74	2	221.8	13.0	86.9	7.8
15	$5Ni/Al-\alpha-CD_{0.1}$	726	522	0	9	79	12	52.3	12.3	81.9	8.2
16	$5Ni/Al-\gamma-CD_{0.1}$	703	511	0	8	81	11	87.0	20.4	136.2	5.0

<sup>a</sup> Estimated by integrating the  $H_2$ -TPR profile from RT to 1000 °C. The numbers in brackets represent the % of reduction of Ni oxide with respect to the theoretical  $H_2$  consumption calculated by considering the Ni loading measured by ICP.

<sup>b</sup> Calculated by dividing the integrated area in the temperature region 100-300 °C by the total H<sub>2</sub> consumption (range 30-1000 °C).

<sup>c</sup> Calculated by dividing the integrated area in the temperature range 300–500 °C for non-CD assisted catalysts and 300–400 °C for CD assisted catalysts by the total H<sub>2</sub> consumption (range 30–1000 °C).

<sup>d</sup> Calculated by dividing the integrated area in the temperature range 450–750 °C for non-CD assisted catalysts and 400–750 °C for CD assisted catalysts by the total H<sub>2</sub> consumption (range 30–1000 °C).

Calculated by dividing the integrated area in the temperature range 750–950 °C by the total  $H_2$  consumption (range 30–1000 °C).

<sup>f</sup> Estimated from the area under the CO pulse signals.

<sup>g</sup> Calculated from the CO uptake using equation:  $(V_{chem} * S.F. * M.W.)/(c/100) * 100$ ; where  $V_{chem}$  is the amount of CO uptake (mol  $g^{-1}$ ), S.F. is the stoichiometric factor (Ni/CO = 2), M.W. is the atomic weight of supported Ni and c is the Ni loading (wt%).

<sup>h</sup> Calculated from the equation:  $(V_{chem} * N_{A^*} * S.F. * \sigma_{m.} * 10^{-18})/c * 100$ ; where N<sub>A</sub> is the Avagadro number and  $\sigma_m$  is the Ni cross section area (0.0649).

Mean particle size calculated from the following equation:  $60c/(A_m * \rho)$  where  $A_m$  is the Ni surface area per gram catalyst and  $\rho$  is the Ni density.



**Fig. 6.** Percentage of reduction of surface Ni species ( $\beta 1 + \beta 2$ ) as a function of the Ni loading for the catalysts synthesized without and with  $\beta$ -CD as measured by H<sub>2</sub>-TPR in the temperature range 300–750 °C without considering Ni aluminate ( $\gamma$  type) species.

measured from CO pulse chemisorption and reflect fairly well the overall beneficial impact of  $\beta$ -CD on the Ni dispersion observed.

#### 3.5. Catalytic performance

# 3.5.1. Amination of benzyl alcohol with aniline (model reaction)

Taken together, the above characterization results for the catalysts both in the dried and calcined forms demonstrate the ability of native CDs to interact with Ni nitrate in the first steps of the impregnation process by forming complexes, which in turn significantly affect the final structure of the catalysts. Ni complexation helps to achieve both a better dispersion with smaller Ni particle



Fig. 7. CO uptake as a function of the Ni loading for the catalysts synthesized without and with  $\beta\text{-CD}.$ 

sizes (2–5 nm) and a higher reducibility of surface-active Ni species ( $\beta$ 1 +  $\beta$ 2). Notably, this trend is readily preserved over a wide range of Ni loadings.

To assess the effect of CD on the properties of the different catalysts for conducting amination processes, the reaction of benzyl alcohol with aniline at 140 °C was initially used as a model reaction using 35 mg of pre-reduced xNi/Al and xNi/Al- $\beta$ -CD<sub>0.1</sub> catalysts (x = 2–20 wt% Ni) (Fig. 10 and Table S2). These conditions were set to facilitate the comparison between the different catalysts.

Interestingly, irrespective of the Ni loading (except for 2 wt% Ni), the xNi/Al- $\beta$ -CD<sub>0.1</sub> catalysts exhibit much higher activities compared to xNi/Al catalysts prepared without  $\beta$ -CD. The highest activity is observed for 10Ni/Al- $\beta$ -CD<sub>0.1</sub> with 62% aniline conversion and 61% BZA selectivity. Nevertheless, the fact that 12Ni/Al-



Fig. 8. TEM micrographs of reduced 10Ni/Al: (A) 100 nm, (B) 20 nm, (C) electron diffraction pattern and (D) normalized particle size histogram.



Fig. 9. TEM micrographs of reduced 10Ni/Al-β-CD<sub>0.1</sub>: (A) 50 nm, (B) 50 nm, (C) 20 nm and (D) normalized particle size histogram.

 $\beta$ -CD<sub>0.1</sub> contains an abnormally high proportion of bulk nickel oxide (11%) at the expense of active surface nickel species (74%) may explain the observed deviation of the catalytic activity from the overall trend that is emerging in this series of catalysts prepared with the aid of  $\beta$ -CD. Note also that *x*Ni/Al catalysts with x = 5 wt% and 8 wt% Ni do not show any activity when Ni impregnation is not assisted by  $\beta$ -CD. For these catalysts, the reaction tem-

perature needs to be increased to  $160 \, ^{\circ}C$  for detecting a conversion (Table S2, entry 3).

Fig. 11 plots the turnover number (TON, calculated by dividing the number of reacted moles of aniline at 1 h by the number of surface Ni atoms) against the mean particle size of the Ni particles measured from pulse CO chemisorption for the different catalysts prepared in this study. Overall, the catalysts with smaller Ni parti-



**Fig. 10.** Performance of the different Ni-alumina catalysts synthesized without and with  $\beta$ -CD ( $\beta$ -CD/Ni = 0.1) in the amination reaction of benzyl alcohol with aniline. *Reaction conditions: Aniline – 2 mmol, Benzyl alcohol – 6 mmol, Cat – 35 mg, T – 140 °C, Time – 1 h, rpm – 600, no solvent, Ar atm.* The number in the histograms indicates the aniline conversion and selectivity to the different N-products.

cles exhibit higher activity. Furthermore, irrespective of the Ni loading, the catalysts prepared in the presence of  $\beta$ -CD displaying smaller Ni particles sizes afford comparatively higher activities. These results suggest that the most active sites for amination are located on smaller Ni particles (i.e. edges, corners or sites) at the Ni-alumina interface. The highest TON is attained for 8Ni/Al- $\beta$ -CD<sub>0.1</sub> exhibiting the highest Ni dispersion (i.e. lower average Ni particle size, ~5 nm) and a large fraction of reducible surface Ni species (86%).

We also surveyed the effect of other native CDs ( $\alpha$ -CD and  $\gamma$ -CD) on the performance of *x*Ni/Al catalysts in the model amination reaction of benzyl alcohol with aniline at 160 °C for 1 h (Fig. S7). The following activity trend is observed:  $\beta$ -CD >  $\gamma$ -CD >>  $\alpha$ -CD > no CD. The observed activity, which dropped by 12% when compar-



**Fig. 11.** Turnover number of the different Ni-alumina catalysts at 1 h in the amination of benzyl alcohol with aniline as a function of the average Ni particle size for the catalysts synthesized without and with  $\beta$ -CD at variable Ni loading. Indexation of alphabets represents the Ni loading: (a) 2 wt%, (b) 5 wt%, (c) 8 wt%, (d) 10 wt%, (e) 12 wt%, (f) 15 wt%, and (g) 20 wt%. *Reaction conditions as in Fig.* 10.

ing the activity between  $\beta$ -CD and  $\gamma$ -CD and by 34% when comparing the activity between  $\beta$ -CD and  $\alpha$ -CD clearly indicates that  $\beta$ -CD is the most active CD. The contrasting activity displayed by the different native CDs can be explained on the basis of a different interaction strength between the CD and the Ni precursor. This can be attributed in turn to the different number of OH groups present on the CD and to the stability of the as-formed adduct during the thermal treatment (i.e. drying and calcination). As confirmed from the ESI-MS experiments, the most stable complex tends to be formed between β-CD and nickel nitrate (Fig. S4-B) and therefore the decomposition pattern of the complex and the subsequent growth of NiO particles should differ with respect to other native CDs ( $\alpha$  and  $\gamma$ -CD) during calcination. Thus, for a CD/Ni ratio of 0.1, the OH/Ni ratio in the complex is slightly different (i.e. 2.1 for  $\beta$ -CD vs 1.8 and 2.4 for  $\alpha$ -CD and  $\gamma$ -CD respectively), likely affecting the final surface properties of the catalysts, both in terms of surface density and reducibility. Finally, our data show that the use of the  $\beta$ -CD-assisted catalyst with a CD/Ni ratio of 0.1 presents a higher amount of reducible surface Ni species, thus leading to most significant effects in the model amination reaction.

#### 3.5.2. Amination of 1-octanol with ammonia (target reaction)

In a subsequent step of our study, we assessed the performance of the xNi/Al and xNi/Al- $\beta$ -CD<sub>0.1</sub> catalysts (x = 2, 5, 8, 10 and 15 wt% Ni) in the amination reaction of 1-octanol with ammonia. The catalytic tests were carried out at 160 °C and 180 °C for 4 h using 55 mg of catalyst pre-reduced at 580 °C for 30 min. Fig. 12 (160 °C), Table S3 (entries 11–16, 180 °C) and Fig. S8 (180 °C) compile the results obtained. The 2Ni/Al catalysts prepared with or without  $\beta$ -CD do not display any activity. The catalytic activity is enhanced with the Ni loading beyond 5 wt%, especially when  $\beta$ -CD is used as additive during Ni impregnation. As a matter of fact, the 1-octanol conversion raises by 20% at 160 °C when the Ni loading increases from 5 wt% to 10 wt% for the Ni/Al catalysts prepared without  $\beta$ -CD, whereas the OA yield reaches almost 60% (Table S3, entries 3 and 7). Meanwhile, an enhancement of the catalytic activity is observed when  $\beta$ -CD is used as additive. For example, when comparing the catalytic performance of 5Ni/Al and 5Ni/Al- $\beta$ -CD<sub>0.1</sub>, the 1-octanol conversion increases from 57% to 68%, while the OA yield is enhanced from 45% to 56%. A similar type of effect is observed for highly Ni-loaded catalysts, the OA yield showing a maximum value of 69% for 15Ni/Al- $\beta$ -CD<sub>0.1</sub>. These results point out the positive effect of  $\beta$ -CD on enhancing the catalytic properties of *x*Ni/Al catalysts for 1-octanol amination. Indeed, the catalysts synthesized with  $\beta$ -CD can save up to 50% of Ni compared to the catalysts prepared without  $\beta$ -CD and also reported in the literature at comparable 1-octanol conversion (Fig. 12) [20]. For example, at short reaction time (4 h), the 5Ni/Al- $\beta$ -CD<sub>0.1</sub> catalyst prepared in this study exhibits a similar TON (87) as that reported by Shimizu and coworkers on 10Ni/ $\theta$ -Al<sub>2</sub>O<sub>3</sub> (TON = 83), but obtained at longer reaction time (13 h) (compare entries 5 and 17 in Table S3) [20].

# 3.5.3. Recycle study and characterization of the spent catalysts

To further assess the potentials of CDs in stabilizing Ni nanoparticles against leaching, a recycling study was conducted on 5Ni/Al- $\beta$ -CD<sub>0.1</sub> and 5Ni/Al for the direct amination reaction of 1-octanol with ammonia in the same conditions (160 °C for 4 h). In both cases, after the 1st run, the reaction mixture was centrifuged and the catalyst was filtered, dried overnight at 100 °C for 10 h and finally calcined at 400 °C for 2 h. The resulting catalyst was further reduced at 580 °C for 30 min and the reaction was conducted in a 2nd run. Fig. 13 and Table S4 collect the results for the fresh and spent catalysts.

It is apparent that the catalyst synthesized without  $\beta$ -CD (i.e. 5Ni/Al) deactivates after the 1st run as the 1-octanol conversion dramatically drops from 57% to 5%. In contrast, a higher stability is noticed for the catalyst synthesized with  $\beta$ -CD (i.e. 5Ni/Al- $\beta$ -CD<sub>0.1</sub>), which shows only a slight drop in activity (68% to 55%). Chemical analysis of the spent 5Ni/Al reveals a Ni loss due to leaching after the 1st run (from 4.4 wt% Ni to 3.9 wt% Ni), which further increases after the 2nd run (from 3.9 wt% Ni to 3.2 wt% Ni). Opposing this behavior, no significant Ni loss is observed after the 2nd run (from 4.6 wt% Ni to 4.1 wt% Ni) (Table S4, entries 3 and 4). These results point out the greater ability of  $\beta$ -CD to retain



**Fig. 13.** Recycling study of  $5Ni/Al-\beta-CD_{0,1}$  and 5Ni/Al catalysts synthesized with and without  $\beta$ -CD. *Reaction conditions:* 1-octanol – 1.3 mmol,  $NH_3 - 7$  bar Cat – 55 mg,  $T - 160 \,^{\circ}$ C, Time – 4 h, rpm – 600, Solvent – 3 mL o-xylene. The numbers in brackets indicate the Ni loadings measured on the solid catalysts by ICP analysis after each reaction run.

the catalyst composition and its structure during 1-octanol amination with ammonia for at least two consecutive runs. The higher stability of CD-assisted catalysts against leaching can be explained on the basis of a much more homogeneous distribution of smaller Ni particles (2–5 nm) in stronger interaction with the alumina support. These trends are in line with the study reported by Claus and co-workers pointing out a higher resistance to leaching for catalysts with low Ni loadings and for small particle size [72].

The dried spent samples (synthesized with and without  $\beta$ -CD) were further subjected to TGA analysis to assess any coke formation during the amination reaction. The thermal profiles of the spent catalysts (Fig. S9, profiles b and d) show in both cases two weight loss regions occurring at low and high temperatures. The weight loss of 2% at about 100 °C can be attributed to physically adsorbed water, whereas the larger weight loss (9%) in the region



**Fig. 12.** Performance of the different Ni-alumina catalysts synthesized without and with  $\beta$ -CD ( $\beta$ -CD/Ni = 0.1) in the amination reaction of 1-octanol with ammonia. <u>Reaction</u> conditions: 1-octanol – 1.3 mmol, NH<sub>3</sub> – 7 bar, Cat – 55 mg, T – 160 °C, Time – 4 h, rpm – 600, Solvent – 3 mL o-xylene. The number in the histograms indicates the 1-octanol conversion and selectivity to the different N-products.

300–400 °C can be ascribed to the combustion of amorphous carbonaceous deposits [73]. No appreciable differences are observed between the thermal profiles of the spent 5Ni/Al and 5Ni/Al- $\beta$ -CD<sub>0.1</sub>, indicating the same nature of carbon deposits. However, since the spent catalysts are re-calcined at 400 °C before the 2nd run, this temperature ensures complete coke removal and regeneration of the catalyst, as supported by the corresponding TG profiles.

# 4. Conclusions

In summary, we have described the preparation of a series of alumina-supported Ni catalysts using native cyclodextrins as a water-soluble additive via wet impregnation. The catalysts were synthesized with a controlled amount of cyclodextrin to the metal precursor and characterized in dried and calcined forms. The use of cyclodextrin during Ni impregnation afforded enhanced catalytic properties in the direct amination of alcohols. Among the native CDs, the catalysts synthesized with  $\beta$ -CD outstand in activity. 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, the Ni dispersion, reducibility and speciation over alumina could be finely controlled and tuned. In particular, a higher density of surface Ni species could be achieved in the CD-assisted catalysts. Interestingly, this effect could be preserved over a wide range of Ni loading. Last but not least, β-CD boosted the stability of the catalysts by discouraging Ni leaching during the amination reaction, thereby maintaining the catalytic activity after at least two consecutive catalytic runs.

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#### Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.jcat.2017.10.006.

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