



# Influence of the textural properties of porous aluminas on the reducibility of Ni/Al<sub>2</sub>O<sub>3</sub> catalysts

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## ABSTRACT

Temperature-programmed reduction (TPR) profiles recorded on calcined Ni/Al<sub>2</sub>O<sub>3</sub> catalysts exhibiting the same Ni(II) surface density (3 Ni<sup>2+</sup> nm<sup>-2</sup>) suggest that nickel speciation and reducibility are significantly influenced by the specific surface area and textural properties of aluminas, and by their stability toward water during impregnation. Limiting the dissolution of Al<sub>2</sub>O<sub>3</sub> and protecting Ni<sup>2+</sup> ions are required to increase the reducibility of Ni/Al<sub>2</sub>O<sub>3</sub> catalysts, especially for mesoporous aluminas presenting a high specific surface area.

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## 1. Introduction

Nickel is widely known for its catalytic activity in the hydrogenation of organic molecules and carbon monoxide, both at the laboratory and in the industry [1–3]. On supported catalysts, nickel is used as nanoparticles dispersed over the surface of a porous oxidic material.  $\gamma$ -Alumina is often selected because, unlike silica, it combines high specific surface area and thermal stability.

Nickel is introduced onto alumina by impregnation of the support porosity with an aqueous solution of precursor salt, most commonly nickel(II) nitrate. After drying and calcination, nickel-containing oxidic species, which may not respond to X-ray diffraction due to their dispersion and small size, can be characterized and quantified by temperature-programmed reduction (TPR). While hydrogen consumption peaks at lower temperatures correspond to the reduction of large NiO nanoparticles, peaks at higher temperatures are assigned to the reduction of smaller nickel oxide particles, or particles “in strong interaction with the support surface”. Finally, a fraction of Ni<sup>2+</sup> ions trapped inside the support and labelled as “nickel aluminate” can only be reduced at temperatures above 700 °C [4,5]. Assignments are similar for cobalt catalysts, but the identification of the phases is more complex because of the various oxidation states of cobalt in oxidic species [6,7]. The

reducibility of a nickel or cobalt catalyst depends on the proportion of each phase and of the ability of the catalyst manufacturer to limit the formation of the least reducible phases, for instance by varying parameters of calcination (temperature, heating rate, time).

Actually, the chemical nature and formation process of these oxidic species is not completely clear. Various hypotheses account for differences in reducibility: size of the nanoparticles, chemical composition, interactions with the support [8–10]. Extrapolation from published studies and models is made difficult by the fact that nickel speciation strongly depends on preparation parameters that are not easily compared (metal loading, support, thermal treatments). We present here a series of experiments carried out on several Ni/Al<sub>2</sub>O<sub>3</sub> catalysts differing by the structure, specific surface area and pore characteristics of their support, but with one common feature: the nominal density of Ni<sup>2+</sup> ions per surface area unit of alumina. Our aim is to propose a model that would precise the nature of nickel species reduced at higher temperatures and the way they are formed during the catalyst preparation. Consequences on catalysts prepared over mesoporous aluminas exhibiting a high specific surface area are considered.

## 2. Experimental

### 2.1. Catalysts preparation

Five aluminas were used as supports. Their characteristics are presented in Table 1. Four of them exhibit closely related crystal

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structures ( $\delta$ - and  $\gamma$ - $\text{Al}_2\text{O}_3$ ), while the last one belongs to the  $\eta$ - $\text{Al}_2\text{O}_3$  variety. They will be referred to by use of their crystalline type and by their specific surface area, noted in subscript characters. Three aluminas were supplied by the Institut Français du Pétrole ( $\delta_{120}$ - $\text{Al}_2\text{O}_3$ , SCM129;  $\gamma_{200}$ - $\text{Al}_2\text{O}_3$ , EC1285) or Axens ( $\eta_{315}$ - $\text{Al}_2\text{O}_3$ , EC08701).  $\gamma_{250}$ - $\text{Al}_2\text{O}_3$  and  $\gamma_{360}$ - $\text{Al}_2\text{O}_3$  were synthesized following [11], using glucose as a porogen.  $\gamma_{250}$ - $\text{Al}_2\text{O}_3$  was synthesized by recovering the white precipitate of boehmite by centrifugation after the 6 h ageing period, and further calcination in air at 600 °C in a muffle oven.  $\gamma_{360}$ - $\text{Al}_2\text{O}_3$  was prepared following the complete procedure of synthesis, concluded by calcination at 600 °C. The five aluminas also differ by their pore size distribution (Fig. 1). While pore size maxima of the distribution shift to lower values when the specific surface area increases along the series  $\delta_{120}$ - $\text{Al}_2\text{O}_3/\gamma_{200}$ - $\text{Al}_2\text{O}_3/\gamma_{360}$ - $\text{Al}_2\text{O}_3$ , the two other supports  $\gamma_{250}$ - $\text{Al}_2\text{O}_3$  and  $\eta_{315}$ - $\text{Al}_2\text{O}_3$  stand out by their narrow size distributions and small pore sizes, close to the micropore range.

Five Ni/ $\text{Al}_2\text{O}_3$  catalysts were prepared by incipient wetness impregnation of the aluminas described above, using different concentrations of aqueous solutions of nickel (II) nitrate ( $[\text{Ni}(\text{H}_2\text{O})_6](\text{NO}_3)_2$ , 99%, Alfa Aesar), and drying at room temperature (Table 1). Solutions were added dropwise onto the supports, with mechanical mixing taking place after addition of each increment; impregnation of 1 g of support was completed after 10 min. After calcination, the nominal  $\text{Ni}^{2+}$  surface density per  $\text{nm}^2$  was approximately 3 on all the systems. A sixth catalyst was prepared on  $\gamma_{360}$ - $\text{Al}_2\text{O}_3$  by impregnation with an excess of 0.1 mol  $\text{L}^{-1}$  solution of nickel(II) nitrate (38 mL of solution for 2.5 g of support) followed by evaporation of water under reduced pressure. Finally, another system was synthesized by incipient wetness impregnation of  $\gamma_{360}$ - $\text{Al}_2\text{O}_3$  using a 3.1 mol  $\text{L}^{-1}$  aqueous solution of nickel (II) citrate (citrate/Ni = 1). 10 mL of this solution were prepared by refluxing a suspension of 2.91 g of  $\text{Ni}(\text{OH})_2$  (Aldrich) contacted with 6.63 g of citric acid monohydrate (Aldrich), till  $\text{Ni}(\text{OH})_2$  was dissolved. Like diamines [3] and aminoacids [12], citrate ions have been shown to chelate  $\text{Ni}^{2+}$  ions and limit their chemical interactions with oxidic supports [13,14]. pH of the solutions were acidic in all cases, varying from 3 for the most concentrated solutions of nickel (II) nitrate and nickel (II) citrate, to 5.3 for the most diluted solution of nickel (II) nitrate.

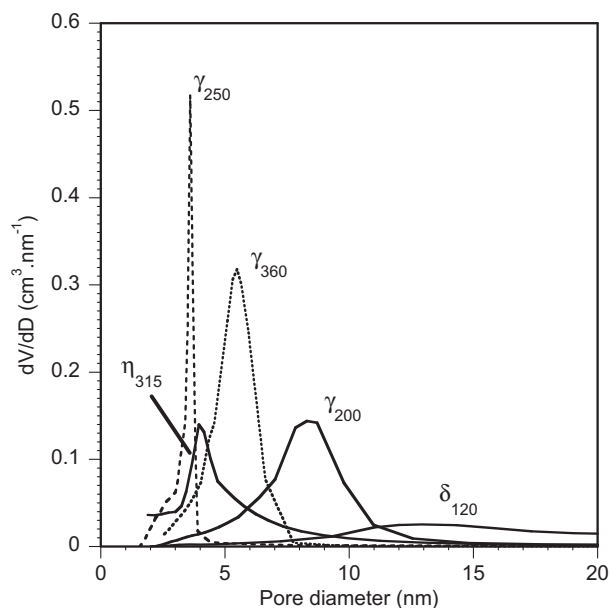


Fig. 1. Pore size distributions for the five aluminas.

## 2.2. Catalysts characterization

Elemental analysis in Ni was performed by ICP AES at the Center of Chemical Analysis of CNRS, Solaize.  $\gamma_{200}$ - $\text{Al}_2\text{O}_3$ ,  $\gamma_{250}$ - $\text{Al}_2\text{O}_3$  and  $\gamma_{360}$ - $\text{Al}_2\text{O}_3$  exhibited contents in Na and Ca lower than the limit of detection (80 ppm), while  $\delta_{120}$ - $\text{Al}_2\text{O}_3$  contained 500 ppm Na and 600 ppm Ca, and  $\eta_{315}$ - $\text{Al}_2\text{O}_3$  2200 ppm Na and 190 ppm Ca, respectively. Specific surface areas and pore characteristics of the catalysts were determined by the BET and BJH models from nitrogen adsorption/desorption experiments carried out at  $-196$  °C on samples outgassed at 250 °C for 4 h prior to analysis, using an automatic Micromeritics ASAP 2010 instrument. Specific surface areas expressed per gram of support were not significantly altered after nickel deposition, except in the case of the sample prepared with excess of impregnation solution (final specific surface area = 300  $\text{m}^2 \text{g}^{-1}$ , nickel surface density = 3.3  $\text{Ni}^{2+} \text{nm}^{-2}$ ).  $\gamma_{360}$ - $\text{Al}_2\text{O}_3$  was formerly shown to be partly unstable toward exposure to a large quantity of water, without changes in the pore size [11].

Calcination of the dried catalysts, purge and subsequent TPR were performed using an Autochem 2910 (Micromeritics), under air (25  $\text{cm}^3 \text{min}^{-1}$ ; heating rate 7.5 °C  $\text{min}^{-1}$  up to 500 °C), Ar (25  $\text{cm}^3 \text{min}^{-1}$ ; down to 20 °C) and 5%  $\text{H}_2/\text{Ar}$  (25  $\text{cm}^3 \text{min}^{-1}$ ; heating rate 7.5 °C  $\text{min}^{-1}$  up to 950 or 1000 °C), respectively. The *in situ* calcination of the dried catalysts, without intermediate exposure to air, allowed us to avoid a possible effect of water on the TPR [15].  $\text{H}_2$  consumption was followed by catharometry. Calibration was done with pure  $\text{Ag}_2\text{O}$  and  $\text{CuO}$  standards. The reduction ratio of  $\text{Ni}^{2+}$  in the catalysts was assessed as 90–95%. A brief description of some of the TPR profiles was presented in [16]. It was checked in parallel experiments that no nickel-containing phase could be detected by XRD on the calcined samples.

## 3. Results and discussion

TPR profiles of calcined Ni/ $\delta_{120}$ - $\text{Al}_2\text{O}_3$ , Ni/ $\gamma_{200}$ - $\text{Al}_2\text{O}_3$ , Ni/ $\gamma_{360}$ - $\text{Al}_2\text{O}_3$  and Ni/ $\eta_{315}$ - $\text{Al}_2\text{O}_3$  are shown on Fig. 2. None of the thermograms exhibits reduction peaks in the lower temperature range

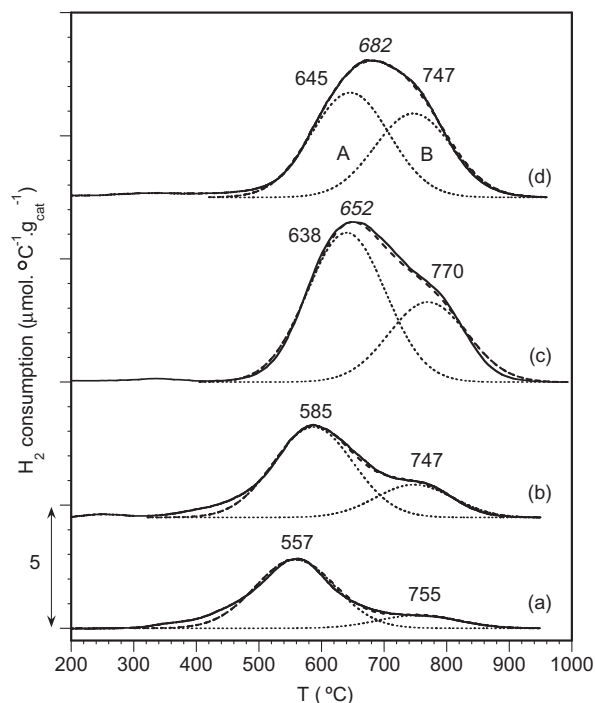


Fig. 2. TPR profiles of: (a) Ni/ $\delta_{120}$ - $\text{Al}_2\text{O}_3$ ; (b) Ni/ $\gamma_{200}$ - $\text{Al}_2\text{O}_3$ ; (c) Ni/ $\gamma_{360}$ - $\text{Al}_2\text{O}_3$ ; and (d) Ni/ $\eta_{315}$ - $\text{Al}_2\text{O}_3$ , expressed per gram of calcined catalyst.

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