



## Gas phase hydrogenation of nitrobenzene over acid treated structured and amorphous carbon supported Ni catalysts

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### ABSTRACT

Carbon supported nickel (1%, w/w) catalysts have been prepared by deposition–precipitation with urea. Two structured, *i.e.* carbon nanofibers (CNF,  $129 \text{ m}^2 \text{ g}^{-1}$ ) and nanospheres (CNS,  $15 \text{ m}^2 \text{ g}^{-1}$ ), and one unstructured, *i.e.* activated carbon (AC,  $686 \text{ m}^2 \text{ g}^{-1}$ ), supports were used. The three supports were treated with  $\text{HNO}_3 + \text{H}_2\text{SO}_4$  to generate oxygen-containing surface groups that served as anchoring sites for Ni introduction. The supports and Ni catalysts have been characterized by scanning and transmission electron microscopy (SEM and TEM), X-ray diffraction (XRD), temperature-programmed reduction (TPR), temperature-programmed decomposition (TPD), Raman spectroscopy,  $\text{N}_2$  adsorption–desorption and acid/base titrations, which have established distinct morphological, graphitic and porous characteristics. CNS and CNF exhibited significant graphitic character when compared with AC, which was essentially microporous in contrast to mesoporous CNF and CNS. Pore volumes were lowered after the  $\text{HNO}_3 + \text{H}_2\text{SO}_4$  treatment, a result that we associate with the incorporation of surface acidity. TPR of the three Ni/C samples resulted in low (620–630 K) and high (823–910 K) temperature hydrogen consumption due to a combined reduction of the Ni precursor and partial decomposition of surface acid groups. Surface area weighted mean Ni particle diameters (post-activation at 623 K) were in the range 7.7–10.4 nm. The three catalysts were tested in the gas phase ( $T = 523 \text{ K}$ ) hydrogenation of nitrobenzene to aniline. Application of pseudo-first order kinetics has delivered the following sequence of increasing specific (per  $\text{m}^2_{\text{Ni}}$ ) activity:  $\text{Ni/CNF} < \text{Ni/CNS} < \text{Ni/AC}$ . Our results demonstrate that nitrobenzene hydrogenation is essentially insensitive to Ni particle size and the higher specific rate delivered by Ni/AC can be attributed to greater surface acidity that serves to enhance nitrobenzene activation.

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### 1. Introduction

Carbonaceous supports are widely used in heterogeneous catalysis due to their resistance to acidic/basic media, adjustable porosity, surface chemistry and easy recovery of the supported metal by controlled combustion [1,2]. Activated carbon (AC) has an amorphous microporous structure (surface area typically  $>600 \text{ m}^2 \text{ g}^{-1}$ ), where the specific structural features depend on the nature of the precursor [1], and is now regarded as a conventional metal support in hydrogenation reactions [3–5]. The discovery of novel carbon nanostructures, such as carbon nanofibers (CNF) and nanospheres (CNS), has led to growing interest in terms of potential catalytic applications. CNF are characterized by a high aspect (length relative to width) ratio with enhanced mechanical

strength and surface areas in the range  $10\text{--}200 \text{ m}^2 \text{ g}^{-1}$  [1,6]. The preponderance of edges in the lattice and basal regions (providing increased metal–support interaction [6]) and the lower mass transfer constraints associated with mesoporous CNF [7] (when compared with conventional AC) offer distinct advantages for use as a metal support. Indeed, there have been recent reports dealing with the application of CNF as a Pd [8], Ru [9] and Pt [10] support in hydrogenation reactions. CNS are typically isolated as a conglomeration of spherical bodies with low surface areas ( $\approx 20 \text{ m}^2 \text{ g}^{-1}$ ) [11] but a high surface chemical activity provided by “unclosed” graphitic layers, reactive open edges and “dangling bonds”, which can enhance reactant adsorption [12]. CNS have been proposed as potential catalyst supports but there is a dearth of studies dealing with their use in catalysis. To the best of the authors’ knowledge, CNS have only been employed as Pt catalyst support in the electro-oxidation of methanol in fuel cells [13].

Taking an overview of the published studies that have compared the catalytic application (in gas phase hydrogen

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mediated reactions) of structured versus non-structured carbon supports, it is worth flagging the work of Amorim et al. who studied the performance of Pd supported on a range of carbonaceous structures in the hydrodechlorination of chlorobenzene and reported decreasing activity in the order Pd/AC  $\approx$  Pd/CNF > Pd/graphite, where larger Pd particles exhibited higher hydrodechlorination rates [7]. It has recently been demonstrated [14] that Ni/AC delivered a higher activity than Ni/graphite (at a comparable Ni dispersion) in the selective hydrogenation of *p*-chloronitrobenzene [14]. In the hydrogenation of phenol over supported Pd, the observed activity sequence, *i.e.* Pd/graphite > Pd/CNF > Pd/AC, was accounted for in terms of metal–support interactions [8]. Regarding liquid phase operation, Pham-Huu et al. [15] reported higher rates for Pd/CNF when compared with Pd/activated charcoal in the hydrogenation of cinnamaldehyde while Zhao et al. [16] recorded a higher activity for Pt supported on carbon nanotubes than Pt/AC in the hydrogenation of nitrobenzene. In the latter two cases, a metal particle size effect was proposed but not explicitly demonstrated in terms of specific (per m<sup>2</sup> of metal) reaction rates. The studies cited above point to a carbon support effect but this has not been irrefutably established and appears to depend on the specific catalytic system/phase/reaction.

Nickel is widely used in hydrogenation applications, offering low cost and moderate activity [9] when compared with Pd and Pt [7,17]. The higher intrinsic hydrogenation rates associated with Pd and Pt may mask, to some extent, the influence of the support in determining catalyst performance. Nickel was accordingly selected in this study to assess the role of three different carbonaceous supports in the hydrogenation of nitrobenzene to aniline. Aniline is a valuable intermediate in the manufacture of plastics, dyes and pigments [18–20] and its production *via* nitrobenzene hydrogenation has been used as a test of catalytic activity in both liquid [19,21–33] and gas [34–43] phases. The reaction has been proposed to be structure sensitive for well dispersed Pt (<2.5 nm) and Pd (<4.7 nm) particles [22,41] but the possible influence of support acidity has not been considered. In this paper, we report the preparation and characterization of Ni supported on (acidified) activated carbon (Ni/AC), carbon nanofibers (Ni/CNF) and carbon nanospheres (Ni/CNS), where a similar mean Ni particle size was achieved using a deposition–precipitation synthesis. We could not find any published work that deals with support effects in the case of nitrobenzene hydrogenation over Ni. Furthermore, this work constitutes the first reported study of CNS based catalysts used in the reduction of a nitroaromatic feed.

## 2. Experimental

### 2.1. Support/catalyst preparation

The CNF and CNS supports were prepared *via* the catalytic decomposition of ethylene (over Ni/SiO<sub>2</sub>) [44] and thermal pyrolysis of benzene (benzene:He = 1:4 (v/v), 1223 K), respectively. The AC support was obtained from NORIT (UK). The CNF sample was subjected to a demineralization treatment with HF (100 cm<sup>3</sup> g<sup>-1</sup>) to remove any residual metal that could contribute to the subsequent hydrogenation reaction; CNS and AC samples received the same HF treatment for comparison purposes. After demineralization, the three supports were refluxed in HNO<sub>3</sub> + H<sub>2</sub>SO<sub>4</sub> (1:1 (v/v), 20 cm<sup>3</sup> g<sup>-1</sup>) for 1 h to introduce surface oxygen groups as anchoring sites for Ni incorporation [45]. The three carbon supported Ni catalysts (1%, w/w) were prepared by deposition–precipitation (DP) using urea as basification agent. In each case, 10 g of carbonaceous support was suspended in 1 dm<sup>3</sup> of Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O solution (1.02 mM) containing excess urea (*ca.* 40 mol<sub>urea</sub> mol<sub>Ni</sub><sup>-1</sup>) and the pH was adjusted to 2–3 by addition of

HNO<sub>3</sub>, which was continuously monitored using a crystal-body pH electrode (Hannah Instruments) coupled to a data collection system (Pico Technology Ltd.). The suspension was then heated to 363 K under constant agitation (250 rpm). This procedure ensured the slow decomposition of urea, which contributes to a more homogeneous metal dispersion [46]. After 18 h, the mixture was cooled to room temperature, filtered and the solid thoroughly washed with deionised water until the wash water approached neutral pH and sieved (ATM fine test sieves) into a batch of 75 μm average diameter.

### 2.2. Support/catalyst characterization

Surface area/porosity measurements were conducted using a Micromeritics ASAP 2010 sorptometer apparatus with N<sub>2</sub> (at 77 K) as sorbate. Prior to analysis, the samples were outgassed at 433 K under vacuum (6.6 × 10<sup>-9</sup> bar) for 16 h. The total specific surface areas were determined by the multi-point BET method and pore size distributions were evaluated using the standard BJH treatment. Acid/base titrations were performed by immersing 25 mg of sample in 50 cm<sup>3</sup> solution of 0.1 M NaCl and 0.1 mM oxalic acid, acidified to pH *ca.* 3 with HCl (0.1 M) with constant stirring under a He atmosphere. A 0.1 M NaOH solution was used as titrant, added dropwise (3 cm<sup>3</sup> h<sup>-1</sup>) using a 100 Kd Scientific microprocessor-controlled infusion pump and the pH was monitored using a Dow-Corning pencil electrode coupled to a data logging and collection system (Pico Technology Ltd.). Surface acidity is presented in this paper as the volume of NaOH required to neutralize surface groups where *pK<sub>i</sub>* ≤ 7, as has been employed in related studies [47–49]; the starting NaCl solution served as a blank. Micro-Raman spectra of the supports were recorded with a Renishaw Raman Microscope System RM1000 equipped with a Leica microscope, an electrically refrigerated CCD camera and a diode laser at 514 nm as excitation source, operating at a power level of 3 mW. The carbon, hydrogen and nitrogen (CHN) content of the carbon supports was determined using a LECO CHNS-932 unit. The carbon (*ca.* 2 mg) combustion (at 1223 K) products were analyzed by IR (for C and H content) and TCD (for N content). The Ni metal loading was determined (to better than ±1%) by atomic absorption (AA) spectrophotometry, using a SPECTRA 220FS analyzer. Samples (*ca.* 0.5 g) were treated in 2 cm<sup>3</sup> HCl, 3 cm<sup>3</sup> HF and 2 cm<sup>3</sup> H<sub>2</sub>O<sub>2</sub> followed by microwave digestion (523 K).

The temperature-programmed reduction (TPR) response was analyzed using the commercial CHEM-BET 3000 (Quantachrome) unit. The samples were loaded into a U-shaped quartz cell (100 mm × 3.76 mm i.d.) and contacted at room temperature with 17 cm<sup>3</sup> min<sup>-1</sup> 5% (v/v) H<sub>2</sub>/N<sub>2</sub> (Brooks mass flow controlled). The samples were then heated (5 K min<sup>-1</sup>) to a final temperature in the range 623–1273 K and maintained at this temperature until the signal returned to baseline. Hydrogen consumption was monitored by a thermal conductivity detector (TCD) with data acquisition/manipulation using the TPR Win<sup>TM</sup> software. The presence of trace methane in the exhaust gas was monitored using a Perkin-Elmer Auto System XL GC equipped with a programmed split/splitless injector and a flame ionization detector (FID), employing a Poropack N 100/120 Mesh (6' × 1/8" o.d.) packed column. Temperature-programmed decomposition (TPD) profiles were recorded using a Micromeritics TPD/TPR 2900 apparatus. The samples were activated *in situ* under H<sub>2</sub> (60 cm<sup>3</sup> min<sup>-1</sup>) at 5 K min<sup>-1</sup> to 623–910 K, cooled to room temperature and then heated (15 K min<sup>-1</sup>) to 873 K in a flow of He (100 cm<sup>3</sup> min<sup>-1</sup>), where changes in outlet gas composition were monitored by TCD and data acquisition/treatment employed the Micromeritics 2900 commercial software. XRD analysis was conducted with a Philips X'Pert instrument using nickel filtered Cu K $\alpha$  radiation; the samples were scanned at a rate of 0.02° step<sup>-1</sup> over the range

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