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Ni-based structured catalyst for selective 3-phase hydrogenation of nitroaromatics

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ABSTRACT

We report herein on the development of Ni-based catalyst using activated carbon fibres (ACFs) as a structured support and its application for the three-phase hydrogenation of nitroarenes (T = 353 K; P = 10 bar). It was shown that metallic Ni^0 nanoparticles (NPs) with a mean diameter of ~2.0 nm stabilized by the ACF microporous network were responsible for the catalytic transformation. To obtain optimum catalytic activity, the Ni/ACF catalyst must be freshly prepared and activated *in situ* by H_2 at T > 353 K. Pre-treatment of the ACFs by nitric acid boosted the activity of the Ni/ACF catalyst, which exhibits high performance in hydrogenation of nitrobenzene to aniline (yield, Y ~100%). The catalyst was tested for the reuse attaining a quasi-steady-state after the sixth reaction thereafter remaining relatively stable over seven consecutive runs. Near-quantitative transformation (Y > 99%) of *p*-chloronitrobenzene to *p*-chloroaniline was achieved under mild conditions over the Ni/ACF catalyst with a *ca.* 20-fold higher activity than conventional Raney Ni. Thus, new catalyst reported here represents a significant step forward towards a simple, heterogeneous catalytic selective hydrogenation of nitroarenes that employs H_2 as the hydrogen source.

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1. Introduction

Functionalized anilines are valuable intermediates used in the synthesis of agrochemicals, pharmaceuticals, pigments and dyes [1]. They are generally prepared by hydrogenation of the corresponding nitroarenes. Traditional non-catalytic processes have been largely abandoned, being replaced by catalytic hydrogenation processes [2]. The catalytic route allows high yields without the generation of toxic wastes and smaller amount of by-products with cost efficient separation and treatment processes. For substituted anilines the preservation of functional groups is one of the main challenges, with the exclusive reduction of the nitro-group while not affecting other groups being crucial [1,3].

The majority of heterogeneous catalytic systems used to hydrogenate nitroarenes are based on precious metals such as Au, Pd, Pt, Rh or Ru [4–14]. Nevertheless, catalysts based on Fe, Co, Cu or Ni [1,9,11,15–19] show promising activity in both liquid and gas-phases [1,18] while Raney nickel is the only commercial catalyst used on the industrial scale for Cl-nitroarenes hydrogenation [1]. The influence of metal nanoparticles (NPs) size on catalytic response including the catalyst selectivity and stability has been widely reported [20–25], although the control of the NP size during the preparation of supported catalysts is difficult to ensure. In general, the highest dispersion of active metal is targeted in order to have a sufficient catalytic performance per mole of active metal.

The majority of hydrogenation catalysts are used as powders to avoid transport limitations, but these powders lead to problems during downstream separation. Possible solutions lie in the use of structured catalysts that allow simple handling and controlled fluid dynamics [14,26]. ACFs in the form of tissues are ideal catalytic structured supports, characterized by a highly porous network, high specific surface areas (SSAs) (up to 3000 m^2 g^{-1}) and low resistance to fluid flow [10,27–30]. ACFs have been used for the deposition of noble metal NPs and exhibit good performances in the multi-phase hydrogenation [31–34]. The carbonaceous surface can be pre-treated in acidic media generating different oxygen-containing groups [35,36]. In this way, the morphology of the supported Me NPs and their catalytic response can be controlled.

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Herein, we present a facile preparation of ACF-based structured catalysts with supported Ni-NPs of high dispersion (1–2 nm) as an active phase. Different pre-treatments of ACF were applied and the influence of preparation conditions on catalytic response has been assessed in nitroarenes hydrogenation. A battery of physico-chemical techniques, such as N_2 physisorption, XRD, XPS, AAS, SEM, STEM-HAADF imaging, temperature programmed decomposition (TPD) and reduction by hydrogen (TPR) was applied for catalysts characterization. The activity/selectivity of the various Ni/ACF catalysts was compared to industrial Raney nickel which serves as a benchmark catalyst.

2. Experimental

2.1. Materials

Nickel(II) nitrate hexahydrate (Fluka, ≥98.0%), nitric acid (VWR chemicals, 65%), hydrogen peroxide (reactolab SA, 30%), nitrobenzene (99%, Acros Organics), 1-chloro-4-nitrobenzene (99%, Acros Organics), 1,3-dinitrobenzene (Tokyo Chemical Industry, ≥99.0%), dodecane (99%, Acros Organics), methanol (MeOH, ≥99.8%, Sigma-Aldrich), ethanol (EtOH, 99.8%, Sigma-Aldrich), toluene (>99%, AppliChem) were used as received. The solvent used for the reaction was technical EtOH (95% + 5% MeOH, Brenntag). All gases (H_2, N_2, and Ar) were of high purity (Carbagas Switzerland, >99.9%). The ACF K-20 (~2000 $m^2\,g^{-1}$) was purchased from Kynol Europa GmbH.

2.2. Catalyst preparation

2.2.1. Structured Ni/ACF
The Ni/ACF catalysts were prepared as follows. Commercial ACF was pre-treated in 15 wt.% HNO_3 aq. solution for 15 min at 373 K ($ACF_{HNO3-373}$) and for 3 min at 298 K ($ACF_{HNO3-298}$) to increase the concentration of oxygen-containing groups on the carbon surface [35,37]. The supports denoted as ACF were not pre-treated and used as received. The ACF was impregnated with an ethanolic solution of the Ni precursor ($Ni(NO_3)_2\cdot6H_2O$) ensuring complete filling of the pores. The Ni loading was adjusted by varying the precursor concentration. The impregnated ACF samples were dried at room temperature (RT) overnight. The precursor decomposition was performed via thermal treatment in a flow reactor (50 cm × 3 cm i.d.) from RT to 673 K, 6 K min⁻¹ under Ar flow (280 cm^3 min⁻¹), maintained at 673 K (1 h) under 17% v/v H_2/Ar flow (340 cm^3 min⁻¹) and cooled to RT under Ar. To prevent oxidation of the pyrophoric Ni/ACF, the samples were passivated (1 h) at RT in 2.8% v/v air/Ar flow (145 cm^3 min⁻¹). Gas flows were controlled using an Agilent Technologies ADM1000 Universal Gas Flowmeter, values are given in IUPAC STP [40].

2.2.2. Raney nickel catalyst
1 g of Ni-Al (50:50 wt.% alloy, Alfa Aesar) was treated with an aq. solution of KOH (10 wt.%) and stirred at RT until bubbling (H_2) stopped (~1 h), then at 333 K for 0.5 h. The resulting solid (Raney Ni) was decanted, washed with distilled water and ethanol.

2.3. Catalyst characterization

The Ni content was determined by absorption atomic spectroscopy (AAS) using a Shimadzu AA-6650 spectrometer with an air-acetylene flame. Temperature-programmed reduction in hydrogen (H_2-TPR) was carried out on a Micromeritics Autochem II 2920 by heating the sample in 17 cm^3 min⁻¹ 5% v/v H_2/N_2 from RT to 973 K at 2 K min⁻¹. The exit gas was passed through a liquid N_2 trap and changes in H_2 consumption/release were monitored by TCD with data acquisition/manipulation using the TPR Win™ software.

BET surface areas were measured using a Micromeritics 3Flex. Prior to analysis, the samples were degassed at 393 K for 3 h under vacuum (<1 × 10⁻⁵ bar). N_2 adsorption/desorption isotherms were recorded over the range 0.000002 ≤ P/P_0 ≤ 0.99. The specific surface area and the total pore volume were obtained using the BET method [38].

Temperature Programmed Decomposition (TPD) was conducted in a He flow (50 cm^3 min⁻¹) from RT to 835 K at 5 K min⁻¹ in a tubular reactor inside an oven (Carbolite MTF 10/25/130) and the outlet flow was continuously monitored using a Pfeiffer Vacuum ThermoStar™ GSD 300 T2. The NO_2 signal was mainly detected as a NO fragment (m/z = 30).

Powder X-ray diffractograms (XRD) were recorded on a Bruker/Siemens D500 incident X-ray diffractometer using Cu Kα radiation. The samples were scanned at 0.004° s⁻¹ over the range 20° ≤ 2θ ≤ 90° (scan time = 5 s step⁻¹). Diffractograms were identified using the JCPDS-ICDD reference standard, i.e. Ni (89-7129), NiO (89-5881) and NiO_2 (89-8397). In situ XRD patterns were obtained using a PANalytical X'Pert PRO θ–θ scan system with Cu$_{K\alpha}$ radiation (λ = 1.5418 Å). The diffraction patterns were recorded at a scanning rate of 0.015° s⁻¹. The $Ni(NO_3)_2$/$ACF_{HNO3-373}$ sample was placed in the heating chamber (XRK 900, Anton Paar) and gas was applied through the mass flow controller (5850 TR, Brooks instrument). About 0.03 g of sample was heated under a 60 cm^3 min⁻¹ flow of N_2 up to 723 K with a heating rate of 2 K min⁻¹. Long scans (30° ≤ 2θ ≤ 85°) were acquired on the fresh sample directly after heating to 723 K. In a separate experiment on the same starting material, the procedure was modified by replacing the N_2 by 10% v/v H_2/N_2. A long scan was performed at the end of the procedure. Peak fitting was performed using the EVA (DIFFRAC.Suite) software.

X-ray photoelectron spectroscopy (XPS) analysis was conducted on PHI VersaProbe II (Physical Instruments AG). The monochromatic Al Kα X-ray source power was maintained at 24.8 W and the emitted photoelectrons were obtained from a 100 μm × 100 μm samples. The spherical capacitor analyser was set at a 45° take-off angle with respect to the sample surface. The analyser pass energy was 188 eV for survey spectra (0–1300 eV) and 47 eV for high resolution spectra (Ni 2p3/2 and Ni 2p1/2). For the latter resolution a full width at half maximum of 0.91 eV for the Ag 3d 5/2 peak was obtained. The adventitious C (284.8 eV) 1 s peak was used as an internal standard to compensate for any charging effects. Sputtering was realized using a 20 kV Ar$_{2500}$⁺ cluster source on a 2 nm × 2 nm sample surface at a rate of 0.45 nm/min (referenced to SiO_2). Curve fitting was performed using the CasaXPS software.

The Ni NPs size distribution was measured from "Z-contrast" or high angle annular dark-field scanning transmission electron microscope (HAADF STEM) images acquired on a FEI Talos F200S instrument operating at 200 keV. The Ni/ACF catalysts were infiltrated-embedded in an EPON 812 epoxy resin and polymerized at 333 K for 24 h, cut (20 nm) by ultramicrotomy to analyse the fibre cross-section. The TEM samples were subjected to mild (10 eV) plasma cleaning for 1 min using a Fischone 8070 plasma cleaner operated with a forward power of 9 W.

Up to 1400 individual metal particles were counted for the investigated catalyst and the circular diameter (d_i) was determined from the area measured using imageJ software from images of different magnifications. The mean circular diameter (d) was calculated using Eq. (1):

$$d = \frac{\sum\limits_{i} n_i d_i}{\sum\limits_{i} n_i} \tag{1}$$

where n_i is the number of particles of diameter d_i.