



Commercial catalysts screening for liquid phase nitrobenzene hydrogenation



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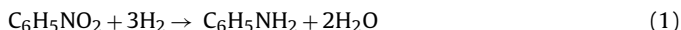
ABSTRACT

In this work, a series of commercially available materials was screened for the catalytic hydrogenation of nitrobenzene (NB). The materials revealed different performances, particularly different activities in what concerns the NB conversion, and notably diverse selectivities towards the industrially desired reaction product, aniline (ANL). The catalysts' active phases are based on Pd and Ni (respectively groups I and II), namely 1 wt.% Pd/Al₂O₃ (catalyst I.1), 0.3 wt.% Pd/Al₂O₃ (catalyst I.2), 0.3 wt.% Pd/Al₂O₃ (catalyst I.3), and 50 wt.% NiO/(Al₂O₃ + SiO₂) (catalyst II.1). The fresh and used materials were characterized by several physical-chemical techniques, specifically scanning electron microscopy (SEM), high resolution transmission electron microscopy (HRTEM), nitrogen adsorption (with BET surface area determination), X-ray diffraction (XRD), H₂ temperature-programmed reduction (TPR), inductively coupled plasma mass spectrometry (ICP-MS) and elemental (CHNS) analysis. It was shown that the catalysts are stable in the conditions studied and no deactivation was found. The characterization results allowed explaining the catalytic behavior of the tested materials. In particular, catalyst I.1 was found to be the less active, probably due to its much lower BET surface area (and larger Pd particle size). On the other hand, catalyst I.2 was the more active, which was well correlated to the smaller average particle size (along with narrower Pd particle size distribution) and smaller pellet size, although the active metal content is low. Finally, it was observed that catalyst II.1 is the most selective towards light by-products (benzene (Bz), cyclohexylamine (CHA), cyclohexanol (CHOL) and cyclohexanone (CHONA)), probably due to its lower pore size dimensions.

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1. Introduction

Aniline (ANL) is an important raw material for the polyurethane industry, being used mainly in the production of methylene diphenyl diisocyanate (MDI) [1,2]. Commercial ANL is predominantly produced by the catalytic hydrogenation of nitrobenzene (NB)—Eq. (1), which can be performed in gaseous or in liquid phase [3,4].



One of the advantages of using liquid phase hydrogenation is to avoid the hot-spots (as a consequence of the reaction exothermicity); moreover, when compared with the vapor-phase and for a given reactor size, it usually shows a greater production capac-

ity and allows using reaction heat to produce steam. Typically, NB liquid-phase hydrogenation is operated at 80–250 °C under pressure with yields of 98–99%. In vapor-phase, although yields of 99% or higher could be achieved, it is operated under pressure at slightly higher temperatures [1,5].

For NB hydrogenation many catalysts offering high activity and selectivity are available, being the choice of the right catalyst to be used in the industrial ANL synthesis a key issue. Usually, for the hydrogenation of nitro groups, the most used metals are palladium, platinum and nickel, supported or not [6]. In the case of NB hydrogenation there is a wider possible choice, including also the use of copper and cobalt [7]. Other reducing agents, such as ferrous salts, tin, zinc, soluble sulfides, sulfur, and carbon monoxide were also proposed [1–8]. Catalyst selection is very important for maximizing ANL selectivity, keeping secondary products formation low.

Palladium and nickel catalysts have shown great success in the NB hydrogenation [9,10]. For instance, it has been reported the use of platinum-palladium catalyst on a carbon support, with iron

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Nomenclature

ANL	Aniline
Bz	Benzene
CH	Cyclohexane
CHA	Cyclohexylamine
CHOL	Cyclohexanol
CHONA	Cyclohexanone
CHANIL	N-Cyclohexylaniline
CHENO	Cyclohexyldeneaniline
DICHA	Dicyclohexylamine
MDI	Methylene diphenyl diisocyanate
NB	Nitrobenzene

as a modifier [11], as well as palladium or palladium-platinum deposited on a lipophilic carbon support [12], palladium supported on iron oxides [13], or using a gel entrapped palladium catalysts [14]. Noble metals can catalyze the NB hydrogenation under mild conditions, since the nitro group was found to be one of the most suitable to be reduced using this type of catalysts. Nevertheless, their use in large-scale production has not been explored due to their high costs [15]. The advantage of Pd-based catalysts is related with their high activity and also to the fact that they do not attack, or even disrupt, the aromatic ring [16]. In the open literature, the most studied catalysts for NB hydrogenation in liquid phase are palladium supported on carbon [17–20]. However, upon consulting the list of commercial catalysts available in the market, it is possible to verify that the most common is palladium supported on Al_2O_3 , with the variations restricted to their shape and metal content [21].

Ni-based catalysts are also well-known and widely studied in the liquid phase reaction, either being supported or on a Raney form [22,23]. Industrially, Ni catalysts are also very used due to their low cost and high yields [3].

The main goal of this work was to test available commercial catalysts suitable for the NB hydrogenation in liquid phase that are active in mild conditions of temperature and pressure. Pd-based catalysts are the most appropriate, and so it was decided to acquire several Pd catalysts (from now on called group I). Industrially, Ni based-catalysts are the most used for ANL production being decided to acquire one of this kind to use as a reference (group II) to compare activity and selectivity to the desired reaction, with less secondary products formation.

2. Material and methods

2.1. Catalyst samples

Materials used in this work are available in the market and are presented as catalysts for the hydrogenation of aromatic nitro groups into aromatic amines. The main characteristics of the as-received catalysts are presented in Table 1 (group I—Pd-based; group II—Ni-based).

Table 1
Catalysts main physical characteristics.

	catalyst I.1	catalyst I.2	catalyst I.3	catalyst II.1
Composition	1 wt.% PdO/ Al_2O_3	0.3 wt.% PdO/ Al_2O_3	0.3 wt.% PdO/ Al_2O_3	50 wt.% NiO/($\text{Al}_2\text{O}_3 + \text{SiO}_2$)
Size (mm)	2–4	1.2–2.5	4–6	0.8–3.2

2.2. Catalysts characterization

The commercial catalysts were characterized by XRD (X-ray Diffraction), SEM (Scanning Electron Microscopy), TEM (Transmission Electron Microscopy), HRTEM (High Resolution Transmission Electron Microscopy), H_2 -TPR (Temperature Programmed Reduction), nitrogen adsorption for BET surface area determination, ICP-MS (Inductively Coupled Plasma Mass Spectrometry) and elemental (CHNS) analysis. Two samples of each catalyst were characterized: without suffering any reaction (fresh samples) and after the catalytic tests (used samples), except for H_2 -TPR, where only the fresh materials were analysed because the used samples have some organic compounds, which interfere in the TCD signal.

The XRD patterns were obtained on a Rigaku diffractometer, Geigerflex, in the angular range of 10 – 100° (2θ) with a scan rate of $3^\circ/\text{min}$. The morphology and surface of the catalysts were analyzed by SEM, performed on a Hitachi SU-70 microscope. TEM, performed on a Hitachi 8100 with ThermoNoran light elements EDS detector and digital image acquisition, was used to monitor the morphological properties of the different samples. HRTEM was performed on a JEOL 2200FS apparatus to determine the Pd particle size distribution in the support.

H_2 -TPR experiments were performed on a Micromeritics AutoChem II 2920 apparatus, using 130 mg of catalyst. Ni catalyst was pre-treated, under argon (flow rate of 25 ml/min NTP), from room temperature (RT) up to 250°C (heating rate of $10^\circ\text{C}/\text{min}$), kept at 250°C for 1 h and then cooled to RT. This pre-treatment was realized with the objective of removing water and impurities from the catalyst surface. Then, the reactor was purged with argon for 10 min at RT. Only the Ni catalyst was pre-treated, because Pd particles are reduced in the presence of Argon. H_2 -TPR was carried out under a mixture of 5% H_2 /Argon with a flow rate of 30 ml/min (NTP), from RT up to 900°C at a heating rate of $10^\circ\text{C}/\text{min}$. Hydrogen consumption was measured with a TCD; water formed during the reduction processes was trapped in a dry ice trap.

Nitrogen adsorption and desorption measurements were carried out at 77 K with an automatic Micromeritics ASAP 2000 apparatus. Prior to analysis, the samples were pretreated at 448 K under vacuum for 6 h. The BET surface area (S_{ext}), the total pore volume (V_{total}), calculated from the adsorbed volume of nitrogen for a relative pressure P/P_0 of 0.99, and the average pore diameter (D_{average}), were estimated.

Elemental (CHNS) analysis was performed on a TruSpec Micro equipment with a nominal sample weight of 2 mg. The determination of elements by ICP-MS was performed on an ICP-MS Thermo X Series apparatus. The sample to be analyzed was rigorously weighed (ca. 0.05 g) and it was added 1 ml $\text{HNO}_3 + 3$ ml $\text{HCl} + 1$ ml de HF. Then the sample was digested under microwave heating (180°C) for 5 min. The sample was finally taken up to 100 ml with ultrapure water and analyzed.

2.3. Catalytic reaction

Hydrogenation of NB, in liquid phase, was carried out in a 1L-capacity Parr batch reactor provided with an air-impelled stirrer (Fig. S.1 of the Supplementary information section). The stirrer was equipped with a basket, where the catalysts were placed. The catalysts used are those indicated in Table 1. Preliminary results have shown that above 1000 rpm no major differences were observed

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