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# Novel microwave synthesis of ruthenium nanoparticles supported on carbon nanotubes active in the selective hydrogenation of p-chloronitrobenzene to p-chloroaniline

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### 1. Introduction

The role of catalysis in the development of clean chemical production with limited hazardous and toxic by-products is now well-established as an essential element of sustainable processing [1]. Today, aromatic haloamines are extensively employed as intermediates in the manufacture of many fine chemicals [2,3]. In particular, p-chloroaniline is applied as curing agent for epoxy resins, as cross-linking agent in some polymer preparations and in pharmaceuticals for the synthesis of tranquilizers [4]. These organic amines are currently produced through the reduction of the corresponding aromatic halonitro compounds either by Bechamp's reaction, using a metal-acid reduction system, or by selective hydrogenation over transition-metal catalysts. The former stoichiometric method has been falling into disuse in industry because it produces a great amount of Fe/FeO sludge which cannot be recycled, thus causing a serious environmental pollution [5]. The second route is characterized by a clean production process, high atom

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### ABSTRACT

Carbon nanotubes (CNTs) have been employed for the preparation of supported ruthenium nanoparticles using, for the first time, a low boiling alcohol or a mixture ethanol/water as solvent/reducing agent under microwave irradiation as heating source. These systems were employed as catalysts in the selective hydrogenation of p-chloronitrobenzene (p-CNB) to p-chloronailine (p-CAN) and resulted efficient systems for the selective reduction of the nitro group in p-CNB under mild reaction conditions (60 °C and 4 MPa of H<sub>2</sub>), while the C—Cl bond remains intact, thus allowing the almost complete substrate conversion with total selectivity to the target product. These supported ruthenium nanoparticles are characterized by small average diameters and narrow particle size distributions, even if synthesized in the absence of any additional stabilizing agents and appear very promising systems also for other catalytic applications.

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economy, cheap operations, easy product separation and can offer high selectivities to the desired product with a significantly lower environmental impact [6]. However, it is still difficult to industrially apply this process because of the extensive dechlorination which lowers the selectivity, producing also corrosive hydrogen chloride [7]. A number of reaction parameters have been shown to affect the activity and the selectivity to chloroanilines, but the secondary dechlorination reaction cannot be completely avoided [8]. Many studies regarding this hydrogenation reaction have been made both in gas [9,10] and in liquid phase [11-16], emerging the last as the cleanest and the most sustainable alternative. Most researches were focused on heterogeneous metal catalysts [11-26], such as Pd [17], Pt [11,12,18,19], Rh [20], Ir [13,21], Ni [14], Raney Ni [22], Au [15], Ru [10,16,23-29] and poly-metallic catalysts [30]. Palladium catalysts are the more widely employed, but though they show high activities, the selectivity to chloroaniline remains low because of the dehalogenation reaction [17,31]. Platinum based catalysts have been also deeply investigated: although they show interesting catalytic performances under mild reaction conditions, now they are not suitable for an industrial expansion due to the high price of platinum [32]. Very few attempts were performed using rhodium and iridium catalysts which, despite promising selectivities, are scarcely active [21]. Well-investigated catalysts were also nickel ones because of their acceptable cost compared to other noble



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Scheme 1. The hydrogenation pathways of p-chloronitrobenzene.

metals. In spite of several attempts have been made in order to suppress the undesired hydrodehalogenation side reaction, this is still an unsolved problem on nickel catalyst, together with their toxicity [14,33,34]. On the other hand, gold catalysts show a reduced activity and they require a high reaction temperature and hydrogen pressure to be competitive with other metals, a response that has been attributed to less effective activation/dissociation of H<sub>2</sub> [13,35,36]. Recently high activity and selectivity (up to 100% in p-chloroaniline) have been ascertained in the hydrogenation of *para*-substituted nitroarenes in gas phase at 200 °C adopting Au/TiO<sub>2</sub> or Ag/TiO<sub>2</sub> [37]. The continuous process is very suitable for large scale processes. However these gas phase operations need high temperatures with extra energy input, more severe maintenance of the plant and safety problems [27].

The employment of bimetallic catalysts or alloy catalysts often results in an improvement in catalytic behaviors, but more complicated procedures and extra processing steps are required for the recovery of metals from the used catalysts [2,38]. Furthermore, the elimination of the undesired dechlorination reaction at high conversion of substrate is still a challenge also on bimetallic supported catalysts [8].

Regarding ruthenium catalysts, it is well-known that they are highly selective but exhibit low activity for haloaromatic amine formation [10,16,23–26] and on this metal the catalytic hydrogenation of p-CNB follows a multi-step reaction pathway, as shown in Scheme 1.

The main side reaction on ruthenium catalyst is the hydrodechlorination, leading to aniline (AN) as the ultimate product. This may happen either by the hydrodechlorination of p-CNB to nitrobenzene (NB), followed by the subsequent hydrogenation to AN or by the hydrodechlorination of the target product pchloroaniline (p-CAN) to AN [17]. For ruthenium catalysts, the best selectivity (>99%) to p-CAN have been reached on alumina [26] and SnO<sub>2</sub> [24] supports, whereas other investigated supports, such as silica [23] or MgF<sub>2</sub> [16], gave selectivities around 90%. The addition of metal cations modifiers, in particular  $Sn^{4+}$ , and the use of protic solvents, enhance the reaction rate and the selectivity of  $Ru/Al_2O_3$  [29]. The effect of metal cations has been related to their interaction with the ruthenium particles which may change the electronic density of the active catalytic site and, as a consequence, the catalytic performance.

The catalytic activity and, in particular, the chemoselectivity of this reaction can also be influenced by strong metal/support interactions which produce electronically altered sites [8].

Now, we have studied supported Ru catalysts for the selective hydrogenation of p-CNB to p-CAN using carbon nanotubes (CNTs) as support: due to their peculiar interaction with metals, they represent a remarkable support and metal nanoclusters adsorbed both inside and outside CNTs usually exhibit very high activities and excellent selectivities [39,40]. These advantages result from their high mechanical strength, excellent thermal properties, absence of microporosity and absence of diffusion and material mass-transfer limitations. In addition, the metal-support interactions can generate electronic perturbations on metal particles. thus inducing a peculiar structure or a modification of the electron density in the metal clusters. Interesting results obtained employing CNTs as supports have been already reported in the literature [41-47], and the catalytic activity in hydrogenation reactions resulted enhanced either due to electronic effects and/or to the absence of diffusion limitations. In particular the charge transfer between CNTs and ruthenium has been well evidenced [41]. As above reported, this type of interactions results determinant for the catalytic performances in the selective hydrogenation of functionalized nitroarenes [8].

Recently, microwave (MW)-assisted preparation represents a major breakthrough in synthetic chemistry methodology, because (i) it provides a rapid and homogeneous heating of the entire sample avoiding detrimental temperature gradients, (ii) it enhances reaction rates facilitating the formation of uniform nucleation centers and (iii) it is energy efficient and environmentally friendly [48,49]. Especially, it presents unique advantages in the synthesis of carbon-based materials because carbon itself is a good microwave absorbent [50]. Regarding the microwave synthesis of ruthenium catalysts, many efforts have been made [48,51-54] and many preparation methods [40,52,53,55-61] employ the microwaveassisted polyol process, where a high boiling polyol, generally ethylene glycol, acts as solvent for the metal precursor as well as reducing agent and grow medium for the metallic product, but the high boiling points and viscosities of used polyols lead to downsides during the isolation of metal nanoparticles. In the present paper, we have synthesized ruthenium nanoparticles supported on CNTs by the reduction of RuCl<sub>3</sub>·3H<sub>2</sub>O in a low boiling point alcohol employing the microwave-assisted synthesis. Very few results are reported in the literature on the synthesis of ruthenium nanocolloids made using low boiling point alcohol solvents, such as n-butanol, n-propanol and ethanol [62]. To the best of our knowledge, no adoption of a low boiling point alcohol as solvent/reducing agent under microwave irradiation for the synthesis of ruthenium nanoparticles supported on CNTs has ever been reported. On the other hand, only few researches report the preparation of ruthenium nanoparticles supported on CNTs [44-46,63]. Recently nanostructured carbon nanotubes and nanofibers have been used as support for the preparation by wet impregnation of ruthenium nanoparticles used in the hydrogenation of p-CNB. These catalysts exhibited excellent catalytic performances in liquid phase, obtaining for both supports a selectivity of 94% to p-CAN at complete substrate conversion [63]

Therefore, the objective of our research is the study of new, sustainable and cost-effective microwave-assisted synthesis of ruthenium nanoparticles supported on CNTs and their use in the selective hydrogenation of p-CNB to p-CAN adopting mild reaction conditions.

# 2. Experimental methods

# 2.1. Chemicals

Ruthenium chloride hydrate (RuCl<sub>3</sub>·3H<sub>2</sub>O), Ru/Al<sub>2</sub>O<sub>3</sub> 0.5 wt% and PVP (poly-N-vinyl-2-pyrrolidone, average molecular weight 29,000) were purchased from Aldrich Chemical Company and were used as received. Unless otherwise stated, all other reagents and products (ethanol, isopropyl alcohol, acetone, diethyl ether, p-chloronitrobenzene, p-chloroaniline, aniline, methanol) were obtained from Aldrich and purified according to the standard distillation procedures.

Ru/C 5 wt% (Escat 40) (catalyst particle size distribution: 10% <4  $\mu$ m, 50% 4–21  $\mu$ m and 40% 21–90  $\mu$ m; surface area 900 m<sup>2</sup>/g; Ru particles in the size range 1–4 nm with mean size 2±0.5 nm [64]) was purchased from Engelhard and used as received.

Carbon nanotubes were produced by chemical vapor deposition from ethylene in the presence of hydrogen on Fe catalysts supported on hydroxyapatite [65]. The as-produced sample was purified by HCl washing for 12 h at room temperature, then filtered, washed with deionized water repeatedly until the pH of the filtrate was around 7 and then dried for 3 days in an oven at 110 °C. The modified supports were oxidized in acid HNO<sub>3</sub> at 140 °C for 4 h, then washed with deionized water until the pH of the filtrate was again around 7 and then dried at 120 °C for 12 h. The complete characterization of the as-produced samples as already been reported [63].

 $\gamma$ -Al\_2O\_3 (BET surface area 138 m²/g) was purchased from Strem and used as support after treatment under vacuum at 180 °C for 6 h.

# 2.2. Preparation of the ruthenium nanoparticles

The MW-assisted synthesis of Ru nanoparticles was performed using a CEM Discover S-class oven with a PC control. The instrument consists of a single-mode, self tuning cavity where the correct position of the reaction vial is automatically tuned to ensure reproducible conditions at each run. The oven operates with a continuous power generator capable of supplying an irradiation power from 0 to 300W (with 1W-step increment) with a fine and automated control of the sample temperature based on the CEM PowerMax technology. The oven allows two different ways of working: at constant temperature (varying the irradiation power in order to maintain the desired temperature value) or at constant power. The 80 ml glass reactor (sealed vessel accessory) was equipped with a magnetic drive stirrer and a vertically focused IR temperature sensor which provided an accurate temperature control during the process. This sealed vessel accessory was equipped with a pressure line and a pressure probe, the latter allowing the control of the internal pressure throughout each run. The reaction conditions adopted for the different preparation are summarized in Table 1. The ruthenium colloidal nanoparticles (Sample 1, 1 bis and 6) were prepared as follows: the selected amount of RuCl<sub>3</sub>·3H<sub>2</sub>O and PVP (stabilizer) were dissolved in the solvent, under stirring at room temperature. The resulting solution was MW-irradiated for 12 min at constant MW power of 250 W working under 1.2 MPa of nitrogen at 150 °C. The reaction was monitored throughout its course by sampling the mixture at different reaction times and controlling the reduction process by means of UV-vis spectroscopy.

For the "in situ" preparation of the supported catalysts (Samples 2, 2 bis, 3–9), the desired support was directly added to the reaction vessel containing the chosen solvent,  $RuCl_3 \cdot 3H_2O$  and PVP when specified. The process was then carried out as above reported for

colloidal samples. In all cases, the work-up of the supported ruthenium nanoparticles was performed as follows: when the reaction was complete, the reactor vessel was rapidly cooled to the safe temperature for the opening of the reactor vessel (50 °C) in about 3 min, the solvent was removed by evaporation under vacuum and the supported samples were washed with acetone and ether, dried under vacuum and stored under nitrogen atmosphere.

#### 2.3. Characterization of the catalysts

Ultraviolet-visible absorption spectral measurements were carried out with a UV-vis spectrophotometer JASCO V-530 operating at room temperature.

TEM images of the samples were taken on a JEOL 1011 transmission electron microscope. High resolution images were obtained on a JEOL JEM 2100F transmission electron microscope with a field emission gun (TEM-FEG). Mean Ru particle sizes are quoted from statistical distributions of measurements as a number average diameter  $\sum_i n_i d_i / \sum_i n_i$  where  $n_i$  is the number of particles of diameter  $d_i$  and  $\sum_i n_i > 200$ . The size limit for the detection of Ru particles is ca. 1 nm.

The BET surface area was determined by nitrogen adsorption, using a single point ThermoQuest Surface Area Analizer Qsurf S1. BET surface area values were reproducible within  $\pm$ 5%.

Micro Raman spectra were taken on powder samples on a Perkin Elmer Raman spectrometer with 785 nm red laser irradiation.

The ruthenium content was established by inductively coupled plasma-optical emission spectrometers (ICP-OES), with a Spectro-Genesis instrument using a software Smart Analyzed Vision.

Elemental analysis of eventual residual chlorine was carried out at ENI S.p.A. (San Donato Milanese, Italy).

X-ray photoelectron spectroscopy analyses were performed with a VG Microtech ESCA 3000 Multilab spectrometer, using the unmonochromatized Al K $\alpha$  source (1486.6 eV) run at 14 kV and 15 mA [57]. The samples were analyzed as powders mounted on a double-sided adhesive tape. In order to avoid the contact with air, the mounting on the sample holder was performed inside a glove bag filled with N<sub>2</sub> and then the holder was loaded inside the XPS machine in a N<sub>2</sub> atmosphere.

## 2.4. Hydrogenation of p-chloronitrobenzene to p-chloroaniline

All the hydrogenation reactions were carried out in a 300 ml mechanically stirred Parr 4560 autoclave equipped with a P.I.D. controller 4843. In a typical procedure the amount of supported catalysts (corresponding to 0.5 mg of metallic Ru) was charged in the autoclave under inert atmosphere. Then the autoclave was closed, evacuated up to 66 mPa and a solution of 0.4 g of pchloronitrobenzene in 50 ml of methanol was introduced inside by suction. Then the autoclave was pressurized with hydrogen to 4 MPa and heated up to 60 °C, adopting a stirring speed of 500 rpm which was ascertained to assure the absence of mass transfer limitations. Reaction mixture samples were periodically removed via the liquid sampling valve, collected in capped vials and analyzed by gas-chromatography with a HP 5890 gas-chromatograph equipped with a HP 3396 integrator, a flame ionization detector and a PONA capillary column (length of the column: 30 m, inner diameter: 0.25 mm and thickness of the stationary phase:  $0.25 \mu \text{m}$ ) with a stationary phase 100% dimethylpolysiloxane. The carrier gas was nitrogen and the flow was 1 ml/min.

Recycling experiments of the catalyst were carried out in a similar manner but, after removing through the sample valve the liquid reaction mixture, the autoclave containing the solid catalysts was evacuated and again charged with the fresh p-CNB solution for a subsequent catalytic cycle.

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Synthetic conditions and characterizations of colloidal and supported ruthenium catalysts (reaction conditions: 250 W; T, 150 °C; and 1.2 MPa of nitrogen for 12 min).

Sample	RuCl₃·3H₂O (mg Ru)	PVP (g)	Solvent (ml)	Support (g)	Ru (wt%) <sup>a</sup>	Average diameter (nm)	Standard deviation $\sigma$ (nm)	BET (m <sup>2</sup> /g)
1	24.6	0.31	<sup>i</sup> PrOH	-	-	2.7	1.0	-
1 bis	26.3	0.33	<sup>i</sup> PrOH	-	-	2.9	1.1	-
2	25.7	-	<sup>i</sup> PrOH	CNT (HNO <sub>3</sub> ) 0.50	1.3	3.4	1.8	152
2 bis	27.0	-	<sup>i</sup> PrOH	CNT (HNO <sub>3</sub> ) 0.52	1.2	3.6	1.7	150
3	25.4	0.33	<sup>i</sup> PrOH	CNT (HNO <sub>3</sub> ) 0.53	1.3	2.7	1.2	137
4	27.1	-	<sup>i</sup> PrOH	CNT (HCl) 0.51	1.8	3.1	1.5	126
5	25.3	0.32	<sup>i</sup> PrOH	CNT (HCl) 0.51	1.3	2.8	0.9	111
6	28.1	0.33	H <sub>2</sub> O/EtOH 80/20	-	-	3.1	1.3	-
7	27.7	0.36	H <sub>2</sub> O/EtOH 80/20	CNT (HNO <sub>3</sub> ) 0.67	1.6	3.3	1.4	142
8	2.47	-	H <sub>2</sub> O/EtOH 80/20	$\gamma$ -Al <sub>2</sub> O <sub>3</sub> 0.50	0.15	2.9	1.3	133
9	25.5	_	H <sub>2</sub> O/EtOH 80/20	γ-Al <sub>2</sub> O <sub>3</sub> 0.51	1.2	3.3	1.2	122

<sup>a</sup> Determined by inductively coupled plasma analysis (ICP).

Repeated catalytic runs using different samples of the same catalyst produced reaction mixtures whose composition was reproducible within  $\pm 5\%$ .

# 3. Results and discussion

The MW-assisted synthesis of ruthenium nanoparticles was preliminarily tested for the preparation of unsupported colloidal ruthenium nanoparticles using poly(N-vinyl-2-pyrrolidone) (PVP) as stabilizing agent and isopropyl alcohol as solvent and reducing agent (Sample 1, Table 1). The capping agent was necessary for the stabilization of the colloid prepared in the absence of any support.

The reduction process was monitored by sampling the reaction mixture at different reaction times and analyzing it by means of UV–vis spectroscopy. In Fig. 1 the UV–vis spectra of the RuCl<sub>3</sub>·3H<sub>2</sub>O solutions stabilized with PVP before and during the progressive reduction by MW irradiation are reported.

A broad absorption peak between 300 and 400 nm, assigned to the  $Ru^{3+}$  ions, was present in the spectrum before MW irradiation. During the radiation this peak progressively disappeared due to the gradual reduction of  $Ru^{3+}$  ions to Ru(0): after 10 min no peaks were



**Fig. 1.** UV-vis absorption spectra of Sample 1 solutions: absorption spectrum before MW irradiation (curve 1), after reduction by MW irradiation at 250W for 1 min (curve 2), 3 min (curve 3), 6 min (curve 4), 10 min (curve 5) and 12 min (curve 6).

found in the UV-vis spectra curves and the plasmon band of Ru shifted at higher energies [66]. Further microwave irradiation gave no change of the spectral pattern. This observation demonstrates that Ru<sup>3+</sup> ions had been totally reduced in the solution to form Ru (0) nanoparticles. The overall reduction was completed in less than 12 min, an extremely short period if compared with the hours required by the traditional heating process. The compete reduction of Ru species was further confirmed by XPS analysis, despite the assignment of Ru BE (binding energies) is not univocal in the literature. Since the C 1s peak covers the Ru 3d<sub>3/2</sub> signal and partially overlaps with the Ru 3d<sub>5/2</sub> peak, the Ru 3p was chosen for the analysis. The Ru 3p spectra are characterized by the two components Ru  $3p_{3/2}$  and Ru  $3p_{1/2}$ . Ruthenium in metallic state is characterized by the Ru  $3p_{3/2}$  at ~462.3 eV and Ru  $3p_{1/2}$  at ~484.5 eV whereas the species in high oxidation states, such as Ru(IV) shows these peaks at about 463.7 eV and 486.2 eV respectively [67]. Hence, the Ru 3p<sub>3/2</sub> region was selected for the measurement. Sample 1 contained only ruthenium in the metallic state characterized by the Ru 3p<sub>3/2</sub> at 462.4 eV, as evidenced in Fig. 2.

The sizes of the Ru nanoparticles were determined by TEM measurement: nanoparticles with an average diameter of 2.7 nm



**Fig. 2.** XPS spectra (Ru  $3p_{3/2}$  and Ru  $3p_{1/2}$ ) of Sample 1.



Fig. 3. TEM images of Sample 2.

and a standard deviation of 1.0 were ascertained. Moreover, this technique resulted highly reproducible as confirmed by TEM and XPS analysis of the colloidal nanoparticles achieved in a duplicate preparation (Sample 1 bis, Table 1). As a consequence, this simple methodology was translated for the "in situ" preparation of supported ruthenium nanoparticles employing CNTs as support (Samples 2-5, Table 1). The "in situ" approach for the synthesis of supported metal nanoparticles has been adopted by us in a solvothermal route carried out under nitrogen overpressure in autoclave in the presence of low-boiling point alcohols [68,69]. This procedure has been also adopted by us [57] and other researchers [58] for the preparation of supported ruthenium nanoparticles under MW irradiation, working in ethylene glycol as solvent. Two kinds of CNTs have been used as support for the preparation of ruthenium nanoparticles: purified CNTs treated with HCl (surface area  $134 \text{ m}^2/\text{g}$ ) and purified CNTs treated with HNO<sub>3</sub> (surface area  $172 \text{ m}^2/\text{g}$ ), where the nitric acid treatment permits the introduction of acidic surface groups [63]. We also investigated the effective role of PVP as stabilizing agent in the nanoparticles synthesis (compare Sample 2 with Sample 3 and Sample 4 with Sample 5). In each case nanoparticles with a small average diameter are obtained, ranging from 2.7 to 3.6 nm, but the metal particle distribution on the two types of nanotubes is different: Samples 2 and 3, synthesized employing functionalized CNTs, show a more homogeneous particle distribution on the support surface, whereas Samples 4 and 5 supported on untreated CNTs present a heterogeneous particle distribution on the nanotubes with some surface parts characterized by full particle agglomeration and others completely without. This is evidenced in Figs. 3 and 4 which shows the TEM images of Sample 2 and of Sample 4.

This result can be related to the presence of carboxylic and oxygenated groups present on the functionalized support, due to the nitric acid treatment, which act as anchoring sites for the ruthenium nanoparticles: the formation of Ru carboxylate bonds can significantly stabilize these ruthenium nanoparticles, giving them a more homogeneous distribution on the support. The comparison between samples synthesized on the same support but in the presence and in the absence of PVP (compare Sample 2 with Sample 3 and Sample 4 with Sample 5) evidenced that PVP is not indispensable for the nanoparticle stabilization and has a detrimental effect on the surface area. The support itself is able to prevent the significant nanoparticle aggregation, thus avoiding the excessive increase of the nanoparticle size and their poorly homogeneous distribution. This was already found for the preparation under MW-irradiation of ruthenium [57] and palladium nanoparticles supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> [70] and on CNTs [71]. In the absence of PVP, the preparation technique is reproducible, as confirmed by the features of Sample 2



Fig. 4. TEM images of Sample 4.

bis, which has been synthesized in the identical reaction conditions of Sample 2 (Table 1).

Elemental analysis of residual chlorine deriving from the chlorinated precursor evidenced the absence of this halogen in the supported catalysts.

In order to improve our synthetic procedure, in the sense of a greener and cheaper solvent/reducing agent, we tested aqueous ethyl alcohol (EtOH/H<sub>2</sub>O 20/80, v/v) working at 150 °C under overpressure. This approach was preliminarily checked for the preparation of colloidal ruthenium nanoparticles (Sample 6, Table 1), by means of UV–vis spectroscopy. Also in this case the UV–vis spectra perfectly fitted with the previous results, as it is possible to appreciate from Fig. 5.

The complete ruthenium reduction was again confirmed by XPS analysis. This result does not contrast with the general observation that the reduction of  $Ru^{3+}$  by low boiling point alcohols, such as ethanol, does not work [27]. In fact, our procedure is carried out adopting more drastic conditions, working under overpressure and MW irradiation at 150 °C. On the basis of these encouraging results, the EtOH/H<sub>2</sub>O mixture was employed for the preparation of supported ruthenium nanoparticles using CNTs treated with HNO<sub>3</sub> as support (Sample 7, Table 1). Sample 7 is characterized by small average diameter and a narrow particle size distribution, as shown in Fig. 6.

This synthetic approach in EtOH/H<sub>2</sub>O medium was then translated for comparison to the preparation of two samples supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> in the absence of PVP (Samples 8 and 9, Table 1). Sample



**Fig. 5.** UV-vis absorption spectra of Sample 6 solutions: absorption spectrum before MW irradiation (curve 1), after reduction by MW irradiation at 250 W for 2 min (curve 2), 4 min (curve 3), 6 min (curve 4), 10 min (curve 5) and 12 min (curve 6).



Fig. 6. TEM image and particle size distribution of Sample 7.

8 was prepared with low ruthenium loading (0.15 wt%), whereas Sample 9 has a loading (1.2 wt%) comparable with those of the samples supported on CNTs. They both evidenced small dimensions and narrow size distributions.

It must be underlined that Raman spectra of pristine and Ru-functionalized CNTs are very similar, this evidencing that the carbonaceous skeleton has not been modified under MWirradiation, as previously reported for Pd/CNTs [71]. Raman spectroscopy represents in fact an important tool for obtaining information on the quality and degree of perfection of CNTs: in our case, the Raman spectra of Ru modified CNTs do not significantly change, thus underlining the absence of significant structural damages [63].

All the above supported systems were tested in the selective hydrogenation of p-CNB to p-CAN in liquid phase and compared with reference commercial catalysts (5 wt% Ru/C catalyst from Engelhard and 0.5 wt% Ru/Al<sub>2</sub>O<sub>3</sub> from Aldrich).

All catalytic p-CNB hydrogenation tests were carried out in the presence of the above supported systems under the same conditions, always using identical amounts of substrate (0.4 g of p-CNB) and of ruthenium (0.50 mg of Ru). Before the catalytic tests, preliminary blank tests were carried out using the two different supports alone, i.e. in the absence of Ru, in order to verify their eventual catalytic activity: both untreated CNTs and CNTs treated with HNO<sub>3</sub> resulted completely inactive under the adopted hydrogenation conditions. Besides, several experiments using different amounts of Ru supported catalysts and different speeds of agitation were performed in order to work without mass-transfer limitations.

Under the adopted conditions, remarkable differences in the catalytic performances of the different systems were observed. The catalytic activity, reported as converted moles of p-CNB/(g Ru h) measured after 30 min of reaction and at 100% conversion is shown in Table 2, together with the selectivity to p-CAN at total substrate conversion, being the unique ascertained by-product always aniline.

Samples 2 and 3 showed better performances with respect to the corresponding Samples 4 and 5, as also evidenced in Fig. 7.

At total p-CNB conversion only Samples 2 and 3 are characterized by 100% selectivity to p-CAN, whereas Samples 4 and 5 show a selectivity of only 95% and 90.3% respectively. These results could be related to the better dispersion of ruthenium nanoparticles on the nanotubes in the samples supported on CNTs treated with HNO<sub>3</sub> (Samples 2 and 3) characterized by a more homogeneous dispersion of ruthenium nanoparticles on the support and a stronger anchorage between ruthenium particles and oxygenated and carboxylic



**Fig. 7.** Catalytic conversion (mol%) of p-chloronitrobenzene for Samples 2–5 (reaction conditions: 60 °C, 4 MPa of hydrogen, 0.5 mg of Ru, 0.4 g of p-chloronitrobenzene and 50 ml of CH<sub>3</sub>OH as solvent).

groups on the surface of the modified CNTs. The good catalytic performances in hydrogenation reactions of ruthenium nanoparticles well dispersed on the nanotubes have been already observed [40,63].

The very low catalytic activity of Sample 5 could be ascribed both to the use of the non-modified support and also, to minor extent, to the presence of PVP which remains on the surface of the catalyst. This passivation could be detrimental for the catalytic activity because it is well known that in the reduction of functionalized nitroarenes also the strong metal/support interactions can exert a significant influence on the catalytic behavior [8]. The catalytic performances of these samples were compared with the commercial Engelhard system Ru/C 5 wt%. The comparison between this catalyst and the more active prepared Samples 2, 3 and 7 is reported in Table 3 and Fig. 8.

The most interesting result regards the selectivity: the prepared catalysts show a total selectivity to the desired product during the whole reaction course, whilst the selectivity of commercial Ru/C system is just lower at 50% of conversion, and further decreases till 96.0% at 100% of p-CNB conversion. Regarding the catalytic performances of Sample 7 it is remarkable that this catalyst shows comparable performances with Samples 2 and 3: this represents



**Fig. 8.** Catalytic conversion (mol%) of p-chloronitrobenzene for Samples 2, 3, 7 and for 5 wt% Ru/C Engelhard (reaction conditions:  $60 \circ C$ , 4 MPa of hydrogen, 0.5 mg of Ru, 0.4 g of p-chloronitrobenzene and 50 ml of CH<sub>3</sub>OH as solvent).

#### Table 2

Catalytic activity of the supported ruthenium catalysts in the hydrogenation of p-CNB to p-CAN for Samples 2–5 (reaction conditions: 60 °C; 4 MPa of hydrogen; 0.5 mg of Ru; 0.4 g of p-chloronitrobenzene; and 50 ml of CH<sub>3</sub>OH as solvent).

Sample	Sample description	A <sub>30 min</sub> (mol/g Ru h) <sup>a</sup>	A <sub>100%</sub> (mol/g Ru h) <sup>b</sup>	Sel. at 100% conversion (%)	
				p-CAN	AN
2	1.3 wt% Ru/CNT (HNO <sub>3</sub> ), no PVP, ( <sup>i</sup> PrOH)	3.66	0.92	100	0
3	1.3 wt% Ru/CNT (HNO3), PVP, ( <sup>i</sup> PrOH)	3.35	0.89	100	0
4	1.8 wt% Ru/CNT (HCl), no PVP, ( <sup>i</sup> PrOH)	1.73	0.85	95	5
5	1.3 wt% Ru/CNT (HCl), PVP, ( <sup>i</sup> PrOH)	0.21	0.46	90.3	9.7

<sup>a</sup> Activity measured at 30 min of reaction.

<sup>b</sup> Activity measured at 100% conversion.

#### Table 3

Catalytic activity of the supported ruthenium catalysts in the hydrogenation of p-CNB to p-CAN for Samples 2, 3, 7 and for 5 wt% Ru/C Engelhard (reaction conditions: 60 °C; 4 MPa of hydrogen; 0.5 mg of Ru; 0.4 g of p-chloronitrobenzene; and 50 ml of CH<sub>3</sub>OH as solvent).

Sample	Sample description	A <sub>30 min</sub> (mol/g Ru h) <sup>a</sup>	$A_{100\%}$ (mol/g Ru h) <sup>b</sup>	Sel. at 100% conversion (%)	
				p-CAN	AN
Comm. Ru/C	5 wt% Ru/C Engelhard	5.99	0.56	96	4
2	1.3 wt% Ru/CNT (HNO <sub>3</sub> ), no PVP, ( <sup>i</sup> PrOH)	3.66	0.92	100	0
7	1.6 wt% Ru/CNT (HNO <sub>3</sub> ), PVP, (H <sub>2</sub> O/EtOH)	3.55	1.69	100	0
3	1.3 wt% Ru/CNT (HNO <sub>3</sub> ), PVP, ( <sup>i</sup> PrOH)	3.35	0.89	100	0

<sup>a</sup> Activity measured at 30 min of reaction.

<sup>b</sup> Activity measured at 100% conversion.

a promising outcome considering that Sample 7 has been synthesized employing the  $H_2O/EtOH 80/20 (v/v)$  medium.

The reuse of Sample 2, recovered after the hydrogenation reaction, leads to reproducible results in terms of both activity and selectivity and two further successive recycle runs give quite analogous catalytic behaviors, thus confirming the stability of this heterogeneous sample under recycling. On the other hand, when the duplicate Sample 2 bis was tested, almost identical performances to those obtained with Sample 2 were ascertained.

This novel synthetic approach in aqueous ethanol was also applied to the preparation of ruthenium catalysts supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (Samples 8 and 9). For the synthesis of these samples PVP was not used because it was previously observed for ruthenium nanoparticles supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> that the presence "in situ" of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was sufficient to limit the metal particles aggregation during the solvothermal reduction process carried out under MW irradiation [57]. These samples, characterized by a different metal loading, were compared with the commercial system 0.5 wt% Ru/Al<sub>2</sub>O<sub>3</sub> Aldrich and their catalytic behavior is reported in Table 4.

The catalytic activity of Sample 8 is very high, as underlined by the activity value after 30 min of reaction, about tenfold higher compared with the corresponding value for commercial  $Ru/Al_2O_3$ catalyst, reaching the first an almost complete substrate conversion in 3 h, as highlighted in Fig. 9.

Sample 9, with a higher ruthenium loading, shows a slower hydrogenation rate, in comparison with Sample 8, leading to 80% of p-CNB conversion after 5 h (Fig. 8). On the other hand, from the point of view of the selectivity, the commercial catalyst among the investigated catalysts shows at 100% of substrate conversion the lowest selectivity value (95.5%).

Finally, the comparison between two corresponding ruthenium catalysts, Samples 2 and 9 having the same ruthenium loading (1.2 wt%), but supported respectively on CNTs treated with HNO<sub>3</sub> and on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> is shown in Table 5 and Fig. 10.

Sample 2, supported on CNTs, shows better activity and selectivity, maintaining total selectivity to the desired product also at high p-CNB conversion. In fact, the use of CNTs with open structure permits the system to avoid diffusion limitations and to maintain the high hydrogen flux at catalyst surface with an easy access to



**Fig. 9.** Catalytic conversion (mol%) of p-chloronirobenzene for Samples 8 and 9 and for 0.5 wt% Ru/Al<sub>2</sub>O<sub>3</sub> Aldrich (reaction conditions:  $60 \,^{\circ}$ C, 4 MPa of hydrogen, 0.5 mg of Ru, 0.4 g of p-chloronitrobenzene and 50 ml of CH<sub>3</sub>OH as solvent).



Fig. 10. Comparison of the catalytic performances of Samples 2 and 9.

# 106 **Table 4**

Catalytic activity of the supported ruthenium catalysts in the hydrogenation of p-CNB to p-CAN for Samples 8, 9 and for 0.5% wt Ru/Al<sub>2</sub>O<sub>3</sub> Aldrich (reaction conditions: 60 °C; 4 MPa of hydrogen; 0.5 mg of Ru; 0.4 g of p-chloronitrobenzene; and 50 ml of CH<sub>3</sub>OH as solvent).

Sample	Sample description	A <sub>30 min</sub> (mol/g Ru h) <sup>a</sup>	$\frac{A_{100\%}}{(\mathrm{mol}/\mathrm{gRuh})^{\mathrm{b}}}$	Sel. at 100% conversion (%)	
				p-CAN	AN
Comm. Ru/Al <sub>2</sub> O <sub>3</sub>	0.5 wt% Ru/Al <sub>2</sub> O <sub>3</sub> Aldrich	0.50	0.73	95.5	4.5
Sample 8	0.15 wt% Ru/γ-Al <sub>2</sub> O <sub>3</sub> , no PVP, (H <sub>2</sub> O/EtOH)	4.87	1.69	100	0
Sample 9	1.2 wt% Ru/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub> , no PVP, (H <sub>2</sub> O/EtOH)	1.32	0.73	97.5	2.5

<sup>a</sup> Activity measured at 30 min of reaction.

<sup>b</sup> Activity measured at 100% conversion.

#### Table 5

Catalytic activity of the supported ruthenium catalysts in the hydrogenation of p-CNB to p-CAN for Samples 2 and 9 (reaction conditions: 60 °C; 4 MPa of hydrogen; 0.5 mg of Ru; 0.4 g of p-chloronitrobenzene; and 50 ml of CH<sub>3</sub>OH as solvent).

Sample	Sample Description	A <sub>30 min</sub> (mol/g Ru h) <sup>a</sup>	A <sub>100%</sub> (mol/g Ru h) <sup>b</sup>	Sel. at 100% conversion (%)	
				p-CAN	AN
Sample 2	1.3 wt% Ru/CNT (HNO <sub>3</sub> ), no PVP, ( <sup>i</sup> PrOH)	3.66	0.92	100	0
Sample 9	1.2 wt% Ru/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub> , no PVP, (H <sub>2</sub> O/EtOH)	1.32	0.73	97.5	2.5

<sup>a</sup> Activity measured at 30 min of reaction.

<sup>b</sup> Activity measured at 100% conversion.

the reaction sites [33]. Besides, CNTs are electron conductors and some charge transfers which can modify the electronic density at ruthenium centres could occur [41]: it is well known that the generation of a positive charge on the ruthenium should increase the catalytic activity for this reaction [10].

# 4. Conclusions

A novel approach for the synthesis of ruthenium nanoparticles supported on CNTs was adopted, working under MW irradiation in the presence of a low boiling point alcohol or of a mixture alcohol (isopropanol/ethanol)/water. These ruthenium catalysts have been employed for the selective hydrogenation of p-CNB to p-CAN and result efficient catalysts for the selective reduction of the nitro group in p-CNB, while the C—Cl bond in the same p-CNB molecule maintains intact. Under mild reaction conditions, the complete substrate conversion with a total selectivity to the target product has been reached.

This study underlines the fast, reproducible and sustainable preparation of these ruthenium catalysts employing not only mild conditions, but also green solvents. This procedure has been translated to the preparation of ruthenium nanoparticles supported on alumina, characterized by catalytic performances overcoming the corresponding commercial system.

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 0.15 wt% Ru/γ-Al<sub>2</sub>O<sub>3</sub>, no PVP, (H<sub>2</sub>O/EtOH)
 4.87
 1.69

 1.2 wt% Ru/γ-Al<sub>2</sub>O<sub>3</sub>, no PVP, (H<sub>2</sub>O/EtOH)
 1.32
 0.73

 30 min of reaction.
 100% conversion.
 100% conversion.

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