DOI: 10.1002/cssc.201000335

Hydrogenation of *p*-Chloronitrobenzene over Nanostructured-Carbon-Supported Ruthenium Catalysts

Mustapha Oubenali,^[a, b] Giuditta Vanucci,^[c] Bruno Machado,^[d] Mohammed Kacimi,^[b] Mahfoud Ziyad,^[b] Joaquim Faria,^[d] Anna Raspolli-Galetti,^[c] and Philippe Serp^{*[a]}

Carbon nanotubes (CNTs) and carbon nanofibers (CNFs) have been used for the first time to support ruthenium nanoparticles for the hydrogenation of *p*-chloronitrobenzene (p-CNB) to produce selectively *p*-chloroaniline. The preparation of well-dispersed ruthenium catalysts from the $[Ru_3(CO)_{12}]$ precursor required activation of the purified supports by nitric acid oxidation. The supports, purified and functionalized, and the sup-

Introduction

The role of catalysis in the development of clean chemical processes with limited hazardous/toxic by-products/wastes is now well established as an essential element of a sustainable chemistry. Aromatic haloamines are important intermediates for the synthesis of many fine chemicals, such as dyes, herbicides, pesticides, pharmaceuticals, and cosmetic products. A current method for producing these haloamines is reduction of the corresponding nitro-compounds, either with a metal acid or by selective hydrogenation over metal supported catalysts.^[1] Thus, *p*-chloroaniline (p-CAN), a high production volume compound, can be synthesized via Bechamp reduction (Fe/HCl) of p-chloronitrobenzene (p-CNB) or by selective hydrogenation using metal supported catalysts.^[1,2] Industrial implementation of the Bechamp reduction is no longer viable due to the generation of metal oxide residues and acid effluents, and liquid-phase selective catalytic hydrogenation has emerged as a cleaner alternative, with little impact on the environment and higher product yields. However, the economic viability depends on catalyst selectivity because unwanted C-Cl bond hydrogenolysis is difficult to fully circumvent. Thus, with a variety of catalysts (e.g., Pt, Pd, Ni, Rh) the hydrogenation of halonitroaromatics to the corresponding haloanilines is always accompanied by some dehalogenation reaction. Reaction selectivity is therefore critical, as p-CNB hydrotreatment can generate a range of intermediates and by-products,^[3] as shown in Figure 1, which presents the reaction pathways proposed for batch liquid-phase hydrogenation. Platinum and nickel are the metals most widely used for the hydrogenation of halonitroaromatics. In this process, the solvent often used is methanol or ethanol. Metals with favorable selectivity patterns are ruthenium,^[4] rhodium,^[5] iridium,^[6] palladium,^[7] and gold.^[8] Among these catalysts, ruthenium is cheaper than the other noble metals and more selective for this reaction, but its catalytic activity is generally low. Therefore, to achieve high yields of haloanilines, many approaches have been developed by ported catalysts have been characterized by a range of techniques. The catalytic activity of these materials for the hydrogenation of *p*-CNB at 35 bar and 60 °C is shown to reach as high as 18 mol_{*p*-CNB} $g_{Ru}^{-1}h^{-1}$, which is one order of magnitude higher than a commercial Ru/Al₂O₃ catalyst. Selectivities between 92 and 94% are systematically obtained, the major by-product being aniline.



Figure 1. The hydrogenation reaction pathways of *p*-chloronitrobenzene.

[a] M. Oubenali, Prof. Dr. P. Serp Laboratoire de Chimie de Coordination UPR CNRS 8241 composante ENSIACET Université de Toulouse UPS-INP-LCC 4 allée Emile Monso B.P. 44362, 31030 Toulouse Cedex 4 (France) Fax: (+ 33) 05 34 32 35 96 E-mail: philippe.serp@ensiacet.fr [b] M. Oubenali, Dr. M. Kacimi, Prof. Dr. M. Ziyad Faculté des Sciences, Département de Chimie Laboratoire de Physico-chimie des Matériaux et Catalyse Avenue Ibn Battouta, B.P. 1017, Rabat (Morocco) [c] G. Vanucci, Dr. A. Raspolli-Galetti Dipartimento di Chimica e Industriale Università di Pisa Via Risorgimento 35, 56100 Pisa (Italv) [d] Dr. B. Machado, Dr. J. Faria Laboratorio de Catalise e Materiais

Rua Dr. Roberto Frias, 4200-465 Porto (Portugal)

Universidade do Porto

Supporting Information for this article is available on the WWW under http://dx.doi.org/10.1002/cssc.201000335.

ChemSusChem 2011, 4, 950-956

either dedicated preparation of the catalysts (colloids,^[9-11] bimetallic catalysis,^[4,12,13] controlling the metal particle dispersion and metal-support interaction^[14, 15]) or the use of specific additives such as water.^[16] One of the most important aspects concerns the catalyst support. Thus, the catalytic performances can be altered significantly by the use of suitable supports that control metal particle dispersion and metal-support interactions. Modification of the electronic state and/or morphology of ruthenium crystals through metal-support interactions creates a chance of obtaining a catalyst with unique catalytic properties. Carbon nanotubes (CNTs) and nanofibers (CNFs) can show unusual behavior compared to classical supports, especially for liquid-phase reactions, and some interesting results have already been obtained.^[17-20] According to these reports the catalytic activity in hydrogenation reactions can be enhanced either due to electronic effects or to the absence of diffusion limitations. Such supports have already been used for the hydrogenation of chloronitrobenzenes. $^{\mbox{\tiny [21-24]}}$ Over PtM/CNT catalysts both catalytic activity and yield of *p*-chloroaniline are improved.^[21,22] Ni/CNF catalysts show very good activity and selectivity for the hydrogenation of chloronitrobenzenes to the corresponding chloroanilines.^[23,24] To the best of our knowledge, no attempt has yet been made to improve the catalytic activity of supported ruthenium catalysts for the selective hydrogenation of *p*-CNB by using CNTs or CNFs as support.

The aim of the present work is to determine the influence of the support and ruthenium precursor on the hydrogenation of p-chloronitrobenzene over Ru/CNT and Ru/CNF catalysts. Pressure and reaction temperature effects in the hydrogenation of p-CNB over Ru/CNT and Ru/CNF catalyst in the liquid phase are also studied. The presented results establish a basis for the development of a sustainable catalytic route for the production of haloamines.

Results and discussion

Support characterization

Two kinds of nanostructured carbons have been used as a support for ruthenium: multiwalled carbon nanotubes and carbon nanofibers. The multiwalled nanotubes are composed of graphene layers that lie perpendicular to the fiber axis; and the "herringbone" carbon nanofibers used present a tilted layer arrangement. These herringbone nanofibers are usually inferior to CNTs in mechanical strength and conductivity, but possess exposed graphene edge sites that make them attractive for some applications, such as catalysis.

In order to obtain a well-dispersed metallic ruthenium phase on CNTs and CNFs some prerequisites have to be fulfilled. First of all, the solvent containing the metal precursor must wet the support. Second, the support must contain anchoring sites in order to immobilize the metal precursor and the subsequent metallic particles. The hydrophobic as-produced carbon nanostructures do not fulfill these prerequisites due to the lack of reactive anchoring sites. Surface activation of CNTs and CNFs by refluxing the support in nitric acid resulted in hydrophilic carbon nanostructures with oxygen-containing surface groups.^[25,26]

The as-synthesized carbon nanostructures have been purified by HCl treatment to remove the remaining catalyst. The purity of the purified supports, CNT_P and CNF_P is 92% and 84%, respectively. The remaining impurities are iron and nickel particles. HRTEM images of the purified supports (CNT_P and CNF_P) are shown on Figure 2, where the orientation of the graphene layers with respect to the fiber axis can be measured: $\sim 0^{\circ}$ for CNT_P and between 18° and 25° for CNF_P



Figure 2. HRTEM images of a) CNT_P and b) CNF_P White bar: orientation of the graphene layers. Black bar: tube or fiber axis.

The textural and chemical characterization of purified and functionalized supports is given in Table 1. The distribution of external diameters for CNT_P is relatively narrow (7–40 nm), while for CNF_P the distribution is wider and bimodal (5–30 nm and 50–200 nm). CNT_P and CNF_P present similar specific surface areas, and the significant contribution of small-diameter CNF_P can explain the higher surface measured for CNF_P .

The Raman spectra of these materials reflect the different organization of the graphene layers in CNT_P with respect to CNF_P as illustrated by the I_D/I_G values that are indicative of the $C_{sp3}/$

Table 1. Textural and chemical characterization of purified and functionalized supports.									
Sample	Purity [%C]	$arPsi_{ext}$ [nm]	d ₀₀₂ [nm]	Raman (I _D /I _G)	BET [m ² g ⁻¹]	Pore vol. [cm ³ g ⁻¹]	PZC	TPD [µm CO	ol g ⁻¹] CO ₂
CNT	02	10	3 30	15	13/	0 302	76	1121	330
CIVIP	92	10	5.59	1.5	1JT	0.302	7.0	1121	552
	92 84	15	3.41	1.2	161	0.411	7.6	601	158
	92 84 92	15 18	3.41 3.39	1.2 1.6	161 172	0.302 0.411 0.344	7.6 3.5	601 2248	158 1365

 C_{sp2} ratio. The lower I_D/I_G ratio measured for CNF_P compared to CNT_P can be attributed either to a higher ordering of the graphene layers and/or to a shorter length for CNF_F compared to CNT_F . In addition, the presence of disordered carbon on the surface of CNT_F (Figure 2a) cannot be ruled out.

Controlling the point of zero charge (PZC) of CNTs or CNFs is important for depositing finely dispersed metal nanoparticles from precursors in solution. The values obtained for the purified supports point towards a neutral surface, and temperature-programmed desoprtion (TPD) spectra are characteristic of a poorly functionalized carbon surface. The CO/CO₂ ratios measured for CNT_P and CNF_P are 3.37 and 3.81, respectively, confirming that the surface is not acidic.

Due to the different reactivity of CNTs and CNFs surface towards oxidation, we decided to use nitric acid solution (69% HNO₃) and low-temperature activation (60°C, 2 h) to activate CNF surfaces, in order to avoid severe burn-off during the process. CNTs were boiled in 69% HNO₃ for 4 h. This treatment permits to increase the CNF purity up to 98%. At this stage, the remaining impurities consist of encapsulated metal particles that are not expected to interfere with the catalytic measurements.

The nitric acid treatment performed on purified supports permits to introduce acidic surface groups, as shown by (i) the PZC values of functionalized supports (CNT_F and CNF_F); (ii) the low CO/CO₂ ratios calculated from the TPD spectra (1.65 and 2.33 for CNT_F and CNF_F respectively); and (iii) the significant contribution of the peak at 285°C, associated to decomposition of carboxylic groups, on the TPD profiles (Supporting Information, Figure SI1). Interestingly, we noticed that the nitric acid oxidation significantly modified the TPD profiles of CNTs. Indeed, for the CNT_P sample the profile is consistent with a transformation of CO into CO_2 at around 835 °C. This can be explained by the presence of traces of iron on CNTs that can catalyze the Boudouard reaction $2CO \leftrightarrow CO_2 + C^{[25]}$ After functionalization this phenomenon disappears, pointing towards the total removal of accessible iron upon nitric acid treatment. This phenomenon was not observed in the case of CNFs. The lower amount of oxygenated groups measured on the CNF surface is due to the milder conditions used for activation. However, the use of these mild conditions has not permitted to completely avoid CNF damage. Indeed, thinner CNFs are destroyed by the treatment, resulting in an increase of the mean diameter and a decrease of the specific surface area and pore volume.

Catalyst characterization

The ruthenium catalysts have been prepared by wet impregnation from the Ru^0 organometallic cluster $[Ru_3(CO)_{12}]$. This precursor was chosen to avoid the effect of chlorine, which could affect the chemisorption and therefore the catalytic

properties. This precursor has already been used for the preparation of well-dispersed Ru/CNF catalysts, which showed high activity for arene hydrogenation.^[27] The chemical composition, adsorption properties, and particle size of the catalysts are presented in Table 2. The ruthenium loading achieved by the im-

Table 2.	Characteriz	ation of the	support	ed Ru/CNT _F	and R	u/CNF _F o	atalysts.
Sample	Ru loading [%]	Ru particle size [nm]	$\begin{array}{l} BET^{[a]} \\ [m^2 g^{-1}] \end{array}$	Pore vol. ^[a] [cm ³ g ⁻¹]	TPR ^[b] [°C]	TPD ^[a] [µ CO	umol g ⁻¹] CO ₂
Ru/ CNT _F Ru/ CNF _F	2 1.5	4 3	185 (172) 134 (117)	0.599 (0.411) 0.302 (0.263)	105 110	2618 (2248) 1587 (1053)	799 (1365) 596 (652)
[a] The values between parentheses correspond to the functionalized supports. [b] Temperature of ruthenium reduction.							

pregnation method corresponds to the immobilization of 30– 40% of ruthenium (5% w/w); the remaining ruthenium species being recovered from the filtrate. The higher loading obtained for CNTs should be correlated to the higher amount of oxygenated surface groups on this support. The TEM images of Ru/ CNT_F and Ru/CNF_F show that the ruthenium particles are welldispersed, with narrow size distributions (Figure 3). The Ru/ CNF_F contains particles in the range 1–9 nm and the Ru/CNT_F in the range 1–16 nm. The larger particle size distribution in the case of the CNT support can be correlated to the higher metal loading, and/or to the different orientation of the graphene layers. The deposition of well-dispersed ruthenium nanoparticles on nanocarbon supports results in an increase of their specific surface area. Such a phenomenon has already been observed in the case of 1–5% Ru/CNT catalysts.^[28]

The H₂ temperature-programmed reduction (TPR) experiments were performed on samples reduced at 300 °C and reexposed to the air. The TPR profiles shown in Figure 4 indicate that the small ruthenium nanoparticles were easily re-oxidized. The ruthenium species can be fully reduced at relatively low temperatures (< 200 °C), without significant differences between the two supports. The higher-temperature peaks may correspond to the reductions of carbon-related functional groups or carbon species on nanocarbon surfaces.^[29] Another possibility is the ruthenium-catalyzed hydrogen gasification of carbon, producing methane, followed by a catalyst deactivation. The higher amount of hydrogen needed for the Ru/CNT_F catalyst reduction compared to Ru/CNF_F is consistent with the difference in ruthenium loading. The TPD spectra correspond-



Figure 3. TEM images of a) Ru/CNT_P and b) Ru/CNF_P



Figure 4. TPR profiles of Ru/CNT_F and Ru/CNF_F.

ing to the reduced Ru/CNT_F and Ru/CNF_F catalysts (Figure SI1) exhibit different features. First, the amount of CO-releasing groups has increased for both samples. This might be due to ruthenium-catalyzed reduction of the CO₂-releasing groups during catalyst reduction. Second, the CO profiles for the supports and the catalysts are very similar, suggesting that the CO groups are not involved in ruthenium anchoring. Finally, the CO₂ profiles are very different for the supports and the catalysts (Figure 5). Thus, for CNT_F and CNF_F the CO₂ is formed and



Figure 5. TPD profiles (CO_2 evolution) of a) CNT_F and $Ru/CNT_{F\prime}$ and b) CNF_F and Ru/CNF_P

released between 150 and 750 °C with a maximum at around 300 °C (290 °C for CNT_F and 310 °C for CNF_F). For the Ru/CNT_F and Ru/CNF_F catalysts the CO₂ is released abruptly at 470 °C for CNT_F and 480 °C CNF_F. The amount of CO₂ released from the Ru/CNT_F catalysts is higher for Ru/CNF_F with a ratio of 1.33, which is similar to the ratio of ruthenium loadings on both supports. We thus propose that the carboxylic groups present on the functionalized support act as anchoring sites for the ruthenium, and that the formation of ruthenium carboxylate bonds significantly stabilizes these groups. The fast decomposition of these groups should be correlated to an autocatalytic decomposition involving ruthenium. Indeed, a sudden stop of release of any gas from a complicated surface (system) is highly unlikely without a catalytic reaction.

Obviously, a significant sintering of these catalysts should occur above a temperature of 470-480 $^\circ\text{C}.$

Hydrogenation of *p*-chloronitrobenzene

The prepared catalysts were tested for the liquid-phase hydrogenation of *p*-CNB to *p*-CAN, and compared to three commercial catalysts: a 5 % Ru/Al₂O₃ catalyst from Fluka, a 0.5 % Ru/ Al₂O₃ catalyst from Aldrich, and a 5 % Ru/C catalyst from Engelhard. Lower alcohols are generally used as solvents in the liquid-phase hydrogenation of *p*-CNB and an examination of the studies reported by different groups^[9–15] prompted us to use methanol as a solvent in the present study. The catalytic hydrogenation of *p*-CNB follows a multi-step reaction pathway (Figure 1). The main side reaction on ruthenium catalyst is hydrodechlorination, leading to aniline (AN) as the ultimate product. This may happen either by hydrodechlorination of *p*-CNB

CHEMSUSCHEM

to nitrobenzene (NB) followed by subsequent hydrogenation to AN, or by hydrodechlorination of the target product *p*-chloroaniline (p-CAN) to AN. The selectivity may depend on the support used; thus, simultaneous hydrogenation of the nitro group and hydrogenolysis of chlorine in *p*-CNB was reported for the reaction over a Pd/C catalyst, whereas on a Pd/polymer catalyst hydrogenolysis of chlorine was a subsequent reaction.^[30] For ruthenium catalysts, the best selectivities (>99%) towards *p*-CAN have been obtained on alumina^[4] or SnO₂ supports,^[14] the other investigated supports such as silica^[16] or MgF₂^[15] permitting to reach high selectivity (>90%).

First, blank experiments using the CNT_F and CNF_F supports were performed to evaluate the catalytic performances of the unloaded supports; indeed the residual iron or nickel particles might became accessible after reduction at 300 °C and present some activity. After 2 h of reaction at 60 °C and under 35 bar of hydrogen the measured conversion and selectivity were 11% and 50%, respectively, whatever the support used. Thus, the contribution of the support can be neglected.

The first set of experiments was performed at a temperature of 60 °C and a hydrogen pressure of 35 bar. Under these conditions there were remarkable differences in the performances of the different catalysts (Figure 6 and Table 3). First, we confirmed that the highest selectivity can be obtained on alumina supports (98–100% selectivity towards *p*-CAN). The only undesirable product was aniline. It is well-known that hydrodehalogenation on ruthenium concerns mainly haloanilines. On carbon supports, activated carbon, or carbon nanostructures, slightly lower selectivities were achieved (92–96%, C>CNF_F>

CNT_F). The most remarkable difference between these different systems concerns the catalytic activity. Indeed, the use of nanostructured carbon as a support permits to increase the catalytic activity by one order of magnitude when compared to the alumina support, by a factor of 2 to 3 compared to activated carbon if we consider the initial activity, and by a factor of 4 to 10 if we consider the activity at 100% conversion. Regarding the structure of the nanocarbon supports, the CNFs permit to reach higher activity and selectivity

than the CNTs. In order to increase the selectivity over the Ru/ CNT_F and Ru/CNF_F catalysts, we performed a second set of experiments at a temperature of 40 °C and a pressure of 10 bar (Table 3). No significant improvement of the catalytic performances was noticed under these milder conditions. The decrease of the activity in the case of the Ru/CNF_F catalyst can be correlated to the different adsorption coefficient of *p*-chloronitrobenzene on the small ruthenium particles supported on CNF surface. It is worth mentioning that the high activity measured for the Ru/CNF_F catalysts, which correspond to a TOF of 1900 h⁻¹, places this systems well above the ruthenium cata-





Figure 6. Catalytic properties of the various ruthenium catalysts: a) conversion, and b) selectivity.

Catalyst	Ru loading [%]	Ru [mg]	$A_{100\%}^{[b]}$ [molg _{Ru} ⁻¹ h ⁻¹]	$A_{in.}^{[c]}$ [molg _{Ru} ⁻¹ h ⁻¹]	Selectivity at 100% conversion [%]		
					<i>p</i> -CAN	NB	AN
Ru/Al ₂ O ₃ Fluka	5	0.48	0.59	1.1	100	0	0
Ru/Al ₂ O ₃ Aldrich	0.5	0.48	1.3	0.4	98	0	2
Ru/C Engelhard	5	0.48	1.7	5.8	96	0.5	3.5
Ru/CNT _F	2	0.72	7.1	12.3	92	1	7
Ru/CNF _F	1.5	0.54	18.8	18.2	94	0.5	5.5
Ru/CNT _F ^[d]	2	0.72	7.6	14.1	94	0.5	5.5
Ru/CNF _F ^[d]	1.5	0.54	4.7	10.4	93	1	7

lysts reported in the literature for the same reaction performed under similar conditions. Indeed, values of TOF ranging between 30 and 400 h⁻¹ have been reported for ruthenium-containing catalysts operating between 60-100 °C and $P_{\rm H2}$ of 10 to 40 bars.^[12, 14, 16]

The increased activity obtained over nanostructured-carbonsupported ruthenium catalyst may have several explanations. First, the use of CNF or CNT supports, which present a very open structure permit to avoid diffusion limitations and maintain a high hydrogen flux at the catalyst surface and an easy access to the reaction sites.^[19,22] Second, these supports are electron conductors, and charge transfer that modifies the electronic density at ruthenium centers could occur. A firstprinciples study of ruthenium clusters adsorbed on carbon nanotubes has shown that a charge transfer occurs from metal to carbon^[31] the transition metal atoms adsorbed on carbon nanotubes donating electrons to the nanotube. It has also been proposed that the generation of a positive charge on the ruthenium centers should increase the catalytic activity for p-CNB hydrogenation.^[13] We should also consider the possible influence of the polarity of the support surface. Indeed, it has been evidenced that in the case of cinnamaldehyde hydrogenation over catalysts supported on CNTs^[32] or CNFs,^[33] the concentration of oxygenated surface species on the nanostructured supports strongly influences the catalytic activity of these systems: the lower the concentration of oxygenated surface groups, the higher the activity. Finally, we cannot rule out an influence of the degree of metal dispersion, even though it has been demonstrated both for ruthenium and platinum catalysts that the catalytic activity for p-CNB hydrogenation decreases when increasing the metal dispersion.^[4]

Conclusion

In summary, to the best of our knowledge, this is the first time that nanostructured carbons (CNFs and CNTs) have been used as supports for ruthenium nanoparticles for the hydrogenation of *p*-chloronitrobenzene. The preparation of well-dispersed Ru/CNT_F and Ru/CNF_F catalysts by wet impregnation from the Ru⁰ organometallic cluster [Ru₃(CO)₁₂] required an activation of the purified supports with HNO₃. These catalysts exhibit excellent performances in the liquid-phase hydrogenation of *p*-CNB and produced *p*-CAN with 94% selectivity and very high activity for a ruthenium catalyst. The results show that the as-synthesized Ru/CNF_F and Ru/CNT_F catalysts for the production of chloroanilines. Studies to elucidate the details of the catalytic mechanism of the Ru/CNFs and Ru/CNT_F systems and on the improvement of their catalytic properties are in progress.

Experimental Section

Carbon nanostructures synthesis

The carbon nanotubes and carbon nanofibers were produced by chemical vapor deposition from ethylene in the presence of hydrogen on iron and nickel monometallic catalysts, respectively, supported on hydroxyapatite. The as-produced samples were purified by HCl washing during 12 h at room temperature, then filtered, washed with deionized water repeatedly until the pH of the filtrate was around 7, and dried for 3 days in an oven at 110 °C to produce CNT_P and CNF_P The complete characterization of these materials is given in the Results and Discussion section.

Catalyst preparation

The CNT_P and CNF_P samples were oxidized in acid HNO₃ at 413 K for 4 h (CNT_P) and 333 K for 2 h (CNF_P), then washed with deionized water repeatedly until the pH of the filtrate was around 6, and then dried at 120 °C for 12 h. The ruthenium catalysts were prepared by a conventional impregnation procedure from triruthenium dodecacarbonyl, 99% in hexane at 293 K. The loading of ruthe-

nium was calculated to reach 5 wt%. The impregnated sample was filtered and washed thoroughly with ethanol, and dried at 120 °C overnight. The catalysts were subsequently reduced in flowing H₂/ Ar mixture (80:20 in volume) at 300 °C for 2 h.

Catalyst characterization

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). Average ruthenium nanoparticle diameters were calculated from statistical distributions of measurements made on 200 particles per sample and the CNT and CNF diameter distribution was measured by counting about 200 CNTs or CNFs on the TEM images. The X-ray diffraction (XRD) patterns were obtained using a modern multipurpose theta/theta powder X-ray diffraction system, equipped with a fast linear detector. Micro Raman spectra were taken on powder samples on a Perkin–Elmer 400F Raman spectrometer with 785 nm red laser irradiation. Thermogravimetric analysis (TGA) of the composite materials was carried out with a SETSYS Evolution (SETARAM Instrumentation) at a heating rate of 20°Cmin⁻1 under air flow.

BET: The textural characterization of the materials was based on the nitrogen adsorption-desorption isotherms, determined at 77 K with a Quantachrome NOVA 4200e multi-station apparatus. The specific surface area (SBET) was calculated by multipoint BET analysis of the isotherm in the relative pressure range from 0.05 to 0.3. TPR/TPD: Spectra were obtained with a fully automated AMI-200 Catalyst Characterization Instrument (Altamira Instruments), equipped with a thermal conductivity detector (TCD) and a quadrupole mass spectrometer (Dymaxion 200 amu, Ametek). For TPR experiments, the sample was placed in a U-shaped quartz tube located inside an electrical furnace and heated at 5 Kmin⁻¹ to 973 K under a 5% (v/v) H_2 flow diluted with He (total flow rate of 30 cm³min⁻¹, STP); for TPD, the sample was heated to 1373 K using a constant flow rate of helium (25 cm³min⁻¹, STP). The H_2 consumption was followed by both TCD and mass spectrometry. The amounts of CO and CO₂ released during the thermal analysis were calibrated at the end of each analysis.

pH_{PZC}: The determination of the point of zero charge (pH_{PZC}) of the sample was carried out according to a procedure described elsewhere.^[34] Briefly, 50 mL of a NaCl solution (0.01 m) was placed in a closed Erlenmeyer flask; the pH was adjusted to a value between 2 and 12 using HCl (0.1 m) or NaOH (0.1 m) following which 0.05 g of each sample was added. The final pH was measured after 72 h continuous stirring at room temperature.

Catalytic activity measurements

The hydrogenation reaction was conducted between 313 and 333 K under a hydrogen pressure of 10 to 35 bar in an autoclave reactor under stirring (750 rpm). Typically, 0.4 g (2.54 mmol) of *p*-chloronitrobenzene and the prereduced catalyst (0.036 g) in 50 mL methanol were added to the autoclave. The reaction lasted for 2 h. Samples were extracted every 15 min and the products were analyzed using a gas chromatograph (Perkin–Elmer Clarus 500, equipped with a stabilawx DA capillary column and a FID detector).

CHEMSUSCHEM

Acknowledgements

M.O. thanks the LIA Laboratoire de Chimie Moléculaire Maroco-Français, and the C'Nano GSO network for financial support.

Keywords: amines • hydrogenation • nanotubes • ruthenium • surface chemistry

- [1] H.-U. Blaser, H. Steiner, M. Studer, ChemCatChem 2009, 1, 210.
- [2] X. Wang, M. Liang, J. Zhang, Y. Wang, Curr. Org. Chem. 2007, 11, 299.
- [3] F. Cárdenas-Lizana, S. Gómez-Quero, M. A. Keane, Appl. Catal. A: Gen. 2008. 334, 199.
- [4] A. Tijani, B. Coq, F. Figueras, Appl. Catal. 1991, 76, 255.
- [5] J. Wrzyszcz, M. Zawadzki, A. M. Trzeciak, J. J. Ziolkowski, J. Mol. Catal. A: Chem. 2002, 189, 203.
- [6] P. Baumeister, M. Studer, F. Roessler, in *Handbook of Heterogeneous Catalysis, Vol. 5* (Eds.: G. Ertl, H. Knözinger, J. Weitkamp), Wiley-VCH, Weinheim, **1997**, pp. 2186–2209.
- [7] V. Vishwanathan, V. Jayasri, P. Mahaboob Basha, N. Mahata, L. Sikhwivhilu, N. J. Coville, *Catal. Commun.* 2008, 9, 453.
- [8] F. Cárdenas-Lizana, S. Gómez-Quero, M. A. Keane, Catal. Commun. 2008, 9, 475.
- [9] M. Liu, W. Yu, H. Liu, J. Mol. Catal. A: Chem. 1999, 138, 295.
- [10] M. Liu, B. He, H. Liu, X. Yan, J. Colloid Interface Sci. 2003, 263, 461.
- [11] M. Liu, W. Yu, H. Liu, J. Zheng, J. Colloid Interface Sci. 1999, 214, 231.
- [12] Q. Xu, L. Wang, J. Chen, X. Li, R. Li, Chin. J. Catal. 2007, 28, 579.
- [13] M. Pietrowski, M. Wojciechowsk, Catal. Today 2009, 142, 211.
- [14] B. Zuo, Y. Wang, Q. Wang, J. Zhang, N. Wu, L. Peng, L. Gui, X. Wang, R. Wang, D. Yu, J. Catal. 2004, 222, 493.
- [15] M. Pietrowski, M. Zieliński, M. Wojciechowska, Catal. Lett. 2009, 128, 31.
- [16] J. Ning, J. Xu, J. Liu, H. Miao, H. Ma, C. Chen, X. Li, L. Zhou, W. Yu, Catal. Commun. 2007, 8, 1763.

- [17] K. P. De Jong, J. W. Geus, Catal. Rev. Sci. Eng. 2000, 42, 481.
- [18] P. Serp, M. Corrias, P. Kalck, Appl. Catal. A: Gen. 2003, 253, 337.
- [19] P. Serp in Carbon Materials for Catalysis (Eds.: P. Serp, J. L. Figueiredo), Wiley, Hoboken, 2009, pp. 309–372.
- [20] J. H. Bitter, J. Mater. Chem. 2010, 20, 7312.
- [21] C. Wang, J. Qiu, C. Liang, L. Xing, X. Yang, *Catal. Commun.* **2008**, *9*, 1749.
- [22] N. Mahata, A. F. Cunha, J. J. M. Órfão, J. L. Figueiredo, Catal. Commun. 2009, 10, 1203.
- [23] X. X. Han, Q. Chen, R. X. Zhou, J. Mol. Catal. A: Chem. 2007, 277, 210.
- [24] J. Yang, C. Xiong, X. Han, L. Zhou, Ind. J. Chem. 2009, 48 A, 1358.
- [25] A. Solhy, B. F. Machado, J. Beausoleil, Y. Kihn, F. Gonçalves, M. F. R. Pereira, J. J. M. Órfão, J. L. Figueiredo, J. L. Faria, P. Serp, *Carbon* **2008**, *46*, 1194.
- [26] J. H. Bitter, in *Nanocatalysis* (Ed.: D. Y. Murzin), Research Signpost, Kerala, 2006, pp. 99–125.
- [27] M. Takasaki, Y. Motoyama, K. Higashi, S.-H. Yoon, I. Mochida, H. Nagashima, Chem. Asian J. 2007, 2, 1524.
- [28] S. Guo, K. Y. Liew, J. Li, J. Am. Oil Chem. Soc. 2009, 86, 1141.
- [29] J. Kang, S. Zhang, Q. Zhang, Y. Wang, Angew. Chem. 2009, 121, 2603; Angew. Chem. Int. Ed. 2009, 48, 2565.
- [30] V. Kratky, M. Kralik, M. Mecarova, M. Stolcova, L. Zalibera, M. Hronec, *Appl. Catal. A: Gen.* 2002, 235, 225.
- [31] H. Gao, J. Zhao, J. Chem. Phys. 2010, 132, 234704.
- [32] H. Vu, F. Gonçalves, R. Philippe, E. Lamouroux, M. Corrias, Y. Kihn, D. Plee, P. Kalck, P. Serp, J. Catal. 2006, 240, 18.
- [33] M. L. Toebes, Y. Zhang, J. Hájek, T. A. Nijhuis, J. H. Bitter, A. J. van Dillen, D. Y. Murzin, D. C. Koningsberger, K. P. de Jong, *J. Catal.* 2004, 226, 215.
- [34] P. C. C Faria, J. J. M. Orfao, M. F. R. Pereira, Water Res. 2004, 38, 2043 2052.

Received: October 4, 2010 Revised: November 3, 2010 Published online on June 7, 2011