Elsevier Editorial System(tm) for Catalysis Today
Manuscript Draft

Manuscript Number: CATTOD-D-14-00406R1

Title: Ir supported over carbon materials for the selective hydrogenation of chloronitrobenzenes

Article Type: SI: Carbocat VI

Keywords: Iridium; graphitic character; nitrobenzene hydrogenation.

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Manuscript Region of Origin: SPAIN

Abstract: In the present work we have studied the effect of carbon supports with different graphitic character (carbon nanotubes, mesoporous graphite and activated carbon) on the catalytic performance of iridium nanoparticles on the liquid phase chemoselective hydrogenation of para-chloronitrobenzene at room temperature. The effect of the oxygen groups was also evaluated by oxidizing a portion of the carbon nanotubes. The Raman and XRD spectra showed that the mesoporous graphite displayed the strongest graphitic character. The characterization of the catalysts by HR-TEM, XPS and TPR-H₂, showed that the catalysts had similar particle size and that the catalysts prepared over the previously oxidized support, Ir/CNT_{ox}, was not fully reduced. The activity and selectivity achieved with the catalyst Ir/CNT was the best among the samples and the presence of iridium oxide on Ir/CNT_{ox} diminished the yield to p-chloroaniline, being the worse catalyst. The reactivity of different isomers was also studied over Ir/CNT and it followed the order m > o > p.

Highlights

- Ir catalysts supported on carbon materials with different graphitic character.
- The effect of oxygen groups in carbon nanotubes has been evaluated.
- Ir/CNT shows the best catalytic performance in p-chloronitrobenzene hydrogenation.
- The reactivity of different isomers on Ir/CNT was $m > o > p$.

Ir supported over carbon materials for the selective hydrogenation of chloronitrobenzenes

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Abstract

In the present work we have studied the effect of carbon supports with different graphitic character (carbon nanotubes, mesoporous graphite and activated carbon) on the catalytic performance of iridium nanoparticles on the liquid phase chemoselective hydrogenation of para-chloronitrobenzene at room temperature. The effect of the oxygen groups was also evaluated by oxidizing a portion of the carbon nanotubes. The Raman and XRD spectra showed that the mesoporous graphite displayed the strongest graphitic character. The characterization of the catalysts by HR-TEM, XPS and TPR-H₂, showed that the catalysts had similar particle size and that the catalysts prepared over the previously oxidized support, Ir/CNTox, was not fully reduced. The activity and selectivity achieved with the catalyst Ir/CNT was the best among the samples and the presence of iridium oxide on Ir/CNTox diminished the yield to p-chloroaniline,

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1. INTRODUCTION

Aromatic substituted amines are important intermediates in the fine chemistry industry. Its high production prompted the development of heterogeneous catalysts for the chemoselective hydrogenation of nitrocompounds to substitute the environmentally unfriendly traditional synthetic routes. Although the activation of the N=O bond is relatively easy, the main problem associated with this reaction is the accumulation of intermediates as nitrosobenzene and competitive hydrogenations if other reducible groups such as -CHO, -CH=CH₂, C≡N or -NO₂ are also present in the molecule. The most studied metals, i.e. Ni, Pt and Pd, offer good activities for this reaction. However, to achieve a high yield of the desired aniline it is necessary to add modifiers (promoters and inhibitors) and/or to work at high temperatures [1,2]. In certain catalytic systems a second metal is added as a poison to decrease the activity of the main phase, this improving the selectivity [3,4]. Nonetheless, it would be advantageous to employ a more selective active phase to avoid the loss of metallic surface area by the addition of poisoning elements. In this sense, iridium has been studied and it has been shown to offer better selectivities compared to other noble metals [5,6]. However, its use in catalysis has been scarce and, to date, very few reports can be found which use iridium as active phase for the hydrogenation of nitrocompounds [6,7].

It has been suggested that positively charged metal species activate the polarized N=O bond *via* metal-O interaction, where oxygen is negatively charged [8]. Moreover, it has been proposed that surface hydroxyl groups on the support surface might be able to activate the nitro group via hydrogen bond [7]. The synthesis of small metal nanoparticles will increase the proportion of M^{+δ} species but the support may also modify their electronic properties. In this sense, the use of carbon nanotubes (CNT) can offer further aid as they have proved to display special properties compared to other supports influencing the size, location and morphology of the metal nanoparticles [9,10]. In some cases it has been suggested that they

are responsible of positively charged metal species due to electron transfer [11]. In addition, its special morphology as a rolling graphene layer(s) may also influence the adsorption of reactants/products and hence the catalytic performance [9]. In general, for the hydrogenation of substituted nitro-compounds CNTs have been employed as supports for Pt and Ni nanoparticles, with modifiers or in bimetallic systems [12, 3]. CNT-supported Ru was also very active and selective for the hydrogenation of para-chloronitrobenzene, although high temperatures were employed in this case [13].

In this sense, we have studied the hydrogenation ability of iridium nanoparticles supported on carbon nanotubes. To asses for the effect of their structure and surface chemistry, iridium catalysts prepared over commercial mesoporous graphite, activated carbon and oxidized carbon nanotubes were also evaluated. In addition, the hydrogenation of other nitrocompounds was also tested.

2. EXPERIMENTAL

2.1 Catalysts

Catalysts were prepared by incipient impregnation of the supports, carbon nanotubes (CNT; Nanocyl 3100, 95% purity), activated carbon (AC; Norit SX Plus) and mesoporous graphite (MG; Timrex 300), with the required amount of Ir(acac)₃ (Sigma-Aldrich) dissolved in toluene to obtain an Ir loading of 1 wt.%. The samples were dried for 16 h at 393 K and then activated by heating under Ar up to 673 K at 5 K/min and reduced with H₂ flow (30 ml/min) for 2 h at 673 K. The prepared catalysts will be labeled Ir/CNT, Ir/AC and Ir/MG. Additionally, a portion of CNTs was oxidized with HNO₃ (65 % w/w) at 403 K for 24 h (CNTox) and the catalyst, Ir/CNTox, was prepared in the same way.

2.2 Characterization

Textural properties of the prepared materials were determined by N₂ adsorption at 77 K on a Micromeritics ASAP 2010 apparatus. Before measurements, the samples were dried at 383 K for 12 h and out-gassed at 523 K under vacuum. The micropore volume was obtained by application of the Dubinin–Radushkevich (DR) equation to the adsorption isotherm. The volume of mesopores was estimated by subtracting the micropore volume from the uptake at a relative pressure of 0.95. The surface area was calculated by application of the B.E.T. method.

X-ray powder diffraction patterns were recorded on a JSO Debye-flex 2002 system, from Seifert, fitted with a Cu cathode and a Ni filter, using a $2^{\circ} \cdot \text{min}^{-1}$ scanning rate.

Raman measurements were performed with a LabRam (Jobin-Ivon) micro-Raman spectrometer at 514 nm. The laser beam was focused onto the sample with a 100x objective. The laser intensity at the sample was kept below the threshold for any laser-induced changes in the Raman spectra and electrical transport characteristics.

The thermogravimetric analyses were performed with a Mettler Toledo Thermogravimetric TGA/SDTA 851 system. The sample was treated under flowing He for 2 h and then heated with a heating rate of $10 \text{ K} \cdot \text{min}^{-1}$ rate up to 1123 K.

TEM images were taken with a JEOL electron microscope (model JEM-2010) working at 200 kV. It was equipped with an INCA Energy TEM 100 analytical system and a SIS MegaView II camera. Samples for analysis were suspended in ethanol and placed on copper grids with a holey-carbon film support.

Temperature-programmed reduction (TPR) with H₂ measurements were carried out on the calcined catalysts in a U-shaped quartz cell using a 5% H₂/He gas flow of $50 \text{ mL} \cdot \text{min}^{-1}$, with a heating rate of $10 \text{ K} \cdot \text{min}^{-1}$. Samples were treated with flowing He at 673 K for 1 h before

the TPR run. Hydrogen consumption was followed by on-line mass spectrometry (Pfeiffer, OmniStar GSD 301).

X-Ray photoelectron spectroscopy (XPS) analyses were performed with a VG-Microtech Multilab 3000 spectrometer equipped with a hemispherical electron analyzer and a Mg-K α ($h\nu = 1253.6$ eV; $1\text{ eV} = 1.6302 \cdot 10^{-19}$ J) 300-W X-ray source. The powder samples were pressed into small Inox cylinders. Before recording the spectra, the samples were maintained in the analysis chamber until a residual pressure of ca. $5 \cdot 10^{-7}$ N/m² was reached. The spectra were collected at pass energy of 50 eV. The intensities were estimated by calculating the integral of each peak, after subtracting the S-shaped background, and by fitting the experimental curve to a combination of Lorentzian (30%) and Gaussian (70%) lines. The binding energy (BE) of the C 1s peak of the support at 284.9 eV was taken as an internal standard. The accuracy of the BE values is ± 0.2 eV.

2.3 Test reactions

Previous to the reactions all the catalysts were reduced in a glass U-shaped reactor at 673 K for 2 h under H₂ (30 mL·min). The hydrogenation of the nitrocompounds was performed in a batch reactor lined with glass employing 25 mg of catalyst in 25 mL of ethanol, 0.2 M of the substrate at 298 K and 20 bar of hydrogen. Small aliquots were taken up to 300 min and analyzed in a GC-MS Shimadzu GCMS-QP5050 with a capillary column β -Dex 225 (Supelco). The activity at 50% conversion was estimated as:

$$\text{Activity} = \frac{\text{mol converted pClNB}}{(\text{time}(\text{min}) \times \text{mol Ir nominal})}$$

3. RESULTS

3.1 Support characterization

The parent supports were characterized to assess for differences on their morphology and surface chemistry. The nitrogen adsorption/desorption isotherms at 77 K are shown in Fig. 1. It can be observed that CNT showed very little nitrogen uptake at low relative pressure, characteristic of a Type II isotherm corresponding to non microporous carbon materials. Then, at a relative pressure of 0.8–0.9 an important increase in the amount of N₂ adsorbed can be observed, along with a well-defined hysteresis loop due to the presence of mesoporosity. This mesoporosity is generated by the space arrangement of the nanotubes. The isotherm of the MG sample was also characteristic of a mesoporous material but, for this sample, a higher amount of N₂ adsorbed was observed at low relative pressures. On the other hand, the isotherm obtained with AC displayed higher adsorption volume at low partial pressures ($P/P_0 \leq 0.1$) which is consistent with a Type I isotherm, indicative of a microporous structure. The hysteresis loop due to capillary condensations at higher partial pressures matches that observed for a Type IV isotherm and is associated with mesoporosity. The isotherm of CNTox is different to that obtained with the parent CNT. The nitrogen uptake at low relative pressures has increased and the hysteresis loop is extended to medium pressures. The oxidation treatment with nitric acid might have also created some defects on the surface, increasing the microporosity but it could also open the carbon nanotubes to some extent, this increasing the mesoporosity [14]. The estimated BET surface areas, V_{micro} and V_{meso} are shown in Table 1, and the values correspond well with the qualitative observations. The apparent surface area estimated after application of the BET equation was very similar for MG, CNT and CNTox, although the pore volume distribution differed and CNT displayed a much higher proportion of mesoporous compared to the other supports.

The graphitic order of the supports was evaluated by XRD, and the patterns are shown in Fig. 2. Both MG and CNT displayed the characteristic reflection at $2\theta = 26^\circ$ of the (002) plane of graphite. However, while MG presented an intense and sharp peak, the diffraction peak of CNT was broad and it was slightly shifted to higher angles. This is consistent with the different interlayer distance due to the curvature of the layers which also leads to a different order degree [15]. Finally, the XRD profile of AC showed a broad hump at $2\theta = 26^\circ$, this confirming the amorphous nature of this support. Activated carbon is formed by turbostratic carbon with stacked graphene layers regularly spaced as in graphite but with different degree of stacking order [16].

The Raman spectra obtained with the different catalysts are shown in Fig. 3. The materials displayed the characteristics G ($1578\text{--}1585\text{ cm}^{-1}$) and D ($1327\text{--}1342\text{ cm}^{-1}$) bands which are ascribed to the in-plane vibrations of C–C and to defective graphitic structures respectively [17]. Therefore the intensity I_D/I_G ratio estimated from the deconvolution of the spectra can be taken as an indication of the graphitic character and it is included as insert in Fig. 3. The lower I_D/I_G ratio for MG indicates a more graphitic character for this sample. The higher D contribution for the CNT is attributed to the defective graphitic structures due to curvature of graphene layer which is caused by pentagons and/or heptagons [18]. The CNTox material displayed the D and G bands at nearly the same wavenumber; however, the I_D/I_G ratio is higher compared to that of CNT, what indicates that the oxidation treatment increased the disorder.

The surface chemistry of the supports was studied by thermogravimetry under He, and the TG profiles are shown in Fig. 4. It can be observed that CNT was very stable up to 873 K and then, a slight weight loss was observed which accounted for 2.5%. The MG and AC supports were also quite stable, but a 2.5–3% weight loss was observed for both samples at 873 K, followed by another step of mass loss which was more pronounced for the AC than

for the MG, the total mass loss being 7 and 4% respectively. Finally, the thermogram of CNTox proved that the oxidation treatment was efficient to incorporate oxygen groups. The CNTox thermal analysis displayed two different slopes in the range 373-723 K and 723-1123 K with a mass loss of 7.5% and 9% respectively. It is well known that the treatment of CNT with HNO_3 introduces a high proportion of oxygen groups that evolve as CO_2 (carboxyl, anhydride and lactone groups) and CO (phenolic, carbonyl, quinone and anhydride groups) upon heating the sample. It can be assumed that below 723 K most of the weight loss is due to CO_2 whereas at temperature above 723 K the mass loss is mainly due to CO and, accordingly, the concentration of oxygen can be estimated [19]. The values, in Table 1, show that the parent supports, CNT and MG, displayed a very low concentration of oxygen. The amount of oxygen groups on AC was higher, and they are mainly ascribed to groups evolving as CO which may have been introduced in the support during the synthesis of AC or after air exposure.

The surface chemistry of the supports was also studied by XPS. The deconvolution of the C1s and O1s levels was employed to estimate the O/C ratio and the proportion of the different oxygen species on the surface which, are shown in Table 1. The trend of the O/C ratio is in quite good agreement with the oxygen concentration estimated from the thermal analyses. The similar value for AC and MG, despite the higher oxygen concentration on AC estimated by TG, can be due to the location of oxygen groups on the micropore area which are not sensitive to XPS.

3.2 Catalysts characterization

Representative TEM images of the catalysts are shown in Fig. 5. The morphology of MG was characterized by extended graphene layers. The CNT are formed by long straight graphitic walls with barely any defects. Furthermore, only few amount of amorphous carbon could be observed on the surface of MG and CNT. These results are in agreement with the

observations by Raman and TG analysis. Moreover, the images showed that most of the tubes in Ir/CNT were closed, and this proportion did not change significantly for the Ir/CNTox, therefore the differences on the isotherms for these samples could be due to the creation of other defects rather than the opening of the tubes. This also indicates that Ir nanoparticles are mainly located on the external surface. As long as the particle size is concerned, it can be observed that nanoparticles are homogeneously distributed on the supports, and very small nanoparticles with a narrow particle size distribution were obtained for all the catalysts. TEM images of the catalysts were used to estimate the average particle size reported in Table 2. The values are in the range of previous reports for Ir supported on Al_2O_3 [20,21] and carbon [22].

Analyses of the XPS spectra of the catalysts were performed. The relative amounts of the different species were calculated from the corresponding peak areas divided by the sensitivity factors, and the most relevant data are shown in Table 2. All the catalysts displayed a peak corresponding to the Ir 4f transition. The Ir/C ratio was also estimated and the values, shown in Table 2, were very similar and in the range 0.001-0.002 for all the catalysts. However, while Ir/CNT, Ir/MG and Ir/AC showed only a single contribution at 61.1-61.5 eV, Ir/CNTox displayed two components in this region, at 61.1 eV and 62.2 eV, which were deconvoluted and the proportion of each component is included in brackets. The component at the lower binding energy is ascribed to the transition $4f_{7/2}$ of Ir^0 and the component at higher binding energy to the $4f_{7/2}$ transition of Ir^{+4} , which have been reported in the range 60.4–61.3 eV and 61.4–62.6 eV, respectively [7,22,23,24]. These results indicate that under the reduction conditions employed iridium oxide was fully reduced to Ir^0 on Ir/CNT, Ir/MG and Ir/AC. However for Ir/CNTox, a certain proportion of IrO_2 was still present. It has been proposed that contact with air may be responsible of the re-oxidation of small nanoparticles; however, considering the absence of this contribution for the other

samples, it is plausible to assume that the oxygen groups on the surface may influence the oxidation state of iridium nanoparticles.

Fig. 6 shows the evolution of H_2 consumption as a function of temperature for the prepared catalysts. All the catalysts showed two main peaks. The first one appeared at a similar temperature for Ir/AC, Ir/MG, and Ir/CNTox, c.a. 518-524 K, and at a lower value for Ir/CNT, 437 K. The contribution at higher temperatures appeared as a broad band with maxima at 667, 793, 890 and 900 K for Ir/CNT, Ir/MG, Ir/AC and Ir/CNTox respectively. The reduction temperature may vary depending on the size of the nanoparticles and the interaction with the support. For example, for Ir/SiO₂ catalysts one reduction peak at 360-460 K, depending on the particle size, has been reported [24]; for Ir/TiO₂ two reduction peaks at 395 and 623 K were observed and ascribed to reduction of iridium oxide with different interaction with TiO₂ [25]. However, the assignation for carbon-based catalysts should also take into account the reduction of surface oxygen groups and possible surface methanation [25,26]. For the CNT support, the possibility of nanoparticles being located inside the nanotube has also been considered to cause a different reduction temperature [27]: However, as observed by TEM, this is not expected in our catalyst.

To evaluate those aspects, the amount of H_2 consumed was estimated and the values are reported in Table 2, assuming IrO₂ as the only starting phase. In addition, the $m/z = 2, 18, 28, 44$, and 16 signals, which correspond to the main fragmentation patterns of H_2, H_2O, CO, CO_2 and CH_4 were followed (Fig.SI1). It was observed that $m/z = 18$ was the major contribution of the first peak, this confirming that the reduction of iridium oxide was the main reaction within this range of temperature. Nonetheless, $m/z = 28$ and 44 signals were also observed in the spectra of Ir/AC and Ir/MG, and more pronounced in the Ir/CNTox spectrum in agreement with the thermogravimetry and XPS analyses of the supports, which suggested the presence of a small amount of oxygen groups on the surface. On the other hand, for the second contribution, Ir/MG, Ir/CNT and Ir/CNTox presented the evolution of

$m/z = 16$ along with $m/z = 18$ signals in a proportion that indicates that $m/z = 16$ corresponds to CH_4 . This was not observed in the spectrum of Ir/AC which only displayed the evolution of $m/z = 18$ on this peak. Moreover, the intensity of $m/z = 16$ was higher on Ir/CNT and Ir/MG than on Ir/CNTox, this being more pronounced for Ir/CNT. Finally, $m/z = 28$ with maxima in the range 923-1173 K was observed for all the samples. As long as the H_2 consumption is concerned, the estimated values for the first peak showed that, even considering the oxide in its higher oxidation state, the consumption in the first stage was below the expected value, except for Ir/CNTox, but for this sample a higher consumption of H_2 to reduce the oxygen groups has also to be considered. The total consumption was above the theoretical value for all the samples.

Therefore, the first peak would be ascribed to the reduction of most of the IrO_2 along with some oxygen groups. The higher reduction temperature of the first peak observed for Ir/CNTox compared to Ir/CNT despite the similar particle size that they displayed would be due to the stronger interaction of the metal precursor with the oxygen surface groups on the surface, as previously reported [28]. The assignment of the second contribution is more complicated, as different factors should be considered. Bearing in mind the XPS analyses and the TPR- H_2 profiles, the reduction of a small fraction of IrO_2 might be also included. The high CH_4 proportion evolving from Ir/CNT, despite its high thermal stability observed by TG, suggests that methanation of the support is taking place and it seems to anticipate the higher activation ability of the iridium nanoparticles deposited over the CNT compared to the other supports. This would also explain the more pronounced difference between the theoretical and the actual value of H_2 consumed by this sample in TPR analysis compared to Ir/MG and Ir/AC. The higher difference observed for Ir/CNTox corresponds to the decomposition of the oxygen groups on the surface, which also appeared on Ir/MG and Ir/AC, but in a lower proportion. Considering TEM results that showed no significant

differences on particle size, the iridium oxide reduced at higher temperatures might correspond to species with stronger interaction with the support.

In summary, XPS and TPR-H₂ analyses have shown that for Ir/CNTox the reduction conditions led to the reduction of the previously introduced oxygen groups, however some IrO₂ was still present. It seems that the reduction of the oxygen groups hindered the reduction of IrO₂ as suggested previously for palladium nanoparticles supported on graphite oxide [29] or for bimetallic Pd-Cu, for which the reduction of copper limited the reduction of palladium [30].

3.2 Reaction

The catalytic performance was firstly studied on the liquid phase hydrogenation of p-chloronitrobenzene and the most relevant results are shown in Table 3. All the catalysts were active and the estimated activity at 50% conversion followed the trend Ir/CNT > Ir/AC $\approx$ Ir/MG > Ir/CNTox. As far as the selectivity is concerned, p-chloroaniline (pCIAN) was the main reaction product for all the catalysts, and only catalyst Ir/CNTox produced 5% of nitrobenzene (NB) at 90% conversion. The yield to p-CIAN at 100% conversion followed the order Ir/CNT > Ir/MG > Ir/AC > Ir/CNTox.

The hydrogenation paths of pClNB are summarized on Scheme 1. The catalytic reduction of pClNB may proceed through the hydrogenation of the nitro group to give the desired product p-chloroaniline (pCIAN). At the same time, pCIAN may suffer dehalogenation to produce AN. The dehalogenation may also take place on the pClNB producing NB, via nitrosobenzene, which could later be hydrogenated to AN [31]. It has been proposed that the dehalogenation reaction occurs via electrophilic attack of the activated hydrogen on the absorbed aromatic halides. In general, dehalogenation always takes place at high p-CNB conversion. For a given metal the dehalogenation depends on the metal dispersion, interactions with the support and the use of additives to suppress the dehalogenation [1].

Iridium supported on the carbon materials was active and very selective to the hydrogenation of pCINB without adding other metal. Moreover the special properties of CNT avoided the accumulation of intermediates and 100% yield to pCIAN was obtained. The better performance of carbon nanotubes compared to the other carbon supports used has been observed for other liquid phase reactions. It was proposed that the higher surface area, the absence of micropores and oxygen groups among the reasons for the better activity/selectivity [32]. The different morphology of the CNT may also change the adsorption properties of the metal creating active sites as reported for the activation of C=O bond of citral [33]. According to the characterization, MG and CNT presented similar surface area as well as metal particle size, and their surface chemistry did not vary significantly. In addition, the excellent yield to pCIAN obtained with Ir/CNT could be due to the higher activity of the iridium nanoparticles supported on the CNT and to the lower affinity of the intermediates to adsorb on the surface. This lower affinity was already suggested to be one of the reasons for the improved selectivity of the hydrogenation of halonitrocompounds with Pd/activated carbon compared to a more acidic support [34].

The iridium nanoparticles supported on CNT were more active than those supported on the other carbon materials employed, in spite of their similar average particle size. It is possible that the nanoparticles located on defects sites of CNT have different properties due to the electron withdrawing by the support. The $\text{Ir}^{+\delta}$ species might be able to interact with the negatively charged oxygen atom on the nitro group which will favor the attack by dissociated hydrogen, thus improving the activity.

As long as the surface chemistry is concerned, it was expected that the remaining oxygen groups on Ir/CNTox could activate the N=O bond via hydrogen bond. However, Ir/CNTox was the less active and selective among the catalysts tested. Although some reports can be found in literature concerning the improvement of the catalytic performance due to the

presence of oxygen groups [35,36] most of the literature reports a decrease of the activity of the catalysts in the presence of surface oxygen groups. Despite the higher dispersion of the nanoparticles that can be achieved by the oxidation of the carbon surface, the remaining oxygen groups may influence on the adsorption of the reactants, obtaining a worse catalytic performance [37,38]. Characterization of Ir/CNT_{ox} shows that the metal particle size was very similar to that of Ir/CNT, and that a low concentration of surface oxygen groups remained on the surface after the reduction treatment. The high activity of the iridium nanoparticles probably favored the reduction of the majority of oxygen groups even at the low temperature employed for the catalysts reduction. This may have hindered the complete reduction of IrO₂ on the surface, as the XPS analysis showed, and these species are inactive in the hydrogenation [7]. Moreover, a slight dehalogenation of pCINB was observed.

In addition, the catalytic performance of Ir/CNT on the selective hydrogenation of the meta- and ortho- isomers was studied. The reactivity followed the order $m > o > p$, and the selectivity to the x-ClAN was 100% for all the isomers. Different reactivity trends have been reported in the literature for the three isomers. For example, with catalysts Pt/TiO₂ and Ni/Cu/CNT the reactivity followed the order $m > p > o$ and $p > o$ respectively [39]. The opposite behavior has been observed, and the catalyst Au/Al₂O₃ in gas phase offered the following reaction rates: $o > p > m$ [40]. Nonetheless, no dependence of the reaction rate with the position of the halogen has also been reported [41]. Our results suggested that the chloride function was acting as an electron withdrawing group and, thus, the meta- position was more activated than ortho- and para-. The similar reactivity of ortho- and para- did not indicate that steric hindrance directed the reaction rate.

4. CONCLUSIONS

This study shows that well dispersed iridium nanoparticles on AC, MG and CNT were active and selective in the p-chloronitrobenzene hydrogenation. The catalyst prepared with

CNT was the most active and 100% yield could be obtained at room temperature. The better catalytic performance of Ir/CNT could be ascribed the lower adsorption affinity of the intermediates for the support and the presence or partially positively charged iridium species. Moreover, the oxidation of the CNT surface resulted in a catalyst with remaining IrO₂ on the surface after the reduction treatment, which was not active in the p-chloronitrobenzene reaction.

ACKNOWLEDGEMENTS

Authors thank to CONICYT (Chile, FONDECYT 3130483) and Generalitat Valenciana (Spain, PROMETEOII/2014/004 – FEDER) for financial support.

5. REFERENCES

- [1] H.U. Blaser, A. Schnyder, H. Steiner, F. Rössler, P. Baumeister in Handbook of Heterogeneous Catalysis (Wiley, 2008), vol. 8 pp. 3284-3307
- [2] R.S. Downing, P.J. Kunkeler, H. van Bekkum, Catal. Today 37 (1997) 121-136.
- [3] N. Mahata, O.S.G. P. Soares, I. Rodríguez-Ramos, M.F.R. Pereira, J.J.M. Órfão, J.L. Figueiredo, Appl. Catal. A: General 464-465 (2013) 28-34.
- [4] F. Cárdenas-Lizana, S. Gómez-Quero, C. Amorim, M.A. Keane, Appl. Catal. A: General 473 (2014) 41–50.
- [5] A. Negoii, K. Triantafyllidis, V. I. Parvulescu, S.M. Coman, Catal. Today 223 (2014) 122– 128.
- [6] E. Auer, M. Gross, P. Panster, K. Takemoto, Catal. Today 65 (2001) 31–37.
- [7] G.Y. Fan, L. Zhang, H.Y. Fu, M.L. Yuan, R.X. Li, H. Chen, X.J. Li, Catal. Commun. 11 (2010) 451–455.
- [8] B. Zuo, Y. Wang, Q. Wang, J. Zhang, N. Wu, L. Peng, L. Gui, X. Wang, R. Wang, D. Yu, J. Catal. 222 (2004) 493-498.
- [9] P. Serp, M. Corrias, P. Kalck, Appl. Catal. A: General 253 (2003) 337–358.
- [10] J. Zhu, A. Holmen, D. Chen, ChemCatChem., 5 (2013) 378 – 401.
- [11] J.M. Nhut, L. Pesant, J.P. Tessonnier, G. Winé, J. Guille, C. Pham-Huu, M.J. Ledoux, Appl. Catal. A: General 254 (2003) 345–363.

- [12] X. X.Han, Q.Chen, R.X.Zhou, J. Mol. Catal. A: Chemical 277 (2007) 210–214.
- [13] C. Antonetti, M. Oubenali, A.M. Raspolli Galletti, P. Serp, G. Vannucci, Appl. Catal. A: General 421– 422 (2012) 99– 107.
- [14] Y. Quan-Hong, H.Peng-Xiang, B. Shuo, W.Mao-Zhang, C. H. Ming. Chem. Phys. Lett., 345 (2001) 18–24.
- [15] J.P. Tessonnier, D. Rosenthal, T.W. Hansen, C. Hess, M. E. Schuster, R. Blume, F. Girgsdies, N. Pfänder, O. Timpe, D. Sheng Su, R. Schlögl, Carbon 47 (2009) 1779–1798.
- [16] V.S. Babu, M.S. Sechra, Carbon 34 (1996) 1259-1265.
- [17] N. Larouche, B.L. Stansfield, Carbon 48 (2010) 620–629.
- [18] E. Castillejos, B. Bachiller-Baeza, I. Rodríguez-Ramos, A. Guerrero-Ruiz, Carbon 50 (2012) 2731-2740.
- [19] A.B. Dongil, B. Bachiller-Baeza, A. Guerrero-Ruiz, I. Rodríguez-Ramos, A. Martínez-Alonso, J.M.D. Tascón. J.Colloid. Interface Sci. (2011) 355, 179-189.
- [20] L.I. Kuznetsova, N.I. Kuznetsova, S.V. Koscheev, V. I. Zaikovskii, A.S. Lisitsyn, K. M. Kaprielova, N.V. Kirillova, Z. Twardowski, Appl. Catal. A: General 427-428 (2012) 8-15.
- [21] A.B. Dongil, B. Bachiller-Baeza, A. Guerrero-Ruiz, I. Rodríguez-Ramos, A. Baiker, C. Mondelli. Appl. Catal .A: General 451 (2013) 14-20
- [22] L.I. Kuznetsova, Nina I. Kuznetsova, S.V. Koscheev, V. I. Zaikovskii, A.S. Lisitsyn , K.M. Kaprielov, N.V. Kirillova, Z.Twardowski, Appl. Catal. A: General 427– 428 (2012) 8– 15
- [23] T. MarzIAletti, J.L. García-Fierro, P. Reyes, Catal. Today, 107–108, 30 (2005) 235-243.
- [24] T. MarzIAletti, M. Oportus, D. Ruiz, J.L. García-Fierro, P. Reyes, Catal. Today 133–135 (2008) 711–719.
- [25] Q. Ma, D. Wang, M. Wu, T.Zhao, Y. Yoneyama, N. Tsubaki, Fuel 108 (2013) 430-438.
- [26] A. Nieto-Márquez, S. Gil, A. Romero, J.L. Valverde, S. Gómez-Quero, M.A. Keane, Appl. Catal. A: General 363 (2009) 188–198.
- [27] Q. Ma, D. Wang, M. Wu, T. Zhao, Y. Yoneyama, N. Tsubaki, Fuel 108 (2013) 430-438.
- [28] B. He, M. Wang, W. Sun, Z. Shen, Mater. Chem. Phys. 95 (2006) 289-293.
- [29]K. H. Lee, S.W. Han, K.Y. Kwon, J.B. Park, J. Colloid. Interface Sci.403 (2013) 127–133.
- [30]Y. Yamamoto, T. Matsuzaki, K.Ohdan, Y.Okamoto, J.Catal. 161 (1996) 577-586.

- [31] F. Cárdenas-Lizana, S. Gómez-Quero, C. Amorim, M.A. Keane, *Appl. Catal. A: General* 473 (2014) 41-50.
- [32] N. Mahata, O.S.G.P. Soares, I. Rodríguez-Ramos, M.F.R. Pereira, J.J.M. Órfão, J.L. Figueiredo, *Appl. Catal. A: General* 464–465 (2013) 28–34.
- [33] E. Asedegbega-Nieto, A. Guerrero-Ruiz, I. Rodríguez-Ramos, *Carbon* 44 (2006) 799–823.
- [34] V. Kratky, M. Kralik, M. Mecerova, M. Stolcova, L. Zalibera, M. Hronec, *Appl. Catal. A: General* 235 (2002) 225–231.
- [35] F. Coloma, A. Sepúlveda-Escribano, J.L.G. Fierro, F. Rodríguez-Reinoso, *Appl. Catal. A: General* 150 (1997) 165–183.
- [36] A.E. Aksoylu, M.M.A. Freitas, J.L. Figueiredo, *Appl. Catal. A: General* 192 (2000) 29–42.
- [37] E. Jardim, M. Goncalves, S. Rico-Francés, A. Sepúlveda-Escribano, J. Silvestre-Albero, *Appl. Catal. B: Environmental* 113 (2012) 72-78.
- [38] M.L. Toebes, F.F. Prinsloo, J.H. Bitter, A. Jos van Dillen, K.P. de Jong, *J. Catal.* 214 (2003) 78–87.
- [39] X. Han, R. Zhou, G. Lai, B. Yue, X. Zheng, *J. Mol. Catal. A: Chemical* 209 (2004) 83–87.
- [40] F. Cárdenas-Lizana, S. Gómez-Quero, M.A. Keane, *Catal. Comm.* 9 (2008) 475–481.
- [41] N. Mahata, A.F. Cunha, J.J.M. Órfão, J.L. Figueiredo, *Catal. Comm.* 10 (2009) 1203–1206.

Figure 1. Nitrogen adsorption/desorption isotherms at 77 K of the supports.

Figure 2. XRD patterns of the supports.

Figure 3. Raman spectra of the supports.

Figure 4. Thermogravimetry under He of the supports.

Figure 5. HRTEM images of the catalysts, a) Ir/AC; b) Ir/CNT; c) Ir/MG; d) Ir/CNTox.

Figure 6. TPR-H₂ profiles of the catalysts.

Table 1. Textural and chemical properties of the supports.

Sample	S_{BET} (m²/g)	V micro (cm³/g)	V meso (cm³/g)	Vt (cm³/g)	[O] mmol/g	O/C
AC	846	0.28	0.03	0.31	2.8	0.04
MG	270	0.09	0.29	0.38	1.6	0.04
CNT	300	0.01	1.76	1.77	0.9	0.01
CNTox	295	0.10	0.49	0.59	6.6	0.10

Table 2. Physicochemical properties of the catalysts.

Sample	XPS data			TPR-H ₂ mmol consumed/g (x10 ³)			dp-TEM (nm)
	O/C	Ir/C	Ir 4f7	Peak1	Total	ΔCons. ¹	
Ir/AC	0.042	0.001	61.5	88	240	136	1.42 ± 0.07
Ir/MG	0.012	0.001	61.2	67	206	102	1.24 ± 0.02
Ir/CNT	0.021	0.001	61.1	46	242	138	1.35 ± 0.03
Ir/CNTox	0.009	0.002	61.1 (78) 62.2 (22)	178	275	171	1.19 ± 0.01

¹Difference between the total amount of H₂ consumed and the theoretical value (104x10⁻³ mmol/g_{Ir})

Table 3. Hydrogenation of p-chloroaniline over Ir supported on carbon materials.

Sample	Activity (mol conv./ (mol Ir*min))	Yield of products (mol %)		
		p-ClAN	NB	Others
Ir/AC	48	86	-	14
Ir/MG	43	93	-	7
Ir/CNT	87	100	-	-
Ir/CNTox	25	73	5*	22

*Appeared at 90 %

Table 4. Hydrogenation of x-Chloro nitrobenzene isomers over Ir/CNT.

Nitrocompound	Activity (mol conv./ (mol Ir*min))	Yield of products (mol %)	
		x-ClAN	Others
p-ClNB	87	100	0
o-ClNB	96	100	0
m-ClNB	209	100	0

Scheme 1. Possible reaction paths for the para-chloronitrobenzene hydrogenation.

Figure SI.1.TPR-H₂ profiles of the catalysts coupled to mass spectrometer.