

Document downloaded from:

<http://hdl.handle.net/10251/123464>

This paper must be cited as:

Blandez, JF.; Navalón Oltra, S.; Alvaro Rodríguez, MM.; García Gómez, H. (2018). N-Hydroxyphthalimide Anchored on Diamond Nanoparticles as a Selective Heterogeneous Metal-free Oxidation Catalyst of Benzylic Hydrocarbons and Cyclic Alkenes by Molecular O₂. *ChemCatChem*. 10(1):198-205. <https://doi.org/10.1002/cctc.201700886>



The final publication is available at

<http://doi.org/10.1002/cctc.201700886>

Copyright John Wiley & Sons

Additional Information

This is the peer reviewed version of the following article: Blandez, Juan F., Navalón Oltra, Sergio, Alvaro Rodríguez, Maria Mercedes, García Gómez, Hermenegildo. (2018). N-Hydroxyphthalimide Anchored on Diamond Nanoparticles as a Selective Heterogeneous Metal-free Oxidation Catalyst of Benzylic Hydrocarbons and Cyclic Alkenes by Molecular O₂. *ChemCatChem*, 10, 1, 198-205. DOI: 10.1002/cctc.201700886, which has been published in final form at <http://doi.org/10.1002/cctc.201700886>. This article may be used for non-commercial purposes in accordance with Wiley Terms and

N-hydroxyphthalimide anchored on diamond nanoparticles as selective heterogeneous metal-free oxidation catalyst of benzylic hydrocarbons and cyclic alkenes by molecular O₂

Juan F. Blandez,^[a] Sergio Navalón,^[a] Mercedes Álvaro,^[a] and Hermenegildo García*^[a,b]

Abstract: N-hydroxyphthalimide (NHPI) derived from trimellitic anhydride has been covalently anchored (4 weight %) through ester bonds to the surface of commercial diamond nanoparticles previously functionalized by chemical and thermal treatments (DH). IR spectroscopy of the NHPI/DH solid shows the presence of a characteristic peak at 1735 cm⁻¹ attributable to the ester bond, while solid-state MAS ¹³C NMR spectroscopy shows two broad bands corresponding to carbon atoms of carbonyl groups (167 ppm) and aromatic carbons (127 ppm). NHPI/DH promotes autoxidation of isobutylbenzene involving superoxide (O₂⁻) and hydroperoxide (HOO[•]) radicals NHPI/DH can be reused at least three times and reach a minimum turnover number as high as 20,600, probably due to the unique inertness of the diamond surface, allowing free diffusion of reactive oxygen species. Analogous materials in where NHPI was anchored on activated carbon and multiwall carbon nanotubes were inefficient as autoxidation catalysts. NHPI/DH is able to promote also selective aerobic oxidation of other benzylic hydrocarbons and cycloalkenes.

Introduction

Commonly, hydrocarbon oxidation is carried out in the presence of inorganic oxidizing agents such as chromium and manganese oxides, nitric and sulfuric acid among others, resulting in generation of toxic wastes of difficult environmental management.^[1, 2] Nowadays, development of environmentally-friendly oxidations involves the use of organic and/or inorganic peroxides or hydroperoxides,^[3] the use of molecular O₂ to promote selective oxidations still being a challenge.^[4] In this context, N-hydroxyphthalimide (NHPI) and its derivatives have shown a wide scope in promoting the aerobic oxidations of organic functional groups including benzylic and alicyclic hydrocarbons, alcohols, oximes, alkenes, etc.^[1, 5-7] The reaction mechanism is known to involve phthalimide N-oxyl (PINO) radical generated from NHPI, the process being easier in the

presence of first-row transition metals, particularly Co²⁺ ions that coordinate, with the hydroxyl group of the diacyloxime and subsequently generate the PINO radicals with the simultaneous change in the oxidation state of the metal.^[1, 5, 6] In spite of the high efficiency and applicability together with affordability of NHPI, its implementation at industrial scale is hampered by the difficulty to recover NHPI from the reaction mixtures. However, the number of studies reporting heterogeneous catalyst in with NHPI or its derivatives has been immobilized on solid supports is relatively scarce.^[5, 8]

A few years ago, we reported the catalytic activity of NHPI adsorbed on porous metal organic frameworks (MOFs), in where there is a synergism between the adsorbed NHPI and the metal nodes of the MOF.^[9] In other reports, NHPI derivatives have been anchored to polymers, based on polystyrene^[10] or acrylates,^[11] and used to promote oxidations of benzylic hydrocarbons in combination or in the absence of Co²⁺ ions. NHPI derivatives have also been anchored on mesoporous silica again using Co²⁺ salts as promoter.^[12]

In spite of the related precedents, it would be still convenient to explore other heterogeneous catalyst in where NHPI is anchored to other supports of different properties. Herein we have used surface-modified diamond nanoparticles (DH) as support to anchor NHPI. The main advantage of DH as support is the inertness of its surface against radicals. In early precedents it was found that even highly aggressive hydroxyl radicals do not react with the surface of modified DH.^[13] The data presented here shows that NHPI/DH in the absence of Co²⁺ or any other transition metals as co-catalyst is able to promote the aerobic oxidation of benzylic hydrocarbons and cyclic alkenes behaving as a solid radical initiator.

Results and Discussion

In the first part of this section the preparation and characterization of NHPI/DH will be described. Then, the performance of NHPI/DH as heterogeneous initiator for autoxidation in benzylic carbons and cyclic alkenes will be presented.

Synthesis and characterization of NHPI/DH

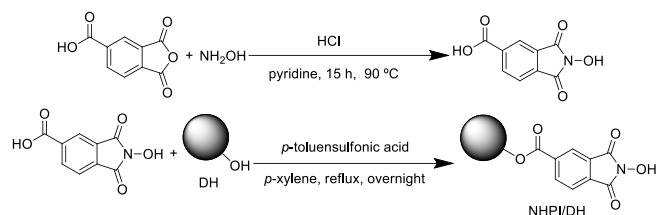
The synthesis of NHPI/DH started with commercially available trimellitic anhydride that was reacted with hydroxylamine to form the 4-substituted carboxylic acid derivative of NHPI. This derivative was characterized by ¹H- and ¹³C-NMR spectroscopy and mass spectrometry (Figures S1-S3). This NHPI acid derivative was reacted with D NPs that were previously purified, then, surface-modified by Fenton oxidation and subsequently

[a] Dr. J. F. Blandez, Dr.S.Navalón, Prof.M.Álvaro Prof. H.García
Departamento de Química and Instituto de Tecnología Química
CSIC-UPV, Universitat Politècnica de Valencia, Consejo Superior
de Investigaciones Científicas, Av. de los Naranjos s/n, 46022
Valencia, Spain.
E-mail: hgarcia@qim.upv.es

[b] Center of Excellence for Advanced Materials Research, King
Abdulaziz University, Jeddah, Saudi Arabia

Supporting information for this article is given via a link at the end of the document.

hydrogenated at 500 °C under H₂ flow (DH). The synthetic route is illustrated in Scheme 1. It is known that commercial D NPs can suffer an oxidative functionalization by Fenton reaction with H₂O₂ using Fe²⁺ salt.^[13, 14] This Fenton treatment gives rise to water dispersible D NPs in where the surface of these D NPs contains a significant population of hydroxylic and carboxylic groups. Treatment of the purified D NPs with H₂ at 500 °C resulted in the chemical reduction of surface carboxylic and carbonyl groups that are converted into hydroxyl group.^[15] These surface -OH groups will form an ester bond with the carboxyl acid substituent of NHPI forming a covalent linkage NHPI and DH.



Scheme 1. Synthetic route for the preparation of the NHPI/DH catalyst.

Similar chemical oxidation reactions but using sulfuric or nitric acid as oxidants followed by reductive hydrogenation and further NHPI derivative anchoring were also applied to commercial activated carbon (AC) and multi-walled carbon nanotubes (MWCNT) samples, leading to the formation of NHPI/ACH and NHPI/MWCNTsH that would be reference materials to compare the performance of NHPI/DH.

The materials containing covalently anchored NHPI were characterized by different techniques including elemental combustion analysis, thermogravimetry, FT-IR, XPS and solid-state ¹³C NMR spectroscopies. Table 1 shows analytical data of the three supports (DH, ACH and MWCNTsH) compared to the elemental analysis of the corresponding materials where NHPI is anchored. As it can be seen in the Table 1, derivatization of DH, ACH and MWCNTsH result in a decrease in the carbon content, while the amount of nitrogen undergoes minor relative variations. These data indicate that the percentage of NHPI anchored to the material should be low. It is also noted that the process introduces elemental sulphur indicating that some adsorbed *p*-toluensulfonic acid must be present in our material.

Table 1. Elemental analysis data for the solid materials before and after NHPI anchoring.

Solid material	N (%)	C (%)	H (%)	S (%)	O (%)
DH	2.07	88.61	0.98	0	8.34
NHPI/DH	1.95	80.32	1.04	0.30	16.39
ACH	1.05	88.54	0.82	0	9.59
NHPI/ACH	1.48	69.68	1.47	0.17	27.20
MWCNTsH	0.06	98.53	0.20	0	1.21
NHPI/MWCNTsH	0.28	82.38	0.94	0.20	16.20

The amount of NHPI present on the support was estimated from TG analysis (TGA) and TGA derivative (DTGA) profiles of the carbon supports covalently functionalized with NHPI on the surface (Figure 1a and S4). Specifically, the weight loss from

250 to 400 °C is attributable to the decomposition of NHPI. These measurements give an estimation of NHPI content in the series of carbon supports of about 4 wt% for NHPI/DH (Figure 1a), NHPI/ACH (Figure S4a) and NHPI/MWCNTsH (Figure S4b). The presence of NHPI on the support can be ascertained by FT-IR spectroscopy, comparing the spectra of NHPI and DH with that of NHPI/DH (Figure 1b). The most characteristic observations were the disappearance of OH band in the DH support (about 3300-3000 cm⁻¹) and the appearance of C=O stretching vibration band about 1735 cm⁻¹ attributable to the formation of the ester groups. Figure 1b shows a comparison of three FT-IR spectra for NHPI, DH and NHPI/DH.

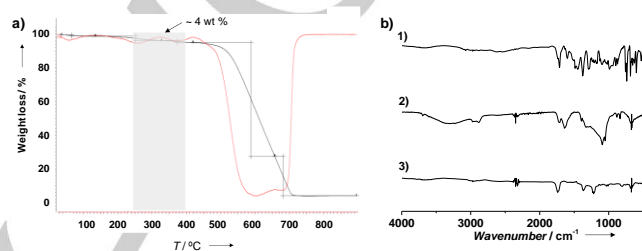


Figure 1. (a) TGA (black line) and DTGA (red line) for NHPI/DH; (b) FT-IR spectra for NHPI (1), DH (2) and NHPI/DH (3).

Comparison of XPS C1s peaks of DH and NHPI/DH shows an increase in the percentage of carbons bonded to oxygen from 33 to 60 % after anchoring the NHPI on DH. The broadness of N 1s peak slightly increases from DH to NHPI/DH due to the presence of imide group in the NHPI that overlaps with that of graphitic N. This XPS data are in general agreement with the amount of NHPI anchored on DH surface (Figure 2).

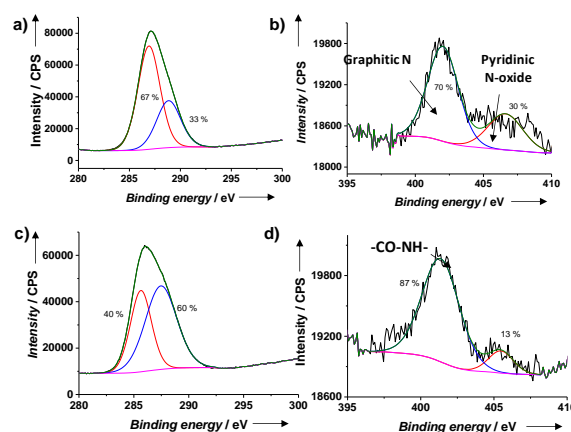


Figure 2. XPS spectra for C 1s and N 1s for the DH (top) and NHPI/DH (bottom) and the percentages of their individual components obtained from the best fit.

Magic-angle spinning (MAS) solid-state ¹³C NMR spectra of NHPI/DH shows two broad weak peaks about 167 and 127 ppm attributable to the carbonyl groups and aromatic carbon atoms of NHPI. These peaks in MAS ¹³C NMR spectroscopy were absent

in the case of DH as support (Figure 3), where only two signal at 35 and 50 ppm corresponding to carbon atoms of DH bonded or not to oxygen, respectively, can be observed.^[15]

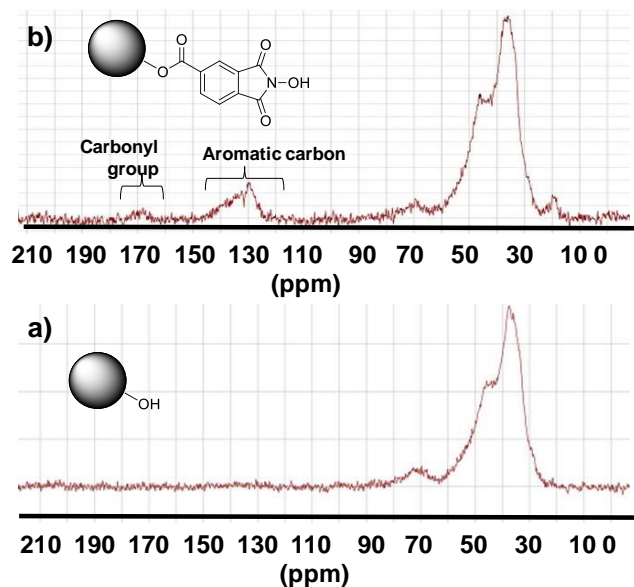


Figure 3. MAS ¹³C-NMR spectra for DH (a) and NHPI/DH (b).

Catalytic data

Comparison of the performance of NHPI anchored to the three types of carbon supports shows that only for NHPI/DH products are formed in significant concentration (Figure 4). In the case of NHPI/ACH and NHPI/MWCNTsH disappearance of isobutylbenzene (IB) was not accompanied by the formation of significant amount of oxidation products (Figures S5 and S6). Moreover, in the cases of NHPI/ACH (Figure S5) and NHPI/MWCNTsH (Figure S6), the comparison of the percentage of IB disappearance under oxygen or argon atmosphere shows that most of the IB is really adsorbed on the material while oxidation is taking place in only a very minor extent as revealed by the presence of reaction products (Figures S5 and S6). This high adsorption of IB on NHPI/ACH or NHPI/MWCNTsH it is agreement with the high adsorption capacity characteristic of these carbonaceous materials.^[16]

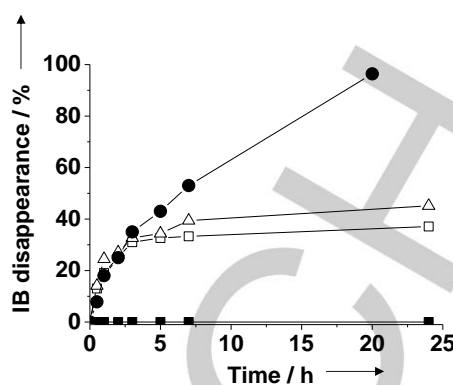


Figure 4. Time profile of IB conversion in the presence of NHPI/DH (●), NHPI/ACH (□), NHPI/MWCNTsH (Δ) and DH (■) as catalyst. Reaction conditions: Catalyst (40 mg), IB (20 mmol), O₂ (1 bar), 140 °C.

Comparison of the performance of NHPI/DH solid, with those of DH, commercial NHPI molecule, and unsupported NHPI carboxylic acid shows that while DH was unable to promote IB autoxidation, the two NHPI molecules promote IB autoxidation, but at much lower reaction rate than for NHPI/DH, even though the reactions using commercial NHPI and unsupported NHPI carboxylic acid were carried out using double amount in comparison with NHPI/DH. Therefore, NHPI/DH was the best performing catalyst to carry out IB autoxidation of IB of all the series (Figure 5). This higher catalytic activity of NHPI anchored to DH is attributed to the combination of a series of factors, easier generation of the corresponding PINO radicals, their longer lifetime when they are anchored to DH and the free diffusion of oxygen-centred radicals to the liquid phase without interaction with the solid surface.

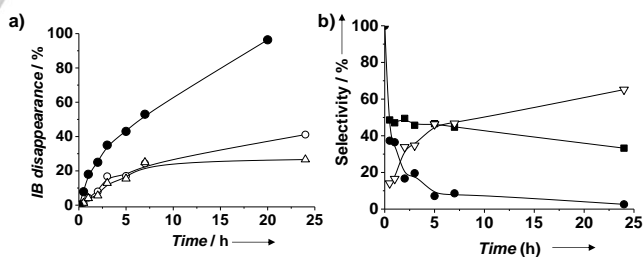


Figure 5. a) Time profile of IB conversion in the presence of commercial NHPI (○), carboxylic acid derivative of NHPI (Δ) and NHPI/DH (●). b) Selectivity evolution for 1-hydroperoxyisobutylbenzene (●), phenyl isopropyl ketone (■) and benzoic acid (Δ) during IB conversion using NHPI/DH as catalyst. Reaction conditions: IB (20 mmol), NHPI/DH (40 mg), commercial NHPI and derived acid NHPI (1.6 mg), O₂ (1 bar), 140 °C.

In all reactions, the products observed in IB autoxidation were the corresponding 1-hydroperoxy IB, phenyl isopropyl ketone and benzoic acid. The 1-hydroperoxy IB cannot be quantified by GC due to its decomposition. Therefore, the reaction mixture was treated with triphenylphosphine at 80 °C to promote

decomposition of the hydroperoxide and, then, the formation 1-hydroxy-1-IB, together with 1-phenyl-1-isobutanol was quantified together with triphenylphosphine oxide and 1-phenyl-2-methyl-1-propanol.^[17] Benzoic acid is a secondary product, coming from oxidation of phenyl isopropyl ketone. Accordingly, the temporal profile of benzoic acid formation shows an induction period, indicating that it is not a primary product. Figure 6b shows the time profile for IB conversion and selectivity towards the main products.

NHPI/DH was reused three times observing that during the first two uses, the temporal profile of IB conversion remains unaltered, while a decrease in the reaction rate was observed in the third use, even though substantially the same conversion was achieved at final reaction time (Figure 6a). This partial deactivation can be attributed to the occurrence of leaching/degradation of NHPI as can be deduced from the changes observed in the IR spectra of the used NHPI/DH catalyst (Figure S7). The most evident change was the decreased intensity of the characteristic band of the ester groups at 1735 cm^{-1} . In addition, TG profiles show that the three times used material contains a significant amount of organic compounds adsorbed on its surface that was estimated to be about 12 wt% (Figure S8).

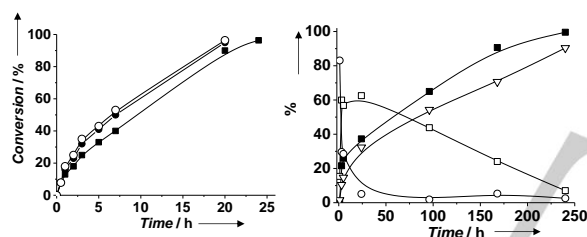


Figure 6. (a) Reusability of NHPI/DH during the oxidation of IB. Legend: 1st use (■), 2nd use (●) and 3rd use (○). Reaction conditions: IB (20 mmol), NHPI/DH (20 mg), O₂ (1 bar), 140 °C. (b) Time conversion (■) and selectivity (○: hydroperoxide IB; □ phenyl isopropyl ketone; Δ: benzoic acid) plots for the maximum IB turnover number reaching a value of 20,600. Reaction conditions: IB (40 mmol), NHPI/DH (10 mg), O₂ (1 bar), 140 °C.

In order to determine the maximum turnover number (TON) of NHPI/DH as catalyst for autoxidation of IB, an additional experiment was carried out in where a large amount of IB was used and the reaction was allowed to proceed for longer times (Figure 6b). Under these conditions, a TON value of 20,600 molecules of IB converted per NHPI molecule in the catalyst was achieved. This value is several orders of magnitude higher than those previously reported using NHPI/MOF^[9, 18] or even using homogeneous NHPI as radical initiator in combination with transition metal ions,^[19] and is also higher or comparable to the TON values reported for other catalysts based on transition metals as active centers.^[20] Selectivity about 90 % for benzoic acid was achieved at full IB conversion (Figure 6b).

The influence of the oxygen content in the atmosphere on the catalytic activity of IB oxidation using NHPI/DH as catalyst was also studied. In contrast to the previously commented adsorption experiment in NHPI/ACH or NHPI/MWCNTsH, in where little

influence of the composition of the atmosphere either oxygen or argon, was observed as consequence of the occurrence of a negligible oxidation reaction, in the case of IB autoxidation by NHPI/DH the initial reaction rate follows an apparent pseudo first order relationship with oxygen pressure and no IB disappearance was observed under argon atmosphere (Figure 7).

The activation energy for IB autoxidation promoted by NHPI/DH was determined from the Arrhenius plot of the natural logarithm of the initial reaction rate versus the inverse of the absolute temperature. The initial reaction rate was obtained from the slope of the temporal profile of IB conversion at temperatures ranging from 120 to 150 °C. In this way, an activation energy of $69\text{ kJ}\cdot\text{mol}^{-1}$ was estimated for the process (Figure 8). This E_a is similar to the values estimated for the aerobic oxidation of benzylic positions using transition metal-based catalysts such as, for instance, the metal-organic framework MIL-101(Cr).^[17]

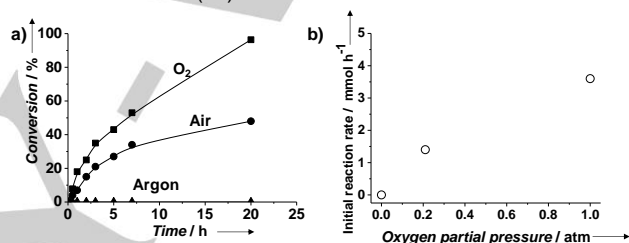


Figure 7. (a) Time-conversion plot under different oxygen pressure (argon, air; molecular oxygen) and relationship of the oxygen atmosphere and the initial reaction rate (b) for the oxidation of IB in the presence of NHPI/DH. Reaction conditions: Catalyst (40 mg), IB (20 mmol), 140 °C, O₂ atmosphere as indicated in the graph.

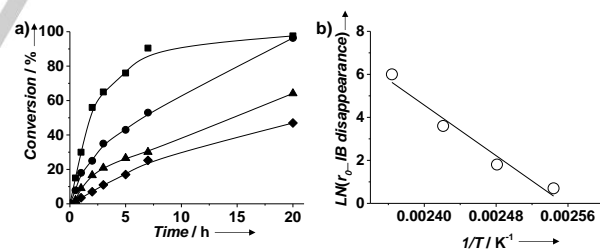


Figure 8. a) Time-conversion plot for IB oxidation at different temperatures and b) Arrhenius plot of the natural logarithm of the initial reaction rate vs the inverse of the absolute temperature. Legend: 150 °C (■), 140 °C (●), 130 °C (▲) and 120 °C (◆). Reaction conditions: IB (20 mmol), NHPI/DH (40 mg), 140 °C, O₂ atmosphere (1 bar).

The fact that the reaction mechanism involves carbon center radicals was supported by performing a hot filtration test in where the reaction is initiated in the presence of solid catalyst and then the catalyst was removed after 4 h, while the reaction is still hot at the reaction temperature. Comparison of the temporal profiles after filtration of the catalyst with that of a twin

reaction where the catalyst was present shows that the reaction does not completely stop in the absence of solid catalyst (Figure S9). It was, however, determined that IB conversion was smaller after filtration of the catalyst than when the catalyst was present. These results can be interpreted considering that during the initial 4 h, of reaction radicals such as hydroperoxide are generated, and these radicals will continue oxidation through a radical chain mechanism even in the absence of solid catalyst. Similar results, i.e. evolution of the reaction after catalyst filtration, have been observed for the aerobic oxidation of benzylic substrates employing metal-based catalysts such as MIL-101(Cr),^[17] Cu-MOF as initiators.^[21] Although the contribution of some leached NHPI from the solid to the solution cannot be ruled out, leached NHPI should promote oxidation in a very minor extent according to the previously commented experiment in where pure NHPI in a much higher amount than possibly leached out was used as catalyst, observing a slow progress of the oxidation reaction (Figure 5a). This radical chain mechanism was also supported by quenching experiment using *p*-benzoquinone as selective $O_2^{\cdot-}$ radical quencher (Figure S9b).^[17, 22, 23] When the reaction is started in the absence of *p*-benzoquinone and then, 20 mol % *p*-benzoquinone was added at 5 h reaction time, an almost complete quenching of the reaction was observed, supporting the intermediacy of superoxide radical ions as a radical intermediate. The use of DMSO as selective hydroxyl radical scavenger also stopped the reaction (Figure S9b).

Additional support for the intermediacy of superoxide radical anions was obtained by Electron paramagnetic resonance (EPR) spectroscopy using *N-tert-butyl- α -phenylnitron* (PBN) as radical trapping agent. Heating *n*-dodecane containing PBN and NHPI/DH under oxygen led to the observation of an EPR spectra corresponding to the adduct of PBN with hydroperoxide (HOO^{\cdot}) radicals (Figure 9). Hydroperoxyl is the protonated form of superoxide ($O_2^{\cdot-}$) that should be the primary oxygen reactive species generated in the system. The good match between the experimental and simulated EPR spectrum for PBN-OOH adduct indicated that no other reactive oxidizing species should be present in comparable amounts to that of $O_2^{\cdot-}$.^[24] The fact that hydroxyl radical was not observed by EPR spectroscopy is interpreted considering that the generated hydroperoxides are quantitatively trapped by PBN and undergo decomposition to the corresponding hydroxyl radical in significant extent.^[17]

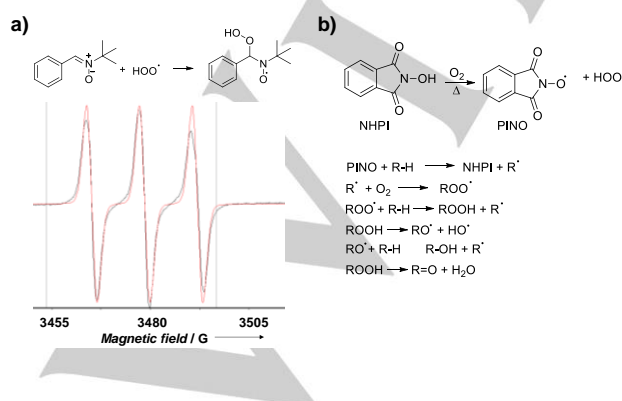


Figure 9. a) Experimental (black line) and simulated EPR spectra (red line) of PBN-OOH. Hyperfine coupling constants of PBN-OOH $AG_N = 13.40$ and $AG_H = 1.25$. Reaction conditions: NHPI/DH (10 mg), PBN (20 mg), O_2 (1 atm) in *n*-dodecane (20 mL) at 140 °C for 2 h. b) Proposed reaction mechanism for the oxidation of benzylic substrates using supported NHPI/DH.

The scope of the aerobic oxidation of benzylic compounds using NHPI/DH as heterogeneous autoxidation catalyst was expanded to other industrially important substrates including cumene, indane, 1-phenylbutane and 2-phenylbutane (Table 2). Excellent to good selectivities to the corresponding ketones or hydroperoxides were obtained for the studied substrates. Of particular importance is oxidation of cumene to 1-hydroperoxycumene with selectivity as high as 93 % at 50 % conversion under solventless conditions (Figure S10). Cumyl hydroperoxide is a commodity largely employed in the chemical industry as primary oxidant and radical initiator for the production of oxygenated compounds or as polymerization initiator. Currently, most of the phenol produced worldwide is obtained by the chemical industry through decomposition of cumyl hydroperoxide with H_2SO_4 (Hock process).^[25] Interestingly, using NHPI/DH acetophenone can be obtained with high selectivity (95 %) at almost full conversion as secondary product from cumyl hydroperoxide in the same reaction. Acetophenone is an important commodity for the production of resins and an important intermediate for the production of fine chemicals. Also indane can be oxidized with good selectivity (82 %) to 2-indanone at high conversions (81 %) (Figure S11). Indanone is an industrial organic intermediate for the production of oximes employed in the production of agrochemicals and pharmaceuticals. As commented earlier, IB is oxidized to phenyl isopropyl ketone and benzoic acid with selectivities of 64 and 30 %, respectively. In the case of 2-phenylbutane the corresponding ketone in benzylic position is obtained with good selectivity (80 %), even at high conversions (~80 %) (Figure S12). In the case of 1-phenylbutane also the major selectivity was achieved for the ketone in benzylic position (66 %) accompanied by benzoic acid (29 %) at 70 % conversion (Figure S13). It is important to highlight the good conversions and selectivities achieved using exclusively molecular O_2 as oxidant, respect to the use of other transition metal^[26] or metal-free catalysts that employ organic or inorganic peroxides as terminal oxidants.^[27] Figure 9b shows the proposed reaction pathway for the oxidation of benzylic compounds using NHPI/DH as radical initiator in the presence of molecular O_2 .

Table 2. Conversion and selectivity for the benzylic oxidation of hydrocarbons promoted by NHPI/DH.^[a]

	Initial reaction rate (mmol h ⁻¹)	Conversion (%)	Time (h)	Main reaction products	Selectivity (%)
Cumene	11.2	97	24	Acetophenone	95
				Benzoic acid	5
Indane	4.8	83	5	Indanone	76
				3-hydroxy-1-indanone	17
IB	1.38	96	24	Phenyl isopropyl ketone	64
				Benzoic acid	31
2-Phenylbutane	1.49	80	72	2-Phenyl-2-butanol	80
				Acetophenone	6
1-Phenylbutane	1.46	55	24	Phenyl propyl ketone	66
				Benzoic acid	29

[a] Reaction conditions: Catalyst (40 mg), substrate (20 mmol), O₂ atmosphere, 140 °C. Reaction time profiles are presented in figures S10 to S13.

As expected in view of the reported activity of NHPI, NHPI/DH is also active to promote oxidation of cycloalkenes, the product distribution depending on the size of the cycloalkene (Table 3). Aerobic oxidation of cycloalkenes is a challenging reaction for the production of fine chemicals such as epoxides, alcohols and ketones. In the case of large cyclooctene, epoxide was the only product observed with almost complete selectivity at significant substrate conversion. This selectivity towards the epoxide decreased as the ring size diminishes. In this way cycloheptene undergoes aerobic oxidation to afford the allylic ketone and the cyclic epoxide in a proportion 2:1. In the case of cyclohexene, no epoxide was observed and the major products were the corresponding allylic alcohol and ketone. No autoxidation was observed in the case of cyclopentene. These results and the product distribution for cycloalkene oxidation parallel well the data that have been reported in the literature for the autoxidation of these cyclic substrates by NHPI adsorbed on Fe-BTC^[9] or using a Cu-MOF.^[23]

Table 3. Oxidation of cycloalkenes. Catalytic data for the aerobic oxidation of cycloalkenes by NHPI/DH.^[a]

Cycloalkene	Conversion (%)	Selectivity (%)		
		Alcohol	Ketone	Epoxide
Cyclooctene ^[b]	33	0	0	100
Cycloheptene	58	0	67.3	32.7
Cyclohexene	25	35.5	57.2	0
Cyclopentene	< 3	-	-	-

[a] Reaction conditions: Catalyst (40 mg), substrate (20 mmol), O₂ atmosphere (5 bars), 150 °C, 24 h

[b] Blank control experiments in the absence of catalyst resulted in a conversion of ~6 %

Conclusions

In the present manuscript it has been shown that the nature of the carbonaceous support in with NHPI is anchored plays a significant role determining its catalytic activity. While covalent anchoring of NHPI through ester bonds to the surface OH group of ACH or MWCNTsH render materials with negligible autoxidation activity, when NHPI is anchored on the surface of treated D NPs, the resulting material is able to promote autoxidation of benzylic hydrocarbons and alicyclic alkenes. In general, good to excellent selectivity were observed even at conversions higher than 60 % under solventless conditions. In the case of IB a TON as high as 20,600 was achieved. Quenching experiments and EPR detection of the adduct of PBN with hydroperoxyl radical indicate that the most likely reaction mechanism involves the superoxide and hydroperoxide species as primary reactive oxygen species. The catalyst can be reused and the activity decay appears to be related to poisoning of the solid surface. NHPI/DH has a broad scope to promote autoxidation of benzylic hydrocarbons and cycloalkenes, following the reactivity pattern already reported for others heterogeneous NHPI catalysts.

Experimental Section

Materials

Diamond nanopowder (ref: 636444, 95%), activated carbon (Norit SX Ultra, ref. 53663), multi-walled carbon nanotubes (MWCNTs) and trimellitic anhydride were supplied by Sigma-Aldrich. The other reagents or solvents used in this work were of analytical or HPLC grade.

Synthesis of NHPI 4-carboxylic acid molecule

The preparation of NHPI 4-carboxylic acid was carried out according reported procedures.^[28] To a suspension of N-

hydroxylamine-HCl (3.06 g, 44 mmol) in pyridine (50 mL), trimellitic anhydride (7.69 g, 40 mmol) was added. The mixture was stirred magnetically at 90 °C for 15 h. After this time, the reaction was quenched by addition of water (50 mL). The mixture was cooled at room temperature and the pH value brought to 2-3 with HCl. A white solid precipitated. The solid was filtered using a Nylon filter (0.2 µm), washed with abundant water and dried under vacuum. The spectroscopic data is provided in Figures S1-S3.

Preparation of surface-modified D support (DH)

Preparation of DH was made following previously reported procedures.^[15, 29] Briefly, commercial diamond NPs (0.5 g) (D NPs) were added to H₂O₂ (150 mL) in a beaker and, the suspension was sonicated. A solution of FeSO₄ (2 g) in water at pH 3 (H₂SO₄) was added to this mixture dropwise. Caution: sudden temperature increase can occur because the high exothermicity of the reaction. When the reaction is finished, the suspension was allowed to settle overnight. The supernatant was removed and the solid exhaustively washed with a diluted sulfuric aqueous solution (0.1 M) until the iron is absent as evidenced by colorimetric titration using KSCN. Then, the solid was washed with Milli-Q water until pH 7. The H₂O was removed by lyophilization. Dry samples of purified D NPs were reduced with H₂ at 500 °C for 6 h and labelled as DH.

Preparation of surface-modified activated carbon support (ACH)

Commercially available activated carbon (Norit SX Ultra; 100 mg) was sonicated in 25 mL of concentrated HNO₃. The suspension was heated at 85 °C for 20 h. After this time, the mixture was cooled to room temperature and the solid recovered by centrifugation. The solid was washed with water several times until pH 7. Finally, the solid was dried under vacuum. Dry samples of purified AC were reduced with H₂ at 500 °C for 6 h and the resulting sample labelled as ACH.

Preparation of surface-modified MWCNTs support (MWCNTH)

Commercial MWCNTs were submitted to purification and pretreatment by adding a sample (150 mg) to a HNO₃ aqueous solution (75 mL, 3 M) in a flask.^[30] The reaction mixture was stirred under reflux temperature for 12 h. Then, the solid was collected by filtration, washed until pH 7 and the sample dried by lyophilization. Subsequently the length of purified MWCNTs was shortened by adding pretreated MWCNTs (150 mg) to an acid mixture of concentrated H₂SO₄ (6 mL) and concentrated HNO₃ (2 mL) in H₂O (20 mL). The suspension was sonicated at 60 °C for 1 h. The solid was washed with water until pH 7 and the H₂O was removed by lyophilization. Dry samples of purified MWCNTs were reduced with H₂ at 500 °C for 6 h and labelled as MWCNTsH

Covalent anchoring of NHPI 4-carboxylic acid to the surface-modified supports

NHPI 4-carboxylic acid was added in at 10 w/w% respect to the support to a suspension of *p*-xylene (40 mL) containing the solid support (DH, ACH or MWCNTsH).^[28] Then, *p*-toluenesulfonic acid (0.1 equivalent) was added to the suspension as catalyst. The suspension was heated overnight at reflux temperature. The solid was filtered and washed with hot dichloromethane. The solid samples were labelled as NHPI/DH, NHPI/ACH or NHPI/MWCNTsH.

Catalyst characterization

Fourier transformed infrared (FTIR) spectra were collected using a Nicolet 6700 instrument (Thermo scientific, USA) within the range of 4000-400 cm⁻¹ range. Thermogravimetric analyses (TGA) were performed on a Perkin Elmer Diamond TGA/DTA STA 6000 in the 25-600 °C temperature range under at 5 °C·min⁻¹ scan rate under an O₂ flow of 20 mL·min⁻¹. Elemental analyses (EA) were carried out with a Euro EA 3000. X-Ray photoelectronic spectroscopy (XPS) measurements were carried out using a spectrometer SPECS equipped with a Phoibos 150 9 MCD detector. The measurements were performed using a monochromatic source of X-Ray (Al) at 200 W. Solid-state and liquid phase NMR spectra were recorded in a Bruker AV 400 and a Bruker Advance de 400 MHz, respectively.

General catalytic procedure

Typically, the catalyst (20 mg) was placed into a round bottom flask (25 mL) having a magnetic stirring bar. The reagent (10 mmol) was added to the flask and the suspension sonicated for 1h. Then, the mixture was purged with O₂ for 15 min. Then, the reaction mixture was stirred at 140 °C in a preheated oil bath under oxygen atmosphere from a balloon. The course of the reaction was periodically followed by extracting aliquots (0.1 mL) of the reaction mixture with a syringe that were diluted with acetonitrile. Then, a known weight of nitrobenzene as calibration standard was added, the solution was filtered and the mixture was immediately injected in GC (6890 Network GC system Agilent technologies) to avoid spontaneous subsequent oxidation. Product quantification was done using calibration data obtained using commercially available products.

Reuse experiments for NHPI/DH sample were performed following the general reaction conditions, but employing the used NHPI/DH sample as catalyst. At the end of each reaction, the solid catalyst was filtered through a Nylon membrane filter (0.2 µm) and washed with hot dichloromethane. Then, the catalyst was dried at 100 °C for 24 h before next use. The catalyst was loaded in a new reaction mixture.

Selective radical quenching experiments were carried out following the general procedure, but with the addition of dimethylsulfoxide (DMSO) as hydroxyl radical quencher^[17, 23, 31] and *p*-benzoquinone as superoxide/hydroperoxide radical quencher^[17, 22, 23] (20 mol % respect to substrate) after the reaction started.

Electron paramagnetic resonance (EPR) measurements

NHPI/DH (20 mg) was added to a round bottom flask (25 mL) containing *N-tert*-butyl- α -phenylnitron (PBN, 1150 mg L⁻¹) dissolved in *n*-dodecane (10 mL). Then, the flask was sonicated (20 min) and purged with a balloon containing O₂. Finally, the system was heated at 120 °C for 4 h. Then, a reaction aliquot was filtered (Nylon filter, 0.2 µm) and the sample purged with N₂ before recording the EPR. EPR spectra were acquired using a Bruker EMX spectrometer with the following parameters: frequency 9.803 GHz, sweep width 3489.9 G, time constant 40.95 ms, modulation frequency 100 kHz, modulation width 1 G, microwave power 19.92 mW

Acknowledgements

Financial support by the Spanish Ministry of Economy and Competitiveness (Severo Ochoa and CTQ2015-69153-CO2-R1 and CTQ2014-53292-R and Generalitat Valenciana (Prometeo 2013/14) and is grateful acknowledged. S.N. is thankful for

financial support by Fundación Ramón Areces (XVIII Concurso Nacional, Ciencias de la Vida y de la Materia, Energía renovable: materiales y procesos 2016).

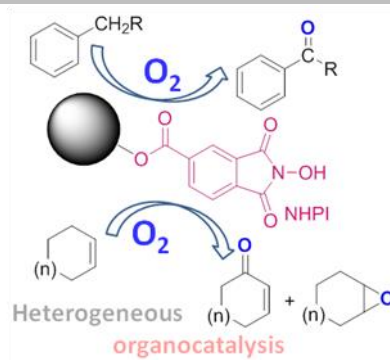
Keywords: Heterogeneous catalysis • aerobic oxidations • N-hydroxylphthalimide • diamond nanoparticles as support • benzylic oxidation • cyclic alkene oxidation

- [1] Y. Ishii, S. Sakaguchi, T. Iwahama, *Adv. Synth. Catal.* **2001**, *343*, 393-427.
- [2] D. G. Lee, V. S. Chang, *J. Org. Chem.* **1979**, *44*, 2726-2730.
- [3] Y. Gao, G. Hu, J. Zhong, Z. Shi, Y. Zhu, D. S. Su, J. Wang, X. Bao, D. Ma, *Angew. Chem. Int. Ed* **2013**, *52*, 2109-2113.
- [4] a) S. Navalon, A. Dhakshinamoorthy, M. Alvaro, M. Antonietti, H. García, *Chem. Soc. Rev.* (doi:10.1039/c7cs00156h) **2017**; b) P. Tang, G. Hu, M. Li, D. Ma, *ACS Catal.* **2016**, *6*, 6948-6958; c) O. A. Kholdeeva, *Catal. Sci. Technol.* **2014**, *4*, 1869-1889.
- [5] S. Coseri, *Catal. Rev.* **2009**, *5*, 218-292.
- [6] a) Y. Ishii, S. Sakaguchi, *Catal. Today* **2006**, *117*, 105-113; b) F. Recupero, C. Punta, *Chem. Rev.* **2007**, *107*, 3800-3842.
- [7] I. Melone, c. Punta, *Beilstein J. Org. Chem.* **2013**, *9*, 1296-1310.
- [8] J. Tong, Z. Li, C. Xia, *Prog. Chem.* **2005**, *17*, 96-110; R. A. Sheldon, I. W. C. E. Arenas, *Adv. Synth. Catal.* **2004**, *346*, 1051-1071.
- [9] A. Dhakshinamoorthy, M. Alvaro, H. Garcia, *J. Catal.* **2012**, *289*, 259-265.
- [10] M. Jian, J. Cui, D. Luo, M. Xie, *RSC Adv.* **2016**, *6*, 68170-68177.
- [11] P. Łątka, K. Kasperczyk, B. Orlińska, M. Drozdek, B. Skorupska, E. Witek, *Catal. Lett.* **2016**, *146*, 1991-2000.
- [12] F. Rajabi, B. Karimi, *J. Mol. Catal. A.-Chem* **2005**, *232*, 95-99.
- [13] S. Navalon, R. Martin, M. Alvaro, H. Garcia, *Angew. Chem. Int. Ed.* **2010**, *49*, 8403-8407.
- [14] A. Dhakshinamoorthy, S. Navalon, D. Sempere, M. Alvaro, H. Garcia *Chem. Commun.* **2013**, *49*, 2359-2361.
- [15] S. Navalon, D. Sempere, M. Alvaro, H. Garcia, *ACS Appl. Mater. Interfaces* **2013**, *5*, 7160-7169.
- [16] a) F. Villacañas, M. F. R. Pereira, J. J. M. Órfão, J. L. Figueiredo, *J. Colloid Interf. Sci.* **2006**, *293*, 128-136; b) S. Navalon, A. Dhakshinamoorthy, M. Alvaro, H. Garcia, *ChemSusChem* **2011**, *4*, 1712-1730.
- [17] A. Santiago-Portillo, S. Navalon, F. Cirujano, F. Llabrés i Xamena, M. Alvaro, H. Garcia, *ACS Catal.* **2015**, *5*, 3216-3224.
- [18] A. Dhakshinamoorthy, M. Alvaro, H. Garcia, *ChemCatChem* **2010**, *2*, 1438-1443.
- [19] Y. Yoshino, Y. Hayashi, T. Iwahama, S. Sakaguchi, Y. Ishii, *J. Org. Chem.* **1997**, *62*, 6810-6813.
- [20] A. Rezaeifard, A. Khoshyan, M. Jafarpour, M. Pourtahmasb, *RSC Adv.* **2017**, *7*, 15754-11576.
- [21] F. X. Llabrés i Xamena, O. Casanova, R. G. Tailleux, H. Garcia, A. Corma, *J. Catal.* **2008**, *255*, 220-227.
- [22] A. Gómez-Paricio, A. Santiago-Portillo, S. Navalón, P. Concepción, M. Alvaro, H. Garcia, *Green Chem.* **2016**, *18*, 508-515.
- [23] P. Cancino, A. Vega, A. Santiago-Portillo, S. Navalon, M. Alvaro, P. Aguirre, E. Spodine, H. García, *Catal. Sci. Technol.* **2016**, *6*, 3727-3736.
- [24] G. R. Buettner, *Free Radic Biol Med.* **1987**, *3*, 259-303.
- [25] O. Fukuda, S. Sakaguchi, Y. Ishii, *Adv. Synth. Catal.* **2001**, *343*, 809-813.
- [26] O. A. Kholdeeva, *Catal. Today* **2016**, *278*, 22-29.
- [27] J. Zhang, Z. Wang, Y. Wang, C. Wan, X. Zheng, Z. Wang, *Green Chem.* **2009**, *11*, 1973-1978.
- [28] N. Sawatari, T. Yokota, S. Sakaguchi, Y. Ishii, *J. Org. Chem.* **2001**, *66*, 7889-7891.
- [29] a) J. C. Espinosa, S. Navalón, M. Álvaro, H. García, *ChemCatChem* **2015**, *7*, 2682-2688; b) J. C. Espinosa, S. Navalón, M. Álvaro, H. García, *Catal. Sci. Technol.* **2016**, *6*, 7077-7085; c) D. Sempere, S. Navalon, M. Dančiková, M. Alvaro, H. Garcia, *Appl. Catal. B-Environ* **2013**, *142-143*, 259-267; d) A. Dhakshinamoorthy, S. Navalon, D. Sempere, M. Alvaro, H. Garcia, *ChemCatChem* **2013**, *5*, 241-246.
- [30] G. G. Stavropoulos, P. Samaras, G. P. Sakellariopoulos, *J. Hazard. Mater.* **2008**, *151*, 414-421.
- [31] J. C. Espinosa, S. Navalón, M. Álvaro, H. García, *ChemCatChem* **2016**, *8*, 2642-2648.

Entry for the Table of Contents

FULL PAPER

In contrast to analogous active carbons and multiwall carbon nanotubes, OH functionalized diamond nanoparticles are suitable supports to develop heterogeneous oxidation catalysts based on anchored N-hydroxyphthalimide.



Juan F. Blandez, Sergio Navalón,
Mercedes Álvaro, Hermenegildo
García*

N-hydroxyphthalimide covalently anchored on diamond nanoparticles as selective heterogeneous metal-free oxidation catalyst of benzylic hydrocarbons and olefins by molecular O₂