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To cite this version:
Camila Rivera-cárcamo, I.C. Gerber, Iker Del rosal, B. Guicheret, Rubén Castro Contreras, et al.. Control of the single atom/nanoparticle ratio in Pd/C catalysts to optimize the cooperative hydrogenation of alkenes. Catalysis Science & Technology, 2021, 11 (3), pp.984-999. 10.1039/d0cy01938k . hal-03148510

HAL Id: hal-03148510
https://hal.science/hal-03148510
Submitted on 10 Nov 2021
Control of the single atom/nanoparticle ratio in Pd/C catalysts to optimize the cooperative hydrogenation of alkenes

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We recently reported (J. Catal., 2019, 372, 226-244) that a structure/activity correlation exists in Pd/C catalysts for myrcene hydrogenation, which integrates the Pd dispersion, and the surface concentration of oxygen groups and defects of the support. Here, through a combined experimental-theoretical study, we provide an explanation of the influence of these three structural characteristics of Pd/C catalysts for alkene hydrogenation. Highly dispersed Pd nanoparticles (PdNP) are necessary to activate dihydrogen. A high concentration of surface defects on the support is necessary to stabilize Pd single atoms (PdSA), which coexist with PdNP on Pd/C catalysts. A high concentration of oxygenated surface groups is also necessary on the support to allow hydrogen spillover. We demonstrate that such combination allows a cooperative catalysis to operate between PdNP and PdSA that involves the formation of PdNP-H species, which are much more active than PdSA-H for alkene hydrogenation but also isomerization. Importantly, we also report an efficient method to control the ratio between PdSA and PdNP in Pd/C catalysts of similar loadings and show that the control of this ratio allows the development of a new generation of stable and highly active catalysts integrating the ultra-rational use of precious metals in short supply. Indeed, for myrcene hydrogenation activity variations of several orders of magnitude were measured as a function of the value of this ratio.

1. Introduction

The hydrogenation of alkenes is among the important technological reactions catalyzed by supported metals, finding application in the pharmaceutical, agrochemical, refining, and commodity chemical industries. As the catalyst active phase is often made of noble metals, expensive and for the most part identified as critical elements, a logical step is to optimize their dispersion on the support. The highest dispersion that can be achieved corresponds to supported isolated metal atoms. Supported single-atoms (SA) have coexisted with metal nanoparticles (NP) for a long time, and may have played significant roles in many catalytic processes, but they have rarely been recognized as active sites. Today, aided by recent advances in synthesis methodologies, characterization techniques and computational modelling, single-atom catalysis has decisively become the most active new frontier in heterogeneous catalysis. Single atoms exhibit distinctive performances from the ones of NP for a wide variety of chemical reactions, and industrial applications employing them already exist. The absence of atomic ensemble effects, and the charge transfer to or from the support, that strongly modifies the electronic structure of the metal atom in SA catalysts, significantly affect the adsorption, and definitively induce a different reactivity compared to metallic NP. Current studies conducted on SA catalysts focus mainly on distinguishing them from NP and the possibility of synergy between these two species have been rarely explored. Interestingly, it was proposed that a synergy may operate between PdNP and PdSA during ketone/aldehyde hydrogenation on Pd/TiO2 catalysts. In this reaction, PdSA contributes for the C=O activation while PdNP allow the easy dissociation of H2. Palladium on carbon is a very common catalyst for alkene hydrogenation. Hydrogenations with PdSA have been already reported, but the metal-support interaction in such catalysts often results in an ionic/electron-deficient state of the metallic atoms that prevents an efficient H2 activation compared to metallic surfaces, and limits their application to specific selective hydrogenation reactions. A direct H2 activation has been reported for Pd/Cu single-atom alloy on PdSA. H2 activation is performed thanks to support-assisted molecular hydrogen heterolytic dissociation. Given that H2 dissociation is often the rate-limiting step in these reactions, efficient strategies toward engineering the minimal catalytic ensemble that can activate H2 would represent a substantial progress in pursuit of highly efficient Pd/C hydrogenation catalysts.

Here, through a combined experimental-theoretical study, we show that for alkene (myrcene, squalene, farnesene) hydrogenation a cooperative catalysis takes place between carbon-supported PdSA and PdNP. First, PdNP dissociate H2 easily, and subsequent hydrogen spillover provides Pd-H species on PdSA (H-PdSA). The H-PdSA are much more active than H-PdNP for the hydrogenation and isomerization of C=C double bonds. Thanks to the control of the SA/NP ratio on the support, which has been achieved in this work, the rational design of highly active catalysts becomes possible.

Electronica Supplementary Information (ESI) available: [Materials, Catalytic experiments, Tests to assess hydrogen spillover, Assessment of the impact of mass transfer for myrcene hydrogenation, Figs. S1 to S16].

Received 00th January 20xx, Accepted 00th January 20xx
DOI: 10.1039/x0xx00000x

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2. Materials and methods

Palladium catalyst synthesis

A wet impregnation method was used to prepare the palladium catalysts supported on carbon nanomaterials. The desired amount of palladium(II) nitrate dihydrate [Pd(NO$_3$)$_2$·2H$_2$O] (Sigma-Aldrich) was added to acetone (100 mL) containing 1 g of carbon nanomaterial, so as to introduce 2 %w/w of metal phase. The solution was sonicated at room temperature for 1 h and magnetically stirred overnight. The solution was then filtered and washed with acetone. The resulting solid was dried in an oven at 120 °C overnight. Finally, the 2% Pd/CNT catalyst was reduced in a horizontal tube oven under a nitrogen and hydrogen flow (20 vol% H$_2$) at 300 °C for 2 h (25°C to 300 °C at 10 °C/min). The same procedure was followed for the 1.6% Pd/CNT, by using theCNT$_{SR}$ Support. For Pd$_{SA}$ synthesis (0.1% Pd$_{SA}$/CNT), the wet impregnation method was also used. The desired amount of palladium(II) nitrate dihydrate [Pd(NO$_3$)$_2$·2H$_2$O] was added to an acetone solution (100 mL) containing 1 g of CNT$_{sa}$ so as to introduce 0.1 %w/w of metal phase. The solution was sonicated at room temperature for 6 h using an ultrasonic finger. The solution was then filtered and washed with acetone. The resulting solid was dried in an oven at 120 °C overnight. Finally, the catalyst was reduced in a horizontal tube oven under a nitrogen and hydrogen flow (20 vol% H$_2$) at 300 °C for 2 h (25°C to 300°C at 10°C/min).

For Pd$_{SA}$/CNT catalysts synthesis where X refers to SA/NP ratio, a recently patented process was used.\textsuperscript{20} The process consists in: i) creating carboxylic groups on the support by nitric acid oxidation (step I); ii) decomposing these groups under an inert atmosphere to produce CO$_2$, some H$_2$ and carbon vacancies (step II); and iii) depositing the metal on this defective support (step III). For a given metal loading, if step III is performed once, only Pd$_{SA}$ are obtained; and if it is performed several times, mixtures of SA and NP are obtained. The number of times that step III is performed for a given metal loading, conditions the SA/NP ratio. For Pd$_{SA}$/CNT catalysts on D-CNT the desired amount of bis(2-methylallyl)palladium precursor (Nanomeps) was added under argon to a pentane solution of D-CNT. At the end of each cycle the catalyst was treated under a nitrogen and hydrogen flow (20 vol% H$_2$) at 80 °C for 1 h.

Finally, a 0.1%Pd$_{1000}$SA/NP with a SA/NP ratio > 1000 was also prepared by the wet impregnation method. The desired amount of palladium(II) nitrate dihydrate [Pd(NO$_3$)$_2$·2H$_2$O] was added to an acetone solution (100 mL) containing 1 g of CNT$_{sa}$ so as to introduce 0.1 %w/w of metal phase. The solution was sonicated at room temperature for 1 h. Then, NaBH$_4$ (0.1 g) was added at room temperature, and let to react for 1 h to complete catalyst reduction. The solution was then filtered and washed with water and then acetone. The resulting solid was dried in an oven at 120 °C overnight.

For comparison purpose in myrcene hydrogenation we also used a commercial 5%Pd/activated carbon catalyst and a 5%Pd/Al$_2$O$_3$ catalyst. The Table S1 presents the different catalysts used in this study.

Characterization

The palladium content in the products was measured by inductively coupled plasma optical emission spectroscopy (ICP-OES) performed at the LCC with a Thermo Scientific ICAP 6300 instrument. Elemental analyses of C, H were carried out on a PERKIN ELMER 2400 series II elemental analyzer. TEM and HR-TEM analyses were performed at the “Centre de microcaracterisation Raimond Castaing, UMS 3623, Toulouse” by using a JEOL JEM 1011 CX-T electron microscope operating at 100 kV with a point resolution of 4.5 Å and a JEOL JEM 1400 electron microscope operating at 120 kV. The high-resolution analyses were conducted by using a JEOL JEM 2100F equipped with a field emission gun (FEG) operating at 200 kV with a point resolution of 2.3 Å and a JEOL JEM-ARM200F Cold FEG operating at 200 kV with a point resolution of > 1.9 Å. The particle size distribution was determined through a manual measurement of enlarged micrographs from different areas of the TEM grid (at least 300 particles).

The size distribution reported as Pd atomic percentage (based on total atoms) in each size range were obtained by calculating the number of atoms (N) in each nanoparticle assuming a spherical shape using an equation described in.\textsuperscript{21} The SA/NP ratio (a number ratio) was measured from the STEM-HAADF analyses of at least 500 elements.

The samples were analyzed by X-ray photoelectron spectroscopy (XPS) using a VG Escalab MKII spectrophotometer operating with a non monochromatized Mg k source (1253.6 eV). A SQuID magnetometer MPPMS5 was used to investigate the magnetic properties. The M(H) loop was measured at T = 300 K after cooling the sample from 300 K to 2 K under a constant applied magnetic field $H_{appl} = 50$ kOe. The M(H) loops were measured between -50 and 50 kOe. EPR data were recorded using an Alexsys E 500 Bruker spectrometer, operating at a microwave frequency of approximately 9.5 GHz. All spectra were recorded using a microwave power of 20 mW across a sweep width of 150 mT (centered at 310 mT) with modulation amplitude of 0.5 mT. Experiments were carried out at 110 K using a liquid nitrogen cryostat.

DFT periodic calculations

Calculations using periodic boundary conditions were performed using the Vienna \textit{ab initio} simulation package VASP,\textsuperscript{22-25} which employs the full-potential projector augmented waves (PAW) framework.\textsuperscript{26,27} Exchange-correlation effects were approximated using the PBE functional and applied in spin-polarized calculations.\textsuperscript{28} A kinetic energy cutoff of 400 eV was found to be sufficient to achieve a total energy convergence within several meV, considering k-point sampling, i.e. with a (3x3x1) \Gamma-centered grid in conjunction with a 0.05 eV/Å Gaussian smearing. All atoms were fully relaxed in order to have forces smaller than 0.005 eV/Å$^{-1}$, and the Nudged Elastic Band method was used to estimate minimum energy paths of transitions, as implemented by Henkelman et al.\textsuperscript{29,30} using 3 intermediates images and force criteria of 0.05 eV/Å$^{-1}$ to control the convergence. We have modeled the carbon support by a single graphene layer presenting a
vacancy in (7x7) supercell, which can be either filled by a single Pd atom (Pd\(_{\text{d}}\)) or served as an anchorage point for a fully hydrogenated Pd\(_{2}\)H\(_{20}\) aggregate (Pd\(_{\text{np}}\)). We recall that a sufficient vacuum height of 16 Å was used to limit spurious interaction between repeated images in the z-direction due to periodic boundary conditions.

**DFT Gaussian calculations**

Calculations were carried out using the Gaussian09 package\(^{31}\) at the DFT level by means of the hybrid density functional B3PW91.\(^{32,33}\) For the Pd atom, the Stuttgart-Dresden pseudopotentials\(^{34}\) were used in combination with their associated basis sets\(^{35}\) augmented by a set of polarization functions (f-orbital polarization exponents of 1.472).\(^{36}\) For the C and H atoms, a double-zeta 6-31G basis set\(^{37-41}\) augmented by a polarization function were used. The different intermediates and transition states were simulated with dispersion corrected functional. More precisely, dispersion corrections were treated with the D3 version of Grimme’s dispersion with Becke-Johnson damping.\(^{44}\) The nature of the optimized stationary point, minimum or transition state, has been verified by means of analytical frequency calculations at 298.15 K and 1 atm. The geometry optimizations have been verified by means of analytical frequency calculations at 298.15 K and 1 atm. The comparison between reactant(s), transition state and product(s). Energy data in kcal/mol are reported in the gas phase.

**Catalytic experiments**

**β-myrcene hydrogenation**

Myrcene catalytic hydrogenation has been carried out in a stirred tank reactor of 200 mL from Top Industrie. This reactor is equipped with 4 baffles and a gas inducing Rushton turbine having 6 straight blades to provide an efficient G-L-S contacting. The catalytic tests were operated at 1200 rpm and 120 °C with 200 mg of catalyst powder (except for Pd/C and Pd/Al\(_{2}\)O\(_{3}\) catalysts where 80 mg of catalyst has been used because of their Pd loading of 5 wt.%) under pure H\(_{2}\) atmosphere at a constant pressure of 20 bar. The liquid phase consists in 80 mL of a 1M β-myrcene (Sigma-Aldrich, 98% purity, corresponding to 3M of C=C double bond) solution in n-heptane (Sigma-Aldrich, 99%) containing a known trace of n-tetradecane as internal standard for final GC-FID analysis (DB17 column). In this configuration, the reactor is operated in batch mode for the solid and liquid phases and in semi-batch mode for the gas because hydrogen was constantly fed via a pressure regulator and supplied by a calibrated reserve. The pressure and temperature monitoring of this reserve provides the hydrogen consumption rate, and thus the apparent and instantaneous activity of the catalysts expressed in moles of H\(_{2}\) consumed per mole of Pd and per second, and being equivalent to an instantaneous Site Time Yield (“STY” in the following).

The instantaneous STY is determined with the local slope of the H\(_{2}\) reserve consumption curve as following, where n\(_{\text{Pd}}\) is the quantity of Pd determined by ICP:

\[
\text{STY} = \frac{\Delta n_{H_2}}{\Delta t \times n_{\text{Pd}}} \ (\text{mol}_{H_2} / \text{mol}_{\text{Pd}} / \text{s})
\]

STY is qualified of apparent because (i) it addresses the overall consumption of H\(_{2}\) through multiple reactions and (ii) depending on the catalyst and the reaction progress, possible external and internal mass transfer resistances are likely. Indeed, the reactivity of the first C=C is very high (terminal and conjugated C=C) and the first moments of the reaction are physically limited. Hopefully, this is not true for the whole range of reaction course. For robust and chemically consistent catalysts comparison, STY at 66% and 83% of reaction progress are thus considered, i.e. when 2.0 and 2.5 equivalents of H\(_{2}\) per β-myrcene are consumed respectively. More details about the characterization of possible internal and external mass transfer limitations throughout the reaction progress are available in the Supplementary Informations in the corresponding section S.4.

For a fair comparison with commercial catalysts, a STY* could be also used where n\(_{\text{cat}}\) is replaced by S\(_{\text{Pd}}\), the quantity of surface Pd determined from metal dispersion (Table S1).

\[
\text{STY*} = \frac{\Delta n_{H_2}}{\Delta t \times S_{\text{Pd}}} \ (\text{mol}_{H_2} / \text{mol}_{\text{Pd}} / \text{s})
\]

For hydrogenation and isomerization reactions, we have also used normalized time (time.cat), a standardized notation that is convenient and usual in catalysis to compare catalysts with different loadings of the active phase. The quantity of Pd was determined by ICP. For comparison with commercial catalysts (Fig. S1a), a time.cat* could be also used where n\(_{\text{Pd}}\) is replace by S\(_{\text{Pd}}\), the quantity of surface Pd determined from metal dispersion (Table S1).

To ensure a reproducible and precise initial times for the tests, heating of the reactor was first done with 1 bar of N\(_{2}\), then agitation was stopped and the N\(_{2}\) atmosphere was replaced by 20 bar of H\(_{2}\) and agitation turned on again, defining the initial time for the experiment. No side-reactions like Diels-Alder or oligomerization are encountered in the experimental domain investigated for this substrate. Thus, no selectivity issue has to be considered. The good matching between the evolution of H\(_{2}\) consumption profiles and of liquid substrate compositions has been checked (not shown here) and validates the experimental approach for reaction progress monitoring.

**Squalene and β-farnesene hydrogenation**

The comparison between β-myrcene, β-farnesene and squalene hydrogenations have been carried out in the same experimental rig following the same procedure with identical experimental conditions excepting a slightly increased catalyst mass (280 mg instead of 200 mg). To illustrate the extension of the concept to other carbon supports, here FLG was chosen and compared to Al\(_{2}\)O\(_{3}\). Squalene has been purchased from Sigma-Aldrich and β-farnesene has been synthesized and purified accordingly to ref.\(^{45}\).
Catalyst stability testing under continuous reactor operation

Catalyst stability has been investigated through a dedicated continuous reactor operation with coated metallic open-cell solid foams (Hollomet Foamet 800 µm). Stainless steel foam cylinders were precisely cut through EDM (Electrical Discharge Machining) to obtain cylindrical objects with a diameter of 4.3 mm and a length of 5 cm. 8 foam pieces were homogeneously coated with 12.5 mg of the Pd$_{2}$SA/NP/CNT catalyst (following the detailed procedure described elsewhere) and inserted into a home-made millimeter-scale tubular reactor (40 cm long, 4.4 mm I. D.) to provide a reactor volume of 6 mL with a total catalyst amount of 100 mg. Fig. S2 shows a photo of the foam coated in the tubular reactor. The continuous experiments were performed at 120 °C and 20 bar applying a gas flowrate of 2 NL/min of pure H$_{2}$ and a liquid flow rate of 2 mL/min of a 1M solution of myrcene in heptane corresponding to a liquid space velocity of 106.4 mol$_{\text{myrcene}}$/mol$_{\text{Pd}}$/min. Analysis by GC-FID (method and apparatus are identical to the one described in the previous \(\beta\)-myrcene hydrogenation section) at the reactor outlet allow to verify the mass balance and to determine the liquid flow composition. The corresponding mean Site Time Yield and Reaction progress are then calculated. It is noteworthy that this mean STY and the instantaneous STY used in the batch experiment are different and cannot be compared directly.

3. Results

Hydrogenation and isomerization of alkenes

As a model substrate \(\beta\)-myrcene, an acyclic polyunsaturated monoterpane with highly reactive 1,3-diene moiety, and an isolated tri-substituted C=C bond, was chosen (Fig. 1a). Complete hydrogenation to 2,6-dimethyloctane usually requires long reaction times, resulting in low average Site Time Yield (STY). A comparison made between two commercial Pd/Al$_{2}$O$_{3}$ and Pd/C catalysts showed that the Pd/C catalyst is significantly more active (Fig. 1b,c). In order to exclude a possible influence of the microporosity of activated carbon, the same reaction was also performed on a Pd catalyst supported on carbon nanotubes (CNT), Pd/CNT showing comparable particle size with Pd/C (Supplementary Informations S1, Fig. S1, and Table S1). The catalytic activity of Pd/CNT and Pd/C are similar (Fig. 1b,c). Since the three catalysts present different Pd NP size, we also calculated the time.cat* and the STY* as a function of surface Pd (Fig. S3). A similar tendency was observed, i.e. higher STY* are obtained on the two carbon-supported catalysts. Analysis of these three catalysts by TEM and STEM-HAADF before and after reaction showed no very significant change in mean particle size after catalysis (Fig. S1). However, a major difference between these catalysts was the presence of Pd$_{\text{SA}}$ on Pd/CNT and Pd/C (Fig. 2a-c). The probable presence of atomically dispersed Pd species on reduced Pd/CNT catalysts has been recently discussed by de Jong and coworkers. For the Pd/CNT catalyst, a ratio SA/NP of 2 was measured and this catalyst will be named Pd$_{2}$SA/NP/CNT from now on (Fig. 2c). We independently checked that the SA/NP ratio of Pd$_{2}$SA/NP/CNT does not change after catalysis. In parallel, mixtures of Pd$_{\text{SA}}$ and Pd$_{\text{NP}}$ were also obtained on other carbon supports such as few layer graphene or carbon nanofibers (Fig. S4). These latter catalysts are also very active compared to Pd/Al$_{2}$O$_{3}$ for the hydrogenation of various terpenes of industrial interest such as squalene or \(\beta\)-farnesene (Fig. S5). We also checked that for these catalysts the mean Pd$_{\text{NP}}$ size and SA/NP ratio does not change significantly after catalysis (Fig. S6).
The existence of Pd_{sa} on carbon supports can be attributed to the presence of specific anchoring sites such as structural defects, which are necessary for their stabilization.\textsuperscript{13,48} From the reaction profiles of Fig. 1b,c, we can see that the reaction starts rapidly, then for Pd/Al_{2}O_{3} it slows down, while a high rate is maintained for the catalysts supported on carbon. The rate decrease observed for the Pd/Al_{2}O_{3} catalyst is probably associated with the difficult hydrogenation of the internal double bonds of myrcene.\textsuperscript{49} In order to explain the stable activity of carbon supported catalysts, the possible involvement of acidic sites on these catalysts, which could assist the isomerization of the relatively crowded double bond to an easier to reduce one, has been investigated. Potentially, two types of acidic sites may coexist on the carbon-supported catalysts. The first one corresponds to carboxylic acid groups arising from the acid functionalization of the carbon material, which withstand the heat treatments carried out during catalyst preparation (Supplementary Informations S1). Temperature programmed desorption experiments performed on both the CNT support and the Pd_{sa}/CNT catalyst (Fig. S7) do not establish the presence of significant amounts of carboxylic groups after Pd deposition, these groups acting as anchoring sites for Pd.\textsuperscript{50} DFT calculations performed on a Pd_{sa}/graphene single vacancy model show a charge transfer from Pd-4d to C-2p of -0.37 e- (Fig. S8). Thus, the second type of acidic sites consists in the Pd_{sa}, due to charge transfer from the metal to the support. The H\textsubscript{2}-assisted isomerization of 1-octene (Fig. S9) was independently studied on various catalysts including: CNT support (with -COOH groups), Pd_{sa}/CNT, Pd/Al_{2}O_{3} and a Pd_{sa}/CNT containing exclusively SA (Fig. 2d). CNT and the Pd_{sa}/CNT catalysts are almost inactive for 1-octene isomerization, and the Pd_{sa}/CNT clearly outperforms the Pd/Al_{2}O_{3} catalyst. Thus, the presence of acidic sites that would assist the isomerization cannot explain the differences in reactivity observed. To gain further insight on the mechanistic pathway, DFT calculations were performed on Pd_{sa} and Pd_{np} supported on graphene.

Mechanistic insights from DFT calculations

To study the isomerization and hydrogenation reactions, 2-butene was used as a model substrate (see Fig. 3). We considered first, the trapping of a Pd_{sa} in a mono-vacancy, which is strongly exothermic, with adsorption energy of roughly 100 kcal/mol. On Pd_{sa}, the hydrogenation and isomerization reactions begin with the exothermic (by 24.6 kcal/mol) \pi-coordination of 2-butene to Pd (1). From 1, the isomerization (Fig. 3a) occurs via the formation of a \pi-allyl hydride intermediate as observed with homogeneous catalysts,\textsuperscript{51} which requires to pass a high energy demanding transition state (36.4 kcal/mol) corresponding to the abstraction of one hydrogen atom from a methyl group. This leads to the formation of an unstable, by +34.4 kcal/mol with respect to 1 allyl intermediate (2). Then, the H atom is transferred with almost no barrier with respect to 2 (2.8 kcal/mol) to the carbon atom in alpha position of the methyl group, leading to the endothermic formation of but-1-ene (+4.8 kcal/mol with respect to 1).

From 1, the hydrogenation of the but-2-ene occurs through the Horiiuti-Polanyi mechanism:\textsuperscript{52} (i) alkene and H\textsubscript{2} coordination to Pd, (ii) H\textsubscript{2} dissociation, (iii) hydrogen transfer to one of the alkene methine carbon with formation of a \sigma-bond between Pd and the second C-methine, and finally (iv) reductive elimination of the free alkane. In our case (Figure 3b), the coordination of the 2-butene (1) and of a H\textsubscript{2} molecule (4) to the Pd_{sa} is exothermic. These initial steps are followed by an endothermic (+21.6 kcal/mol with respect to 4) and kinetically demanding (activation barrier = +24.5 kcal/mol) H-H activation (5). This reaction exhibits a lower barrier than the isomerization reaction, by 9.9 kcal/mol. From 5, the reaction continues by the transfer of one of the hydrogen atoms to one of the methine carbon atoms. The energy barrier of this last step is only +8.1 kcal/mol with respect to 5 but +29.7 kcal/mol with respect to 4. This transfer induces the formation of a 2-butyl complex \sigma-coordinated to the Pd center (6), located at -11.7 kcal/mol with respect to the entrance channel. The subsequent reductive elimination occurs via an accessible transition state (+4.1 kcal/mol with respect to 6) and leads to the exothermic formation of butane (-42.1 kcal/mol with respect to the separated reactants).

Figure 2. STEM-HAADF micrographs of: a Pd/Al_{2}O_{3}; b Pd/C; c Pd_{sa}/CNT; d Pd_{sp}/CNT; e Pd_{sa}/CNT_{sc}; and f Pd_{sa}/CNT catalysts. Scale bar = 10 nm.

\textbf{Journal Name} \textbf{ARTICLE} 2013, \textbf{00}, 1-3 | 5
Figure 3. DFT mechanistic study. Reaction mechanisms of isomerization a and hydrogenation b of 2-butene mediated by Pd\(_{\text{SA}}\) and H-Pd\(_{\text{SA}}\) (in orange).

In summary, the hydrogenation of the 2-butene into butane is preferred both from a kinetic and thermodynamic point of view over the isomerization to 1-butene. However, according to the high barriers, a poor catalytic activity is expected in both cases, as experimentally observed for hydrogenation using single Pd atoms.\(^{53,54}\) For comparison, an activation energy of 18 kcal/mol has been reported for the hydrogenation of 2-butene on a Pd\(_9\)/CNT catalyst.\(^{55}\) In this context we also verified that the Pd\(_{\text{SA}}\)/CNT catalyst shows a very low activity for \(\beta\)-myrcene hydrogenation (see Fig. 7 in the section Control of the single atoms/nanoparticles ratio).

At this point, it is interesting to note that a completely different potential energy landscape is obtained if the catalyst is a hydrogenated SA (H-Pd\(_{\text{SA}}\)). A plausible scenario for the formation of this active site is: (i) a nearly barrierless activation of H\(_2\) on Pd\(_{\text{NP}}\) (< 2 kcal/mol on Pd\(_{\text{13}}\) supported on defective graphene monolayer), and (ii) hydrogen spillover. The latter has been widely studied in the context of hydrogen storage and catalysis, and many experimental studies report on that H-spillover can operate at low temperature on some carbon materials.\(^{48,56-58}\) The entire spillover mechanism remains not fully understood; especially since some energy barriers remain high to be accessible at room temperature on non-defective carbon supports, but should correspond to a multi-step process after the dissociative adsorption of H\(_2\) on Pd\(_{\text{NP}}\). The H-migration from the NP to the carbon support is supposedly the first step with large energy barrier to overcome, and this step is not thermodynamically favorable for non-defective carbon supports. For instance a 60 kcal/mol energy barrier has been reported in the case of a Pt cluster on pristine graphene model, the final step being 35 kcal/mol above the initial one,\(^{59}\) but when the graphene support is already hydrogenated the energy barrier is decreased and the thermodynamics become favorable.\(^{50}\) However, it remains obscure how the support can be initially hydrogenated. Then H-diffusion on the carbon support occurs, with a relatively high energy barrier associated to a nearest-neighbor hopping process (> 20 kcal/mol on pristine carbon support).\(^{44,58}\) Interestingly, it has also been proposed that the presence of oxygenated functional groups on the carbon support can facilitate the diffusion.\(^{61}\) H-Clustering could also play a role by disturbing the \(sp^2\) network around the H-adsorption site, decreasing significantly the energy barrier.\(^{57,62}\) As we can see on Fig. 3b, the coordination of 2-butene to H-Pd\(_{\text{SA}}\) (1\(^H\)) remains exothermic, -23.3 kcal/mol with respect to the separated reactants. However, in this case the isomerization reaction takes place through a so-called metal hydride addition–elimination mechanism, strongly preferred for monohydrides. Thus, the isomerization proceeds via an initial hydrogen transfer to one of the −CH= carbons, followed by the dehydrogenation of the methyl group at a position with respect to the second methine carbon. This reaction is kinetically accessible with two low activation barriers (3.5 and 11.9 kcal/mol, respectively). However, even if the formation of the 2-butyl intermediate (2\(^H\)) is exothermic...
with respect to \( 1^\text{st} \) by -6.0 kcal/mol, that of the 1-butene product (\( 3^\text{rd} \)) remains endothermic by +2.8 kcal/mol. Concerning the hydrogenation, the coordination of H2 is followed by the transfer of the hydrogen atom to one of the methine carbons without H2 dissociation. The corresponding activation barrier (8.4 kcal/mol above \( 4^\text{th} \)) corresponds to an easily kinetically accessible process. In the same way, the formation of the alkyl intermediate is found to be exergonic with respect to \( 4^\text{th} \) (-3.2 kcal/mol with respect to \( 4^\text{th} \)). The last step corresponds to the heterolytic splitting of H2 leading to the regeneration of the H-Pd\text{SA} and the butane product (\( 7^\text{th} \)). The formation of butane is an exothermic process, by 25.2 kcal/mol with respect to \( 4^\text{th} \) (-42.4 kcal/mol with respect to the separated reactant). The corresponding activation barrier for this step is 12 kcal/mol, compared to energy of 18 kcal/mol for a Pd\text{d} cluster supported on CNT\text{55} and 20 kcal/mol for a Pd/Al2O3 catalyst.\text{63} Therefore, this last step is the rate-determining step of an overall facile and exergonic reaction.

In order to confirm the key role of H-spillover in the cooperative catalysis between Pd\text{SA} and Pd\text{NP}, a Pd\text{2_SA/NP/CNT\text{HT}} catalyst (Fig. 2e) was prepared on CNT, from which the oxygen surface groups have been removed by thermal annealing at 1000 °C,\text{47} which should prevent H-spillover. Although this catalyst contains also a mixture of Pd\text{SA} and Pd\text{NP} (SA/NP = 2), with mean particle size similar to the Pd\text{2_SA/NP/CNT} catalyst (Fig. S10) it shows a significantly reduced activity for myrcene hydrogenation (Fig. 4a), which is quite similar to the one of the Pd/Al2O3 catalyst that contains only Pd\text{NP}. It is important to note here that such a behavior (i.e. a lower activity of Pd/C catalysts in the hydrogenation of myrcene on supports treated at 1000 ° C) has been systematically observed on various carbon supports and for catalysts exhibiting different particle sizes.\text{47} It is also worth mentioning that the two catalysts Pd\text{2_SA/NP/CNT} and Pd\text{2_SA/NP/CNT\text{HT}} present a similar amount of Pd clusters (Pd\text{NP} < 1 nm, Fig. S10), so that the observed high activity measured for the Pd\text{2_SA/NP/CNT} catalyst cannot be only related to the presence of Pd clusters, even if it has been reported that noble metal clusters are often more active than nanoparticles.\text{64-67}

The hydrogen spillover was experimentally probed for these two CNT-supported catalysts. As it is well known that the spilled-over hydrogen migrates and readily reacts with the yellow WO3 oxide to form dark blue H3WO4,\text{68,69} we used the WO3 tungsten oxide to diagnose the activation of H2 on these two catalysts (Supplementary Informations S3). Such simple test was already used with success for Rh/zeolithe catalysts.\text{70}

As shown in the photographs of Fig. 4b, the pure WO3 did not change color after hydrogen treatment. When mixed with the Pd\text{2_SA/NP/CNT\text{HT}} catalyst, no significant change in color after the hydrogen treatment was observed. While this Pd catalyst should activate hydrogen, the absence of surface oxygen groups on the support does not allow extended hydrogen spillover. In contrast, when WO3 was mixed with the Pd\text{2_SA/NP/CNT} catalyst this resulted in the darkest color of the tungsten species after hydrogen treatment at 20 °C for 3 min, demonstrating that hydrogen dissociation and extended spillover occurred on this catalyst. We infer that the significant spillover should be attributed to the presence of oxygenated surface groups on the carbon support. These latter experiments confirm that the presence of oxygen surface groups is necessary for the cooperative catalysis to proceed via H-spillover.

The hydrogen spillover was also investigated by DFT, to propose a complete pathway, see Fig. 5, for the formation of H-Pd\text{SA} species through the migration of H atoms initially adsorbed on H-saturated Pd\text{NP}. As we can see on Fig. 5, the overall reaction is kinetically accessible and thermodynamically favorable. Our starting geometry is a H-saturated Pd\text{NP} deposited on a defective di-vacancy with an oxygen atom in its vicinity. From this starting configuration the first H migration from the Pd\text{NP} to the closest C atom in front of the ether group is thermodynamically favorable (-38 kcal/mol), with a reasonable energy cost (activation barrier = 10.2 kcal/mol). Then a second H can easily migrate (the energy barrier is less than 2 kcal/mol) to the same carbon atom leading to the formation of a -CH_2 group. Then we have evaluated the migration of one H from the -CH_2 group to a neighbor C carbon atom, still involved in the di-vacancy ring.
This step, with an energy barrier of 29.7 kcal/mol, is the rate-determining step of the proposed profile. Then a second hopping process can proceed with a lower activation barrier (24.2 kcal/mol) to yield almost a single H atom adsorbed on the non-defective part of the carbon support. The adsorption of an extra H$_2$ molecule on Pd$_{np}$ ensures the overall stability of the H-migration process. Then H-diffusion can occur with an energy barrier of around 24 kcal/mol, in line with previous works, or can be significantly decreased to less than 9 kcal/mol, when the H atom is surrounded by other H atoms, 6 in the present case. Finally, the formation of the H-Pd$_{sa}$ product takes places through a barrierless H transfer to Pd$_{sa}$ with largely favorable stabilization energy of ca. -60.5 kcal/mol.

Thus, the correlation we have recently reported between the activity of Pd/C catalysts for β-myrcene hydrogenation and their structure, which integrates the dispersion of the metal, and the quantity of oxygen groups and defects on the support, arises from a cooperative catalysis between Pd$_{sa}$ and Pd$_{np}$ that involves H-spillover. It is certainly necessary to have highly dispersed Pd$_{np}$ on the support to activate H$_2$, but a high concentration of surface defects and oxygenated surface groups are also necessary on the carbon support, which favors the stabilization of Pd$_{sa}$ and H-spillover, respectively. The resulting H-Pd$_{sa}$ are highly active for alkene hydrogenation/isomerization.

**Control of the single atoms/nanoparticles ratio**

From the previous results, it becomes obvious that in heterogeneous catalysis, an ultra-rational use of precious metals often in short supply could pass by an accurate control of the SA/NP ratio. With this in mind, we have developed a simple process allowing the control of this ratio on carbon supports to produce Pd$_{X_{sa}/np}$/CNT catalysts where X refers to the SA/NP ratio. Briefly, the process consists in: i) creating carboxylic groups on the support by nitric acid oxidation (step I); ii) decomposing these groups under an inert atmosphere to produce CO$_2$, carbon vacancies and some H$_2$ (step II); and iii) depositing the metal on this defective support (D-CNT, step III). On CNT support, the defective CNT produced after step II (D-CNT) contain defects that we have characterized by electron spin resonance (ESR) and vibrating sample magnetometry (VSM), and which can be used to stabilize metal single atoms. As for highly ordered pyrolytic graphite, the EPR spectrum of CNT presents a single peak, while that of D-CNT consists of two contributions (Fig. S11). The narrow line is associated to interacting conduction electrons, while the broad one corresponds to spin-polarized localized electronic states.

As in the case of graphite, the magnetization curve of CNT presents a diamagnetic behavior, while for D-CNT ferromagnetism appears at room temperature, presumably due to the presence of defects (Fig. S12). Although the exact nature (vacancies or edges) of the localized electronic states created by the thermochemical process is not known, these defects efficiently stabilized Pd$_{sa}$. For a given metal loading, if step III is performed once, Pd$_{sa}$ are selectively produced; and if it is performed several times, mixtures of SA and NP are obtained. The number of times that step III is performed for a given total metal loading, conditions the SA/NP ratio. Figure 6 shows TEM images of four 1.2% Pd/CNT samples prepared by this process, for which the SA/NP ratio is controlled between 200/1 (a single deposition cycle of 1.2% Pd) and 10/1 (four deposition cycles of 0.3% Pd).

---

**Figure 5.** DFT mechanistic study. Spillover mechanism corresponding to the migration of H adsorbed on Pd$_{np}$ leading to the formation of H-Pd$_{sa}$ species.
The particle size distribution based on total particle number and on total atom number are shown in Fig. S13. As transmission electron microscopy only informs us thanks to a very local analysis of the samples (poor statistic value), we decide to use a more general probe to characterize the whole samples. Since traditional probe molecule infrared spectroscopy cannot been used for carbon supported catalyst, and EXAFS is not sensitive enough to identify SA in many cases, we rely on XPS analyses. It is worth mentioning that the XPS analyses were performed on the four samples with introduction of the samples by vacuum transfer cell from a glove box under a controlled argon atmosphere, so we can exclude any air oxidation of this sample. The O 1s spectra exhibit large bands of the order of 5 eV, which suggests superposition of different oxygenated groups. The line shapes are very similar for all samples and are close to the one of the D-CNT support (Fig. S14). Figure 7 shows the deconvolution of the Pd 3d spectra of the four samples. The binding energy at 335.3 eV is in agreement with the value reported in the literature for metallic palladium. For the sample Pd$_{200}$/CNT, this binding energy is slightly upshifted presumably due to charge transfer between the very small particles present on this sample and the support or to particle size-dependent shift.

The binding energy at 337.3 eV can be attributed to surface oxides and/or to electron-deficient palladium species (Pd$^{0+}$) such as SA or small clusters in strong interaction with the support. The Pd$^{0+}$/Pd$^{0}$ ratio for the four samples are shown on Table 1 as well as the fraction of SA in the same samples determined from STEM. A good correlation was found between the results obtained with these two techniques (Fig. S15). These data, in association with the STEM-HAADF observations, confirm that the proportion of Pd$_{SA}$ is much higher in the sample Pd$_{200}$/CNT than in Pd$_{10}$/CNT. Thus, this strategy allows engineering the minimal catalytic ensemble that will activate H$_2$ for the cooperative catalysis to operate. For β-myrcene hydrogenation at 120 °C, regarding the catalysts tested, the optimum SA/NP ratio was found at 10/1 (Fig. 8). This optimal ratio offers the best control for the balance between H$_2$ activation on Pd$_{NP}$, the H-spillover and H-Pd$_{SA}$ catalyzed β-myrcene hydrogenation rates. The activity of the Pd$_{20}$/CNT (SA/NP = 10/1, Fig. 2f) outperformed the one of the Pd$_{2}$/CNT catalyst (Fig. 8). At a reaction progress of 2, the STY with Pd$_{20}$/CNT (SA/NP = 200), Pd$_{2}$/CNT (SA/NP = 2), and Pd$_{5}$/CNT (SA/NP = 10) are 10, 44 and 272 s$^{-1}$, respectively (Fig. 8c). Once again, it is interesting to note that for this sample series, for which the surface chemistry of the support is the same, it is not the sample that presents a higher proportion of palladium clusters that is the more active.

**Figure 6.** Mixtures of SA and NP at different ratio in 1.2% Pd/CNT catalysts.

**Figure 7.** XPS spectra of Pd 3d of Pd$_{20}$/CNT, Pd$_{6}$/CNT, Pd$_{4}$/CNT and Pd$_{1}$/CNT samples.
Table 1. Fraction of SA in the same samples determined from STEM and ratio Pd\(^0\)/Pd\(^{\delta}\) determined by XPS.

<table>
<thead>
<tr>
<th>Sample</th>
<th>STEM fraction of SA (%)</th>
<th>XPS atomic percentage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Pd(^0)</td>
</tr>
<tr>
<td>Pd(_{200})_SA/NP/CNT</td>
<td>0.97</td>
<td>14.21</td>
</tr>
<tr>
<td>Pd(_{60})_SA/NP/CNT</td>
<td>0.77</td>
<td>15.25</td>
</tr>
<tr>
<td>Pd(_{40})_SA/NP/CNT</td>
<td>0.61</td>
<td>22.00</td>
</tr>
<tr>
<td>Pd(_{10})_SA/NP/CNT</td>
<td>0.25</td>
<td>41.75</td>
</tr>
</tbody>
</table>

Thus, the sample Pd\(_{60}\)_SA/NP/CNT present a similar proportion of Pd\(^{\delta}\) < 1 nm based on total atoms than the sample Pd\(_{10}\)_SA/NP/CNT (Fig. S13) but is significantly less active (Fig. 8c). Similarly, the sample Pd\(_{200}\)_SA/NP/CNT, which presents a significant amount of clusters of different atomicity, is the less active of the series.

Finally, at a reaction progress of 2, there is a 44-fold increase of STY between the Pd\(_{10}\)_SA/NP/CNT catalyst and Pd\(_{2}\)_SA/NP/CNT (a catalyst containing NP with no possibility of hydrogen spillover, see Fig. 4) and 195-fold increase with Pd\(_{1000}\)_SA/NP/CNT (a catalyst containing almost exclusively SA). The evolution of STY with SA/NP ratio remains nearly the same for the reaction progress of 2.5 (Fig. 8c). This fact further confirms the consistency of these results.

Catalyst stability

Instead of running successive recyclability batch experiments catalyst stability was investigated through a dedicated continuous reactor operation. When a single typical batch experiment allows us to reach a moderate turn-over number (TON) of 6200 mol\(_{H_2}\)/mol Pd, the chosen continuous testing mode leads to TON values as high as 600 000 mol\(_{H_2}\)/mol Pd. This represents a more intensive and powerful way to test catalyst stability. This contacting mode has also been chosen because of future developments within an intensified compact continuous reactor.

The continuous experiments were run with the Pd\(_{2}\)_SA/NP/CNT catalyst coated on metallic open-cell solid foam cylinders. It is first worth mentioning that the coating process, performed at 300 °C under a nitrogen flow did not significantly modify the particle size distribution and the SA/NP ratio of the catalyst (Fig. S16a-f), pointing its good thermal stability. Such internals in milli-channels are ideal candidates to promote such powdered catalysts in a continuous reactor. The particularly confined hydrodynamics lead to interesting heat and mass transfer performances as well as a small pressure drop due to the wide-open structure of open-cell solid foams. This contacting mode has also been chosen because of future developments within an intensified compact continuous reactor.

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Figure 8. Catalytic results for myrcene hydrogenation at different SA/NP ratio. a Reaction progress as a function of time catalyst. b STY as a function of reaction progress. c STY at a reaction progress of 2 and 2.5 as a function of SA/NP ratio. Catalysts nomenclature is Pd\(_{X}\)_SA/NP/CNT where X refers to the SA/NP ratio.
The corresponding evolution of the outflow composition indicates that the reaction progress decreases also with decreasing contributions of the second and third hydrogenation while the first one remains constant. As in the batch experiments, this behavior for the first hydrogenation is explained by the gas-liquid external mass transfer limitation that hinders the intrinsic catalyst activity. For the slower second and third successive hydrogenations, the deactivation was logically more noticeable.

The coated catalyst was qualitatively examined by STEM-HAADF before and after this stability experiment (Fig. S16). After the test the SA/NP ratio changes from $\approx 2$ to $\approx 3$ and the mean PdNP size increased slightly from 2.5 to 3.2 nm. The slight deactivation could thus be structural but could also be explained by the strong adsorption of impurities from the natural starting material (β-myrcene). Although they could not be detected in the charge by GC because of their too low concentration, these impurities could continuously be absorbed on the catalyst, resulting in a gradual decrease in activity at high TON numbers. Studies are in due course to recover and characterize these adsorbed impurities.

Overall, the catalysts developed in this study appear resistant to sintering due to the stabilization of the SA by the functionalized carbon support and can undergo very long TON either in batch or continuous mode. Nonetheless in the chosen reaction, the catalysts appear sensible to a charge impurity and purification steps may be required to reach very high TON with a more stable activity over time. This fact was only detectable with the continuous mode operation because of its easier operability and ability to reach a very high TON. Moreover, in addition to efficient catalyst stability testing, the continuous mode operation appears very promising for the compact intensified and secure operation of this reaction.

**Conclusion**

Here, we have reported that a cooperative catalysis operates between carbon-supported Pd$_{SA}$ and Pd$_{NP}$ for alkene hydrogenation and isomerization, which involved: i) dihydrogen activation on Pd$_{NP}$, ii) H-spillover on the support, and iii) the catalytic reaction on H-Pd$_{SA}$ species. This discovery provides a rational explanation for the structure/activity correlation that exists in Pd/C catalysts for myrcene hydrogenation, which associates the metal dispersion (Pd$_{NP}$ are necessary to activate H$_2$), the concentration of oxygen surface groups on the support (necessary for H-spillover), and the concentration of defects on the support (necessary for Pd$_{SA}$ stabilization). While such a cooperative effect may occur in many Pd/C catalysts, it has never been recognized or exploited to improve catalytic performances in industrial catalysts. While this finding alone is important, major advances in heterogeneous catalysis can be achieved only if the SA/NP ratio can be controlled. Indeed, the control of this ratio, a major achievement of this work, allows tuning the catalyst performances. For β-myrcene hydrogenation, STY variations of several orders of magnitude were measured as a function of the value of this ratio. This work can also provide an explanation to the fact that many organic chemists experienced much contrasted catalytic performances for hydrogenation reactions with commercial Pd/C catalysts provided by different suppliers, since the Pd$_{SA}$/Pd$_{NP}$ ratio is not controlled in such systems. Of course, other types of cooperative catalysis than the one reported herein can be envisioned, such as bifunctional catalysis with a single metal: metallic NP ensuring one function, and SA of the same element exploited to improve catalytic performances in industrial catalysts. Finally, our results demonstrate an interesting point for the single atom catalysis literature. Even when a very small number of metal NP are present (here Pd$_{SA}$/Pd$_{NP}$ ratios of $>1000$ or $200$), the activity is quite different than the SA alone. This can be a common issue in studies that try to examine only the properties of SA but actually have a distribution of structures. Recent studies have started to point this out.

**Conflicts of interest**

*J. Name.*, 2013, **00**, 1-3 | 11
The authors declare no competing financial interest.

Acknowledgements

We thank Vincent Collière (LCC, UPR8241 CNRS, Toulouse, France) for STEM analyses. B.F.M. acknowledges the exploratory project under the FCT Investigator Programme (ref. IF/00301/2015) with financial support from FCT/INESC, through national funds (PIDDAC). C.R.C. thanks CONICYT for the financial support (Becas de doctorado en el extranjero “Becas Chile” - n° 72170200). R.C.C. thanks CONICYT for the financial support (PhD grant). I.C.G. and I.R. acknowledge the Calcul en Midi-Pyrénées initiative, CALMIP (Projects p0812 and p1214), for computer time allocation. This work was also granted access to the HPC resources of CINES and IDRIS under the allocation 2019-A0060906649 made by GENCI. Part of this work was performed within the framework of the “DEEPER” project (in which LGPC members were involved) funded by the region Auvergne-Rhône-Alpes (contract number 15 021131 01 – CNR006) through the 20th FUI call. Part of this work was also supported by the Agence Nationale de la Recherche (ANR project ANR-19, COMET), which is gratefully acknowledged.

Notes and references

Herein, we show that the control of the single atom/nanoparticle ratio in Pd/C allows the development of a new generation of highly active hydrogenation catalysts integrating the ultra-rational use of Pd.
Electronic Supplementary Information

Control of the single atoms/nanoparticles ratio in Pd/C catalysts to optimize the cooperative hydrogenation of alkenes

Authors: C. Rivera-Cárcamo, I. C. Gerber, I. del Rosal, B. Guicheret, R. Castro Contreras, L. Vanoye, A. Favre-Réguillon, C. de Bellefon, R. Philippe, P. Serp

This file includes:

Materials and Methods
  S.1 Materials
  S.2 Catalytic experiments
  S.3. Tests to assess hydrogen spillover
  S.4. Assessment of the impact of mass transfer for myrcene hydrogenation
    S.4.1. G-L external mass transfer
    S.4.2. L-S external mass transfer
    S.4.3. Internal mass transfer
    S.4.4. Global conclusion on the presence of mass transfer limitations

Figs. S1 to S16

Additional references:[1]-[13]
Materials and Methods

S.1 Materials

**Carbon nanotube synthesis.** A homemade AlFeCoO$_4$ catalyst was reduced in a fluidized bed reactor under a nitrogen (225 mL·min$^{-1}$) and hydrogen (150 mL·min$^{-1}$) flow at 650 °C. After the reduction step, the ethylene flow was adjusted to 225 mL·min$^{-1}$ for 30 min to produce CNT. The CNT were recovered and then purified using an aqueous solution (50 vol% H$_2$SO$_4$) under reflux at 140 °C for 3 h. The acidic solution was then filtered and the solid washed with distilled water. The resulting solid was dried in an oven at 80 °C overnight. A portion of purified CNT was then functionalized with HNO$_3$ under reflux at 140 °C for 3 h. The acidic solution was filtered and washed with distilled water. The resulting solid was dried in an oven at 80 °C overnight to produce functionalized CNT (CNT). Another portion of purified CNT was treated in a horizontal tube oven under a nitrogen flow at 1000 °C for 1 h to produce high-temperature-treated CNT$_{HT}$. Finally, for EPR and VSM analyses, a portion of CNT (CNT$_{ox}$) was treated at 2800 °C for 1 h to produce high-temperature-treated CNT free of metallic impurities.

**Palladium catalyst synthesis.**

**Supplementary Table 1.** Catalysts properties.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Pd loading (%)</th>
<th>NP size from TEM (nm)$^a$</th>
<th>Pd dispersion (%)$^c$</th>
<th>SA/NP ratio$^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd/Al$_2$O$_3$</td>
<td>5</td>
<td>3.9 ± 1.1</td>
<td>31</td>
<td>n.d.$^e$</td>
</tr>
<tr>
<td>Pd/C</td>
<td>5</td>
<td>2.4 ± 1.0</td>
<td>46</td>
<td>n.d.$^e$</td>
</tr>
<tr>
<td>Pd/CNT</td>
<td>2</td>
<td>2.2 ± 1.1</td>
<td>49</td>
<td>2</td>
</tr>
<tr>
<td>also named Pd$^{2+}$SA/NP/CNT</td>
<td>1.6</td>
<td>2.2 ± 1.1</td>
<td>49</td>
<td>2</td>
</tr>
<tr>
<td>Pd$^{2+}$SA/NP/CNT$_{HT}$</td>
<td>0.1</td>
<td>-</td>
<td>-</td>
<td>no NP</td>
</tr>
<tr>
<td>Pd$_{1000}$SA/NP/CNT</td>
<td>0.1</td>
<td>1 ± 0.5$^b$</td>
<td>-</td>
<td>1000</td>
</tr>
<tr>
<td>Pd$_{200}$SA/NP/CNT</td>
<td>1.2</td>
<td>0.5 ± 0.1</td>
<td>-</td>
<td>200</td>
</tr>
<tr>
<td>Pd$_{60}$SA/NP/CNT</td>
<td>1.2</td>
<td>0.8 ± 0.3</td>
<td>-</td>
<td>60</td>
</tr>
<tr>
<td>Pd$_{40}$SA/NP/CNT</td>
<td>1.2</td>
<td>0.9 ± 0.3</td>
<td>-</td>
<td>40</td>
</tr>
<tr>
<td>Pd$_{10}$SA/NP/CNT</td>
<td>1.2</td>
<td>1.1 ± 0.6</td>
<td>-</td>
<td>10</td>
</tr>
<tr>
<td>Pd/FLG</td>
<td>1.9</td>
<td>2.6 ± 1.6</td>
<td>43</td>
<td>10</td>
</tr>
<tr>
<td>Pd/CNF</td>
<td>1.7</td>
<td>1.5 ± 0.9</td>
<td>67</td>
<td>n.d.$^e$</td>
</tr>
</tbody>
</table>

a) Calculated over 300 NP from STEM-HAADF micrographs
b) Calculated over 20 NP from STEM-HAADF micrographs
c) Metal dispersion was evaluated from a universal mathematical relation between the mean relative size of metallic crystallites and their dispersion [1].
d) SA/NP ratio in number calculated over 500 elements from STEM-HAADF micrographs.
e) n.d.: not determined
S.2 Catalytic experiments

**H$_2$-assisted isomerization of 1-octene**

Isomerization of alkenes was assessed using a dedicated experience. 1-octene was used as a molecular probe (see scheme below). The different isomers and by-product that could be obtained during the isomerization of 1-octene by Pd catalysts is shown below:

```
\[\text{m/z: 112}\]
```

```
\[\text{m/z: 114}\]
```

**H$_2$-assisted isomerization of 1-octene**

60 mL of a solution of 1-octene (Sigma Aldrich, 99%) in heptane (1 M) was added in a 100 mL round bottom flask and then heat at reflux under H$_2$ atmosphere. A sample was taken for *ex-situ* analysis and then catalyst was added in one portion. The mass of the catalyst was adjusted in order to have 3.75 $\mu$mol of Pd (0.4 mg, 60 ppm). Samples were taken as the function of time and were analyzed using GC-FID analysis. The concentration of isomers of 1-octene and octane could be easily followed by GC as shown below.

**GC-FID of the reaction mixture**

The absence of hydrogenation product (*i.e.* n-octane) was assessed by comparison with pure octane and by GC-MS analysis (see chromatogram below). Under those conditions, no hydrogenation product (*i.e.* n-octane) could be identified in the reaction mixture. This was
confirmed by comparison with pure octane and by GC-MS analysis in SIM mode (see chromatogram below).

**GC-MS chromatogram TIC and SIM ion count of a sample at 75 % of isomerization.**
Reaction conditions: 1 M 1-octene in heptane (1 M), reflux (98°C), H₂ 1 atm.

The comparison of the 1-octene isomerization by the Pd catalysts is shown in Fig. S.

**S.3. Tests to assess hydrogen spillover**
To check for the H-spillover, we used WO₃ to diagnose the activation of H₂ in the various catalysts, because the spilled-over hydrogen migrates and readily reacts with the yellow WO₃ to form dark blue HₓWO₃ [2]. Samples made with 500 g of WO₃ were mixed or not with 5 mg of catalyst and treated with H₂ (100 mL/min) at 20 °C for 3 min.

**S.4 Assessment of the impact of mass transfer for myrcene hydrogenation**
Mass transfer limitations have been evaluated using common chemical engineering approaches regarding the limiting reagent H₂. The physical properties of the different phases involved in the reaction are listed in the following Supplementary Table 2. Gas and liquid properties are given for 20 bar and 120 °C.
**Supplementary Table 2**: Physical properties of the different phases at 120 °C and 20 bar.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Name</th>
<th>Symbol</th>
<th>Value</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Viscosity</strong></td>
<td>Viscosity</td>
<td>( \mu )</td>
<td>1.71x10^{-4}</td>
<td>Pa.s</td>
</tr>
<tr>
<td><strong>Density</strong></td>
<td>Density</td>
<td>( \rho )</td>
<td>703</td>
<td>kg/m^3</td>
</tr>
<tr>
<td><strong>Surface tension</strong></td>
<td>Surface tension</td>
<td>( \sigma )</td>
<td>1x10^{-2}</td>
<td>N/m</td>
</tr>
<tr>
<td><strong>H2 diffusivity</strong></td>
<td>Diffusivity</td>
<td>( D_{m,H2} )</td>
<td>1.99x10^{-9}</td>
<td>m^2/s</td>
</tr>
<tr>
<td><strong>H2 solubility</strong></td>
<td>Solubility</td>
<td>( C^*_H2 )</td>
<td>187</td>
<td>mol/m^3</td>
</tr>
<tr>
<td><strong>Viscosity</strong></td>
<td>Viscosity</td>
<td>( \mu )</td>
<td>1.07x10^{-5}</td>
<td>Pa.s</td>
</tr>
<tr>
<td><strong>Density</strong></td>
<td>Density</td>
<td>( \rho )</td>
<td>1.22</td>
<td>kg/m^3</td>
</tr>
<tr>
<td><strong>Skeleton density</strong></td>
<td>Skeleton density</td>
<td>( \rho_s )</td>
<td>1900</td>
<td>kg/m^3</td>
</tr>
<tr>
<td><strong>Pore volume</strong></td>
<td>Pore volume</td>
<td>( V_{pore} )</td>
<td>2.5</td>
<td>mL/g</td>
</tr>
<tr>
<td><strong>Dry particle density</strong></td>
<td>Dry particle density</td>
<td>( \rho_d )</td>
<td>600</td>
<td>kg/m^3</td>
</tr>
<tr>
<td><strong>Wetted particle density</strong></td>
<td>Wetted particle density</td>
<td>( \rho_w )</td>
<td>1080</td>
<td>kg/m^3</td>
</tr>
<tr>
<td><strong>Internal porosity</strong></td>
<td>Internal porosity</td>
<td>( \beta_p )</td>
<td>70%</td>
<td>m^3/cm^3</td>
</tr>
<tr>
<td><strong>Tortuosity</strong></td>
<td>Tortuosity</td>
<td>( \tau )</td>
<td>1/3</td>
<td>-</td>
</tr>
<tr>
<td><strong>Mean Particle</strong></td>
<td>Mean Particle</td>
<td>( d_p )</td>
<td>1.2</td>
<td>( \mu ) m</td>
</tr>
<tr>
<td><strong>Viscosity</strong></td>
<td>Viscosity</td>
<td>( \mu )</td>
<td>1.07x10^{-3}</td>
<td>Pa.s</td>
</tr>
<tr>
<td><strong>Density</strong></td>
<td>Density</td>
<td>( \rho )</td>
<td>1.22</td>
<td>kg/m^3</td>
</tr>
<tr>
<td><strong>Skeleton density</strong></td>
<td>Skeleton density</td>
<td>( \rho_s )</td>
<td>3650</td>
<td>kg/m^3</td>
</tr>
<tr>
<td><strong>Dry particle density</strong></td>
<td>Dry particle density</td>
<td>( \rho_d )</td>
<td>1460</td>
<td>kg/m^3</td>
</tr>
<tr>
<td><strong>Wetted particle density</strong></td>
<td>Wetted particle density</td>
<td>( \rho_w )</td>
<td>1880</td>
<td>kg/m^3</td>
</tr>
<tr>
<td><strong>Internal porosity</strong></td>
<td>Internal porosity</td>
<td>( \beta_p )</td>
<td>60%</td>
<td>m^3/cm^3</td>
</tr>
<tr>
<td><strong>Tortuosity</strong></td>
<td>Tortuosity</td>
<td>( \tau )</td>
<td>( \approx ) 3</td>
<td>-</td>
</tr>
<tr>
<td><strong>Mean Particle</strong></td>
<td>Mean Particle</td>
<td>( d_p )</td>
<td>25</td>
<td>( \mu ) m</td>
</tr>
<tr>
<td><strong>Viscosity</strong></td>
<td>Viscosity</td>
<td>( \mu )</td>
<td>1.07x10^{-3}</td>
<td>Pa.s</td>
</tr>
<tr>
<td><strong>Density</strong></td>
<td>Density</td>
<td>( \rho )</td>
<td>1.22</td>
<td>kg/m^3</td>
</tr>
<tr>
<td><strong>Skeleton density</strong></td>
<td>Skeleton density</td>
<td>( \rho_s )</td>
<td>1900</td>
<td>kg/m^3</td>
</tr>
<tr>
<td><strong>Pore volume</strong></td>
<td>Pore volume</td>
<td>( V_{pore} )</td>
<td>2.5</td>
<td>mL/g</td>
</tr>
<tr>
<td><strong>Dry particle density</strong></td>
<td>Dry particle density</td>
<td>( \rho_d )</td>
<td>760</td>
<td>kg/m^3</td>
</tr>
<tr>
<td><strong>Wetted particle density</strong></td>
<td>Wetted particle density</td>
<td>( \rho_w )</td>
<td>1180</td>
<td>kg/m^3</td>
</tr>
<tr>
<td><strong>Internal porosity</strong></td>
<td>Internal porosity</td>
<td>( \beta_p )</td>
<td>60%</td>
<td>m^3/cm^3</td>
</tr>
<tr>
<td><strong>Tortuosity</strong></td>
<td>Tortuosity</td>
<td>( \tau )</td>
<td>( \approx ) 3</td>
<td>-</td>
</tr>
<tr>
<td><strong>Mean Particle</strong></td>
<td>Mean Particle</td>
<td>( d_p )</td>
<td>10</td>
<td>( \mu ) m</td>
</tr>
<tr>
<td>a) Estimated using correlations found in [3].</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>b) Thermodynamic calculations with PPR78 group contribution using PROSIM software for a flash equilibrium at constant P &amp; T.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>c) Commonly taken equal to the graphite density.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>d) See for example [4,5] for such typical orders of magnitudes.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>e) Calculated from skeleton density and pore volume.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>f) See [6] for a discussion about mass transfer inside nanotubes bundles.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### S.4.1. G-L external mass transfer

To evaluate the efficiency of the reactor set up to transfer hydrogen in the liquid phase, the mass transfer coefficient \( k_{L_aGL} \) of the reactor has been measured experimentally with a classical physical absorption technique \([7, 8]\) following the H\(_2\) consumption in the regulated and calibrated gas tank. Identical conditions to the experimental ones have been used but without any catalyst (1200 rpm, 80mL of 1M myrcene solution in heptane, 120°C, constant P\(_{H2} = 20\) bar).

The H\(_2\) consumption profile of the reserve allowed adjusting and recovering 2 parameters of the system mass balance (eq. S1-S3): the mass transfer coefficient \( k_{L_aGL} \) and the final saturation concentration of H\(_2\) in the solution (solubility) \( C^*_H2 \).

\[
dn_{H2}(t) = -dn_{H2}^{Res}(t) = -dp^{res}(t) = \frac{V_{res}}{RT} \exp\left(-\frac{\Delta H_{H2}}{RT} - \frac{\Delta S_{H2}}{R}t\right) \quad \text{(S1)}
\]

\[
k_{L_aGL}V_H(C_{H2} - C_{H2}^{res}(t)) = \frac{dn_{H2}^{Res}(t)}{dt} = \frac{dC_{H2}(t)}{dt} = \frac{V_{res}}{RT}C_{H2}^{res}(t) \left(1 - \exp\left(-\frac{k_{aGL}}{\epsilon_L}t\right)\right) \quad \text{(S2)}
\]

\[
dp^{res}(t) = \frac{RT}{V_{res}}C_{H2}^{res}(t) \left(1 - \exp\left(-\frac{k_{aGL}}{\epsilon_L}t\right)\right) \quad \text{(S3)}
\]

In these equations, \( dn_{H2}(t) \) is the variation of the quantity of dissolved H\(_2\) in the liquid phase between \( t_0 \) and \( t \) (mol); \( dn_{H2}^{Res}(t) \) is the corresponding variation of H\(_2\) in the calibrated reserve (mol); \( dp^{res}(t) \) is the corresponding pressure variation in the reserve (Pa); \( V_{res} \) is the volume of
the reserve (m$^3$); $T_{res}$ is the temperature of the reserve (K); $V_L$ is the liquid volume inside the reactor (m$^3$); $\varepsilon_L$ is the liquid fraction inside the reactor (m$^3$L/m$^3$R); $C_{H2}$ is the solubility of H$_2$ in the liquid mixture (mol/m$^3$); $k_La_{GL}$ is the G-L mass transfer coefficient (s$^{-1}$) with $a_{GL}$ the specific surface area for G-L mass transfer (m$^2$GL/m$^3$Reactor).

$k_La_{GL}$ and $C_{H2}$ were estimated as 0.2 s$^{-1}$ and 190 mol H$_2$/m$^3$L respectively. The $k_La_{GL}$ appears typical of well-equipped laboratory stirred tank reactor (for H$_2$). The experimental solubility is in agreement with the one calculated with the PPR78 thermodynamic model (187 mol/m$^3$L).

Based on these mass transfer measurements, a theoretical maximum H$_2$ consumption, $F_{H2}^{max, GL}$ (in mol H$_2$/s) can be defined for each experiment (S4). This consumption can be linked to the corresponding theoretical apparent reaction rate, $r_p^{max, app}$ (S5), or to the corresponding theoretical Site Time Yield, $STY^{max}$ (S6), both in full G-L mass transfer regime:

$$F_{H2}^{max, GL} = k_La_{GL}V_RC^*_H$$ (S4)

$$r_p^{max, app} = \frac{F_{H2}^{max, GL}}{V_{cata}} = \frac{k_La_{GL}V_RC_{H2}}{V_{cata}}$$ (S5)

$$STY^{max, GL} = \frac{F_{H2}^{max, GL}}{V_{cata}} = \frac{k_La_{GL}V_RC_{H2}}{V_{cata}}$$ (S6)

Independently, following the instantaneous consumption curves of H$_2$, experimental instantaneous apparent reaction rates or STY can be determined at any reaction progress. These latter can be compared to the corresponding theoretical ones to appreciate a fraction of external G-L mass transfer limitation, $f_{ex}^{GL}$ (S7), on the measurements and is analogous of the L-S external mass transfer one because no reaction occurs inside the liquid, only on the catalyst surfaces.

$$f_{ex}^{GL} = \frac{STY}{STY^{max, GL}} = \frac{r_p^{app}}{r_p^{max, app}}$$ (S7)

The relationship between the instantaneous STY and the instantaneous apparent reaction rate $r_p$ (per volume of wetted catalyst) is recalled in (S8):

$$r_p = \frac{STY \times \rho_p \times wt\%_{pd}}{H_{pd}}$$ (S8)

Supplementary Table 3 presents this determination for most of the catalysts of the study (those of Figures 1 and 7) at three different reaction progresses: 0.5 mol H$_2$/mol myrcene, 2.0 mol H$_2$/mol myrcene and 2.5 mol H$_2$/mol myrcene.
**Supplementary Table 3:** Appraisal of G-L mass transfer limitations.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>( n_{\text{Pd}} ) (µmol)</th>
<th>( STY_{\text{max}} ) (mol ( \text{H}_2 )/s/mol ( \text{Pd} ))</th>
<th>( STY_{0.5} ) (mol ( \text{H}_2 )/s/mol ( \text{Pd} ))</th>
<th>( f^{GL}_{0.5} ) (-)</th>
<th>E (-)</th>
<th>( STY_{2.0} ) (mol ( \text{H}_2 )/s/mol ( \text{Pd} ))</th>
<th>( f^{GL}_{2.0} ) (-)</th>
<th>( STY_{2.5} ) (mol ( \text{H}_2 )/s/mol ( \text{Pd} ))</th>
<th>( f^{GL}_{2.5} ) (-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd/Al(_2)O(_3)</td>
<td>37.6</td>
<td>199</td>
<td>109</td>
<td>55%</td>
<td>1.0</td>
<td>10.2</td>
<td>5%</td>
<td>4.6</td>
<td>2%</td>
</tr>
<tr>
<td>Pd/C</td>
<td>36.5</td>
<td>205</td>
<td>168</td>
<td>82%</td>
<td>1.0</td>
<td>72</td>
<td>35%</td>
<td>26</td>
<td>13%</td>
</tr>
<tr>
<td>Pd/CNT also named Pd(_{2})SA/NP/CNT</td>
<td>38.3</td>
<td>195</td>
<td>144</td>
<td>74%</td>
<td>1.0</td>
<td>44</td>
<td>23%</td>
<td>22</td>
<td>11%</td>
</tr>
<tr>
<td>Pd(_{100})SA/NP/CNT</td>
<td>1.9</td>
<td>3979</td>
<td>184</td>
<td>5%</td>
<td>1.0</td>
<td>1.4</td>
<td>0.04%</td>
<td>N.A.</td>
<td>N.A.</td>
</tr>
<tr>
<td>Pd(_{20})SA/NP/CNT</td>
<td>25.0</td>
<td>299</td>
<td>104</td>
<td>35%</td>
<td>1.0</td>
<td>10.4</td>
<td>3%</td>
<td>4.5</td>
<td>2%</td>
</tr>
<tr>
<td>Pd(_{50})SA/NP/CNT</td>
<td>25.8</td>
<td>290</td>
<td>544</td>
<td>187%</td>
<td>1.9</td>
<td>104</td>
<td>19%</td>
<td>50</td>
<td>9%</td>
</tr>
<tr>
<td>Pd(_{100})SA/NP/CNT</td>
<td>24.2</td>
<td>308</td>
<td>672</td>
<td>218%</td>
<td>2.2</td>
<td>272</td>
<td>40%</td>
<td>106</td>
<td>16%</td>
</tr>
</tbody>
</table>

First of all, it is noticeable that the \( STY_{\text{max}} \) reached different values depending on the different amounts of Pd in each experiment. The \( f^{GL}_{ex,0.5} \), for most of the catalysts (except the \( \text{Pd}_{1000}\)SA/NP/CNT catalyst which contains a very low amount of metal) is revealed to be high indicating a strong G-L mass transfer impact on the \( STY_{0.5} \) measurements and the impossibility to discuss robustly these \( STY_{0.5} \). This is indicated in the main text of the article. Interestingly, the 2 more active catalysts present a higher \( STY_{0.5} \) compared to the theoretical \( STY_{\text{max}} \). This is a phenomenon already observed and explained in stirred tank reactors with very active fine slurry catalyst particles [9, 10]. The approach detailed in [9] is very close to an enhancement factor, \( E(-) \), for mass transfer G-L reactive absorption already well established [11]. In the present work, this situation is encountered. Thus, the first points at a reaction progress of 0.5 are used to estimate an experimental \( E \) factor as shown in the 6th column of the table. The values are equal to 1 when \( f^{GL}_{0.5} < 100\% \) and equal to the value of \( f^{GL}_{0.5} \) when >100%. The values obtained here for the two more active catalysts are consistent with those reported in [9]. For the other reaction progress, accordingly to these measurements, the \( F^{max,GL}_H2 \) (and \( STY_{\text{max}} \)) takes into account this factor accordingly to (S9):

\[
F^{max,GL}_H2 = E k_L a_H2 V_p C^*_H2
\]  

(S9)

For reaction progresses of 2.0 and 2.5 mol \( \text{H}_2 \)/mol myrcene, the impact of G-L mass transfer on the STY is drastically decreased as shown in the Table and a satisfactory comparison of the observed STY can be drawn on a chemical basis. The \( \text{Pd}_{100SA}\)NP/CNT, which is the most active one, is the only catalyst that may still present a possible partial G-L mass transfer hindrance of its intrinsic performance. This partial leveling is a signature of its very high intrinsic activity and does not change the conclusions made in this article. In a quantitative point of view, one can just expect an increase of the observed differences between this catalyst and the other ones.

**S.4.2. L-S external mass transfer**

In G-L-S slurry reactors, L-S external mass transfer is often less limiting than the G-L one. To verify this common assumption, the classical external mass transfer fraction, \( f^{LS}_{ex} \) (defined in S10) has been used for reaction progresses of 0.5, 2.0 and 2.5 mol \( \text{H}_2 \)/mol myrcene:

\[
f^{LS}_{ex} = \frac{r_{PL}}{k_L C_{H2}} = \frac{STY}{STY^{max,LS}} \quad \text{with} \quad STY^{max,LS} = \frac{M_{Pd} k_L a_{H2} V_p C^*_H2}{\rho \omega \eta \eta_{H2L}} \tag{S10}
\]
L is the characteristic length of the catalyst (dp/6 for spherical particles) and $k_S$ is the L-S mass transfer coefficient. It has been estimated using the correlation of Armenante & Kirwan [12]. The different results are presented in Supplementary Table 4:

**Supplementary Table 4:** Appraisal of L-S external mass transfer limitations.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>$STY_{max,LS}$ (molH$_2$/s/molPd)</th>
<th>$STY_{0.5}$ (molH$_2$/s/molPd)</th>
<th>$f_{LS,0.5}^S$ (+)</th>
<th>$STY_{2.0}$ (molH$_2$/s/molPd)</th>
<th>$f_{LS,2.0}^S$ (+)</th>
<th>$STY_{2.5}$ (molH$_2$/s/molPd)</th>
<th>$f_{LS,2.5}^S$ (+)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd/Al$_2$O$_3$</td>
<td>137</td>
<td>109</td>
<td>79%</td>
<td>10.2</td>
<td>7.5%</td>
<td>4.6</td>
<td>3.4%</td>
</tr>
<tr>
<td>Pd/C</td>
<td>541</td>
<td>168</td>
<td>31%</td>
<td>72</td>
<td>13.3%</td>
<td>26</td>
<td>4.8%</td>
</tr>
<tr>
<td>Pd/CNT also named Pd$_2$SA/NP/CNT</td>
<td>31 486</td>
<td>144</td>
<td>0.5%</td>
<td>44</td>
<td>0.1%</td>
<td>22</td>
<td>0.07%</td>
</tr>
<tr>
<td>Pd$_{100}$SA/NP/CNT</td>
<td>642 309</td>
<td>184</td>
<td>0.03%</td>
<td>1.4</td>
<td>0.0002%</td>
<td>0.7</td>
<td>0.0001%</td>
</tr>
<tr>
<td>Pd$_{200}$SA/NP/CNT</td>
<td>48 294</td>
<td>104</td>
<td>0.2%</td>
<td>10.4</td>
<td>0.02%</td>
<td>4.5</td>
<td>0.01%</td>
</tr>
<tr>
<td>Pd$_{40}$SA/NP/CNT</td>
<td>46 884</td>
<td>544</td>
<td>1.2%</td>
<td>104</td>
<td>0.2%</td>
<td>50</td>
<td>0.1%</td>
</tr>
<tr>
<td>Pd$_{10}$SA/NP/CNT</td>
<td>49 791</td>
<td>672</td>
<td>1.4%</td>
<td>272</td>
<td>0.6%</td>
<td>106</td>
<td>0.2%</td>
</tr>
</tbody>
</table>

At a reaction progress of 0.5 molH$_2$/mol myrcene, only Pd/Al$_2$O$_3$ and Pd/C present a L-S mass transfer limitation. All the CNT catalysts appear free of external L-S mass transfer limitation.

At reaction progress of 2.0 and 2.5 mol/mol, no L-S mass transfer limitation remains at all for all the catalysts (except slightly for the Pd/C) and STY comparisons are consistent and chemically robust.

**S.4.3. Internal mass transfer**

To evaluate a possible internal mass transfer limitation, the classical Weisz-Prater criterion $\varphi'$ [13] has been evaluated. When the criterion is inferior to 1 a surface efficiency of 1 is stated. When it is superior to 1, a surface efficiency is approximated as $\frac{1}{\varphi'}$ The Supplementary Table 5 presents the results and equations (S11) to (S13), the formula used for $\varphi'$:

$$\varphi' = \frac{r_p^2}{D_{eff}C_{HL2}}$$  (S11)

$$D_{eff} = \frac{\beta \nu}{\tau}D_{m,HL2}$$  (S12)

For $\varphi' > 1$: $\eta_{su} \approx \frac{1}{\varphi'}$ and for $\varphi' < 1$: $\eta_{su} \approx 1$  (S13)

**Supplementary Table 5:** Appraisal of possible internal mass transfer limitations.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>$Deff$ (m$^2$/s)</th>
<th>$STY_{2.0}$ (molH$_2$/s/molPd)</th>
<th>$\varphi'$ (+)</th>
<th>$\eta_{su}$ (+)</th>
<th>$STY_{2.5}$ (molH$_2$/s/molPd)</th>
<th>$\varphi'$ (+)</th>
<th>$\eta_{su}$ (+)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd/Al$_2$O$_3$</td>
<td>4.0x10$^{-8}$</td>
<td>10.2</td>
<td>2.10</td>
<td>=0.5</td>
<td>4.6</td>
<td>0.95</td>
<td>=1</td>
</tr>
<tr>
<td>Pd/C</td>
<td>4.0x10$^{-8}$</td>
<td>72</td>
<td>1.44</td>
<td>=0.5</td>
<td>26</td>
<td>0.52</td>
<td>=1</td>
</tr>
<tr>
<td>Pd/CNT also named Pd$_2$SA/NP/CNT</td>
<td>1.6x10$^{9}$</td>
<td>44</td>
<td>0.004</td>
<td>22</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pd$_{100}$SA/NP/CNT</td>
<td>1.4x10$^{9}$</td>
<td>1.4</td>
<td>1x10$^{-3}$</td>
<td>0.7</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pd$_{200}$SA/NP/CNT</td>
<td>1.4x10$^{9}$</td>
<td>10.4</td>
<td>6x10$^{-3}$</td>
<td>4.5</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pd$_{40}$SA/NP/CNT</td>
<td>1.4x10$^{9}$</td>
<td>104</td>
<td>6x10$^{-3}$</td>
<td>50</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pd$_{10}$SA/NP/CNT</td>
<td>1.4x10$^{9}$</td>
<td>272</td>
<td>0.015</td>
<td>106</td>
<td>1</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
All the CNT catalysts at reaction progress 2.0 and 2.5 mol_{H2}/mol_{myrcene} are free of internal limitations. This remains true for the reference Pd/Al_{2}O_{3} and Pd/C at the reaction progress of 2.5 mol_{H2}/mol_{myrcene}. For these catalysts, an intermediate regime with little mass transfer resistance may be present at a reaction progress of 2.0 mol_{H2}/mol_{myrcene} because 1 < \varphi^\prime < 3. This is due to the bigger size of the catalyst particles.

**S.4.4. Global conclusion on mass transfer limitations**

Due to the high reactivity of the terminal alkene and the conjugated double bond of myrcene, the first hydrogenation is very fast and the overall hydrogenation of this study is subject to external mass transfer limitations (either G-L, L-S or both) at low reaction progress (typically < 1.0 mol_{H2}/mol_{myrcene}). For the usual reference hydrogenation catalysts (Pd/Al_{2}O_{3} and Pd/C), at higher reaction progress, (2 or 2.5 mol_{H2}/mol_{myrcene}), most of the experimental instantaneous STY measurements are free of external or internal limitations. Only the most active catalysts (Pd_{40,SA/NP}/CNT and Pd_{10,SA/NP}/CNT) can be subject to a little G-L limitation that may hinder slightly their true performance.

Regarding internal mass transfer limitations, only Pd/Al_{2}O_{3} and Pd/C may be subject to a little hindrance of their true kinetics at a reaction progress of 2.0 mol_{H2}/mol_{myrcene}. This latter tends to disappear at a reaction progress of 2.5 mol_{H2}/mol_{myrcene}.

Overall, comparison of instantaneous STY of this study is allowed and consistent for reaction progresses higher than 2.0. The conclusions drawn in this paper can be linked with chemical phenomena.
**Fig. S1.** STEM-HAADF and TEM micrographs, and histograms of Pd$_{NP}$ sizes of: **a** fresh Pd/Al$_2$O$_3$; **b** Pd/Al$_2$O$_3$ after $\beta$-myrcene hydrogenation; **c** fresh Pd/C; **d** Pd/C after $\beta$-myrcene hydrogenation; **e** fresh Pd/CNT; and **f** Pd/CNT after $\beta$-myrcene hydrogenation. Scale bar = 50 nm.
Fig. S2. Photo of the metallic foam coated in the tubular reactor for catalyst stability study under continuous reactor operation.
Fig. S3. Catalytic results on Pd/Al₂O₃, Pd/C and Pd₂_SA/NP/CNT as a function of surface Pd. β-myrcene hydrogenation reaction. The reaction was carried out over supported Pd catalysts. P_{H₂} = 20 bar - T = 120°C - myrcene 1 M (80 mL) - solvent heptane - 200 mg cat. a Reaction progress as a function of time.cat*. b STY* as a function of reaction progress.
**Fig. S4.** STEM-HAADF images of **a** and **b** Pd/FLG (FLG = few layer graphene); and **c** and **d** Pd/CNF (CNF = carbon nanofibers), showing the coexistence of Pd SA and Pd NP.
Fig. S5. Comparison of the catalytic performances of Pd/Al₂O₃ and Pd/FLG for the total hydrogenation of myrcene, farnesene and squalene. Hydrogenation reactions carried out over supported Pd catalysts. P_H₂ = 20 bar - T = 120°C - substrate 1 M (80 mL) - solvent heptane - 280 mg cat.
Fig. S6. STEM-HAADF micrographs, particle size distribution and Pd_{SA}/Pd_{NP} ratio for the Pd/FLG catalyst: a) and b) before catalysis; and c) and d) after myrcene hydrogenation.
Fig. S7. CO$_2$ TPD profiles of the CNT support and the Pd$_{2\text{SA/NP}}$/CNT catalyst showing the disappearance of most of the surface carboxylic groups after catalyst preparation, and the appearance of a Pd-OOC- interface.
Fig. S8. Isosurface plot of the electronic density differences ($\Delta \rho = \rho_{Pd} - \rho_{SA} - \rho_{Pd} - \rho_{SA}$) for negative (in cyan) and positive (in yellow) isovalues of 0.002 e$/\text{Å}$. The charge transfer from Pd SA 4d orbitals to the defective (single vacancy in graphene) support is estimated to be 0.37 e$^-$. 
**Fig. S9.** Evolution of the composition of the solution during 1-octene hydrogenation as the function of time and catalysts $\text{Pd}_{\text{SA}}$/CNT, $\text{Pd}/\text{Al}_2\text{O}_3$ and $\text{Pd}_{2\text{ SA}}$/NP/CNT. Reaction conditions: 1-octene (1M) in heptane, Pd 0.4 mg (60 ppm), reflux (98 °C), $\text{H}_2$ 1 atm. In the case of the CNT catalyst no measurable activity was noticed.
Fig. S10. STEM-HAADF micrographs of Pd$_{2\text{SA/NP/CNT}}$ and Pd$_{2\text{SA/NP/CNT-HT}}$ catalysts and related particle size distribution based on total particles and on total atoms.
Fig. S11. EPR spectra of CNT$_{HT}$ and D-CNT$_{HT}$. For these measurements, CNT have been heat-treated at 2800 °C before the thermochemical process in order to remove any traces of remaining metal arising from their synthesis.
Fig. S12. VSM magnetization curves of CNT_{HT} and D-CNT_{HT}. For these measurements, CNT have been heat-treated at 2800 °C before the thermochemical process in order to remove any traces of remaining metal arising from their synthesis.
Fig. S13. STEM micrographs and particle size distribution based on total particles and on total atoms for Pd$_{200}$$_{SA}$/NP/CNT, Pd$_{60}$$_{SA}$/NP/CNT, Pd$_{40}$$_{SA}$/NP/CNT and Pd$_{10}$$_{SA}$/NP/CNT samples.
Fig. S14. O 1s XPS spectra of Pd$_{200}$SA/NP/CNT, Pd$_{60}$SA/NP/CNT, Pd$_{40}$SA/NP/CNT, Pd$_{10}$SA/NP/CNT and D-CNT.
Fig. S15. Correlation between the ratio $\text{Pd}^0/\text{Pd}^{\delta+}$ determined by XPS and the fraction of SA in the same samples determined from STEM.
Fig. S16. TEM and STEM micrographs and particle size distribution based on total particles and on total atoms for: a) to c) $\text{Pd}_{2-\text{SA/NP}}$/CNT; d) to f) $\text{Pd}_{2-\text{SA/NP}}$/CNT coated on metallic open-cell solid foam cylinders before catalysis; and g) to i) $\text{Pd}_{2-\text{SA/NP}}$/CNT coated on metallic open-cell solid foam cylinders after catalysis.
Additional references

Statement of contributions

Author contributions. P.S. conceived the idea of cooperative catalysis and coordinated the work. I.C.G. and I.R. performed the DFT calculations. C.R.C. prepared and characterized the mixtures of single atom catalysts and nanoparticles. B.G. and L. V. performed the catalytic experiments and GC-FID and GC-MS analyses. R.P., C.B. and A.F.R. conceived, supervised and analyzed the catalytic experiments. R.C.C. prepared and characterized the Pd catalysts. B.F.M. performed and analyze the TPD experiments.