Supporting information

Palladium-catalyzed aerobic oxidation of 1-phenylethanol with an ionic liquid additive

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Experimental section

Materials: Multi-walled carbon nanotubes (MWCNT) was purchased from Cnano Technology Ltd (purity: 97.1%, S_{BET}: 241 m^2/g, bulk density: 0.05 g/cm^3). $PdCl_2$ (99%), HNO_3 (69%), HCl (36%), H_2SO_4 (98%), diethyl ether (>99%), 1-phenylethanol (98%) and dodecane (≥99.8%) were provided by Sigma-Aldrich. Ionic liquids 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [emim][NTf_2], 1-butyl-3-methylimidazolium chloride [bmim]Br and Nafion solution (5 wt.% in isopropanol) were purchased from Regent Chemicals Pte Ltd. All chemicals were used as received without further purification.

Measurements: X-ray photoelectron spectroscopy (XPS) measurement was carried out on a VG Escalab 250 spectrometer equipped with an Al anode (Al Kα= 1486.6 eV). The background pressure in the analysis chamber was lower than 1×10^{-7} Pa. Measurements were performed using 20 eV pass energy, 0.1 eV step and 0.15 min dwelling time. The correction for the binding energies (BE) was carried out using the C 1s peak of adventitious C at 284.6 eV. Transmission electron microscopy (TEM) was performed on JEOL JEM-2100F, operated at 200 kV. The sample was suspended in ethanol and dried on holey carbon-coated Cu grids. Raman spectra were collected on a Renishaw via Raman system in the backscattering configuration using 633 nm (1.96 eV) laser over five random spots on each sample.

Synthesis: The pristine MWCNT was pretreated with concentrated HNO_3 at 120 ^oC for 2 h to remove the amorphous carbonaceous and metallic impurities as well as to introduce surface oxygen functional groups. Palladium catalyst supported on MWCNT was prepared by an adsorption-reduction method [1] with a Pd loading of 1 wt.%: 375.9 μL of H_2PdCl_4 (0.05 M) aqueous solution was added to 0.2 g of acid-pretreated MWCNT suspended in 20 mL of deionized water, followed by vigorous stirring at 80 ^oC for 5 h. The catalyst, donated as Pd/CNT, was obtained by filtering, washing with deionized water, and drying at 60 ^oC overnight. The catalyst was activated in a H_2 flow of 20 mL/min at 400 ^oC for 2 h.

Determination of electrochemical active surface (EAS) area and dispersion (D_{Pd}) of Pd: The measurement of EAS was carried out using CO-stripping voltammetry at room temperature in a three-electrode cell connected to an electrochemical analyzer (Eco Chemie B. V., Autolab PGSTAT 30). Typically, 3 mg of catalyst was dispersed in 1.5 mL of Nafion/ethanol solution (0.025 wt.%) and ultrasonicated to form a 2 mg/mL homogeneous ink suspension. 50 μL of the ink was cast on the polished surface of a glassy carbon electrode (GCE) and dried at atmosphere. Pt foil and Ag/AgCl electrodes were used as the counter and reference electrodes, respectively. Gaseous CO was bubbled for 2 min to form a CO adlayer on the electrode while the potential maintained at -0.22 V. Excess CO in the electrolyte was purged by N_2. 10 consecutive cyclic voltammogram (CV) sweeps were recorded between -0.22 and 1.20 V in 0.5 M H_2SO_4 solution (sweep rate 50 mV/s) versus Ag/AgCl. The first anodic sweep was performed to electro-oxidize the irreversibly adsorbed CO and the subsequent sweeps was carried out in order to verify the completion of CO oxidation. The coulombic charge for CO oxidation Q (C) was employed to calculate the EAS of Pd as below:

$$EAS\ (m^2/g_{\ Pd}) = \frac{Q}{q_{Pd}^{s} \cdot (m_{Pd})}$$

Where q_{Pd}^{s} is the reference charge of oxidizing a full monolayer of CO (4.2 C/m^2) and m_{Pd} is the amount of Pd dispersed on GCE.[2] Therefore, the dispersion of Pd defined as the fraction of surface-active Pd atoms in all of Pd atoms can be obtained:

$$D_{Pd} = \frac{EAS}{\frac{1}{M_{Pd}} \cdot (N_A \cdot 4\pi r_{Pd}^2)}$$

Where M_{Pd} is the relative molecular weight of Pd (106.42 g/mol), N_A is Avogadro constant (6.02E23) and r_{Pd} is Pd atomic radius (0.137 nm). To examine the accuracy of D_{Pd} derived by CO-stripping, a comparison was made with the dispersion estimated using the mean diameter of Pd nanoparticles from TEM observations (D_{TEM}). Assuming a full-shell model that each Pd nanoparticle is cuboctahedral in shape with *fcc* close-packed crystal structure; the number of total atoms (N_T) and surface atoms (N_S) can be calculated from: [3]

$$d_{Pd} = 1.105 d_{at} \cdot N_T^{1/3}$$

$$N_T = \frac{10m^3 - 15m^2 + 11m - 3}{3}$$

$$N_S = 10m^2 - 20m + 12$$

$$D_{TEM} = \frac{N_S}{N_T}.$$

Where d_{Pd} is the mean diameter of Pd crystallites in Pd/CNT catalyst obtained from statistical TEM analysis (2.3±0.4 nm), d_{at} is the atomic diameter of Pd (0.274 nm), m is the shell number. D_{TEM} obtained from TEM is 47.3%, while the dispersion estimated from CO-stripping is lower (32.4%), which may be caused by the adsorption configuration of CO on Pd.[2] Since TEM results only provide local and microscopic information, in this study, CO-stripping is considered as a more reliable method to evaluate Pd dispersion D_{Pd}.

Catalytic reaction: The selective oxidation of 1-phenylathanol using molecular O_2 was carried out in a bath-type reactor operated under atmospheric conditions: a three-necked glass flask (25 mL) precharged with 25 mmol of 1-phenylethanol, 5 mg of Pd/CNT catalyst and certain amounts of IL (1 mL except for the IL molar ratio study otherwise mentioned), as well as a stirring bar, was heated by a silicon oil bath, where a thermocouple was applied to control the temperature and a reflux condenser to condense the vapor of products. In each reaction run, the mixture was heated to the desired reaction temperature under vigorous stirring (stirring rate: 1200 rpm). Oxygen flow was bubbled at 20 mL/min controlled by a mass flow controller into the mixture to initiate the reaction. For O_2 partial pressure effect study, N_2 and air instead of pure oxygen were employed. For O_2 total pressure effect examination, the reaction was alternatively carried out in a stainless steel reactor with Telfon liner (Parr 4950, controller 4843). The residual air inside the reactor was expelled by pressurizing and releasing O_2 several times. The reaction was performed at 100 ^{o}C for 1 h under different O_2 pressures. For reaction time effect examination, the reaction was performed from 10 min to 1 h with 5 min interval. For reaction temperature effect investigation, the oxidation was carried out from 60 to 160 ^{o}C with 20 ^{o}C interval.

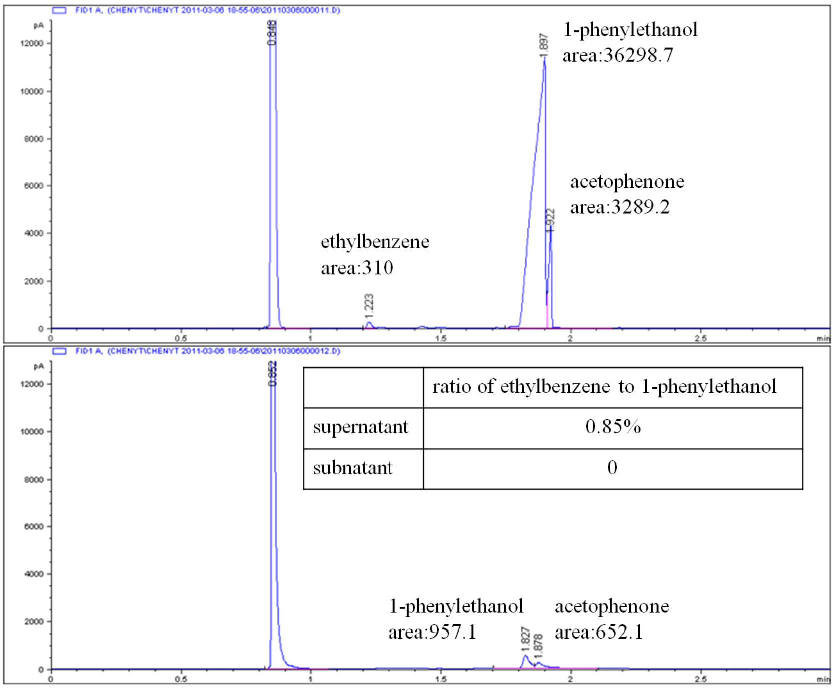
After reaction, the solution was quickly quenched for further extraction. The catalyst powder was separated from the liquid by filtration, affording a clear single-phase homogeneous mixture of residual reactant, products and IL without any visible interface or cloudiness. The liquid phase was extracted using diethyl ether (3×10 mL). The IL was in the subnatant while the supernatant (mixture of residual reactant, products and diethyl ether) was analyzed using an Agilent gas chromatograph 6890 equipped with a HP-5 capillary column (30 m long and 0.32 mm in diameter, packed with silica-based supel cosil) and flame ionization detector (FID). Dodecane was the internal standard. The injector temperature was 250 ^{o}C and the spilt is 0.1 μL. The column head pressure of the carrier gas (helium) during the analysis was maintained at 22.57 psi. Temperature program: 100 ^{o}C to 120 ^{o}C; 20 ^{o}C/min; hold for 3 min.

For the recovery of [emim] [NTf_2], the residual subnatant after extraction was evaporated under vacuum and re-used in a new reaction. For the recovery of Pd/CNT catalyst, the spent catalyst powder was recollected, washed with acetone, dried at 60 ^{o}C overnight. All the recycling experiments were conducted using Pd/CNT in [emim][NTf_2] following the same procedure described above. The Pd loading after 5 consecutive reaction cycles was almost the same as that of fresh catalyst, and Pd cannot be detected by ICP analysis in the filtrate after the reaction, confirming the absence of Pd leaching. To evaluate the catalyst activity, the turnover numbers (TON) and turnover frequencies (TOF) were defined as follows:

$$TON = \frac{M_{PE} \cdot X}{M_{Pd} \cdot D_{Pd}};\ TOF(h^{-1}) = \frac{M_{PE} \cdot X}{M_{Pd} \cdot D_{Pd} \cdot t}$$

Where M_{PE} and M_{Pd} are the amount of 1-phenylethanol and Pd in feed (mol), respectively, X is the conversion of 1-phenylethanol, D_{Pd} is the Pd dispersion calculated using CO-stripping method, and t is the reaction time (h). The uncertainties based on five repeated experiments are ±0.15%, ±0.35% and ±118 (h^{-1}) for conversion, selectivity and TON (TOF), respectively.

Product isolation controls: Two control experiments were carried out to examine the validity of product isolation process. The comparative images shown below are GC signals of the supernatant and subnatant after extracting by diethyl ether (3×10 mL) after the reaction, where the first peak stands for diethyl ether solvent. It is clear that almost all the organic reactant and products can be extracted and only trace and negligible amount of residues is detected in IL. Therefore, the selectivity in this study is reliable and not isolation artifact.



	ratio of ethylbenzene to 1-phenylethanol
supernatant	0.85%
subnatant	0

Supplemental results and discussions

Intrinsic activity examination: The steadily increased conversion of 1-phenylethanol in [emim][NTf_2] (Fig. 1(a)) indicates that the Pd catalyst is stable even at high temperatures. According to the fitted result, this is a 1^{st}-order reaction respect to 1-phenylethanol (reaction rate constant k=1.96±0.05, R_{adj}^2=0.9902). Nevertheless, the reaction may be in a deactivation region due to the high conversion. To interpret the activity in a more precise way, we repeated the reactions listed in Table 1 and controlled the substrate conversion at/below 20% by increasing the amount of substrate fourfold while maintaining the catalyst amount and IL molar fraction constant. In these reactions, 100 mmol of 1-phenylethanol, 5 mg of Pd/CNT catalyst and a corresponding amount of [emim][NTf_2] were used. The catalytic results are shown in Table S1 where TOFs are reported to evaluate the intrinsic activity.

The low activity in the absence of catalyst and IL (entry 1) is due to the non-catalytic oxidation. The conversion is almost doubled (entry 2) by adding Pd/CNT. Mixture of substrate and IL [emim][NTf_2] shows a moderate activity and rather poor ketone selectivity (entry 8), confirming the essential role of heterogeneous Pd/CNT catalyst. The molar fraction of [emim][NTf_2] remarkably affects the catalytic activities. The TOF increases sharply and then declines in the presence of excess [emim][NTf_2], concomitant with good selectivities (entry 3-7). The best activity is achieved when IL is 16.0 mol% and can be well maintained using recovered IL (entry 9). When using N_2 or air as alternatives, it is distinct that higher O_2 partial pressures contribute to better catalytic activities, implying that sufficient O_2 is crucial to enhance the dehydrogenation and suppress the hydrogenolysis side reaction. Noteworthily, regardless of the variation of reaction conditions and as far as intrinsic activity concerned, TOFs for 100 mmol-scale 1-phenylethanol oxidation show comparable values of TONs within 1 h reaction to 25 mmol-scale oxidation when using same amounts of Pd/CNT catalyst. The steady catalytic performance, regardless of changing the substrate/catalyst ratio, verifies that reaction is conducted in a kinetic region; dehydrogenation is the rate-limiting step without any mass transfer limitation.

Oxidation of various alcohols over Pd/CNT in [emim][NTf$_2$]: The scope of Pd/CNT catalyst with additive [emim][NTf$_2$] for a wide variety of alcohols was examined and the results are listed in Table S2. The selectivities toward the corresponding aldehydes or ketones are high for all the alcohols investigated. Benzyl alcohol is oxidized to benzaldehyde with a 60.8% conversion and 94.9% benzaldehyde selectivity, whereas 4-methylbenzyl alcohol exhibits a better performance (71.5% conversion) (entry 1-2). For the oxidation of 4-methoxybenzyl alcohol, the conversion is moderate (12.2%) (entry 3). Poor activity is observed in the oxidation of 4-nitrobenzyl alcohol and 4-bromobenzyl alcohol (entry 4-5), suggesting that the catalyst is more active for substituted aromatic alcohols containing electron-donating groups (-CH_3 and -CH_3O) than those containing electro-withdrawing groups (-NO_2 and -Br).[1, 4] It also confirms that the electrophilicity of [emim][NTf$_2$] is critical in the catalytic oxidation and electron transfer steps. When an electron-donating group substitutes the *p*-position of benzylic alcohol, the electron density is enriched on α-C atom. In an electrophilic environment, the electron transfer from substrate to Pd active sites is accelerated, *i.e.*, the dehydrogenation is promoted. The oxidation of cinnamyl alcohol displays a high conversion (entry 6), suggesting the efficient oxidation of allylic alcohols. 1-octanol is proven as a poor substrate and hardly converted, while 2-octanol shows a better conversion (entry 7-8), indicating that secondary alcohol is more reactive than primary one, which is also shown by the higher activity of 1-phenylethanol than benzyl alcohol.

TEM observations: TEM observations were carried out for the fresh and spent Pd/CNT catalysts in reactions with/without IL media (Fig. S2). One of the major disadvantages for poor recyclability of Pd-supported catalysts is the aggregation and agglomeration of Pd nanoparticles during the reaction, leading to the drastic decrease in the catalytic performance of spent catalysts. This can be avoided to a large extent in this study. Fresh Pd/CNT presents a mean particle size of 2.3±0.4 nm, and does not undergo a significant change in either solvent-free condition or [emim][NTf_2] additive (2.5±0.4 and 2.6±0.3 nm, respectively). However, large and irregular particles of 4.5±1.1 nm in diameter with a broad size distribution were observed after recovering the catalysts from [bmim]Br additive (Fig. S2(d)). Anions in ILs are prone to coordinate with metal centers and Br^- shows intimate coordination to Pd nanoparticles.[5] This coordination complex exhibits a strong affinity to the adjacent Pd nanoparticles to form large aggregates due to Pd-Br-Pd interactions (similar to the H-bonding in aqueous solutions). On the other hand, [emim][NTf_2] acts as a stabilizing spacer which provides both steric and electronic protection against the aggregation/agglomeration of Pd nanoparticles.[6] Therefore, [emim][NTf_2] acts not only as an effective and green reaction additive, but also an excellent stabilizer for the Pd nanoparticles.

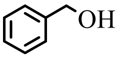
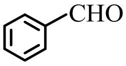
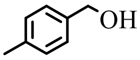
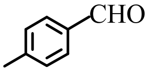
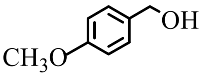
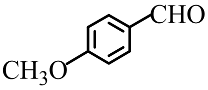
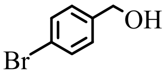
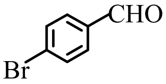
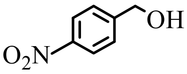
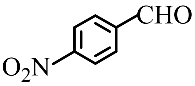
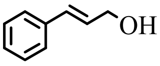
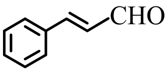
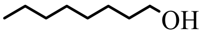
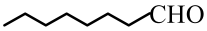
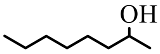
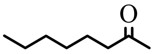
Raman spectra: MWCNT support is stable in the mixture of ionic liquids and organic compounds (alcohols and products), which is evidenced by the Raman spectra of fresh and spent catalysts shown in Fig. S3. All spectra exhibit the characteristic peaks of G-band at around 1600 cm^{-1} showing the sp^2 (graphitic) feature and D-band at around 1300 cm^{-1} showing the disorder of sp^3-hybridized (defect) feature. Reactions in [emim][NTf_2] and solvent-free conditions show negligible effect on MWCNT support evidenced by similar I_D/I_G ratios. Using [bmim]Br as the additive results in a noticeably decreased I_D/I_G ratio, implying the diminished defect sites due to accumulation and coverage of [bmim]Br on catalyst, which leads to rapid catalyst deactivation and extremely poor activity.

Table S1. Variation of reaction conditions for the oxidation of 1-phenylethanol to acetophenone over Pd/CNT catalyst[a]

Entry	Ionic liquid	V_{IL} (mL)	IL molar fraction(%)	Conv.(%)	Select.[b](%)	TOF $\times 10^{4c}$ (h^{-1})
1	-[d]	-	0	7.0	99.9	-
2	-	-	0	13.5	86.6	8.9
3	[emim][NTf_2]	2	8.7	17.3	87.5	11.3
4	[emim][NTf_2]	4	16.0	24.8	94.9	16.3
5	[emim][NTf_2]	8	23.7	20.4	87.7	13.4
6	[emim][NTf_2]	12	31.8	17.6	86.1	11.5
7	[emim][NTf_2]	16	38.3	14.5	85.3	9.5
8	[emim][NTf_2][d]	4	16.0	8.8	50.1	-
9	[emim][NTf_2][e]	4	16.0	20.7	91.6	13.6
10	[emim][NTf_2][f]	4	16.0	6.2	71.6	4.0
11	[emim][NTf_2][g]	4	16.0	12.4	90.2	8.1

[a] reaction conditions: 100 mmol of 1-phenylethanol, 5 mg of Pd/CNT, 40 mL/min of O_2, 160 °C, 1h. Uncertainties: conv.±0.15%, select.±0.35%, TOF(h^{-1})±0.08%. [b] ethylbenzene is the only byproduct. [c] TOF (h^{-1}) was calculated based on D_{Pd} obtained from CO-stripping (conversion is controlled in the low range, ≤20%) and values are identical with TON. [d] no catalyst. [e] IL recovered after the reaction. [f] N_2 used. [g] air used.

Table S2. Oxidation of various alcohols by Pd/CNT in [emim][NTf$_2$] ionic liquid[a]

Entry	Substrate	Product	Conv.(%)	Select.(%)	TON $\times 10^{4}$[b]
1			60.8	94.9[c]	10.0
2			71.5	94.8[d]	11.7
3			12.1	100	2.0
4			2.9	100	0.5
5			1.0	100	0.2
6			36.5	100	6.0
7			0.3	100	0.05
8			11.5	100	1.9

[a] reaction conditions: 25 mmol of substrate, 5 mg of Pd/CNT, 4 mL of [emim][NTf$_2$], 20 mL/min of O_2, 160 °C, 1h. Uncertainties: conv.±0.15%, select.±0.35%, TON±0.08%. [b] TON was calculated based on D_{Pd} obtained from CO-stripping. [c] byproduct: toluene (2.2%) and benzoic acid (2.9%). [d] byproduct: p-xylene (5.2%).

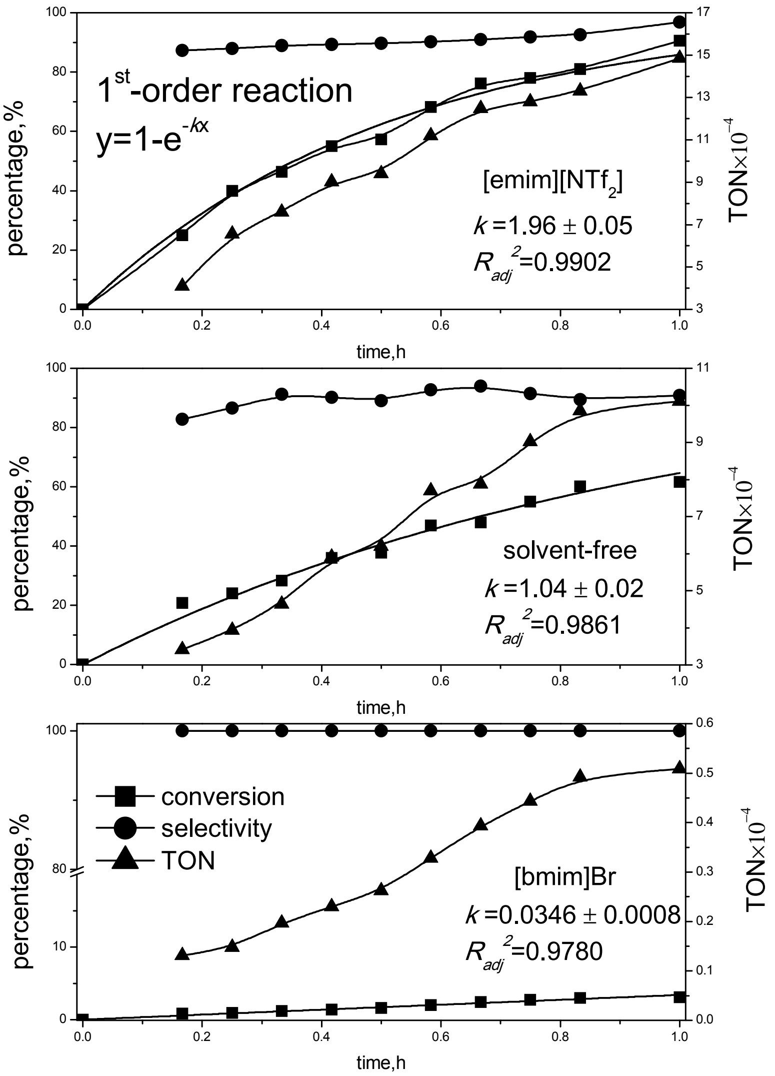


Fig. S1 Time course of 1-phenylethanol oxidation in different media. The conversion was connected by the trend line fitted based on the 1st-order kinetic model.

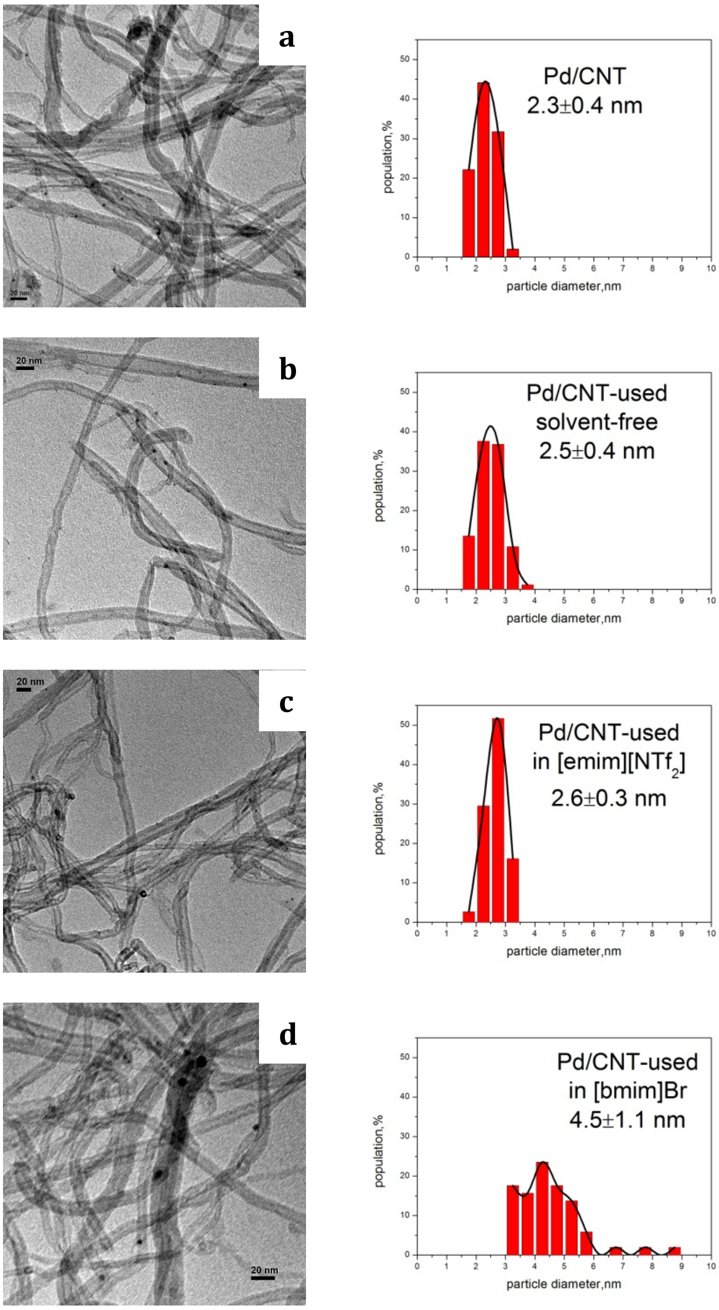
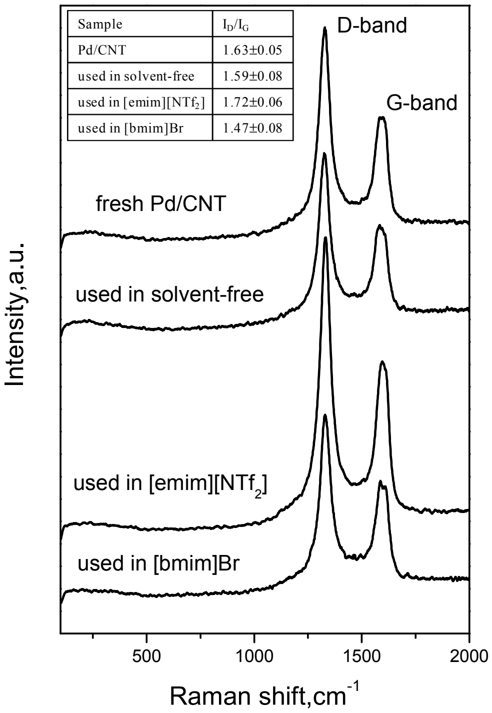


Fig. S2 TEM micrographs and size distributions: (a) fresh Pd/CNT; (b) Pd/CNT used under solvent-free condition; (c) Pd/CNT used in [emim][NTf$_2$]; (d) Pd/CNT used in [bmim]Br.



Sample	I_D/I_G
Pd/CNT	1.63±0.05
used in solvent-free	1.59±0.08
used in [emim][NTf$_2$]	1.72±0.06
used in [bmim]Br	1.47±0.08

Fig. S3 Raman spectra of fresh and used Pd/CNT catalysts.

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2. L. L. Fang, Q. A. Tao, M. F. Li, L. W. Liao, D. Chen and Y. X. Chen, *Chin. J. Chem. Phys.*, 2010, **23**, 543-548.
3. K. Mori, T. Hara, T. Mizugaki, K. Ebitani and K. Kaneda, *J. Am. Chem. Soc.*, 2004, **126**, 10657-10666.
4. Y. T. Chen, H. M. Lim, Q. H. Tang, Y. T. Gao, T. Sun, Q. Y. Yan and Y. H. Yang, *Appl. Catal. A: Gen.*, 2010, **380**, 55-65.
5. T. Welton, *Coord. Chem. Rev.*, 2004, **248**, 2459-2477.
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