Supported ionic liquid phase catalysis on functionalized carbon nanotubes†

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Highly active rhodium catalysts have been prepared by immobilization of an ionic liquid film on carbon nanotubes functionalized with imidazolium-based ionic moieties.

One of the main drawbacks in homogeneous catalysis concerns the difficulty in separating the reaction products from the soluble catalyst and any solvent. This problem becomes even more crucial when expensive noble metal based catalysts are involved. Furthermore, the use of distillation columns increases the energy consumption and often leads to catalyst degradation, increasing the overall cost of the process. Many alternative approaches have been attempted using supported homogeneous catalysts or biphasic systems.[1] One very attractive concept combines these approaches by immobilising the catalyst in a thin film of either water or an ionic liquid, absorbed within the pores of a high surface area solid.[2] When ionic liquids (ILs), green, non volatile solvents, are used as a supported phase (supported ionic liquid phase catalysts, SILPCs), long-term reactions have shown promising results.[3] Indeed, the ionic character of ILs confers to these media a spatial organization over several nanometres that induces peculiar solvation phenomena and specific reactivity, which can be linked either to confinement effects in these organized structures or to molecular interactions.[4,5] However, these solvents are expensive and supporting them should allow us to significantly reduce the volumes used. Moreover, this concept allows for a simple filtration step for liquid and solid recovery, and may contribute to catalyst stability (no metal leaching) compared to conventional supported homogeneous catalysis.[1] The use of SILPCs is thus one of the most elegant and efficient ways to solve the problem of catalyst recovery[6] that induces energy consumption *via* distillation, and to diminish the use of organic solvents that contribute considerably to volatile organic compounds' emissions. Up to now, most of the SILPCs have been prepared on oxide supports, and we believe that the use of carbon nanotubes (CNTs) should offer significant advantages such as: (i) high catalytic activities arising from the mesoporous nature of these supports that avoids mass transfer limitations; increases in activity of up to 100% have been reported for metal supported on CNTs systems;[7] (ii) high activity/selectivity due to the possibility to operate in the inner cavity of carbon nanotubes (confinement effect); a recent report has shown an increase in activity of more than one order of magnitude when CNTs are used as a support;[8] (iii) these supports exhibit a well defined and tunable structure;[9] and (iv) the possibility to build a micro-reactor by selective growth of nanocarbons by catalytic chemical vapour deposition (C-CVD) on defined substrates.[10]

Herein we report on the preparation of rhodium based SILPCs using high purity multi-walled carbon nanotubes (MWCNTs) as a support. The synthetic route involves two steps: (i) external surface functionalization of MWCNTs to improve their compatibility with and dispersion in ionic liquids, and (ii) rhodium complex immobilization in the IL film. In addition, our experimental results show that the [Rh/IL]/CNT system exhibits high stability and more catalytic efficiency for 1-hexene hydrogenation than SILPCs prepared on oxide supports, including silica support.

One major drawback of CNTs is their difficult processability/dispersibility linked to the inert and apolar character of their surface, and so very often covalently modified CNTs should be used.[11] Three types of CNTs and 1-butyl-3-methylimidazolium hexafluoro-phosphate ([bmim][PF_6]) as the IL have been used here for SILPC preparation. The first type of MWCNTs consists of a high purity material (>95%, <5% remaining iron particles encapsulated in CNTs, determined by TGA and ICP) without external functionalization. These CNTs, named CNT0, have been prepared by C-CVD.[12] The second type of CNTs, named CNT1, results from CNT0 functionalization by nitric acid treatment (12 g CNT0, 500 mL HNO_3 at 37%, 140 °C, 8 h), and polar hydrophilic surface groups, mainly –COOH groups but also carbonyl, quinones and phenol, are present on its surface.[13] The surface –COOH groups concentration is 0.85 COOH nm^{-2}, as determined from chemical titration and CNT specific surface area measurements.[14] To prepare the third type of CNTs, named CNT2, CNT1 was successively treated with thionyl chloride, a controlled amount of imidazole, butyl bromide and finally potassium hexafluorophosphate (Scheme 1).[15] The aim of this treatment, which does not affect MWCNT morphology, is the covalent modification of the CNTs with imidazolium-based ionic functionalities. Increasing amounts of imidazolium groups lead to the production of CNT2a, CNT2b and CNT2c materials (Table 1). The efficiency of surface functionalization has been checked by IR and XPS spectroscopies, elemental analysis and TGA. Compared to CNT0, CNT1s are distinguished by their slightly larger specific surface area due to the opening of some MWCNTs, and by the

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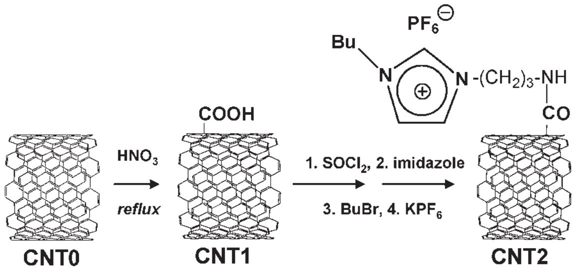

Scheme 1 Surface functionalization of CNTs with imidazolium-based ionic groups.

presence of significant amounts of oxygen containing surface groups. It is noteworthy that during this aggressive oxidative treatment a carbon burn-off of 7.7% has been measured by weighing and confirmed by TGA and elemental analysis (Table 1). The IR spectrum of CNT1 shows, besides the band due to the CNTs' skeletal in-plane vibration at 1570 cm^{-1}, two bands at 1717 cm^{-1} (C=O vibration) and at 1200 cm^{-1} (C–O stretching) attributed to the carboxylic groups.[16] For CNT2, the effective grafting of the imidazolium functionalities onto the CNT surface is confirmed by the presence of the amide band at 1641 cm^{-1}, the aliphatic C–H stretching bands located between 2850 and 2950 cm^{-1}, bands at 1250–1500 cm^{-1} assigned to C–H bendings,[17] and the intense stretching vibration ν(P–F) bands of $[PF_6]^-$ at 830 cm^{-1} (see ESI†). For the less functionalized samples CNT2a and CNT2b, the band at 1717 cm^{-1} could be still observed, indicating the presence of COOH groups. The bulk-quantitative (elemental analysis) and surface-semiquantitative (XPS) analysis confirm the CNT functionalization, and show that the amount of imidazolium-based ionic functionalities can be controlled. TGA analyses (see ESI†) under air show that the imidazolium-based ionic functionalities are less stable than the pure [bmim][PF_6], the decomposition temperature being 425 °C for the pure IL and310 °C for the grafted species. Similarly, the surface functionalization has an effect on CNT thermostability since for all CNT2s the temperature of maximum gasification rate is 750 °C whereas for CNT0 it is 640 °C. The dispersibility of MWCNTs in [bmim][PF_6] is clearly improved upon surface functionalization (see ESI†) and follows the following trend: CNT2 > CNT1 ≫ CNT0.

To prepare the SILPCs, 200 mg of support were contacted for 18 h with a solution of $[Rh(nbd)(PPh_3)_2][PF_6]$ (10 mg, 1.39×10^{-2} mmol) and [bmim][PF_6] (50, 150, 250 or 350 mg, corresponding to 20, 37, 55 or 64% w/w) in 15 mL of acetone at 20 °C; acetone was removed under vaccum. The CNTs supported ionic liquid phase composites (CNT*x*–SIL(y% w/w)), similarly prepared but without Rh, have been characterized by TEM, TGA and XRD.

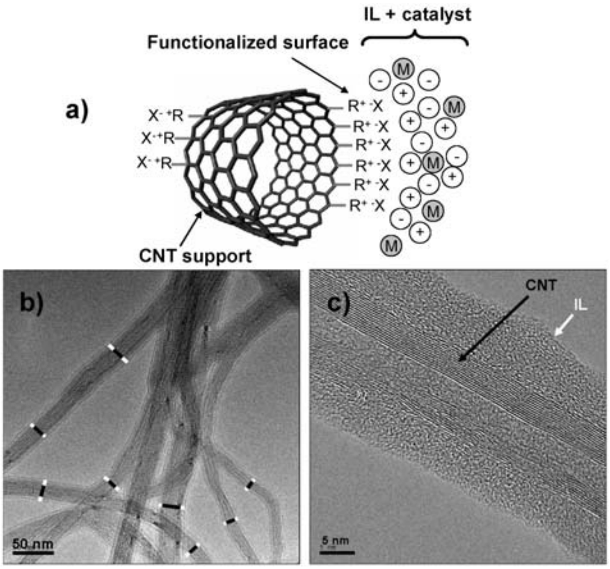

Fig. 1 (a) Schematic representation of SILPC, (b) TEM, white bar: IL film, black bar: CNT and (c) HRTEM micrographs of CNT2b–SIL(55%).

The effective grafting of an ionic liquid film on CNT2 walls, producing CNT–SILs samples, could be observed by TEM and HREM micrographs (Fig. 1). The thickness of the [bmim][PF_6] film depends on the amount of IL, and for CNT2b–SIL(55%), the film shows a mean thickness of 3.3 nm (1 nm < thickness < 10 nm). Thus, the mean CNT diameter shifts from 10.5 nm for CNT0 to 17.1 nm for CNT2b–SIL(55%) (see ESI†). TGA confirms the presence of the [bmim][PF_6] film on the MWCNT surface; the thermostability of these films is lower than that of pure IL, since the [bmim][PF_6] film decomposes between 340 °C and 360 °C, depending on the film thickness, in contrast to 425 °C for pure IL (see ESI†). The influence of IL–CNT interaction on IL film thermostability is not yet clear and remains to be solved. The degree of functionalization by ionic moieties also has an influence on the texture of the CNT–SILs produced. Therefore, CNT2a and CNT2b in the presence of different IL amounts, are always obtained as powders. On the contrary, CNT2c, which presents the highest concentration of ionic groups, containing ≥ 250 mg of [bmim][PF_6] (CNT2c–SIL(55%)), is a gel. This phenomenon has already been reported for CNTs mixed with imidazolium-based ILs, leading to gels, often called bucky gels, of ILs.[18] The gels can be formed either by physical CNT bundles cross-linking, mediated by local molecular ordering of the ILs or by CNT entanglement. If such gels can find promising applications as soft materials for electrochemical applications,[19] for SILPC their formation should be avoided since it induces low catalytic activity due to a poor

Table 1 Elemental and XPS analyses of functionalized CNT materials

	wt% (elemental analysis)				Atomic % (XPS)			
MWCNT	C	H	N	O	C	O	N	F
CNT0[a]	95	0.16	0	0.64	100	—	—	—
CNT1[b]	87.3	0.3	0.15	5.3	92.4	7.6	—	—
CNT2a[c]	88.66	0.7	1.51	—	89.5	4.2	1.8	4.6
CNT2b[c]	82.6	1.5	1.85	7.5	82.7	10.3	1.8	5.2
CNT2c[c]	80.85	1.26	2.69	—	82.5	7.2	3.0	7.3

[a] CNT0: $S_{BET} = 227\ m^2/g$, 7 nm < $\varnothing_{ext.}$ < 20 nm, $\varnothing_{mean.}$ = 10.5 nm, 3 nm < $\varnothing_{int.}$ < 11 nm, pore volume: 0.67 cm^3/g. [b] CNT1: $S_{BET} = 244\ m^2/g$, pore volume: 0.89 cm^3/g. [c] CNT1 functionalized with imidazolium-based ionic groups.

contact between the catalyst, the gas and the liquid phases (*vide supra*). The XRD patterns of CNTx–SIL samples (see ESI†) show the peaks of MWCNTs at $2\Theta = 30.37°$ ($d_{002} = 3.37$ Å) and $50.21°$ ($d_{100} = 2.09$ Å) and broad peaks at $2\Theta = 16.54°$, 22.28° and 24.30° distinctive of the amorphous IL phase. No characteristic peak of a transition of [bmim][PF_6] from liquid to high melting point crystal due to confinement in the CNT cavity was observed.[20]

The catalytic activity of SILPCs ([Rh] = 1.39×10^{-5} mol) was evaluated for the hydrogenation of 1-hexene (0.04 mol) in heptane (55 mL) at 40 °C under 25 bar of hydrogen.

First, we have demonstrated the importance of CNT functionalization on the performances of SILPCs. Indeed, after 2 h reaction, although Rh/CNT0–SIL and Rh/CNT2–SIL allow a complete conversion (determined by GC), for Rh/CNT0–SIL a severe IL and Rh leaching was observed, whatever the IL concentration (20 to 64% w/w). Neither IL nor Rh leaching was observed for Rh/CNT2–SIL. For Rh/CNT1–SIL, the conversion was not complete (~60%) and IL/Rh leaching was also noticed. Thus, surface functionalization of the CNT is important for the design of stable and recyclable catalysts. Then, we have evaluated the optimum amount of grafted immidazolium groups on the CNT surface. For CNT2a and CNT2b, the activity was markedly better than that for CNT2c, this latter giving a lower activity whatever the amount of added IL (20 to 64% w/w). This should be induced by the poor dispersibility of CNT2c-SIL and thus low surface of contact (gel formation). The CNT2a support was chosen in order to evaluate the influence of the IL loading on the catalytic activity of the SILPCs. The optimum value was clearly reached between 37 and 55% of IL w/w, the TOF being 1270, 2880, 2550 and 1140 h^{-1} for 64%, 55%, 37% and 20% IL w/w, respectively. We compared the catalytic activity of the Rh/CNT2a–SIL(55%) catalyst with that of SILPCs prepared on a large variety of supports (see Fig. 2). For Al_2O_3 ($S_{BET} = 155\ m^2\ g^{-1}$), TiO_2 ($S_{BET} = 75\ m^2\ g^{-1}$), ZrO_2 ($S_{BET} = 31\ m^2\ g^{-1}$), MgO ($S_{BET} = 130\ m^2\ g^{-1}$) and ZnO ($S_{BET} = 20\ m^2\ g^{-1}$), the optimal IL concentration was 20%, beyond this value the formation of soft pastes induces a drastic decrease of the catalytic activity. For silica (SiO_2, Crossfield EP100, $S_{BET} = 315\ m^2\ g^{-1}$, pore volume = $1.80\ cm^3\ g^{-1}$) and activated carbon ($S_{BET} = 705\ m^2\ g^{-1}$), similar conversions were obtained whatever the IL loading (20 to 55% w/w). It is clear from Fig. 2 that the Rh/SILPCs prepared with CNT2a show much better performances than SILPCs supported on oxide supports, including SiO_2 or activated carbon. Indeed, Rh/CNT2a–SIL(55%) showed more than twice the catalytic activity of Rh/SiO_2–SIL. This result is probably related to the very open structure of MWCNT aggregates that facilitates mass transport and improves the kinetics. The highest selectivity towards *n*-hexane was obtained on SiO_2, followed by Rh/CNT2a–SIL(55%); significant isomerization being observed on activated carbon and TiO_2 supports. Rh/CNT2a–SIL(55%) catalyst was reused five times without any loss of catalytic activity, and the selectivity towards *n*-hexane was found to increase up to 100% after the second cycle. The level of leached Rh was below the detection limit and the isolated organic phase did not show any reactivity.

In summary, rhodium based SILPCs have been prepared using MWCNTs functionalized with imidazolium-based ionic groups as a support. The control of the degree of surface functionalization as well as the thickness of the IL film avoids the formation of bucky gels, inappropriate for catalytic purposes. We demonstrated the importance of CNT surface functionalization on the performances of SILPCs for the hydrogenation of 1-hexene, since the use of unfunctionalized supports induces severe leaching of the IL film. The Rh/CNT2a–SIL(55%) catalyst presents a significant higher activity than SILPCs supported on oxide supports, including silica or activated carbon, with full retention of the Rh/IL active phase upon recycling.

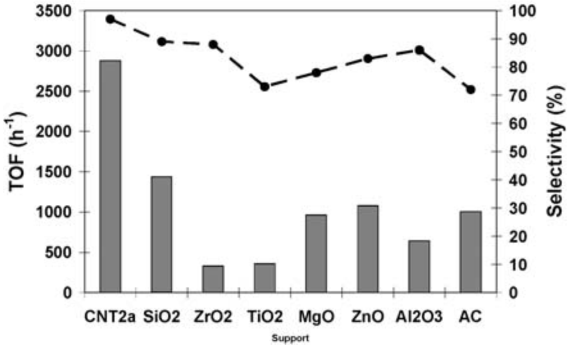

Fig. 2 Hydrogenation of 1-hexene using Rh/SILPCs.

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