

NON-COVALENTLY FUNCTIONALIZED MULTIWALLED CARBON NANOTUBES AS NOVEL ACTIVE AND REUSABLE ACID CATALYSTS

J. Souquet-Grumey¹, H. Plaisantin², J. Thébault², F. Jérôme¹,
J. Barrault¹, J.-M. Tatibouët¹, S. Valange¹

¹ LACCO, University of Poitiers-CNRS, ESIP, 40 Av. Recteur
Pineau, Cedex, F-86022, Poitiers, France

² Snecma Propulsion Solide (SPS), 33187 Le Haillan, France

Introduction

Since the discovery of carbon nanotubes (CNTs) in 1991 by Iijima [1], they have attracted considerable attention because of their unique electronic, thermal and mechanical properties that make them valuable materials for a variety of applications, including nanocomposites, gas storage materials, electronics and chemical sensors. Moreover, their intrinsic properties along with their high surface area make them promising supports for a variety of advanced heterogeneous catalytic systems [2]. However, as CNTs are relatively chemically inert, it is necessary to activate their graphitic surface in order to use them as catalyst supports for metallic nanoparticles or organometallic complexes, as well as for the anchoring of acidic or basic functional groups. As compared to covalent surface modification of CNTs based on traditional harsh oxidative methods, such as refluxing in concentrated mixtures of H₂SO₄ and HNO₃ [3-4], non-covalent functionalization has the benefit of preserving the π - π electronic structures of the outer CNT surface. This strategy includes wrapping of CNTs with polymers [5], as well as modification of the CNTs graphene layers through π - π stacking with imidazolium ionic liquids or aromatic units as stabilizers to produce metal nanoparticles [6-7]. This contribution reports for the first time on a versatile and general strategy for the immobilization of acidic catalytic centers on the surface of carbon nanotubes in one step. More precisely our aim consisted in the non-covalent modification of CNTs surface through π - π stacking with pyrene moieties that already contain the acidic functional groups and in evaluating the catalytic properties of that solid acid carbon-based nanomaterial in fine chemistry reactions. In this work, the adsorption of 1-pyrenesulfonic acid (PSA) was carried out over the surface of the CNTs (Fig. 1) and the performances (activity and stability) of the resulting functionalized acid/CNT catalyst were determined in the Michael reaction of indole with trans β -nitrostyrene (Fig. 2).

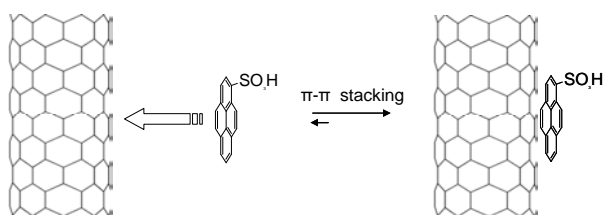


Fig. 1 Immobilization of PSA over the surface of MWCNT.

Such reaction gives access to the 3-alkylated indole derivatives which constitute an important class of compounds that display diverse pharmacological activities.

This approach based on the direct interaction of CNTs with pyrene moieties with terminal groups (-SO₃H) acting as catalytic acid sites opens a new way to be explored for performing heterogeneous catalytic reactions.

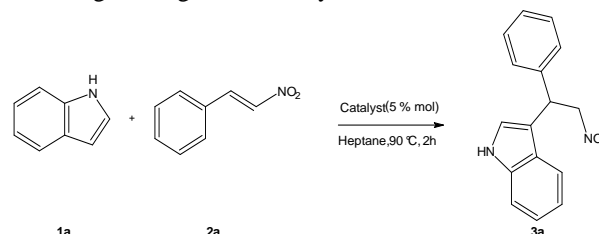


Fig. 2 Michael reaction of indole with trans β -nitrostyrene.

Experimental

The non-covalent functionalization of carbon nanotubes was carried out by mixing the MWCNT support (1g) with 1-pyrenesulfonic acid (100 mg, 10% wt) in ethanol (100 mL). The resulting mixture was bath-sonicated during 30 min at room temperature. The solvent was then evaporated under vacuum and the catalysts were dried under vacuum at 40°C for 24 h. 1-pyrenesulfonic acid (PSA) was also supported on the surface of coal (PSA/Vulcan XC72), as well as on non porous silica (PSA/SiO₂) and used for comparison.

The catalytic reaction was conducted at atmospheric pressure in a Pyrex reactor equipped with a magnetic stirrer. Indole (1.0 mmol), trans- β -nitrostyrene (1.0 mmol) and the PSA-based catalyst (5% mol) were mixed in heptane (2.5 mL) under air and stirred at 90 °C. At the end of the reaction, the products were extracted two times with ethyl acetate/heptane (1:3), diluted with ethyl acetate and washed with NaOH solution. The crude products were then purified by silica column chromatography and their purity checked by NMR.

Results and Discussion

PSA was found to be strongly adsorbed on the surface of the investigated supports (CNTs, Vulcan, silica) in non polar solvents. Among all the solvents tested, heptane led to the highest adsorption of 1-pyrenesulfonic acid onto these solids, as confirmed by NMR quantification. As the solubility of the reaction products was poor in heptane, a more polar mixture containing ethyl acetate and heptane (1:3) was used for the extraction of the products at the end of the catalytic reaction. However, by contrast to the silica and coal supports for which a high PSA desorption was observed (26 and 12%, respectively), NMR data revealed that the amount of desorbed PSA was as low as 0.7%, confirming the strong interaction of PSA with the CNTs graphene layers through π - π stacking.

In order to compare the catalytic properties of the CNT and coal supported PSA solids, the amount of catalyst in the reactor was adjusted in each case, so that the content of proton exchange sites was the same in all systems.

As shown in Table 1, when the reaction was performed in the absence of catalyst, no reaction occurred. After 2h of reaction at 90°C, Vulcan XC72-SO₃H and Vulcan XC75-PSA afforded the corresponding 3-alkylated indole with 66% and 75% yield, respectively.

Table 1. Heterogeneous Michael reaction over different type of solid acid catalysts.

Entry	Catalyst	TOF (h ⁻¹) ^c	Yield after 2h (%)
1	MWCNT-PSA ^(a)	25.3	88
2	PSA	25	83
3	Vulcan XC72-PSA ^(a)	17.9	75
4	Vulcan XC72-SO ₃ H ^(b)	9.6	66
5	No catalyst	-	<1

Proton exchange capacity: ^{a)} 0.35 mmol g⁻¹ ^{b)} 0.8 mmol g⁻¹. ^{c)} determined after 10 min of reaction (conversion <20%).

To our delight, we found that MWCNT-PSA was far more active (TOF = 25.3 h⁻¹) than the carbonaceous Vulcan XC75-PSA catalyst (TOF = 17.9 h⁻¹), affording the desired product with 88% yield. Such difference of behavior might come from the highly hydrophobic nature of MWCNTs surface with their unique π -conjugated system which favors a better approach of the aromatic based reagents (indole and trans β -nitrostyrene). The high activity of the CNT material can therefore be attributed to the very high dispersion of 1-pyrenesulfonic acid over the carbon nanotubes surface.

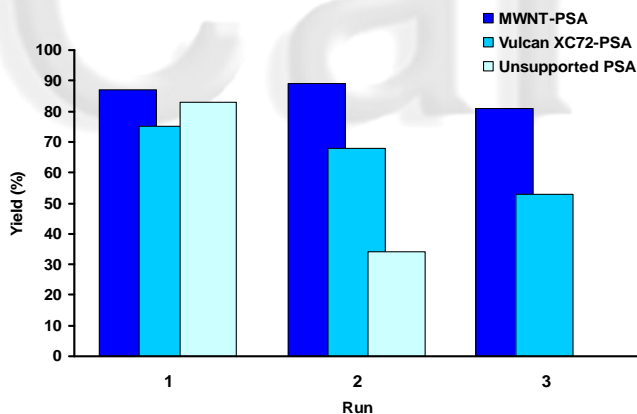


Fig. 3 Catalytic recycling over CNT and Vulcan supported PSA and over free PSA after 2h of reaction at 90°C.

To prove the efficiency of the various supported PSA catalysts, a series of three tests was performed. At the end of the reaction, the reaction mixture was centrifuged and the recovered catalyst was reintroduced inside the reactor without washing. The results reported in Fig. 3 showed that the activity of the non-supported 1-pyrenesulfonic acid decreased considerably during the second cycle of reaction (only 34% yield). This could indicate either that the free PSA was partially removed from the reaction mixture during the

products extraction procedure after the first cycle, either that it was damaged in the course of the catalytic reaction.

A significant drop of yield was still observed after three runs (75 to 53%) when immobilizing PSA on Vulcan (VulcanXC72-PSA). By contrast, after three cycles of reaction, the catalytic activity of MWCNT supported 1-pyrenesulfonic acid was almost unchanged since the yield was above 81% (compared with 88% after the first run), thereby confirming that PSA/MWCNT is a very stable and reusable catalyst. Such phenomenon obviously stems from the hydrophobic nature of the carbon nanotubes, as well as from the strong interaction of PSA with the CNTs graphene layers through π - π stacking. This effect is far more pronounced in that case than when PSA is supported on Vulcan.

On the course of our work, we next investigated the scope of the PSA/MWCNT catalyst in the Michael reaction. Various indole (i.e. 2-methylindole, 5-bromoindole, 5-methoxyindole, ...) and nitrostyrene (4-hydroxy- β -nitrostyrene, ...) derivatives were successfully converted with 82–95% yield.

Conclusions

By contrast to less straightforward covalent chemical routes, our approach is based on a non-covalent functionalization with aromatic sulfonic acid through π - π interactions in order to prepare a reusable acid/CNT catalyst. This method is non-destructive and very simply to handle. Strongly adsorbed acidic functional groups on the CNT surface were generated and proved particularly active in Michael reaction whatever the indole and nitrostyrene degree of substitution. Moreover compared with the unsupported counterpart or with functionalized active coal, for which a high leaching level was observed, this novel acid/CNT catalyst is stable, which is also a crucial property in catalysis.

Acknowledgment. This work was supported by the French Ministry of Economy, Finance and Industry under the NACOMAT consortium (062906227).

References

- [1] Iijima S. Helical microtubules of graphitic carbon. *Nature* 1991;354:56-58.
- [2] Andrews R, Jacques D, Qian D, Rantell T. Multiwall carbon nanotubes: synthesis and application. *Acc. Chem. Res.* 2002;35:1008-1017.
- [3] Yu H, Jin Y, Peng F, Wang H, Yang J. Kinetically controlled side-wall functionalization of carbon nanotubes by nitric acid oxidation. *J. Phys. Chem. C* 2008;112:6758-6763.
- [4] Pompeo F, Resasco D. E. Water Solubilization of Single-Walled Carbon Nanotubes by Functionalization with Glucosamine. *Nano Lett.* 2002;2:369-373.
- [5] Tasis D, Tagmatarchis N, Bianco A, Prato M. Chemistry of Carbon Nanotubes. *Chem. Rev.* 2006;106:1105-1136.
- [6] Georgakilas V, Tzitzios V, Gourmis D, Petridis D. Attachment of Magnetic Nanoparticles on Carbon Nanotubes and Their Soluble Derivatives. *Chem. Mater.* 2005;17:1613-1617.
- [7] Wu B, Hu D, Y. Kuang Y, Liu B, Zhang X, Chen J. Functionalization of Carbon Nanotubes by an Ionic-Liquid Polymer. *J. Angew. Chem. Int. Ed.* 2009; 48:4751-4754