

## Nitrogen-functionalized carbon nanotubes as a basic catalyst for biomass conversion reactions.

Jean-Philippe Tessonnier\*, Alberto Villa, Olivier Majoulet, Dangsheng Su and Robert Schlögl  
Fritz Haber Institute of the Max Planck Society, Berlin, D-14195 (Germany)  
\*tesso@fhi-berlin.mpg.de

### Introduction

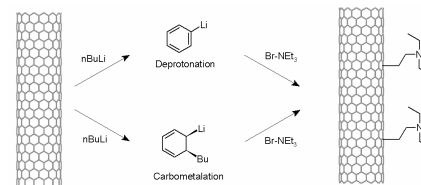
Biomass conversion to transportation fuels and chemicals is a growing field of research due to the depletion of fossil fuels feedstock. New catalysts, optimized for carbohydrates conversion, need to be developed. In this context, basic heterogeneous catalysts will play a major role for dehydration, hydrolysis, (trans)esterification, aldol condensation, alkylation or isomerization reactions for example. In contrast to existing basic heterogeneous catalysts, MWCNTs-based catalysts are chemically stable (no leaching) and relatively easy to tailor on a nano- and macro-level (controlled porosity). Therefore, nitrogen-functionalized multiwalled carbon nanotubes (N-MWCNTs) appear to be a promising basic catalyst and catalyst support [1,2]. Unfortunately, the nitrogen concentration, its location in/on the nanotube and the nature of the formed N-containing functional groups are difficult to control by common synthesis techniques like by catalytic chemical vapor deposition (CCVD) or by post-treatments [3]. In addition, it is still unclear which functional groups are required to reach high catalytic activities. Thus, we synthesized N-MWCNTs catalysts by grafting desired N-containing molecules on the MWCNTs' surface. In order to avoid the drawbacks of the traditional  $\text{SOCl}_2$  route, a new procedure has been designed. The obtained catalysts have been tested in the transesterification of glyceryl tributyrates, as a model triglyceride for biodiesel synthesis

### Materials and Methods

Typically, 2 g of MWCNTs (Nanocyl, Belgium) were suspended in dry diethylether. Butyllithium (BuLi) was added and the mixture was stirred for 5h. An halogenated nitrogen-containing compound, e.g. 2-bromo-N,N-diethyl-ethylamine, was then added and allowed to react for 1.5h. The resulting solid was finally filtrated and thoroughly washed with methanol. A catalyst was also prepared using the traditional  $\text{SOCl}_2$  route for comparison [4]. The catalytic tests were performed at 333K with 2 wt.% catalyst (relative to the triglyceride) and with a methanol to triglyceride ratio of 12. A commercial hydrotalcite activated at 623K for 6h was used as reference.

### Results and Discussion

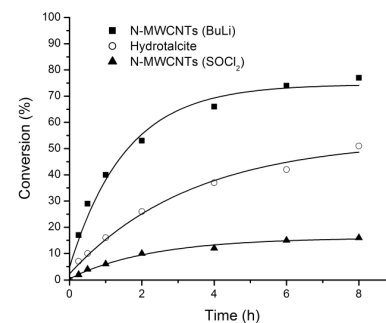
Grafting of molecules on MWCNTs is typically carried out in 3 successive steps. The nanotubes are first oxidized with nitric acid to create surface carboxylic acid groups. These groups are further activated by acylation with  $\text{SOCl}_2$  and the desired molecules are finally grafted by amidation. Although this procedure is very popular, we found that it suffers several drawbacks for further application in heterogeneous catalysis. SEM and TEM showed that the grafted amine wrapped and filled the nanotubes, thus leading to a 50% loss in the specific surface area. In addition, the amine was found to be mainly adsorbed and not chemically bonded to the nanotube surface. Thus, the active sites were progressively lost when recycling the catalyst. The sample also contained many impurities like S and Cl. In order to circumvent



**Figure 1.** Schematic view of our synthesis procedure with BuLi.

these drawbacks, we developed a procedure to directly graft the desired basic molecules by C-C coupling. The surface of the nanotubes was first activated by deprotonation and/or carbometallation with n-butyllithium (nBuLi). The amine was then anchored by electrophilic attack as shown in Figure 1. BET, Raman, SEM and HRTEM revealed that the initial structure of the MWCNTs was preserved. XPS and

acid/base titrations confirmed that the desired groups were anchored to the surface. Titrations led to a basic site concentration of 1 mmol.g<sup>-1</sup>. TG-MS analysis did not show any weight loss below 400K. In addition, 60% of the anchored groups were stable up to 843K. The transesterification of glyceryl tributyrates was used as a model reaction for biodiesel synthesis. The catalytic tests (Figure 2) show that the activity of the N-MWCNTs samples is strongly influenced by the synthesis procedure. The catalyst prepared via the  $\text{SOCl}_2$  route deactivates rapidly due to the leaching of the amino groups and therefore it cannot be regenerated. In contrast, the catalyst prepared via the BuLi route exhibits a higher activity than hydrotalcite, which is a reference catalyst for this reaction. Analysis by TG-MS of the solution after reaction does not show any amine, thus meaning that the active sites are not lost during the reaction. In this case, the catalyst could be regenerated by simple washing with methanol.



**Figure 2.** Catalytic results obtained with the reference hydrotalcite and the different N-MWCNTs samples.

### Significance

The developed nitrogen-grafting procedure leads to very active and stable heterogeneous catalysts for biodiesel synthesis. Similar catalysts should be applicable for a wide range of biomass conversion reactions. In addition, model single-site N-MWCNTs catalysts, as synthesized in the present work, will deliver precious information to understand the chemistry of carbohydrates as well as to optimize N-MWCNTs obtained by scalable techniques, e.g. CCVD or post-treatments.

### References

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