

DEFECT MEDIATED FUNCTIONALIZATION OF MULTIWALLED CARBON NANOTUBES: A NOVEL ROUTE TO DESIGN BASIC HETEROGENEOUS CATALYSTS FOR THE SYNTHESIS OF FUELS AND CHEMICALS FROM BIOMASS

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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]. 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 [2]. 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 SOCl_2 route, a new procedure has been designed. The obtained catalysts have been tested in the transesterification of glyceryl tributyrate, as a model triglyceride for biodiesel synthesis

Experimental

Typically, 2 g of MWCNTs (Nanocyl, Belgium) were suspended in 400 ml dry diethylether. 20 ml n-butyllithium (2.5 M in hexane) was added and the mixture was stirred for 4 h at room temperature. $5 \cdot 10^{-2}$ mol of an halogenated nitrogen-containing compound, e.g. 2-bromo-N,N-diethyl-ethylamine, was then added and allowed to react for 1.5 h at 308 K. The resulting solid was finally filtrated and thoroughly washed with methanol. A catalyst was also prepared using the traditional SOCl_2 route for comparison [3]. Catalytic tests were performed in a thermostated glass reactor (30 ml) with samples withdrawn periodically for analysis. A commercial hydrotalcite activated at 623 K for 6 h was used as reference. The reaction was carried out at 333 K, with a methanol to glyceryl tributyrate molar ratio of 12:1 and with a stirring rate of 1200 rpm. The catalyst concentration was 2 wt.% based on the glyceryl tributyrate weight. The quantification of the

products was performed using an Agilent 6890N gas chromatograph equipped with a HP-5 column and FID detector. GC-MS was used for identification of the products. For the recycling experiments, the catalyst was recovered after each cycle by simply decanting the reaction solution. In order to identify species leached from the catalysts during the reaction in liquid phase, the solution after reaction was analyzed using GC-MS. Details about the various techniques employed to characterize the catalysts can be found elsewhere [4-6].

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 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 or weakly 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 these drawbacks, we developed a procedure to directly graft the desired basic molecules by C-C coupling. Commercial MWCNTs exhibit many structural defects such as vacancies for instance (observed by HRTEM and Raman spectroscopy). Most carbon atoms located near defects are saturated with hydrogen. Therefore, there is a relatively high concentration of C-H bonds which can be employed to graft desired molecules onto the MWCNTs. The surface of the nanotubes was first activated by deprotonation and/or carbometalation with n-butyllithium (nBuLi). The amine was then anchored by electrophilic attack as shown in Fig. 1 [4].

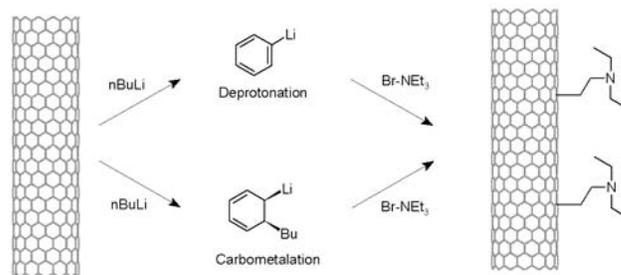


Fig. 1 Schematic view of our synthesis procedure with BuLi.

BET, Raman, SEM and HRTEM revealed that the initial structure of the MWCNTs was preserved. As expected, grafting occurred only on existing defects. Additional defects were not created during the synthesis. 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⁻¹. TG-MS analysis did not show any weight loss below 400 K. In addition, 60 % of the anchored groups were stable up to 843 K.

The transesterification of glyceryl tributyrate was used as a model reaction for biodiesel synthesis. The catalytic tests (Fig. 2) show that the activity of the N-MWCNTs samples is strongly influenced by the synthesis procedure. The catalyst prepared via the SOCl₂ route deactivates rapidly due to the leaching of the amino groups, and therefore it cannot be regenerated. N-MWCNTs synthesized by CCVD also exhibit a poor activity. CCVD leads to relatively high concentrations of nitrogen-containing groups. However, the nitrogen is mainly involved in pyrrolic and pyridinic groups which are only weakly basic. Although it was demonstrated that CCVD N-MWCNTs catalyze condensation reactions [1], they only show a modest activity for more demanding reactions such as biodiesel synthesis. 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.

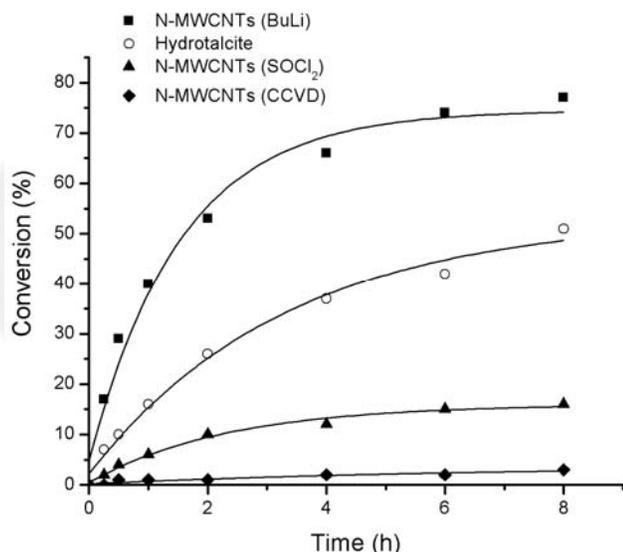


Fig. 2 Triglyceride conversion as a function of time for N-MWCNTs synthesized by grafting (BuLi and SOCl₂) and by CCVD, as well as for a reference hydrotalcite.

N-MWCNTs synthesized via the BuLi route lead to a maximum conversion of 77 % under standard reaction conditions (333 K, triglyceride to methanol ratio 1:12). The deactivation observed is due to the strong adsorption of the triglyceride on the lipophilic walls of the MWCNTs, thus encapsulating the active sites. However, it is possible to avoid this phenomenon by raising the temperature or increasing the methanol concentration [6]. For example, full conversion was reached in only 2 h when the reaction is performed at 363 K (Fig. 3). Similarly, a deactivation is observed when recycling the catalyst. However, HRTEM and GC-MS analysis demonstrated that it is a result of the strong triglyceride

adsorption inside the MWCNTs, thus blocking the internal channel. A simple washing with methanol between each cycle completely regenerates the catalyst (Fig.3).

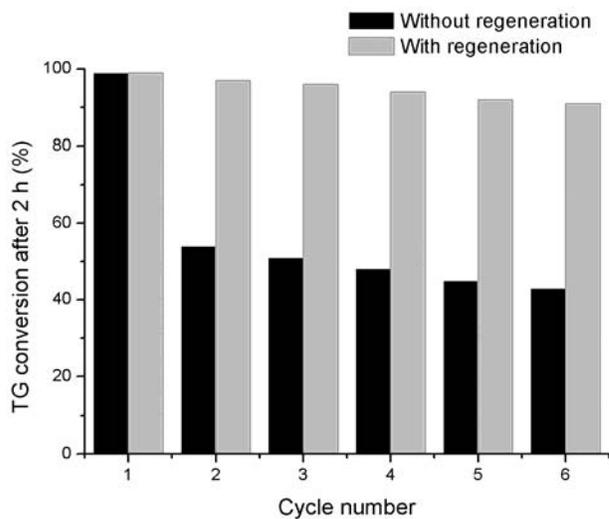


Fig. 3 Recycling tests performed with N-MWCNTs (BuLi) at 363 K. The catalyst can be regenerated by simple washing with methanol.

Conclusions

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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