

Amino-functionalized carbon nanotubes as solid basic catalysts for the transesterification of triglycerides†

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Multiwalled carbon nanotubes grafted with various amino groups show high activity and stability when used as basic catalysts for the transesterification of triglycerides.

The decline of fossil fuel energy resources is the driving force in the development of new alternative sustainable energy sources. Biomass could be a suitable solution, as it is the only accessible non-fossil source of carbon and can serve as a sustainable resource of renewable fuels and chemicals.^{1–4} Biomass feedstocks can be classified into three general groups: lignocellulose, carbohydrates and triglycerides. Various reactions are involved in the transformation of biomass, such as depolymerization, dehydration, isomerization and transesterification.⁵ The classical heterogeneous basic catalysts used for biomass conversion include alkaline earth oxides, calcined hydrotalcites and nano-MgO.^{6–8} However, these catalysts show various drawbacks, for instance small surface area and partial dissolution into the reaction media. Therefore, much effort has to be exerted in the development of new basic heterogeneous catalysts which show a high stability during the liquid phase reaction.

During the last few years, functionalized carbon nanotubes (CNTs) have attracted much attention. The physical and chemical properties of nitrogen-doped CNTs (N-CNTs) are modified compared to conventional CNTs due to the incorporation of nitrogen in the basal planes and defects of the CNTs.^{9–13} Several synthesis methods of nitrogen-doped carbon materials have been reported, including sputter deposition, graphitization of nitrogen-containing polymers, and grafting desired functional groups onto their surface.^{14–17} Bitter *et al.* reported the preparation of basic nitrogen containing CNTs by chemical vapour deposition. The good activity in the Knoevenagel condensation is related to the amount of pyridinic nitrogen incorporated in the CNTs structure.¹⁸ Furthermore, different groups reported the preparation of amino grafted CNTs, modifying their solvation properties.^{19–22} The resulted N-CNTs can lead to important platforms and devices for drug delivery and biosensor applications. However, to the best of our knowledge, applications of amino-grafted CNTs as solid basic catalysts have not been reported yet. In this communication we report a new methodology for the

preparation of amino-functionalized CNTs. The resultant N-CNTs have been used as solid basic catalysts for the transesterification of triglycerides. In a first step, the CNTs are reacted with *n*-butyllithium (*n*BuLi) in excess, then in a second step, bromo amino derivatives are added to the activated CNTs to form the corresponding N-CNTs.²³ Three catalysts were prepared by grafting three different amines (triethylamine, ethylamine and pyrrolidine, denoted as Et₃-CNT, EtNH₂-CNT and C₄H₉N-CNTs) with the aim to correlate the different basicity of the amines to the catalytic activity. These catalysts were tested in the transesterification of glyceryl tributyrates, a model reaction to evaluate their basicity. In particular the aim was to show the stability of the anchored groups during liquid-phase reactions. All the catalysts have been analyzed by ICP in order to demonstrate the total absence of Li on the catalyst and to study the single effect of the grafted amines on the activity of the catalyst.

TG-MS measurements and acid–base titrations were performed in order to study the thermal stability of the catalysts and to quantify the anchored groups.

Table 1 shows a comparison between the thermal stability of the catalysts and the boiling point of the corresponding amines. The TG-MS data show that the catalysts are stable at a temperature higher than the boiling point of the corresponding amines, thus proving that the amino groups were successfully anchored on the CNTs.

The basic properties and the amount of accessible basic sites were characterized by acid–base titration with HCl as titrant (Table 1). The generated pH values of the functionalized CNTs were 10.30, 10.15 and 9.5 for grafted-Et₃N, -EtNH₂ and -C₄H₉N, respectively.

The total number of basic groups was calculated by the amount of HCl added and was found to be 1 mmol g^{−1} for Et₃N, and 0.99 for EtNH₂, whereas for the pyrrolidine it was found to be only 0.54 mmol g^{−1}. C₄H₉N-CNTs showed a lower basicity in comparison to the other catalysts, in disagreement with the higher p*K*_a of the corresponding amine. This result can be explained by the lower amount of grafted groups for the C₄H₉N-CNTs catalyst (0.54 mmol g^{−1} for C₄H₉N-CNTs vs. 1 and 0.99 mmol g^{−1}, respectively for Et₃N-CNTs and EtNH₂-CNTs).

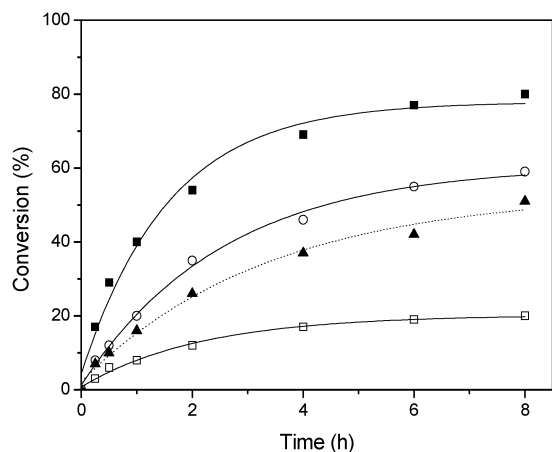
The catalytic performance of the amino-grafted CNTs was investigated for the transesterification of glyceryl tributyrates at 60 °C with a glyceryl tributyrates : methanol ratio of 1 : 12, which are typical conditions for this reaction. Et₃N-CNTs resulted in the most active catalyst with a conversion of 77% after 8 h (Fig. 1). In comparison the EtNH₂-CNTs catalyst

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Table 1 Characteristics of the amino-grafted carbon catalysts

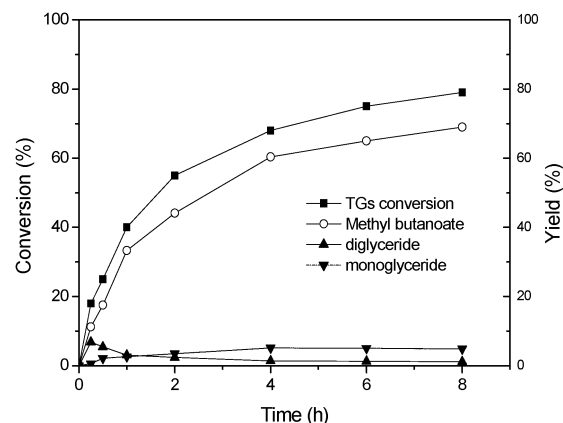
Sample	TGA results	Amine bp/°C	pH	pK _a (amine)	Basic site density/mmol g ⁻¹
Et ₃ N-CNTs	Stable up to 130 °C	89.7	10.3	10.75	1.00
EtNH ₂ -CNTs	Stable up to 80 °C	16.6	10.1	10.63	0.99
C ₄ H ₉ N-CNTs	Stable up to 120 °C	87.0	9.5	11.31	0.54

**Fig. 1** Effect of the different amines grafted on CNTs in the transesterification of glyceryl tributyrate: (■) Et₃N-CNTs, (○) EtNH₂-CNTs, (▲) hydrotalcite, (□) C₄H₉N-CNTs.

reaches a conversion of 55% after the same time, whereas C₄H₉N-CNTs shows a much lower conversion. The different catalytic performance of Et₃N-CNTs and EtNH₂-CNTs can be assigned to the different pK_a of the grafted amine. In the case of C₄H₉N-CNTs, the lower catalytic performance can be addressed to the lower number of grafted amino groups (0.54 mmol g⁻¹) in comparison to the other two catalysts (1 mmol g⁻¹ for Et₃N-CNTs and 0.99 mmol g⁻¹ EtNH₂-CNTs). In fact, upon repeating the experiment, using the amounts of catalyst in order to have the same number of basic sites as in Et₃N-CNTs and EtNH₂-CNTs, C₄H₉N-CNTs led the highest initial activity. The reason of the lower amount of grafted pyrrolidine groups could be due to the different reactivity of 1-(2-chloroethyl)pyrrolidine hydrochloride in comparison to the bromo derivatives used to graft the other two amines.

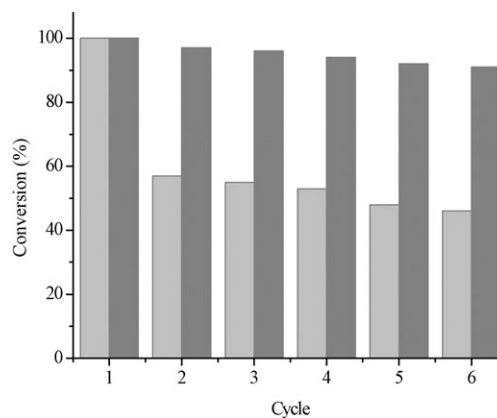
The activity of amino-grafted CNTs was also compared to a commercial hydrotalcite, which is a standard catalyst for this reaction. Et₃N-CNTs and EtNH₂-CNTs showed a better catalytic performance, with a conversion of 77 and 55%, respectively, whereas the hydrotalcite reaches 51% conversion after 8 h. Fig. 2 shows a typical reaction profile obtained using Et₃N-CNTs (60 °C, glyceryl tributyrate–MeOH 1 : 12). Glyceryl tributyrate is immediately converted to methyl butanoate and to the diglyceride. After 15 min, the second transesterification of the diglyceride to monoglyceride is initiated also. The yield of diglyceride has a maximum after 15 min. After this time the yield of diglyceride declines with the concomitant production of monoglyceride.

Recycling tests were carried out in order to study the stability of amino-grafted CNTs. In this study, Et₃N-CNTs were used as a test catalyst at a temperature of 90 °C instead 60 °C in order to accelerate the process. After each run, the

**Fig. 2** Product distribution for Et₃N-CNTs.

solid catalyst was separated from the reaction mixture by filtration and reused for the next cycle.

As shown in Fig. 3, the catalyst underwent a significant deactivation during the first run. Furthermore, the catalyst slightly deactivated during the subsequent cycles. A possible reason for the strong deactivation between the first two cycles is the strong adsorption of the triglyceride on the active sites. In fact the TEM images (Fig. 4(a)) of the used catalysts show that amorphous species are present around the CNTs and inside their channels. In order to remove the adsorbed triglyceride, a new cycle of recycling tests regenerating the catalysts after each run was performed. The regeneration was performed by washing the used catalyst several times with methanol and by drying it at 80 °C. Fig. 3 shows that, by regenerating the catalyst after each run, only a slight deactivation was detected. It was observed (Fig. 4(b)) that after these new cycles the amorphous species were successfully removed after the regeneration-recycling steps. Furthermore, the reason

**Fig. 3** Et₃N-CNTs deactivation during multiple 4 h reaction cycles (light gray) and regeneration effect (gray).

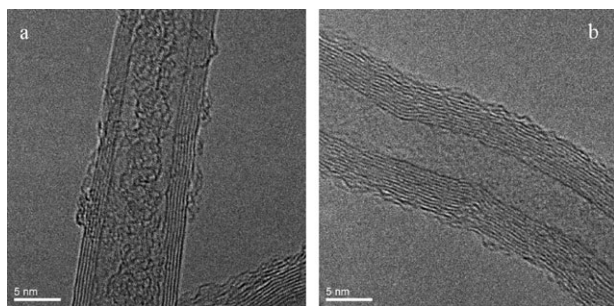


Fig. 4 HRTEM image of Et₃N-CNTs catalyst after (a) recycling cycles and (b) regeneration-recycling cycles.

for the slight deactivation present during the regeneration-recycling tests was investigated. In particular the possible leaching of the grafted amine was studied. Acid–base titration was performed on the used catalyst and the reaction solution was analysed after each reaction by GC-MS. Titration data showed that the generated pH of the used Et₃N-CNTs catalyst was 10.26 and the total number of basic groups was 0.96 mmol g⁻¹ (Table 2). Thus we can conclude that the amino groups were well anchored on the surface of the CNTs with a leaching of the basic groups of only 4% after six cycles.

The analysis of the solution by GC-MS did not present the characteristic peaks of Et₃N, probably because the concentration of the amines leached into the solution was so low that it was impossible to detect. Moreover, the slight deactivation during the regeneration cycles could also be due to the inevitable catalyst loss during sampling and recovering steps. The use of different amino-grafted CNTs has been investigated in the transesterification of glyceryl tributyrate with methanol. TG-MS measurement demonstrated that the grafted amines are covalently anchored on the surface of the CNTs and the system is stable at the temperature used for the reaction.

All the catalysts showed basic properties and the number of basic groups was found to be 1 mmol g⁻¹ for Et₃N- and EtNH₂-CNTs, whereas for C₄H₉N-CNTs the amount is only 0.54 mmol g⁻¹. The most active catalyst is Et₃N-CNTs. The higher activity in comparison to EtNH₂-CNTs can be assigned to the higher basicity of triethylamine compared to ethylamine. C₄H₉N-CNTs showed the lowest activity. Despite the higher pK_a of the pyrrolidine, the number of anchored amino groups is halved compared to the other two catalysts.

Table 2 Generated pH and total number of basic groups of Et₃N-CNTs before reaction and after regeneration-recycling test

Sample	pH	Basic site density/mmol g ⁻¹
Et ₃ N-CNTs (before)	10.30	1.00
Et ₃ N-CNTs (after)	10.26	0.96

Recycling tests were performed using Et₃N-CNTs as the catalyst. The strong deactivation of the catalyst was demonstrated to be due to the strong adsorption of the triglycerides. This drawback can be avoided by regenerating the catalyst *via* washing with methanol. In this latter case only a slight deactivation was detected, due to the leaching of a small amount of the anchored amines (4%) and the inevitable loss of catalyst during the recycling test in the batch reactor. Thus we can conclude that the grafting of amino groups onto CNTs is a suitable method to obtain active and stable basic catalysts for application in liquid phase reactions.

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