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Transesterification of Triglycerides Using Nitrogen-Functionalized Carbon Nanotubes

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Nitrogen-functionalized carbon nanotubes were synthesized by grafting amino groups to the surface of the nanotubes. The nanotubes exhibited promising results in the base-catalyzed liquid phase transesterification of glyceryl tributyrate with methanol, which is a model reaction for the production of biodiesel. The concentration of the active sites and the reaction parameters, such as temperature and glyceryl tributyrate to methanol ratio, were shown to significantly affect catalytic performance. The grafting technique employed allowed for design and control of the active sites. As a consequence, it was possible to design a nitrogen-functionalized carbon nanotube catalyst with a few strong, basic groups. This might be of interest for carbohydrate conversion reactions where strong basic sites are required but the pH of the solution should remain mild to avoid the degradation of the reactants and/or products.

Introduction

Chemical routes to biodiesel from renewable resources such as plant oils have attracted much attention over the last years.^[1-3] The conventional production of biodiesel from lipid feedstocks involves the use of homogenous basic catalysts such as sodium or potassium hydroxides, or alkoxides, which are very active, but also present many problems.^[4,5] These processes require an aqueous wash step to remove the dissolved catalyst and glycerol from the product phase. This step often suffers from separation problems owing to the formation of emulsions, and also leads to waste treatment issues. The substitution of homogeneous catalysts with heterogeneous catalysts is crucial to eliminate these problems. A wide variety of solid bases have been examined for this purpose, for example, alkaline earth oxides,^[6] potassium and lithium-promoted oxides,^[7] calcined hydrotalcites,^[8] zeolites,^[9] and nano-magnesium oxide.^[10] However, most of these catalysts do not dissolve in the reaction media. These solids are Lewis bases and in the presence of polar species, for example methanol and glycerol, they can form methoxylates and glycerates with the consequence of leaching from the solid catalyst. Therefore, many efforts have been made to develop basic heterogeneous catalysts that show high stability throughout transesterification reactions. Liu et al. reported the high catalytic activity of aminofunctionalized silica and resin in the transesterification of triacetin with methanol.^[11] They also highlighted a partial leaching of the grafted amino functionalities using silica as the support, whereas with resin this problem was not observed. It appears the support plays an important role on the stability and activity of the catalyst. Resin-based catalysts show better stability, however, several groups observed that approximately 65% of the active sites are not accessible, the active sites are poorly dispersed, and their basic character is strongly influenced by the structure of the resin.^[11] In few cases, a strong deactivation was also observed in the case of the anionic resins. It is thus necessary to study new supports, which are easy to synthesize and to functionalize. Carbon nanotubes (CNTs) are suitable for this purpose as they can be chemically modified with heteroatoms, which are either inserted in their structure^[12-18] or grafted on their surface.^[19,20]

We recently reported on the importance of the methodology in grafting organic amine molecules on the surface of CNTs to obtain active and stable catalysts for the transesterification of glyceryl tributyrate.^[21,22] In particular, we developed a synthetic route where CNTs are reacted with an excess of *n*-butyllithium (nBuLi), followed by addition of bromo amino derivates to the activated CNTs to form the corresponding nitrogen-CNTs (N-CNTs).^[21,22] The catalysts show high stability during regeneration/recycling cycles, thus proving that the amino groups are strongly anchored to the surface of the CNTs.^[22] We also proved that the basicity of the catalyst can be tuned by grafting amines with different pKa values. Herein, we studied the effect the amount of grafted amines has on the basicity of the catalyst. Furthermore, we studied the effect the reaction parameters, such as temperature and molar ratio of glyceryl tributyrate to methanol, have on catalytic performance.

Results and Discussion

We previously demonstrated that the synthetic procedure for grafting N-containing groups onto the surface of multi-walled CNTs (MWCNTs) has a dramatic role on the subsequent catalyt-

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ic activity of the N-CNTs.^[21,22] The most common synthetic route consists of three steps; oxidation of the surface to create carboxylic acid groups, acylation with thionyl chloride, and the anchoring of the desired molecule by amidation.^[19,20] Although this technique is efficient, we found that the proximity of acidic O-containing functional groups to basic amino groups leads to weakly basic samples, showing poor catalytic activity and poor stability. This observation is consistent with the results obtained by several groups when grafting amines on silica or SBA-15 materials.^[11] Therefore, we developed a synthetic route where the desired molecules are directly grafted to the surface defects by C-C coupling reactions. Indeed, contrary to single-walled CNTs, MWCNTs synthesized by catalytic chemical vapor deposition (CCVD) exhibit a number of structural defects, such as vacancies and terminations, where the carbon atoms are saturated by hydrogen atoms. In our procedure, commercial MWCNTs are reacted with nBuLi to activate the terminal C-H bonds near the defects and create nucleophilic carbon atoms (C-Li).^[21] In a second step, a bromoalkylamine is added to perform an electrophilic attack on the C-Li bonds. As a result, the desired molecule is directly anchored to the MWCNT surface through the created C-C bond. Lithium bromide is formed as a side-product. This synthetic route is an elegant way to graft various amines, for example triethylamine, ethylamine, or pyrrolidine, which can be employed as active sites for base-catalyzed reactions.^[22] Herein, we investigated the role of the concentration of the active sites on the subsequent catalytic activity of the N-CNTs. The number of active sites was controlled by adjusting the concentrations of nBuLi and 2-bromo-N,N-diethyl-ethylamine used during the synthesis.

The basicity properties and the number of accessible basic sites were characterized by acid-base titration with HCl as the titrant (Table 1). The pH generated by the N-CNTs suspended

Table 1. Properties of Et ₃ N-CNTs catalysts.		
Catalyst	рН	Basic site density
		[mmol g ⁻¹]
Et ₃ N-CNTs 1 Et ₃ N-CNTs 2 Et ₃ N-CNTs 3	7.8 9.9 10.3	0.11 0.73 1.00

in a 10^{-3} M KCl solution was 7.8, 9.9, and 10.3, for Et₃N-CNTs 1, Et₃N-CNTs 2, and Et₃N-CNTs 3, respectively. The total number of basic groups was calculated by the amount of HCl added and was found to be 0.11, 0.73, and 1.00 mmolg⁻¹ for 1, 2, and 3, respectively. In all cases the yield of the grafting procedure ranged from 15–19%.

Attention was dedicated to the washing of the catalyst; the presence of trace amounts of lithium in the catalyst may considerably change its catalytic activity as lithium is known to catalyze transesterification reactions.^[7] To study the effect of the presence of lithium, the N-CNTs samples were washed after synthesis following two different procedures. The first procedure was a fast washing of the catalyst with methanol.

Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) analysis of this sample revealed the presence of lithium (2.6% of the Li added). Thus, the washing procedure was improved by washing the catalyst overnight, and in this case, no lithium was detected. To confirm the role that lithium can have on the transesterification reaction, we performed catalytic tests using both the fast-washed and long-washed catalysts. The catalysts were tested in the transesterification of glyceryl tributyrate with methanol to form methyl butanoate. Figure 1



Figure 1. Glyceryl tributyrate conversion after the fast and improved washing procedures (catalyst, Et₃N-CNTs 3).

shows the observed catalytic activities and, as expected, the sample containing lithium was more active. Thus, all samples were thoroughly washed with methanol to exclusively study the catalytic performances of the grafted amines.

Experiments were performed to study the possible effect on the catalytic activity of a pre-contact between the catalyst and reagents. In the first test the catalyst was introduced at the same time as glyceryl tributyrate and methanol, whereas in the second experiment the catalyst and methanol were stirred for ten minutes before addition of the oil.

Figure 2 shows that the activity is drastically lowered without the catalyst-methanol pre-contact. This decrease in activity can be attributed to the strong adsorption of glyceryl tributyrate to the inner and external surfaces of the carbon nanotubes (Figure 3). The strong adsorption of the oil to the active sites is also the reason for deactivation during recycling tests.^[22] Thus, to have an active system it is necessary to adsorb methanol onto the active sites before the introduction of glyceryl tributyrate.

The effect on catalytic activity of various loadings of the amino functionality on the CNTs was investigated. The typical reaction conditions of 60 °C with a glyceryl tributyrate to methanol ratio of 1:12 were used (Figure 4). The catalyst with the highest concentration of basic groups (Et₃N-CNTs **3**) proved to be most active. In particular, Et₃N-CNTs **1** showed a very low activity and immediately deactivated. The abundance of amino groups is a key factor for highly active catalysts.



Figure 2. Influence of the methanol-catalyst pre-contact (temperature, 60 °C; glyceryl tributyrate/methanol 1:12, 2% catalyst).



Figure 3. TEM image of Et₃N-CNTs 3 after transesterification.



Figure 4. Effect of the amount of grafted triethylamine on the activity in the transesterification of glyceryl tributyrate (temperature, 60 °C; glyceryl tributyrate to methanol ratio, 1:12; 2 wt% catalyst).

To compare the grafting route with more classical methods for nitrogen functionalization, we compared our best catalyst, **3**, to a N-CNTs sample prepared by a gas phase procedure.^[23] In this case, the N-CNTs were obtained by previous acid oxidation and further amination with gaseous ammonia. X-ray photoelectron spectroscopy (XPS) and thermogravimetry mass spectrometry (TG-MS) revealed that these samples mainly contain pyridinic and pyrrolic groups. Hence, they are similar to N-CNTs synthesized by CCVD.^[18] The performance of the catalysts were compared (Figure 5); the N-CNTs synthesized by gas phase led to a very low conversion of 3% compared to 77% for Et₃N-CNTs **3**.



Figure 5. Catalytic activities of Et₃N-CNTs 3 and gas phase synthesized N-CNTs for the glyceryl tributyrate transesterification (60 $^{\circ}$ C, glyceryl tributy-rate/methanol 1:12; 2% catalyst).

The effects of the reaction parameters on the catalytic activities were also investigated. Figure 6 shows the influence of the reaction temperature. Increasing the reaction temperature leds not only to a faster reaction but also improved phase miscibili-



Figure 6. Influence of the reaction temperature on the transesterification of glyceryl tributyrate (glyceryl tributyrate to methanol ratio, 1:12; catalyst, Et_3N -CNTs 3, 2 wt%).

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ty, in particular when using heavy oils. At 90 °C the glyceryl tributyrate was fully converted in 2 h, whereas at 75 °C it took 6 h to achieve 90% conversion (Figure 7).



Figure 7. Influence of the ratio of glyceryl tributyrate to methanol on the transesterification of glyceryl tributyrate (temperature, 60 °C; catalyst, Et₃N-CNTs 3, 2 wt%).

The use of higher temperatures increases energy consumption. Moreover, at higher temperatures a higher pressure is necessary to keep the methanol in liquid phase. Hence, the best temperature despite the transport limitation is still 60°C, which is below the boiling point of methanol. The molar ratio of the oil and methanol is another important factor in the transesterification of triglycerides. Three moles of methanol per mole of triglyceride are required stoichiometrically. However, as the transesterification is a reversible reaction, a large excess of methanol is required to displace the equilibrium. In our study, different glyceryl tributyrate to methanol molar ratios (1:60, 1:24, 1:12, 1:6) were used, at a fixed temperature of 60°C and a fixed amount of catalyst (2 wt%). By increasing the amount of methanol the system became more active. When using molar ratios of 1:60 or 1:24, complete conversion was achieved after 2 h and 4 h, respectively. With a ratio of 1:12, only 77% conversion was reached after 8 h and in the case of the ratio 1:6, fast deactivation was observed. Despite high activity, an optimal molar ratio must balance the cost of separation of the main products from the excess methanol. Hence, a ratio of 1:12 can be regarded as the optimal ratio.

Conclusions

Three N-CNTs were synthesized following a published procedure.^[21] When the amount of grafted triethylamine was increased, the basicity and the catalytic performance in the transesterification of glyceryl tributyrate increased. An activity ten times greater than that for N-CNTs synthesized by ammonolysis of oxygen functional groups was observed. The catalytic performance was significantly improved if the catalyst was pre-contacted with methanol or through optimization of the operating conditions. High temperatures and high methanol to glyceryl tributyrate molar ratios improved the catalytic performances. The limiting factors were the vapor pressure of methanol and the energy required for the separation of the product from methanol. Optimal reaction parameters were identified with respect to these limitations. The results may serve as orientation for other applications of N-CNTs in synthetic chemistry. For practical applications, scalable procedures need to be identified, as the gas phase ammonolysis or CCVD techniques do not seem suitable.

Experimental Section

The reactants for the synthesis of catalysts and those used in the catalytic tests, that is, glyceryl tributyrate (98%), methanol (99.8%), dimethyl ether, *n*-butyllithium (2.5 μ in *n*-hexane, and 2-bromo-*N*,*N*-diethyl-ethylamine (98%) were purchased from Aldrich. *n*-Hexane obtained from Sigma–Aldrich (>99%) and hexyl ether from Aldrich (97%) were used respectively as the solvent and the internal standard for gas chromatography (GC) analysis. MWCNTs were purchased from Nanocyl (Nanocyl 3100, >95% C purity).

Three N-CNT catalysts with different amounts of grafted triethylamino groups were prepared following the published procedure.^[21] Pristine CNTs (2 g) were added to freshly distilled dimethyl ether (400 mL) and placed in an ultrasonic bath for 20 min at RT. nBuLi (2.5 M solution in *n*-hexane) was then added and the mixture was stirred for 5 h under argon at RT. 2-Bromo-N,N-diethyl-ethylamine was added and the solution was heated at 35°C for 90 min. The samples were washed following two different procedures; for the fast washing procedure, the N-CNTs were simply filtered on a Büchner funnel and rinsed with methanol (300 mL). For the improved washing procedure, the N-CNTs were first filtered and rinsed following the fast washing procedure. They were then suspended in methanol (600 mL) and stirred for overnight. Finally, they were filtered and rinsed with distilled water (500 mL) and methanol (200 mL). In all cases, the catalyst was dried overnight at 80 °C. The different amounts of nBuLi and of 2-bromo-N,N-diethyl-ethylamine used in the synthesis are shown in Table 2.

Transesterification reactions were performed in a thermostatted glass reactor (30 mL) with samples periodically withdrawn for analysis. The reactants were always loaded into the reactor at RT. The reactor was then purged with nitrogen to expel air before heating up and pressurized with nitrogen. The catalyst concentration was 2% based on glyceryl tributyrate weight. The quantification of the products was performed using an Agilent 6890 N GC equipped with a HP-5 column (30 m length, 0.32 mm internal diameter, 0.25 μ m film thickness) and free induction decay (FID) detector. GC-MS was used for identification of the products.

The Li content was analyzed by ICP-AES using a Jobin Yvon JY24 instrument. Morphologies and microstructures of the catalysts were characterized by transmission electron microscopy (TEM). The

Table 2. Amount of reagents.			
Catalyst	<i>n</i> BuLi	2-Bromo-N,N-diethyl-ethylamine	
	[mmol]	[mmol]	
Et ₃ N-CNTs 1 Et ₃ N-CNTs 2	2.75 27.5	2.75 27.5	
Et ₃ N-CNTs 3	55	50	

powder samples of the catalysts were ultrasonically dispersed in chloroform and mounted onto holey carbon coated copper grids. A Philips CM200 FEG electron microscope, operating at 200 kV and equipped with a Gatan imaging filter, GIF100, was used for TEM observation. A Mettler Toledo titrator equipped with a DGi 114-SC electrode was used for acid-base titration measurements

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