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NITROGEN-FUNCTIONALIZED CARBON NANOTUBES AS A BASIC CATALYST FOR BIOMASS CONVERSION REACTIONS

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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, in the present work, we synthesized N-MWCNTs catalysts by grafting desired N-containing molecules on the MWCNTs' surface. The obtained catalysts were tested in the transesterification of triglycerides with methanol (biodiesel synthesis), as a model reaction for biomass conversion.

Common grafting techniques require a first step of oxidation of the carbon nanotubes in order to create surface oxygen-containing groups which can then be further chemically modified. We found that these techniques lead to catalysts with a large variety of acidic as well as basic functional groups. Therefore, we developed an original method which allows to graft desired molecules directly on the surface of the MWCNT by electrophilic attack (Fig. 1). SEM, TEM, BET, Raman as well as TG-MS and acid-base titrations confirm that the desired groups were anchored and well dispersed on the surface of the MWCNTs. This procedure was used to graft triethylamine as well as ethylamine and pyrrolidine groups.

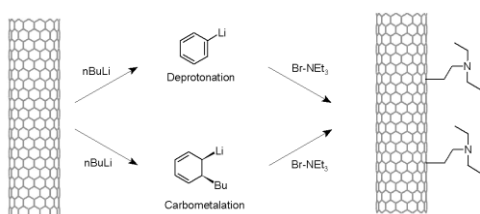


Fig. 1. Schematic view of our synthesis procedure.

The catalytic tests (Fig. 2) show that the activity of the N-MWCNTs samples is strongly influenced by the synthesis procedure. The catalyst prepared by electrophilic attack exhibits a higher activity than hydrotalcite, which is a reference catalyst for this reaction. In contrast, N-MWCNTs samples prepared by other procedures deactivate rapidly.

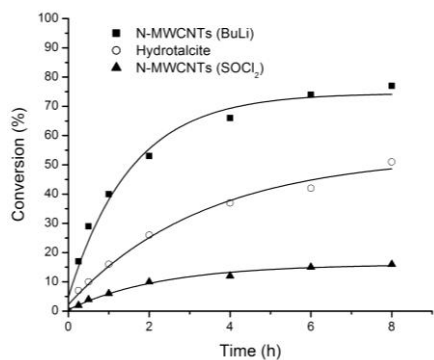


Fig. 2. Triglyceride conversion as a function of time obtained with different catalysts: N-MWCNTs synthesized with our procedure (■), a reference hydrotalcite (○) and N-MWCNTs synthesized with a traditional grafting procedure (▲).

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