Supplementary Material (ESI) for Chemical Communications

Amino-funtionalized carbon nanotubes as solid basic catalyst for transesterification of triglycerides

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Electronic supporting information

Experimental

Catalyst preparation

N-functionalized MWCNTS catalysts have been prepared following the procedure. As an example the preparation of Et_3N grafted MWCNTS is reported.

Pristine MWCNTs (2g) were added to a solution of 400 ml of dried ether and placed in an ultrasonic bath for 20 minutes at room temperature. Butyllithium (20 ml), 55 mmol from a 2.5 M solution in hexane) is added and the mixture then is stirred for 5h at room temperature. 2-bromo-N,N-diethyl-ethylamine (5.20g, 50 mmol) is finally added and the solution is heated at 35°C for 90 minutes. The solution was then filtered and washed several times with methanol in order to remove all the Li present and the amines not grafted on the surface. The catalyst was then dried overnight at 80°C.

Catalytic test

Reactions were performed in a thermostatted glass reactor (30 ml) with samples withdrawn periodically for analysis. The reactants were always loaded into the reactor at room temperature. The reactor was then purged by nitrogen to expel the air left before heating up and pressurizing with N_2. A typical reaction temperature was 60°C, molar ration methanol to glyceryl tributyrate 12:1 and stirring rate 1200 rpm. The catalyst concentration was 2% based on glyceryl tributyrate weight. The quantification of the products was performed using an Agilent 6890N gas chromatograph equipped with a HP-5 column (30m length, 0.32 mm internal diameter, 0.25 μm film thickness) and FID detector. GC-MS was used for identification of the products. In the recycling experiments, catalysts were recovered after a particular cycle by simply decanting the reaction solution. In the regeneration cycle the catalyst was washed several times with methanol before the newt experiment in order to remove the adsorbed triglycerides. In order to identify species leached from the catalysts during the reaction in liquid phase, the solution after reaction were analyzed using GC-MS.

Catalyst characterisation

The Lithium content was checked by ICP analysis of the filtrate burned off, using a Jobin Yvon JY24 instrument. TG-MS measurements were performed using a TG-DTA/DSC (Netzsch STA 449) equipped with a Pfeiffer OmniStar^{TM} mass spectrometer. 5 mg of sample were heated from 30 to 900°C at 2 °C.min^{-1} in a 100 ml.min^{-1} Ar flow. A Mettler Toledo titrator equipped with a DGi 114-SC electrode was used for acid-base titration measurements. Typically, 100 mg of sample were dispersed in 50 ml of a 10^{-3} M KCl solution. The mixture was kept under vigorous stirring overnight. Prior to measurement, the mixture was degassed under Ar for at least 1 h, until the pH value was constant. The titration was then performed under Ar, using a 10^{-2} M HCl solution.
Morphology and microstructures of the catalysts are characterised by TEM. The powder samples of the catalysts were ultrasonically dispersed in ethanol and mounted onto copper grids covered with holey carbon film. A Philips CM200 FEG electron microscope, operating at 200 kV and equipped with a Gatan Tridiem imaging filter, was used for TEM observation.