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Supplementary information for

Mesoporous polymeric catalysts synthesized from self-assembled organic nanotubes as templates.

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Experimentals

Materials

Compound **1** was synthesized according to previously described procedure.[1] Ethylene glycol diacrylate (EGDA) and diphenyl (2,4,6-trimethylbenzoyl)-phosphine oxide (TPO) were purchased from Aldrich, and used as received.

Preparation of the catalyst

A solution of diphenyl (2,4,6-trimethylbenzoyl)-phosphine oxide (TPO) (1 wt. %) in EDGA was prepared and stored in opaque vessel. Equal weights of this stock solution and BHPB-10 (typically 300 mg) were mixed in a sealed vial and heated until complete dissolution of BHPB-10 (around 60 °C). The resulting solution was cooled at 25 °C to yield a thermoreversible gel which was then exposed to a UV mercury lamp (366 nm, 100 W) for 2 hrs. The obtained resin was then immersed in CH_2Cl_2 for 24 hrs. The extracted solution was replaced by fresh solvent. The combined extracted solutions were evaporated to measure the weight of extractible materials, analyze their composition, and recover BHPB-10.

Treatment of the resin

The resin is ground coarsely and treated with NaOH (1 M in CH_3OH-H_2O) for 4h20 without stirring. The resin is then decanted and washed more than 7 times with water, with EtOH in a Soxhlet extractor for 24 hrs and then with H_2O again in Soxhlet extractor for 24 h before drying under vacuum.

Titration of carboxylates

The treated resin was mixed with a 0.1 N aqueous HCl solution (20 mL) and stirred gently for 3 days in a sealed flask under Ar. 5 mL of this solution were titrated with a 0.1 N aqueous NaOH solution by using a pH-meter. The experiments were conducted three times.

Catalytic experiments

Benzaldehyde (0.6 g, 5.65 mmol) and the catalytic resin (0.15 g, 0.21 mmol of COO^-, 0.036 equiv.) in EtOH (8 mL) were stirred at 25 °C for 10 min. under Ar and ethyl cyanoacetate (0.9 g, 7.90 mmol, 1.4 equiv.) was added at once. After 4h30 the mixture was filtered, the obtained resin was rinsed with EtOH (3 x 5 mL); the filtrate was evaporated under vacuum and the residue was chromatographed (SiO_2, EtOAc/C_6H_{12} : 15/85 eluent) to afford pure 2-cyano-3-phenyl-acrylic acid ethyl ester (0.97 g, 85 %) with physical properties identical to the previously reported material. M. p. 51 °C, lit. 52 °C.[2]

For the kinetics experiments, the reaction was performed in the same conditions, with tetradecanol (300 mg) as an internal standard. Every 10 min, the reaction medium was analyzed by gas chromatography (6890 Agilent) by injecting 10 µL aliquots on a ZB-WAX column (coated with PEG, length 60 m, internal diameter 250 µm) at 230 °C.

Transmission electronc microscopy

The resin was attached to the holder of a Ultracut microtome from Leica and trimmed with a glass knife to obtain a square section of 1 mm x 1 mm. The latter was then cut in microsections 40 to 80 nm thick with a diamond knife. The sections were retrieved in a water bath fixed under the knife and picked directly by carbon coated grids. They were observed by TEM without staining agent.

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2. J. S. Yadav, B. V. S. Reddy, A. K. Basak, B. Visali, A. V. Narsaiah and K. Nagaiah, *Eur. J. Org. Chem.*, 2004, **2004**, 546-551.