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Efficient cycloaddition of CO_2 to epoxides using novel heterogeneous organocatalysts based on tetramethylguanidine-functionalized porous polyphenylenes

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ABSTRACT

The conversion of CO_2 into cyclic carbonates by cycloaddition to epoxides is achieved under relatively mild reaction conditions (without solvent, 7 bar of CO_2, 100 °C) using easily available heterogeneous tetramethylguanidine(TMG)-polyphenylene organocatalysts. These new highly stable catalysts were easily prepared by reaction of tetramethylurea in the presence of oxalyl chloride with aminomethyl polyphenylenes. The TMG-functionalized polyphenylene ($2PhCH_2TMG$) prepared from a pre-functionalized network was efficient and competitive compared with other reported catalysts achieving high epoxides conversion (> 90%) and 100% selectivity towards the corresponding cyclic carbonates. The catalyst was easily separated from the reaction media and reused after basic regeneration without loss of activity.

1. Introduction

The chemical conversion of carbon dioxide in value-added products and fuels is of great importance in catalysis and industrial chemistry [1]. Homogeneous catalysts [2], halide metals [3], ionic liquids [4], and metal organic complexes [5] have been applied for the synthesis of cyclic carbonates from the cycloaddition of CO_2 to epoxides. However, the homogeneous catalysts are difficult to separate from the reaction medium, while the heterogeneous can be isolated by simple filtration [6].

Many porous materials have been developed to be used as heterogeneous catalysts from inorganic networks (zeolites [7], carbon [8], silica [9]) or hybrid organo-inorganic frameworks (MOFs) [10] to pure organic polymers (POPs) [11]. Many synthetic strategies are applied to prepare different kind of POPs such as covalent organic frameworks (COFs) [12], hypercrosslinked polymers (HCPs) [13], conjugated microporous polymers (CMPs) [14], polymers of intrinsic microporosity (PIMs) [15], covalent triazine frameworks (CTFs) [16] and porous aromatic frameworks (PAFs) [17,18,19]. Recently, a new class of porous polymers has been emerged (using $AlCl_3$ or $FeCl_3$ as reagents), with a network predominantly based on direct aryl-aryl couplings, via the Scholl reaction, and some methylene cross-links via a Friedel-Crafts reaction generated from the solvent [20]. These porous polyphenylenes have similar surfaces areas that PAFs or porous polymers networks (PPNs), but with the advantages of using inexpensive starting materials (benzene, biphenyl, spirobifluorene, triphenylbenzene, triptycene, etc) and mild reaction conditions [20b,21].

Regarding to the application of these porous polyphenylene networks, CO_2 capture has been the more studied application [20–22]. Taking into account the good properties as heterogeneous catalysts demonstrated for similar porous polymeric networks [23], should be of great interest to explore also the use of these new porous polymer networks as supports to incorporate active sites.

Solid base catalysts such as metal oxides [24], organic [25] or alkali-doped mesoporous materials [26], zeolites [27] or other solid supported materials [28], have been studied over the decades; by other hand, solid organocatalysts have emerged as a favorable alternative for green catalysis applications [29]. Guanidines are important class of compounds that have many applications within organic chemistry, being the most common use as organic bases [30]; in particular, 1,1,3,3-tetramethylguanidine (TMG) catalyzes different reactions acting as nucleophilic catalyst in many cases [31]. Guanidines are good candidates for immobilization, among various supports used to heterogenize catalysts, mesoporous silica were the most habitual for guanidines [32]. In fact, guanidine and some of its silica-supported guanidine counterparts have been effective catalysts in cycloaddition of

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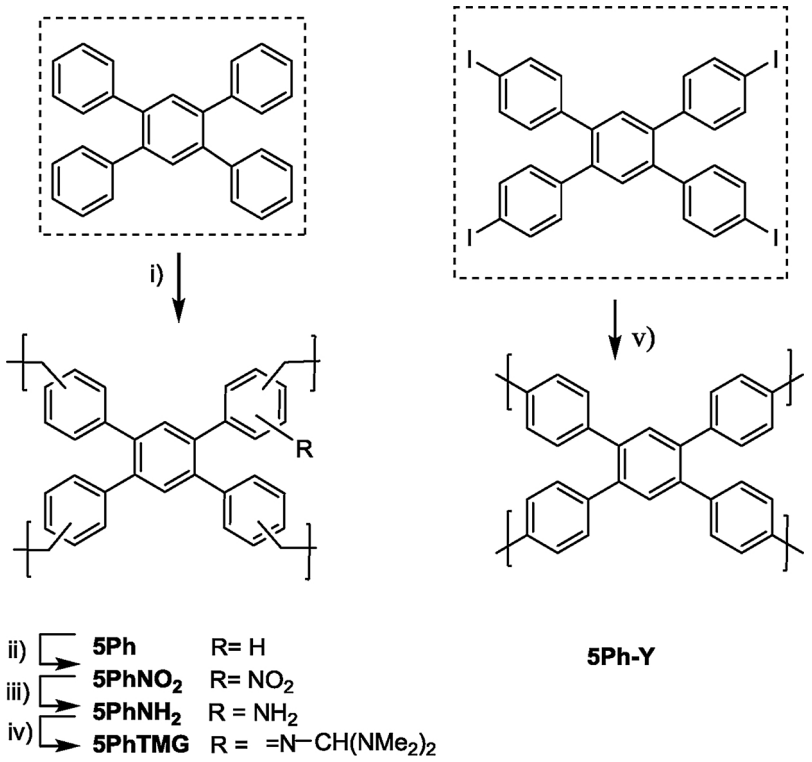
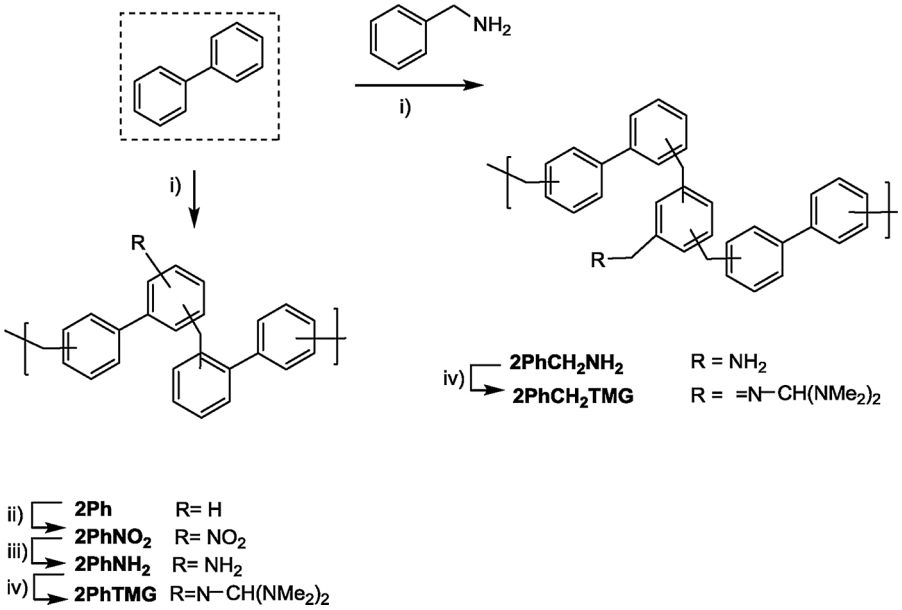


Scheme 1. Synthetic procedures for preparation of 5 Ph based polyphenylene networks: i) $AlCl_3$, CH_2Cl_2, 40 °C, 48 h; ii) HNO_3/CF_3COOH, 5 h; iii) $SnCl_2.2H_2O$, THF, 24 h; iv) $(CH_3)_2NCON(CH_3)_2$, ClCOCOCl, 24 h, Toluene; v) $Ni(cod)_2$, 2,2´-bipyridyl, DMF, 80 °C, 4 d.



Scheme 2. Synthetic procedures for preparation of 2 Ph based polyphenylene networks: i) $AlCl_3$, CH_2Cl_2, 40 °C, 48 h; ii) HNO_3/CF_3COOH, 5 h; iii) $SnCl_2.2H_2O$, THF, 24 h; iv) $(CH_3)_2NCON(CH_3)_2$, ClCOCOCl, 24 h, Toluene.

CO_2 to epoxides [33]. Now, we report a simple approach for the preparation of a guanidine group immobilized on easily available porous polyphenylenes, where the guanidine group is attached to the network directly or through a methylene spacer group. The performance of the novel materials as heterogeneous organocatalysts, is explored for the cycloaddition of CO_2 to epoxides.

2. Experimental section

2.1. Materials and methods

Biphenyl was supplied by Fluka with a purity > 98%; $AlCl_3$ (anhydrous) and CH_2Cl_2 (extra dry) were supplied by Acros Organics with purities > 98.5% and > 99.8% respectively. The other reagents and solvents were supplied by Aldrich with analytical grade and were used as received. Fourier Transform Infrared Spectra (FTIR) were recorded on a Perkin-Elmer RX-1 instrument. The solid-state ^{13}C NMR spectra