

Imidazolium-Functionalized Carbon Nanohorns for the Conversion of CO₂ Unprecedented Increase of Catalytic Activity after Recycling

**Carla Calabrese,^{a,b} Leonarda F. Liotta,^c Esther Carbonell,^b Francesco Giacalone,^a
Michelangelo Gruttadauria,^a Carmela Aprile^{b,*}**

^aDepartment of Biological, Chemical and Pharmaceutical Sciences and Technologies, University of Palermo, Viale delle Scienze Ed. 17, Palermo, 90128, Italy

^cIstituto per lo Studio dei Materiali Nanostrutturati (ISMN-CNR), Via Ugo La Malfa 153, Palermo, 90146, Italy

^bUnit of Nanomaterial Chemistry (CNano), University of Namur (UNAMUR), Department of chemistry, Rue de Bruxelles, Namur, 5000, Belgium

*Corresponding author: carmela.aprile@unamur.be

Carbon nanohorns (CNHs) were selected as a novel catalytic platform for the design of imidazolium based hybrid materials able to promote the conversion of carbon dioxide into cyclic carbonates. Several heterogeneous catalysts were prepared using a one-step procedure based on the radical polymerization of various bis-vinylimidazolium salts in the presence of pristine CNHs. The as-synthesized materials were tested for the fixation of CO₂ into epoxides. The excellent catalytic performances were evaluated in terms of turnover number and productivity. The versatility of the above hybrids was proved using several epoxides as substrate. Catalysts recyclability was successfully verified for several consecutive runs.

1. Scope

The design of novel nanostructured catalytic systems for the conversion of carbon dioxide is envisaged. In order to achieve this objective, imidazolium-functionalized carbon nanohorns were prepared and used as heterogeneous catalysts for the synthesis of cyclic carbonates (Figure 1a).

2. Results and discussion

Imidazolium-functionalized CNHs were synthesized starting from pristine CNHs and a series of bis-vinylimidazolium salts with different organic linker between the two imidazolium units. The degree of functionalization of the supported CNHs was estimated by thermogravimetric analysis. The polymeric networks displayed good thermal stability as their degradation started in the 210-240 °C range, which is promising for their possible repeated use under heating regimes. The morphology of such materials was studied by transmission electron microscopy. A screening of synthesis conditions was performed using a bis-vinylimidazolium bromide salt bearing a *p*-xylyl group as a linker connecting the two imidazolium units. Styrene oxide was selected as the target reagent to check the recyclability of the most promising materials. An unprecedented increase in the catalytic activity after recycling was observed (Figure 1b).

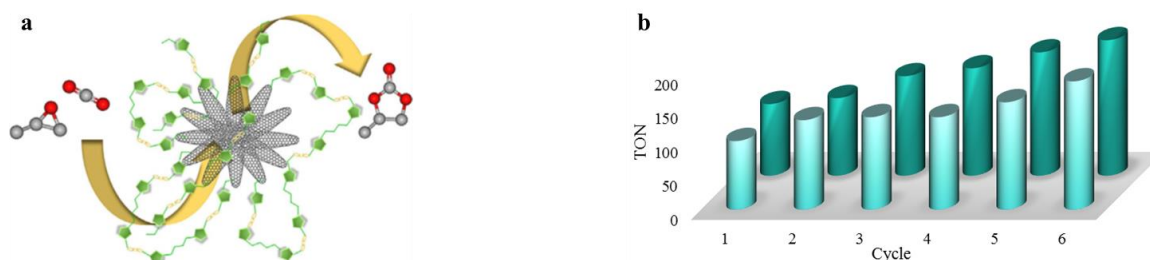


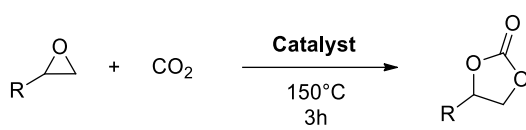
Figure 1. Synthesis of cyclic carbonates catalyzed by imidazolium-functionalized CNHs (a); recycling tests of imidazolium-functionalized CNHs using styrene oxide as target reagent (b).

This catalytic behavior could be ascribed to self-condensation phenomena between the free dangling vinyl moieties and consequent generation of a more stable cross-linked structure with an increased percentage of

porosity. The above hypothesis was supported by thermogravimetric and mercury porosimetry analysis performed on both fresh and reused catalysts. The possible leaching of imidazolium active species was excluded by quantifying the amount of organic functionalizing before and after the 6th cycle.

Based on preliminary investigations, bis-vinylimidazolium bromide salts with butyl or octyl linkers between imidazolium units were used for the synthesis of additional functionalized CNHs using the previously optimized reaction conditions. A trend in the catalytic performances based on the nature of the linker was observed. Imidazolium-based catalyst prepared using the octyl chain as a linker emerged as the best performing material. This catalyst was used in further tests for deeper investigations (Table 1). A first screening of the catalyst amount was performed using epichlorohydrin as starting epoxide (entries 1-3). In this context, the turnover number (TON) and productivity increased when the amount of the catalyst was reduced. This behavior was ascribed to a better dispersion of the solid in the reaction mixture with the decreased amount of catalyst. A second screening was performed for the same reaction to study the effect of CO₂ pressure (entries 3-5). The activity of the catalyst remained almost the same at a working pressure of 40 and 80 bar. Then, the versatility of such catalyst was studied with different epoxides (entry 3, 6-8).

Table 1. Synthesis of cyclic carbonates catalyzed by imidazolium functionalized CNHs. ^[a]



Entry	-R	Catalyst		Conv. ^[a] [%]	S ^[a] [%]	TON	P ^[a]
		mg	mol%				
1	-CH ₂ Cl	60	0.070	95	95	1367	624
2	-CH ₂ Cl	30	0.035	76	95	2186	998
3	-CH ₂ Cl	15	0.017	44	95	2532	1156
4 ^[b]	-CH ₂ Cl	15	0.017	49	95	2819	1287
5 ^[c]	-CH ₂ Cl	15	0.017	44	95	2532	1156
6 ^[d]	-CH ₂ OH	15	0.017	44	95	2532	1000
7	-CH ₃	15	0.017	44	95	2532	865
8 ^[e]	-Ph	240	0.409	36	95	112	62

[a] Conversion (Conv.), Selectivity (S), Productivity (P). Reaction conditions: epoxide (303.8 mmol), CO₂ (40 bar), 150°C. [b] CO₂ (50 bar). [c] CO₂ (80 bar). [d] 100°C. [e] Styrene oxide (206.3 mmol).

To investigate the influence of the nucleophile, a bis-vinylimidazolium iodide salt with octyl as the linker was employed for the synthesis of a further catalytic material. As expected, functionalized CNHs with iodide as a nucleophile led to higher conversion, turnover number, and productivity than the analogous material with a bromide as a counterion. Moreover in the reaction of CO₂ with epichlorohydrin this catalyst achieved excellent catalytic performances with extremely high TON (3226) and productivity (1235).

3. Conclusions

Several CNHs/cross-linked imidazolium salt hybrid materials were prepared using a straightforward one-step procedure by radical polymerization of various bis-vinylimidazolium salts in the presence of pristine CNHs. The as-synthesized materials were used as catalysts for the conversion of epoxides into cyclic carbonates by reaction with CO₂ without the presence of any co-catalysts. The reactions were performed using catalytic materials prepared with different CNHs/imidazolium ratios, different linkers, and by modifying the reaction conditions. Moreover, several epoxides were tested. Cyclic carbonates were obtained with high TON and productivity values. Catalytic materials were also tested in recycling experiments with styrene oxide. Two materials, with the same linker between the imidazolium moiety (*p*-xylyl) and the same anion and different imidazolium loadings, displayed an unprecedented increase of the catalytic activity from the first to the sixth cycle. TGA of the recycled catalysts showed that the materials were very stable. The trends of the catalytic activity could be ascribed to self-condensation phenomena between the free dangling vinyl moieties and consequent generation of a more stable cross-linked structure.

References

1. C. Calabrese, L.F. Liotta, E. Carbonell, F. Giacalone, M. Gruttadauria, C. Aprile, *ChemSusChem* **2017**, DOI: 10.1002/cssc.201601427.