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Cadmium catalyst with industrial polymeric nitrogen-containing ligand for the addition of carbon dioxide to oxiranes

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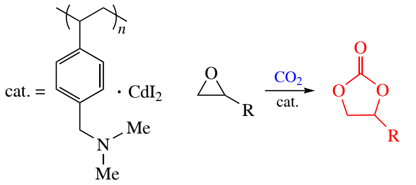
An industrial polymeric dimethylamino-containing ligand for the CdI_2-catalyzed CO_2 addition to oxiranes provides nearly quantitative yields of the cyclic carbonates. The catalyst can be recycled 9 times without loss of conversion.



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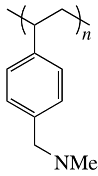
Carbon dioxide is an inexpensive and abundant chemical feedstock. One of the important catalytic processes in which carbon dioxide can be used is its addition to oxiranes to form organic carbonates.[1] The latter are used as fuel additives, electrolytes for lithium-ion batteries, polar solvents, monomers for the production of polycarbonates and non-isocyanate polyurethanes.[2] Transition metal complexes, inorganic salts and non-metallic catalysts such as organic ammonium, imidazolium, phosphonium salts and molecular iodine complexes were used as catalysts for the addition of CO_2 to oxiranes.[3–19] Heterogeneous catalysts are crucial for chemical processes since they are characterized by the ease of separation, opportunity for reuse and the applicability of the flow reaction mode. Of particular importance in heterogeneous catalysis are the structural features of the carrier material. One of the types of modern polymer structures characterized by a very high specific surface area (usually about 1000 $m^2\ g^{-1}$) are hypercrosslinked copolymers of styrene and divinylbenzene.[20] These materials are compatible or even swell in all types of organic reagents, which facilitates diffusion processes. This property of highly porous polystyrene matrices provides opportunities for their use in various catalytic processes. We have recently shown that CdI_2 in combination with organic amines could be an effective catalyst for the CO_2 addition to oxiranes.[21] One of the interesting matrices that combines the structure of an amine and hyper-crosslinked polystyrene is the industrial sorbent Purolite MN-100 produced by treatment of chloromethylated styrene/divinylbenzene copolymer with dimethylamine.

In this paper we present the results of testing the Purolite MN-100 copolymer treated with CdI_2 in the CO_2 addition to oxiranes. The catalyst was prepared by treating Purolite MN-100 with a methanol solution of CdI_2 followed by washing.[†] Elemental analysis showed the presence of 4.3% cadmium. Initial catalytic experiment was carried out with 1 mol% Cd in the addition of CO_2 (initial pressure at ~20 °C was 56 atm) to propylene oxide **1a** at 120 °C for 3 h (Scheme 1, Table 1, entry 1). In this case, 90% conversion was achieved. Reducing the initial carbon dioxide pressure to 30 atm determined an increase in conversion to 95% (entry 2). In order to obtain quantitative conversion, the reaction temperature was raised to 130 °C, which led to the desired result (entry 3). It should be noted that the conversion remains unchanged over 9 catalytic cycles, at the 10th cycle the conversion decreases to 95%.



Purolite MN-100

Under optimized reaction conditions (30 atm CO_2, 130 °C), the catalyst was tested in the CO_2 addition reaction to a series of oxiranes **1**.[†] Oxiranes **1d–g** were converted into the corresponding carbonates **2** with quantitative conversion in 3 h (see Table 1). Using 1,2-epoxybutane **1b** and epichlorohydrin **1c** required 4 h to achieve quantitative conversion.

The catalyst was also tested in the reaction of CO_2 addition (30 atm) to bisoxirane **3** at 130 °C for 20 h (Scheme 2). Under these conditions, 85% conversion was obtained. Prolongation the reaction to 24 h resulted in quantitative conversion. It should

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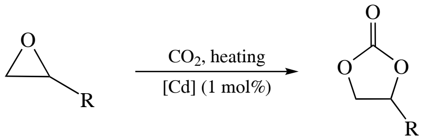
[†] Oxiranes **1a–e**, **3**, and the polymer Purolite MN-100 are commercially available compounds, **1g** was obtained by a known technique.[25]

Catalyst synthesis. A solution of CdI_2 (300 mg) in methanol (10 ml) was added to Purolite MN-100 beads (1 g). The mixture was kept for 40 min, the beads were filtered and washed with water and methanol (10 ml each). The weight of the product after drying (105 °C, 1 h) was 1.165 g. The specific surface area determined by nitrogen adsorption method was 1160 $m^2\ g^{-1}$.

Catalytic experiments. The catalyst (155 mg) was placed in a 10 ml autoclave and the corresponding epoxide (6 mmol) was added at room temperature, CO_2 gas was introduced to adjust the required pressure at room temperature, and then the autoclave was heated in a thermostat. After the reaction, the autoclave was cooled to 5 °C, excess CO_2 was released, liquid products **2a–c**,**f**,**g** were separated using a Pasteur pipette, solid products **2d**,**e** and **4** were dissolved in acetonitrile with filtration of the catalyst. The yields were determined at full conversion in the 2nd catalytic cycle to exclude product sorption by catalyst. The spectral characteristics of carbonates **2a–g** and **4** (see Online Supplementary Materials) correspond to the literature data.[26–28] In the case of recycle, substrate **1a** and CO_2 were added to the catalyst again.



1a–g **2a–g**

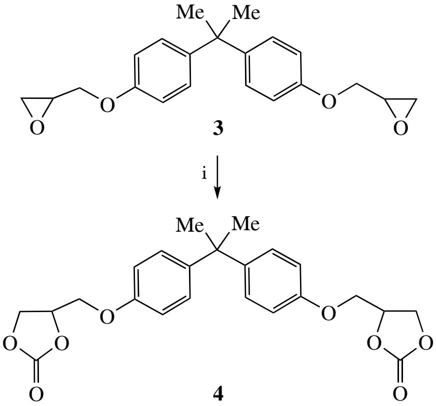
a R = Me
b R = Et
c R = CH_2Cl
d R = Ph
e R = CH_2OPh
f R = $CH_2OCH_2CH{=}CH_2$
g R = CH_2NEt_2

Scheme 1

Table 1 Addition of CO_2 (initial pressure at ~20 °C: 30 atm) to oxiranes **1a**–**g**.

Entry	Oxirane/ carbonate	*T*/°C	*t*/h	Conversion (%)
1[a]	**1a/2a**	120	3	90
2	**1a/2a**	120	3	95
3	**1a/2a**	130	3	100 (96)[b]
4	**1b/2b**	130	3	92
5	**1b/2b**	130	4	100 (97)[b]
6	**1c/2c**	130	3	92
7	**1c/2c**	130	4	100 (95)[b]
8	**1d/2d**	130	3	100 (96)[b]
9	**1e/2e**	130	3	100 (94)[b]
10	**1f/2f**	130	3	100 (97)[b]
11	**1g/2g**	130	3	100 (95)[b]

[a] Initial pressure of CO_2 was 56 atm. [b] Isolated yields of products **2a**–**g** are given in parentheses.



3

4

Scheme 2 *Reagents and conditions*: i, CO_2 (initial pressure 30 atm), catalyst (1 mol%), 130 °C, 20–24 h.

be noted that biscarbonate **4** is used to obtain high-temperature and mechanically stable adhesives and hydrophilic coatings.[22,23]

To summarize, a convenient industrial ligand for the reaction of CO_2 addition to oxiranes was suggested. The catalyst can be reused up to nine times without decrease in catalytic activity. It should be noted that the polymer coordination approach is more successful compared to the preparation of ammonium structures based on close high-molecular compounds.[24] The polymer ligand may be of interest for other catalytic applications. It should be also noted that the processing involved heated pressurized CO_2 gas rather than the supercritical substance, which is essential for industry. We are aware that the true catalyst for the transformation should be the iodide anion while cadmium cation is necessary to tightly support the salt at the polymer matrix (for the mechanism of the carbonate formation, see refs. 5–7 and 21).

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.71267/mencom.7741.

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