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Mn(III)(salen)-catalyzed synthesis of cyclic organic carbonates from propylene and styrene oxide in "supercritical" CO_2

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Abstract

Various homogeneous and immobilized manganese-salen complexes were synthesized and tested as catalysts for the formation of cyclic organic carbonates from two liquid epoxides (propylene oxide and styrene oxide) and CO_2, which served as reactant and solvent. Reaction rates in terms of turnover frequencies up to 255 $\mathrm{mol_{product}\,mol_{Mn}^{-1}\,h^{-1}}$ at 98% selectivity were achieved by optimizing the salen ligand as well as the reaction temperature and CO_2 pressure. The reaction rates did not only strongly depend on the kind of salen ligand, the phase behaviour, and the reaction conditions but significant differences were also observed between the epoxide reactants. In addition, two different and simple ways for the immobilization of Mn-salen complexes were examined, among which one led to a highly active, stable and reusable heterogeneized catalyst. In this heterogeneous catalyst the salen ligand was covalently bound to the silica surface and showed low deactivation and almost no leaching of Mn during repetitive use. A coordinatively bound Mn-salen complex resulted in a high loading of the Mn-salen complex on a specially modified silica surface, but was not stable enough. Furthermore, phase behaviour studies and ATR-IR spectroscopic investigations on the product formation are reported that gave further insight into this catalytic reaction taking place at elevated pressure.

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Keywords: Carbon dioxide fixation; Phase behaviour; Propylene oxide; Styrene oxide; Propylene carbonate; Styrene carbonate; Infrared spectroscopy; Expanded liquid; Immobilization; Manganese salen complexes

1. Introduction

Using CO_2 as an environmentally benign, safe, and cheap C_1 building block in synthetic chemistry has gained considerable attention in fine chemistry [1–3]. CO_2 can potentially substitute toxic and hazardous reactants, such as phosgene and carbon monoxide [4], and at the same time serve as solvent with peculiar properties [5–7]. Among other applications, CO_2 is increasingly used in the synthesis of organic carbonates from epoxides, both polycarbonates and cyclic carbonates [8]. Cyclic organic carbonates such as propylene carbonate (4-methyl-[1,3]dioxolan-2-one) are used in different areas, e.g. as polar and aprotic solvents for lithium batteries, resins, cleaning, cosmetics, and personal care, or as intermediate for polymer synthesis [9]. Various catalysts have been developed for the synthesis of cyclic organic carbonates from CO_2 and epoxides, among which are several homogeneous and heterogeneized salen complexes, bearing Sn, Al, Co, Cr, Zn, and further metal centres [10–18]. Salen complexes (=bis(salicylidene)ethylenediamine) have the advantage of a cheap and simple synthetic preparation, high modifiability (ligand tailoring and immobilization on a support), and excellent thermal and chemical stability [19].

Cr(III)-salen and especially Mn(III)-salen complexes are also well known and extensively studied in a related reaction, the asymmetric epoxidation of olefins [20–22]. This epoxidation reaction usually has to precede as separate step the production of the organic carbonates. However, only Cr-salen complexes have been employed either for the copolymerization of CO_2 and epoxides [23] or the synthesis of cyclic carbonates [15,17,24]. Mn-salen complexes do not seem to have any activity in direct copolymerization [25], and, hence have not been considered in the formation of cyclic organic carbonates yet.

However, in the present study, we show that Mn(III)-salen complexes can be successfully used for the "solventless" synthesis of cyclic organic carbonates as well, and they even slightly

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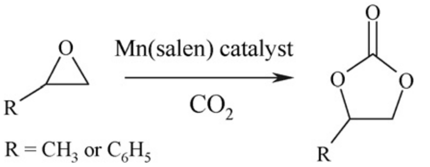

Scheme 1. General reaction scheme of the carbon dioxide fixation to propylene carbonate or styrene carbonate from the corresponding epoxides.

exceed the analogous Cr-salen catalysts in terms of catalytic performance under the same conditions. Therefore they may lead in future to a direct synthetic way from olefins to cyclic carbonates with the same catalyst for both steps. Here we focussed on the formation of cyclic organic carbonates from the epoxide (Scheme 1) and we have investigated and optimized the catalytic activity of several homogeneous and heterogeneized Mn(III)-salen complexes under various reaction conditions. Facile synthetic routes for both homogeneous and immobilized catalysts were chosen. The two model substrates propylene oxide and styrene oxide with different physical properties were tested, and the system was thoroughly studied employing phase behaviour studies and ATR-IR spectroscopy to investigate and optimize the reaction conditions.

2. Experimental

2.1. Synthesis of the homogeneous manganese-salen complexes

2.1.1. Synthesis of the salen ligands

In general, all chemicals were used as commercially obtained without any further purification, and the liquids were of spectroscopic grade. All ligands were analyzed by NMR spectroscopy and the homogeneous complexes by elemental analysis. The salen-type ligands were synthesized according to the literature [26] from the corresponding salicylaldehyde derivates and 1,2-ethanediamines with good yields (82–93%).

Ligand characterization of catalyst **1a–c** was as follows: ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): $\delta = 3.92$ (d, 4H, $CH_2CH{=}CH_2$), 6.82–6.85 (m, 2H, ArH), 6.92 (m, 2H, ArH), 7.20–7.28 (m, 4H, ArH), 8.34 (s, 2H, CH=N), 11.9 (s, 2H, OH); ^{13}C NMR (500 MHz, $CDCl_3$, 300 K): 59.7, 116.9, 118.6, 118.7, 131.5, 132.4, 161.0, 166.5.

Ligand characterization of catalyst **1d** and **1e** was as follows: ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): $\delta = 4.7$ (d, 2H, $CH{=}NCH$), 6.78 (m, 2H, ArH), 6.9 (m, 2H, ArH), 7.04–7.06 (m, 2H, ArH), 7.21–7.44 (m, 12H, ArH), 8.06 (s, 2H, CH=N), 11.86 (s, 2H, OH); ^{13}C NMR (500 MHz, $CDCl_3$, 300 K): 79.9, 116.8, 118.6, 127.8, 127.9, 128.2, 128.5, 131.7, 132.5, 139.5, 160.7, 165.8.

Ligand characterization of catalyst **1f** was as follows: ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): $\delta = 3.4$ (d, 4H, $CH_2CH{=}CH_2$), 3.87–3.95 (m, 4H, $CH{=}NCH_2$), 5.03–5.07 (m, 4H, $CH{=}CH_2$), 5.97–6.02 (m, 2H, $CH{=}CH_2$), 6.79 (m, 2H, ArH), 7.08–7.28 (m, 4H, ArH), 8.35 (s, 2H, CH=N), 11.32 (s, 2H, OH); ^{13}C NMR (500 MHz, $CDCl_3$, 300 K): 31.1, 33.7, 59.8, 115.8, 118.3, 128.0, 129.8, 132.8, 136.7, 159.1, 166.8.

2.1.2. Synthesis of the Mn(III)-salen complexes

The manganese complexes were synthesized in the way reported in [26] from the ligands described above. Bromide- and iodide complexes were obtained by employing LiBr and KI, respectively. In a typical synthesis, the ligand was dissolved in ethanol and heated to reflux. After stopping the heating and employing a dropping funnel, a saturated solution of $Mn(OAc)_2{\cdot}4H_2O$ in ethanol was added slowly into the still hot solution. Instantly, a dark brown color was observed. The mixture was heated to reflux again and left for 1 h. After that, an excess of LiCl (or the corresponding Br^- or I^- salt) was added, followed by another 30 min of reflux. Then, the solution was cooled to room temperature and the solvent was removed employing vacuum. CH_2Cl_2 was afterwards added to the dark brown residue and it was extracted with water. All the homogeneous catalysts were received easily by filtration from the water phase, typically as brown or maroon colored crystals, after cooling in the fridge over night.

Results of the elemental analyses were as follows:

- *Catalyst **1a***. Theoretical values ($C_{16}H_{14}N_2O_2MnCl{\cdot}2H_2O$): C 48.93%, H 4.62%, N 7.13%, O 16.30%, Cl 9.03%; obtained values: C 48.63%, H 4.45%, N 7.05%, O 16.88%, Cl 9.16%.
- *Catalyst **1b***. Theoretical values ($C_{16}H_{14}N_2O_2MnBr$): C 47.91%, H 3.52%, N 6.98%, Br 19.92%; obtained values: C 47.47%, H 3.57%, N 6.82%, Br 19.61%.
- *Catalyst **1c***. Theoretical values ($C_{16}H_{14}N_2O_2MnI{\cdot}2H_2O$): C 39.69%, H 3.75%, N 5.79%, I 26.21%; obtained values: C 39.84%, H 3.40%, N 5.69%, I 25.62%.
- *Catalyst **1d***. Theoretical values ($C_{28}H_{22}N_2O_2MnCl{\cdot}H_2O$): C 63.83%, H 4.59%, N 5.32%, O 9.11%, Cl 6.73%; obtained values: C 65.72%, H 4.93%, N 5.30%, O 9.03%, Cl 5.96%.
- *Catalyst **1e***. Theoretical values ($C_{28}H_{22}N_2O_2MnBr{\cdot}H_2O$): C 58.86%, H 4.23%, N 4.90%, O 8.40%, Br 13.99%; obtained values: C 58.65%, H 4.23%, N 4.80%, O 8.69%, Br 12.95%.
- *Catalyst **1f***. Theoretical values ($C_{22}H_{24}N_2O_2MnBr$): C 54.68%, H 5.01%, N 5.80%, Br 16.53%; obtained values: C 55.02%, H 4.63%, N 5.75%, Br 16.18%.

2.2. Syntheses of the heterogeneous catalysts

2.2.1. Synthesis of catalyst **2**

2.2.1.1. Synthesis of aminopropyl-modified silica. Following the procedure from [17], 5.0 g silica (Fluka Silica Gel 60; BET surface area 460 $m^2\,g^{-1}$; mean pore size 5.1 nm) was filled into a three-neck flask and covered with 50 ml $CHCl_3$ under argon. One milliliter of triethylamine was added, and the suspension was stirred for 30 min. After that, 4.5 g (20.4 mmol) 3-aminopropyltriethoxysilane in 20 ml chloroform was slowly dropped into the suspension. The mixture was then refluxed at 60 °C for 4 h. Silica was filtered off after cooling, washed with 20 ml $CHCl_3$ and dried under vacuum. The yield of the modified silica, denoted in the following as "silica-NH_2", was 7.23 g.

2.2.1.2. Coordinative anchoring of the Mn-salen complex. 2.03 g of silica-NH_2 was filled into a two-neck flask under argon and covered with 50 ml dichloromethane. 1.059 g (2.6 mmol) of

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