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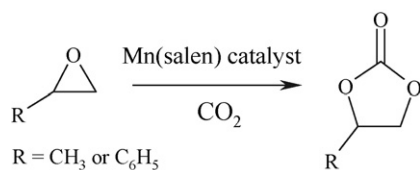
Scheme 1. General reaction scheme of the carbon dioxide fixation to propylene carbonate or styrene carbonate from the corresponding epoxides.

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): δ = 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): δ = 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): δ = 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)$_2$·4H$_2$O 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$_2$Cl$_2$ 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$_2$O$_2$MnCl·2H$_2$O): 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$_2$O$_2$MnBr): 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$_2$O$_2$MnI·2H$_2$O): 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$_2$O$_2$MnCl·H$_2$O): 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$_2$O$_2$MnBr·H$_2$O): 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$_2$O$_2$MnBr): 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

complex **1b** was added and the suspension refluxed at 50 °C for 4 h and left stirring overnight at ambient temperature. A brown fine powder was obtained which was filtered off, washed with CH_2Cl_2, and dried under vacuum. Yield was 2.88 g.

2.2.2. Synthesis of catalyst 3

0.6 g (1.25 mmol) of complex **1f** was filled into a three-neck flask under argon atmosphere and dissolved in 50 ml dry toluene. After that, 0.41 g (2.5 mmol) triethoxysilane was added with a syringe, followed by addition of a small amount of H_2PtCl_6 to the reaction mixture. The brown colored solution was heated to 40 °C and stirred at this temperature for 1 h. Then, 2.5 g dried silica (Fluka Silica Gel 60; BET surface area 460 $m^2 g^{-1}$; mean pore size 5.1 nm) was added, and the suspension was left stirring overnight at ambient temperature. The silica was filtered off and transferred into another flask, where it was refluxed in 100 ml diethyl ether for 3 h in order to remove impurities. After this, the now brownish silica was separated again, washed with diethyl ether and dried under vacuum. Yield was 2.45 g.

2.3. Carbon dioxide insertion reaction

The catalytic reactions were performed in a 500 ml high pressure stainless-steel autoclave (Medimex No. 128) equipped with an active heating and cooling system. The quantity of liquid CO_2 was measured by a RHEONIK mass flow controller (RHM 01, RHE 02). Stirring was done by a motor of type EMOD EEDF 56L/2A equipped with a magnetic-coupled gas stirrer. The stirring rate was set at 1000 rpm.

In a typical reaction, exactly determined amounts of the corresponding liquid epoxide and the catalyst were filled into the reactor. After closing, the reactor was carefully flushed once with carbon dioxide (PANGAS, 99.995%). A defined amount of carbon dioxide from a liquid CO_2 gas cylinder equipped with a dip tube was then dosed into the reactor by employing a compressor (NWA PM-101), and heating and stirring were started. After having reached the working temperature (normally 140 °C), the reaction proceeded for 3 h, then rapid cooling down to room temperature was initiated by a water flow system.

After reaching room temperature, the CO_2-pressure was released by opening the outlet valve. This decompression was carried out slowly during half an hour, in order to minimize the loss of reaction mixture and to allow the liquid phase to degas properly. After this, the autoclave was opened and immediately a defined amount of tert-butylbenzene was added as an internal standard, and the compounds were analyzed by a gas chromatograph (HP-6890) equipped with a HP-FFAP capillary column (30 m × 0.32 mm × 0.25 μm) and a flame ionization detector (FID). Products were identified by gas chromatography (HP-6890) coupled with mass-selective detection (HP-5973) and reference chemicals. As co-products, glycols and oligomers were found in traces, but always appear to be below 1%.

2.4. View-cell experiments

The phase behaviour experiments were performed in a computer-controlled high-pressure view-cell of variable volume (23–63 ml), consisting of a horizontal cylindrical cell with a sapphire window on one side and a movable piston for volume adjustment on the other side [27]. Temperature was controlled by an oil-containing heating jacket and a combined thermo-/cryostat (JULABO F25 HD). The pressure was measured by a pressure transmitter with integrated amplifier for high temperature and pressure (DYNISCO MTD422H-1/2-2C-15/46). The reaction mixture was stirred by a teflon coated stirring bar inside the cell, driven by a magnetic stirrer plate (HEIDOLPH MR 2002) placed below. The amount of CO_2 to be introduced into the cell was measured by a mass-flow meter (RHEONIK, RHM015) and electronically steered by an automated needle valve (KÄMMER). Pictures were taken by an attached 8-bit CCD camera (KAPPA CF 8/4). The whole system was controlled by a standard computer running the software BridgeVIEW (National Instruments).

In a typical experiment, the cell was set to the desired volume and charged with the required amount of liquid epoxide. After closing, CO_2 was first carefully used to flush the system and then the desired amount was introduced. The cell was heated to the working temperature under moderate stirring. Pictures were taken when the desired state was reached after turning off the stirring.

2.5. Further characterization

2.5.1. Nuclear magnetic resonance spectroscopy (NMR)

^1H NMR and ^{13}C NMR spectra were taken on a Bruker Avance 500 instrument at an operation frequency of 500.12 MHz.

2.5.2. Inductively coupled plasma optical emission spectrometry (ICP-OES)

ICP-OES measurements to determine the Mn-content in the heterogeneous samples were performed at ENVILAB AG (Zofingen, Switzerland).

2.6. In situ ATR-IR spectroscopy

IR-spectroscopic studies were performed in a home-built high pressure batch cell, consisting of three mobile parts. Mounted on a moveable holder, a round disk-shaped bottom piece holding a cavity for the internal reflection element (IRE) was placed, below which also the mirrors for the IR-beam were attached. On top of this bottom piece, a hollow stainless steel cylinder (8 cm outer diameter, 5.7 cm inner diameter) was fixed. This cylinder comprised a diminution of volume towards the bottom, which together with the IRE surface and the cap, formed the reactor volume (10 ml). A Viton O-ring placed in a rectangular shaped chamfer was used to tighten the cell on the ATR-IR crystal. The cap as third part contained the lines for inlet, outlet, pressure transducer (WIKA tronic line) and on top the burst plate (Swagelok, 190 bar). The whole setup withstands a pressure up to 200 bar and a temperature up to 200 °C. Note that the spectra get noisier above 120 °C due to vicinity to the detector or perturbing IR radiation generated by the heating process. The cell was heated by a 160 W cartridge heater (SUVAG), which was built

into the bottom plate, together with a NiCr/Ni thermocouple. Temperature control was achieved by a commercial controller (PMA, KS-20-1, Omni Ray). As internal reflection element for the ATR-IR measurements, a trapezoidal crystal of ZnSe was used (50 mm × 20 mm × 2 mm, angle of incidence 60°). Stirring was performed by a small magnetic stirring bar, able to be placed into the reactor volume. A motor with magnet was placed below the holder of the cell. The gas inlet line for CO_2 at the cap was connected to a compressor unit (NWA PM-101 and a flow controller (RHEONIK, RHM015), attached to a dip-tube bottle of liquid CO_2 (PANGAS, 99.9995%). The whole cell, together with the holder was placed in a BRUKER EQUINOX 55 spectrometer equipped with a liquid nitrogen-cooled mercury cadmium telluride (MCT) detector.

In a typical experiment, the liquid epoxide (2 ml) and the catalyst **1b** (7.5 mmol) were filled into the ready and aligned cell. After having closed the cap and flushed the cell carefully, CO_2 (2.7 g) was introduced into the cell. Under moderate stirring, the heat source was turned on and repeated measurements were started to be taken. Above 100 °C the first product signals could be identified. The temperature was kept at 120 °C. The measurements were repeated in definite time intervals until no further change in the spectra was visible.
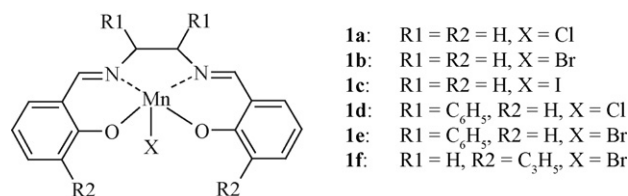
Safety note: The experiments described in this paper involve the use of high pressure and require equipment with an appropriate pressure rating.

3. Results and discussion

3.1. Syntheses of the homogeneous and heterogeneized catalysts

The preparation of the salen ligands and the homogeneous complexes depicted in Scheme 2 was straightforward and successful as described in Section 2.1. The ligands could be synthesized in high yields (82–93%) and high purity by double recrystallization, and the desired structure could be confirmed by NMR.

The corresponding Mn complexes used as homogeneous catalysts **1a**–**f** could also be synthesized with little synthetic effort. The yields were moderate (47–78%) due to the fact that the complexes were obtained by filtration after crystallizing over night in the fridge, possibly leaving considerable amounts dissolved in solution. Note that intensive work-up of the complexes was omitted at this stage. The catalysts all showed a typical brown color, and elemental analysis confirmed the desired composition. The small divergence between some of the theoretical and the measured values of the elemental analyses can be explained by strong coordination of solvent molecules to the manganese centre, especially water. This effect was also observed elsewhere with similar salen complexes [15,17].

The immobilized catalysts **2** and **3** required a more extensive synthetic route, following closely the analogous syntheses of immobilized chromium-salen complexes (cf. Ref. [17]). Both heterogeneized catalysts consisted of a fine, brownish powder, which in both cases was refluxed in various pure solvents and filtered off repeatedly, until the solvent remained colorless. Since the synthetic route was known and followed closely, only the Mn-content was analyzed by ICP-OES for characterization. The resulting weight percentage of Mn on the support was in the expected range of 1–1.5 wt% for **3**. In contrast, it was high (over 5 wt%) for **2**. This is probably associated with the high loading of aminopropyl-anchors on the support for **2**.

3.2. Catalytic activity of the homogeneous catalysts

The catalytic results from the cycloaddition of CO_2 and propylene oxide or styrene oxide are given in Table 1. The rate of the cyclic carbonate synthesis is given as turnover frequencies (TOF, $mol_{product} \, mol_{Mn}^{-1} \, h^{-1}$) calculated on the assumption that all Mn-complexes were active. This is certainly a conservative estimate since some of the complexes may not contribute to the reaction due to possible agglomeration or incomplete dissolution. The selectivity towards the cyclic carbonate was very high in all reactions, at least 98%, as observed when analyzing the product mixture by GC and GC–MS. Only traces of by-products such as diols and oligomers were found, which could not all be completely identified by GC–MS due to their low concentration.

The highest TOFs measured were 213 h^{-1} with catalyst **1c** in the reaction of styrene oxide and 233 h^{-1} with catalyst **1f** in the reaction of propylene oxide. Hence, manganese salen complexes seem to be more active than similar manganese catalysts for this reaction, using peraza macrocyclic ligands [28],

Scheme 2. Overview on the homogeneous catalysts synthesized and tested in this work; the halide and the salen ligand were varied. The nomenclature given is used throughout the paper.

Table 1
Catalytic activity of the different homogeneous catalysts (Scheme 2) in the reaction of the epoxides and carbon dioxide

Catalyst (–)	Epoxide (–)	Yield[a] (%)	TOF[b] (h^{-1})
1a	PO (propylene oxide)	12	18
	SO (styrene oxide)	10	11
1b	PO	70	106
	SO	92	183
1c	PO	31	203
	SO	49	213
1d	PO	64	146
	SO	3	11
1e	PO	16	111
	SO	52	109
1f	PO	34	233
	SO	67	117

[a] Reaction conditions: 10–20 ml epoxide, 27 g CO_2, 50–80 mg catalyst. Reaction time was 3 h at 140 °C. Yield of cyclic carbonate was based on epoxide amount, selectivity was always higher than 99%.
[b] Turnover frequency [$mol_{product} \, (mol_{Mn \, on \, catalyst} \, h)^{-1}$].

manganese porphyrins [29] or manganese-PPN salts [30]. It is also noteworthy that the catalytic reaction investigated in this work was performed without any additional solvent or co-catalyst which are usually applied in similar metal-salen systems [12,15,16,18,31]. The, in this study undesired, direct copolymerization reaction of CO_2 and epoxides seems to be less prominent when using manganese-salen complexes compared to chromium-salen catalysts. Recently, Darensbourg et al. investigated this copolymerization reaction with a variety of metal salen complexes [25]. Manganese-salen complexes turned out to be inactive in direct copolymerization, which is more favoured at low temperatures. At higher temperatures (above 100 °C), the cyclic carbonate product is the main product in all comparable systems. This is also the case for chromium-salen catalysts employed for the production of both carbonate products [17,24], and for cobalt-salen complexes used at higher temperatures [32], which at low temperatures also selectively produce the copolymerization product [33]. Thus, when targeting towards cyclic carbonate products, manganese-salen complexes seem to offer an advantage in selectivity, but they also require relatively high temperatures.

Regarding the effect of the halide anion, the activity of the catalysts corresponds to the nucleophilicity of their halide anions, where $I^- > Br^- > Cl^-$. This trend is clearly visible for the unsubstituted salen complexes **1a**, **1b**, and **1c**. The bromo-complex **1b** was much more active for both tested substrates than the chloro-complex **1a**, while the increase in activity using the iodo-complex appears tremendous for PO, but only moderate for SO. This observation agrees with Sun et al. [34], who found the same dependence for the catalytic activity of Zn-halide catalysts in the cycloaddition of CO_2 to styrene oxide.

When using propylene oxide as substrate, the phenyl-substituted complexes **1d** and **1e** were more active than their unsubstituted salen-analogs **1a** and **1b**. A similar observation was made for chromium salen complexes in the formation of propylene carbonate under the same conditions [17]. In this case a TOF of $90\,h^{-1}$ was reached with Cr(salen)Cl and $170\,h^{-1}$ with its phenyl-substituted analog. Since the same trend is visible here, the reason may be a strong difference in solubility between the original salen complex and its phenyl-substituted counterpart in the mixture of PO, PC and CO_2. Apolar groups, such as phenyl substituents, may increase the solubility of the catalyst in this reaction mixture. This observation is also supported by the fact, that complex **1f**, which bears allyl-groups on its aromatic ring, shows also better performance than catalyst **1b** without the substituents. Interestingly enough, this trend is reversed when using styrene oxide as substrate. There, the complexes with a standard salen ligand performed best, and any substituents appeared to be an impediment for the reaction. Obviously, when using propylene oxide as substrate, the solubility effects seem to be stronger than a possible steric hindrance, which occurs more in substituted ligands. In styrene oxide, this seems to be reversed. Beside the different solubility of the catalysts in styrene oxide, also the chemical properties of the two epoxide substrates differ. Styrene oxide is generally considered to react slower than propylene oxide, due to a sterically demanding phenyl group and the relatively low reactivity of its β-carbon atom [34,35].
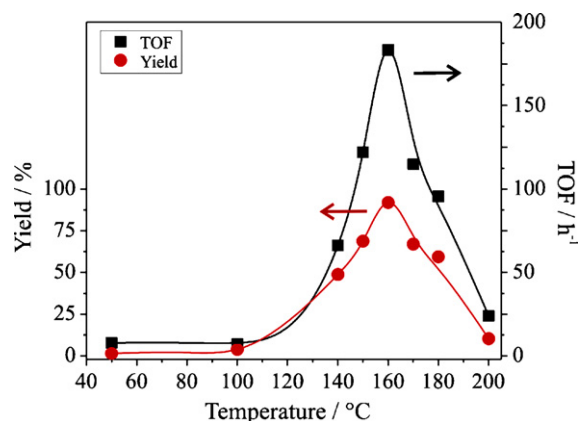

Fig. 1. Temperature dependence of the catalytic performance of Mn(salen)Br **1b** in the chemical fixation of carbon dioxide to styrene carbonate. The catalytic activity in terms of turnover frequency (TOF, related to the total amount of Mn present in the catalyst) and styrene carbonate yield (Y) is depicted. In all experiments, epoxide (90 mmol), catalyst (0.18 mmol) and CO_2 (614 mmol) remained in the same ratio while the working temperature was varied.

This difference in reactivity was also observed by *in situ* ATR-IR studies described in Section 3.5.

3.3. Parametric studies

3.3.1. Influence of temperature

The influence of the reaction temperature on the performance of Mn(salen)Br **1b** was tested by employing a defined ratio of styrene oxide, CO_2 and catalyst in a series of experiments covering a broad temperature range. The results of this study are shown in Fig. 1. Interestingly, a very sharp maximum of activity is visible at a temperature of about 160 °C, and higher reaction temperatures lead to a fast decrease in activity and product yield. This behaviour could be influenced by a change in phase distribution of the reactants occurring at higher temperatures, where increasing amounts of styrene oxide are dissolved in the supercritical CO_2-phase and less remains in the liquid CO_2-expanded phase where the reaction takes place. This effect was also observed in the phase behaviour studies (vide infra, Fig. 3), especially when using a high CO_2 to epoxide ratio. The same dependence of the volume of the liquid phase on the temperature was observed in the solvent-less cycloaddition of CO_2 to propylene oxide, where a strong influence of the temperature on the phase behaviour and reactant distribution was found. Yasuda et al. [36] also observed an activity maximum at around 200 °C in their solvent-less propylene oxide system. Further increase of the temperature led to a drastic decrease in activity and selectivity.

3.3.2. Influence of CO_2 pressure

The amount of CO_2 employed in this reaction is a crucial parameter, since it acts as reactant and reaction medium at the same time. For the solvent-less synthesis of propylene carbonate from propylene oxide and CO_2, an optimal ratio of 1:4 (PO:CO_2) was found [37]. Although working with a different epoxide (styrene oxide), the same behaviour was observed in this study (Fig. 2). Variation of the amount of CO_2 while employing the
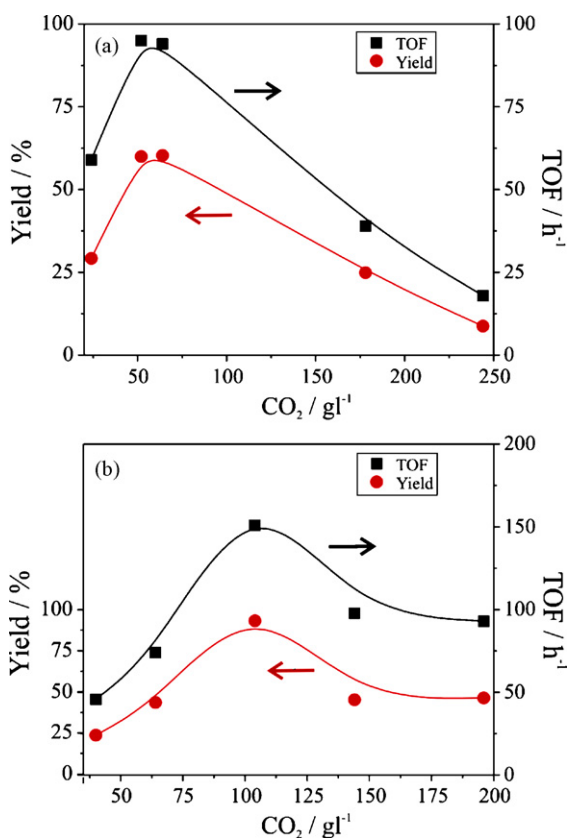
Fig. 2. Influence of the amount of CO_2 on the reaction. The amount of epoxide and the temperature (140 °C) were kept constant to investigate the optimal CO_2 to epoxide ratio. (a) 20 ml epoxide in a 500 ml autoclave. The maximum is reached at around 27 g CO_2, which is a molar ratio of styrene oxide:CO_2 close to 1:4. (b) The same trend but higher activity is visible when the concentrations of epoxide and CO_2 are doubled while maintaining the same ratio.

same amount of styrene oxide led to a maximum in catalytic activity and yield of product when the epoxide:CO_2 ratio was close to 1:4, resulting in a two phase system with a dense, CO_2-expanded liquid-like phase and a more gas-like phase on top. This effect is independent from the overall density of the system (Fig. 2). When the overall density of the reaction system was doubled, the absolute activity in terms of TOF and yield was higher, while the same maximum appeared at an epoxide:CO_2 ratio at around 1:4. In both cases, a further increase of the CO_2-pressure led to a decrease in activity, and unlike other reactions in CO_2, the single-phase region finally reached turned out to be very unfavourable for this reaction. Yasuda et al. found a similar dependency in their solvent-less propylene oxide system [36], where a distinct maximum in terms of propylene carbonate yield was achieved at around 80 bar. These observations indicate, that especially under solvent-less conditions the ratio of CO_2 and liquid epoxide has a tremendous influence on the reaction. Although the chemical properties of the epoxides themselves are different, the CO_2:SO and CO_2:PO ratio had a minor influence. Note however, that carbon dioxide is rather unpolar and the properties can be especially tuned in expanded liquids, which can also be CO_2-expanded reactants [38–40].

3.4. Phase behaviour

A series of phase behaviour studies were performed to investigate the influence of the fluid phases present on the catalytic activity. Selected snapshots are shown in Fig. 3. In general, addition of CO_2 to the liquid styrene oxide (SO) led to a strong expansion of the dense liquid-like phase at ambient temperature. An increase in temperature then lowered the CO_2-content of the liquid phase continuously (Fig. 3, volume decrease). A similar behaviour was found for propylene oxide (cf. Ref. [37]). The influence of the temperature was much stronger when a high CO_2:SO-ratio was employed (Fig. 3A–C). In this case, the primary expansion of the liquid phase was tremendous (Fig. 3B), but was then completely reversed at higher temperatures as needed for the reaction (Fig. 3C). When using the optimal ratio of a fourfold excess of CO_2, the initial expansion during carbon dioxide addition appeared relatively moderate (Fig. 3E), but remained stable also at higher temperatures (Fig. 3F). This turned out to be beneficial for the catalytic reaction. The homogeneous catalyst remains in the expanded liquid phase under reaction conditions, where probably the whole catalytic process takes place. To follow the reaction and product formation in this expanded liquid phase at the bottom of the reactor, the incorporation of spectroscopic techniques, i.e. in situ ATR-IR spectroscopy offers an adequate tool [41].

3.5. IR-spectroscopic study

To compare the catalytic activity of Mn(salen)Br **1b** in the cycloaddition of CO_2 to the two model substrates propylene oxide and styrene oxide, in situ spectroscopic measurements were performed in a batch reactor cell with built-in ATR-IR crystal (see Section 2 for details). The volume of this cell (10 ml) was much smaller than the conventional batch reactor for catalytic studies, but the ratio of epoxide and CO_2 was kept at 1:4, thus in optimal range. Fig. 4 shows the superimposed spectra of both experiments, where the arrows indicate the temporal development. Both the epoxide and upon reaction the carbonate are visible together with the CO_2-bands in the ATR-IR spectra. The ν_2 bending mode of carbon dioxide was typically located below 660 cm^{-1}, which supports the phase behaviour experiments which indicated that an expanded liquid is present, because the density (for correlation of infrared band and density, cf. Ref. [42]) is significantly higher than in scCO_2. For quantification of the formation of cyclic carbonate, mainly the C=O stretching band at around 1800 cm^{-1} was used. It has a strong absorbance and no interfering bands are located in this area for both epoxides. The measurements were kept running until no further increase of this band was visible. Beside the C=O stretching band, also increasing C–O stretching bands were observable in both cases (Fig. 4). The most prominent decreasing band was the C–O stretching of the epoxide in the region of 850 cm^{-1} in both cases.

The areas below the C=O stretching band at 1800 cm^{-1} for both epoxides were then analyzed in their chronological development (Fig. 5). The time resolution was obtained by taking spectra in regular intervals after a temperature of 100 °C was
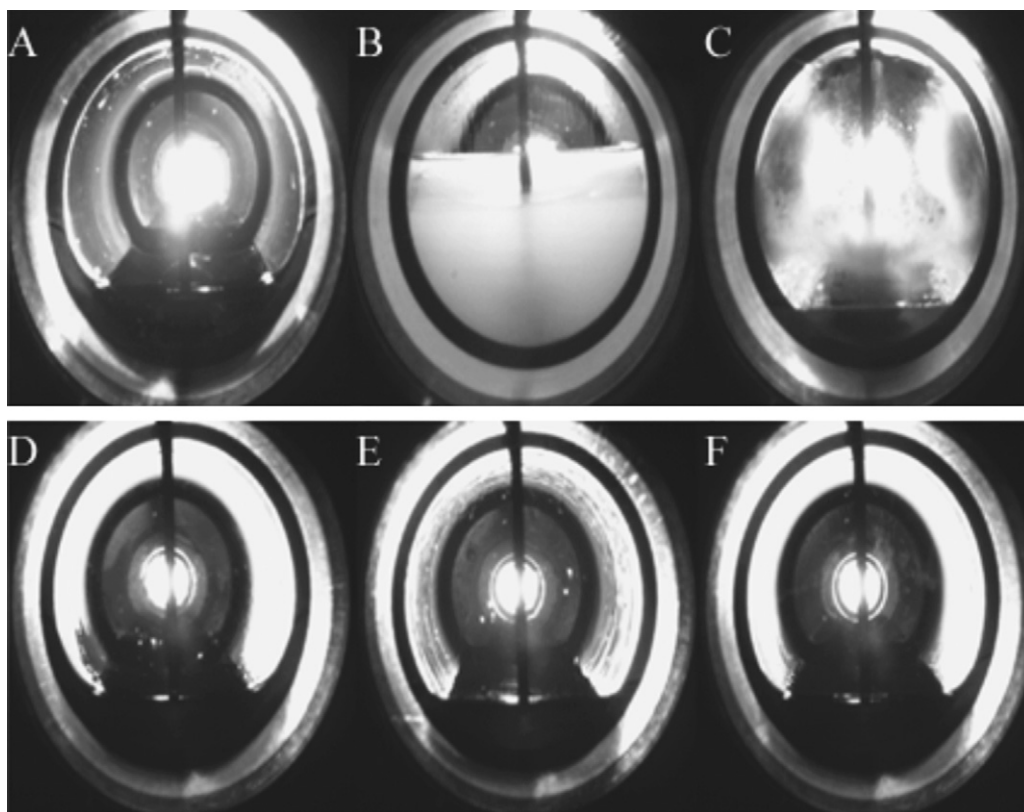
Fig. 3. View cell experiments undertaken to clarify the phase behaviour during reaction and its influence on the reaction. Pictures A to C show a reaction with 10 ml styrene oxide and 60 g CO_2 (approximate molar ratio epoxide:CO_2 = 1:16), where A shows the liquid phase (epoxide) without CO_2, B after CO_2-introduction, and C at the temperature of 100 °C. Pictures D to F show the same experiment with only 27 g CO_2 (approximate molar ratio epoxide:CO_2 = 1:4), where D is the pure epoxide, E after CO_2-introduction at ambient temperature, and F at 100 °C. The larger amount of CO_2 (A to C) is expanding the liquid phase only at low temperatures; in the high temperature regions the liquid phase is even slightly smaller as if less CO_2 is present (E to F).
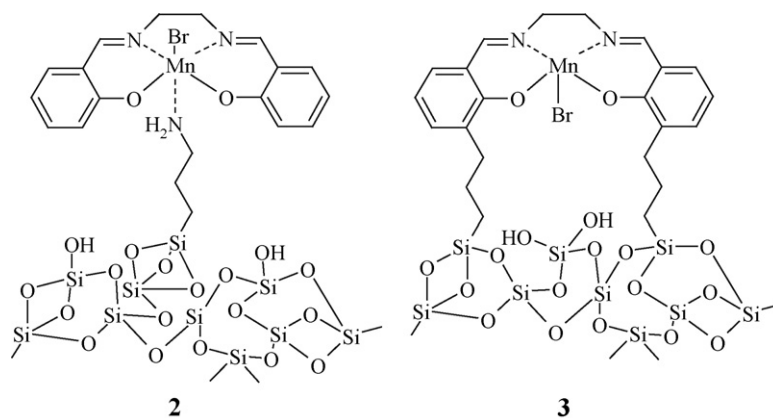
Scheme 3. Two kind of immobilization of the Mn(salen)Br catalysts employed in this work. Catalyst **2** is coordinated to an aminopropyl group which was previously attached to the silica support, while catalyst **3** is covalently bond to the silica support by anchoring functional groups attached to the ligand.

reached during heating (no signal could be observed below that temperature). The final constant temperature was 120 °C, limited by the spectrometer setup. Comparing Fig. 5a and b shows that styrene oxide reacts much slower in the beginning than propylene oxide. At 120 °C, the reaction was far from completion after the normally employed testing time of 3 h. Propylene oxide on the other hand seems to react much faster, reaching almost maximum conversion after 3 h. Interestingly, also the maximum conversion was considerably different for both substrates. The

yield of propylene carbonate at 120 °C was 78.4%, whereas the yield of styrene carbonate remained as low as 20.8% after the total time measured, which also corresponds to batch reactor experiments performed at 120 °C, and not at 140 °C as listed in Table 1. The long initiation time for styrene oxide could stem from a poorer solubility of the catalyst in the expanded SO-CO_2-phase than in the expanded PO-CO_2-phase, especially when no product is formed yet. Also the volume of the expanded phase may increase upon organic carbonate formation in the beginning.
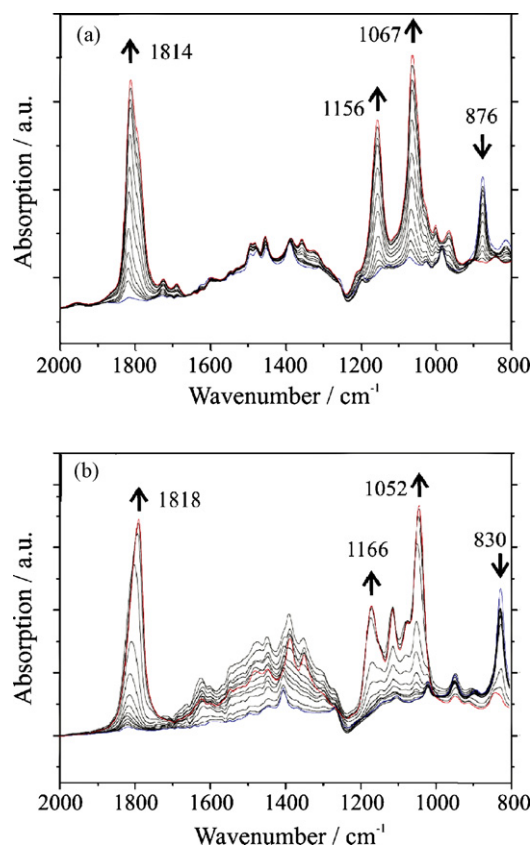
Fig. 4. Changes over time in IR-absorption during reaction. The spectra were obtained using *in situ* ATR-IR spectroscopy and put on top of each other to show the evolution of product bands and the coeval disappearance of the reactant bands. The arrows indicate the temporal development. (a) Reaction of styrene oxide and CO_2 to styrene carbonate. The rising band at $1814 \, cm^{-1}$ depicts the C=O stretching mode of the formed cyclic carbonate, the bands at 1156 and $1067 \, cm^{-1}$ are assigned to the C–O stretching modes of the carbonate. The most clearly visible vanishing band is that of the C–O–C ring structure of the epoxide at $876 \, cm^{-1}$. (b) Reaction of propylene oxide and CO_2 to propylene carbonate. Similar assignments of the vibrational bands can be employed. In both cases, the experimental procedure was the same: 15 mmol epoxide, 0.04 mmol Mn(salen)Br **1b** and 25 mmol CO_2 were filled in the spectroscopic cell (10 ml) and heated to 120 °C until completion of the reaction.

Another experiment performed under the same conditions with 5 wt% styrene carbonate already present at the beginning showed a much shorter initiation time with an increase in product content already after 60 min, indicating a larger volume and probably better solubility of the salen complexes in the carbonate-enriched expanded SO-CO_2 phase. On the other hand, the slope of the curve was flatter, thus the reaction proceeded slower. Higher styrene carbonate content may also increase the viscosity of the liquid phase. Another factor may be the different CO_2-expansion ability of pure and carbonate-containing styrene oxide. The relative density of CO_2 can be estimated by observing the shift of its ν_2 rotation-vibration band in the infrared-spectrum. An increase in density leads to a shift towards lower wavenumbers [42]. While working with pure styrene oxide, the initial ν_2 band at ambient temperature was found at $657 \, cm^{-1}$, then shifted towards lower wavenumbers gradually upon heating and proceeding of the reaction, until reaching $655 \, cm^{-1}$. The second experiment with 5 wt% styrene carbonate present had a ν_2

band at $662 \, cm^{-1}$ at ambient temperature, which then shifted quickly towards $656 \, cm^{-1}$ upon heating and reaction progress. The density of the CO_2-expanded liquid phase seems to increase gradually with styrene carbonate formation, especially at higher temperatures, showing that less CO_2 is dissolved in the liquid-like phase at the bottom in the end of the reaction.

3.6. Catalytic activity of the immobilized catalysts

The catalytic activity of the two immobilized catalysts **2** and **3** are given in Table 2. Among the different routes proposed in literature [43], the simple coordination of the catalysts via an amino ligand and the covalent fixation were selected (Scheme 3). The immobilized catalysts were tested for the substrate styrene oxide and were employed repeatedly in order to investigate their stability and reusability. Catalyst **2**, immobilized by coordination to the aminopropyl-modified silica support, showed a very poor catalytic activity, although the Mn loading was very high. In addition, it deactivated during reuse (Table 2, entries 1–3). This is in contrast to other reports, where this immobilization technique by coordination produced active and reusable ruthenium catalysts [44]. A similar coordinatively immobilized chromium catalyst used by Ramin et al. [17] showed trends of fast deactivation upon repeated employment, but turned out to be very active during its first use. This deactivation was also observed by Garcia and coworkers [11]. Apart from the successive loss of Mn by leaching, catalyst **2** seems to form inactive species on its surface, thus appearing unsuitable for this catalytic reaction. Another possibility may be that Mn(III) is less suitable to form stable six-coordinated complexes with an amino-ligand than Cr(III). Other publications report similar immobilization routes for manganese-salen complexes, but either link the aminopropyl-anchor directly to the salen ligand [45] or use a different anchoring ligand such as an anionic phenoxy-group [46] to form immobilized six-coordinated manganese-salen complexes. Also Zhou et al. found that chromium-salen complexes could be easily immobilized on zeolites by this technique [47], while ana-

Table 2
Catalytic activity of the immobilized catalysts **2** and **3** (Scheme 3) in the reaction of styrene oxide and carbon dioxide in repetitive use

Catalyst (–)	Run (–)	Yield[a] (%)	TOF[b] (h^{-1})	Mn content[c] (wt%)
2	1	6.2	1.2	5.7
2	2	4.5	8.3	3.5
2	3	1.7	4.1	2.6
3	1	95	196	1.4
3	2	0.6	1	1.1
	2[d]	85	244	1.1
3	3[d]	78	255	1.2
SiO_2	–	1.1	–	–

[a] Reaction conditions: 20 ml epoxide, 27 g CO_2, 900–1000 mg catalyst. Reaction time was 3 h at 140 °C. Yield of cyclic carbonate was based on epoxide amount, selectivity was always higher than 98%.
[b] Turnover frequency [$mol_{product}$ ($mol_{Mn\,on\,catalyst}$ h)$^{-1}$].
[c] Total Mn content of the silica-supported catalysts in weight percent, determined by ICP-OES.
[d] Catalyst was regenerated by addition of an equimolar amount of $(Et)_4NBr$ to the reaction mixture.
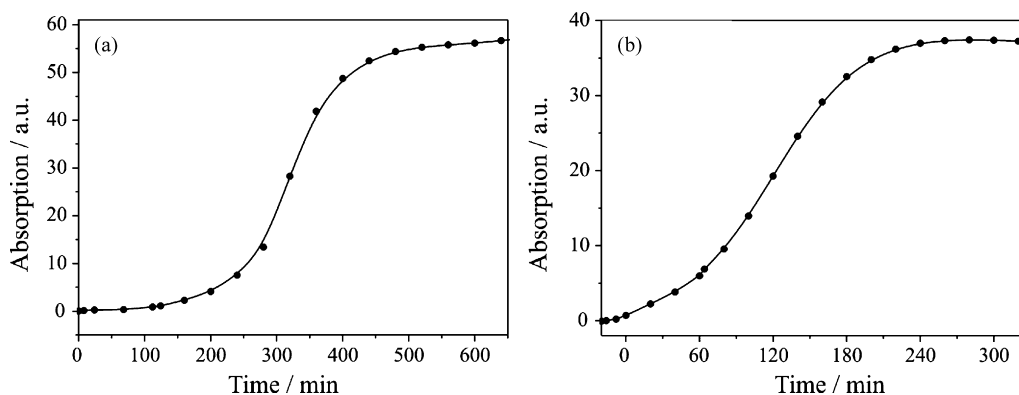
Fig. 5. On-line ATR-IR measurements of the reaction progress of the epoxide in the CO_2-expanded liquid phase at 120 °C, where (a) is the reaction of 2 ml styrene oxide and (b) the reaction of 2 ml propylene oxide. In both cases, 10 mg of homogeneous Mn(Salen)Br **1b** was employed as catalyst. The curves were obtained by integrating the peak area of the C=O stretching mode at around 1800 cm^{-1} of the *in situ* ATR-IR measurements (Fig. 4).

logue manganese-complexes on the same support suffered from a faster deactivation upon reuse [48].

In contrast, the covalently immobilized catalyst **3** showed a tremendously better overall performance and reusability (Table 2, entries 4–7), reaching TOFs between 196 and 255 h^{-1}, which are in the range of the homogeneous catalyst **1b**. Moreover, it is striking that the conversion is higher than for catalyst **2**, even though its initial Mn content was much lower than the one of catalyst **2**. Due to the twofold covalent anchoring of the quadridentate ligand on the silicagel support, also the leaching effect upon reuse could be successfully minimized. Apparently, this way of immobilizing salen-type complexes provides a relatively easy route towards almost real heterogeneous catalysts with the advantage of a defined structure as in homogeneous catalysts. Apart from the higher leaching resistance of **3** compared to **2**, the original coordination sphere of the Mn centre remains unchanged. This may also be a reason why **2** lost the major part of its catalytic activity after immobilization via anchored coordinating amino-ligands. During reuse, catalyst **3** needs regeneration though. The catalyst looses its halide ligand during the catalytic reaction, since the halide acts as nucleophile in the activation of the epoxides. Without addition of a halide source like (Et)$_4$NBr, the catalytic activity drops down drastically already after one use. This effect could be compensated by adding an amount of halide equimolar to the manganese content of the catalyst to the reaction mixture and shows that not only the transition metal but also the nucleophilic halogen ion are important for the reaction mechanism, also for the Mn-catalyzed CO_2-addition to epoxides. This is in contrast to mechanisms suggested for other catalyst systems, where the halide remains coordinated to the transition metal [49,50].

4. Conclusions

Salen complexes of Mn(III) show good catalytic performance in the cycloaddition of CO_2 to epoxides. These catalysts are easily accessible by a straightforward synthetic route and, since being air-stable, insensitive towards light, and non-toxic, can be stored and handled without excessive precaution. Furthermore,

they can be immobilized on silica and used as heterogeneized catalysts with all related advantages while maintaining good catalytic performance and reusability.

Parameter studies undertaken reveal the optimal conditions for the cycloaddition of CO_2 to liquid epoxides without any additional solvent catalyzed by Mn-salen complexes, where yields of cyclic carbonate as high as 95% and turnover frequencies up to 255 h^{-1} could be reached. The optimum reaction medium is an expanded solvent, improved in the presence of the carbonate. Depending on the epoxide used, Mn-salen complexes with different ligands have been found most active. In case of heterogeneous catalysts only covalently immobilized catalysts appeared sufficiently stable under the reaction conditions applied here. Since Mn-salen complexes are well known and intensively studied catalysts for the asymmetric epoxidation of olefins, a reaction preceding the reaction presented in this paper, they may be interesting candidates for a direct synthetic route from olefins to cyclic carbonates.

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