

Solventless synthesis of propylene carbonate catalysed by chromium–salen complexes: Bridging homogeneous and heterogeneous catalysis

Michael Ramin, Fabian Jutz, Jan-Dierk Grunwaldt, Alfons Baiker*

Department of Chemistry and Applied Biosciences, Swiss Federal Institute of Technology, ETH-Hönggerberg, CH-8093 Zürich, Switzerland

Received 6 June 2005; received in revised form 2 August 2005; accepted 2 August 2005

Available online 6 September 2005

Abstract

Various homogeneous chromium–salen complexes were synthesised and tested concerning their catalytic performance in the synthesis of propylene carbonate from carbon dioxide and propylene oxide. The most active complexes were immobilised on a silica support and tested in the same reaction. Different immobilisation methods were applied including anchoring of the complex through coordination with the metal, and covalent bonding via the ligand. Rates up to $300 \text{ mol}_{\text{product}} \text{ mol}_{\text{Cr}}^{-1} \text{ h}^{-1}$ at 98% selectivity were achieved with the heterogeneous catalysts without the use of any additional solvent or co-catalyst. The coordinatively-bound complexes showed low stability and a very strong deactivation during reuse, whereas the corresponding covalently-bound complexes hardly showed any chromium leaching during catalyst recycling experiments. The catalysts were characterised by means of X-ray photoelectron spectroscopy (XPS), thermal analysis, inductively-coupled plasma optical emission spectrometry (ICP-OES) and diffuse reflectance IR spectroscopy (DRIFTS) in as-prepared state and after use.

© 2005 Elsevier B.V. All rights reserved.

Keywords: Carbon dioxide fixation; Propylene carbonate; Propylene oxide; Carbon dioxide; Chromium–salen complexes; Immobilisation; Catalyst deactivation; Infrared spectroscopy; Thermal analysis; XPS

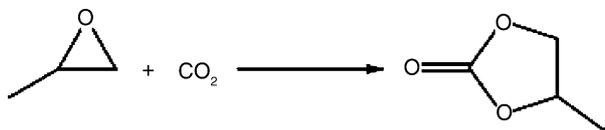
1. Introduction

The synthesis of propylene carbonate by the use of carbon dioxide as C_1 -building block (Scheme 1) is a step towards greener production of propylene carbonate. Toxic and hazardous reactants, such as phosgene and carbon monoxide [1–4] can be substituted by carbon dioxide which simultaneously serves as a solvent. Various homogeneous catalysts were reported for this reaction [5–14] usually carried out in the presence of a solvent. Heterogeneous catalysis would be desirable due to easier product separation and because the process can be simplified [15]. However, the activity and stability of heterogeneous catalysts is still not satisfying [16–20]. Homogeneous chromium–salen complexes were reported as active homogeneous catalysts for carbon

dioxide fixation [21–23]. Due to the use of chelate complexes with high complexation ability, the immobilisation of these complexes represents an attractive strategy towards heterogeneous catalysts with improved stability. Different immobilisation strategies have been reported in literature [24], among them is coordination of the metal centre to a modified support surface or covalently-bound inorganic complexes.

In this work we aimed at the heterogeneous catalytic synthesis of propylene carbonate in a process without the use of co-solvents. In the first step we searched for suitable homogeneous catalysts that were also sufficiently active in the absence of co-solvents. By variation of the structure of salen ligands of the corresponding chromium–salen complexes, the influence of these ligands on the catalytic behaviour was investigated. In a further step the most promising homogeneous complexes were grafted onto a silica support using different immobilisation methods. Finally, the resulting het-

* Corresponding author. Tel.: +41 1 632 31 53; fax: +41 1 632 11 63.
E-mail address: baiker@chem.ethz.ch (A. Baiker).



Scheme 1. Synthesis of propylene carbonate from propylene oxide and carbon dioxide.

erogeneous catalysts were compared with respect to their catalytic performance and their reusability.

2. Experimental

2.1. Synthesis of the homogeneous chromium–salen complexes

In general, the chemicals were used without any further purification, and the liquids were of spectroscopic grade. All products were analysed by NMR and elemental analysis.

According to Scheme 2, the syntheses of the complexes **1–8** (Scheme 3) were performed similarly as reported in [25,26]. All reactants for the syntheses were commercially available except 3-allylsalicylaldehyde, an essential reactant of complex **8**. It was synthesised as described in [27]. The yield of the different supported complexes ranged from 42 to 86%. In the last step, chromium dichloride was added to the ligand and oxidised in the presence of air.

2.1.1. Synthesis of 3-allylsalicylaldehyde

Tributylamine (4.35 g, 80 mmol) and SnCl_4 (4.125 g, 20 mmol) were given to a solution of 2-allylphenol (25.05 g, 187 mmol) in toluene (500 ml). After stirring for 20 min at ambient temperature, paraformaldehyde (9.05 g, 0.4 mmol)

was added. The mixture was heated to 100 °C for 8 h, afterwards quenched in cold water (75 ml), and a pH 2 was adjusted with HCl (2 N). The water phase was extracted three times with diethyl ether (20 ml), and finally the organic phases were united. After removal of the solvent, the remaining dark yellow oil was purified by chromatography (ethyl acetate:hexane = 1:9). Yield was 11.67 g (28% based on 2-allylphenol). ^1H NMR (500 MHz, CDCl_3 , 300 K): δ = 3.4 (d, 2H, $\text{CH}_2\text{CH}=\text{CH}_2$), 5.15 (m, 2H, $\text{CH}=\text{CH}_2$), 5.90–6.15 (m, 1H, $\text{CH}=\text{CH}_2$), 6.90–7.00 (m, 1H, ArH), 7.38–7.48 (m, 2H, ArH), 9.85 (s, 1H, CHO), 11.32 (s, 1H, OH); ^{13}C NMR (500 MHz, CDCl_3 , 300 K): 33.0, 116.5, 119.8, 131.2, 136.0, 137.5, 196.6.

2.2. Syntheses of the heterogeneous catalysts

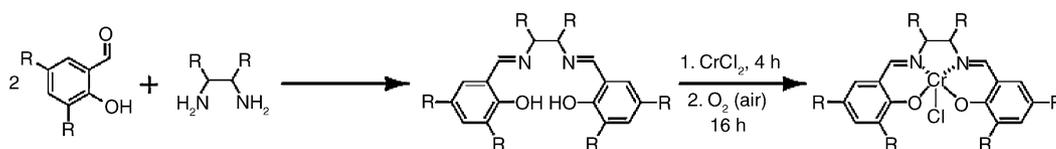
2.2.1. Synthesis of catalyst **9**

(a) Modification of the silica

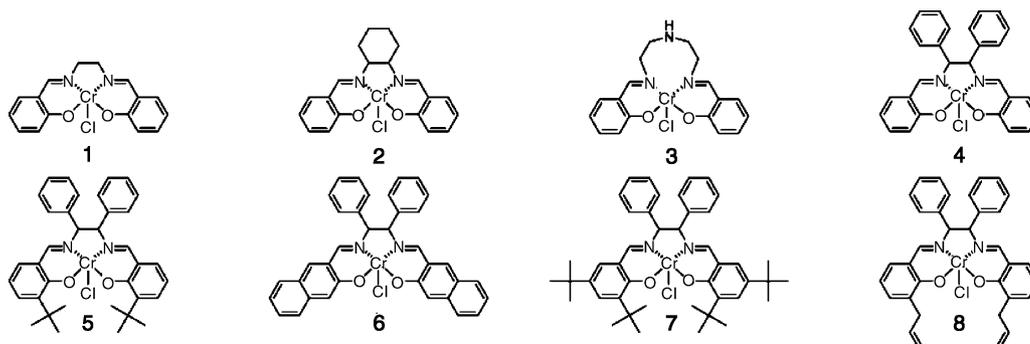
Silica (16.0 g; Fluka Silica Gel 60; BET surface area, $460\text{ m}^2\text{ g}^{-1}$; mean pore size, 5.1 nm) was filled into a three-neck flask. Under argon, triethylamine (1 ml) in chloroform (100 ml) was given to the silica. After 30 min of stirring, 3-aminopropyltriethoxysilane (8.89 g, 40.2 mmol) in chloroform (100 ml) was slowly dropped to the suspension. Afterwards, the mixture was refluxed for 4 h at 60 °C. The silica was cleansed in Soxhlet extractor with dichloromethane (200 ml) and dried under vacuum. Yield of the modified silica denoted in the following as “silica- NH_2 ” was 17.36 g.

(b) Anchoring of the Cr–salen complex

Dichloromethane (50 ml) was added to silica- NH_2 (2.16 g) in a two-neck flask under argon. After addition of complex **4** (0.92 g, 1.8 mmol), the suspension was



Scheme 2. General route applied for the synthesis of the different chromium–salen complexes.



Scheme 3. Overview of the chromium–salen complexes used in homogeneous catalysis.

refluxed for 3 h at 40 °C and stirred overnight at ambient temperature. Yield was 2.48 g.

2.2.2. Synthesis of catalyst **10**

(a) Modification of the silica

Under argon, triethylamine (1 ml) was added to silica (15.5 g) and toluene (150 ml) in a three-neck flask. Then 3-chloropropyltriethoxysilane (9.00 g, 37 mmol) in toluene (15 ml) was slowly dropped to the mixture. The slurry was heated for 4 h at 80 °C. Soxhlet extraction with a mixture of ether and dichloromethane (1:1, 200 ml) was carried out for 3 h. Yield was 20.64 g of white silica modified powder denoted “silica–Cl”.

(b) Anchoring of the ligand via the aminopart

N,N'-Bis(2-hydroxybenzylidene)-3-aza-1,5-pentanediamine dissolved in some toluene was dropped to a two-neck flask filled with silica–Cl (10.01 g) and toluene (180 ml). Thereafter, this mixture was refluxed for 8 h at 110 °C. The yellow silica material obtained was cleansed with Soxhlet extractor with dichloromethane (200 ml) for 3 h until the solvent was colourless. After drying under vacuum, ligand-modified silica was obtained as a yellow powder (7.90 g).

(c) Complexation of the immobilised ligand

CrCl₂ (1.175 g, 9.61 mmol) was added to the immobilised ligand (7.00 g) in toluene (150 ml). The suspension was stirred for 4 h at ambient temperature under argon. Afterwards, silica was transferred into Soxhlet extractor and washed for 2.5 h with dichloromethane (200 ml). The silica was filtrated and dried under vacuum. Yield was 7.21 g of a greenish brown powder.

2.2.3. Synthesis of catalyst **11**

Two different preparation routes were used to synthesise catalyst **11** depending on the sequence of the reaction steps.

(a) Variant **11a**: immobilisation of the free ligand

Firstly, *N,N'*-Bis(2-hydroxy-3-allylbenzylidene)-1,2-diphenylethylene-1,2-diamine (2.83 g, 5.65 mmol) was dissolved in a mixture of cyclohexane (10 ml) and toluene (10 ml). Then triethoxysilane (1.64 g, 10 mmol, 2 equivalent) was added and the mixture was heated to 40 °C. H₂PtCl₆ was previously dried at 150 °C for 4 h, and finally a bit of H₂PtCl₆ was dissolved in propylene carbonate (20 ml). This catalytic solution was dropped to the reaction mixture at 40 °C. After 1 h of stirring, dried silica (10.9 g) was added, and the suspension was stirred overnight at ambient temperature. The silica was separated and washed with diethyl ether. 12.5 g of brownish silica was obtained. Secondly, CrCl₂ (0.75 g, 6.14 mmol) was added to a suspension of the modified silica (10.00 g) in tetrahydrofuran (100 ml). The suspension was stirred for 4 h at ambient temperature under argon. Finally, the silica was transferred into Soxhlet extractor and washed for 2 h with dichloromethane (200 ml). The silica was

filtrated and dried under vacuum. Yield was 9.3 g of a green powder.

(b) Variant **11b**: immobilisation of the Cr complex

Complex **8** (3.00 g, 5.99 mmol) was dissolved in toluene (50 ml) and propylene carbonate (2 ml). After heating to 40 °C, triethoxysilane (4 ml) was added, followed by a small amount of H₂PtCl₆. The solution became maroon coloured. The mixture was stirred for 4 h at 40 °C and after cooling down to ambient temperature, stirred overnight.

In parallel, dried silica (5.81 g) was suspended in purified toluene (75 ml) and activated with triethylamine (1 ml). After 1 h of stirring, the maroon-coloured solution was dropped into the suspension with the help of a syringe. The mixture was stirred overnight. The yellow green catalyst was filtrated and washed with diethyl ether. Yield was 6.83 g.

2.3. Carbon dioxide insertion reaction

The catalytic reactions were performed in a 250 ml high pressure MEDIMEX HPM-P stainless-steel autoclave equipped with an active heating and cooling system. The quantity of carbon dioxide was measured by a balance (type METTLER Toledo IP5 Multirange) on which the whole reactor system was placed. The temperature profile was controlled by a EURO THERM 900 EPC thermostat, the stirring was done by a motor of type EMOD EEDF 56L/2A equipped with a magnetic-coupled gas stirrer. Stirring rate was 1000 min⁻¹. Propylene oxide (FLUKA, spectroscopic grade) and the catalyst were poured into the reactor, and the reactor was once flushed with carbon dioxide (PANGAS, 99.995%). A defined amount of carbon dioxide was dosed into the reactor with the help of a compressor (NWA PM-101), and heating and stirring were started. The reactor was heated to 140 °C for 30 min. After a certain reaction time the reactor was cooled down to room temperature for 40 min. Afterwards, CO₂ was released by opening the outlet valve. This decompression was carried out slowly over a 30 min period. To the reaction mixture *tert*-butylbenzene was added as an internal standard, and the compounds were analysed 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, only propylene and dipropylene glycols were found.

For the leaching and reuse experiments, the reaction mixture was filtrated, and the catalyst washed, dried and reused in the same way as described above.

2.3.1. Safety note

The experiments described in this paper involve the use of high pressure and require equipment with an appropriate pressure rating.

2.4. Analytical and physicochemical characterisation

The carbon content of the grafted ligands was analysed by thermal analysis (TA). The samples were heated to 800 °C in a stream of 20 vol.% oxygen in helium. A mass spectrometer was used to detect the formation of carbon dioxide and water (traces $m/e = 44$ and 18, respectively). When the combustion finished, a defined pulse of carbon dioxide was injected into the helium gas stream to calibrate the area of the $m/e = 44$ peak. This calibration allowed determining the carbon content of the sample.

Surface analysis of the immobilised catalysts (**9–11**) by XPS was performed on a Leybold Heraeus LHS11 MCD instrument using Mg K α (1253.6 eV) radiation. The apparatus is described in detail in [28]. The sample was pressed into a sample holder, evacuated in a load lock to 10^{-6} mbar and transferred to the analysis chamber (typical pressure $<10^{-9}$ mbar). The peaks were energy-shifted to the binding energy of the C(1s) peak to correct for the charging of the material. The surface composition of the catalysts was determined from the peak areas of C(1s), O(1s), N(1s), Si(2p), Cl(2p) and Cr(2p) which were computed after subtraction of the Shirley type background by empirically-derived cross-section factors [29]. The relative error of the analysis was $\pm 5\%$.

DRIFT spectra were recorded at room temperature in a BRUKER Equinox 55 spectrometer, accumulating 100 scans at a resolution of 4 cm^{-1} ; the measured range was $4000\text{--}400\text{ cm}^{-1}$. The solid samples were diluted in potassium bromide.

The chromium content was measured by inductively coupled plasma optical emission spectroscopy (ICP-OES), performed at ALAB AG (Urdorf, Switzerland).

3. Results and discussion

3.1. Syntheses of the free complexes

The preparation of the salen ligands and the corresponding chromium complexes according to Scheme 2 was straightforward and thus, successful as described in Section 2. Partly, the yields (42–86%) were somewhat lower than expected but the main goal of this work was to obtain pure catalyst with reasonable effort. Hence, intensive work-up of the complexes was omitted at this stage. NMR of the ligands and element analysis of the complexes confirmed the desired structure. Strong coordination of solvent molecules to the chromium centre usually hampered the removal of these molecules by high vacuum, so the element analysis showed a slight difference in the calculated and measured values. This behaviour is also reported in literature for similar compounds [21].

3.2. Catalytic activity of the homogeneous catalysts

In the first step, we varied the diamine part of the ligand, and the most active component was aromatic

Table 1

Catalytic activity of the different catalysts (Schemes 3 and 4) in the reaction of propylene oxide and carbon dioxide

Catalyst	Yield ^a (%)	TOF ^b (h ⁻¹)	PO/catalyst ratio
1	26.6	90	1000
2	47.3	150	1000
3	47.1	150	1000
4	62.0	170	900
5	17.9	60	1000
6	24.4	90	1100
7	18.4	60	1000
8	12.3	50	1100
9	41.0	330	2500
10	29.7	200	2000
11a	0.9	7	2400
11b	9.2	70	2400

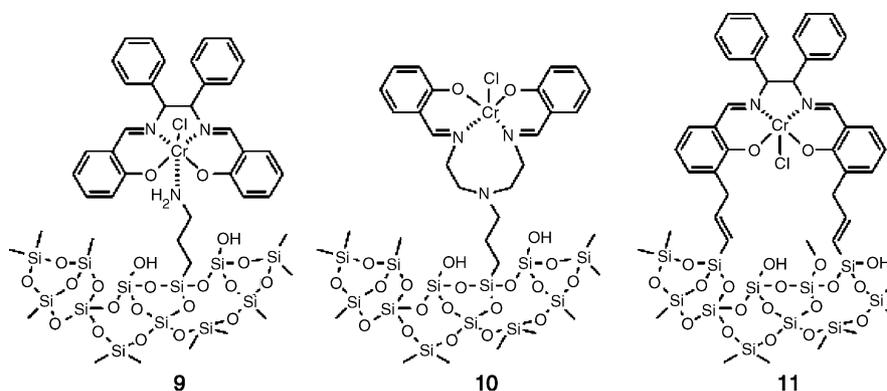
^a Reaction was carried out in 10 ml (140 mmol) of propylene oxide, catalyst, carbon dioxide (480–550 mmol, 3.4–3.9 equivalent), reaction time was 3 h at 140 °C. Yield of propylene carbonate was based on propylene oxide, the selectivity was always higher than 98%.

^b Turnover frequency [$\text{mol}_{\text{product}} / (\text{mol}_{\text{Cr on catalyst}} \text{ h})^{-1}$].

diphenylethylenediamine (Scheme 3, catalyst **4**), but the catalytic activity towards propylene carbonate (Scheme 1) in terms of the turnover frequency (TOF, $\text{mol}_{\text{product}} \text{ mol}_{\text{Cr}}^{-1} \text{ h}^{-1}$) of the other substituted diamines (catalysts **2** and **3**) was quite similar (150 h^{-1} versus 170 h^{-1}). Note that we assumed for the calculation of the TOF that all Cr-complexes were active. This is certainly a conservative estimate of the TOF since some of the complexes may not contribute to the reaction due to possible agglomeration or incomplete dissolution. The higher conversion using catalyst **4** could be due to the higher solubility of the aromatic rings in carbon dioxide.

Hence, diphenyldiaminoethane was used for further testing of the catalysts prepared from different hydroxybenzaldehydes. As Table 1 shows that the alkyl chains in *ortho* position to the hydroxy group decreased the activity due to steric reasons, either by blocking access to the active centre or inhibiting the transition state. An alkyl chain in *meta* position (catalyst **6**) halved the activity, alkyl chains in *ortho* position even decreased the activity to one-third of the non-substituted complex. Catalyst **7** showed no further drop in the activity compared to catalyst **5**. So, additional substitution in *para* position had no negative effect on the activity of the complex. The most active catalyst prepared from hydroxybenzaldehyde was the catalyst derived from the unsubstituted hydroxybenzaldehyde itself.

The homogeneous chromium–salen catalysts showed good catalytic performance reaching a TOF of 170 h^{-1} at a conversion of 70% and a selectivity higher than 98% in the cycloaddition of CO_2 to propylene oxide. It should be stressed that this performance has been achieved without any additional solvent or co-catalysts as applied in [21–23], which has distinct advantages because the reactant can easily be separated from the product. The variation of the diamine compound (catalysts **1–4**) had a strong influence in line with the results of Paddock and Nguyen [21], although they used a Lewis-base and an additional solvent. In their



Scheme 4. Immobilised chromium–salen complexes: **9** coordinated complex; **10** covalently-bound complex **3**; **11** covalently-bound complex **8**.

experiments also the diphenyl compound showed the highest activity, the difference to the cyclohexane compound was however much higher than the one we found in this work.

The choice of the benzaldehyde component was also important, though the substitution position seemed to have a stronger influence on the activity than the structure of the side chain itself. Substitution in *ortho* position of the hydroxy group (catalysts **5**, **7**, **8**) hampered the reaction much more than substitution in *meta* position (catalyst **6**). The influence of a group in *ortho* position is much bigger than a corresponding substitution in *para* position, though the double-substituted catalyst **7** showed no additional decrease in the activity compared to catalyst **5**. Similar results were achieved by Lu et al. [30] for cobalt salen complexes for the synthesis of ethylene carbonate in the presence of additional solvents. The additional group in *para* position also lowered the activity in this study by 25%. A group in *ortho* position decreased the yield by 65% (catalysts **4** and **5**). In conclusion, the impact of substitution seems to be more related to steric factors than to the solubility or the electronic properties of the different ligands. In contrast, Darensbourg et al. [31] found an opposite effect for the influence of groups on the phenolic ligand. They used a different substrate and an additional co-catalyst, so the solubility of the salen complexes was probably more important than steric factors.

3.3. Syntheses and characterisation of the heterogeneous catalysts

Considering the results from the homogeneous catalysts, corresponding salen complexes were immobilised using different grafting methods (Scheme 4). Catalyst **9** was prepared by anchoring the metal to a modified silica surface by coordination of the Cr³⁺-centre to an amine group. As there is no special requirement for the complex structure, the most active complex **4** was chosen. The modification of the silica surface by reaction with different ethoxysilanes is well known in literature, and preliminary tests with ²⁹Si NMR measurements showed good feasibility of this synthesis. The NMR spectra mainly showed silicon bound by two oxygen atoms to the

bulk silica (−58 ppm) and the rest by three oxygen atoms (−66 ppm). Single bound silicon was not found.

Immobilisation via the amino part of the salen ligand could be easiest achieved with complex **3** by modification of the amino group and using hydroxybenzaldehyde as an aldehyde component (see Section 2). This led to one covalent bond (catalyst **10**). In contrast, modification of the aldehyde part resulted in the immobilisation via two covalent bonds on the silica surface (catalyst **11**). In this case, complex **8** was chosen, because the synthesis with a vinyl group in *ortho* position is much simpler than the one in *para* position, and the interest in the heterogeneous catalysts was triggered by their stability.

For characterising the immobilised catalysts, DRIFT spectra were recorded (Fig. 1). The bands of the C=N imine vibration appeared at 1636 and 1613 cm^{−1} for the immobilised ligand of catalyst **10** without chromium in accordance with literature [26]. After addition of the chromium, the signals were shifted to 1619 and 1598 cm^{−1} [32]. The intensive bands of catalyst **9** appeared at higher wavenumbers (1628 and 1602 cm^{−1}); the bands of catalysts **11a** and **11b** appeared at significantly lower wavenumbers. Catalyst **11b** showed bands at about 1620 and 1592 cm^{−1}, whereas catalyst **11a** only showed a very weak, but broad signal at 1630 cm^{−1}. This indicates a small total amount of C=N bonds and in addition, that both chromium–salen complexes and uncomplexed ligands are present. Obviously, the structure of the salen complex was destroyed during the synthesis of the catalyst. Hence, chromium was not coordinated to the grafted ligand. The spectra of catalysts **9**, **10** and **11b** showed all the typical shifted bands of the C=N group. Consequently, in this case the chromium was well immobilised in an intact anchored complex. Additionally, with both catalysts **11a** and **11b** weak bands appeared between 1700 and 1670 cm^{−1} together with bands over 3000 cm^{−1} due to small amounts of residual vinyl side chains.

TA-MS measurements were conducted to gain information on the ligand loading for the immobilised catalysts by determination of the carbonaceous compounds (Fig. 2). Note that only the chromium-free immobilised ligands were examined to avoid contamination of the TA equipment. The

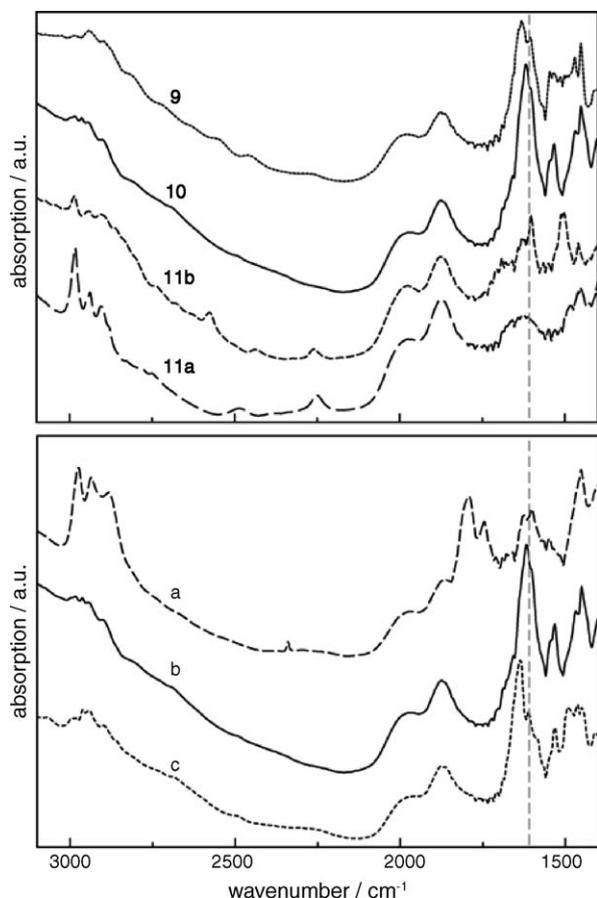


Fig. 1. DRIFT spectra of the immobilised catalysts (top). The labels of the catalysts correspond to those indicated in Scheme 4. Different states of catalyst **10** (bottom): (a) after one reaction cycle; (b) catalyst **10** as prepared; and (c) immobilised salen ligand without chromium. The dotted line serves as a guide for the eyes for better comparability.

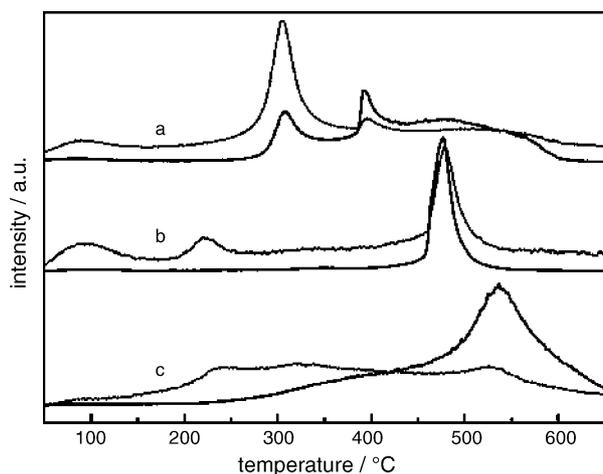


Fig. 2. TA-MS measurements of (a) aminopropyl grafted on silica—precursor of catalyst **9**; (b) immobilised ligand of catalyst **10** without chromium; and (c) grafted ligand of catalyst **11a** without chromium. The samples were heated in 20 vol.% O₂ in He. The solid black lines are the signal of $m/e = 44$, corresponding to CO₂, the grey dotted lines are the signal of $m/e = 18$, due to H₂O formation.

Table 2
Surface analysis of the heterogeneous catalysts by XPS

Element (%)	9	10	11a	11b
C(1s)	13.0	10.7	17.8	8.7
O(1s)	68.0	69.6	63.8	73.8
N(1s)	2.3	1.1	2.1	0.3
Si(2p)	14.8	15.7	13.3	16.3
Cl(2p)	0.5	1.2	1.4	0.2
Cr(2p)	1.4	1.7	1.7	0.8

sterically-demanding ligand of catalyst **11a** showed a carbon loading of 1.0 mg C/g catalyst. The combustion of carbon occurred in a narrow temperature range with a maximum at 478 °C. This is typical for species that were placed on the same part of the surface. The small aminopropyl anchor of catalyst **9** decomposed in a broad temperature range with two different narrow maxima at 308 and 390 °C. The loading (2.2 mg C/g) was higher than for the sterically-demanding complex **11a** probably because the molecule is smaller and immobilisation is sterically less hindered. Finally, the highest carbon loading of the silica surface showed complex **10** (3.1 mg C/g), due to the sum of immobilised complex **3** and 3-chloropropyltriethoxysilan. The curve of the mass loss of carbon as function of temperature looked like the superimposed curves of the former two experiments. This could be traced to the method of catalyst preparation. First, the silica surface was modified by grafting of 3-chloropropyltriethoxysilane. Afterwards, complex **3** reacted partly with the already immobilised precursor. Thus the results of the TA-MS indicated that not all grafted precursors reacted with the salen complex.

The highest bulk chromium content (1.5%) quantified by ICP-OES was found for catalyst **10**. Catalyst **9** and the two variants of catalyst **11** showed similar metal content (about 0.6%). In contrast, the chromium surface concentration of catalyst **11a** determined by XPS (Table 2) was higher than the surface concentration of catalyst **11b**. This supports the observation from IR measurements that in catalyst **11a** chromium was not found as Cr–salen complex on the surface, because XPS is surface sensitive and thus more sensitive for uncomplexed chromium (in case of catalyst **11b** the bulky salen ligands can shield the chromium). XPS further showed that in catalyst **11a** both Cr and Cl are adsorbed on the surface. As expected, catalyst **9**—grafted on a silica surface with aminopropyl anchors—had the highest nitrogen content on the surface. Also catalyst **11a** showed a high nitrogen content, whereas the nitrogen content of catalyst **11b** was very low. This implied a higher ligand loading of catalyst **11a** compared to **11b**, but the ligands of catalyst **11a** did not coordinate to any chromium centre.

3.4. Catalytic activity of the heterogeneous catalysts

The activity in terms of TOF of the immobilised catalysts (**9**, **10**) for propylene carbonate formation (Scheme 1) was higher than that of the free complexes. One reason for this behaviour may be the site isolation of the immobilised

complexes, whereas the homogeneous complexes may partly agglomerate during reaction. Note that also the concentration of the Cr-complexes in the reaction mixture was higher in case of the homogeneous catalysts (Table 1). Homogeneous catalysts with comparable catalytic activity were reported in literature to be more active only in the presence of additional solvents [21].

The simplest approach for anchoring the active complex to a support was applied for the preparation of catalyst **9**. The fresh catalyst showed a very high TOF of 330 h^{-1} . Also the activity of catalyst **10** is high in comparison to the homogeneous catalysts. Catalyst **11a** was nearly inactive, whereas the activity of catalyst **11b** prepared by a different procedure was higher by one order of magnitude. This is perfectly in line with the structural analysis of the complexes which showed that only in the procedure where the complete complex was grafted, the salen complex was intact in the resulting heterogeneous catalyst (catalyst **11b**). The catalytic activity of catalyst **11b** was lower than that of catalyst **10** due to its side chains in *ortho* position, as also observed for the homogeneous counterparts **8** and **3**.

In conclusion, both catalysts **10** and **11b** showed the same dependence on structural influences as the homogeneous ones, and even the catalytic activity was comparable for the free and grafted complexes. Hence, the presented strategy to immobilise the most active salen complexes was a reasonable approach.

3.5. Reuse of the heterogeneous catalysts

An important criterion for heterogeneous catalysis is reusability. Catalyst **9** showed a strong loss of activity (Fig. 3). After one use, the yield dropped from 41 to 1.4%. Since one-third of the chromium content remained on the catalyst, not only leaching of the salen complex, but also deactivation of the remaining chromium species occurred. A similar deactivation of coordinatively-bound catalysts was observed for a styrene oxide system with additional solvent by Garcia and co-workers [32,33], but no leaching was reported in [34,35]. In conclusion, anchoring via the Cr metal atom was not strong enough for the title reaction and led to leaching and ligand exchange. This may be traced back to the rather drastic conditions during the reaction or the strong propensity for complexation of propylene oxide and its derivatives. In summary, this simple approach is not suitable and the observed activity probably originates from homogeneous catalysis.

Significantly more stable were the covalently-bound catalysts **10** and **11b** (Fig. 3). However, this required a compromise in the catalytic activity, since either the amine or benzaldehyde component had to be modified. A certain loss of the chromium content was observed for catalyst **10** after the first use. The high stability in subsequent runs indicates that this may have resulted from adsorbed chromium that was not removed at the work-up of the synthesis by washing under atmospheric conditions. Catalyst **10** was prepared step by step on the silica surface and finally the chromium

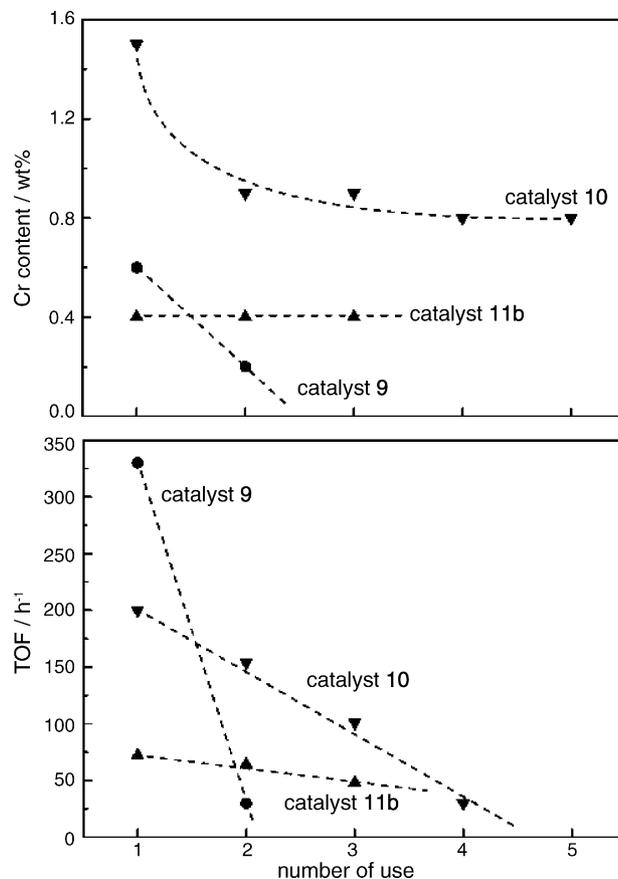


Fig. 3. Chromium content (top) and catalytic activity (bottom) of the different immobilised catalysts (Scheme 4) after reuse in the synthesis of propylene carbonate (activity is expressed as TOF [$\text{mol}_{\text{product}} (\text{mol}_{\text{Cr on catalyst h}})^{-1}$]).

chloride was added. This final step could have caused the high adsorption of chromium. In contrast no strong “washing” effect was observed with catalyst **11b**. In the latter case the complete complex was grafted, the chromium content was stable over the whole time. The observed loss in activity of catalyst **11b** was less pronounced than that of catalyst **10**.

DRIFTS measurements of a used catalyst **10** showed decreased signals at 1622 and 1600 cm^{-1} (Fig. 1). In accordance with the loss of chromium content the signals of the C=N vibration became weaker. This indicated that the whole complex and not only chromium was washed out during reaction. Further, strong bands appeared in the DRIFTS of the used catalyst **10** at 2977 , 2935 and 2883 cm^{-1} , and at 1794 and 1745 cm^{-1} , corresponding to the adsorbed propylene carbonate species. Strong adsorption of propylene oxide and similar compounds was also reported in [36]. Hence, polymerisation probably occurs as a side reaction during the cycloaddition of carbon dioxide to propylene oxide leading to some deactivation of the catalyst during reuse. This may also explain why the activity of both catalysts **10** and **11b** still decreased while hardly any leaching was observed. Thus, the decreasing “TOF” at stable chromium content was caused by blockage or disintegration of an active chromium centre. Note that no deactivation was reported in literature for

a related substrate, ethylene oxide [37,38], probably due to less pronounced adsorption on the silica support.

Therefore, the use of modified silica or other supports, which are less polar together with the immobilisation strategies shown in this study, may lead to catalysts with improved stability for propylene carbonate synthesis from propylene oxide and carbon dioxide. Research towards this aim is presently pursued in our laboratory.

4. Conclusions

A series of chromium–salen complexes with different ligands has been synthesised and tested for carbon dioxide fixation in propylene oxide without additional solvents and co-catalysts. The structure of the salen ligand had a strong effect on the catalytic activity, whereas selectivity to propylene carbonate was always high (>98%). The most active complexes were immobilised on silica by coordinative or covalent bonding.

The study shows that only covalently-bound complexes exhibit reasonable stability under reaction conditions. Coordinated complexes are too weakly anchored during propylene oxide reaction with carbon dioxide under high pressure. No advantage of double tethered complexes compared to complexes anchored by single covalent bond was found. Instead, the structure of the ligand had a pronounced influence on the catalytic activity, similarly as observed with the corresponding homogeneous catalysts.

Acknowledgements

Financial support by the Bundesamt für Energie (BFE) is gratefully acknowledged. Thanks are due to Marek Maciejewski for TA, Carsten Beck for ICP-OES measurements, and Davide Ferri for the support during the DRIFTS measurements.

References

- [1] A.A.G. Shaikh, S. Sivaram, *Chem. Rev.* 96 (1996) 951.
- [2] A. Behr, *Angew. Chem. Int. Ed.* 27 (1988) 661.
- [3] H. Arakawa, M. Aresta, J.N. Armor, M.A. Barteau, E.J. Beckman, A.T. Bell, J.E. Bercaw, C. Creutz, E. Dinjus, D.A. Dixon, K. Domen, D.L. DuBois, J. Eckert, E. Fujita, D.H. Gibson, W.A. Goddard, D.W. Goodman, J. Keller, G.J. Kubas, H.H. Kung, J.E. Lyons, L.E. Manzer, T.J. Marks, K. Morokuma, K.M. Nicholas, R. Periana, L. Que, J. Rostrup-Nielsen, W.M.H. Sachtler, L.D. Schmidt, A. Sen, G.A. Somorjai, P.C. Stair, B.R. Stults, W. Tumas, *Chem. Rev.* 101 (2001) 953.
- [4] M. Aresta, E. Quaranta, *Chemtech* 27 (1997) 32.
- [5] G. Rokicki, W. Kuran, *Bull. Chem. Soc. Jpn.* 57 (1984) 1662.
- [6] G. Rokicki, W. Kuran, B. Pogorzelskamarciński, *Monatsh. Chem.* 115 (1984) 205.
- [7] M. Ratzenhofer, H. Kisch, *Angew. Chem. Int. Ed.* 19 (1980) 317.
- [8] A. Baba, T. Nozaki, H. Matsuda, *Bull. Chem. Soc. Jpn.* 60 (1987) 1552.
- [9] D.J. Darensbourg, S.J. Lewis, J.L. Rodgers, J.C. Yarbrough, *Inorg. Chem.* 42 (2003) 581.
- [10] H.S. Kim, J.J. Kim, B.G. Lee, O.S. Jung, H.G. Jang, S.O. Kang, *Angew. Chem. Int. Ed.* 39 (2000) 4096.
- [11] H.S. Kim, J.J. Kim, S.D. Lee, M.S. Lah, D. Moon, H.G. Jang, *Chem.-Eur. J.* 9 (2003) 678.
- [12] F.W. Li, C.G. Xia, L.W. Xu, W. Sun, G.X. Chen, *Chem. Commun.* (2003) 2042.
- [13] H. Kawanami, A. Sasaki, K. Matsui, Y. Ikushima, *Chem. Commun.* (2003) 896.
- [14] R.L. Paddock, Y. Hiyama, J.M. McKay, S.T. Nguyen, *Tetrahedron Lett.* 45 (2004) 2023.
- [15] A. Baiker, *Appl. Organomet. Chem.* 14 (2000) 751.
- [16] S. Fujita, B.M. Bhanage, Y. Ikushima, M. Shirai, K. Torii, M. Arai, *Catal. Lett.* 79 (2002) 95.
- [17] H. Yasuda, L.N. He, T. Sakakura, *J. Catal.* 209 (2002) 547.
- [18] K. Yamaguchi, K. Ebitani, T. Yoshida, H. Yoshida, K. Kaneda, *J. Am. Chem. Soc.* 121 (1999) 4526.
- [19] M. Tu, R.J. Davis, *J. Catal.* 199 (2001) 85.
- [20] R. Srivastava, D. Srinivas, P. Ratnasamy, *Catal. Lett.* 89 (2003) 81.
- [21] R.L. Paddock, S.T. Nguyen, *J. Am. Chem. Soc.* 123 (2001) 11498.
- [22] D.J. Darensbourg, J.C. Yarbrough, *J. Am. Chem. Soc.* 124 (2002) 6335.
- [23] D.J. Darensbourg, R.M. Mackiewicz, J.L. Rodgers, A.L. Phelps, *Inorg. Chem.* 43 (2004) 1831.
- [24] M.H. Valkenberg, W.F. Holderich, *Catal. Rev.* 44 (2002) 321.
- [25] F. Minutolo, D. Pini, A. Petri, P. Salvadori, *Tetrahedron Asymmetry* 7 (1996) 2293.
- [26] R.G. Konsler, J. Karl, E.N. Jacobsen, *J. Am. Chem. Soc.* 120 (1998) 10780.
- [27] S.K. Hwang, A. Juhasz, S.H. Yoon, N. Bodor, *J. Med. Chem.* 43 (2000) 1525.
- [28] J.D. Grunwaldt, M.D. Wildberger, T. Mallat, A. Baiker, *J. Catal.* 177 (1998) 53.
- [29] C.D. Wagner, L.E. Davis, M.V. Zeller, J.A. Taylor, R.H. Raymond, L.H. Gale, *Surf. Interface Anal.* 3 (1981) 211.
- [30] M.B. Lu, J.H. Xiu, R. He, K. Jin, L.M. Luo, X.J. Feng, *Appl. Catal. A* 275 (2004) 73.
- [31] D.J. Darensbourg, R.M. Mackiewicz, J.L. Rodgers, C.C. Fang, D.R. Billodeaux, J.H. Reibenspies, *Inorg. Chem.* 43 (2004) 6024.
- [32] C. Baleizao, B. Gigante, M.J. Sabater, H. Garcia, A. Corma, *Appl. Catal. A* 228 (2002) 279.
- [33] M. Alvaro, C. Baleizao, D. Das, E. Carbonell, H. Garcia, *J. Catal.* 228 (2004) 254.
- [34] Y.P. Zhang, J.H. Fei, Y.M. Yu, X.M. Zheng, *Catal. Lett.* 93 (2004) 231.
- [35] X.G. Zhou, X.Q. Yu, J.S. Huang, S.G. Li, L.S. Li, C.M. Che, *Chem. Commun.* (1999) 1789.
- [36] B.S. Uphade, T. Akita, T. Nakamura, M. Haruta, *J. Catal.* 209 (2002) 331.
- [37] H.S. Kim, J.J. Kim, H.N. Kwon, M.J. Chung, B.G. Lee, H.G. Jang, *J. Catal.* 205 (2002) 226.
- [38] X.B. Lu, H. Wang, R. He, *J. Mol. Catal. A: Chem.* 186 (2002) 33.