Simple preparation routes towards novel Zn-based catalysts for the solventless synthesis of propylene carbonate using dense carbon dioxide

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Abstract

Differently prepared supported and unsupported zinc-based catalysts were tested in the solventless synthesis of propylene carbonate from propylene oxide and carbon dioxide. ZnO–SiO_2 xerogels prepared by the sol–gel method and flame-made ZnO–SiO_2 materials synthesized by flame spray pyrolysis resulted in catalysts with high surface area (640 and 460 $m^2\,g^{-1}$, respectively) and exhibited in the presence of tetrabutyl ammonium bromide a good catalytic activity towards propylene carbonate. Also undoped and doped zinc oxides prepared via flame spray pyrolysis were catalytically active. A significant improvement of the flame-made ZnO–SiO_2 system could be achieved by depositing the zinc precursor on pre-formed silica particles. Yields >99% at principally 100% selectivity were achieved with 200 mg catalyst and 140 mmol propylene oxide at 120 °C in 6 h. The results indicate that not single site zinc but rather zinc oxide clusters play an important role in the catalytic activity of the system, as also evidenced by EXAFS results and SEM.
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1. Introduction

In green chemistry, the substitution of poisonous substances, circumvention of additional solvents and energy minimization using an efficient catalytic process are important targets [1,2]. An attractive route is the insertion of carbon dioxide (CO_2) into the oxirane ring of propylene oxide (PO) [3–5] (Scheme 1). The resulting propylene carbonate (PC) is a commercially important chemical product, used e.g. as aprotic solvent or intermediate in fine chemistry [6]. In this reaction CO_2 serves as C_1-building block instead of toxic carbon monoxide or phosgene. Particularly, application of "solventless conditions" in the sense that CO_2 acts as both solvent and reactant and the use of an easy-separable heterogeneous catalyst are desirable [7,8]. However, up to now mostly homogeneous catalysts that make use of a transition metal complex or an aluminum complex in combination with Lewis bases [9–19] were in the focus due to their superior activity. Simple heterogeneous catalysts based on oxides [20–25] and halides [26–28] require a much higher catalyst/substrate ratio. Only the use of specially designed catalysts with immobilized organometallic complexes achieved satisfying catalytic performance in heterogeneously catalyzed solventless processes [11,29–35]. We recently found that immobilized $ZnBr_2Py_2$-complexes exhibited high turnover rates that are nearly as high as those of the homogeneous counterparts. However, the synthesis of such functionalized catalysts is time consuming and quite expensive. Hence, the design of a simple and efficient catalyst for the coupling of PO and CO_2 according to Scheme 1 is still required. Intrigued by the observation of our and other groups that zinc-based complexes are catalytically active in this or related reactions [12,29,34,36], we focused in the present study on zinc-based mixed oxide catalysts synthesized by different preparation techniques. Ideally, these catalysts should be easily accessible and toxicologically harmless. Emphasis was laid on achieving high yields at solventless conditions with a relatively low amount of catalyst at short reaction times to reduce the use of chemical products and waste

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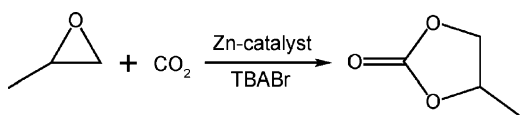
Scheme 1. Reaction scheme of carbon dioxide fixation to propylene carbonate.

to a minimum. We chose as preparation routes for the zinc-based catalysts both the synthesis of xerogels via the sol–gel route [37] and flame-made materials using flame spray pyrolysis [38]. The latter allows fast and cheap one-step catalyst synthesis without any work-up and minimized effluents. For comparison, zinc hydroxyapatite was tested. It was recently used in the synthesis of higher and thus more reactive cyclic carbonates [36].

Tetrabutyl ammonium bromide (TBABr) was added as base/co-catalyst.

2. Experimental

2.1. Catalyst synthesis

In Tables 1–6 the compositions of the various catalysts are given together with the corresponding results of catalytic tests. Specific designations were used throughout the paper, which included the loading, support, and preparation method (gel: sol–gel-based synthesis; TEOS: flame-made with tetraethoxysilane (TEOS); disp: flame-made with colloidal silica precursors), as specified in the corresponding tables.

Table 1
Results of the propylene carbonate synthesis catalyzed by different sol–gel-derived zinc containing oxides

Catalyst	Catalyst composition	Amount (mg)	Surface area ($m^2 g^{-1}$)	Yield (%)
$2.5Zn/SiO_2$-gel	2.5 wt.% ZnO/SiO_2	100.2	645	10.8
$2.5Zn/Al_2O_3$-gel	2.5 wt.% ZnO/Al_2O_3	100.6	643	0.4
$2.5Zn/TiO_2$-gel	2.5 wt.% ZnO/TiO_2	100.3	465	0.4
$2.5Zn/AlSi_5O_x$-gel	2.5 wt.% $ZnO/Al_2O_3(SiO_2)_5$	99.7	201	0.4
$2.5Zn/TiSi_5O_x$-gel	2.5 wt.% $ZnO/TiO_2(SiO_2)_5$	100.1	185	7.0
$2.5Zn/ZrSi_5O_x$-gel	2.5 wt.% $ZnO/ZrO_2(SiO_2)_5$	100.1	216	4.3
TBABr	–	10.0[a]	–	2.0

Note that the selectivity to PC of all the tested catalysts was always ca. 100% so that the yield can directly be used as a measure of conversion (activity).

[a] For all other reactions, 10 mg TBABr was used as co-catalyst.

Table 2
Influence of zinc content on the synthesis of propylene carbonate with sol–gel-derived catalysts

Catalyst	Catalyst composition	Amount (mg)	Surface area ($m^2 g^{-1}$)	Yield (%)
$0.6Zn/SiO_2$-gel	0.6 wt.% ZnO/SiO_2	99.9	582	3.2
$1.3Zn/SiO_2$-gel	1.3 wt.% ZnO/SiO_2	100.2	220	7.1
$2.5Zn/SiO_2$-gel	2.5 wt.% ZnO/SiO_2	100.2	645	10.8
$6.3Zn/SiO_2$-gel	6.3 wt.% ZnO/SiO_2	100.8	172	16.3
$12.5Zn/SiO_2$-gel	12.5 wt.% ZnO/SiO_2	100.6	639	19.2

Table 3
Catalytic results of the propylene carbonate synthesis on flame-made silica prepared with TEOS

Catalyst	Catalyst composition	Amount (mg)	Surface area ($m^2 g^{-1}$)	Yield (%)
$1.3Zn/SiO_2$-TEOS	1.3 wt.% ZnO/SiO_2	100.2	283	11.8
$2.5Zn/SiO_2$-TEOS	2.5 wt.% ZnO/SiO_2	100.2	423	13.4
$7.0Zn/SiO_2$-TEOS	7.0 wt.% ZnO/SiO_2	100.3	337	12.1
$7.0Zn/SiO_2$-TEOS	7.0 wt.% ZnO/SiO_2[a]	100.5	453	13.3
$12.5Zn/SiO_2$-TEOS	12.5 wt.% ZnO/SiO_2	99.7	480	15.5

[a] $Zn(acac)_2$ and TEOS were dissolved in 100 mL instead of 40 mL precursor solution.

Table 4
Catalytic results of the propylene carbonate synthesis on different zinc oxides prepared by flame synthesis

Catalyst	Catalyst composition	Surface area ($m^2 g^{-1}$)	Yield, Y (%)	$Y/100\, m^2 g^{-1}$ (%)
ZnO	ZnO	59.6	16.6	27.9
Li/ZnO	0.3 wt.% Li/ZnO	67.6	16.4	24.3
Mg/ZnO	1.5 wt.% Mg/ZnO	67.2	20.9	31.1
Ca/ZnO	2.5 wt.% Ca/ZnO	58.3	18.8	32.2
Sr/ZnO	5.5 wt.% Sr/ZnO	41.5	15.8	38.1
Ba/ZnO	8.6 wt.% Ba/ZnO	80.6	20.3	25.2

Table 5
Catalytic results of the propylene carbonate synthesis over doped flame synthesized materials

Catalyst	Catalyst composition	Amount (mg)	Surface area ($m^2 g^{-1}$)	Yield (%)
2.5-HAp	2.5 wt.% Zn/HAp[a]	101.1	63.5	11.2
1.0ZnPO$_4$/SiO$_2$-TEOS	1.0 wt.% ZnO, 4.0wt.% PO$_4$/SiO$_2$	100.2	360	9.6
2.5ZnMg/SiO$_2$-TEOS	1.0 wt.% MgO, 2.5wt.% ZnO/SiO$_2$	100.2	359	14.9
12.5ZnMg/SiO$_2$-TEOS	5.5 wt.% MgO, 12.5 wt.% ZnO/SiO$_2$	100.2	445	12.7
12.5ZnSr/SiO$_2$-TEOS	6.1 wt.% Sr, 12.5 wt.% ZnO/SiO$_2$	100.0	419	15.3
12.5ZnSr/MgO-TEOS	2.7 wt.% Sr, 12.5 wt.% ZnO/MgO	100.3	232	13.3
1.0ZnPO$_4$/SiO$_2$-disp	1.0 wt.% ZnO, 4.0 wt.% PO$_4$/SiO$_2$	100.5	60.2	11.9
1.0ZnCaPO$_4$/SiO$_2$-disp	0.7 wt.% Ca,1.0 wt.% ZnO, 4.0 wt.% PO$_4$/SiO$_2$	100.3	54.9	11.8

[a] The hydroxyapatite was prepared by a sol–gel process and afterwards ion exchanged. Note: the pure zinc content is given and not the content of zinc oxide.

2.1.1. Sol–gel-based synthesis of zinc containing catalysts with oxide support

Oxide-supported xerogels containing different weight percentages of Zn have been prepared applying a sol–gel process and subsequent drying according to Ref. [39]. Zinc acetate (Zn(OAc)$_2$) has been used as Zn precursor and tetraethoxysilane (TEOS) as silica precursor. For non-silica supports, zinc acetylacetonate (Zn(acac)$_2$) has been used as Zn precursor, aluminum and titanium isopropylate as precursor for the silica-free supports, and the corresponding acetylacetonates for the mixed oxides.

2.1.2. Flame-made catalysts

Zinc on silica samples were prepared via flame spray pyrolysis (FSP) [40,41]. In the FSP process, the liquid reactant mixture containing soluble metal-precursors is pumped through a capillary to a nozzle. At the tip of the capillary, an oxygen flow disperses the liquid, resulting in a fine spray. This spray is ignited by a supporting methane/oxygen flame around the capillary. The powders were collected on a cooled glass-fibre filter located 50 cm above the burner plate. Zn(acac)$_2$ or corresponding metal complexes and TEOS were dissolved in 40 mL of 50/50 (vol.%) MeOH/AcOH. These precursor solutions were fed through the capillary to the flame with 5 mL/min and dispersed with 5 L$_n$/min oxygen. In addition, Zn(acac)$_2$ was also deposited on SiO$_2$ using pre-formed silica particles. For this purpose, colloidal silica (Ludox TMA, 34 wt.% suspension in water, Sigma–Aldrich) was used. The colloidal silica was sprayed together with the zinc precursor.

2.2. Catalytic measurements

The coupling of CO$_2$ and PO according to Scheme 1 was performed in a 250 mL high-pressure stainless-steel autoclave. Typically, PO, TBABr (10 mg) and the respective catalyst (see Tables 1–5) were first poured into the reactor. Then the reactor was flushed with CO$_2$. By means of a compressor (NWA PM–101), 0.6 mol of CO$_2$ was pressed into the reactor, followed by heating to 100 °C and stirring of the reaction mixture. The pressure was 45 bar during reaction. After 3 h the reactor was cooled down to room temperature, and CO$_2$ was released. *tert*-Butylbenzene was added as internal standard to the reaction mixture 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).

2.3. General catalyst characterization

Ex situ characterization was performed by X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) spectroscopy at the X1 beamline at HASYLAB and at the XAS-beamline at ANKA. For these experiments the catalysts were pressed to pellets with polyethylene as additive. The leaching experiment was performed using the procedure described in Ref. [34]. The raw data were energy calibrated, background corrected and normalized using the WINXAS 3.0 software [42]. The EXAFS spectra were fitted in R-space using theoretical scattering

Table 6
Catalytic results of the propylene carbonate synthesis over flame synthesized materials using pre-formed silica particles

Catalyst	Catalyst composition	Amount (mg)	Surface area ($m^2 g^{-1}$)	Yield (%)
1.0Zn/SiO$_2$-disp	1.0 wt.% ZnO/SiO$_2$	100.2	81.2	14.8
2.5Zn/SiO$_2$-disp	2.5 wt.% ZnO/SiO$_2$	100.3	46.6	20.1
5.0Zn/SiO$_2$-disp	5.0 wt.% ZnO/SiO$_2$	100.0	54.4	28.1
7.0Zn/SiO$_2$-disp	7.0 wt.% ZnO/SiO$_2$	100.0	46.5	26.8
9.0Zn/SiO$_2$-disp	9.0 wt.% ZnO/SiO$_2$	100.1	49.6	20.7
12.5Zn/SiO$_2$-disp	12.5 wt.% ZnO/SiO$_2$	100.2	42.4	21.3
17.0Zn/SiO$_2$-disp	17.0 wt.% ZnO/SiO$_2$	99.6	47.3	23.0
5.0Zn/SiO$_2$-disp	5.0 wt.% ZnO/SiO$_2$[a]	200.1	54.4	84.7
7.0Zn/SiO$_2$-disp	7.0 wt.% ZnO/SiO$_2$[b]	200.1	46.5	100.0

[a] Reaction conditions: temperature 120 °C, time 5 h, 20 mg TBABr.
[b] Reaction conditions: temperature 120 °C, time 6 h, 20 mg TBABr.

amplitudes and phase shifts, similarly as reported in Ref. [34].

3. Results

3.1. Catalytic studies

First, a series of 2.5 wt.% zinc oxide on different supports was synthesized by the sol–gel method to examine, which support was most suitable for this reaction (Table 1). The specific surfaces of the catalysts varied (see Table 1), but the nature of the support had a much stronger influence on the reaction rate than the surface area. No leaching of active zinc complexes could be observed. Surprisingly, supports containing aluminum oxide and silica-free titanium oxide showed an even lower yield (conversion) than the blank experiment only containing tetrabutyl ammonium bromide (TBABr). This could be explained by a strong interaction of support and product. Interestingly, mixed Mg/Al oxides were reported to be active as catalysts for the synthesis of PC, but in these studies an additional solvent [20], a much higher catalyst/substrate ratio and/or more drastic conditions were used (80–140 bar, 200 °C, 8 h) [21,22].

Table 2 shows the catalytic data for PC formation as function of different zinc loading on silica. With increasing zinc loading, more PC was formed. However, the yield did not increase linearly with the zinc content. The average catalytic activity per zinc atom decreased at higher loading, probably due to the growth of larger zinc-clusters.

The flame-made catalysts shown in Table 3 were slightly more active than the corresponding catalysts prepared by sol–gel method at a low zinc oxide content of 2.5% (13.4% instead of 10.8%). One reason could be the lower number of free hydroxyl groups on the catalyst surface [43], which may result in by-products and blocking of the active sites. Also flame-made silica samples with higher zinc contents were tested. In general, the yields of catalysts with higher Zn loading were not higher than for the $2.5Zn/SiO_2$ sample and lower than the yields of the corresponding sol–gel-derived silica. Note that the surface areas of the sol–gel catalysts were higher than those of the flame-made materials (generally in the sol–gel series $640 \pm 20\,m^2\,g^{-1}$). Another reason for the lower activity of the flame-made catalysts could be the favored incorporation of the zinc into the silica during flame pyrolysis. Furthermore, different precursor concentrations during flame spray pyrolysis resulted only in a slight change of the catalytic activity (Table 3, $7.0Zn/SiO_2$-TEOS).

Since the highest zinc loadings of sol–gel and flame-made catalysts resulted in the highest yield, zinc oxides without silica as support were catalytically tested (Table 4). These zinc oxides were varied by addition of different dopants. Also with these zinc oxides the flame-made materials showed higher yields than commercial zinc oxide, which only gave a conversion of 8.8%. Doping of the zinc oxide by Mg, Ca, and Sr led to an improved activity. Although the additives influenced the surface, still different activities were achieved when the yield was related to the surface area, which could be due to the variation in strength of the basic sites depending on the dopant used [20,44].

Encouraged by the results of the doped zinc oxides, we prepared a series of differently doped catalysts (Table 5). Again, as observed when comparing sol–gel and flame-derived catalysts, only at low zinc loadings a beneficial effect of Mg-doped material was observed. The $2.5ZnMg/SiO_2$-TEOS catalyst showed a slightly higher catalytic activity than the undoped catalyst $2.5Zn/SiO_2$-TEOS. Since it was reported that zinc hydroxyapatite was quite active in the synthesis of other cyclic carbonates [36], we tested also a hydroxyapatite catalyst 2.5-HAp in the synthesis of PC (Table 5). The yield of PC obtained with hydroxyapatite was lower per zinc loading than the yield of both silica catalysts $2.5Zn/SiO_2$-gel and $2.5Zn/SiO_2$-TEOS. Also no beneficial effect of doping the flame-made catalysts with phosphate or calcium was observed.

With all tested catalytic materials increasing the zinc loading led after a maximum to a decrease in the yield (activity) per zinc atom. Possible explanations for this behavior are a higher amount of zinc incorporated into the silica lattice or a larger particle size of the zinc oxide clusters on the silica surface. To avoid incorporation of the zinc an additional series of flame-made zinc/silica catalysts was synthesized. In this series, instead of TEOS a dispersion of silica was used. Thus, the zinc particles had to be preferentially deposited on the silica surface. In fact, the catalytic activity was higher than the activity of the materials synthesized with TEOS (Table 6). Note additionally that the surface area was significantly lower than for the Zn-based xerogels (Table 2) and the prior series of flame-made materials (Table 3). With increasing content of zinc the surface area of the catalysts was slightly decreasing. Nevertheless, the influence of the surface area was rather low compared to the zinc content. The highest conversion was found at a zinc oxide content of 5%. Possibly, lower zinc content led to a decrease of the number of active zinc particles. Higher zinc content afforded predominantly larger particles and thus not a higher amount of accessible active centers. The use of colloidal silica during synthesis greatly enhanced the catalytic activity of

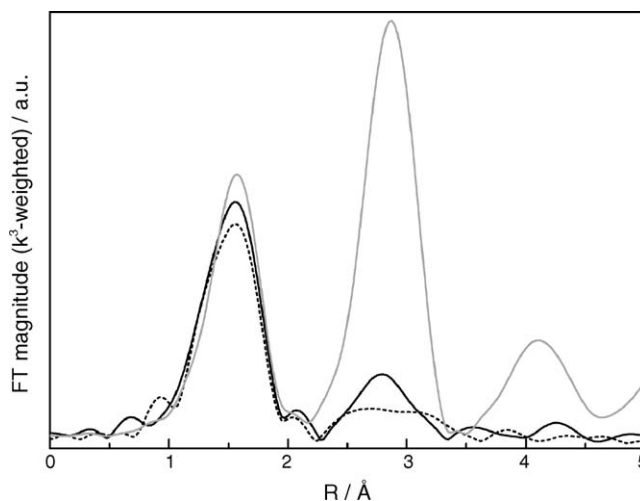Fig. 1. Fourier transformed EXAFS spectra. Fourier transformed $k^3\,\chi(k)$ function ($k = 2.2$–$14\,Å^{-1}$) of catalyst $7.0Zn/SiO_2$-disp (solid line) and catalyst $7.0Zn/SiO_2$-TEOS (dotted line). As reference the spectrum of ZnO is given (grey line).
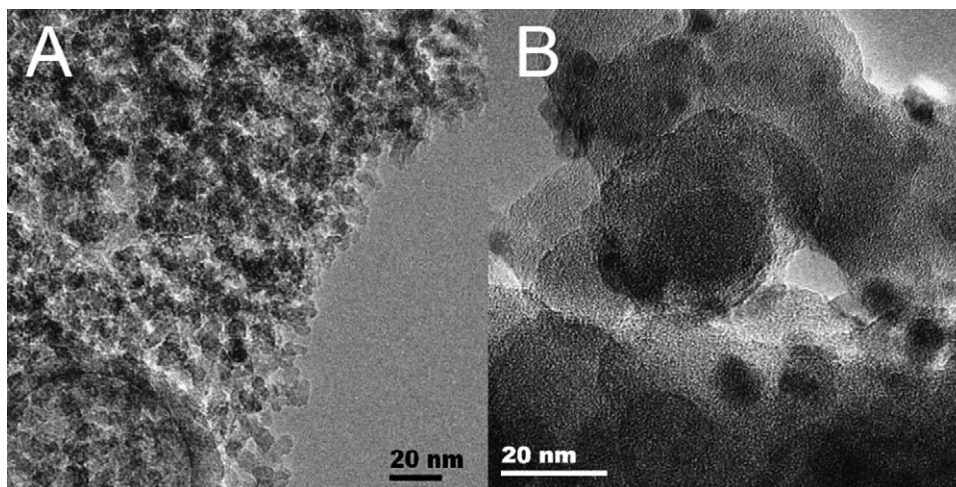
Fig. 2. TEM pictures of (a) 7.0Zn/SiO$_2$-TEOS and (b) 7.0Zn/SiO$_2$-disp made by flame synthesis.

zinc/silica (7.0Zn/SiO$_2$-disp (Table 6), compared to 7.0Zn/SiO$_2$-fm (Table 3)).

All the test reactions in Tables 1–6 were performed at differential conversion to demonstrate the difference in the catalytic activity. Yet, at modified conditions (120 °C; 6 h; 45 bar; 200 mg catalysts; 20 mg TBABr; 10 mL/140 mmol PO) the flame-made catalyst showed 100% yield in reasonable reaction time and at moderate temperature (Table 6, last entry). The selectivity was always >99% even at a conversion of 100%.

3.2. Further characterization of selected samples

To clarify the difference in activity of the flame-made catalysts prepared from TEOS and from colloidal silica solutions, XAS spectra were recorded. The XANES region was very similar, but significant differences were found in the EXAFS region. The Fourier transformed EXAFS spectra are shown in Fig. 1. The signal at about 1.6 Å can be assigned to the oxygen neighbor and no difference is found between the two catalysts. The curve-fitting analysis resulted in an interatomic Zn–O distance of 1.95 Å, which is in accordance to the Zn–O distances observed in a silica matrix [45]. This is shorter than the Zn–O distance of 1.97 Å in silica-free zinc oxide. At higher R-values significant differences were found. Whereas the flame-made catalyst using a solution of TEOS had only small contributions at higher R-values, the catalyst resulting from the dispersed silica solution featured a signal at 2.8 Å (not corrected for phase shift), which can be assigned to Zn–O–Zn species. This contribution is significantly higher than in the TEOS derived flame-made catalysts. In addition, we performed in situ spectroscopic studies with a batch reactor cell that can measure both the solid and liquid phase (experiments performed analogously to Ref. [34]). No significant changes of the solid catalyst could be observed, probably because only a fraction of the zinc atoms was involved in the reaction. Moreover, the investigation of the liquid phase proved no leaching of zinc into the liquid phase during and after reaction. Bromide was detected both on the solid catalyst and in the solution.

STEM measurements coupled with EDX were performed to investigate the different dispersion of zinc oxide on the catalyst 6.3Zn/SiO$_2$-gel, 7.0Zn/SiO$_2$-TEOS and 7.0Zn/SiO$_2$-disp. Rather large zinc containing particles were found on the sol–gel-derived catalysts 6.3Zn/SiO$_2$-gel, typically between 30 and 100 nm. In contrast, an extremely high dispersion was observed for the flame-made catalyst using a solution of 7.0Zn/SiO$_2$-TEOS (see Fig. 2a). The average silica particle size was 7 nm and hardly any zinc oxide particle could be detected by TEM measurements. Furthermore, EDX spectra of different positions showed a constant but low zinc signal over the whole sample. This is consistent with the EXAFS measurements, where only a small Zn–O–Zn contribution at higher R-values was found. The zinc oxide particle size of the catalyst resulting from dispersed silica solution 7.0Zn/SiO$_2$-disp ranged from 5 to 10 nm (see Fig. 2b). This observation is corresponding to the signal found at the Fourier transformed EXAFS spectrum at 2.8 Å, which also showed the formation of Zn–O–Zn clusters.

4. Discussion

Our results show that Zn-based xerogels and flame-made materials are good catalysts for the solventless insertion of CO$_2$ into PO. As outlined in the introduction, up to now, only homogeneous catalysts [9–19] or heterogeneous organometallic complexes [11,29–35] were reported to be efficient catalysts. Simple solid oxide or halide catalysts were found to be much less active and the materials investigated in this work seem to be an interesting alternative. Catalysts investigated for the solventless PC formation from PO and CO$_2$ like cesium–phosphorous–silicon-mixed oxide [21], zeolite-based organic–inorganic hybrid catalysts [46] as well as polymer-supported nanogold [33] required a higher catalyst/substrate ratio, higher temperatures and/or longer reaction times. Furthermore, the synthesis of flame-made catalysts is simple and fast. The reactants were dissolved and afterwards sprayed into the flame without any work-up. The highest yields were achieved with catalysts where zinc is decorating the silica particles and, surprisingly, the undoped
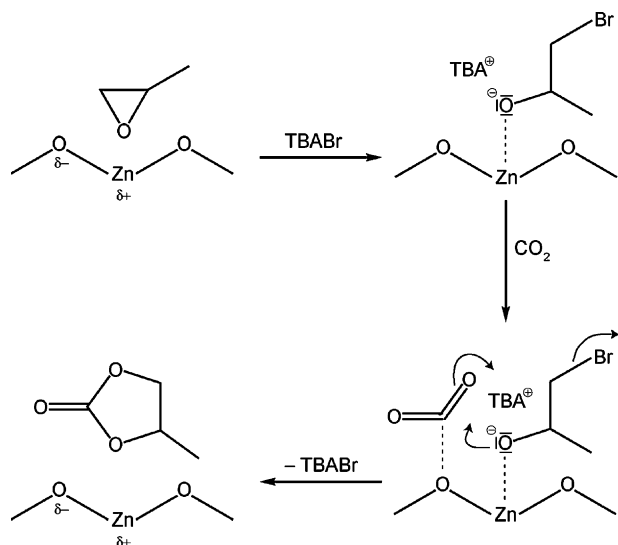
Scheme 2. Reaction mechanism proposed for cycloaddition of CO_2 to propylene oxide on a zinc oxide surface with TBABr as co-catalyst.

and doped zinc oxides turned out to be fairly good catalysts as well.

In general, Zn–O–Zn entities seemed to be advantageous for the catalytic activity. With higher loading the catalytic activity increased to a maximum and deposition of zinc on the silica support in the flame synthesis procedure led to a higher catalytic activity although the surface area was smaller (Table 6). Notably, small zinc oxide particles in the range of 5–10 nm were beneficial for the catalytic activity. The incorporation of Zn in the silica matrix led to a lower catalytic activity and also Zn-exchanged hydroxyapatite was significantly less active. Particularly, the high activity of the ZnO itself supports the assumption that ZnO-clusters are beneficial for the catalytic activity.

These observations are significantly different from that reported in the literature. Mori et al. [36] reported that single site zinc hydroxyapatite would be an efficient catalyst for the synthesis of other cyclic carbonates like styrene carbonate. In the present study, it appears both from the catalytic results and the EXAFS data that for the PC formation from PO and CO_2 the appearance of Zn–O–Zn entities is beneficial. In the most efficient systems we could evidence Zn–O–Zn interactions by spectroscopy. Since the catalysts are hardly active in the absence of TBABr we propose the reaction mechanism shown in Scheme 2. This mechanism is based on the earlier suggested mechanisms reported in Ref. [23] for the CO_2 absorption on zinc oxides during cycloaddition, and on Ref. [12] where the epoxide ring opening by tetrabutyl ammonium halide is described. In studies of immobilized zinc pyridine catalysts TBABr was found to be a co-catalyst for the PC synthesis [34]. According to our proposal the reaction is initiated by coordination of the PO on zinc as a Lewis acidic site. Secondly, a bromide attacks the less-hindered carbon atom of the coordinated PO followed by ring opening. In parallel CO_2 is activated by the Lewis basic site (O^{2-}) of the ZnO/SiO$_2$. Here Zn–O–Zn species may be beneficial compared to Zn–O–Si species. Finally, the oxygen of the activated CO_2 attacks nucleophilically the carbon atom

bonding with Br$^-$, and the PO oxygen attacks the CO_2 carbon atom to close the PC ring. This reaction mechanism can explain the requirement of a halide co-catalyst and the influence of the Lewis acid and basic site strength.

5. Conclusions

Zinc–silicon-oxide materials are effective catalysts for the solventless propylene carbonate synthesis in dense carbon dioxide using TBABr as co-catalyst. Both xerogel synthesis and one-step flame spray pyrolysis, which could be performed without any work-up procedure, turned out to be well-suited synthesis methods resulting in high surface area materials. Strikingly, the selective deposition of zinc oxide on silica by using colloidal dispersion of silica in flame synthesis resulted in a significant improvement of the catalyst performance. In general, this approach may be interesting to avoid substantial incorporation of the catalytically active transition metal into the support matrix during flame synthesis. Both from the catalytic results and the spectroscopic studies we conclude that not single site zinc but rather zinc oxide clusters are important for the title reaction.

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