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Catalytic coupling of epoxides and CO_2 to cyclic carbonates by carbon nanotube-supported quaternary ammonium salts

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ABSTRACT

Quaternary ammonium chlorides bound to multi-walled carbon nanotubes as a catalyst for coupling of CO_2 and epoxides to produce cyclic carbonates were explored. Reaction variables such as the epoxide structure, the length of alkyl substituents in the quaternary ammonium salts and the spacer chain on the catalytic performance were discussed. The yield of the cyclic carbonates varied between 7 and 89% after 6 h at 110 °C under low pressure (2 MPa of CO_2). The epoxide:catalyst mass ratio was 20–30, while 1 mmol g^{-1} of the quaternary salt was grafted on the carbon nanotubes. A synergy between carboxyl moiety and ammonium moiety grafted on carbon nanotubes was found, and a strong impact of the length of the spacer group used for grafting of the quaternary ammonium salt on nanotubes was observed. The best performance was achieved with short (2 carbon atoms) and long (10 atoms) spacer groups, while a middle-sized spacer group (6 atoms) was not suitable. The length of the alkyl chain of the substituents of the ammonium salt (head group) had a low impact where ethyl and methyl groups performed better than butyl. The reactivity of epoxides was as follows: epichlorohydrin > propylene oxide > styrene oxide. Observations were rationalized by a mechanism where Brønsted's sites on the surface of nanotubes play an important role during carboxylation of epoxides. The catalyst can easily be separated by filtration recycled without a significant decrease in the catalytic activity if dried properly between the runs.

1. Introduction

The issue of carbon dioxide utilization is particularly important, especially in the view of toughening the regulations on the discharge limits of greenhouse gases into the atmosphere. The necessity of lowering carbon dioxide emission to the atmosphere has brought about advancements in the research on using this feedstock for chemical syntheses. This is evidenced in the substantial number of publications, which is constantly growing, or the number of subsidies granted to the research on the new methods of CO_2 management. Regardless of the environmental policy, CO_2 is a cheap, abundant and readily available C1 source for chemical synthesis [1]. One of the possible uses of CO_2 is in the cyclic carbonate synthesis, which enabled to eliminate the environmentally unfriendly process of phosgenation of glycols. The cyclic carbonate synthesis from carbon dioxide and epoxide was patented in 1943 by IG Farben [2]. In 2010, the annual output of cyclic carbonates reached 0.1 Mt [3]. These compounds are widely used in producing polymers and polycarbonates. Ethylene and propylene carbonates are used as polar aprotic solvents. They dissolve both small-molecule compounds and polymers, e.g., polyacrylonitrile and polysuccinimide. Since propylene carbonate is not toxic, it is used as a solvent for paint strippers, plastics and epoxy resins. Typically, cyclic carbonates are used as solvents in electrolytes for lithium-ion batteries. Alkylene carbonates are also utilized as modifiers of solid fast-crosslinking polyurethanes and polyurethane glues. Moreover, these compounds may be used as intermediate products in the fine chemicals synthesis, e.g., of polycarbonates or polyurethanes. Cyclic carbonates have also found their use in pharmaceutical and cosmetic industries as an additive for clay gellants [4].

Major research effort in recent years has been devoted to the development of a new catalytic system for the cyclic carbonates synthesis from CO_2 and various reagents, such as epoxides or alkenes. Among others, quaternary onium salts and ionic liquids were found to be one of the most effective ones. The current

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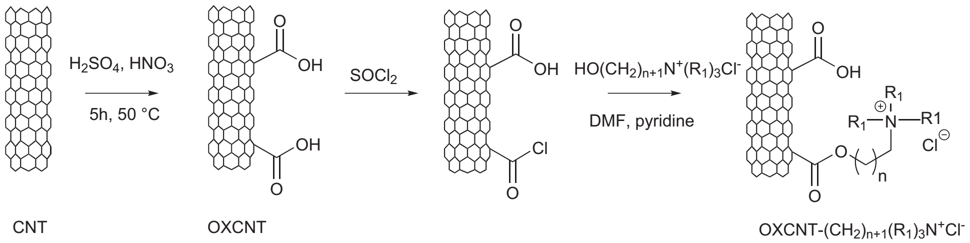


Scheme 1. General procedure of the synthesis of CNT-ammonium salt catalysts.

research is focused on the improvement of the existing systems to develop highly active catalytic agents that would be non-toxic and environmentally friendly. Due to the potential cost reduction, it is vital to apply immobilized catalysts, as they can be easily separated from the post-reaction mixture [5].

Recently, Luo and co-workers have used a series of cross-linked polydivinylbenzene polymers covalently grafted with hydroxyl, carboxyl and amino functionalized ionic liquid as effective heterogeneous catalysts for the synthesis of cyclic carbonates in the reaction of CO_2 with epoxides. These catalysts showed excellent reusability and stability [6]. Park and co-workers described the application of a series of heterogeneous zinc-containing ionic liquids on the silica gel as catalysts in the synthesis of cyclic carbonates from epoxides and CO_2. The incorporation of zinc ions in the immobilized ionic liquids significantly enhanced the catalytic activity [7]. Dyson and co-workers [8] reported that cross-linked ionic polymers based on styrene-functionalized imidazolium with chloride are stable and can be easily recycled and reused.

Carbon nanotubes (CNTs), among other nanomaterials, have been the object of extensive research in recent years. This arose from the fact that they have numerous beneficial properties, such as a substantial surface area, high mechanical and thermal resistance. This material found a handful of application in the cyclic carbonate synthesis. For example, 1-hydroxyethyl-3-methylimidazolium halides immobilized on CNTs have high catalyst activity, and may be recirculated five times without any substantial drop in activity. The studies have shown that these catalysts exhibited significantly enhanced catalytic activity in the CO_2 and epoxides reaction in comparison to conventional heterogeneous supports based on silica and polymers [9].

Herein, the aim of the research was to develop an effective method of the cyclic alkylene carbonate synthesis from carbon dioxide and selected epoxides with the use of catalysts based on the quaternary ammonium salts immobilized on CNT. The scope of the research included the synthesis of catalysts and immobilization, as well as performing a reaction of obtaining cyclic carbonates using these immobilized catalysts in order to select an effective and stable system suitable for practical application.

2. Experimental

2.1. Materials

Carbon dioxide (99.5%, from SIAD) was used without further purification. Octane (>99%), (chloromethyl)ethylene carbonate, propylene oxide (>99.5%), 2-chloroethanol (99%), 6-chloro-1-hexanol (>95%), 10-chloro-1-decanol (90%), trimethylamine (>99%) CNT (6–9 nm × 5 μm) were purchased from Sigma Aldrich. Epichlorohydrin (>99%) was obtained from Fluka. Propylene carbonate (99.5%), styrene oxide (>97%), triethylamine (99%), tributylamine (99%), (2-hydroxyethyl)trimethylammonium chloride (99%) were bought from Acros Organics. Other chemicals were of reagent grade supplied by local manufacturers.

2.2. Synthesis of quaternary ammonium salts

The method of hydroxyl functionalized quaternary salts has been described elsewhere [10]. In a typical procedure, triethylamine (0.08 mol), dry toluene (25 mL) and 2-chloroethanol (0.08 mol) were stirred for 24 h at 70 °C under nitrogen atmosphere. Upon completion of the reaction, the mixture was cooled to the room temperature, filtered out and washed successively by anhydrous ether (3 × 15 mL) and dry acetonitrile (2 × 10 mL). Next, the product was dried under vacuum (60 °C, 10 mbar, 24 h). The other quaternary ammonium salts were obtained following a similar procedure (see supporting information).

2.3. Immobilization of quaternary ammonium salts on CNTs

The synthesis was conducted according to Scheme 1. Commercial CNT (5.3 g) were oxidized for 5 h with 320 mL of the HNO_3–H_2SO_4 mixture (1:3, v/v) in an ultrasonic bath at 50 °C. The resulting black viscous suspension was diluted with water (1500 mL), filtered through a 0.2 μm nylon filter and washed thoroughly with water, acetone, methanol and dried in an oven (100 °C). The dry product (5.1 g) was mixed with an excess of thionyl chloride (60 g) and stirred overnight at the room temperature. The excess of $SOCl_2$ was removed at reduced pressure to give 4.7 g of the product. A sample of dry activated oxidized carbon nanotubes (OXCNTs) (0.8 g) was dispersed in dry DMF (75 mL) and the excess of hydroxyl functionalized quaternary salt was added (0.45 g). The reaction was conducted in an ultrasonic bath at 50 °C for 1 h; then dry pyridine (20 mL) was added and the reaction was continued overnight with magnetic stirring at the room temperature. The suspension was then filtered through a 0.2 μm nylon filter and thoroughly washed with DMF, water, acetone, methanol and cyclohexane. Finally, it was azeothropically dried for 3 h using cyclohexane. The yield of the dry product was 0.7 g.

2.4. Synthesis of cyclic carbonates

All the reactions were carried out in a 100 mL stainless steel pressure reactor (Mettler Toledo) with a mechanical stirrer (pitched-blade) immersed in a solid-state thermostat (EasyMax^{TM} 102) with an automatic temperature control system. The pressure reactor was also equipped with temperature and pressure sensors and a rupture disk. In a typical procedure, propylene oxide (15 mL, 0.21 mol) and the appropriate amount of the catalyst (Table 1 and Table 3) were added into the reactor. The reactor was purged with carbon dioxide twice and then heated to 110 °C. CO_2 was charged into the reactor from a reservoir tank to a chosen constant pressure (2 MPa). The reaction progress was monitored by means of CO_2 consumption rate. After the reaction was completed, the reactor was cooled to the ambient temperature, and the excess CO_2 was vented. The catalyst system was separated from the reaction mixture by simple filtration. Samples from the organic layer were taken, dissolved in CH_2Cl_2 and analyzed by gas chromatography (Perkin Elmer GC, Clarus 500) equipped with a capillary column (SPB^{TM}-5:

Table 1
Synthesis of a cyclic carbonate in the presence of OXCNT and ammonium catalyst from propylene oxide and CO_2.

No.	System	OXCNT loading (g)	Quaternary ammonium salt loading (mmol)	CO_2 conversion (%)	Selectivity[a] (%)
1	No catalyst	0	0	0	–
2	OXCNT	0.65	0	Trace	–
3	Choline chloride	0	1	16	95
4	Trimethyl-(6-hydroxyhexyl)ammonium chloride	0	1	15	95
5	Trimethyl-(10-hydroxydecyl)ammonium chloride	0	1	18	95
6	OXCNT + choline chloride	0.65	1	35	96
7	Choline chloride + 1 mmol CH_3COOH	0	1	37	96
8	Choline chloride + 10 mmol CH_3COOH	0	1	38	95

Reaction conditions: epoxide (0.214 mol, 15 mL); 110 °C; 2 MPa of CO_2; 500 rpm; reaction time 6 h.

[a] Analysed by GC.

30 m × 0.25 mm × 0.25 μm film thickness). 1-Octane was used as an internal standard.

3. Results and discussion

The investigation of the possibility of application of the quaternary ammonium salts immobilized on OXCNTs was initiated by a set of experiments in which a non-immobilized quaternary ammonium salt and OXCNTs were investigated as potential catalysts for the cyclic carbonate synthesis. The results are presented in Table 1.

From the control runs presented in Table 1, it was clear that the reaction of CO_2 with propylene oxide did not proceed in the absence of a catalyst. Interestingly, the addition of OXCNTs increased slightly the yield of the cyclic carbonate but the concentration of the product remained at trace level. More pronounced effect had the presence of a quaternary ammonium salts (entries 3–5) when the conversion of CO_2 reached 15–18%. No significant effect of the structure of the ammonium salt was observed (entries 3–5). In contrast, the presence of both the quaternary ammonium catalyst and oxidized CNTs yielded a 35% conversion of CO_2, and equal selectivity. Those preliminary results encouraged us to investigate the possibility of immobilizing an ammonium salt on the CNT surface chemically to obtain a recyclable catalyst of high activity. To confirm whether the CNT itself or carboxylic acid moieties

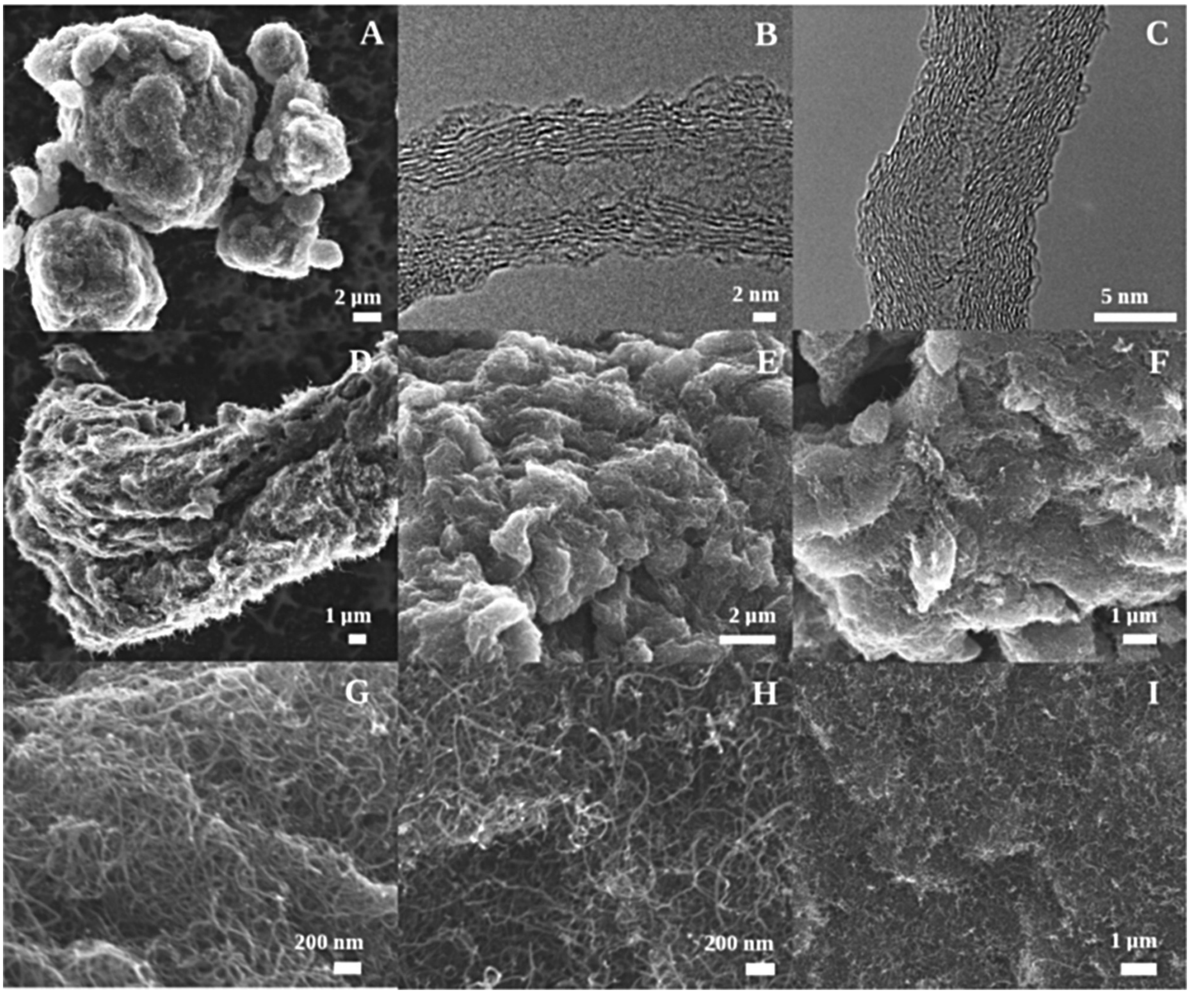


Fig. 1. TEM and SEM characterization of catalysts and intermediate materials. (A, B) CNT; (C, D) OXCNT; (E–I) OXCNT-$(CH_2)_{n+1}(R_1)_3N^+Cl^-$; (E, G) R_1 = Et, n = 1; (F) R_1 = Bu, n = 9; (H, I) R_1 = Me, n = 5.

Table 2
Structural features and elemental composition of CNT-supported ammonium chlorides OXCNT-$(CH_2)_{n+1}(R_1)_3N^+Cl^-$.

R_1	*n*	C (%)	H (%)	N (%)	N ($mmol\,g^{-1}$)
Bu	1	83.54	>0.09	1.43	1.02
Et	1	83.1	0.13	1.65	1.18
Me	1	75.72	0.55	2.36	1.69
Me	9	89.67	0.33	1.99	1.42
Et	9	83.67	0.15	1.30	0.93
Bu	9	74.34	1.08	1.19	0.85
Me	5	84.7	>0.09	1.32	0.94
Et	5	84.15	0.96	0.79	0.56
Bu	5	83.64	0.99	1.34	0.96

display catalytic activity we added acetic acid to the reaction system instead of OXCNT (entries 7–8). Results were similar as with OXCNTs. Therefore, carboxylic moieties play a dominant catalytic role in the process.

3.1. Catalysts synthesis and characterization

Catalysts were synthesized according to Scheme 1. In total, nine different substances were obtained and characterized by elemental analysis (Table 2), SEM and TEM (Fig. 1), IR (Fig. 2), and TGA (Fig. 3).

From Fig. 1, it is clear that oxidation of CNTs did not substantially change the length of the tubes. Probably functional groups were only introduced randomly on the surface where structural defects facilitate the oxidation. Further functionalization with ammonium salts did not alter the microscopic structure of the material. However, small differences in arrangement of bundles of nanotubes may be identified while comparing images A, C, E, F and I. Also higher resolution images G and H suggests more loosely packed bundles when *n* = 9 group was used.

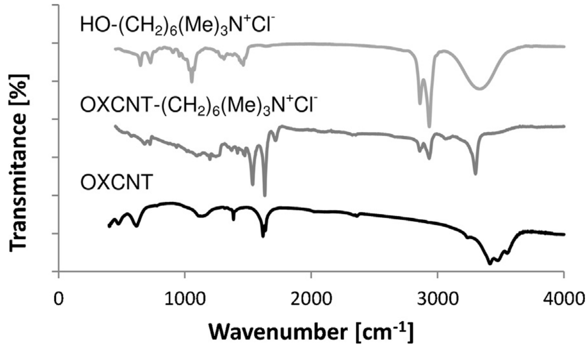


Fig. 2. IR spectra of OXCNT, free ammonium salt and one of the final products.

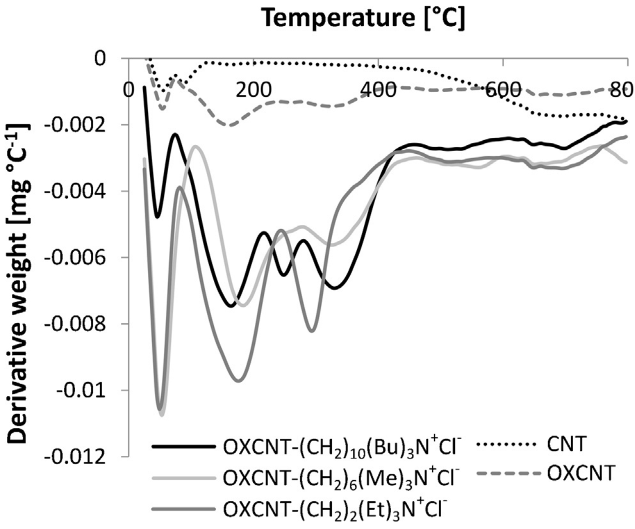


Fig. 3. Representative DTG curves of catalysts and intermediate materials.

FT-IR analysis confirmed successful immobilization of the quaternary ammonium salts onto carbon nanotubes. Fig. 2 shows the FT-IR spectra of the homogeneous catalyst, oxidized CNTs and immobilized catalyst. The characteristic peaks of oxidized CNTs around 1617 and 1385 cm^{-1} was observed. They can be ascribed to C=O and C-O stretching of carboxyl group. Free quaternary ammonium salt exhibited the characteristic bands which occurred in the region of 2869–2934 cm^{-1}. This stretching vibrations of C-H bond are specific for the molecules having a tertiary N-CH_3 group. Moreover, the spectra contained peak appearing at 1055 cm^{-1} corresponding to the C-N stretch. The peak appeared in the region of 3347 cm^{-1} is ascribed to H_2O that was not removed during drying of the samples. In the case of immobilized ammonium salt, characteristic peaks of support (1635, 1538 cm^{-1}) and quaternary ammonium salt (1199, 2861, 2934 cm^{-1}) confirmed successful immobilization.

The results of the TGA analysis (shown in Fig. 3) of catalysts, OXCNTs and CNTs can be clearly distinguished. CNTs themselves are thermally stable and only small peaks (53 and 85 °C) which most likely corresponds to the desorption of water or other substances. Significant decomposition of this material is visible only above 400 °C. OXCNTs were more susceptible to decomposition, and additional peaks between 200 and 400 °C appeared. In the case of catalysts, the degradation occurred in the same range of temperature. In all cases, 2–3 peaks were visible at approximately 200 and 300 °C. Exact position of those peaks depended on the structure of alkyl substituents. If weight loss that occurred between 200 and 400 °C was used to calculate the nitrogen content, the results were in good agreement with those obtained by means of elemental analysis.

3.2. Catalysts performance

Among possible factors that affect the yield of cyclic carbonate synthesis using immobilized ammonium catalysts are the structure of alkyl substituents of ammonium nitrogen, halide type and the epoxide structure. In the case of halides, the views on that matter are divided.

In a series of recently published papers, where tetraalkylammonium halides were considered as a possible factor in carboxylation of epoxides, it was demonstrated that the impact of the halide type strongly depends on a particular reaction system. The reason is that the opening of the epoxy ring occurs through the nucleophilic attack of a halide anion on the less-hindered carbon atom of epoxide. Therefore, the nucleophilicity of the halide is very important to facilitate this step while its leaving ability is crucial during the last step when cyclic carbonate is formed. However, experimental data vary and different orders of reactivity of halides were reported.

In the case of ionic liquids immobilized on the carboxymethyl cellulose (CMIL), it was found that propylene carbonate yield increased in the order of CMIL-I (98.6%) > CMIL-Br (81.7%) > CMIL-Cl (73.2%) [11]. Similar order was reported for imidazolium ionic liquids immobilized on chitosan (CS) where the yield of propylene carbonate increased with the increase in nucleophilicity of the anion (CS-EMImBr 96% > CS-EMImCl 74%) [12]. More profound effect was observed when quaternary phosphonium salts immobilized on silica was used for the same reaction. In that case chloride resulted in 29% yield comparing with 100% for iodide [13]. Other authors reported that fluctuations of catalytic activity of different halides was in a narrow range of 1–15% [9,14,15] or no apparent influence was visible [9,12,16,17].

Interestingly, it was found that in certain instances the yield of carbonates did not rise according to the increase of the catalyst's

Table 3
Effect of the structure of a catalyst and type of epoxide on the cyclic carbonate formation.

R_1	n	Epoxide	Catalyst loading (g)	CO_2 conversion (%)	Yield of carbonate[a] (%)	Selectivity[a] (%)	$k_1 \times 10^6$ (s^{-1})[b]	TOF[c] (mol epoxide mol $N^{-1} s^{-1}$)	$k_{1N} \times 10^6$ (mmol $N^{-1} s^{-1}$)[a]
Me	1	Styrene oxide	0.57	23	22	96	20.3	0.0023	21.1
Et	1	Propylene oxide	0.66	68	66	98	66.7	0.0083	85.6
Bu	1	Epichlorohydrin	0.46	53	50	96	24.9	0.0107	53.0
Me	9	Epichlorohydrin	0.77	86	81	94	110.6	0.0073	101.0
Et	9	Styrene oxide	0.58	17	16	97	14.4	0.0030	26.7
Bu	9	Propylene oxide	0.70	21	20	98	8.9	0.0034	15.0
Me	5	Propylene oxide	0.53	7	6.8	97	3.4	0.0014	6.80
Et	5	Epichlorohydrin	0.55	13	12	92	5.5	0.0039	17.7
Bu	5	Styrene oxide	0.62	16	15	96	13.4	0.0025	22.6

Reaction conditions: epoxide (0.214 mol); 110 °C; 2 MPa of CO_2; 500 rpm; reaction time 6 h.

[a] Analysed by GC.

[b] Measured within the period of 3000–7000s.

[c] Averaged over the entire 6 h.

anion nucleophilicity [18]. In one case, it was rationalized by lower stability of an iodide comparing with a bromide under employed reaction conditions [14]. In 2008, an article was published regarding the reaction of carbon dioxide with butyl glycidyl ether (BGE). This article showed that steric hindrance can have stronger influence on the course of the reaction of obtaining cyclic carbonates than the nucleophilicity of anions. In connection with this, the conversion of BGE increased in the order of $Cl^- > Br^- > I^-$ [19].

Some authors reported that cyclic carbonates can be obtained in similar yields regardless of the catalyst's halide type if reaction conditions are changed to offset different reactivity [20]. For example, catalytic activity of $Zn_3[Co(CN)_6]_2$/TBAB (bromide) system at 120 °C was the same as in the case of $Zn_3[Co(CN)_6]_2$/TBAC (chloride) at 140 °C. In both cases, the yield of styrene carbonate amounted in to 97% [16]. A similar phenomenon was described by Zhao et al. [21].

Another view on the subject was presented by other authors who attributed variation in catalytic activity to physical properties of halides. Shim et al. [22] claimed that the yield of styrene carbonate depend on the melting point of quaternary ammonium salt they applied. Zhou et al. [23] noticed that HBetCl (1-carboxy-*N*,*N*,*N*-trimethylmethanaminium chloride) showed higher catalytic activity than HBetBr, which can be explained by the difference in the catalyst solubility in the reaction mixture. HBetBr precipitated from the product, and HBetCl not.

At this stage of our research, we selected ammonium chlorides as they are cheaper comparing with bromides or iodides, and we focused only on the length of alkyl substituents of the ammonium salt (head group) and the length of a spacer between the CNT functional site and the ammonium nitrogen. As the reported reactivity of epoxides towards CO_2 varies and depends on the reaction system [9,12,18,24], we included this factor in our research. Each experimental variable was investigated at three levels.

With three factors that could be set at three levels, the total of a 27-reaction system was possible. Investigations were performed with various catalysts according to the orthogonal array of experiments presented in Table 3 in order to limit the number of required runs. Instead of 27, only 9 runs were performed to investigate three factors: the length of the spacer group (n), the size of alkyl groups of the quaternary ammonium salt (R_1) (Scheme 1) and the epoxide type.

In all cases, the reaction followed the first-order kinetics at least for the first 3 h. Within this period, the relationship between the reaction time and the CO_2 consumption was linear on the logarithmic scale as showed in Fig. 4. The exception was a short initial period, which could be attributed to the formation of a dispersion of the catalyst in the epoxide. For the same reason, in one case the reaction rate increased during the 6th hour (curve 8, Fig. 4).

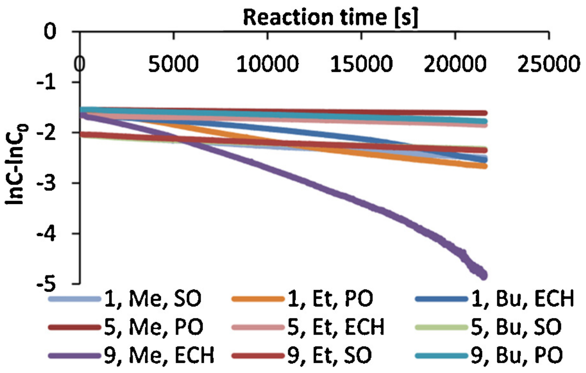


Fig. 4. Progress of the cyclic carbonate synthesis from epoxides followed by the consumption of CO_2. Reaction conditions: epoxide (0.214 mol); catalyst (≈0.5 g); 110 °C; 2 MPa; 500 rpm. ECH, epichlorohydrin; PO, propylene oxide; SO, styrene oxide.

Table 4
Impact of the investigated factor on the carbonate yield. Reaction conditions: catalyst loading, 0.46-0.77 g; epoxide,0.214 mol; 110 °C; 2 MPa of CO_2; 500 rpm; reaction time 6 h (see Table 3).

Factor	Factor value	Averages of $k_{1N} \times 10^6$ $(s^{-1}$ mmol $N^{-1})$[a]
R_1	Me	43
	Et	43
	Bu	30
n	1	53
	5	16
	9	48
Epoxide	Propylene oxide	36
	Styrene oxide	23
	epichlorohydrin	57

[a] k_{1N}, reaction rate per mmol of the ammonium nitrogen present in the reaction system. Estimated uncertainty of $k_{1N} \times 10^6 = 6$ $(s^{-1}$ mmol $N^{-1})$.

For comparison of the catalyst's performance, the interval between 3000 and 7000s was used. The corresponding slopes of kinetic curves are given in Table 3. As the quantity of the ammonium salt grafted on CNTs was different for each catalyst, we decided to compare not directly the yield of the carbonate, but the rate of the reaction divided by the amount of the ammonium nitrogen present during the reaction (k_{1N}). For the same reason, the quantity of the catalyst was not maintained strictly constant. The results are given in Table 4.

Each of nine main runs conducted according to the orthogonal array allowed to establish the main effect of three experimental variables simply by averaging the reaction rates of the carbonates obtained for a given setting (Table 3). In other words, based on the nine results, nine averages could be calculated and compared (Table 4).

According to Table 4, the impact of the head group on the reaction rate was small. Between ethyl and methyl groups, there was no difference, whilst R_1 = Bu gave lower yield compared with the other two. A more important factor was the epoxide type as the variation between the possible rates was higher. The reactivity of epoxides was as follows: epichlorohydrin > propylene oxide > styrene oxide.

Compared with other published data, the observed differences were higher especially between epichlorohydrin and propylene oxide. Often it was reported that the reactivity of propylene oxide is higher than epichlorohydrin [12,16,24–31] but other teams observed the same order of reactivity as presented here [32,33]. The different behaviour of epoxides in various systems is probably a consequence of different structures of reaction sites. The presence of an electron-withdrawing chlorine atom in epichlorohydrin results in reduced electron density of the oxygen atom in epoxide [34] [35]. This probably disfavours the coordination of epoxide by carboxylic acid but facilitates the reaction of epoxide with halide ion as C1 carbon is more positively charged. In our case, the latter process is likely to be important as we used ammonium chlorides which are often reported to be less reactive comparing with bromides or iodides. The other factor that may contribute to the reactivity of epoxides is the size of molecules. In our case, the heterogeneity of the catalyst disfavours more bulky substrates such as styrene oxide which is less reactive comparing with propylene oxide or epichlorohydrin.

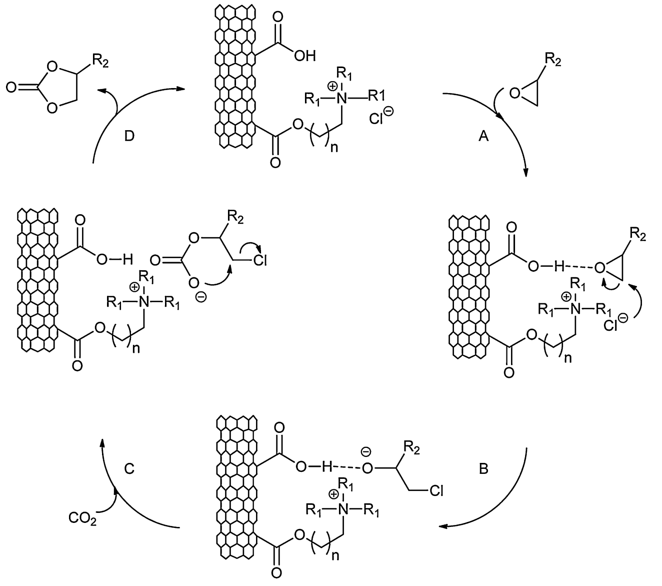
Because in our experiment, only nine runs were performed and nine averages were calculated, there are no degrees of freedom left to calculate the significance of results. The precision of k_{1N} measurements is high (RSD of linear regression < 0.5%). However, using the data obtained during recycle of a catalyst, we estimated the potential variations between runs as high as 15%. Taking into account all results from Table 3, it means that the differences of averages higher than 6 units of k_{1N} 10^6 can be treated as significant.

Based on the obtained results, it is clear that in our system the main factor that influences the yield of carbonate was the length of the spacer group. The average rates were 16, 48 and 53 $\times 10^{-6}$ s^{-1} mmol N^{-1} for hexyl, ethyl and dodecyl chains, respectively. Clearly, the middle-sized spacer was the worst performer, while the shortest was similar to the longest one.

Such observation, counterintuitive at first sight (see Table 1, entries 3–5), could be rationalized on the basis of the mechanism as presented in Scheme 2. The mechanism was derived from a proposition given in previous publications [24,27,36].

Initially (Scheme 2, step A), the epoxide molecule is adsorbed at a Brønsted's site (COOH) on the surface of CNT [37]. Based on the elementary analysis, the number of carboxylic acid sites on an oxidized CNT that was used in this study was approximately 5 mmol g^{-1}. Further functionalization affords the material containing 1 mmol g^{-1} of ammonium groups; therefore, a large number of carboxylic acid sites randomly distributed on the surface are available for the coordination of the epoxide.

As short (n = 1) and long (n = 9) spacer groups are more effective in the process compared with the middle-sized one (n = 5), but only when grafted on the CNT (entries 3–5 in Table 1) surface, it means that the chain length plays an important role during the rate-determining step. It is likely that the distance between positively charged nitrogen and carboxylic acid moiety decreases with the increase in the chain length as longer chains are more flexible. However, long alkyl chain may inhibit the approach of epoxide to the CNT surface because of steric hindrance. This effect is probably negligible for short spacer group and offset by flexibility of the longest one. Comparable effect was reported recently for amino alcohols potassium iodide catalytic system [38]. Other authors reported irregular dependence of carbonate yield on the alkyl substituents in the case of imidazolium ionic liquid catalysts [9,39,40]. However, in that research the distance between the solid support and reaction centre was not varied.



Scheme 2. Mechanism of the synthesis of cyclic carbonates catalysed by OXCNT-$(CH_2)_n(R_1)_3N^+Cl^-$.

Further steps (Scheme 2) include nucleophilic attack of chloride to the epoxide (B) with the subsequent ring opening, addition of CO_2 (C), formation of an alkylcarboante anion stabilized by an ammonium cation and, finally, intramolecular substitution leading to abstraction of chloride and regeneration of the catalyst and cyclic carbonate desorption from the site (D). In comparison with the chloride attack and coordination of the epoxide, those steps are not likely to be affected by the structure of the ammonium salt, which supports our observation of the dominant role of the chain length.

The mechanism also allowed to explain the observed impact of the remaining two factors. A small effect of the head group indicates that the epoxide–nitrogen distance is comparable to two C-C bond lengths during the initial step. For that reason we did not observe any difference in activity between catalysts containing Et or Me groups. In the case of larger Bu substituents, the epoxide approach to the carboxylic group is probably more difficult because of the overall steric hindrance around the reaction centre.

The observed order of epoxides reactivity reflects the increasing positive charge on the carbon that is attacked by the chloride anion and the steric effects of the R_2 group (epoxide). Compared with another publication devoted to CNT-supported catalyst for the cyclic carbonates synthesis from epoxides, we observed a higher difference of reactivity between epoxides, especially between styrene oxide comparing with propylene oxide [17]. It is therefore likely that the quaternary ammonium salts are more sensitive to the reagent's structure compared with imidazolium ionic liquids. Probably, the presence of CNTs favours only parallel orientation of aromatic ring-CNT (due to π–π interaction), which may hamper the attack of the chloride ion on the epoxide comparing with non-aromatic epoxides. This effect might be diminished by the presence of the imidazolium ring. Important role of CNT support in differentiating the reactivity of different epoxides was confirmed by two experiments analogous to entry 3 of Table 1. If styrene oxide and epichlorohydrin were used instead of propylene oxide with choline chloride as a catalyst observed conversions of CO_2 were 14 and 16%, respectively (95 and 96% selectivity). Therefore, the observed

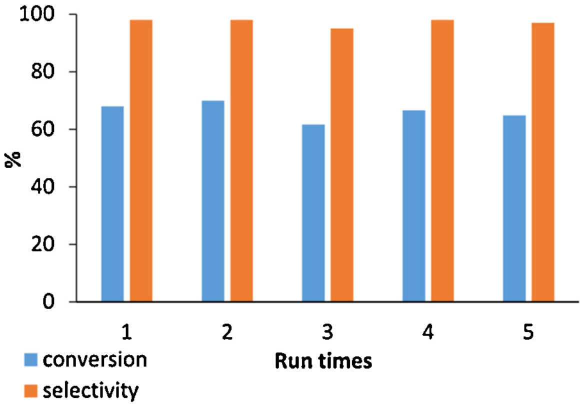


Fig. 5. Catalytic activity of the reused immobilized catalyst ($n = 1$ and $R_1 = Et$). Reaction conditions: propylene oxide (0.214 mol); catalyst (≈0.6 g); 110 °C; 2 MPa; 6 h; 500 rpm.

differences of reactivity were lower comparing with immobilized ammonium salts.

3.3. *Reuse of the catalyst*

A series of cycles of catalyst's reuse was performed with the catalyst of $n = 1$ and $R_1 = Et$ using propylene oxide as a model epoxide. After correcting the results for slight losses of the catalyst during its separation from the reaction mixture, it was clear that the catalyst retains its activity (Fig. 5). Nevertheless, it was crucial to carefully dry the sample between the runs. Typically the catalyst was azeotropically dried for 1 h with cyclohexane. After evaporation of the solvent, the solid was dried over NaOH under vacuum (50 mbar). In the case of the third cycle, the drying period was only 15 min, which appeared to be not enough to remove water. If no drying was performed and the catalyst was used immediately after filtering only, the yield of epoxide was approximately halved. The observation was surprising as water was demonstrated as a possible solvent for the cyclic carbonate synthesis [18]. In our system, water probably competes with the epoxide for Brønsted's sites on the nanotube's surface (Scheme 2, step A) and decreases the likelihood of the catalyst–epoxide contact. In order to confirm our assumption, we deliberately added water to the reaction system using 0.35 g of $OXCNT\text{-}(CH_2)_{10}(CH_3)_3N + Cl^-$ and propylene oxide (0.214 mol) as a model system. With the addition of 0.018 g of water, the carbonate yield was 12% (97% selectivity) after 6 h while 0.18 g of water in the system diminished the yield to 3% only (88% selectivity).

4. Conclusions

In summary, quaternary ammonium chlorides covalently bound to CNTs are proved to be efficient and recyclable heterogeneous catalysts for the solvent-free synthesis of cyclic carbonates under mild conditions. The nanotubes are not only a solid support that facilitates the reuse of the catalyst, but carboxylic moieties present on CNT surface also participate in the reaction presumably by coordination of an epoxide. The synergistic effect is clearly visible comparing the results for free, immobilized ammonium salts and for carboxylic acid-catalysed systems. The activity of the catalyst is fully retained upon reuse; however, it should be thoroughly dried between the runs. Strong impact of alkyl chain that links the surface of carbon nanotube with ammonium nitrogen indicates that steric effects play an important role in the activity of the catalyst.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apcata.2014.09.034.

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