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One-Pot Synthesis of Styrene Carbonate from Styrene and CO_2 Over the Nanogold-Ionic Liquid Catalyst

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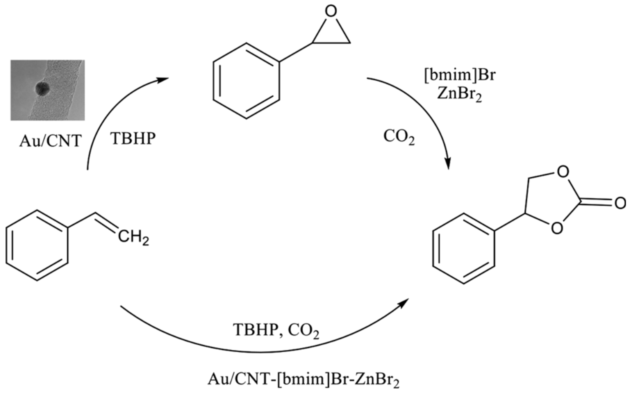
Abstract A catalyst system for the efficient two-step coupling of CO_2 and styrene to styrene carbonate was developed. Gold nanoparticles immobilized on multi-walled carbon nanotubes (Au/CNT) of 6 nm in diameter were used as a catalyst for the epoxidation step. The process was carried out at 80 °C for 4 h in the presence of anhydrous tert-butyl hydroperoxide as an oxidant. The reaction of the resulting epoxide and CO_2 was catalyzed by the 1-butyl-3-methylimidazolium bromide [bmim]Br-$ZnBr_2$ system under the CO_2 pressure (1.2 MPa) at 120 °C. A high styrene carbonate yield of 60 % was achieved. After the reaction, Au/CNT could be easily separated and reused without any significant loss of activity.

Graphical Abstract



Keywords Immobilization · Epoxidation · CO_2 valorization · Nanoparticles · Cycloaddition

1 Introduction

In recent years, a number of research teams have engaged in intense investigations on the use of CO_2 as a raw material for the chemical industry [1, 2]. Owing to the thermodynamic stability of carbon dioxide [3], the commercial use of carbon dioxide is accomplished on a wide scale only in the case of urea, methanol, salicylic acid, and cyclic carbonates synthesis. The latter have found applications as solvents, electrolytes, intermediates in organic synthesis and for polymer production. The annual production of cyclic carbonates was estimated at 0.1 Mt per year in 2010 [4]. One of the examples of cyclic carbonates is styrene carbonate (SC). It is employed as an additive for polymer-coated fertilizer granules [5], and as a component

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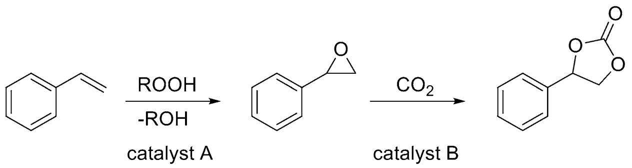
of nonaqueous electrolyte in alkali metal batteries or lithium secondary batteries [6]. SC is also applied in the synthesis of compounds, such as aromatic carbamate, dialkyl carbonate, vicinal diol [7], beata-amino alcohol, thermoplastic aromatic polycarbonate, non-isocyanate polyurethane [8] and aliphatic polycarbonate polyol.

Currently, SC is obtained on an industrial scale in the reaction of carbon dioxide with styrene epoxide, and the most common method of producing styrene epoxide is by the epoxidation of styrene (Scheme 1). An analogous reaction pathway can be applicable to other cyclic carbonates.

Synthesis of SC from styrene without the necessity of the intermediate epoxide separation is highly desirable from the economic and environmental point of view. There are only a limited number of studies reporting such a process. The literature review demonstrates that the synthesis of SC proceeds under both solvent-free and solvent conditions at 30–150 °C and under both low-pressure and high-pressure conditions [9]. Metal oxides were among the first catalysts employed in this process [10]. However, it was found that such a reaction proceeds with a low yield due to the formation of a number of by-products. The use of tetrabutylammonium bromide (TBAB) as a catalyst and *tert*-butyl hydroperoxide (TBHP) as an oxidant under relatively mild conditions (80 °C, 1 MPa, 6 h) [11] improved the yield of SC up to 38 %. A further improvement of the yield in the presence of quaternary ammonium salts was achieved with other oxidants, such as O_2 (SC yield: 76 %) [12] or H_2O_2 (SC yield: 57–70 %) [13, 14]. A more advantageous approach which resulted in higher yields of SC (51–83 %) involved a two-component catalytic system and a two-step protocol [15–17].

The obtained results were relatively poor because of the incompatibility of conditions (type of catalyst, temperature, pressure) during the alkene epoxidation and the cycloaddition of CO_2. Thus, to resolve this problem, the separation of catalysts at an intermediate stage or shifting of the reaction conditions was required. Such a strategy applied to a system consisting of Mn(salen)-O_2-isobutyraldehyde (epoxidation, 80 °C) and choline chloride-CO_2 (cyclocarbonatation, 1.5 MPa, 120 °C) resulted in the formation of SC with a 24 % yield. Such a process was possible only if isobutyraldehyde was completely consumed [18].

Supported gold nanoparticles are ones of possible epoxidation catalysts which have gained a considerable attention. They show excellent catalytic activity for the epoxidation of olefins, and due to low by-products yields they are a promising choice for the cyclic carbonates synthesis from olefins [19–23]. However, until now, only three publications have described such a synthesis in the presence of gold nanoparticles immobilized on various carriers (SiO_2, resin R201, $Fe(OH)_3$) [15, 24, 25]. The reported good yields of cyclic carbonates (42–53 %) depending on the presence of Au-based catalysts encouraged us to investigate different types of support that would increase the efficiency of the catalyst and simultaneously facilitate the separation and stability of gold nanoparticles. Multi-walled carbon nanotubes (CNT) seem to be a promising material as they are widely used as catalyst supports due to their mechanical stability and supreme surface areas.



Scheme 1 Synthesis of SC from CO_2

In this paper, we investigated the possibility of simultaneous application of cycloaddition and epoxidation catalysts for a one-pot coupling of CO_2 with styrene. Highly efficient cycloaddition catalysts reported earlier in the literature, such as TBAB, [bmim]Br-$ZnBr_2$, [bmim]Br-$ZnCl_2$, were used. For the epoxidation step nanogold supported on CNT was proposed.

2 Experimental

2.1 Materials

Carbon dioxide of the 99.5 % purity was obtained from SIAD. Octane (>99 %), styrene (>99 %), TBHP (5.0–6.0 M in decane), CNT (6–9 nm × 5 µm), tetrabutylammonium bromide (>99 %) were purchased from Sigma Aldrich. Urea hydrogen peroxide (UHP), TBHP (70 wt% in water), styrene oxide (>97 %) were bought from Acros Organics. $AuCl_3$ and other chemicals were supplied by local manufacturers. 1-Butyl-3-methylimidazolium bromide and 1-butyl-3-methylimidazolium chloride were synthesized according to the previous reports [26, 27].

2.2 Instruments

The investigations of the structure and morphology of Au/CNT were carried out on a Cs-corrected FEI S/TEM TITAN 80/300 kV and on a high-resolution scanning electron microscope ZEISS SUPRA 35 (Carl Zeiss, Jena, Germany). ICP-AES measurements were done on a Varian 710-ES ICP optical emission spectrometer. The conditions for the determination of Au by ICP-AES were: RF power 1.0 kW, plasma flow 15 L min^{-1}, auxiliary flow 1.5 L min^{-1}, nebulizer pressure 200 kPa, pump rate 15 rpm, Au emission lines: 208.207 and 242.794 nm. The gas chromatography analyses were performed with

PerkinElmer GC, Clarus 500 equipped with a capillary column (SPB-5: 30 m × 0.25 mm × 0.25 μm film thickness) and a FID detector. The detector temperature was 250 °C. The flow rate of He was 45 mL min^{-1} and air 450 mL min^{-1}. The initial column temperature was 45 °C and it increased to 150 °C (20 °C min^{-1}). After a further increase at 45 °C min^{-1} to 200 °C the temperature was held for 2 min, and finally increased to 250 °C (45 °C min^{-1}) and held for 5 min. The crystal structure of the Au nanoparticles supported on CNT was determined by a powder XRD diffractometer (Panalytical X'Pert Pro, Co Kα radiation, $\lambda = 0.1789$ nm). The X-ray Photoelectron Spectroscopy (XPS) measurements were performed on a PHI 5700/660 spectrometer, while IR on FT-IR Nicolet 6700 (KBr pellet method).

2.3 Synthesis and Characterization of the Au/CNT Catalyst

0.1 gram of $AuCl_3$ was dissolved in 50 mL of water and then 1 mL of concentrated ammonia was added. This turbid solution was then added to a 200 mL aqueous dispersion of 0.5 g of CNT placed in a large beaker under continuous mechanical stirring. Next, $NaBH_4$ (1 g) was slowly added portionwise over a period of 1.5 h. After addition, the suspension was stirred for further 2 h. The pH was then adjusted to 5 using concentrated HCl. The Au/CNT were separated by filtration through a 0.2 μm nylon filter, washed with water, acetone and acetonitrile, and dried in a vacuum desiccator. The content of Au in Au/CNT was determined by ICP-AES after partial digestion of approximately 0.01 g of Au/CNT in 1.6 mL of aqua regia. After 48 h, the solution was diluted with water to 10 mL, unreacted CNT were separated by centrifugation, and finally filtered through a PTFE syringe filter. The determined content of Au in the solution was 101 ± 1 mg L^{-1}, which corresponds to 8 % of Au in Au/CNT. The fraction of gold incorporated into CNT was 62 % of the $AuCl_3$ quantity, and the material yield was 0.5 g.

Samples for the transmission electron microscopy were prepared by dispersing the tested materials (black powder) in ethanol, placing them in an ultrasonic bath, then putting droplets onto 3 mm copper grids coated with an amorphous carbon film, and air-dried at room temperature. The morphology of Au/CNT was characterized by TEM, as shown in Fig. 1. The material contained CNT which had similar diameter of approximately 10–20 nm. Based on the TEM images, we estimated the size distribution of Au nanoparticles. The nanoparticles had a spherical shape with an average diameter of 6 nm. The size distribution was narrow between 1 and 13 nm.

The XRD pattern for the sample is shown in Fig. 2a. The diffraction peaks in each XRD pattern at 45.0, 52.5, 77.1, 93.8 and 99.4 ° can be assigned to reflections from the (111), (200), (220), (311) and (222) planes of the face-centered-cubic Au. The average crystallite size of gold nanoparticles calculated using the Debye–Scherrer formula was approximately 10 nm. The IR spectrum (Fig. 2b) of the catalyst (after use) shows no specific features that can be attributed to the Au nanoparticles. Only oxygen-containing functional groups O–H (3420 cm^{-1}), C–O–C (1185 cm^{-1}), and the remains of [bmim]Br (2360; 2920 cm^{-1}) can be identified. Figure 2C shows the XPS spectrum of the Au/CNT catalyst, where C1s is the dominant peak. The XPS signature of the Au 4f doublet ($4f_{7/2}$ and $4f_{5/2}$) for the Au particles was shown in Fig. 2D. The line shapes, and peak-to-peak distance of the Au 4f doublet are consistent with the Au^0 state, which confirms the earlier reports, where it was shown that in this type of material Au nanoparticles are non-covalently adsorbed onto CNT [28].

2.4 Epoxidation of Styrene

Styrene (5 mmol) was placed in a round bottomed flask (5 mL) equipped with a magnetic stirrer and a reflux condenser. The appropriate quantity of the oxidant and then the catalyst were added to the flask. The content of the flask was heated with the agitation speed of 500 rpm. After completion of the reaction, the mixture was cooled down to room temperature.

2.5 Synthesis of SC from Styrene or Styrene Oxide

All the reactions using CO_2 as the reagent were performed in a 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.

2.5.1 Synthesis of SC from Styrene Oxide

Styrene oxide (32 mmol) and the appropriate amount of the catalyst were introduced into the autoclave reactor. The reactor was purged twice using carbon dioxide and then heated to the desired temperature. After the stabilization of temperature, CO_2 was charged into the reactor from a reservoir tank to maintain a constant pressure. The consumption of CO_2 was controlled during the process using iControl^{TM} software (version 5.1.2.9). At the end of the reaction the reactor was cooled down to 25 °C, and then the excess of CO_2 was released slowly.

2.5.2 Synthesis of SC from Styrene

The research on the direct synthesis of SC from styrene was conducted in a similar way as in the case of the

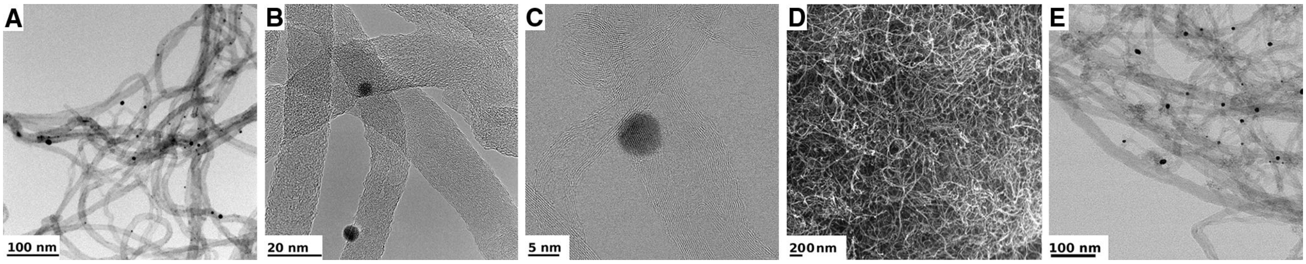


Fig. 1 TEM images of the Au/CNT catalyst (**a**–**c**); SEM image of pristine CNT (**d**); TEM image of the catalyst after 6 cycles (**e**)

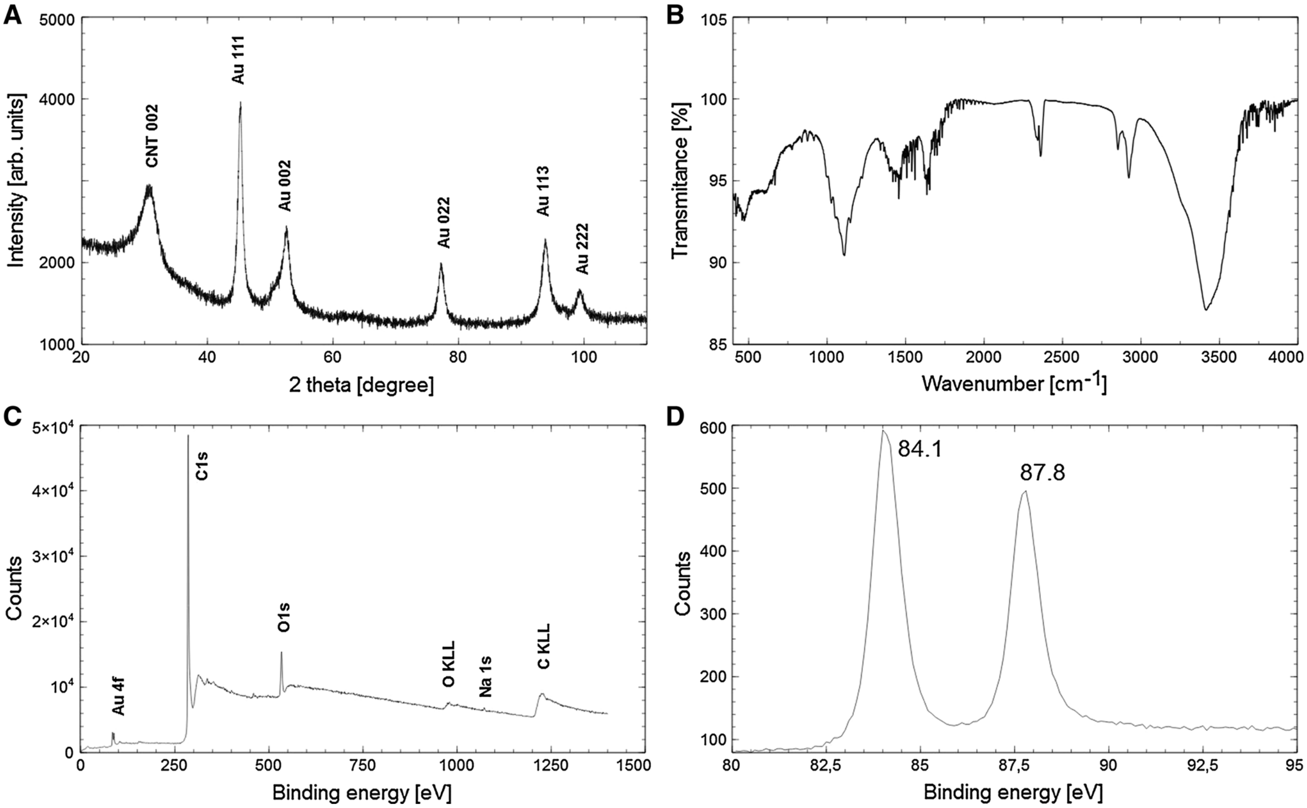


Fig. 2 Au/CNT catalyst characterization. **a** XRD; **b** IR; **c**, **d** XPS

reaction of styrene oxide with CO_2. In an autoclave reactor 32 mmol of styrene, 64 mmol of the oxidant and an appropriate quantity of catalysts were placed. The further procedure was the same as described in Sect. 2.5.1.

2.5.3 Analysis

Au/CNT were separated from the post-reaction mixture by filtration. The filtrate was diluted with 15 mL of ethyl acetate containing 0.2 g of 1-octane as an internal standard. A sample (50 µL) was further diluted with 900 µL of ethyl acetate. The solution was analyzed by GC-FID using a 1 µL injection and the temperature gradient described in Sect. 2.2. The retention times (in min) of the analyzed compounds were as follows: 1-octane (2.3), styrene (3.0), benzaldehyde (3.5), styrene oxide (4.4) and styrene carbonate (7.4). Appropriate quantities were determined using the calibration line method.

3 Results

The aim of this work was to obtain styrene carbonate in a one-pot process from styrene. The catalyst for the epoxidation step was Au/CNT. It was a challenge to find a suitable catalyst system for the second stage and to combine both reactions into one process. We developed our catalytic system by optimizing both steps separately, and then we attempted to couple both processes.

3.1 Epoxidation of Styrene

Epoxidation of alkenes using gold nanoparticles is a well-known process. The mechanism of the nanogold-assisted epoxidation was proposed by Liu et al. [23]. Usually an average catalyst particle size is less than 15–30 nm and the gold content is less than 1 % [21, 23, 29]. It was demonstrated that the activity of a catalyst increases as the particle size decreases [29, 30]. Nevertheless, the selectivity of the epoxidation process might be negatively affected [29]. In order to obtain high epoxidation yields and a stable material, we synthesized the Au/CNT catalyst with a small size of particles (6 nm), while keeping the high Au loading (8 %). It was possible due to a high surface area of CNT, as well as its good dispersity in water or other solvents. The role of CNT was to stabilize gold nanoparticles and to allow a facile separation and reuse of the catalyst. The investigations on the epoxidation of styrene catalyzed by the Au/CNT catalyst were started by examining the type of the oxidant. The progress of the reaction was monitored by the GC analysis. In all cases, the yield of styrene reached its plateau after 4 h. The results are summarized in Table 1.

The best results were obtained with anhydrous TBHP. In that case, a high conversion of styrene was observed and epoxidation proceeded selectively to give styrene oxide. The results showed low and trace yields in the presence of H_2O_2, and UHP, respectively. It was likely due to the poor solubility of UHP in styrene and limited miscibility of H_2O_2 with styrene. Apparently, the presence of water also had a negative impact on the epoxidation reaction—the usage of aqueous TBHP gave worse results in terms of selectivity and conversion. One of the possible reasons is the hydrolysis of the epoxide.

A further investigation of the system included such factors as the catalyst loading, the reaction temperature, and the molar excess of TBHP. The results are summarized in Table 2. The most significant impact was exerted by the temperature and the amount of the catalyst, while the impact of the oxidant excess was low. A higher yield of styrene oxide was obtained at higher temperatures; however, the selectivity was lower due to the formation of a higher amount of by-products. The quantity of the catalyst had no impact on selectivity, and good yields could be obtained with a low amount of the catalyst by prolonging the reaction time. Similar observations were made by other authors [23].

In order to examine the reusability of Au/CNT, the epoxidation of styrene was conducted under optimized reaction conditions (80 °C, 4 h, twofold excess of TBHP). Au/CNT were separated from the post-reaction mixture by filtration, washed with ethyl acetate, and dried in a desiccator. The catalyst could be reused multiple times (at least five times) with a negligible loss of activity. The results are presented in Fig. 3. The small decrease in yield results from the loss of the catalyst during separation.

A comparison with the results from the literature [23, 29] shows that the obtained Au/CNT catalyst exhibited good activity and allowed to reach a better yield of styrene epoxide at a shorter reaction time. The undoubted advantage of the Au/CNT catalyst is the possibility of its easy separation and reuse.

3.2 The Reaction of Styrene Oxide with CO_2

Until now, a number of different catalysts have been suggested for the reaction of CO_2 with epoxides. The most often studied were quaternary ammonium salts and ionic liquids [4, 31–33]. In order to select the best system from amongst the ones proposed in the literature, we investigated the performance of three of the most promising homogeneous catalysts for the cycloaddition of CO_2 with styrene oxide (TBAB, [bmim]Br-$ZnBr_2$, [bmim]Cl-$ZnBr_2$). The reaction conditions and the amounts of the catalysts were based on average values given in appropriate literature sources. The results are presented in Table 3.

The data presented in Table 3 indicate that SC is formed with a high yield if the temperature of the reaction is above 100 °C for all the catalysts tested. This is likely due to the increased reactivity of epoxide. The other possible reason is an improved contact between TBAB and the reaction mixture, because the melting point of TBAB is above

Table 1 The effect of type of oxidant on the epoxidation of styrene using Au/CNT

Type of oxidant	Yield of styrene oxide (%)	Selectivity (%)		
		Styrene oxide	Benzaldehyde	*tert*-Butyl benzoate
Anhydrous TBHP	51	71	15	3
Aqueous TBHP	37	59	17	2
H_2O_2	4	30	55	–
UHP	Trace	–	–	–

Reaction conditions: styrene (5 mmol); oxidant (10 mmol); Au/CNT (10 mg); 80 °C; 500 rpm; 4 h. Yield and selectivity of styrene oxide were determined by GC analysis. Anhydrous TBHP—5.5 M in decane; aqueous TBHP—70 wt% in water; H_2O_2—30 wt% in water

Table 2 Epoxidation of styrene in the presence of Au/CNT, using anhydrous TBHP as an oxidant

Temperature (°C)	Amount of catalyst Au/CNT (mg)	Oxidant/styrene (molar ratio)	Yield of styrene oxide (%)	Selectivity (%)			TON[a]
				Styrene oxide	Benzaldehyde	*tert*-Butyl benzoate	
30	75	2	7	81	10	Trace	11
30	10	2	5	84	9	Trace	62
80	50	2	62	73	15	4	153
80	10	2	51	71	15	3	628
80	1	2	32	70	17	4	3939
80	10	1.5	44	74	13	3	542
80	10	1	33	66	18	5	406

Reaction conditions: styrene (5 mmol); 500 rpm; 4 h. Yield and selectivity of styrene oxide were determined by GC analysis

[a] Turnover number (TON) = moles of styrene oxide/moles of gold in the catalyst. TON values ranged from 11 to 3939 if calculated for entire gold present. However, TON values 10^5–10^7 times higher can be obtained if only Au atoms on the surface of nanoparticles were considered

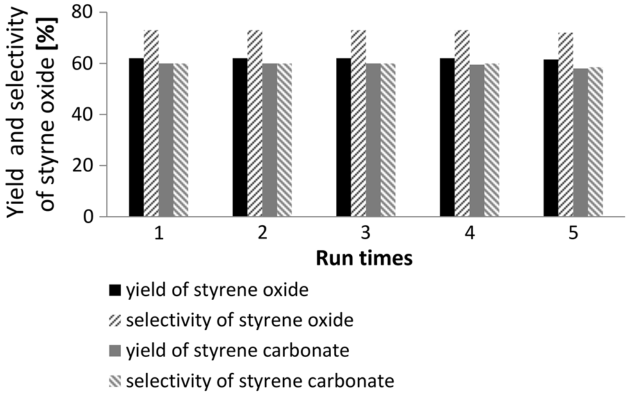


Fig. 3 Catalytic activity of the reused immobilized catalyst (Au/CNT) in epoxidation or one-pot cycloaddition

102–106 °C. In order to obtain a high yield of carbonate, the molar ratio of catalyst/styrene oxide should be 0.03. A further increase in TBAB quantity to 0.06 (relative to styrene oxide) does not have a significant impact. The best results were obtained for the [bmim]Br-ZnBr$_2$ system. The influence of the anion of the ionic liquid on the activity of a two-component catalyst system ([bmim]Cl/Br-ZnBr$_2$) was also checked. The yield of SC increased with the increase of the nucleophilicity of the anion. Interestingly, the rise of the CO$_2$ pressure from 1.2 to 2 MPa resulted in a decrease in the SC yield. Optimal reaction conditions for the [bmim]Br-ZnBr$_2$ system were as follows: 100 °C, 2 h, molar ratio of [bmim]Br/styrene oxide equal to 0.06, CO$_2$ at 1.2 MPa. The same conditions could be used in the case of TBAB; however, a higher temperature (110 °C) was more adequate. Based on the mechanism of the [bmim]Br-ZnBr$_2$ catalysis [31] the negative effect of CO$_2$ pressure can be attributed to the competition of CO$_2$ and the epoxide for coordination centers of [bmim]Br-ZnBr$_2$.

3.3 One-Pot Synthesis of Styrene Carbonate from Styrene

In order to determine how to couple the nanogold-catalyzed epoxidation with the [bmim]Br-ZnBr$_2$ catalytic systems for the reaction of styrene oxide with CO$_2$, we investigated the effect of each catalyst on the course of the styrene epoxidation (Table 4). Control reactions showed that if the epoxidation of styrene was carried out in the absence of a catalyst (entry 1), the yield of styrene epoxide was low (5 %). Interestingly, the presence of CNT tripled the yield of styrene oxide (entry 2). Au/CNT alone were active in the epoxidation of styrene (entry 3). Slightly lower activity in epoxidation was showed by [bmim]Br-ZnBr$_2$ (entry 4). If both catalysts were simultaneously used, no further improvement of styrene oxide yield was possible (entry 5). It indicates that Au/CNT play a dominant role during the epoxidation step. CO$_2$ exerted a negative effect on the selectivity of styrene epoxidation catalyzed by Au/CNT (entry 6). A similar phenomenon was also observed by other researchers [15]; however, it is not clearly explained in the available literature. A potential requirement for O$_2$ presence [34] as a radical initiator during epoxidation was excluded using Ar as an atmosphere (entry 7). As the conversion of styrene remained unchanged whereas the yield of epoxide decreased, it is likely that in the presence of CO$_2$ the epoxide reacts towards side products, such as linear polycarbonate [35] or other oligomers.

Further investigations of the catalysts' effect were focused on the cycloaddition of CO$_2$ to styrene oxide. The results are presented in Table 5. No reaction occurred without the use of [bmim]Br (entries 1–3). The best results were obtained with [bmim]Br and zinc bromide (93 % after 2 h). The presence of Au/CNT had no impact on the cycloaddition step (entries 6–7).

Table 3 Synthesis of SC in the presence of homogeneous catalyst from styrene oxide and CO_2

Type of catalyst	CO_2 pressure (MPa)	Temperature (°C)	Time (h)	Molar ratio of catalyst/styrene oxide (mol/mol)	Yield of SC (%)	Selectivity of SC (%)
TBAB	1.2	80	5	0.01	5	97
TBAB	1.2	110	2	0.01	34	97
TBAB	1.2	110	2	0.03	69	97
TBAB	1.2	110	2	0.06	72	97
TBAB	1.2	100	2	0.06	63	97
[bmim]Br-$ZnBr_2$	1.2	100	1	0.06	89	98
[bmim]Br-$ZnBr_2$	1.2	100	2	0.06	93	98
[bmim]Cl-$ZnBr_2$	1.2	100	1	0.06	78	96
[bmim]Br-$ZnBr_2$	2	100	1	0.06	66	98

Reaction conditions: styrene oxide (32 mmol); molar ratio of $ZnBr_2$/styrene oxide (1:357); 500 rpm. Yield and selectivity of SC were determined by GC analysis

Table 4 The effect of catalysts combinations on epoxidation step

Entry	Type of catalyst	Conversion of styrene (%)	Yield of styrene oxide (%)
1	–	9	5
2	CNT	17	14
3	Au/CNT	85	62
4	[bmim]Br-$ZnBr_2$	88	48
5	Au/CNT-[bmim]Br-$ZnBr_2$	87	61
6	Au/CNT + CO_2	88	40
7	Au/CNT + Ar	88	62

Reaction conditions: styrene (5 mmol); anhydrous TBHP (10 mmol); 80 °C; 4 h; 500 rpm; ratio of substrate/Au/CNT (100 mmol/g); ratio of substrate/CNT (500 mmol/g); molar ratio of [bmim]Br/$ZnBr_2$/substrate (22:1:357). Yield of styrene oxide and conversion of styrene were determined by GC analysis. Reaction was conducted in a round-bottom flask

Table 5 The effect of catalysts combinations on cycloaddition step

Entry	Type of catalyst	Conversion of styrene oxide (%)	Yield of SC (%)
1	–	0	0
2	CNT	0	0
3	$ZnBr_2$	0	0
4	[bmim]Br	70	68
5	[bmim]Br-$ZnBr_2$	95	93
6	Au/CNT-[bmim]Br-$ZnBr_2$	96	93
7	Au/CNT	0	0

Reaction conditions: styrene oxide (32 mmol); 100 °C; 1.2 MPa of CO_2; 2 h;, 500 rpm; ratio of substrate/Au/CNT (100 mmol/g); ratio of substrate/CNT (500 mmol/g); molar ratio of [bmim]Br/$ZnBr_2$/substrate (22:1:357). Yield of SC and conversion of styrene oxide were determined by GC analysis

As both catalytic systems could be used simultaneously, as long as CO_2 was not present during the epoxidation step, we finally attempted to adjust the operating conditions during the cycloaddition step to offset the potential effect of compounds remained in the reaction mixture after the first step. The results are showed in Table 6.

The decrease in the CO_2 pressure strongly increased the yield of SC. The impact was nearly 30 % on average comparing entries 1 and 4 with 2 and 3. The effect of temperature was lower and only a 5 % change of yield of SC could observed when it was raised from 100 to 120 °C. The yield of benzaldehyde remained practically unchanged

Table 6 One-pot synthesis of SC from styrene and CO_2 under different reaction conditions

Entry	CO_2 pressure for cycloaddition step (MPa)	Temperature for cycloaddition step (°C)	Yield (%)		Conversion of styrene (%)
			BA	SC	
1	1.2	120	9	60	100
2	2	120	10	33	99
3	2	100	8	27	100
4	1.2	100	12	56	100
5[a]	1.2	120	9	58	99

Reaction conditions: styrene (32 mmol); anhydrous TBHP (64 mmol); ratio of substrate:Au/CNT (100 mmol/g); molar ratio of [bmim]Br:$ZnBr_2$:substrate (22:1:357); 500 rpm

[a] Au/CNT was separated after epoxidation. The epoxidation step was carried out in the absence of CO_2 at 80 °C, for 4 h and the cycloaddition step for 2 h. *SC* styrene carbonate, *BA* benzaldehyde; Conversion of styrene and yields were determined by GC analysis

between those experiments. As the conversion of styrene was complete, as well, no epoxide was detected in the reaction mixture; the lower yield of SC at higher pressure could be attributed to the formation of side products. Removing of Au/CNT from the reaction mixture after epoxidation had no significant effect. The reusability of Au/CNT was investigated in the one-pot synthesis of SC from styrene and no loss of activity was observed despite harsher conditions of the second step. The results are presented in Fig. 3.

4 Conclusions

The synthesis of SC can be carried out as a one-pot two-step process in the presence of the Au/CNT-[bmim]Br-$ZnBr_2$ catalyst under different conditions of temperature and pressure suitable for each step. Supported gold nanoparticles of 6 nm in size were applied as the catalyst for the styrene epoxidation step at 80 °C. This catalyst could be easily separated by filtration and reused at least five times without any evident reduction of its activity. The reaction of CO_2 with the epoxide should be carried out at a higher temperature (100–120 °C) under a CO_2 pressure of 1.2 MPa. [bmim]Br-$ZnBr_2$ was found to be the most suitable catalyst for that step. The separation of the epoxide or Au/CNT from the reaction mixture was not necessary. The overall yield of the one-pot multistep synthesis of 60 % was comparable to the product of the yields (62 × 93 %) of epoxidation and cycloaddition carried out separately.

The convergence of the yields was not affected by the difference in reaction conditions, indicating that the activity of [bmim]Br-$ZnBr_2$ was not significantly affected by the formation of by-products during epoxidation. It also implies that further research should be primarily focused on the improvement of the epoxidation step.

The advantages of the proposed system comprise: a short reaction time, a high yield, and mild conditions of the running process. Xiang et al. reported a comparatively high SC yield (51 %) using the Au/R201 catalytic system [15]; however, we were able to conduct the second step under lower both temperature and CO_2 pressure conditions. The process could be further improved by using a heterogeneous catalyst at the second step, as well.

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