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A direct synthesis of styrene carbonate from styrene with the Au/SiO_2–$ZnBr_2$/Bu_4NBr catalyst system

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Abstract

This paper reports a direct route for the preparation of cyclic styrene carbonate from styrene, which avoids the preliminary synthesis and isolation of styrene oxide. A catalyst system consisting of Au/SiO_2, zinc bromide, and tetrabutylammonium bromide (Bu_4NBr) has been applied to the one-pot synthesis of styrene carbonate from styrene, organic peroxide, and CO_2. Au/SiO_2 is active for the epoxidation of styrene, and zinc bromide and Bu_4NBr cooperatively catalyze the subsequent CO_2 cycloaddition to epoxide. The influence of various reaction parameters, such as CO_2 pressure, reaction temperature, reaction time, catalyst amount, ratio of oxidant to styrene, and oxidant type, has been investigated in detail.

Keywords: Styrene carbonate; One-pot synthesis; Epoxidation; Carbon dioxide; Supported gold catalyst; Zinc bromide; Ammonium salt

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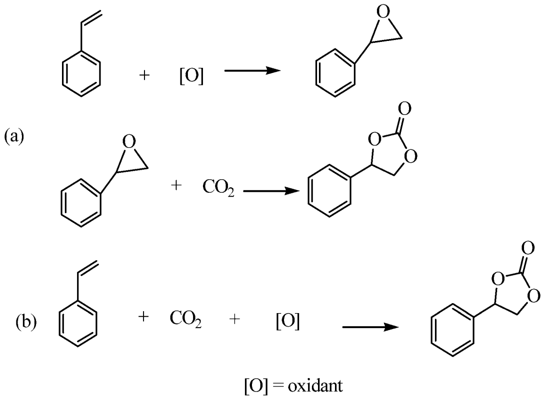
1. Introduction

Chemical fixation of carbon dioxide (CO_2) has received much attention recently for its use in the preservation of the environment and because CO_2 is a cheap and abundant raw material [1,2]. The formation of cyclic carbonates is an effective CO_2 chemical fixation route [3–6]. Cyclic carbonates can be used extensively in various fields [7,8] and are currently manufactured from epoxides produced by the epoxidation of olefins (Scheme 1). Thus one-pot synthesis of cyclic carbonates from olefins and CO_2 should be more interesting and economical, because the reaction uses readily available and low-priced chemicals olefins, and the preliminary synthesis of epoxides is avoided.

Only a few studies of the direct synthesis of cyclic carbonates from olefins have been reported so far. Aresta et al. carried out one-pot synthesis of styrene carbonate (SC) from styrene, CO_2, and molecular oxygen with homogeneous rhodium complex catalysts [9,10]. They also used various metal oxide catalysts [11], and the highest yield was obtained with niobium oxide. The SC yield obtained was low



Scheme 1. Two-step (a) and one-step (b) synthesis of styrene carbonate from styrene.

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because of low SC selectivity due to the formation of byproducts such as benzaldehyde and benzoic acid [10,11]. Srivastava et al. [12] used titanosilicate catalysts for the synthesis of cyclic carbonate in a single reactor; initially they conducted the epoxidation of olefin with H_2O_2 or *tert*-butyl hydroperoxide (TBHP) at 60 °C and then added CO_2 and a cocatalyst with an organic base at a temperature of 120 °C. The yield was not high, and their catalyst system required the toxic organic solvent CH_2Cl_2 and a long reaction time. We have also reported the one-pot synthesis of SC from styrene with TBHP as an oxidant in the presence of quarternary ammonium halides or imidazolium salts [13,14]. The most effective catalyst was tetrabutylammonium bromide (Bu_4NBr) [14]. Although the SC yield was higher than those reported previously, a long reaction time was required and the homogeneous nature of Bu_4NBr was a drawback in separation and recycling. Thus, effective catalysts are still being sought for the one-pot synthesis of cyclic carbonates from olefins and CO_2.

Recently we have found that the catalytic performance of Bu_4NBr in the coupling reaction of CO_2 and styrene oxide is greatly enhanced by the presence of zinc bromide ($ZnBr_2$) [15]. Styrene oxide is quantitatively transformed to SC in a very short reaction time of 30 min at a low reaction temperature of 80 °C. If this $ZnBr_2/Bu_4NBr$ were to be combined with another active species effective for epoxidation, the resulting system would be a novel catalyst for the one-pot synthesis of cyclic carbonates. Gold catalysts have successfully been applied to many reactions, such as low-temperature CO oxidation [16,17], gas-phase epoxidation of propylene [18–20], water–gas-shift reaction [21,22], and hydrogenation of unsaturated hydrocarbons [23,24]. In addition, supported Au catalysts are also effective for liquid-phase epoxidation [25–32]. Thus, it is interesting to apply supported Au catalysts together with the catalyst system of $ZnBr_2/Bu_4NBr$ for the one-pot synthesis of cyclic carbonates.

In the present work, a catalyst system consisting of Au/SiO_2, $ZnBr_2$, and Bu_4NBr is applied to the one-pot synthesis of SC from styrene and CO_2. The effects of reaction parameters, such as Au loading, CO_2 pressure, temperature, reaction time, catalyst amount, type of oxidant, and ammonium salts, have been investigated in detail to achieve high SC yields under optimal conditions. Good SC yields have been obtained under mild reaction conditions (at 80 °C for 4 h with 1 MPa CO_2).

2. Experimental

2.1. Materials

Tetrachloroauric acid ($HAuCl_4 \cdot 4H_2O$), 25 wt% aqueous ammonia solution, sodium tetrahydroborate ($NaBH_4$), zinc bromide, tetrabutylammonium bromide (Bu_4NBr), tetrabutylammonium chloride (Bu_4NCl), tetrabutylammonium iodide (Bu_4NI), styrene, aqueous *tert*-butyl hydroperoxide (TBHP) (70 wt% in water), cumene hydroperoxide (CHP) (80 wt% in cumene), and ethyl acetate were purchased from Wako. Silica gel (Davisil grade 646) and anhydrous *tert*-butyl hydroperoxide (5.0–6.0 M solution in decane) were supplied by Aldrich.

2.2. Preparation and characterization of Au/SiO_2 catalysts

Several silica-supported gold catalysts with different gold loadings were prepared according to methods described in the literature [33]. Silica was suspended in distilled water with vigorous stirring, and the required amount of an aqueous solution of tetrachloroauric acid (10^{-2} mol dm^{-3}) was added dropwise to the suspension. During the addition, the pH value of the suspension was adjusted to 8.5 with the ammonia solution. Then, the suspension was further aged at room temperature for 2 h with stirring while the pH was kept constant with the addition of a diluted ammonia solution. A solution of $NaBH_4$ (10^{-2} mol dm^{-3}) was prepared in ice water, and the appropriate amount of the solution was added to the suspension with stirring. The total amount of $NaBH_4$ added was equivalent to that of tetrachloroauric acid. On the addition of the $NaBH_4$ solution, the colour of the mixture turned to dark purple from yellow, indicating that the reduction of the auric ion had occurred. A purple colour is characteristic of metallic small gold particles [34]. After aging for 2 h, solids in the resulting suspension were filtered off, washed thoroughly with distilled water, and dried in air at 110 °C overnight. The filtrate was colourless, suggesting that all of the gold species had been loaded onto the silica support.

For comparison with the $NaBH_4$ reduction, 1 wt% Au/SiO_2 samples were also prepared by reduction with flowing H_2 at 400 °C for 2 h after the loading of Au precursors in the same manner as described above.

All of the supported gold catalysts we prepared were characterized by X-ray diffraction (XRD) and UV–vis spectroscopy. XRD patterns of the catalysts were measured with a JEOL JDX-8020 powder diffractometer operating at 30 kV and 30 mA and Cu-K_α monochromatized radiation ($\lambda = 0.154178$ nm). We evaluated the size of supported gold crystallites, D, from the full peak width at half-maximum by using the Scherrer equation [35], $D = 0.9\lambda/(\beta \cos\theta)$, where λ is the wavelength of the X-ray radiation, and β is the peak width at half-maximum. A correction for the instrumental broadening was made with silicon powder. Diffuse reflectance UV–vis spectra were recorded with a Shimadzu UV-3100 PC spectrophotometer.

2.3. Catalytic reactions

One-pot synthesis of SC was conducted in a 50-ml stainless-steel autoclave. In a typical run, the reactor was charged with Au/SiO_2 (0.1 g), $ZnBr_2$ (0.44 mmol), Bu_4NBr (0.88 mmol), styrene (17.3 mmol), and TBHP (25.4 mmol)

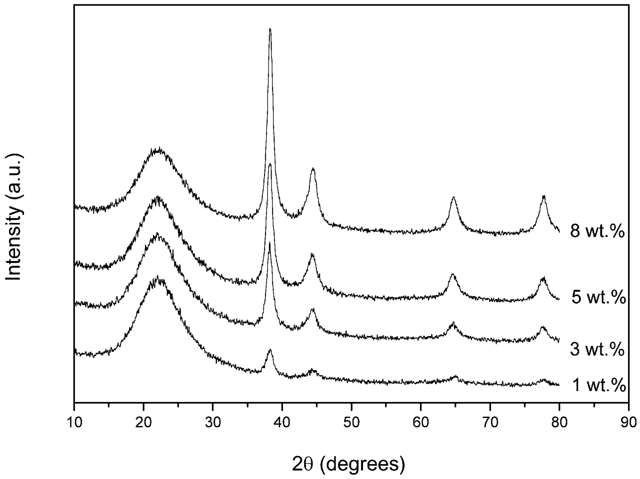


Fig. 1. XRD patterns of supported Au/SiO_2 catalysts with different Au loadings of (a) 1 wt%, (b) 3 wt%, (c) 5 wt%, and (d) 8 wt%.

in decane and heated to a desired temperature. Then CO_2 was fed into the reactor with an HPLC pump equipped with a cooler. The pressure inside of the reactor was monitored and controlled by a back-pressure regulator. After the reaction, the reactor was cooled to room temperature and depressurized to atmospheric pressure. Then the Au/SiO_2 catalyst was filtered off from the reaction mixture. After the filtration, the organic phase was diluted to 25 ml with ethyl acetate and analyzed with a gas chromatograph (Shimadzu 390B) with a capillary column (GL Science TC-17). The quantities of styrene substrate consumed and products formed were determined from the results obtained from authentic standards. The structure of the products was further confirmed with a mass spectrometer (Shimadzu QP5050A). In some runs, either an aqueous solution of TBHP or a cumene solution of CHP was used instead of the TBHP decane solution.

3. Results and discussion

3.1. Catalyst characterization

XRD patterns of Au/SiO_2 catalysts with various metal loadings are presented in Fig. 1. The diffraction peaks ascribed to metallic gold [23] are observed along with a broad one for SiO_2 at $2\theta = 22°$ and tend to sharpen with increasing gold loading. The average sizes of metallic gold crystallites were determined from the most intense diffraction peaks at $2\theta = 38.1°$, which are 8.0, 9.6, 10.0, and 11.6 nm for 1, 3, 5, and 8 wt% Au/SiO_2 catalysts, respectively. The size of gold crystallites determined increases with the gold loading, and this is contrary to the trend observed for Au samples dispersed on a structured support of MCM-41 [36].

Because of their plasmon vibration arising from the collective oscillations of the free conduction band electrons, crystallites of metallic gold have a characteristic absorption in the visible region of the electromagnetic spectrum at 500–600 nm [17,37]. The position and the width of this absorption depend on the crystallite size, and larger gold crystallites show a broader band at a higher wavelength [38,39]. As a source of complementary information on the chemical state and particle size of gold particles, diffuse reflectance UV–vis spectra of the Au/SiO_2 samples were measured. Fig. 2 gives the UV–vis spectra obtained. Bands observed around 510 nm indicate the existence of metallic gold over the catalysts. With increasing gold loading, the absorption band red-shifts slightly and the bandwidth increases. These results show that the size of gold particles increases with the gold loading, which is consistent with the results of XRD (Fig. 1).

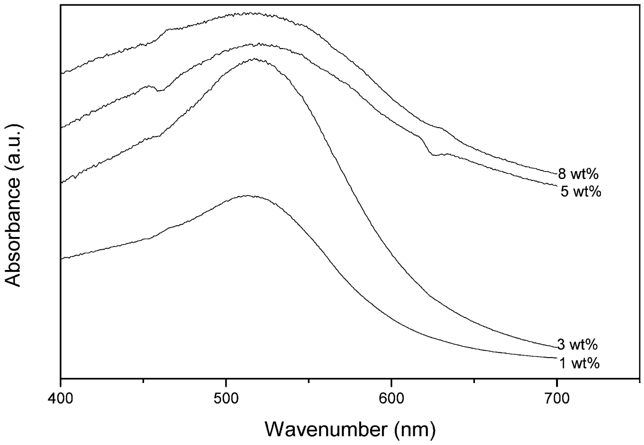


Fig. 2. UV–vis spectra of supported Au/SiO_2 catalysts with different Au loadings of (a) 1 wt%, (b) 3 wt%, (c) 5 wt%, and (d) 8 wt%.

3.2. Catalytic activity

Effects of various catalyst preparation and reaction parameters on the one-pot synthesis of SC have been examined in detail to maximize the SC yield. Under the present reaction conditions, SC and styrene epoxide (SO) were formed along with benzaldehyde (BA) and other by-products, which were oligomers of the substrate and those of SO and/or SC. The total styrene conversion and the product distribution depend strongly on the conditions used, as described in the following. The overall conversion of styrene was calculated from moles of styrene consumed against the initial moles of styrene used. The yield and selectivity of a product were determined from moles of the product formed against the initial moles of styrene used and against the moles of styrene consumed, respectively:

$$\text{yield (\%)} = \text{total conversion (\%)} \times \text{selectivity (\%)}.$$

3.2.1. Influence of catalyst preparation conditions

Table 1 shows the influence of Au loading on the one-pot synthesis of SC. It can be seen that the SC yield increases slightly with the Au loading; however, the differences observed in the yield and in the total conversion are small under the conditions used. These results are discussed in Section 3.3.

Table 1
Influence of Au loading on the activity of Au/SiO_2 catalyst in the one-pot synthesis of SC[a]

Entry	Au loading (wt%)	Conversion (%)	Yield (%)		
			SC	SO	BA
1	1	83	31	5	22
2	3	81	33	7	16
3	5	88	35	4	16
4	8	81	37	4	20

[a] Reaction conditions: Au/SiO_2, 0.1 g; $ZnBr_2$, 0.44 mmol; Bu_4NBr, 0.88 mmol; styrene, 17.3 mmol; TBHP (in decane), 25.4 mmol; CO_2 pressure, 8 MPa; 80 °C; 4 h.

Table 2 shows the influence of the preparation conditions of 1 and 5 wt% Au/SiO_2 catalysts on the one-pot synthesis of SC. With an unreduced 1 wt% Au/SiO_2 sample, a low SC yield of 21% is obtained (entry 1). When this sample is reduced with H_2 or $NaBH_4$, the SC yield increases to more than 30% (entries 2 and 3). However, when the reduced catalyst is used after calcination at 400 °C, the SC yield decreases to a value similar to that obtained with the unreduced sample (entry 4). A decrease in the SC yield with calcination is also observed with a 5 wt% Au/SiO_2 sample (entries 5 and 6). XRD measurements showed that the size of gold crystallites increased with calcinations, but this change was not significant, suggesting that the decrease in the activity is ascribable to the change in the state of gold crystallites. Thus, both the metallic and cationic gold species are active, but the former is more active than the latter.

3.2.2. *Influence of CO_2 pressure, quaternary ammonium salts, and oxidants*

Fig. 3 demonstrates the influence of CO_2 pressure on the styrene conversion and the yields of SC, SO, and BA. At atmospheric pressure (0.1 MPa), the styrene conversion is 83% and the yields of SC, SO, and BA are 21, 6, and 16%, respectively. When the pressure is raised to 1 MPa, the conversion and the SC yield increase to 89 and 35%, respectively. In the region between 1 and 12 MPa, the CO_2 pressure does not significantly affect the conversion and the yields; however, both the conversion and the SC yield decrease at 15 MPa. According to visual observations of the reaction mixture [14], it includes three phases of CO_2-rich gas, liquid (styrene, TBHP or CHP, $ZnBr_2$/Bu_4NBr), and solid (Au/SiO_2) at lower pressures, whereas it exists in two phases (fluid phase and catalyst solid phase) at a high pressure of 15 MPa. This phase change would cause an increase in the volume where the reaction proceeds, and, hence, the concentration of the substrate would be low at this elevated pressure, resulting in lowered styrene conversion and SC yield. It was also found that much oligomer was produced at such a high pressure. In addition to the change in the reaction volume, differences in the properties between the liquid and CO_2 gas phases where the reacting species are dissolved should also be significant in determining the reaction rates. The results in Fig. 3 indicate that high CO_2 pressures are not necessary for the synthesis of SC, and so the influence of other reaction conditions has been examined at a CO_2 pressure of 1 MPa.

Table 2
Influence of preparation conditions on the activity of Au/SiO_2 catalysts in the one-pot synthesis of SC[a]

Entry	Au loading (wt%)	Preparation conditions	Conversion (%)	Yield (%)		
				SC	SO	BA
1	1	No reduction	79	21	4	14
2	1	H_2 reduction	73	35	7	23
3	1	$NaBH_4$ reduction	83	31	5	22
4	1	$NaBH_4$ reduction and calcination[b]	78	26	5	14
5	5	$NaBH_4$ reduction	88	35	4	16
6	5	$NaBH_4$ reduction and calcination[b]	84	28	4	25

[a] Reaction conditions: Au/SiO_2, 0.1 g; $ZnBr_2$, 0.44 mmol; Bu_4NBr, 0.88 mmol; styrene, 17.3 mmol; TBHP (in decane), 25.4 mmol; CO_2 pressure, 8 MPa; 80 °C; 4 h.

[b] Calcination was carried out at 400 °C for 2 h in air.

Quaternary ammonium salts with different counter-anions have been examined. Table 3 shows that bromide counter-ion is better than chloride and iodide anions. In the cycloaddition of CO_2 (the second step of SC synthesis), the ring opening of epoxide occurs by nucleophilic attack of the halide anion to a carbon of the epoxide group [40]. The nucleophilic tendency decreases in the order $I^- > Br^- > Cl^-$, but the yield of SC observed is the highest with Bu_4NBr. In

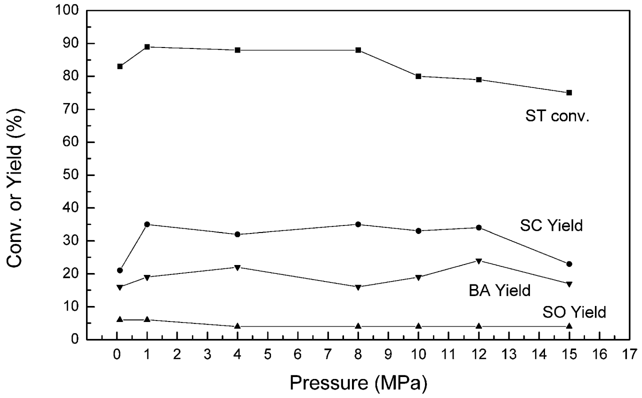


Fig. 3. Effect of CO_2 pressure on the conversion and product yields. Styrene, 17.3 mmol; anhydrous TBHP, 25.4 mmol; 5 wt% Au/SiO_2, 0.1 g; $ZnBr_2$, 0.44 mmol; Bu_4NBr, 0.88 mmol; 80 °C; 4 h.

Table 3
Influence of quaternary ammonium salts on the one-pot synthesis of SC[a]

Entry	Ammonium salt	Conversion (%)	Yield (%)		
			SC	SO	BA
1	Bu_4NCl	82	31	8	13
2	Bu_4NBr	89	35	6	19
3	Bu_4NI	71	30	4	15

[a] Reaction conditions: 5 wt% Au/SiO_2, 0.1 g; $ZnBr_2$, 0.44 mmol; Bu_4NX (X = Cl, Br, I), 0.88 mmol; styrene, 17.3 mmol; TBHP (in decane), 25.4 mmol; CO_2 pressure, 1 MPa; 80 °C; 4 h.

the case of Bu_4NI, TBHP was consumed for its oxidation in addition to the desired epoxidation reaction, thus leading to the decrease in SC and SO yields as observed. When Bu_4NI was added into the mixture of TBHP and styrene, the color of the mixture rapidly changed to dark orange, indicative of the formation of iodine by oxidation with TBHP. Thus Bu_4NBr is more suitable than the other two quaternary ammonium salts examined.

The influence of the kinds of oxidants and the molar ratio of oxidant to styrene is shown in Table 4. When the TBHP/styrene ratio is raised from 1 to 1.5, the styrene conversion and the SC yield increase from 82 to 89% and from 24 to 35%, respectively (entries 1, 2); the selectivity of SC increases from 29 to 39%. However, a further increase in the ratio does not improve the styrene conversion and the SC yield (entry 3). In the case of CHP as an oxidant, the yield of SC is also markedly enhanced with an increase in the CHP/styrene ratio from 1 to 1.5, but the yield at a ratio of 2 is not so different from that at 1.5 (entries 4–6). Thus, the optimal molar ratio of oxidant to styrene is 1.5 for both TBHP and CHP.

Table 4 also indicates that CHP is more effective for the synthesis of SC than is TBHP. Previously CHP had been found to show better performance than anhydrous TBHP in the epoxidation of cyclohexene catalyzed by a mesoporous titanosilicate catalyst [41]. When aqueous TBHP is used instead of anhydrous TBHP, the SC yield decreases from 35 to 21% (entry 7 of Table 4). Thus the choice of oxidant is very important, and CHP is a better oxidant for the one-pot synthesis of SC.

The water contained in the oxidant is detrimental to the carbonate synthesis. An important factor is the hydrolysis of epoxide to phenyl glycol [42], which would decrease the quantity of the starting material for the second step of SC synthesis. Indeed, the formation of a small amount of phenyl glycol was observed after the reaction when aqueous TBHP was used, whereas it was not detected after the reaction when anhydrous TBHP was used. The miscibility of reacting species in organic and water phases would also be important. It was observed that $ZnBr_2$ and TBAB were soluble in a mixture of TBHP and styrene. For further discussion, the phase behavior and solubility should be measured in detail.

Table 4
Influence of the kinds of oxidants and the oxidant/styrene molar ratio on the one-pot synthesis of SC[a]

Entry	Oxidant	Oxidant/styrene molar ratio	Conversion (%)	Yield (%)		
				SC	SO	BA
1	Anhydrous TBHP	1	82	24	3	16
2	Anhydrous TBHP	1.5	89	35	6	19
3	Anhydrous TBHP	2	90	36	8	21
4	CHP	1	75	24	2	10
5	CHP	1.5	76	42	1	19
6	CHP	2	79	45	3	21
7	Aqueous TBHP	1.5	85	21	6	17

[a] Reaction conditions: 5 wt% Au/SiO_2, 0.1 g; $ZnBr_2$, 0.44 mmol; Bu_4NBr, 0.88 mmol; styrene, 17.3 mmol; CO_2 pressure, 1 MPa; 80 °C; 4 h.

3.2.3. *Influence of catalyst amount, temperature, and time*

Table 5 shows the effect of catalyst amount on the formation of SC. The carbonate yield increases when the amount of Au/SiO_2 is increased from 0.05 to 0.1 g (entries 1, 2). When it is further increased, however, the SC yield does not increase (entry 4). It is also shown that even if the amounts of $ZnBr_2$ and Bu_4NBr are doubled while the amount of Au/SiO_2 is kept at 0.1 g, the SC yield is not improved (entry 5). As described below, Au/SiO_2 catalyzes the epoxidation of styrene only, and it is the rate-determining step of the one-pot synthesis of SC. Thus the yield of SC is not improved when the amounts of $ZnBr_2$ and Bu_4NBr are increased under the conditions used.

The reusability of Au/SiO_2 catalyst was examined. After a reaction run, the solid catalyst was removed from the reaction system by filtration, washed with acetone, dried at room temperature, and then subjected to the next catalytic run, in which fresh $ZnBr_2$ and Bu_4NBr were added. The results with the used catalyst are similar to those obtained with fresh catalyst (entry 3), indicating that Au/SiO_2 is recyclable without any loss of activity.

The influence of reaction temperature on the styrene conversion and the product distribution is given in Table 6; for these the reaction temperature was varied from 60 °C to 90 °C. As expected, the styrene conversion increases with

Table 5
Influence of the amounts of catalysts on the one-pot synthesis of SC[a]

Entry	Au/SiO_2[b] (g)	$ZnBr_2$ (mmol)	Conversion (%)	Yield (%)		
				SC	SO	BA
1	0.05	0.44	70	34	3	17
2	0.1	0.44	76	42	1	19
3[c]	0.1	0.44	78	41	2	17
4	0.2	0.44	75	42	1	15
5	0.1	0.88	74	42	5	16

[a] Reaction conditions: $Bu_4NBr/ZnBr_2 = 2$ (molar ratio); styrene, 17.3 mmol; CHP, 25.4 mmol; CO_2 pressure, 1 MPa; 80 °C; 4 h.

[b] Au loading: 5 wt%.

[c] With the used Au/SiO_2 and fresh $ZnBr_2$ and Bu_4NBr.

Table 6
Influence of reaction temperature and time on the one-pot synthesis of SC[a]

Entry	Temperature (°C)	Time (h)	Conversion (%)	Yield (%)		
				SC	SO	BA
1	60	4	54	18	2	9
2	70	4	58	27	2	10
3	80	4	76	42	1	19
4	90	4	77	40	3	15
5	80	1	53	18	3	8
6	80	3	66	40	3	13
7	80	6	75	43	2	15

[a] Reaction conditions: 5 wt% Au/SiO_2, 0.1 g; $ZnBr_2$, 0.44 mmol; Bu_4NBr, 0.88 mmol; styrene, 17.3 mmol; CHP, 25.4 mmol; CO_2 pressure, 1 MPa.

temperature. The SC yield also increases with temperature, reaching a maximum value at 80 °C. Further increase in the reaction temperature to 90 °C causes a slight decrease in the SC yield. In contrast, the yield of SO increases a little, probably because of the decomposition of SC to SO [43,44]. Thus, a relatively low temperature of 80 °C is sufficient for the one-pot synthesis of SC.

Table 6 indicates that the styrene conversion and the SC yield are 53 and 18%, respectively, for 1 h at 80 °C (entry 5), which increase to 66 and 40% for a longer time of 3 h (entry 6). However, a further increase of the reaction time to 6 h does not increase the conversion and the yield as much (entry 7), probably because of complete decomposition of the oxidant. Table 6 also shows that the yield of BA is small, but it increases with a reaction time similar to that of SC. It is reported in the literature that the epoxidation of olefin proceeds in parallel with the formation of benzaldehyde through the cleavage of the C=C bond [45]. Moreover, as described in the next section, the cycloaddition of CO_2 to SO proceeds much faster than the epoxidation, and, hence, the yields of SC and BA should increase similarly with time.

3.3. Reaction processes considerations

In the above sections, the influence of catalyst preparation and reaction variables on the one-pot synthesis of SC has been examined in detail to find optimum conditions. Although the present catalyst system is a little complex compared with our previous one, with Bu_4NBr alone as catalyst [14], the improved yield of the desired product of SC can be achieved in a shorter reaction time of 4 h and at a mild temperature of 80 °C.

Table 7
Results of epoxidation of styrene (ST) and cycloaddition of CO_2 to styrene oxide (SO) using different combinations of catalysts[a]

Entry	Au/SiO_2	Bu_4NBr	$ZnBr_2$	Substrate[b]	Conversion (%)	Yield (%) SC	SO	BA
1	○			ST	71	0	40	15
2	○	○	○	ST	73	0	41	17
3[c]	○			ST	67	0	42	11
4[d]	○			ST	72	0	35	9
5	○			SO	0	0	–	–
6	○	○	○	SO	100	100	–	–
7[e]		○		SO	28	28	–	–
8[e]			○	SO	0	0	–	–
9[e]		○	○	SO	100	100	–	–

[a] Reaction conditions: 5 wt% Au/SiO_2, 0.1 g; $ZnBr_2$, 0.44 mmol; Bu_4NBr, 0.88 mmol; styrene (ST) and SO, 17.3 mmol; TBHP (in decane), 25.4 mmol; CO_2 pressure, 8 MPa; 80 °C; 4 h. The catalysts marked with ○ were used.

[b] ST and SO represent styrene and styrene oxide, respectively.

[c] CHP was used as the oxidant instead of TBHP.

[d] 1 wt% Au/SiO_2 (0.1 g) was used.

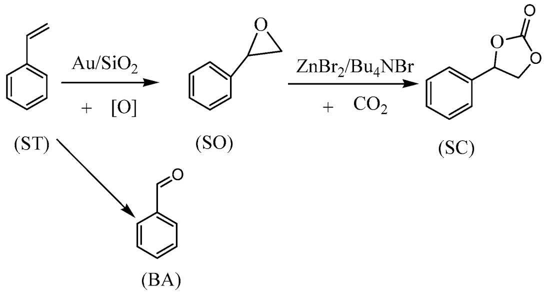
[e] Reaction time was 1 h.

Table 8
Influence of CO_2 pressure on epoxidation of styrene[a]

Entry	Pressure (MPa)	Conversion (%)	Yield (%) SO	BA
1	0[b]	67	32	4
2	8	80	30	4
3	15	55	18	2

[a] Reaction conditions: 8 wt% Au/SiO_2, 0.1 g; styrene, 17.3 mmol; TBHP (in decane) 25.4 mmol; 80 °C; 4 h. SO: styrene oxide; BA: benzaldehyde.

[b] Under ambient atmosphere.



Scheme 2. Reaction pathways for the one-pot synthesis of SC from ST.

To obtain more information on the roles of catalyst components, epoxidation of styrene (first step) and CO_2 cycloaddition to styrene oxide (second step) were conducted separately (Table 7). It is shown that Au/SiO_2 is active for the epoxidation, and $ZnBr_2$ and Bu_4NBr have no effect on this reaction (entries 1, 2). When CHP is used instead of TBHP, the conversion decreases slightly and the SO yield does not change; but the BA yield decreases (entry 3), and so the selectivity of SO increases from 56 to 63%. The gold loading has a marginal effect on the SO yield (entry 4). On the other hand, Au/SiO_2 has no activity for the CO_2 cycloaddition, and both $ZnBr_2$ and Bu_4NBr are required for this addition to proceed smoothly (entries 5–8), although $ZnBr_2$ has no activity for the reaction. It is strongly suggested that Lewis acid ($ZnBr_2$) and Lewis base (Bu_4NBr) work together to open the epoxy ring, as proposed in the literature [46–50]. In addition, the influence of CO_2 pressure on the epoxidation of styrene was examined in the presence of an Au/SiO_2 catalyst alone. The results obtained are given in Table 8, indicating that the conversion at 8 MPa is slightly larger than that in the absence of CO_2, and the conversion decreases significantly at a higher pressure of 15 MPa, similar to the trend in the one-pot synthesis of SC, as shown in Fig. 3. The reaction pathways are illustrated in Scheme 2. First styrene oxide and benzaldehyde are formed in parallel, and then the styrene oxide formed is converted to SC. It can be seen from a comparison of the styrene and styrene oxide conversion levels and of the effects of CO_2 pressure (Fig. 3, Table 8), the CO_2 cycloaddition proceeds much more rapidly than the epoxidation. All of the styrene oxide used can be consumed in a reaction time of 1 h. These results demonstrate that the epoxidation reaction (the first step) is the rate-determining step in the one-pot synthesis of SC.

A comparison of the results with 5 wt% and 1 wt% Au/SiO_2 catalysts given in Table 7 (entries 1, 4) shows that the yield of SO is slightly larger with the former than with the latter, although the conversion levels are almost the same; the quantity of by-products, including BA, is smaller with the former than with the latter. The influence of Au loading was studied with Au/TiO_2 for epoxidation of styrene [31]; the total conversion and the SO selectivity did not change much with the Au loading, except for at very small loading [31].

As illustrated in Scheme 2, the epoxidation of styrene and the CO_2 addition to the epoxide are catalyzed by Au/SiO_2 and $ZnBr_2/Bu_4NBr$, respectively. There are three phases in the reaction mixture below 15 MPa, which are the Au/SiO_2 solid phase; the liquid phase containing styrene, the oxidant, and $ZnBr_2/Bu_4NBr$; and the CO_2-rich gas phase. Some CO_2 can dissolve in the liquid phase. The epoxidation reaction occurs at the interface between the solid and the liquid phase. Then the styrene epoxide formed reacts with CO_2 dissolved in the liquid phase. This reaction could occur partly at the interface between the liquid and the gas phases. When the pressure was elevated to 15 MPa or above, the liquid and gas phases change into a homogeneous fluid phase, and so the cycloaddition of CO_2 took place in the fluid phase at the elevated pressures.

The epoxidation of styrene with 5 wt% Au/SiO_2 in the absence of CO_2 gives SO with a yield of 40% (Table 7). This value is close to the total yield of SC in the one-pot synthesis with the same gold catalyst (Table 1). Similar results are also obtained with 1 wt% Au/SiO_2 catalyst. These results suggest that the efficiency of the SC one-pot synthesis would be determined mostly by the catalytic performance of the gold catalyst. Hence, if more active and selective catalysts for the epoxidation reaction were to be explored, more effective catalyst systems for the one-pot synthesis would be realized.

4. Conclusions

SC synthesis by the direct oxidative carboxylation of styrene, which couples the epoxidation of styrene and subsequent CO_2 cycloaddition, is preferable because starting materials are easily available and cheap, preliminary synthesis and separation of epoxide are avoided, and the work-up procedures are simple. The Au/SiO_2–$ZnBr_2/Bu_4NBr$ catalyst system is effective for the one-pot synthesis of SC, and a good yield of SC (42%) can be obtained under mild reaction conditions (80 °C, 1 MPa CO_2) in a short reaction time of 4 h. The Au/SiO_2 is active for the first step (epoxidation), and $ZnBr_2$ and Bu_4NBr cooperatively catalyze the subsequent CO_2 cycloaddition to epoxide (second step). It is shown that both the metallic and cationic gold species are active for the epoxidation reaction, and the former is more active than the latter. In addition, cumene hydroperoxide is better as an oxidant than anhydrous/aqueous *tert*-butyl hydroperoxide, and Bu_4NBr is more effective than Bu_4NCl or Bu_4NI. Carbon dioxide pressure has no significant effect on the yield of SC under the reaction conditions used. It should be noted that our reaction system does not need an organic solvent, a high reaction temperature, a long reaction time, or high CO_2 pressure. Furthermore, the two sequential steps (epoxidation and CO_2 cycloaddition) can be conducted in a single reactor under the same reaction conditions. Thus, the one-pot synthesis of SC studied in this work has these advantages, and it would make a simple carbonate synthesis process with industrial potential, from environmental and economic points of view.

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