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A novel route for synthesis of styrene carbonate using styrene and CO_2 as substrates over basic resin R201 supported Au catalyst

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ABSTRACT

This paper introduces a novel and convenient synthetic route for styrene carbonate from styrene and CO_2 over nano-gold catalyst supported R201 resin. The simple synthesis route avoids the preliminary synthesis and isolation of intermediate styrene oxide, which couples the two sequential reactions of epoxidation of styrene and cycloaddition of CO_2 to epoxide into one pot. With Au/R201 catalyst, synthetic process has great influence on the carbonate yield. By multistep protocol the carbonate yield reaches 51% with anhydrous TBHP as oxidant. In the synthesis, CO_2 acts as both a reagent and a solvent and the use of additional organic solvents can be avoided. The pronounced cooperative effect of quaternary ammonium cation of the support and nano-gold particle results in its good performance in the one-pot synthesis of styrene carbonate directly from styrene. The simple one-component heterogeneous catalyst Au/R201 was readily separated after the reaction and reused without catalyst leaching, which is of great interest in industrial potential.

1. Introduction

Recently carbon dioxide fixation has received much attention from the viewpoint of preservation of the earth, and the reaction of carbon dioxide with epoxides to produce cyclic carbonates has been of great interest as a useful method for the fixation of CO_2 by chemical processes [1,2]. In addition, cyclic carbonates have found extensive uses as excellent aprotic polar solvents, electrolytes in secondary batteries, precursors for polycarbonates and other polymeric materials, and intermediates in the production of pharmaceuticals and fine chemicals [3,4].

Although the production of cyclic carbonate from epoxide and CO_2 is attractive from the viewpoint of Green Chemistry [5] and chemical fixation of CO_2 [6–10], there are some shortcomings in that commercial epoxides, as raw materials, are more expensive and toxic compared with olefins. Moreover, epoxides are mostly synthesized from olefins. If a simpler and cheaper approach for synthesis of cyclic carbonate starting from olefin and CO_2 is achieved, it must be of potential application in industry because the process uses low-priced and easily available organic substrates, olefins, for the synthesis of valuable chemicals—carbonates. More importantly, preliminary synthesis of epoxides and separation of them after the first step would be avoided (Scheme 1).

In view of industrial applications, the one-pot synthesis of cyclic carbonate from olefin may be promising. However, such a three-component coupling, also called oxidative carboxylation of olefins, has been known since 1962 [11], up to now, only sporadic works were made on the direct synthesis of cyclic carbonate from olefins. Aresta [12–14] reported the synthesis of styrene carbonate from styrene in the presence of O_2 and CO_2 at 135 °C for 12 h reaction time, and very low styrene carbonate yields of 1.9% over Nb_2O_5 catalyst and 11% over $Nb_2O_5 + NbCl_5$ catalysts were obtained. Recently, Srivastava et al. [15] reported that styrene carbonate could be synthesized from styrene by two steps in a single reactor over titanium silicalite in the presence of DMAP (N,N-dimethylaminopyridine) as cocatalyst. However, high temperature, long reaction time, and toxic organic solvents such as DMF and CH_2Cl_2 were needed for a higher styrene carbonate yield of 33%. Styrene carbonates were formed efficiently with 89% yield in water by using metal-free bromide ion catalyst together with organic base 1,8-diazabicyclo [5.4.0] undecenc-7-ene (DBU) and H_2O_2 as oxidant [16]. Inspired by biomimetic oxybromination, He and coworkers [17] developed a binary catalyst system composed of sodium phosphotungstate and Bu_4NBr for facile synthesis of styrene carbonate in a single operation from styrene and CO_2 using 30% H_2O_2 as an oxidant. The presence of a base markedly improved the formation of styrene carbonate. Interestingly, the selective formation of phenacyl benzonate and cyclic carbonate could be

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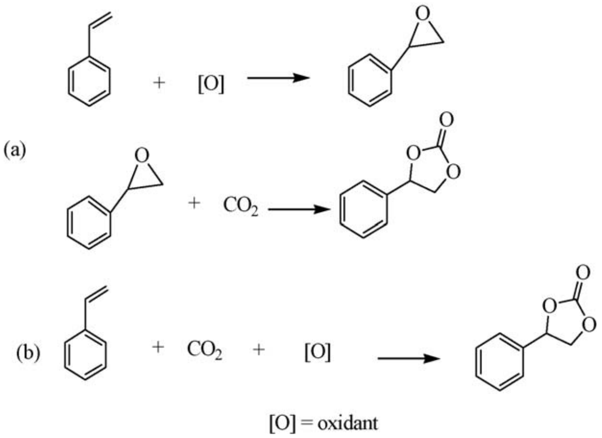


Scheme 1. (a) Two-steps and (b) one-step synthesis of styrene carbonate from styrene.

controlled by subtly tuning the quantities of CO_2 and H_2O_2. Later, Yokoyama and coworkers [18] used a four-component catalysts system MTO/UHP/Zn[EMIm]$_2$Br$_4$/[BMIm]BF$_4$ for the direct preparation of styrene carbonate from styrene using multistep synthetic process, the yield of styrene carbonate was improved to 83%.

In our previous work, it was shown that a catalyst system of $ZnBr_2$/tetrabutylammonium bromide (Bu_4NBr) had excellent activity and selectivity for the coupling of CO_2 with styrene oxide [19]. By combining with an epoxidation catalyst, the catalyst system can be efficiently applied for the direct oxidative carboxylation of styrene [20,21]. Over the three-component catalysts system including $ZnBr_2/Bu_4NBr$ and supported nano-gold as epoxidation catalyst, moderate yield of 53% styrene carbonate was obtained under mild conditions. In the direct oxidative carboxylation of styrene to styrene carbonate, the supported Au catalyzed the epoxidation reaction and $ZnBr_2/Bu_4NBr$ cooperatively catalyzed subsequent CO_2 cycloaddition. However, the complicated catalyst systems limited their wide use in industry. So the simple catalyst with high activity and selectivity is being sought for.

In the pursue of simple catalyst, we have found that direct oxidative carboxylation of styrene to styrene carbonate is feasible in the presence of ionic liquids [22–24]. However, the homogeneous nature of ionic liquid Bu_4NBr is the main drawback in separation and recycling. Therefore, the development of actively one-component heterogeneous catalyst for direct synthesis of cyclic carbonate from olefin is still of great importance.

Herein, we synthesized a strong basic resin R201 supported nano-gold catalyst, which was very active for the oxidative carboxylation of styrene to styrene carbonate. The influence factors such as Au loadings, CO_2 pressure, temperature of CO_2 cycloaddition reaction and CO_2 addition order were investigated in detail. 51% of styrene carbonate yield was obtained over 0.01 wt.% Au loading of catalyst using multistep synthetic process. To optimize the reaction conditions in one-pot synthesis of styrene carbonate, epoxidation of styrene and CO_2 coupling with epoxide were conducted separately over Au/R201 catalyst, and possible mechanism for the direct oxidative carboxylation of styrene to styrene carbonate was proposed.

2. Experimental

2.1. Preparation of Au/R201 catalyst

2 g of dried resin (Amberlite IRA-400, Dandong Mingzhu Resin Industry Company, China) was pretreated with 2 M NaOH solution for 6 h, and then filtrated and washed by distilled water thoroughly. After drying at 80 °C for 3 h, the above resin was dipped in 0.001–0.006 M solution of $HAuCl_4$, stirred at room temperature for 12 h then dried at 150 °C for overnight. Resin supported nano-gold catalysts with various gold loading at 0.005, 0.01, 0.05, 0.1 and 1 wt.% Au/R201 were obtained.

2.2. Characterization of catalyst

Au contents were analyzed by inductively coupled plasma (ICP) technique with a PerkinElmer 2400 elemental analyzer. X-ray powder diffraction (XRD) data were collected on a Siemens D5005 diffractometer with Cu Kα radiation (λ = 1.5418 Å). Transmission electron microscopy (TEM) experiment was performed on a Rigaku H-8100 IV microscope.

2.3. The direct oxidative carboxylation of styrene to styrene carbonate

The one-pot synthesis of styrene carbonate using multistep protocols was conducted in a 50 ml stainless steel autoclave. First, the catalyst and substrates (styrene and oxidant) were fed into the reactor, the epoxidation reaction was conducted at 80 °C for 3 h in the absence of CO_2. After the reaction, the liquid CO_2 of the desired pressure was charged at 80 °C with a high-pressure liquid pump. Then CO_2 cycloaddition was reacted at elevated temperature for 4 h. After the reaction was finished, the reactor was cooled to room temperature and depressurized to atmospheric pressure. The products were extracted into ethyl acetate then the organic products were analyzed by a gas chromatograph (Agilent GC 6890 N) with a capillary column (HP-5). The quantities of styrene consumed and products formed were determined from the results obtained from authentic standards.

For comparison, the one-pot synthesis of styrene carbonate using single step process was carried out in a 50 ml stainless steel autoclave. In a typical run, the reactor was charged with all the raw materials including styrene, oxidant and catalyst successively, and heated to a desired temperature. Then CO_2 at fixed pressure was charged into the reactor at the beginning of the reaction. After the reaction proceeded for certain time, the analysis procedure for products was the same as that in multistep protocol for direct synthesis of styrene carbonate.

The used Au/R201 catalyst was removed from the reaction system by filtration, washed with acetone, dried at room temperature, and then reused for subsequent one-pot synthesis styrene carbonate for testing the catalyst reusability.

3. Results and discussion

3.1. Characterization of supportedAu/R201 catalyst

XRD patterns of Au/R201 catalysts with various Au loadings are presented in Fig. 1. Because of the too low Au loading, Au/R201 sample with Au loading at 0.01 wt.% did not give crystalline gold peaks from 35° to 80° (Fig. 1a). With the loading increasing to 0.1 wt.%, the metallic gold peaks appeared (Fig. 1b). When the Au loading reached 1 wt.%, the typical diffraction peak at 38.1° ascribed to Au (1 1 1) was intensified, and the peaks at $2\theta \approx 44.8°$, 64.8° and 78° characteristic diffraction lines of Au (2 0 0), Au (2 2 0) and Au (2 2 2) appeared [25]. TEM characterization (Fig. 2) indicated the formation of nano-gold particles and the average gold particle sizes was 20 nm for 1 wt.% Au/R201.

As a source of complementary information on the chemical state, diffuse reflection UV–vis spectra of the Au/R201 sample was measured (Fig. 3). Band observed at around 500–600 nm depending upon the particle size indicates the existence of metallic gold

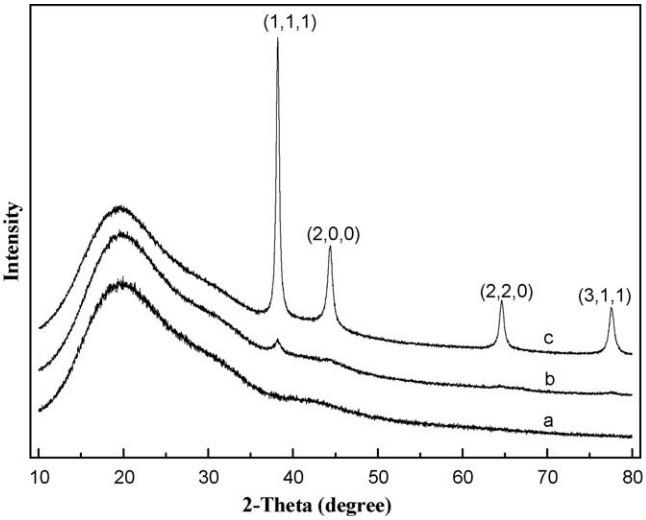


Fig. 1. XRD patterns of Au/R201 samples with various Au loadings (a) 0.01 wt.%; (b) 0.1 wt.%; (c) 1 wt.%.

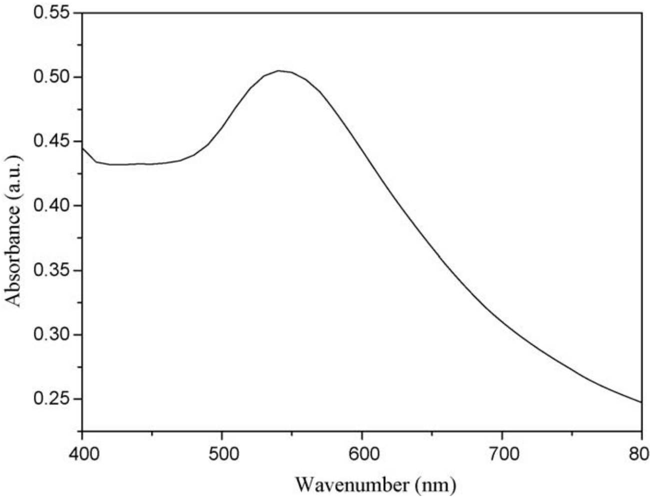


Fig. 3. UV–vis spectra of Au/R201 catalyst with Au loading at 1 wt.%.

over the catalyst [26], which is consistent with the result of XRD (Fig. 3).

3.2. Optimization of the reaction parameters for styrene epoxidation and CO_2 coupling reaction with styrene oxide catalyzed by Au/R201 catalyst

Deng and coworkers [27] reported that a polymer-supported gold nanoparticle showed unexpected catalytic activity for CO_2 coupling reaction to epoxides. Moreover, He and coworkers [28] reported an efficient and environmentally benign process for a highly selective synthesis of propylene carbonate from supercritical carbon dioxide and propylene oxide using insoluble basic anion exchange resins, one type of polystyryl supported catalysts containing an ammonium salt or amino group. Under supercritical conditions (373 K, 8 MPa), a quantitative yield together with excellent selectivity (>99%) was obtained without additional organic solvent. Cycloaddition of CO_2 to epoxides could efficiently proceed over quaternary ammonium salts as catalyst or cocatalyst [29–36]. Furthermore, supported nanocrystalline gold catalysts displayed good activity for epoxidation reaction and high selectivity to epoxides [37–41]. These research works induced us to select Au supported basic resin R201, whose functional group is quaternary ammonium, as catalyst for one-pot synthesis of styrene carbonate from styrene. As anticipated, Au/R201 catalyst was found to be active in both the epoxidation reaction of styrene and cycloaddition reaction of CO_2 to epoxide. In order to get the optimal carbonate yield in the direct oxidative carboxylation of styrene, two separate reactions of epoxidation of styrene and CO_2 coupling with epoxide were studied. Optimization of the reaction parameters such as Au loadings and the ratio of oxidant to styrene for the epoxidation of styrene were shown in Table 1. The basic resin R201 alone had no activity for the epoxidation reaction (entry 1). With the supported Au particle, styrene epoxidation proceeded with high selectivity to styrene oxide, suggesting Au is the main active species in the epoxidation reaction. Styrene oxide yield increased markedly with the gold loading increasing from 0.005 wt.% to 0.01 wt.%. Further increase of gold loading to 0.1 wt.% resulted in decrease of oxide yield, possibly due to the significant effect of the gold particle size [42–44]. Amount of the oxidant was another factor that exerted an important influence on the epoxidation reaction. The effect of the oxidant/styrene ratio was investigated at 1 and 1.5. As can be seen, stoichiometric amount of *tert*-butyl hydroperoxide (TBHP) afforded a lower conversion of styrene and selectivity to styrene oxide. While increasing the oxidant/styrene ratio to 1.5, the yield of styrene oxide improved a little. These results suggested that 1.5 can be viewed as the optimal ratio of TBHP/styrene for the styrene epoxidation reaction. The needs of excessive amounts of oxidant were employed in many epoxidation reactions [20,22,23,45].

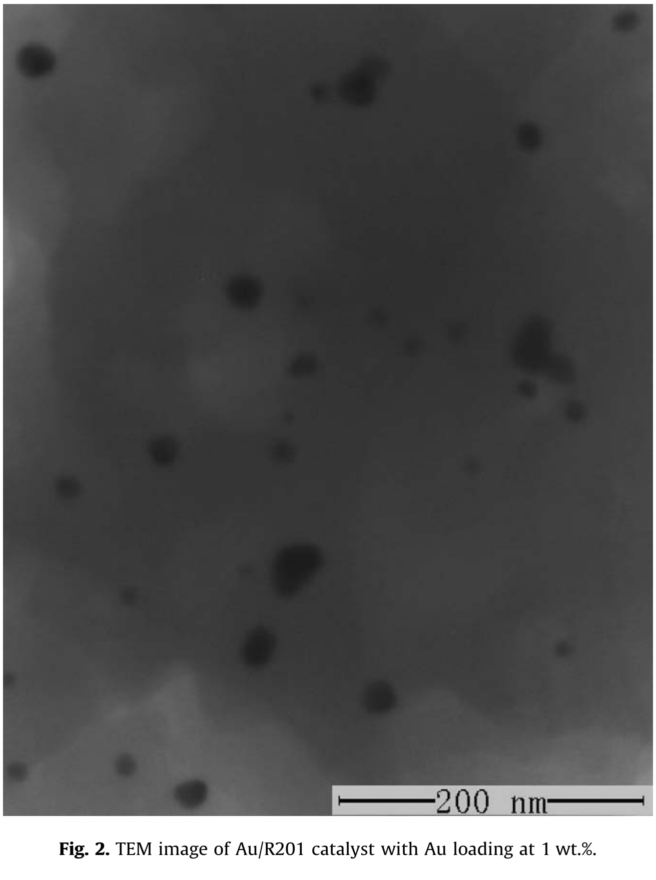


Fig. 2. TEM image of Au/R201 catalyst with Au loading at 1 wt.%.

The CO_2 cycloaddition to styrene oxide was examined in order to get the optimal reaction conditions for the direct oxidative carboxylation of styrene to styrene carbonate (Table 2). With resin R201 alone, styrene carbonate was obtained with very low yield at mild temperature of 85 °C. The yield was improved a little in the

Table 1
The effect parameters in styrene epoxidation reaction over Au/R201 catalyst.

Entry	Au loading (wt.%)	Oxidant/styrene (molar ratio)	Conv. (%)	SO sel. (%)	Others sel. (%)	SO yield (%)
1	0	1.5:1	N.R.			
3	0.005	1.5:1	21.9	79.6	20.4	17.4
3	0.01	1.5:1	40.6	67.3	32.7	27.3
4	0.01	1:1	37.8	64.2	35.8	24.3
5	0.1	1.5:1	37.1	63.2	36.8	23.4
5	0.1	1:1	34.5	61.4	38.6	21.2
2	1.0	1.5:1	24.4	82.0	18.0	20.0

Reaction conditions: catalyst, 0.2 g; styrene, 10 mmol; TBHP (*tert*-butyl hydroperoxide, anhydrous) as oxidant; time, 3 h; temperature, 80 °C. SO = styrene oxide; others include benzaldehyde and phenalacetaldehyde.

presence of Lewis acid $ZnBr_2$ (Table 2, entries 1 and 2). Previous study [19,46] showed that the addition of Lewis acid $ZnBr_2$ could improve the catalytic activity greatly in the CO_2 cycloaddition to styrene oxide catalyzed by quaternary ammonium bromide. With supported Au catalyst, the yield was similar with the bare resin (entries 3 and 4), indicating nano-gold is not necessary for the CO_2 coupling reaction. However, the coupling reaction was very sensitive to the reaction temperature. When the reaction temperature was improved to 100 °C, the conversion increased remarkably. At 150 °C, the conversion achieved 95.4% even in the absence of a second catalyst $ZnBr_2$. Almost 100% selectivity to styrene carbonate were obtained for all the reactions. So with Au/R201 catalyst alone, the optimal reaction temperature was 150 °C for CO_2 cycloaddition to styrene oxide.

3.3. *The direct oxidative carboxylation of styrene to styrene carbonate over Au/R201 catalyst*

Table 3 summarizes the influences of Au loadings and reaction temperature of CO_2 cycloaddition on the product yields in direct synthesis of styrene carbonate. Almost no styrene carbonate was obtained with very low conversion of styrene by one-step synthetic process (entry 3). Interestingly, the desired product styrene carbonate was increased significantly by changing to multistep protocol, implying CO_2 played a negative effect on the epoxidation reaction over Au/R201 catalyst. So the following results were obtained by multistep synthetic protocol, which was viewed as a more attractive and practical route for this catalyst. It was expected that the conversion of styrene and carbonate yield increased with Au loadings. When Au loading was 0.01 wt.%, the conversion and carbonate yield increased to 88.3% and 27.7%, respectively. However, with further increase Au loading to 0.05 wt.%, carbonate yield and conversion decreased sharply, this trend was consistent with that in the epoxidation reaction. The influence of cycloaddition temperature was obvious in the direct synthesis of carbonate from styrene under 4 MPa of CO_2 (entries 2 and 4). As observed, increasing of the reaction temperature was a favorable factor that enhanced the CO_2 coupling reaction with styrene oxide. Almost complete conversion of styrene was achieved with great enhancement of 50.6% carbonate yield at 150 °C.

The influences of CO_2 pressure on the styrene conversion and product yields are shown in Table 4. At low CO_2 pressure, the carbonate yield was very low. The styrene conversion and carbonate yield increased significantly with pressure increasing from 2 MPa to 4 MPa. Increasing the pressure beyond the optimal level at 4 MPa resulted in a sharp reduction in carbonate yield to 10.2% at 7 MPa. Such a decrease in the product yield with increasing pressure of carbon dioxide was also reported previously [21,10,47,48]. High CO_2 pressure may retard the interaction between styrene and catalyst as a result of lower concentration

Table 2
The effects of reaction temperature and co-catalyst addition on the activity in the reaction of CO_2 cycloaddition to styrene epoxide.

Entry	T (°C)	$ZnBr_2$ (mmol)	Conv. (%)	SC sel. (%)	Others sel. (%)	SC yield (%)
1[a]	85	0	14.8	97.0	3.0	14.4
2[a]	85	0.2	36.3	98.2	1.8	35.7
3	85	0	15.2	97.2	2.8	14.8
4	85	0.2	39.0	97.9	2.1	38.2
5	100	0.2	90.5	96.8	3.2	87.6
6	120	0.2	98.3	100	0	98.3
7	150	0	95.4	97.0	3.0	92.5

Reaction conditions: catalyst Au (0.01 wt.%)/R201, 0.2 g; styrene oxide, 0.03 mol; CO_2 pressure, 4 MPa; time, 4 h. SC = styrene carbonate; others include the oligomers of the styrene carbonate.

[a] Bare R201 resin was used as catalyst, the other conditions were the same as above.

Table 3
The effect of reaction parameters on the activity in the direct oxidative carboxylation of styrene to styrene carbonate.

Entry	Au loading (wt.%)	T_2 (°C)	Conv. (%)	SC yield (%)	SO yield (%)	BA yield (%)	Others yield (%)
1	0.005	100	89.1	13.4	7.7	31.7	36.3
2	0.01	100	91.2	27.7	5.4	24.2	33.9
3[a]	0.01	100	20.2	1.5	9.6	4.6	4.5
4	0.01	150	98.1	50.6	7.0	17.9	22.6
5	0.05	100	90.7	15.6	5.4	30.6	39.1
6	0.1	100	88.9	11.2	6.2	31.1	40.4

Reaction conditions: catalyst, 0.2 g; styrene, 17.3 mmol; TBHP, 25.4 mmol; T_1 (epoxidation reaction temperature), 80 °C; t_1, 3 h, T_2 (cycloaddition reaction temperature); t_2, 4 h; CO_2 pressure, 4 MPa. SC = styrene carbonate; SO = styrene oxide; BA = benzaldehyde; others include oligomers of the substrate and those of SO and/or SC.

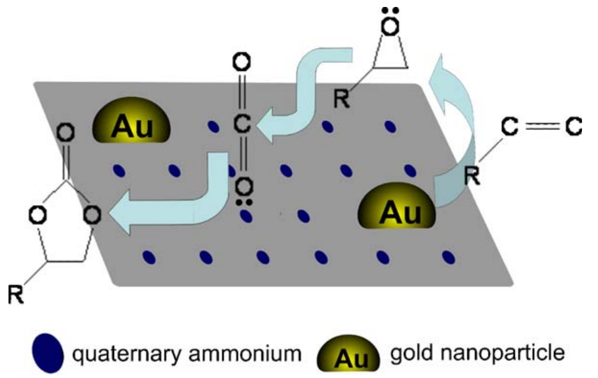
[a] One-step synthetic process.

Table 4
The influence of CO_2 pressure on the activity in the direct oxidative carboxylation of styrene to styrene carbonate by multistep protocol.

Entry	Pressure (MPa)	Conv. (%)	SC yield (%)	SO yield (%)	BA yield (%)	Others yield (%)
1	2	85.7	7.5	9.3	30.4	38.5
2	4	98.0	50.6	7.0	17.9	22.5
3[a]	4	96.5	48.7	6.2	21.2	20.4
4	7	100	10.4	4.6	39.3	45.7

Reaction conditions: catalyst Au (0.01 wt.%)/R201, 0.2 g; styrene, 17.3 mmol; TBHP, 25.4 mmol; T_1 = 80 °C; t_1 = 3 h; T_2 = 150 °C; t_2 = 4 h.

[a] With the used Au/R201 catalyst.



Scheme 2. Possible mechanism for one-pot synthesis of styrene carbonate from styrene and CO_2 over Au/R201 catalyst.

of the substrate at this elevated pressure, moreover, much oligomers were produced at high pressure [49].

In order to check if the reaction is effectively heterogeneous, the Au/R201 catalyst was filtered off after catalytic reaction, then the resultant final reaction solutions were further reacted with the fresh reactants for another run. It was shown that no reaction occurred with the remaining solution, indicating that Au/R201 was indeed heterogeneous catalyst. The reusability of Au/R201 catalyst was examined. After one 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. The results with the used catalyst were similar to those obtained with fresh catalyst (Table 4, entry3), displaying the catalyst was readily separated and reused without any loss of activity.

Based on the present and literature results, a reaction mechanism was postulated (Scheme 2). Styrene epoxidation proceeds over the nano-gold particles and carbon dioxide is activated by quaternary ammonium salts of the support R201 surface. Then CO_2 attacks styrene oxide forming the styrene carbonate over R201 resin. The synergistic effect of the nano-gold particles and quaternary ammonium salts is important for its better catalytic performance for direct oxidative carboxylation of styrene to styrene carbonate.

4. Conclusion

The novel and direct route presented here for cyclic carbonate synthesis is of practical interest from environmental and economic points of view because of one-component heterogeneous catalyst, simplicity of the procedure, and abundant and cheap raw materials of olefin and CO_2. To optimize the reaction conditions for the higher styrene carbonate yield, the epoxidation of styrene and CO_2 cycloaddition to styrene oxide, which are integrated for the one-pot synthesis of styrene carbonate from styrene, were separately investigated. With Au/R201 catalyst, synthetic process had great influence on the carbonate yield. By multistep protocol the carbonate yield reached 51% with anhydrous TBHP as oxidant. In this novel synthesis, CO_2 acted as both a reagent and a solvent, the use of additional organic solvents could be avoided. Over the basic resin supported Au catalyst, the pronounced cooperative effect of quaternary ammonium cation of the support and nano-gold particle resulted in its good performance in the one-pot synthesis of styrene carbonate. The heterogeneous catalyst Au/R201 was readily separated after the reaction and reused without catalyst leaching. The single-component heterogeneous catalyst is of great potential in industry compared with the multi-components catalysts system and homogenous catalyst.

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