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Article

Transformation of carbon dioxide into valuable chemicals over bifunctional metallosalen catalysts bearing quaternary phosphonium salts

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ABSTRACT

The chemical transformation of CO₂ under mild conditions remains a great challenge because of its exceptional kinetic and thermodynamic stability. Two important reactions in the transformation of CO₂ are the *N*-formylation reaction of amines using hydrosilanes and CO₂, and the cycloaddition of CO₂ to epoxides. Here, we report the high efficiency of bifunctional metallosalen complexes bearing quaternary phosphonium salts in catalyzing both of these reactions under solvent-free, mild conditions without the need for co-catalysts. The catalysts' bifunctionality is attributed to an intramolecular cooperative process between the metal center and the halogen anion. Depending on the reaction, this activates CO₂ by permitting either the synergistic activation of Si–H bond via metal–hydrogen coordinative bond (M–H) or the dual activation of epoxide via metal–oxygen coordinative bond (M–O). The one-component catalysts are also shown to be easily recovered and reused five times without significant loss of activity or selectivity. The current results are combined with previous work in the area to propose the relevant reaction mechanisms.

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1. Introduction

The development of green chemistry and atom economy approaches and the fact that carbon dioxide (CO₂) is an inexpensive, highly abundant and renewable C1 building block, have caused the chemical fixation of CO₂ to produce high-added-value chemicals to attract much interest in recent years [1]. A particularly common example is the cycloaddition reaction between CO₂ and epoxides to synthesize cyclic car-

bonates. This reaction may be facilitated by numerous catalytic systems, including alkali metal halides [2], quaternary onium salts [3], ionic liquids (ILs) [4–6], metal complexes [7], metal oxides [8], metal-organic frameworks (MOFs) [9,10], and porous organic polymers (POPs) [11,12]. Another promising reaction with CO₂—its reduction to formamides using amines and hydrosilanes [13]—has also been developed using various catalysts, including organic bases [14], inorganic salts [15,16], strong polar solvents [17], ILs [18], metal complexes [19], and

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N-heterocyclic carbenes [20]. Recently, our group reported that one-component Al(salen) complexes with additional imidazolium-based IL moieties catalyzed the CO₂/epoxide cycloaddition reaction under ambient conditions [21,22]. Additionally, the IL-functionalized Zn(salen) analogues have been shown to promote the CO₂-based *N*-formylation reaction of organic amines to yield formamide derivatives when reacted with hydrosilanes [23].

Analysis of the homogeneous catalytic systems above that involve CO₂ (Scheme 1) revealed a dual activation at the metal center (Lewis acid) and at the halogen anion (nucleophile) which may explain the high efficiency [24]. It is possible for the intramolecular cooperative effect to either activate the Si-H bond within hydrosilane through a metal–hydrogen coordinative bond (M–H), or to activate the epoxide through a metal–oxygen coordinative bond (M–O). The highly active intermediates (Zn–H or Al–O species) may make the CO₂ insertion more favorable, thereby facilitating the activation of CO₂. However, when using traditional quaternary ammonium salts as synthetic units instead of imidazolium-based ILs, low catalytic activity was observed, probably because of the poor solubility exhibited by the simple synthetic method when using ethylenediamine as a feedstock [21,23]. Thus, drawing on other work reported in this area [25,26], we envisioned that bifunctional catalysts bearing quaternary phosphonium salts could exhibit better catalytic performance on account of their superior solubility and stability.

Herein, quaternary phosphonium salts were successfully introduced into the framework of a salen ligand at the 3,3'- and 5,5'-positions as shown in Scheme 2. After metalation with ZnEt₂ or AlEt₂Cl, the Zn-based catalysts (denoted as 5-PSZ-Cl, 3-PSZ-Cl and 3-PSZ-Br) we describe the novel demonstration of their use as bifunctional catalysts to catalyze the CO₂-based *N*-formylation of amines with hydrosilanes. Meanwhile, the Al-based complexes (denoted as 5-PSA-Cl, 3-PSA-Cl and 3-PSA-Br) are shown to promote the CO₂/epoxide cycloaddition reaction at ambient conditions. Accordingly, such efficient intramolecular cooperative catalysis indicates that CO₂ can be

Scheme 2. Bifunctional catalysts developed in (a) previous and (b) the current work.

transformed under mild conditions. The bifunctional metallo-salen catalysts are shown to be very active, highly selective, stable, and easily recycled by manipulating the solvent. A kinetic analysis is also carried out to investigate the reaction mechanism and help understand larger scale development of these bifunctional catalysts that are useful for converting CO₂.

2. Experimental

Propylene oxide, styrene oxide, epichlorohydrin, epibromohydrin, allyl glycidyl ether, *n*-butyl glycidyl ether, *iso*-propyl glycidyl ether, glycidyl methacrylate, cyclohexene oxide, *N*-methylaniline, 4-methoxy-*N*-methylaniline, 4-chloro-*N*-methylaniline, morpholine, diethylamine, 4-methylpiperidine, 4-phenylpiperidine, diphenylsilane, and poly(methylhydrosiloxane) were obtained from J&K Scientific Ltd. Phenylsilane was purchased from Energy Chemical Ltd. The corresponding bifunctional catalysts were synthesized according to procedures detailed in our previous work [21–23,27].

The reaction was carried out in a 10-mL stainless steel autoclave which was coupled with a magnetic stirrer. In a typical experiment for the *N*-formylation of amines with CO₂ and hydrosilanes, *N*-methylaniline, the catalyst 3-PSZ-Br (or other catalysts when performing comparisons), and phenylsilane were added into the reactor. Subsequently, CO₂ was charged into the reactor until the pressure reached 0.5 MPa and the reactor was then heated by an oil bath to 40 °C while being stirred continuously. After the reaction, the autoclave was quickly cooled to 0 °C and depressurized to atmospheric pressure [14]. The cycloaddition reactions with epoxides and CO₂ were carried out in a similar fashion. Conversions and yields were determined using naphthalene or biphenyl as the internal standard and measured by a gas chromatograph (GC2010, Shimadzu Corporation, Japan) equipped with a capillary column (Rtx-5, 30 m × 0.32 mm × 0.25 μm) and a flame ionization detector (FID). The structure and the purity of the corresponding products were identified by ¹H NMR, ¹³C NMR, and GC-MS

Scheme 1. The dual activation of the metal center and the halogen anion.

analysis.

Larger scale (kinetics) experiments were carried out using an EasyMax™102 system (Mettler Toledo, OH, USA) equipped with a 100-mL stainless steel autoclave operated in semi-batch mode with the reaction progress monitored by *in situ* infrared (IR) spectroscopy [22].

3. Results and discussion

3.1. *N*-formylation of amines with CO₂ and hydrosilanes

Formamide derivatives are important platform compounds in the chemical industry [28]. Therefore, we first investigated the catalytic performance in the solvent-free *N*-formylation of amines using CO₂ and hydrosilanes as raw materials. On the basis of our previous work [23], it was demonstrated that the Zn(salen) catalysts bearing additional imidazolium-based IL units exhibited high catalytic efficiency because of the synergistic effect between the Zn active center and the halogen anions. Accordingly, we supposed that the Zn(salen) catalysts functionalized by quaternary phosphonium salts might also present similar catalytic performance given their structural features. Therefore, three kinds of the functional Zn(salen) catalysts were successfully synthesized using the same method as used in the previous work. The simple Zn(salen) complex (denoted as SZ) was also obtained for comparison.

A loading of 0.5 mol% of the catalyst SZ was unable to catalyze the transformation at 40 °C and 0.5 MPa CO₂ pressure even when the reaction time was extended to 12 h (Table 1, entry 2). Low yields (< 5%) were obtained for 5-h experiments with the simple catalyst P-Br and the simple salen ligand 3-PSL-Br at loadings of 1.0 mol% (Table 1, entries 3 and 4). Conversely, the bifunctional catalyst 3-PSZ-Br exhibited excellent catalytic activity and a 96% yield under identical conditions (Table 1, entry 5). Extending the reaction time to 6 h for the homogeneous catalytic system increased the conversion and chemoselectivity to > 99%, still under mild conditions (Table 1, entry 6). The catalytic performance of Cl-based 3-PSZ-Cl was slightly inferior to that of Br-based 3-PSZ-Br (Table 1, entry 7 vs entry 5), especially during the later stages of the reaction (as shown in the kinetic results presented in Fig. 1). We suggest that the difference may be caused by the nucleophilicity of the halogen anion, which is crucial for the activation of Si–H bond in hydrosilanes [29]. The Zn(salen) catalyst 5-PSZ-Cl that was functionalized by the quaternary phosphonium salts at the 5,5'-position of the salen ligand exhibited a lower catalytic performance than that of the same catalyst functionalized at the 3,3'-position (Table 1, entry 8 vs entry 5). This implied that these bifunctional catalysts required a specific spatial structure to actively catalyze the reduction of CO₂. The *N*-formylation of amine with CO₂ under the same reaction conditions was found to depend on the inherent structure of the hydrosilane (Table 1, entries 9 and 10), with either Ph₂SiH₂ or polymethylhydrosiloxane (PMHS) being observed as an unreactive reductant because of steric or electronic effects [16]. Interestingly, the performance of 3-PSZ-Br was better than that

Table 1

Results of the *N*-formylation reaction of *N*-methylaniline with CO₂ and hydrosilanes.

Entry	Catalyst	Hydrosilane (mmol)	<i>t</i> (h)	Conversion ^a (%)	Yield ^a (%)
1	—	PhSiH ₃ (1.0)	24	—	—
2	SZ	PhSiH ₃ (1.0)	12	<1	<1
3	P-Br	PhSiH ₃ (1.0)	5	5	<5
4	3-PSL-Br	PhSiH ₃ (1.0)	5	5	<5
5	3-PSZ-Br	PhSiH ₃ (1.0)	5	96	96
6	3-PSZ-Br	PhSiH ₃ (1.0)	6	>99	99
7	3-PSZ-Cl	PhSiH ₃ (1.0)	5	83	83
8	5-PSZ-Cl	PhSiH ₃ (1.0)	5	68	68
9	3-PSZ-Br	Ph ₂ SiH ₂ (1.0)	6	<1	<1
10	3-PSZ-Br	PMHS (1.0)	6	<1	<1
11 ^b	ISZ1	PhSiH ₃ (1.0)	6	88	88

Reaction conditions: 10-mL stainless-steel autoclave, *N*-methylaniline 1 mmol, catalyst 0.01 mmol, 40 °C, CO₂ pressure 0.5 MPa.

^a Determined by GC using naphthalene as the internal standard.

^b From previous work [23].

of the imidazolium-based ILs ILZ1 reported previously under identical conditions (Table 1, entry 11 vs entry 5). This may be caused by the strong leaving-ability of the halogen anion for the current catalysts. Overall the bifunctional catalyst system was shown to catalyze the *N*-formylation of amine with PhSiH₃ through the reduction of CO₂ thanks to the cooperative effect between the zinc active center and the bromide anion.

To analyze the range of substrates, the *N*-formylation reaction was carried out with a range of primary and secondary amines (and CO₂ and PhSiH₃) over 3-PSZ-Br under the same reaction conditions (40 °C, 0.5 MPa CO₂). The results (Table 2) demonstrate the generality of the bifunctional catalytic system. Aromatic, alicyclic and aliphatic amines afforded moder-

Fig. 1. Change in the concentration of reactant (PhSiH₃) and product (*N*-methylformanilide) with time using 3-PSZ-Cl or 3-PSZ-Br as the catalyst. Reaction conditions: *N*-methylaniline 1.0 mmol, PhSiH₃ 1.0 mmol, catalyst loading 1.0 mol%, CO₂ pressure 0.5 MPa, 40 °C.

Table 2

Results of *N*-formylation of various amines to produce formamides from CO₂ and hydrosilanes over the 3-PSZ-Br catalyst.

Entry	Substrate	Product	Yield (%)
1			96
2			>99
3			85
4			82
5			98
6			96
7			>99
8			39
9			15
10			56:44
11			59:41

Reaction conditions: 10-mL autoclave, amine 1.0 mmol, PhSiH₃ 1.0 mmol, CO₂ pressure 0.5 MPa, 3-PSZ-Br loading 1.0 mol%, 40 °C, 6 h.

ate-to-excellent yields and excellent chemoselectivities [30]. Both steric and electronic effects were thought to have played an important role in the *N*-formylation of amines. For example, the yields obtained from *N*-methylaniline derivatives with electron-donating groups at the *para*-position of the phenyl group were generally lower than those with *para* electron-withdrawing groups under identical conditions (i.e., methoxyl > hydrogen > chloride, see Table 2, entries 1–3). Notably, the mono- and di-formylated formamides were obtained for most of the primary amines with two active N–H bonds (Table 2, entries 10 and 11) [18]. In summary, the bifunctional Zn(salen) catalysts exhibited excellent substrate compatibility.

3.2. Cycloaddition reaction between CO₂ and epoxides

Cyclic carbonates were widely used as electrolyte components in lithium batteries, polar aprotic solvents, and intermediates in the production of pharmaceuticals and fine chemicals. Generally speaking, the cycloaddition reaction between CO₂ and epoxides is regarded as a promising and ‘greener’ alternative to the traditional phosgene (COCl₂) and carbon monoxide (CO) production process. We previously proposed a mechanism that details the dual activation of epoxides through a cooperative effect between an active metal center and a nucleophile [21]. To further understand the bifunctionality of the cat-

alysts studied here, we also investigated their use in the cycloaddition reaction between CO₂ and allyl glycidyl ether (AGE) to afford allyl glycidyl carbonate (AGC). The results from reactions operated in a semi-continuous mode under mild, solvent-free conditions are shown in Table 3.

No reaction occurred when the traditional Al(salen) complex (denoted as SA) was used as the sole catalyst (Table 3, entry 1). In 2007, He and coworkers [31] reported that polyethylene glycol-functionalized phosphonium halide could catalyze the transformation of CO₂ because of liner effects. Nevertheless, both the simple quaternary phosphonium salts P-Br (1.0 mol%) and the simple salen ligand 3-PSA-Br (0.5 mol%) were unable to catalyze the cycloaddition reaction after 2.5 h at 100 °C and a CO₂ pressure of 2.0 MPa (Table 3, entries 2 and 3). Combining the catalysts using a molar ratio of 1:2 to give a binary catalytic system produced an AGC yield of 25% under identical conditions thanks to the intermolecular synergistic effect between the aluminum cation and the bromide anion (Table 3, entry 4). These promising results encouraged us to synthesize bifunctional Al(salen) catalysts bearing quaternary phosphonium salts. Making use of the intramolecular cooperative effect, three kinds of Al-based bifunctional catalysts were successfully prepared and gave high yields (the mechanisms of which are shown in Scheme 1). A loading of 0.5 mol% 3-PSA-Br efficiently catalyzed the cycloaddition reaction under the same conditions to produce a 97% yield without adding any co-catalyst (Table 3, entry 5). Regrettably, under the same conditions the two other bifunctional catalysts (5-PSA-Cl and 3-PSA-Cl) presented low catalytic activity for structural reasons

Table 3

Results of the cycloaddition reaction between AGE and CO₂ using various catalysts.

Entry	Catalyst	Catalyst loading (mol%)	<i>T</i> (°C)	<i>P</i> (CO ₂) (MPa)	Conversion ^a (%)	Yield ^a (%)
1	SA	0.5	100	2.0	—	—
2	P-Br	1.0	100	2.0	<1	<1
3	3-PSL-Br	0.5	100	2.0	<1	<1
4	SA/P-Br	0.5/1.0	100	2.0	26	25
5	3-PSA-Br	0.5	100	2.0	98	97
6	5-PSA-Cl	0.5	100	2.0	10	8
7	3-PSA-Cl	0.5	100	2.0	16	15
8	3-PSA-Br	0.35	100	2.0	51	50
9	3-PSA-Br	0.15	100	2.0	12	11
10	3-PSA-Br	0.5	90	2.0	58	56
11	3-PSA-Br	0.5	80	2.0	28	26
12	3-PSA-Br	0.5	100	1.0	91	90

Reaction conditions: 10-mL stainless-steel autoclave, AGE 6 mmol, 2.5 h.

^a Determined by GC using biphenyl as the internal standard.

and because of the poor nucleophilicity of the chloride anion (Table 3, entries 6 and 7). Decreasing the catalyst loading of 3-PSA-Br to 0.35 mol% gave a moderate yield of 51% (Table 3, entry 8) while decreasing the loading further to 0.15 mol% further decreased the yield (Table 3, entry 9). Decreasing the reaction temperature from 100 to 90 and to 80 °C caused the the ACG yield to fall sharply from 97% to 56% and to 26%, respectively (Table 3, entry 5 vs entries 10 and 11). However, the ACG yield changed only slightly when the CO₂ pressure was halved from 2.0 to 1.0 MPa (Table 3, entry 12 vs entry 5).

Subsequently, a variety of terminal epoxides, including glycidyl ether with various functional groups, styrene oxide (SO), epichlorohydrin (ECH), epibromohydrin (EBH), and aliphatic epoxides, were evaluated using a low (0.5 mol%) loading of 3-PSA-Br under relatively mild (100 °C, 2.0 MPa CO₂), solvent-free conditions. Table 4 shows that the desired cyclic carbonates were exclusively produced from the investigated terminal epoxides in reactions that exhibited good-to-excellent yields and excellent chemoselectivities (Table 4, entries 1–9). Both steric and electronic effects played an important role in determining the success of the reaction. For example, the activity of the epoxides decreased as their alkyl length increased. Similar yields were obtained when the reaction time was ex-

tended (Table 4, entry 2 vs entry 3 and entry 6 vs entry 7). The low activity with cyclohexene oxide (an internal epoxide that is known to be a challenging substrate in this reaction [32]) was probably caused by a high degree of steric hindrance (Table 4, entry 10). Overall, the bifunctional catalyst exhibited excellent tolerance to the various (alkyl, phenyl, alkenyl, halogen, ether, and alkoxy) functional groups, demonstrating its applicability to a wide range of industrial uses [33].

3.3. Recyclability

We analyzed the recyclability of 3-PSA-Br (chosen for its special solubility) using AGE as the model substrate under mild conditions (100 °C, 2.0 MPa CO₂). After adding ethyl acetate or ethyl ether to the reaction mixture, the bifunctional catalyst was easily separated for use in the next cycle. The results in Fig. 2 show that the recycled 3-PSA-Br still presented high activity with yields of up to 90% and ACG selectivity of approximately 95%. This suggests that manipulating the solvent can permit 3-PSA-Br to take part in “one-phase catalysis and two-phase separation” [21].

3.4. Kinetic investigation

The catalytic performance described above was caused by a cooperative effect between the active metal center and the halogen anion. To further understand the intramolecular synergistic catalysis of the Al(salen) complexes functionalized by quaternary phosphonium salts, a larger scale investigation was conducted for the cycloaddition of CO₂ to epoxides using 3-PSA-Br as the sole catalyst. Styrene oxide (SO) was chosen as the representative substrate for the large-scale synthesis of styrene cyclic carbonate (SC).

The *in situ* IR spectra results (Fig. 3) showed an increase in the intensity of the characteristic peaks at 1159 and 1065 cm⁻¹ (C–O), and 1810 cm⁻¹ (C=O). Meanwhile, a decrease was observed in the intensity of the peak around 816 cm⁻¹, which was attributed to vibrations of the epoxy ring skeleton and was used to monitor the degree of conversion and yields [34]. An SC yield of >85% was obtained after 20 h when using a modest

Table 4
Results of the cycloaddition of CO₂ to various epoxide substrates over 3-PSA-Br.

Entry	Substrate	Product ^a	<i>t</i> (h)	Conversion ^a (%)	Yield ^b (%)
1			4	>99	99
2			4	95	95
3			5	87	87
4			2.5	98	97
5			4	97	95
6			2	>99	99
7			6	>99	99
8			3	90	90
9			1	>99	99
10			6	<1	<1

Reaction conditions: 10-mL stainless-steel autoclave, epoxide 6 mmol, 3-PSA-Br loading 0.03 mmol, CO₂ pressure 2.0 MPa, 100 °C. ^a Product identification via FT-IR, ¹H NMR, ¹³C NMR, and GC-MS. ^b Determined by GC.

Fig. 2. Recyclability of 3-PSA-Br used for the coupling of AGE with CO₂.

Fig. 3. (a) *In situ* IR spectra during reaction and (b) change in SO content over time and (inset) plot to obtain observed rate constant. Reaction conditions: 100-mL stainless-steel autoclave, SO 350 mmol, CO₂ pressure 2.0 MPa, 100 °C, catalyst loading 0.05 mol%.

amount of (0.05 mol%) at mild (100 °C and 2.0 MPa CO₂), solvent-free conditions. The observed rate constant (k_{obs}) of $4.62 \times 10^{-5} \text{ s}^{-1}$ was determined from the slope of a linear plot of the natural logarithm of the changing sample concentration ($\ln[\text{SO}]$) against time (t). The results indicated that a selectivity of 99% was achievable in this larger-scale production (Fig. 3) [22].

The kinetic experiments for the 3-PSA-Br-catalyzed cycloaddition reaction were carried out on the basis of the steady-state approximation method we have detailed previously [22]. Using the Arrhenius equation, the activation energy can be calculated from the relationship between k_{obs} and the absolute temperature (T). Therefore, an activation energy of 67.7 kJ/mol was determined as a function of the reaction temperature in the range 60–90 °C by fitting the data from a plot of the natural logarithm of the observed pseudo-first-order rate constant ($\ln[k_{\text{obs}}]$) against the reciprocal of the absolute temperature ($1/T$) (Fig. 4) [35]. Compared with values reported

elsewhere, this lower activation energy appeared characteristic of the excellent catalytic activity observed under relatively mild conditions. The kinetic data were also analyzed by fitting a line to a plot of the natural logarithm of the observed pseudo-first-order rate constant ($\ln[k_{\text{obs}}]$) against the natural logarithm of the catalyst concentrations ($\ln[\text{CAT}]$). The corresponding double logarithmic plot had a slope of 1.04, further suggesting that the reaction was first-order for the bifunctional catalyst (Fig. 5) [36], and indicating that the catalytic system followed a monometallic reaction mechanism [22].

3.5. Reaction mechanisms

In the *N*-formylation reaction of amine with PhSiH₃ and CO₂ over 3-PSZ-Br, the cooperative effect between the zinc center and the bromide anion activates the Si–H bond of PhSiH₃ [23]. This affords the highly active zinc–hydrogen (Zn–H) species and permits a mechanism that involves the transi-

Fig. 4. (a) Decrease in SO concentration ($[\text{SO}]_0 = 4.0 \text{ mol/L}$) with time using a catalyst loading of 3-PSA-Br in PC (20 g) at 2.0 MPa CO₂ over the temperature range 60–90 °C; (b) Linear fit to a plot of the natural logarithm of the observed pseudo-first-order rate constant ($\ln[k_{\text{obs}}]$) against the reciprocal of the absolute temperature ($1/T$).

Fig. 5. (a) Decrease in SO concentration ($[\text{SO}]_0 = 4.0 \text{ mol/L}$) with time for different catalyst loadings of 3-PSA-Br (0.0034–0.0084 mol/L) in PC (20 g) at 80 °C and 2.0 MPa CO_2 ; (b) Linear fit to a plot of the natural logarithm of the observed pseudo-first-order rate constant ($\ln[k_{\text{obs}}]$) against the natural logarithm of the catalyst concentration ($\ln[\text{CAT}]$).

tion-metal-promoted hydride transfer from PhSiH_3 to CO_2 , based on an intermediate silyl formate [29]. In other words, PhSiH_3 can be activated to react with CO_2 to yield formoxysilane [37]. The organic amines can also be activated by the bifunctional catalyst 3-PSZ-Br via the hydrogen bond (as determined by ^1H NMR spectra), with the corresponding formamides then obtained via the nucleophilic reaction (Scheme 3(a)) [38].

Drawing on our previous work on the cycloaddition reaction between epoxides and CO_2 , we propose the mechanism illustrated in Scheme 3(b) [21,22]. The aluminum center and bromide ion of these bifunctional catalysts promote an intramolecular synergistic catalysis process that was applicable to the CO_2 /epoxide cycloaddition reaction. The epoxide was activated by the Lewis-acidic metal center of 3-PSA-Br, and subsequently attacked by the nucleophile (halogen anion). The metal-oxygen (alkoxide) intermediate could be afforded via the ring-opening of the epoxide [39], which made the insertion of CO_2 more favorable and facilitated the activation of CO_2 . The intramolecular ring-closing reaction then resulted in the formation of cyclic

carbonate and the regeneration of the catalyst [40].

4. Conclusions

Synthesized metallocalen catalysts bearing quaternary phosphonium salts (3-PSA-Br and 3-PSZ-Br) were successfully applied to the two important reactions: the CO_2 /epoxide cycloaddition reaction; and the *N*-formylation of amine with PhSiH_3 and CO_2 . In both situations, the catalyst exhibited excellent performance and selectivity under mild, solvent-free conditions. No co-catalysts were required; instead, an intramolecular cooperative effect between the active metal center and the halogen anion was responsible for the catalysts' activity. An investigation into the reaction kinetics and mechanism were carried out to better understand the novel properties of the actions of these catalysts in organic reactions with CO_2 .

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Scheme 3. Proposed mechanisms for (a) the *N*-formylation of amines with CO_2 and PhSiH_3 over 3-PSZ-Br and (b) the cycloaddition of CO_2 to epoxides over 3-PSA-Br.

Graphical Abstract

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Transformation of carbon dioxide into valuable chemicals over bifunctional metallosalen catalysts bearing quaternary phosphonium saltsWuying Zhang, Rongchang Luo *, Qihang Xu, Yaju Chen, Xiaowei Lin, Xiantai Zhou, Hongbing Ji[#]
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The use of bifunctional metallosalen complexes bearing quaternary phosphonium salts under solvent-free, mild conditions without co-catalysts exhibited high efficiencies catalyzing both the CO₂-based *N*-formylation reaction of amines from hydrosilanes and the cycloaddition of CO₂ to epoxides.

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季磷盐型双功能金属Salen配合物催化二氧化碳转化为高附加值化学品

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摘要: 随着全球“温室效应”和能源危机的加剧, 近几年二氧化碳作为一种丰富、无毒、廉价的碳一原料广受关注. 目前, 在温和条件下实现二氧化碳的化学转化仍然是一个十分具有挑战性的课题, 其关键的科学问题是二氧化碳分子的有效活化. 本文发现, 在不添加任何助催化剂的条件下, 季磷盐型双功能金属Salen配合物不仅能够以有机胺、含氢硅烷和二氧化碳为原料, 在温和条件下通过N-甲酰化反应实现系列甲酰胺类衍生物的高效合成, 而且能够催化二氧化碳和环氧化合物的环加成反应, 从而实现环状碳酸酯的宏量制备.

催化实验及动力学研究表明, 该双功能催化剂通过金属活性中心和卤素阴离子之间的分子内协同催化作用, 既可利用高活性锌氢键调控含氢硅烷中的硅氢键, 又能通过高活性铝氧键激活环氧化物的三元环, 进而导致二氧化碳的方便插入及高效活化. 譬如: 当使用1.0 mol% 锌催化剂时, 仅加入1倍当量的苯硅烷, 在25 °C和0.5 MPa的条件下, 反应6 h后N-甲酰苯胺收率高达99%; 而当使用0.5 mol% 铝催化剂时, 在100 °C和2.0 MPa的条件下反应2 h, 环加成反应转化率接近100%, 环状碳酸酯选择性可达99%.

另外, 上述两个反应都表现出优异的底物扩展性, 具有良好的官能团相容性. 在此基础上通过构建反应动力学模型, 采用在线红外跟踪技术, 阐明了协同活化机制在二氧化碳催化转化过程中的作用原理及共性/个性规律, 丰富并发展了二氧化碳活化的基本理论. 最后, 单组分催化剂可通过溶剂调变的方式很容易实现回收及再利用, 表现出“均相催化, 两相分离”的特点. 循环使用五次后催化活性和选择性未见明显下降.

关键词: 二氧化碳; Salen催化剂; 季磷盐; 协同作用; 反应机理

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