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Zinc single atoms on N-doped carbon: An efficient and stable catalyst for CO_2 fixation and conversion

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ABSTRACT

The cycloaddition of epoxides and carbon dioxide represents a straightforward and atom-efficient method for synthesis of cyclic carbonates and utilization of CO_2. So far, homogeneous metal complexes have been mainly applied for such transformations. Here, we describe the synthesis of novel heterogeneous Zn-based catalysts, which were conveniently prepared by pyrolysis of an active-carbon-supported phenanthroline-ligated $Zn(OAc)_2$ complex. Detail structural characterizations proved the existence of single zinc sites in the active material. Compared to a Zn-based nanoparticle (Zn-NP) catalyst, the resulting single metal atom catalyst (SAC) displayed improved activity and stability for the cycloaddition of epoxides. By applying the optimal catalyst, a variety of carbonates were successfully obtained in high yields with good functional group tolerance.

1. Introduction

The development of new procedures for fixation and utilization of carbon dioxide (CO_2), which is emitted about 36 billion tons per year (https://www.co2.earth/global-co2-emissions), continues to attract significant attention from both academic and industrial researchers [1–12]. In this respect, important progresses for the valorization of CO_2 to energy carriers (methane [13–17]), bulk (methanol [18–22]) and fine chemicals (formats [7,23–27]) as well as for organic specialties (*N*-methylated amines [28–37]) have been reported in recent years. Apart from all these redox transformations, the synthesis of cyclic carbonates by cycloaddition of epoxides with CO_2 has been intensely investigated, which proceeds with high atom efficiency and does not need any stoichiometric amounts of reductants [38–40].

The most widely employed catalysts for the formation of cyclic carbonates from CO_2 are homogeneous metal-based complexes, including mainly salen-type and metalloporphyrin complexes [41–43]. For example, North et al. [44,45] reported bimetallic salen complexes which exhibited high activity for the preparation of cyclic carbonates from both terminal and internal epoxides. In addition, Kleij and co-workers [46] demonstrated an easily accessible aluminum complex to be highly active and productive. Other notable investigations described homogeneous catalysts based on Zn [47], Cr [48], Co [49,50], Fe

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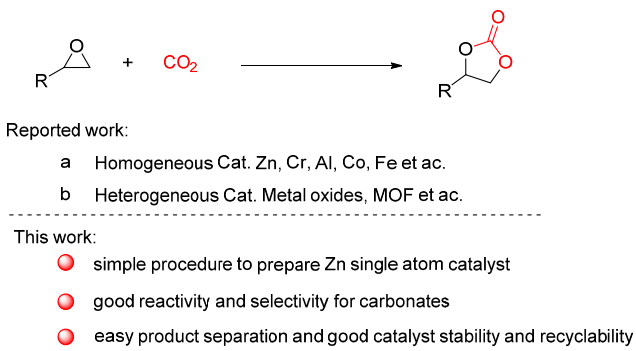


Scheme 1. Known systems and our catalyst for cycloaddition of epoxides and CO_2.

[51–53], Mg [41], and Nb [54].

Although several of the reported homogeneous catalysts show impressive activity and work under mild conditions, and thus allow the formation of sensitive products, the design of heterogenous catalysts is interesting due to their increased stability, simple separation and purification of the products as well as easier integration into continuous flow systems. Compared to molecular-defined complexes, relatively few heterogeneous systems, e.g. metal oxides [55] and metal organic frameworks [56,57], have been explored for the transformation of epoxides to carbonates. Very recently, metals (Zn, Mg and Ni) coordinated to mesoporous *o*-hydroxyazobenzene-based polymers displayed remarkable activity for the formation of propylene carbonate [58,59]. However, so far these materials showed only a narrow substrate scope, and the long reaction time might limit their potential applications.

Recently, single atom catalysts (SACs) provide new opportunities to design catalytic materials at the molecular level because the individual active metal centers can be controlled precisely by the nature of the neighboring atomic species. Hence, we thought that such SACs allow for improved activity in carbonate synthesis due to metal utilization of up to 100%. Encouraged by our recent investigations on the preparation and utilization of N-doped metal nanoparticles and platinum-based single atom catalyst [60–63], here we describe the preparation, characterization and catalytic testing of a novel Zn single atom catalyst (Zn-SAC) supported on N-doped carbon material. The resulting catalyst allows for efficient and general activation of functionalized terminal epoxides to give the corresponding carbonates in high yields.

2. Experimental

2.1. Typical preparation of Zn-SAC@N-C-700 catalysts

$Zn(OAc)_2$ (0.5 mmol) and 1,10-phenanthroline (1.5 mmol) were dissolved in 50 mL ethanol. The reaction mixture was heated to 60 °C and stirred for 1 h under air atmosphere. Next, carbon support (VULCAN®XC72R, which is order from PT. Cabot Indonesia) was used as support and added into the mixture. After further stiring for another 2 h at 60 °C, the reaction mixture was cooled to room temperature naturally. After evaporating the ethanol solvent, a black solid material was obtained and dried at 60 °C for 3 h by vacuum and was grinded to a fine solid powder. Then, the grinded powder was pyrolyzed at 700 °C for 2 h with a step of 25 °C under Ar. The resulting catalyst was grinded to get the final catalyst as Zn-SAC@NC-700. As comparison, other samples were prepared using the similar procedure by varying the pyrolysis temperature (Zn@N-C-600, Zn@N-C-800, Zn@N-C-1000) and organic and inorganic supports such as SiC, SiO_2, MgO_2 and chitosan.

2.2. Preparation of Zn-NP@C catalyst

The support (N-doped carbon) was prepared according to above procedure in the absence of $Zn(OAc)_2$ and pyrolyzed at 700 °C for 2 h with a step of 25 °C under Ar. The Zn-NP@C catalyst was prepared as the literature [64].

2.3. Catalyst recycling experiments

With the similar procedure used above, the catalyst was simply separated by centrifugation, washed with ethyl acetate and *n*-hexane, respectively, and used without further reactivation or purification for the next run.

2.4. Analytic measurements

STEM measurements were performed at 200 kV with an aberration-corrected JEM-ARM200F (JEOL, Corrector: CEOS). The microscope was equipped with a JED-2300 (JEOL) energy-dispersive X-ray-spectrometer (EDXS) and an Enfinium ER (GATAN) eletron energy loss spectrometer for chemical analysis and spectrum imaging. The samples were deposited without any pretreatment on a holey carbon supported Cu-grid (mesh 300) and transferred to the microscope. The high-angle annular dark field (HAADF) and annular bright field (ABF) images were recorded with a spot size of approximately 0.1 nm, the collection semi-angles for HAADF and ABF were 70–170 mrad and 11–22 mrad, respectively.

XPS measurements were performed with a VG ESCALAB220iXL with monochromated Al K_α radiation (E = 1486.6 eV). The electron binding energies (EB) were obtained without charge compensation. For quantitative analysis the peaks were deconvoluted with Gaussian-Lorentzian curves, and the peak areas were divided by a sensitivity factor obtained from the element specific Scofield factor and the transmission function of the spectrometer.

Extended X-ray absorption fine structure (EXAFS) experiments were performed at the Beijing Synchrotron Radiation Facility (BSRF) in Beijing Institute of High Energy Physics, Chinese Academy of Sciences with storage ring energy of 2.5 GeV and a beam current between 150 and 250 mA. The Zn K-edge absorbance of powder catalysts was measured in transmission geometry at room temperature. EXAFS data analysis was carried out using the IFEFFIT analysis program (http://cars9.uchicago.edu/ifeffit/). Radial distribution functions were obtained by Fourier-transformed k^3-weighted χ function.

3. Results and discussion

At the start of this work, we synthesized Zn catalysts supported on different carriers. The preparation of these catalysts commenced with the impregnation of different supports (carbon, alumina, silica, SiC, etc.) with ethanolic solutions of a phenanthroline-ligated $Zn(OAc)_2$ complex (Zn-phen). The resulting ZnN_x@X-Y (N_x denotes the coordinated nitrogen atoms, while X and Y represent the support and pyrolysis temperature) catalysts were obtained upon solvent evaporation and subsequent pyrolysis under inert conditions. Control samples of Zn nanoparticles on carbon (NG) and a Zn-containing catalyst on carbon with no N doping were also prepared. A detailed preparation procedure is described in the Supporting Information. Preliminary testing of all the different catalysts in the model reaction of styrene epoxide revealed the best results for the ZnN_x@C-700 system (Table S3). This optimal catalyst was characterized by high-resolution transmission electron microscopy (HRTEM) and high-angle annular dark field-scanning transmission electron microscopy (HAADF-STEM). Surprisingly, despite the relatively high metal loading (1.56 wt%), no Zn nanoparticles or clusters were observed. Instead, as shown in Fig. 1a, isolated Zn atoms were finely dispersed on the surface of carbon. N atoms were distributed homogeneously on the surface of the support rather than embedded in the carbon support matrix proved by electron energy loss spectroscopy (EELS) (Fig. 1b). These findings indicate the stabilization of Zn single atoms by coordination with nitrogen. To further determine the electronic structure and chemical property of this Zn-SAC, an EXAFS measurement was performed. As shown in Fig. 1c, the strong peak of *R* space between 1 and 2 Å is due to a Zn-N shell which is different from the Zn-O shell. A small peak in the region of 2–3 Å, which is characteristic for a Zn-Zn shell, is observed, thus confirming the presence of isolated Zn atoms and a small portion of Zn nanoparticles.

The contents of Zn and N on ZnN_x@C-700 were detected as 1.56 wt% and 2.56 wt% measured by ICP-MS and EA, respectively. The composition of this Zn-SAC on N-doped carbon was further investigated by X-ray photoelectron spectroscopy (XPS). As shown in Fig. 1d, three N 1*s* peaks at 397.9, 400.9, and 402.54 eV are assigned to pyridinic (60%), graphitic (24%), and oxidic (15%) nitrogen, respectively. Clearly, these N species are derived from the pyrolysis of Zn-phen complexe. The XPS of Zn shows two peaks at a binding energy of 1022.54 and 1045.64 eV (Fig. S6), corresponding to the $2p_{3/2}$ and $2p_{1/2}$, respectively. Note that the binding energy of Zn $2p_{3/2}$ is higher than the standard of 1022.0 eV for metallic Zn and lower than that of 1023.0 eV for ZnO [65], which again confirms that main species in ZnN_x@C-700 is Zn-N rather than ZnO or metal Zn^0.

The catalytic activity of all the prepared materials was evaluated in the cycloaddition of styrene oxide with CO_2. To improve the general reactivity, all experiments were performed in the presence of 2 mol% of tetrabutyl ammonium bromide (TBAB), which showed little product formation in this benchmark reaction. Hence, control experiments in the absence of Zn catalyst revealed styrene carbonate in 19% yield under neat

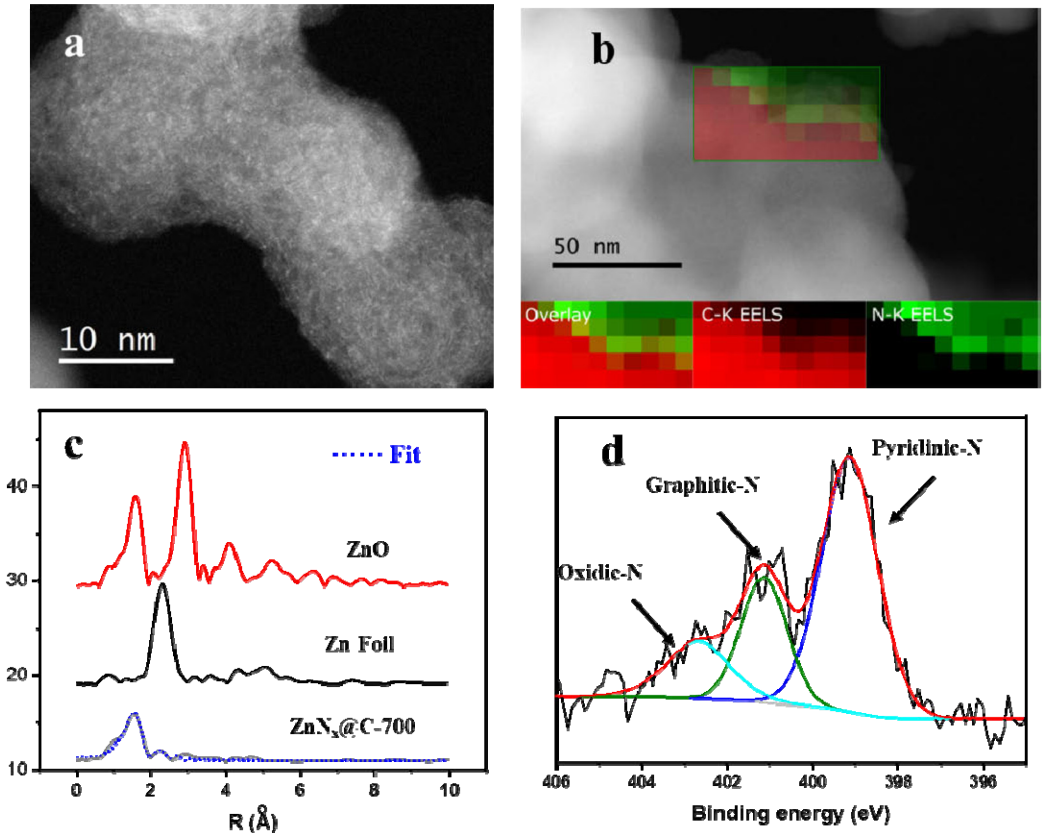


Fig. 1. Characterization for ZnN_x@C-700. (a) HAADF-STEM, (b) EELS of C and N, (c) Zn *K*-edge EXAFS, (d) XPS spectra.

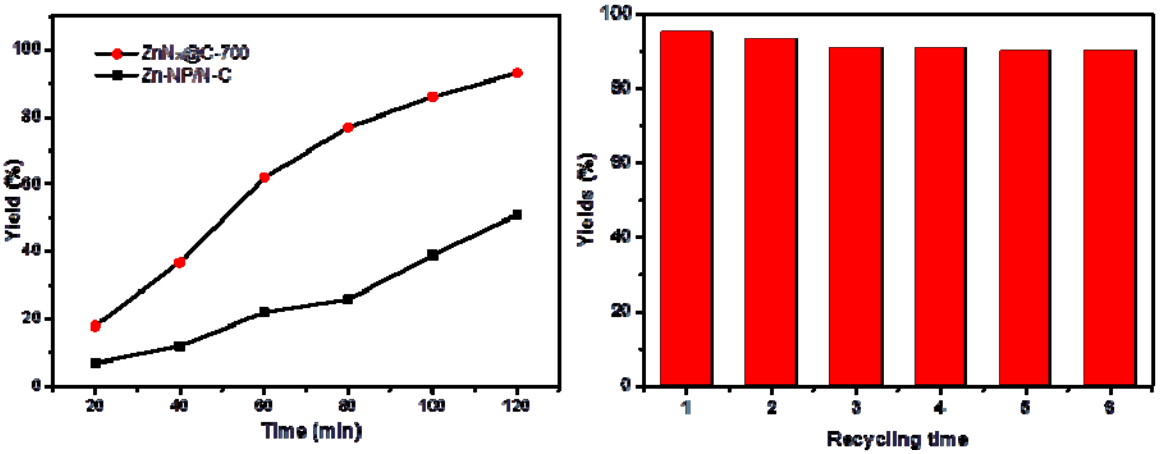


Fig. 2. Reaction of styrene epoxide with CO_2. (a) Time course; (b) Recycling experiments.

condition at 100 °C (Table S3, entry 1). Adding a standard ZnN_x@C catalyst obtained by pyrolysis at 600 °C showed significantly improved activity (70% yield; Table S3, entry 2). To the best of our knowledge, this is the first single atom catalyst that allows for the cycloaddition of epoxides with CO_2. Applying the ZnN_x@C catalyst prepared by pyrolysis at 700 °C exhibited even better activity with the desired product obtained in 93% yield (Table S3, entry 3). In comparison, samples pyrolyzed at higher temperature (800, 900, and 1000 °C) showed lower yields for this transformation (60%–72%, Table S3, entries 4–6). Zn catalysts immobilized on other supports such as SiO_2, MgO, and SiC yielded much lower yields (29%–55%, Table S3, entries 7–10). Notably, Zn nanoparticles supported on carbon gave also lower yield (46%) compared to the single atom catalyst. To compare the reactivity for ZnN_x@C-700 and Zn-NP@N-C appropriately, conversions were measured in detail (Fig. 2a). Under the optimized reaction conditions the Zn single atom catalyst displayed in general better catalytic performance compared to Zn nanoparticles. We assume that this higher activity derives from the better dispersion of the zinc centers on the surface, which activate the epoxide. In addition, basic nitrogen species on the support are favorable to adsorb CO_2 [66].

Obviously, stability and recyclability of a given catalyst are most important parameters for any application in industry. Hence, ZnN_x@C-700 was recycled by centrifugation and reused up to six times (Fig. 2b). To our delight, 90% of **2a** was still achieved at the sixth run. We considered that the loss of the catalyst after washing operation leads to the slightly decreased catalytic activity. This is also confirmed by EXAFS that there is no obvious change of catalyst after reaction, indicating the stability of the catalysts during the reaction (Fig. S7).

Next, the catalytic activity of the Zn-SAC was studied in the presence of different CO_2 concentrations (Table 1). Although no carbonate was detected when the cycloaddition was preceded in air (1 bar), at higher pressure (40 bars) some formation of **2a** is observed, which corresponds to approximately 25% conversion of CO_2 in air. This result showed that the Zn-catalytic system displays certain activity even at very low CO_2 concentration which might be interesting for further applications. Notably, at ambient pressure the desired product was observed at CO_2 concentration of 4000 ppm. In general, at low CO_2 concentrations, the product yields were increased significantly at pressured conditions (results in the parentheses in Table 1). Under gas flow, the yield of **2a** was increased to 31% with increasing the content of the CO_2 to 25 vol%. Even higher activity is seen at CO_2 contents from 50 vol% to 100 vol%, yielding **2a** in 43% and 55%, respectively. The synthesis of carbonate proceeded best at 5 bar and 100 vol% CO_2 leading to an excellent yield (Table S4).

Interestingly, the novel active and stable Zn single atom catalyst (ZnN_x@C-700) displayed also broad scope with simple and functionalized epoxides. As shown in Table 2, under the optimized conditions, various substrates including sensitive derivatives with chloride, bromide and iodine groups were converted to the corresponding cyclic carbonates (Table 2, entries 1–4). Moreover, the cycloaddition of **1e** proceeded well in 95% yield. When oxygen containing substrates were used as starting materials, **2f** and **2g** were obtained in 97% and 95% yields, respectively. Furthermore, when using 100 mmol of **1a** instead of 5 mmol, a 90% yield of **2a** was achieved. This result indicates that the protocol can be scaled up easily.

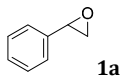
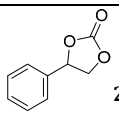
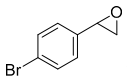
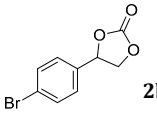
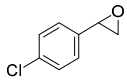
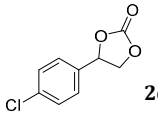
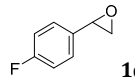
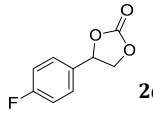
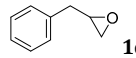
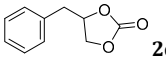
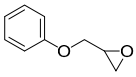
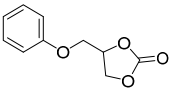
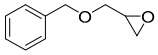
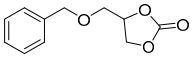
Short chain aliphatic carbonates have been widely applied as solvents, electrolytes, additives, and important intermediates [67]. We then focused on the further investigation of

Table 1
Reaction of styrene epoxide with CO_2 under different CO_2 concentration [a].

Entry	CO_2 concentration (%)	Conversion [b] (%)	Yield [b] (%)
1	0.0400	0 (2)	0 (1)
2	0.4	1 (10)	Trace (9)
3	1	2 (17)	2 (15)
4	5	8 (30)	7 (29)
5	25	32	31
6	50	45	43
7	100	55	55

[a] Reaction conditions: 5 mmol substrates, TBAB (2 mol%), 20 mg catalyst, gas flow, neat condition, 100 °C, 2 h. [b] Detected by GC and the results in parentheses were obtained at 40 bar.

Table 2
Synthesis of cyclic carbonates from arene containing epoxides and CO_2 with ZnN_x@C-700 [a].

Entry	Substrate	Product	Yield [b] (%)
1	 **1a**	 **2a**	93 (90)
2	 **1b**	 **2b**	94
3	 **1c**	 **2c**	90
4	 **1d**	 **2d**	98
5	 **1e**	 **2e**	95
6	 **1f**	 **2f**	97
7	 **1g**	 **2g**	96

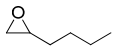
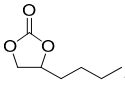
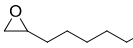
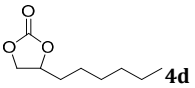
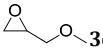
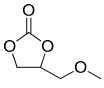
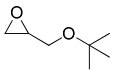
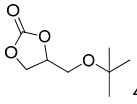
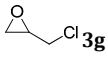
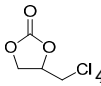
[a] Reaction conditions: 5 mmol substrate, TBAB (2 mol%), 20 mg catalyst, 5 bar CO_2, neat condition, 100 °C, 2 h. [b] Isolated yields. The result in parentheses was obtained at 100 mmol of **1a**.

Zn-SAC on the scope of cross transformation of aliphatic epoxides to a variety of carbonates with different functional groups. Indeed, in the case of the cycloaddition of low and medium chain aliphatic epoxides, higher CO_2 pressure (10 bar) was used to inhibit the evaporation of the low boiling point substrates. For example, propylene oxide, 1-butene oxide, and 1-hexene oxide were converted to the corresponding products in 92%–96% yields (Table 3, **4a**–**4d**). Interestingly, glycidyl methyl ether is transformed into the corresponding carbonates in 91% yield (Table 3, **4e**). However, only 67% yield of cyclic product was achieved in the presence of *tert*-butyl group (Table 3, **4f**). Interestingly, the epichlorohydrin was converted to the corresponding adduct in 97% yield (Table 3, **4g**). For the alkene containing substrates the yields of the corresponding products were obtained in excellent yields (Table 3, **4h**, **4i**, and **4j**). Moreover, **4k** with alkyne group could also be obtained in 88% yield. Cycloaddition of epoxides with steric hindrance groups proceeded smoothly to the carbonates in good to excellent yields (Table 3, **4l**–**4n**). The electron-withdrawing effect of Cl probably leads to the low yield for **4m**. Finally, silicon containing carbonates (Table 3, **4o**–**4q**), which are useful intermediates and are used for the preparation of surfactants, release coatings and lubricants, are obtained by the cycloaddition of corresponding epoxides and CO_2 in the presence of the Zn-SAC.

4. Conclusions

In conclusion, we describe the first heterogeneous single atom Zn catalyst with high metal content, which is synthesized by a simple pyrolysis procedure. The resulting material is used as a heterogeneous catalyst for the cycloaddition of epoxides to carbonates and offers high activity with wide substrate scope

Table 3
Synthesis of cyclic carbonates from aliphatic epoxides and CO_2 with ZnN_x@C-700 [a].

Entry	Substrate	Product	Yield [b] (%)
1	 **3a**	 **4a**	92
2	 **3b**	 **4b**	93
3	 **3c**	 **4c**	96
4	 **3d**	 **4d**	89
5	 **3e**	 **4e**	91
6	 **3f**	 **4f**	65
7	 **3g**	 **4g**	97
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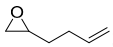
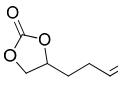
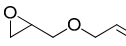
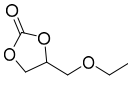
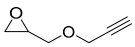
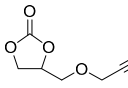
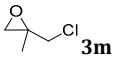
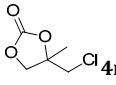
9	 **3i**	 **4i**	93
10	 **3j**	 **4j**	93
11	 **3k**	 **4k**	88
12	 **3l**	 **4l**	90
13	 **3m**	 **4m**	57
14	**3n**	**4n**	93
15	**3o**	**4o**	91
16	**3p**	**4p**	96
17	**3q**	**4q**	97

[a] Reaction conditions: 5 mmol substrates, TBBA (2 mol%), 20 mg catalyst, 5 bar CO_2, neat condition, 100 °C, 2 h. [b] Isolated yields.

and excellent stability. Compared to Zn nanoparticles, the Zn-SAC exhibited the superiority for this transformation. This investigation offers a new approach for the preparation of single atom catalysts and the prepared Zn-SAC may show interesting applications in other areas.

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Graphical Abstract

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Zinc single atoms on N-doped carbon: An efficient and stable catalyst for CO_2 fixation and conversion

Xinjiang Cui, Xingchao Dai, Annette-Enrica Surkus, Kathrin Junge, Carsten Kreyenschulte, Giovanni Agostini, Nils Rockstroh, Matthias Beller*
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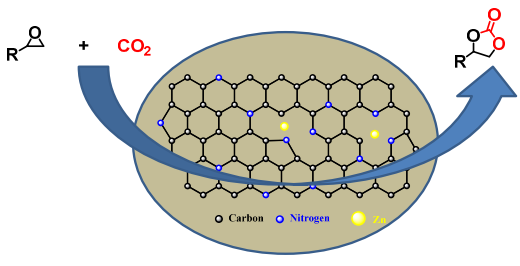
A novel Zn single atom catalyst (Zn-SAC) supported on N-doped carbon material was prepared. The resulting catalyst allows for efficient and general activation of functionalized terminal epoxides to give the corresponding carbonates in high yields.



Single Atom Catalyst

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氮掺杂碳上单原子锌: CO_2固定和转化的高效稳定催化剂

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摘要: 环氧化合物与CO_2环加成反应是环状碳酸酯合成和CO_2利用的一种直接的原子经济方法, 目前主要采用均相金属络合物催化此类转化反应. 本文报道了一种新型多相Zn基催化剂, 它可方便地通过热解活性炭负载的邻菲啰啉络合$Zn(OAc)_2$而得到. 详细的结构表征证实该材料中存在单原子Zn活性位. 与Zn基纳米粒子催化剂相比, 本文制备的单原子Zn催化剂在环氧化物环加成反应中表现出更高的活性和稳定性. 采用该优化的催化剂成功地以高产率得到了一系列碳酸酯, 该催化剂具有较好的基团容忍性.

关键词: 多相催化; 单原子催化剂; 锌; 二氧化碳; 环加成; 碳酸酯

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