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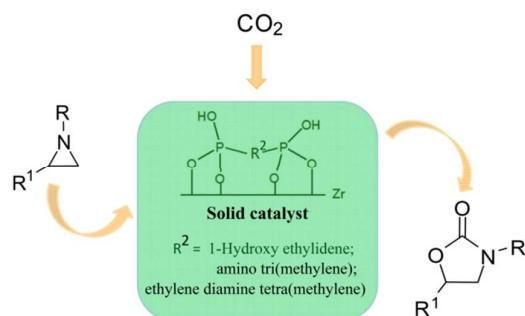
Mesoporous zirconium phosphonates were used as a highly effective catalyst for the heterogeneously catalyzing cycloaddition reaction between aziridines with CO_2.

ARTICLE TYPE

Mesoporous zirconium phosphonates as efficient catalysts for chemical CO₂ fixation

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Mesoporous zirconium phosphonates were demonstrated as a highly effective catalyst for the heterogeneously catalyzing cycloaddition reaction between aziridines with CO₂ to yield oxazolidinones in solvent-free system without introducing any
10 **co-catalysts or halogen species, with outstanding activity and selectivity, as well as excellent recyclability.**
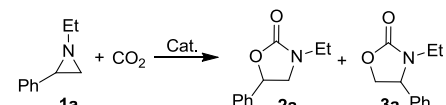
Considering the greenhouse and the depletion of fossil fuels, development of highly efficient methods for chemical fixation of carbon dioxide (CO₂) is one of the urgent and attractive subjects
15 to be investigated. Up to now, various methodologies have been developed to transform CO₂ into useful chemicals,[1-4] of which the utilization of small-membered ring compounds such as epoxides and aziridines to react with CO₂ as a C1 building block is a feasible route. Because of the high reactivity of aziridine that can
20 react with relatively inert CO₂ without its intensive activation, and the importance of the corresponding product oxazolidinones in medicinal chemistry [5-7] and synthetic chemistry,[8-10] many homogeneous catalysts such as alkali metal halide,[11,12] iodine,[13] α-amino acid [14] and tetraalkylammonium salt system [15] have been
25 investigated for the catalytic reaction of aziridine with CO₂, showing rather good activity. However, organic solvents, co-catalysts, stringent synthetic conditions as well as toilsome purification of products were required. Although heterogeneous catalysis may supply an alternative way to solve these problems,
30 the rarely reported heterogeneous catalysts for CO₂ and aziridine cycloaddition reaction, for instance, quaternary ammonium bromide functionalized polyethylene glycol,[16] ZrOCl₂,[17] and pyridinium halide functionalized chitosan,[18] all are halogen-containing as is not environmentally benign, and suffer from
35 gradually lost activity after recycling. It is thus still a challenge to develop efficient and environmentally friendly solid catalysts for chemical CO₂ fixation.

Porous metal phosphonates are promising inorganic-organic hybrids with multifunctionality for potential applications in
40 adsorption, separation, catalysis, energy storage and biology.[19,20] They have significant capability for CO₂ adsorption and intrinsic ion-exchange feature for solid acid-base catalysis.[21-25] However, the use of porous metal phosphonate materials as a catalyst for CO₂ activation is still scarcely reported.[26] In this work, we report
45 for the first time the mesoporous zirconium phosphonates as a highly effective catalyst for the heterogeneously catalyzing cycloaddition reaction between aziridines with CO₂ to yield oxazolidinones in solvent-free system without introducing any

co-catalysts or halogen species, under mild conditions.
50 Mesoporous zirconium organophosphonates were synthesized by using 1-hydroxyethylidene-1,1'-diphosphonic acid (HEDP), amino tri(methylene phosphonic acid) (ATMP) and sodium salt of ethylene diamine tetra(methylene phosphonic acid) (EDTMPS) as the coupling molecules in the presence of surfactant
55 cetyltrimethyl ammonium bromide (see ESI†). After removal of surfactant species in the pore structures by extraction in acidic ethanol solution,[25] the obtained materials were designated as ZrHEDP, ZrATMP and ZrEDTMPS, and their textural properties are listed in Table S1 (see ESI†). In a 25 mL autoclave reactor
60 equipped with a magnetic stirrer, aziridine (1 mmol, synthesized according to the published procedure [16,17,27]) and the mesoporous zirconium phosphonate catalyst were first charged into the reactor. Then CO₂ was introduced into the autoclave, followed by stirring at predetermined temperature for 5 min to reach the equilibration.
65 The pressure was adjusted to the desired pressure and the mixture was stirred continuously for certain time. After the reaction was completed, the reactor was cooled in ice water and CO₂ was ejected slowly. An aliquot of sample was taken from the resultant mixture and dissolved in dry CH₂Cl₂ with the addition of
70 biphenyl as an internal standard for GC analysis. The residue was purified by column chromatography on silica gel (200–300 mesh, eluting with 8:1 to 1:1 petroleum ether/ethyl acetate) to provide the desired products. The products were further identified by ¹H NMR, ¹³C NMR and MS (see ESI†), being in good agreement
75 with the assigned structures and consistent with those reported in the literature [16,17,27] for known compounds.

Table 1. Cycloaddition reaction of CO₂ with aziridine into oxazolidinones under various catalysts [a].

Entry	Catalyst	Conv. (%)	Yield [b] (%)	Regio-sel. [c]	CO₂ uptake (mmol/g)	
					0 ℃	25 ℃
1 [d]	–	37	27	95:5	-	-
2	ZrHEDP	98	85	96:4	0.94	0.83
3	ZrATMP	>99	79	95:5	1.31	1.13
4	ZrEDTMPS	>99	90	90:10	1.15	1.05

80 [a] Reaction conditions: **1a**, 1 mmol; catalyst loading (based on metal centre), 2.5 mol%; CO₂ pressure, 3 MPa; 120 °C; 6 h. [b] Total yield of **2a** and **3a** determined by GC using biphenyl as an internal standard. [c] Molar ratio of **2a** to **3a**. [d] Ref. [28], under pressure 3.5 MPa at 120 °C for 10 h.

In the preliminary study, the cycloaddition of 1-ethyl-2-phenylaziridine (**1a**) with CO_2 catalyzed by various catalysts (Table 1, entries 2-5) was carried out at 120 °C and 3 MPa CO_2 pressure for 6 h in solvent-free system. ZrHEDP, ZrATMP and ZrEDTMPS gave high yield of 79% – 90% for **2a**+**3a** with rather excellent selectivity (90% - 96%) to desired product (**2a/3a**), showing a much higher yield than that obtained without catalyst carried out at 120 °C under 3.5 MPa CO_2 pressure for 10 h (Table 1, entry 1).[28] The high yields and excellent selectivity catalyzed by mesoporous zirconium phosphonates were comparable to the quaternary ammonium bromide functionalized polyethylene glycol [16] and $ZrOCl_2$,[17] under much lower pressure. Among those catalysts, ZrHEDP exhibited relatively higher regioselectivity. Hence, as below we would take ZrHEDP as a representative to investigate the influences of temperature, pressure, reaction time and catalyst loading on the cycloaddition of 1-ethyl-2-phenylaziridine with CO_2, as well as the recyclability of mesoporous zirconium organophosphonate catalysts.

Table 2. Cycloaddition reaction of CO_2 with aziridine into oxazolidinones under various reaction conditions with ZrHEDP as solid catalyst [a].

Entry	Catalyst loading (mol%)	Temp. (°C)	Pressure (MPa)	Time (h)	Conv. (%)	Yield [b] (%)	Regio-sel. [c]
1	2.5	120	3	6	>99	85	96:4
2	2.5	100	3	6	97	89	97:3
3	2.5	80	3	6	84	62	97:3
4	2.5	60	3	6	27	2	-
5	2.5	100	6	6	>99	89	97:3
6	2.5	100	2	6	>99	85	98:2
7	2.5	100	1	6	93	64	99:1
8	2.5	100	2	8	94	89	98:2
9	2.5	100	2	10	98	89	98:2
10	5	100	2	8	97	96	98:2

[a] Reaction conditions: **1a**, 1 mmol. [b] Total yield of **2a** and **3a** determined by GC using biphenyl as an internal standard. [c] Molar ratio of **2a** to **3a**.

The carboxylation of 1-ethyl-2-phenylaziridine (**1a**) with CO_2 catalyzed by ZrHEDP under various reaction conditions were shown in Table 2. When the temperature was over 120 °C, 85% yield of **2a**+**3a** was attained with a conversion > 99% (Table 2, entry 1). An increase in the yield was observed by the decrease in the reaction temperature to 100 °C. Whereas a further decrease of the reaction temperature resulted in a drop of the yield and almost no activity could be obtained at 60 °C (Table 2, entries 2-4). Clearly, the reaction temperature 100 °C was optimal for this reaction. Interestingly, the yield of **2a**+**3a** and the selectivity for **2a** to **3a** obtained under 6 MPa were the same to that obtained at 3 MPa, and no remarkable decrease in yield was found when the pressure was reduced to 2 MPa. Probably because of the CO_2 diluting effect, the higher pressure did not improve much on the yield.[28,29] Further decreasing the reaction pressure to 1 MPa, only a 64% yield was gained (Table 2, entries 5-7). While, a properly prolonged reaction time from 6 to 8 h gave an increase in yield from 85% to 89% (Table 1, entry 6 and 8) and kept constant after 10 h (Table 2, entry 9). In addition, when doubled the catalyst content, the yield was increased to 96 % (Table 2, entry 10). Therefore, the preferable reaction conditions herein should be over 100 °C under 2 MPa CO_2 pressure with catalyst loading 5 mol% for 8 h.

Another advantage of this approach could be related to the heterogeneous catalytic process under solvent-free conditions

without any co-catalysts. Also, the catalyst recycling process was investigated. The catalyst was easily recovered from the reaction mixture by filtration, and reused for the next run after washing with a large amount of CH_2Cl_2 and drying at 60 °C for 6 h in vacuum. As shown in Table 3, the catalyst can be reused for five times without significant loss in catalytic activity. The elemental analysis showed that P/Zr molar ratio was 3.31 for the freshly prepared ZrHEDP and it slightly decreased to 3.05 after five-time recycling. The mesopore ordering of the used ZrHEDP was a little deteriorated, as revealed by the slightly broadened diffraction peaks (Figure S2, ESI†), but the mesoporosity of the catalyst was still retained well with considerable specific surface area (Figure S3 and Table S1, ESI†). Hence, the excellent recyclability of the catalyst was ascribed to its stable skeletal composition and well maintenance of mesoporosity as well as high specific surface area.

Table 3. Catalyst recyclability [a]

Run	Conv. (%)	Yield [b] (%)	Regio-sel. [c]
1	>99	94	98:2
2	>99	97	98:2
3	>99	93	96:4
4	>99	95	95:5
5	>99	92	93:7

[a] Reaction conditions: **1a**, 1 mmol; catalyst, ZrHEDP, 5 mol% for the first time. [b] Total yield of **2a** and **3a** determined by GC using biphenyl as an internal standard. [c] Molar ratio of **2a** to **3a**.

In order to evaluate the generality and utility of mesoporous zirconium phosphonates as solid catalyst for chemical CO_2 fixation with aziridines, the reactions of other various aziridines with CO_2 were catalyzed by ZrHEDP as a representative. The results are summarized in Table 4. Under the optimized reaction conditions, ZrHEDP was found to be applicable to a variety of aziridines, providing the corresponding oxazolidinones in a high yield and excellent selectivity (Table 4, entries 1-5). 1-Ethyl-2-phenylaziridine was found to be the most reactive aziridine because of the relatively low steric hindrance of ethyl group bearing on the nitrogen atom, while 1-ethyl-2-(4-chlorophenyl)-aziridine exhibited the relatively low activity among the aziridines tested, which may be attributed to the presence of electro-donating methyl group on benzene ring compared to the electro-withdrawing chloride group.

Table 4. Substrate scope [a]

Entry	R, R^1	Conv. (%)	Yield [b] (%)	Regio-sel. [c]
1	Et, Ph	97	96	98:2
2	n-Pr, Ph	86	75	93:7
3	n-Bu, Ph	>99	89	98:2
4	Et, p-Cl-Ph	94	81	96:4
5	Et, p-Me-Ph	>99	60	96:4

[a] Reaction conditions: Aziridine, 1 mmol; ZrHEDP (based on metal centre), 5 mol%; CO_2 pressure, 2 MPa; 100 °C; 8 h. [b] Total yield of **2** and **3** determined by GC. [c] Molar ratio of **2** to **3**.

In order to understand the present catalysis, the CO_2 adsorption behavior for ZrHEDP, ZrATMP and ZrEDTMPS were measured at 0 and 25 °C (Figure S4, ESI†), and their corresponding CO_2

capture capacities are summarized in Table 1. The CO_2 uptake for these three materials are close to each other, which was in the range of 0.94 – 1.15 mmol/g measured at 0 ℃ and 0.83 – 1.13 mmol/g at 25 ℃. It was reported that the introduction of polar groups such as sulphonate, -COOH, -OH and N-contained basic sites was favorable for increasing the CO_2 adsorption capability and selectivity.[30-34] Therefore, the CO_2 adsorption capability for ZrHEDP, ZrATMP and ZrEDTMPS should come from the polar surface of zirconium phosphonate network interacted with CO_2, such as the CO_2-philic species like -OH groups connected with carbon on HEDP or N-contained moieties on ATMP and EDTMPS in the hybrid network.

Although in the initial preparation of ZrHEDP, $ZrOCl_2$ and CTAB were used as zirconium source and surfactant template which contained chloride and bromide respectively, and ethanol/HCl solution was used to extract the involved surfactant, no Cl^- or Br^- was detected in the final product, as evidenced by the XPS (Figure S5, ESI†). Therefore, the reaction mechanism catalyzed by ZrHEDP should be different from that described for $ZrOCl_2$.[17] Also, it would be different from the reported halide-contained proticonium salts by the activation of aziridine through the formation of hydrogen bonding with the assistance of halide to stabilize the activated carbamate.[27] Actually, the reaction mechanism for mesoporous zirconium organophosphonates was not clear at this stage. However, in considering the acidic property of mesoporous ZrHEDP hybrid framework offered by P-OH species resided on the zirconium organophosphonate framework,[25] which probably tended to form hydrogen-bond with N-contained aziridine, and the CO_2 adsorption capability of mesoporous zirconium organophosphonate materials discussed above, a plausible route could be proposed by taking ZrHEDP as an example via a cooperative way depicted in Scheme S2 (ESI†). Firstly, the proton from $-PO^-H^+$ species on the zirconium phosphonate surface is coordinated with the nitrogen of the aziridine through a hydrogen bond, resulting in the activation of aziridine molecules. In parallel, an activated CO_2 was achieved through the electrostatic force between the hydroxyl groups connected to organic moieties and the CO_2 molecules adsorbed onto the pore surface. Then, nucleophilic attack of the activated CO_2 on the active aziridine produces the carbamate. Finally, oxazolidinone is formed by subsequent intramolecular ring-closure and the catalyst is regenerated.

In summary, mesoporous zirconium phosphonates (ZrHEDP, ZrATMP and ZrEDTMPS) have been demonstrated as a new type of chemical CO_2 fixation catalysts, serving as efficient heterogeneous solid to catalyze the cyclization of aziridines with green and sustainable CO_2 as C1 building block under mild conditions without using co-catalysts and solvents. The whole process is non-halogen-contained, economic, safe and environmentally benign, along with the high yields (60% – 96%), excellent regio-selectivity (93% – 98%) and good recyclability for the reactions of various aziridines with CO_2. Even though the reaction mechanism is not totally clear yet at this stage, the cooperative interaction of the catalyst with substrate and CO_2 might be the key step. It is expected that these mesoporous metal phosphonate multifunctional materials may be useful in other reactions for chemical CO_2 fixation, suggesting their significance in CO_2 capture and conversion.

Notes and references

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† Electronic Supplementary Information (ESI) available: [Catalyst preparation and characterization, CO_2 adsorption, reaction mechanism]. See DOI: 10.1039/b000000x/

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