

A single-site hydroxyapatite-bound zinc catalyst for highly efficient chemical fixation of carbon dioxide with epoxides†

Kohsuke Mori, Yohei Mitani, Takayoshi Hara, Tomoo Mizugaki, Kohki Ebitani and Kiyotomi Kaneda*

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A zinc-based hydroxyapatite catalyst in conjunction with a Lewis base proved to be efficient for the coupling of CO₂ and epoxide in the absence of additional organic solvents under an atmospheric CO₂ pressure; the work-up procedure is straightforward and the catalyst could be reused without loss of catalytic activity and selectivity.

In order to avoid greenhouse effects, much effort has been devoted to reduce the amount of carbon dioxide (CO₂) that is released from industry. The chemical fixation of CO₂ into synthetically beneficial compounds is of great interests in terms of “green and sustainable chemistry” because CO₂ can be considered as an inexpensive, nontoxic, and abundant C₁ feedstock.¹ One of the most powerful approaches is the coupling of CO₂ and epoxides to provide five-membered cyclic carbonates with 100% atom efficiency, which are predominantly utilized for the production of engineering plastics as well as for the synthesis of pharmaceuticals and fine chemicals.² With the goal of improving the reaction, a variety of catalytic systems have been developed. Homogeneous transition metal complexes in combination with a Lewis base have proven to be efficient catalyst systems,³ but their utility is often limited by difficulties in catalyst separation and recovery. On the other hand, only a few reports exist on heterogeneous catalysts, e.g., MgO,⁴ Mg–Al mixed oxide,⁵ (PVP)ZnBr₂,⁶ and solid bases;⁷ unfortunately, they usually require a high catalyst concentration, an additional co-solvent, and high CO₂ pressures.‡

We have recently presented a new strategy for the design of nanostructured heterogeneous catalysts based on the desirable properties of hydroxyapatite (HAP).⁸ Various transition metals, which have high potential for functioning as the catalytically active centers, can be readily accommodated into the apatite framework to generate stable monomeric phosphate complexes. Herein we report the synthesis of a hydroxyapatite-bound zinc complex (ZnHAP) possessing robust stability and describe its unprecedented catalysis of the chemical fixation of CO₂ onto epoxides in the presence of a Lewis base as a co-catalyst. In addition to the advantages of a simple work-up procedure and the ability to recycle the catalyst, the present catalytic system has successfully overcome the previously mentioned drawbacks.

Using this approach, numerous metal cation-exchanged HAPs were synthesized by treatment of stoichiometric HAP, Ca₁₀(PO₄)₆(OH)₂, with an aqueous solution of the corresponding metal ions at room temperature for 24 h.^{8a} In this way, the ZnHAP was obtained from Zn(NO₃)₂·6H₂O as a white powder

(Zn content: 0.3 mmol g⁻¹). The XPS spectra of the ZnHAP and ZnO showed identical binding energy values of 1021.5 and 1021.4 eV for Zn 2p_{3/2}, respectively. The edge position of the Zn K-edge XANES spectra of the ZnHAP was also comparable with that of ZnO. It is clear that the Zn species in the ZnHAP exist in a tetrahedral geometry having a +2 oxidation state.⁹ The lack of peaks assignable to the Zn–O–Zn bond in the Fourier transform of the *k*³-weighted Zn K-edge EXAFS spectrum, which was detected for ZnO at around 2.8 Å, showed that the Zn species is monomeric ((a) vs. (b) in Fig. 1A). The curve-fitting analysis for the inverse FT of the main peaks revealed the existence of a Zn–O bond having an interatomic distance and coordination number of 1.88 Å and 4.0, respectively. The Zn–O distance was slightly shorter than the values of 1.99 Å in ZnO¹⁰ and 1.95 Å in bis(salicylaldimin) Zn^{II} complex,¹¹ indicating that the interaction between Zn and O atoms in the ZnHAP might be stronger due to structural contraction around the Zn species.¹⁰ The above results demonstrate the creation of a monomeric Zn^{II} phosphate complex surrounded by four oxygen atoms in tetrahedral coordination on the surface of the HAP, as illustrated in Fig. 1B.

The coupling of styrene oxide and CO₂ using several cation-exchanged HAPs proceeded in the presence of Lewis base co-catalysts under a CO₂ pressure of 5 atm at 100 °C, as summarized in Table 1. The ZnHAP has proved to be the best catalyst among all those examined, affording the corresponding carbonate in 98% yield with >99% selectivity (entry 1). It is notable that both the ZnHAP and Lewis base were indispensable components for attaining high carbonate yields (entry 1 vs. entries 12 and 13). The choice of Lewis base has a crucial influence on the efficiency of

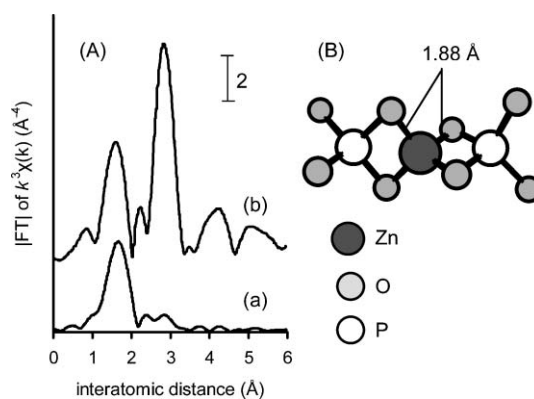
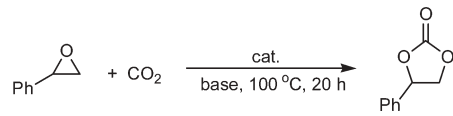


Fig. 1 (A) Fourier transform of *k*³-weighted Zn K-edge EXAFS spectra for (a) ZnHAP and (b) ZnO. (B) Proposed surface structure around Zn²⁺ in the ZnHAP. The nearest oxygen and phosphorus atoms are shown.

† Electronic supplementary information (ESI) available: experimental details. See <http://www.rsc.org/suppdata/cc/b5/b502636a/index.sht>
*kaneda@cheng.es.osaka-u.ac.jp

Table 1 Coupling of styrene oxide and CO₂ by various HAP catalyts^a


Entry	Catalyst	Metal (mol%)	Base	Solvent	Yield (%) ^b
1	ZnHAP	0.3	TEA	—	98
2	CuHAP	0.3	TEA	—	60
3	AlHAP	0.3	TEA	—	50
4	CoHAP	0.3	TEA	—	21
5	CrHAP	0.3	TEA	—	19
6	ZnHAP	0.15	DMAP	—	79
7	ZnHAP	0.15	TEA	—	62
8	ZnHAP	0.15	DBU	—	60
9	ZnHAP	0.15	Pyridine	—	57
10 ^c	ZnHAP	0.15	TEA	DMF	29
11 ^c	ZnHAP	0.15	TEA	CH ₂ Cl ₂	5
12	—	0.15	DMAP	—	12
13	ZnHAP	0.15	—	—	trace

^a Reaction conditions: catalyst (0.05–0.1 g), styrene oxide (10 mmol), base (4 equiv. relative to catalyst metal), CO₂ (5 atm), 100 °C, 20 h.


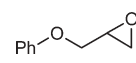
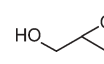
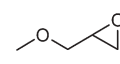

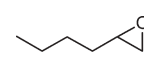
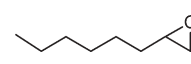
^b Determined by GC using an internal standard technique. ^c Solvent (5 mL).

the coupling reaction; 4-(dimethylamino)pyridine (DMAP) gave the best result (entry 6). Other bases such as triethylamine (TEA), 1,8-diazabicyclo[5.4.0]-7-undecene (DBU), and pyridine were slightly less effective (entries 7–9). Interestingly, the ZnHAP exhibited superior activity under solvent-free conditions, whereas the use of organic solvents led to a significant decrease in the catalytic activity (entries 10 and 11).

The work-up procedure is reasonably simple due to heterogeneous catalysis under solvent-free conditions. The product is automatically separated by filtration of the ZnHAP and then the spent catalyst can be reused without any loss in catalytic performance; yields of over 95% and selectivities of almost 100% could be attained for the three recycling experiments of styrene oxide with CO₂. ICP analysis of the filtrate confirmed that the Zn content was below the detection limit. More significantly, the recovered ZnHAP catalyst maintained its original monomeric Zn²⁺ structure as proved by XAFS analysis, suggesting that the Zn center is not only catalytically active but also extremely durable under the present reaction conditions.

As can be seen from Table 2, a variety of terminal epoxides possessing aromatic, aliphatic, and both electron-donating and -withdrawing substituents were successfully converted into the corresponding cyclic carbonates in excellent yields. In all cases, the selectivities were almost 100% without the formation of the corresponding diols and polycarbonates. The present catalytic system is also highly suitable for large-scale operations. For example, a 100 mmol scale reaction of epichlorohydrin provided 4-(chloromethyl)-1,3-dioxolan-2-one in 90% yield within 24 h (entry 1). It is noteworthy that the coupling reaction could be performed even under an atmospheric CO₂ pressure, giving a remarkably high TON of up to 28 600 with a TOF of approximately 1100 h⁻¹ (entry 2). These values for epichlorohydrin are considerably higher than those of analogous binary catalyst systems comprising a metal complex and a Lewis base under high CO₂ pressures, such as salen-Cr^{III} (50 psig, TON and TOF, 98 and 65 h⁻¹),^{3b} binaphthyldiamino salen-Zn^{II} (500 psi,

Table 2 Coupling of epoxides and CO₂ catalyzed by the ZnHAP^a

Entry	Epoxide	Zn (mol%)	Yield (%) ^b	TON
1		0.003	90	30 000
2 ^c		86	28 600	
3 ^d		0.003	95	31 600
4 ^{c,d}			90	30 000
5 ^e		0.006	96	16 000
6 ^{c,e}			84	14 000
7 ^e		0.006	95	15 800
8 ^{f,g}		0.012	89	7400
9 ^f		0.012	86	7100
10 ^f		0.012	81	6700

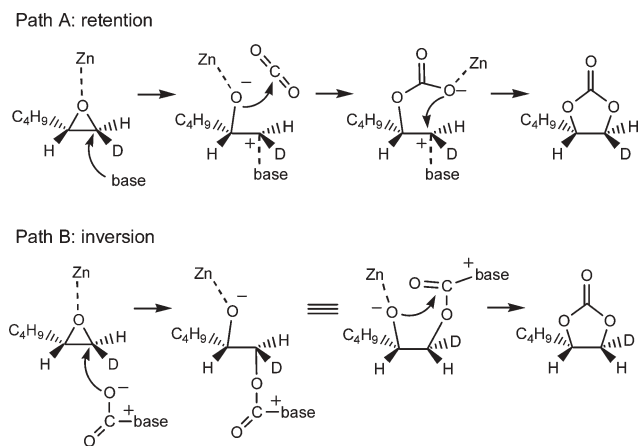
^a Reaction conditions: ZnHAP (0.01 g, Zn: 0.003 mmol), epoxide (100 mmol), DMAP (0.02 mmol), CO₂ (10 atm), 100 °C, 24 h.

^b Determined by GC using an internal standard technique. ^c CO₂ (1 atm). ^d DMF (5 mL) was used as solvent due to the solid nature of product. ^e Epoxide (50 mmol). ^f Epoxide (25 mmol). ^g 130 °C.

100, 6 h⁻¹),^{3c} and Co^{III}-porphyrin (300 psig, 250, 250 h⁻¹).^{3e} Furthermore, the ZnHAP-catalyzed coupling reactions proceeded exclusively with retention of the configuration of epoxides; the reactions of enantiomerically pure (*R*)- and (*S*)-benzyl glycidyl ethers with CO₂ yielded (*R*)- and (*S*)-4-(benzyloxymethyl)-1,3-dioxolan-2-one in 82% and 84% chemical yields with over 99% *ee*, respectively.

We propose here a possible catalytic cycle of the ZnHAP in consideration of the reaction mechanism for the binaphthyldiamino salen-Zn^{II} complex system.^{3c} The coupling reaction proceeds through effective cooperation between the ZnHAP and the Lewis base; the former activates the epoxide as a Lewis acid, while the latter attacks the less sterically hindered carbon atom to open the epoxide ring. The generated oxy anion species then reacts with CO₂ to give the corresponding cyclic carbonate (Path A in Scheme 1). The above mechanism can be well evidenced by the reaction of *trans*-1-deuterio-1,2-hexene oxide with CO₂, in which the corresponding *trans*-1-deuterio-1,2-hexene carbonate was formed in 82% selectivity.¶ The minor formation of the *cis*-isomer cannot rule out participation of the activated CO₂ by Lewis base, *i.e.* zwitterion [R₃N⁺C(O)O⁻], in the ring opening step of epoxide (Path B in Scheme 1).¹²

In summary, the combination of the ZnHAP and Lewis base has been developed as an extremely active and versatile catalyst system for the coupling of epoxides and CO₂. Our protocol can be considered as environmentally-benign due to the following attractive features: (i) high activity and selectivity under mild reaction conditions, (ii) additional organic solvents are unnecessary, and (iii) the simple work-up procedure and ability to recycle the solid catalyst. We are continuing to design nanostructured



Scheme 1

hydroxyapatite catalysts with the aim of realizing simple and clean organic synthesis including asymmetric catalysis.

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Kohsuke Mori, Yohei Mitani, Takayoshi Hara, Tomoo Mizugaki, Kohki Ebitani and Kiyotomi Kaneda*

Department of Materials Engineering Science, Graduate School of Engineering Science, Osaka University, 1-3 Machikaneyama, Toyonaka, Osaka 560-8531, Japan. E-mail: kaneda@cheng.es.osaka-u.ac.jp; Fax: +81-6-6850-6260; Tel: +81-6-6850-6260

Notes and references

‡ For example, Mg–Al mixed oxide requires a substantial amount of co-solvent (85% v/v DMF) and a very high catalyst loading of 1.8 g catalyst per g of substrate under a CO₂ pressure of 5 atm.

§ The reaction of cyclic epoxides such as cyclohexene oxide gave a mixture of the corresponding carbonate and polycarbonates.

¶ We think that the high *trans* selectivity is attributable to the steric hindrance imposed by the solid surface, which severely limits the C₁–C₂ rotation of the epoxide in formation of the *cis*-isomer.

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