NJC

PAPER

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Cite this: DOI: 10.1039/c9nj05831a

Lanthanide clusters as highly efficient catalysts regarding carbon dioxide activation⁺

A series of tetranuclear lanthanide clusters supported by organic ligands ($[Ln_4L_6(NO_3)_4]$ -4(MeCN), Ln = La,

catalytic system also displays a wide substrate scope and high catalytic activity. Unfortunately, the

catalytic efficiency of the catalysts for some sterically hindered reaction substrates is not very satisfactory.

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Nd, Sm) has been synthesized and characterized. The Lewis acidic Ln^{3+} sites were investigated as highly Received 22nd November 2019, Accepted 19th February 2020 efficient catalysts regarding CO₂ activation. The clusters showed significant thermal stability after 4 reaction cycles of CO₂ insertion into epoxides to form cyclic carbonates, with TOF up to 6700 h^{-1} . The

DOI: 10.1039/c9nj05831a

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Introduction

Crystalline lanthanide clusters are one of the most promising classes of inorganic-organic hybrid materials.¹ Besides their high structural diversity, they have shown interesting physical and chemical properties in the fields of luminescence, magnetism and catalysis.² Most of these applications benefit from the unique f-orbitals of rare earth ions compared with transition metal ions. On the other hand, with the use of fossil fuels, a large amount of greenhouse gas carbon dioxide (CO_2) was released, which has been considered the main cause of global warming.³ However CO₂ can also be regarded as an environmentally friendly C1 reagent, compared to toxic chemicals like carbon monoxide, isocyanates or phosgene.⁴ The chemical fixation of CO₂ into the value-added chemical reagent cyclic carbonate is among the most significant topics in green and sustainable chemistry. To date, numerous nanomaterials and metal-organic frameworks have been synthesized and applied in the reaction between epoxides and CO2 to obtain cycle carbonates with good results.⁵ However, in many cases, the inner catalytic sites of these materials cannot be exposed to the substrates. Thus, they usually require more catalyst and relatively harsh reaction conditions to accomplish the conversion.

Lanthanide clusters have preliminarily shown high efficiency regarding CO_2 capture. Tang *et al.* reported the fixation of CO_2 with tetranuclear lanthanide clusters.⁶ Our group has developed a pair of chiral heptameric lanthanide clusters, which are

La³⁺ HN La ČC.

Scheme 1 Self-assembly of lanthanide clusters 1-3 (N blue, O red).

self-assembled with the aid of CO32- ions derived from atmospheric CO₂.⁷ However, further activation of CO₂ with lanthanide clusters is still relatively rare. As isolated molecules, multiple Ln³⁺ sites with strong Lewis acidity are able to be sufficiently exposed to the substrates. Thus, the generation and study of functional lanthanide clusters with novel structures has become very attractive in the field of contemporary materials research.

Triggered by the structural diversity and abundance of Schiff base ligands, we designed and synthesized a series of novel tetranuclear lanthanide clusters supported by hydrazide Schiff base ligands ($[Ln_4L_6(NO_3)_4]$ ·4(MeCN), Ln = La, Nd, Sm; Scheme 1). These clusters were isolated by introducing Ln(NO₃)₃·6H₂O into the acetonitrile and methanol mixed solutions (1:2) of H₃L, with the existence of a certain amount of triethylamine. Satisfyingly, these clusters serve as high-efficiency catalysts in the cycloaddition of epoxides and CO2 to obtain cyclic carbonates under mild conditions.

Results and discussion

Complexes 1-3 (complex 1: $[La_4L_6(NO_3)_4] \cdot 4(MeCN)$; complex 2: $[Nd_4L_6(NO_3)_4] \cdot 4(MeCN);$ complex 3: $[Sm_4L_6(NO_3)_4] \cdot 4(MeCN))$ are isostructural, featuring a tetranuclear structure. Cluster 1



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[†] Electronic supplementary information (ESI) available: Experimental section, characterization and ¹H NMR spectra of the substrates and products. CCDC 1922297, 1922298 and 1922299. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c9nj05831a

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was selected as a representative model for discussion, as shown in Fig. 1b. The asymmetric unit of complex **1** consists of a La₂ core with different coordination modes. The La1 center is ninecoordinated with [LaO₇N₂] environment in the shape of Tri-hat triangular prism, while the La2 center has [LaO₈N] environment in the shape of Tri-hat triangular prism. La1 and La2 are connected *via* three μ_2 -O, which are derived from three ligands. Two La₂ cores are further connected by two ligands to form the La₄ cluster. In addition, La1 and La2 each have one NO₃⁻ involved in coordination. The single crystal structure analysis revealed that complexes **1**–3 have potential catalytic sites for the coupling of epoxides with CO₂ to form cyclic carbonates.

Nitrate ions are involved in the coordination of the three complexes, and the steric hindrance opposite the coordination direction of the NO₃⁻ is weak, which provides a guarantee for the oxygen in the epoxy compounds to participate in the coordination to Ln³⁺.⁸ In order to determine which of the three compounds has the best catalytic performance, we started from the reaction between styrene oxide and CO_2 . 3.5 mg of 1, 2 and 3, respectively, and 0.075 mol% of TBAB as the co-catalyst were used for the reaction to obtain cyclic carbonate in solvent-free conditions at 120 °C and 1 MPa. After reacting for 1.5 h, the three catalysts show different behavior, which is reflected by the conversion and selectivity (75%, 85% and 96%, respectively) and TOF (5076 h^{-1} , 5753 h^{-1} and 6497 h^{-1} , respectively). Since 3 showed the best catalytic activity, we chose 3 as a representative catalyst to further investigate the reactions. Then, the effects of different co-catalysts were tested on this reaction, where TBAB showed the best catalytic performance (Fig. 2a). At the same time, we also explored the corresponding change in reaction conversion when the amount of TBAB is changed. From Fig. 2b, the conversion of the product increased with the increase of TBAB dosage (0 mol%, 0.25 mol%, 0.5 mol%, 0.75 mol% and 1 mol%, respectively). The catalyst also showed excellent catalytic activity when the amount of catalyst 3 was gradually increased from 0.0025 mol% to 0.015 mol% with 0.75 mol% TBAB, with the highest initial TOF up to 6700 h^{-1} (Fig. 2c). When the content of the catalyst is above 0.01 mol%, the increase in the catalyst content is not very significant for the reaction conversion, so it is necessary to select 0.01 mol% as the catalyst amount. Reactions at different temperatures (Fig. 2d) showed outstanding catalytic activity with 0.01 mol% catalyst 3, and the TOF was up to 6497 h^{-1} at 120 °C.



Fig. 1 (a) Structural formula of the ligand with potential multicoordination sites capturing metal ions; (b) molecular structure of complex 1 (hydrogen atoms and solvent molecules are omitted for clarity).



Fig. 2 The conversion of cyclocarbonate under different reaction conditions. Reaction conditions: (a) 10 mmol styrene oxide, 0.01 mol% catalyst, 0.75 mol% co-catalyst, 120 °C, 1.5 h, 1 MPa CO₂; (b) 10 mmol styrene oxide, 0.01 mol% catalyst, 0–1 mol% TBAB, 120 °C, 1.5 h, 1 MPa CO₂; (c) 10 mmol styrene oxide, 0–0.0125 mol% catalyst, 0.75 mol% TBAB as the co-catalyst, 120 °C, 1.5 h, 1 MPa CO₂; (d) 10 mmol styrene oxide, 0.01 mol% catalyst, 0.75 mol% TBAB as the co-catalyst, 60–140 °C, 1.5 h, 1 MPa CO₂.

Subsequently, the catalyst was utilized for cycloaddition of CO_2 with a range of different epoxides and the results are summarized in Table 1. The epoxides were converted to their corresponding cyclic carbonates with high selectivity and conversion due to the good catalytic activity of the catalyst. There are two main important factors which affect this reaction, namely the steric effect of the reaction substrate and the electronic effect of substituent groups in the reaction substrate.9 The steric effect of the epoxide plays a predominant role in this reaction. The activities are higher when the steric effect is decreased.¹⁰ Conversions are up to 99% for the epoxides with weak steric hindrance, such as propylene oxide, butylene oxide and epoxy chloropropane (Table 1, entries 1, 2 and 4).¹¹ Due to steric hindrance, the cyclic carbonate conversion and selectivity of the internal epoxides (cyclohexene oxide and cyclopentene oxide) and 1,2-epoxyhexane were very low (Table 1, entries 3, 12 and 13).12 The electronwithdrawing effects of the substituents of epoxy chloropropane, epibromohydrin and glycidol (Table 1, entries 4, 5 and 10) favour nucleophilic attack of Br⁻, which affords the conversion of 99% epoxy carbonate under the investigated reaction conditions.13 Similarly, the better activity of t-butyl glycidyl ether and 1-allyloxy-2,3-epoxypropane (Table 1, entries 8 and 9) may be related to the oxygen atom in the molecule. The oxygen atom in an epoxy compound can strongly attract the electron clouds of neighboring groups due to its high electronegativity, which leads to the easier attack of its neighboring epoxide by a nucleophilic agent. Thus, the existence of O can facilitate the ring opening of epoxide and improve the reaction rate.¹⁴

Furthermore, the recycling of the rare earth catalyst was investigated by using epoxypropane as a representative substrate. After completion of the reaction, the catalyst was easily recovered by centrifuging at 6000 rpm for 5 min, washing with fresh

Table 1 Various carbonates from different epoxides catalysed by 3

	R +	$CO_2 \qquad \frac{Cat.7}{T.P.}$	3 and TBAB Solvent free	
Entry	Substrate	Product	Conversion ^{<i>a</i>} (%)	TOF (h^{-1})
1	گ		99	6700
2	\checkmark		99	6700
3	\sim		75	5076
4	CI	cio	99	6700
5	Br	o Br	98	6633
6			97	6565
7			96	6497
8	Xor	\rightarrow°	99	6700
9	~°~^^		99	6700
10	но	HOO	99	6700
11	Lo~A		99	6700
12	\bigcirc		29	1963
13	Ô		34	2301

 a Reaction conditions: 10 mmol epoxide, 0.01 mol% catalyst, 0.75 mol% TBAB, 1.5 h, 1 MPa CO₂, 120 $^\circ C.$ Determined by $^1 H$ NMR spectra.

acetonitrile and then drying at 80 $^{\circ}$ C in an oven. The recovered catalyst was used for subsequent reactions using fresh substrates under the conditions of 120 $^{\circ}$ C, 1.5 h. To solve the problem of loss of catalyst dosage by washing, we scaled the amount of substrate added to perform the next experiment. The recovered catalyst was tested for four subsequent runs and showed almost consistent activity with a slight decrease in the conversion (Fig. 3). The conversion decrease may be attributed to the deactivation of a small amount of catalyst in the experiment.¹⁵ As illustrated in Fig. 4, the PXRD pattern of the recycled catalyst showed that the original structure of the catalyst remained stable after four catalytic reaction cycles.

Based on the structure of the lanthanide clusters and previous literature reports,¹⁶ a possible mechanism (shown in Fig. 5) could be used to explain the cycloaddition reaction. First, an epoxide was captured and activated by the Lewis acidic Ln^{3+} site. Then the ring







Fig. 4 The PXRD patterns of the as-synthesized (black) complex **3** and after recycling four times (red).

opening step was driven by the activation effect of the Ln^{3+} site¹⁷ and the carbon–bromine bond was formed through nucleophilic attack by Br^- on the less hindered side of the epoxide.¹⁸ The carbon atom in CO₂ was then attacked by the oxygen anion, while the electrons in the carbon–oxygen double bond moved toward the



Fig. 5 A possible mechanism for the cycloaddition reaction.

carbon atom that was bound to bromine.¹⁹ Finally, an acyclic carbonate molecule was formed, which was converted to a cyclic carbonate by intramolecular cyclization, releasing the original catalyst for the next catalytic cycle. The increasing TOF from 1 to 3 is in line with the increasing Lewis acidity from La to Sm.²⁰

Conclusions

In summary, a series of highly active tetranuclear lanthanide clusters was synthesized and characterized. The unique structures of these clusters provide catalytically active sites for CO_2 conversion.²¹ 3 was selected as a representative efficient and recyclable catalyst to illustrate the reaction of CO_2 with different substituted epoxides.²² In addition, cluster 3 can be recycled at least 4 times without significant loss or structural damage. These results provide new insights for designing lanthanide clusters as efficient CO_2 conversion catalysts.

Conflicts of interest

The authors declare no competing financial interests.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (NSFC, Grant 21431002, 21871122, 21701070) and the Fundamental Research Funds for the Central Universities (Grant No. lzujbky-2018-kb12).

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