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A multi-component polyoxometalate and its catalytic performance for CO₂ cycloaddition reactions†

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A multi-component polyoxometalate based on earth-abundant elements (NH₄)₁₀[Co₈(H₂O)₁₀V₁₀Mo₂₃O₁₀₄(OH)₆].34.5H₂O (**1**) has been successfully obtained and characterized. Furthermore, compound **1** acted as a Lewis acid catalyst and promoted the conversion of carbon dioxide to a cyclic carbonate under mild reaction conditions.

In recent years, the carbon dioxide (CO₂) concentration in the atmosphere has been deemed to be the main contributor to the greenhouse effect and global warming. Therefore, the fixation and transformation of CO₂ has become a hot research topic.¹ In particular, the synthesis of cyclic carbonates by the coupling of epoxides with CO₂ has attracted increasing attention due to their potential applications in pharmaceutical and fine chemical industries.² Although CO₂ is an attractive C₁ building block, efficient chemical fixation of CO₂ remains difficult due to its inert nature. Over the past few decades, various catalysts have been widely used in CO₂ cycloaddition reactions,³ but only at high temperatures (>100 °C) and pressure (>2 MPa) as well as under rigorous separation and purification conditions for the products. Therefore, it is still needed to search for new catalysts that are capable of catalysing cycloaddition of CO₂ with epoxides. In this field, polyoxometalates (POMs) exhibit efficient catalyst activity due to their unique structural and compositional varieties.⁴ Generally, POMs were utilized as Brønsted acids and oxidation catalysts.⁵ On the other hand, the POMs decorated with transition metal moieties were reported to act as Lewis acid catalysts. In 2004, a zinc-substituted sandwich-type Na₁₂[WZn₃(H₂O)₂(ZnW₉O₃₄)₂] was reported as the catalyst for CO₂ cycloaddition reaction at moderate CO₂ pressure (0.4–1.0 MPa) in the temperature range of 100–160 °C.⁶ Subsequently, in 2005, Sakakura's group

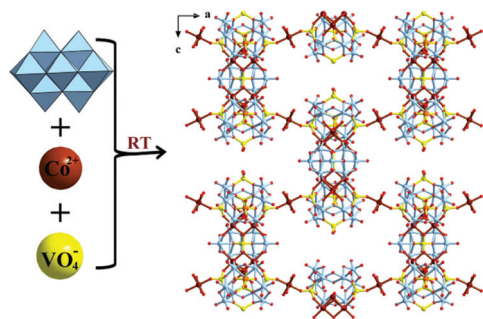
reported that monosubstituted α -Keggin-type POMs [(*n*-C₇H₁₅)₄N]_x[α -SiW₁₁M(H₂O)O₃₉] (M = Co^{II}, Mn^{II}) catalyzed the formation of cyclic carbonates from CO₂ at 150 °C.^{7a} In 2007, α -Wells–Dawson-type [(*n*-C₄H₉)₄N]_xP₂W₁₇M(Br)O₆₁ (M = Co^{II}, Cu^{II}, Mn^{III}) were reported by Zhai^{7b} as the catalyst and tetrabutylammonium bromide as the co-catalyst in polyethylene glycol (PEG) for coupling reaction of CO₂ and propylene oxide or ethylene oxide at 120 °C. Then, Hu reported monosubstituted α -Keggin-type POMs [(*n*-C₇H₁₅)₄N]_x[α -GeW₁₁M(H₂O)O₃₉] (M = Co^{II}, Mn^{II}, Ni^{II}) for catalytic conversion of CO₂ to cyclic carbonates in 2010^{8a} and proposed the mechanism of the cycloaddition of CO₂ to epoxides in 2012.^{8b}

Recently, our group reported an example of transition metal rhenium substituted POM [(CH₃)₄N]₅H₂₃[(PW₁₁O₃₉)-{Re(CO)₃]₃(μ_3 -O)(μ_2 -OH)]₄·24H₂O,⁹ which catalyzed the conversion of CO₂ to cyclic carbonates under mild reaction conditions. Nevertheless, Re is neither abundant nor inexpensive and thus very likely prohibitive for use on a realistic scale. The synthesis of active, environmentally benign, and recyclable catalysts is expected to be of great industrial interest.

In continuation of our studies, we focused our attention on a new strategy to address the problem by exploring an efficient catalyst. Multi-component systems, which combined the intrinsic properties of distinct elements into optimized devices for synergistic effects and new applications, should be effective in cycloaddition reactions. By mixing (NH₄)₆Mo₇O₂₄·4H₂O, NH₄VO₃ and CoCl₂·2H₂O in aqueous solution at a pH value of 4.7, a novel POM (NH₄)₁₀[Co₈(H₂O)₁₀V₁₀Mo₂₃O₁₀₄(OH)₆].34.5H₂O was obtained (Scheme 1), which displayed a two dimensional (2D) layer framework built up of the [Co₆(H₂O)₂V₁₀Mo₂₃O₁₀₄(OH)₆]¹⁴⁻ polyanion (abbreviated as {Co₆Mo₂₃V₁₀}₆) and {Co(H₂O)₄} bridges. It is noteworthy that the labile aqua ligand of {Co(H₂O)₄} could be removed during the activation stage prior to use in catalysis, which may leave a free coordination position in the metal as the Lewis acidic site. Compound **1** with a 2D sheet, which has a high density of well-oriented Lewis acid sites, is desirable for high catalytic activity for the chemical fixation of CO₂ into cyclic carbonates under mild reaction conditions.

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Scheme 1 Synthetic procedure of **1**. Color codes: the atoms of Co, V and O are brown, yellow and red, respectively. The MoO₆ polyhedra are shown in LT cyan.

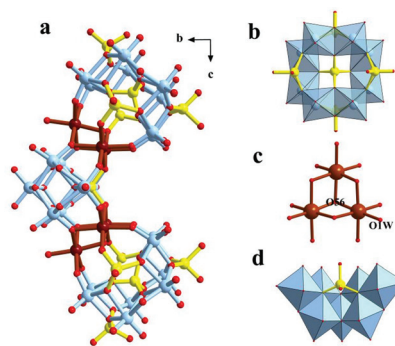


Fig. 2 Polyhedral/ball-and-stick representation of (a) {Co₆Mo₂₃V₁₀}; (b) {V_{4.5}Mo₈O₄₀}; (c) {Co₃O₁₃} and (d) {VMo₇O₂₈}.

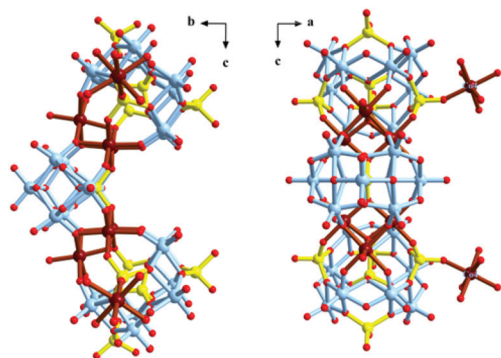


Fig. 1 Ball and stick representation of the anion {Co₈Mo₂₃V₁₀} viewed along (left) the *a*-axis and (right) the *b*-axis.

Single-crystal X-ray analysis indicates that **1** crystallizes in the orthorhombic space group *pnm*, and consists of a [Co₈(H₂O)₁₀V₁₀Mo₂₃O₁₀₄(OH)₆]¹⁰⁻ (abbreviated as {Co₈Mo₂₃V₁₀}) anion (Fig. 1), 34.5 lattice water molecules and ten ammonium cations. According to the bond valence sum (BVS) calculations,¹⁰ the oxidation state of all Co, Mo and V atoms is +2, +6 and +5, respectively (Tables S2 and S3†). The lower BVS values of O7 (1.317) and O14 (1.287) in the frameworks of the {VMo₇O₂₈} unit suggest monoprotection of these oxygen atoms. Similarly, the BVS values also suggest monoprotection of O56 (1.216) in the {Co₃O₁₃} unit and that of O58 (1.391) in the {V_{4.5}Mo₈O₄₀} unit (Table S4†).

{Co₆Mo₂₃V₁₀} is composed of two subunits {V_{4.5}Mo₈O₄₀} and a {VMo₇O₂₈} fragment linked by trinuclear Co^{II} clusters, leading to a banana-shaped structure with the idealized *C*_{2v} symmetry (Fig. 2a). In other words, {Co₆Mo₂₃V₁₀} can also be considered as a double-sandwich structure, where two {V_{4.5}Mo₈O₄₀} and a {VMo₇O₂₈} are separated by two distinct {Co₃O₁₃} triads. The subunit {V_{4.5}Mo₈O₄₀} (Fig. 2b) is similar to the reported {V₅Mo₈O₄₀}.¹¹ The subunit contains eight edge-sharing {MoO₆} octahedra forming a ring in a two-up-two-down fashion and four VO₄ tetrahedra filling the gaps between the pairs of octahedra. The V(2) atom is found in the center of the subunit (Fig. S3†). It should be noted that V(6) occupies a

special position with an occupancy factor of 0.5 for each and the {VMo₇O₂₈} (Fig. 2d) fragment can be considered as a derivative of the (B-β-VMo₉O₃₃) structure by removing one edge-shared {Mo₃O₁₃} group. Each monomeric unit of **1** contains two truncated {Co₃O₁₃} cubane cores (Fig. 2c), three Co(II) cations reside in the CoO₆ octahedral geometry and three edge-sharing CoO₆ octahedra generate the triangular cobalt cluster. Furthermore, in the triplet Co(1)–Co(2)–Co(3), Co(3) has a terminal water molecule, as shown in Fig. 2c. Such water molecules can be removed or replaced by other ligands, the loss of the coordinated water molecules leads to coordinatively unsaturated sites,¹² where the Lewis acidic site may be produced.

The polyanion is extended to a 2D infinite network, in which each {Co₆Mo₂₃V₁₀} is linked to four others through {Co(H₂O)₄} bridges (Fig. S1 and S2†). The six-coordinate Co(4) atom resides in octahedral geometry, which is defined by six oxygen atoms from four coordinated water molecules and two terminal oxygen atoms of {V_{4.5}Mo₈O₄₀}. These coordinated water molecules of Co(4) could be expediently removed, thus Co(4) could be used as a Lewis acid catalyst. Successive 2D sheets are further stacked in the –A–B–A–B– type to produce a 3D architecture framework with a 1D channel along the *b* axis, and the active sites of the Lewis acid catalysts are well aligned in the channels (Fig. S4†). The accessible pores are about 4211.1 Å³ (23.9% of the unit cell volume) calculated by PLATON analysis.¹³ The porous structure benefits guest molecules getting into the channels interacted with the catalyst site.

Based on previous reports,^{3e} **1** was used to catalyze the chemical fixation of CO₂ with glycidyl phenyl ether in the ionic liquid pyrrolidinium bromide. The reactions were carried out under the conditions described in Table 1. We explored the catalytic reaction of the coupling of glycidyl phenyl ether (**1a**) with CO₂ to produce 3-phenoxy-1,2-propylene carbonate (**2a**). In the absence of **1** (Table 1, entry 1), **1a** was found to be able to convert into **2a** in 36.5% yield. With 0.28 mol% of **1** (entry 4), the yield was increased to 76.1% and over 99% selectivity. If addition of **1** was increased incrementally from 0.28 to 0.31 mol%, the yield increased from 76.1 to 79.0% (entry 6).

Table 1 Effect of reaction parameters on the coupling of CO₂ and epoxides catalyzed by catalyst **1** with ionic liquid **2**^a

Entry	Substrate	Cat. 1 (mol%)	2 (mmol)	Pres. ^c (MPa)	Temp. (°C)	Yield ^d (%)
1 ^b		—	8	1.5	70	36.5
2		0.28	8	1.5	60	36.8
3		0.28	8	1.5	65	63.7
4		0.28	8	1.5	70	76.1
5		0.28	8	1.0	70	68.3
6		0.31	8	1.5	70	79.0
7 ^e		0.28	8	1.5	70	71.3
8 ^f	0.28	8	1.5	70	63.3	
9	0.28	—	1.5	70	0.00	
10 ^g		0.28	8	1.5	70	78.6
11 ^h		0.28	8	1.5	70	86.2

^a Reaction conditions: epoxide (5 mmol), ionic liquid (8 mmol, 80 mg), reaction time 1 h. ^b 1,2-Epoxy-3-phenoxypropane (5 mmol, 680 μL). ^c Initial pressure at room temperature. ^d Determined by GC using dimethyl phthalate as an internal standard, the selectivity was over 99% in all cases. ^e The 2nd run. ^f The 3rd run. ^g Glycidyl methacrylate (5 mmol, 660 μL). ^h Chloromethyloxirane (5 mmol, 390 μL).

The effect of the CO₂ pressure was also investigated (entry 5), and the yield of **2a** was decreased at a lower pressure of 1.0 MPa. As shown in Table 1 (entries 2–4), the catalyst system was quite sensitive to the reaction temperature. When the temperature was decreased from 70 °C to 60 °C, the yields decreased from 76.1% to 36.8%. Consequently, the best yield of **2a** can be achieved under reaction conditions such as in entry 4 in Table 1. The possibility of recycling complex **1** in the synthetic process was investigated. **1** was used to catalyze the cycloaddition of CO₂ for 3 cycles, and showed a relative recyclability (entries 7 and 8). The IR spectra of the recovered catalyst were similar to the fresh catalyst (Fig. S7†), indicating that the catalytic system was stable.

The catalytic activities of other epoxides like glycidyl methacrylate and chloromethyloxirane were also tested under the same reaction conditions. The results showed that **1** was active for these epoxides as well (entries 10 and 11). The catalytic activity of **1** seemed to depend on the substrate size. The yield of **1a**, with dimensions of 10.0 × 4.4 × 3.2 Å³, was 76.1%. The yields of glycidyl methacrylate and chloromethyloxirane, the smaller epoxides with dimensions of 8.8 × 4.4 × 2.4 Å³ and 3.5 × 3.2 × 2.2 Å³, were increased to 78.6% and 86.2% under similar conditions, respectively. Furthermore, highly polar glycidyl methacrylate and chloromethyloxirane also give relative conversion.

The reaction mechanism for the cycloaddition of CO₂ to epoxides was proposed by Manikandan *et al.* in 2004, which is the cooperative effect of Zn-POM (Lewis acid site) and DMAP (Lewis base site).⁶ In 2012, Hu *et al.*^{8b} reported a computational study of the mechanism of Co-substituted-POM catalyzing cycloaddition of CO₂ to epoxides. They confirmed that the reaction occurred through attack of the catalyst on the

epoxides which formed a Co^{III} radical intermediate. Here, we supposed that the reaction mechanism was similar to that reported by Manikandan *et al.* Firstly, the epoxide is activated by coordination to the Co center (Lewis acid site), and then it is attacked by Br[−] (Lewis base site) followed by ring opening; finally, the subsequent interactions of the nucleophilic alkoxide intermediate with the electrophilic CO₂ form the cyclic carbonate. A control experiment demonstrated that no detectable conversion was observed for the model reaction in the absence of the pyrrolidinium bromide cocatalyst (Table 1, entry 9), which gave preliminary evidence to support this hypothesis.

Conclusions

In this paper, a multi-component polyoxometalate based on earth-abundant elements (Co, V, Mo) was synthesized at a low cost and it catalyzed the cycloaddition of CO₂ to epoxides under mild conditions, which paves an avenue for the design and synthesis of a novel environmentally benign catalytic system for chemical fixation of CO₂.

Acknowledgement

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Notes and references

‡ Crystal data for **1**: CSD 429071. *M*_r = 5935.64, orthorhombic, space group *Pnmm*, *a* = 28.1420(16) Å, *b* = 24.2136(13) Å, *c* = 25.7921(14) Å, *V* = 17 575.2(17) Å³, *Z* = 4,

$\mu = 2.922 \text{ mm}^{-1}$, $F(000) = 11\,412.0$, $\text{GOOF} = 1.117$. Of 88 020 total reflections collected, 15 773 reflections are unique ($R(\text{int}) = 0.0672$). $R_1 = 0.0778$, $wR_2 = 0.2161$ for 828 parameters and 15 773 reflections [$I > 2\sigma(I)$].

- 1 (a) M. Mikkelsen, M. Jorgensen and F. C. Krebs, *Energy Environ. Sci.*, 2010, **3**, 43; (b) S. Ravi, D. H. Kang, R. Roshan, J. Tharun, A. C. Kathalikkattil and D. W. Park, *Catal. Sci. Technol.*, 2015, **5**, 1580; (c) C. Maeda, T. Taniguchi, K. Ogawa and T. Ema, *Angew. Chem., Int. Ed.*, 2015, **54**, 134.
- 2 I. Omae, *Coord. Chem. Rev.*, 2012, **256**, 1384.
- 3 (a) R. L. Paddock and S. T. Nguyen, *J. Am. Chem. Soc.*, 2001, **123**, 11498; (b) F. W. Li, C. G. Xia, L. W. Xu, W. Sun and G. X. Chen, *Chem. Commun.*, 2003, 2042; (c) D. J. Darensbourg and M. W. Holtcamp, *Coord. Chem. Rev.*, 1996, **153**, 155; (d) W. J. Kruper and D. V. Dellar, *J. Org. Chem.*, 1995, **60**, 725; (e) W. L. Wong, K. C. Cheung, P. H. Chan, Z. Y. Zhou, K. H. Lee and K. Y. Wong, *Chem. Commun.*, 2007, 2175.
- 4 (a) F. W. Chen, T. Dong, X. F. Li, T. G. Xu and C. W. Hu, *Chin. Chem. Lett.*, 2011, **22**, 871; (b) J. Langanke, L. Greiner and W. Leitner, *Green Chem.*, 2013, **15**, 1173.
- 5 (a) L. Huang, S. S. Wang, J. W. Zhao, L. Cheng and G. Y. Yang, *J. Am. Chem. Soc.*, 2014, **136**, 7637; (b) L. X. Shi, X. W. Zhang and C. D. Wu, *Dalton Trans.*, 2011, **40**, 779; (c) C. Boglio, K. Micoine, P. Rémy, B. Hasenknopf, S. Thorimbert, E. Lacôte, M. Malacria, C. Afonso and J. C. Tabet, *Chem. – Eur. J.*, 2007, **13**, 5426; (d) Y. Kikukawa, S. Yamaguchi, K. Tsuchida, Y. Nakagawa, K. Uehara, K. Yamaguchi and N. Mizuno, *J. Am. Chem. Soc.*, 2008, **130**, 5472; (e) Y. Kikukawa, S. Yamaguchi, Y. Nakagawa, K. Uehara, S. Uchida, K. Yamaguchi and N. Mizuno, *J. Am. Chem. Soc.*, 2008, **130**, 15872.
- 6 M. Sankar, N. H. Tarte and P. Manikandan, *Appl. Catal., A*, 2004, **276**, 217.
- 7 (a) H. Yasuda, L. N. He, T. Sakakura and C. W. Hu, *J. Catal.*, 2005, **233**, 119; (b) D. W. Sun and H. J. Zhai, *Catal. Commun.*, 2007, **8**, 1027.
- 8 (a) F. W. Chen, T. Y. Dong, Y. N. Chi, Y. Q. Xu and C. W. Hu, *Catal. Lett.*, 2010, **139**, 38; (b) F. W. Chen, X. F. Li, B. Wang, T. G. Xu, S. L. Chen, P. Liu and C. W. Hu, *Chem. – Eur. J.*, 2012, **18**, 9870.
- 9 Z. Y. Huo, J. Zhao, Z. W. Bu, P. T. Ma, Q. S. Liu, J. Y. Niu and J. P. Wang, *ChemCatChem*, 2014, **6**, 3096.
- 10 I. D. Brown and D. Altermatt, *Acta Crystallogr., Sect. B: Struct. Sci.*, 1985, **41**, 244.
- 11 (a) M. Cindrić, N. Staukan, Z. Veksli and B. Kamenar, *Polyhedron*, 1996, **15**, 2121; (b) A. Björnberg, *Acta Crystallogr., Sect. B: Struct. Sci.*, 1980, **36**, 1530.
- 12 (a) D. E. Katsoulis and M. T. Pope, *J. Am. Chem. Soc.*, 1984, **106**, 2737; (b) A. Corma, H. Garcia and F. X. Llabres i Xamena, *Chem. Rev.*, 2010, **110**, 4606.
- 13 A. L. Spek, *J. Appl. Crystallogr.*, 2003, **36**, 7.