

Communication

A Ca(II) Coordination Polymer of 2-Carboxybenzaldehyde: Synthesis, Crystal Structure, and Catalytic Activity in Oxidation of Benzyl Alcohol

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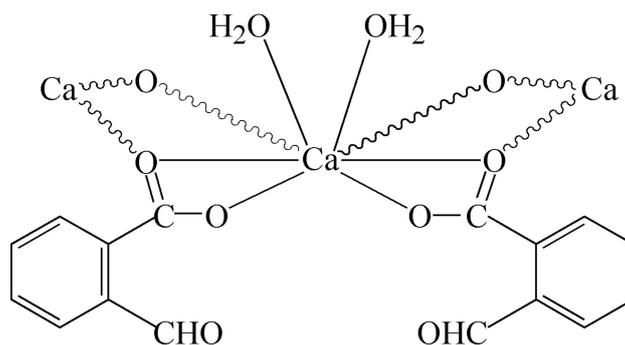


Abstract: The coordination polymers constructed by carboxylate ligand have shown novel structures and excellent properties. Therefore, a new Ca(II) coordination polymer with 2-carboxybenzaldehyde ligand, $[\text{Ca}(\text{L})_2(\text{H}_2\text{O})_2]_n$ (L = 2-carboxybenzaldehyde), has been synthesized. Its structure has been identified by elemental analysis, FT-IR, and single-crystal X-ray diffraction technique. The Ca(II) coordination polymer exhibits a 1D chained structure by the bridging effect of carboxylate groups. The Ca(II) coordination polymer exhibited relatively good catalytic activity in the benzyl alcohol oxidation reaction with benzyl alcohol conversion (53.8%) and moderate benzaldehyde selectivity (83.3%).

Keywords: Ca(II) coordination polymer; synthesis; crystal structure; catalytic activity

1. Introduction

Metal coordination polymers have attracted much attention in recent years, which is due to their novel structures and potential applications in luminescence, catalysis, magnetism, gas storage, and biological activity [1–14]. Among them, the coordination polymers were mainly composed by transition metal ions and rare earth metal ions with organic ligands [15–18]. The study on structure and property of alkaline earth coordination polymers are relatively few. Benzaldehyde is an important intermediate of organic synthesis and fine chemical products, widely used in medicine, dyes, spices, resins, and other industries [19]. Traditionally, the benzaldehyde was prepared by oxidation of benzyl alcohol with toxic metal oxides, peroxides, halides, and so on [20–22]. So, the development of environmentally friendly catalysts is very attractive. Our group has been working on the synthesis and catalytic properties of cheap and environmentally friendly catalysts [23–27]. In this paper, we reported a new Ca(II) coordination polymer, $[\text{Ca}(\text{L})_2(\text{H}_2\text{O})_2]_n$, and its application in aerobic oxidation of benzyl alcohol as catalyst. The chemical diagram of the Ca(II) coordination polymer is shown in Scheme 1.



Scheme 1. The chemical diagram of the Ca(II) coordination polymer.

2. Materials and Methods

2.1. Materials and Instrumentation

The 2-Carboxybenzaldehyde (analytical reagent), $\text{Ca}(\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ (analytical reagent), and benzyl alcohol (analytical reagent) were used as received. Element analyses (C, H, and N) were measured with an Elementar Vario III EL elemental analyzer (Elementar, Hanau, Germany). The IR spectra of 2-carboxybenzaldehyde and $[\text{Ca}(\text{L})_2(\text{H}_2\text{O})_2]_n$ ($4000\text{--}400\text{ cm}^{-1}$) were recorded using a Nicolet AVATAR 360 FT-IR spectrometer (Nicolet Instrument Inc., Madison, WI, USA).

2.2. Synthesis of $[\text{Ca}(\text{L})_2(\text{H}_2\text{O})_2]_n$

Amounts of 0.1501 g (1.0 mmol) 2-Carboxybenzaldehyde and 0.040 g (1.0 mmol) NaOH were dissolved in 95% ethanol (10.0 mL). The water (5.0 mL) solution of $\text{Ca}(\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ (0.1375 g, 0.5 mmol) was dropped into the mixture solution. Then, the reactant mixture was stirred at $70\text{ }^\circ\text{C}$ for 6 h. The white precipitation of $[\text{Ca}(\text{L})_2(\text{H}_2\text{O})_2]_n$ was collected by filtration. The colorless block crystals of $[\text{Ca}(\text{L})_2(\text{H}_2\text{O})_2]_n$ were received in 15 days through slowly evaporating the filtrate at room temperature. Yield: 71. Anal. Calcd. for $\text{C}_{16}\text{H}_{14}\text{CaO}_8$: C, 51.29; H, 3.74; Found: C, 51.01; H, 3.96. IR (KBr disc): 3545 cm^{-1} , 3365 cm^{-1} , 1695 cm^{-1} , 1583 cm^{-1} , 1560 cm^{-1} , 1415 cm^{-1} , 756 cm^{-1} .

2.3. Crystal Data Collection and Refinement

Single-crystal data of the Ca(II) coordination polymer were obtained at 293(2) K on a Bruker Smart CCD diffractometer (Bruker, Billerica, MA, USA) using graphite-monochromated Mo $\text{K}\alpha$ radiation ($\lambda = 0.71073\text{ \AA}$). The *SHELXL-2014/7* program [28] was used to solve the structure by direct method. The *OLEX2* [29] program was used to refine the structure. The key collection and handling information for $[\text{Ca}(\text{L})_2(\text{H}_2\text{O})_2]_n$ are given in Table 1.

Table 1. Data collection and handling for $[\text{Ca}(\text{L})_2(\text{H}_2\text{O})_2]_n$.

Empirical formula	$\text{C}_{16}\text{H}_{14}\text{O}_8\text{Ca}$
Formula weight	374.35
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$\text{C}2/c$
$a/\text{\AA}$	18.693(4)
$b/\text{\AA}$	11.465(2)
$c/\text{\AA}$	7.8746(16)
$\beta/^\circ$	92.83(3)
Volume/ \AA^3	1685.6(6)

Table 1. Cont.

Z	4
$\rho_{\text{calc}}/\text{mg}/\text{mm}^3$	1.475
μ/mm^{-1}	0.414
S	1.063
F(000)	776
Index ranges	$-22 \leq h \leq 22, -13 \leq k \leq 13, -9 \leq l \leq 9$
Reflections collected	6457
Independent reflections	1491 [R(int) = 0.0338]
Data/restraints/parameters	1491/0/114
Goodness-of-fit on F^2	1.063
Final R indexes ($I \geq 2\sigma(I)$)	$R_1 = 0.0326, wR_2 = 0.0831$
Final R indexes [all data]	$R_1 = 0.0339, wR_2 = 0.0841$

The crystallographic data for the structure reported in this paper has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC 1580374. Copy of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk).

2.4. Catalytic Measurements

The $[\text{Ca}(\text{L})_2(\text{H}_2\text{O})_2]_n$ was treated at 100 °C for 24 h under vacuum to remove the terminal water molecules before catalytic reaction, thus providing coordinatively unsaturated calcium metal sites. The procedure for the aerobic oxidation of benzyl alcohol is as follows: 0.0216 g benzyl alcohol (0.2 mmol), 1.50 g tetrahydrofuran, and the catalyst (0.06 g, containing 0.0171 mmol coordinatively unsaturated calcium metal sites) were placed into a 10 mL stainless steel autoclave. Then, the 99.999% pure O_2 was pumped to replace the atmosphere three times. The reaction mixture was kept at 130 °C with vigorous stirring. Then, the $[\text{Ca}(\text{L})_2(\text{H}_2\text{O})_2]_n$ catalyst was removed from the reaction mixture by centrifugation. The gas chromatography equipped with a SE-54 capillary column was used to measure the benzyl alcohol conversion and the benzaldehyde selectivity. The qualitative analysis was carried out by an external standard method.

3. Results and Discussion

3.1. IR Spectra

The IR spectra of 2-carboxybenzaldehyde and $[\text{Ca}(\text{L})_2(\text{H}_2\text{O})_2]_n$ are shown in Figure 1. As shown in Figure 1, the important bands of 2-carboxybenzaldehyde appear at 3330 cm^{-1} , 1758 cm^{-1} , 1463 cm^{-1} , 1265 cm^{-1} , 1201 cm^{-1} , 1124 cm^{-1} , 1072 cm^{-1} , 906 cm^{-1} , 783 cm^{-1} , 748 cm^{-1} , 713 cm^{-1} , 690 cm^{-1} , and 584 cm^{-1} . The important bands of $[\text{Ca}(\text{L})_2(\text{H}_2\text{O})_2]_n$ appear at 3545 cm^{-1} , 3365 cm^{-1} , 1695 cm^{-1} , 1583 cm^{-1} , 1560 cm^{-1} , 1415 cm^{-1} , and 756 cm^{-1} . The strong bands of $\nu_{\text{as}}(\text{COO})$ and $\nu_{\text{s}}(\text{COO})$ in free ligand appear at 1758 cm^{-1} and 1463 cm^{-1} , respectively, and they appear at 1695 cm^{-1} and 1415 cm^{-1} in Ca(II) complex, which show that the ligand, 2-carboxybenzaldehyde, has taken part in coordination with Ca(II) ion.

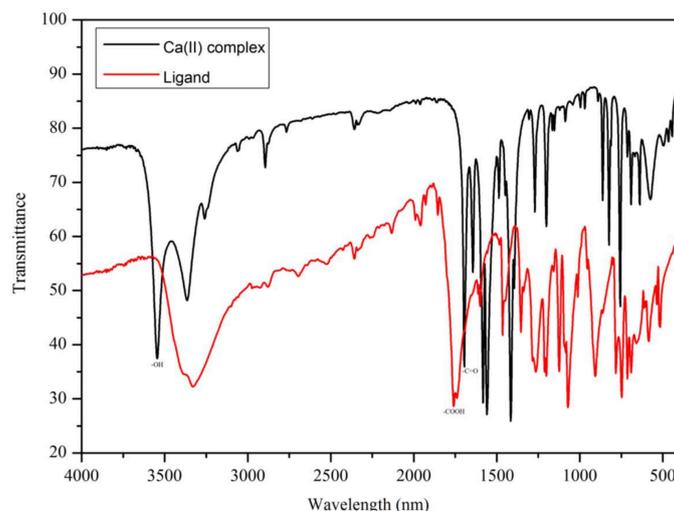


Figure 1. The IR spectra of 2-carboxybenzaldehyde and $[\text{Ca}(\text{L})_2(\text{H}_2\text{O})_2]_n$.

3.2. Structural Description of $[\text{Ca}(\text{L})_2(\text{H}_2\text{O})_2]_n$

The $[\text{Ca}(\text{L})_2(\text{H}_2\text{O})_2]_n$ crystallizes in the monoclinic space group $C2/c$, and its asymmetric unit contains a Ca(II) ion, two 2-carboxybenzaldehyde ligands, and two coordinated water molecules. Figure 2 shows the coordination environment of Ca(II) ion in the Ca(II) coordination polymer. The Ca(II) ion is eight-coordinated with four O atoms of COO^- from two different 2-carboxybenzaldehyde ligands, two O atoms of COO^- from other two different 2-carboxybenzaldehyde ligands, and two O atoms from two coordinated water molecules, and adopts a distorted doubly capped octahedral geometry. The Ca–O distances range from 2.3666(12) Å to 2.6902(12) Å (Ca1–O1W and Ca1–O1WA: 2.3803(13) Å; Ca1–O2 and Ca1–O2A: 2.4488(13) Å; Ca1–O3 and Ca1–O3A: 2.6902(12) Å; Ca1–O3B and Ca1–O3D: 2.3666(12) Å), indicating that the O atoms are coordinate to Ca(II). In the Ca(II) coordination polymer, the dihedral angle of benzene ring 1 (C2–C3–C4–C5–C6–C7) and benzene ring 2 (C2A–C3A–C4A–C5A–C6A–C7A) is 38.6° , showing that the two benzene rings are planar. In addition, the Ca(II) ions are bridged by the O atoms of bridging COO^- groups to form 1D chained structure (Figure 3).

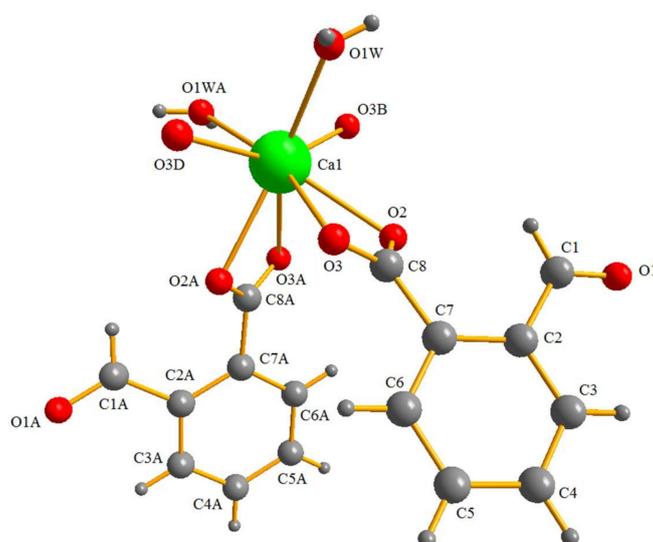


Figure 2. The coordination environment of Ca(II) ion in the Ca(II) coordination polymer. Symmetry codes: A: $-x, y, -1/2-z$; B: $-x, -y, -1/2-z$; D: $x, -y, 1/2+z$.

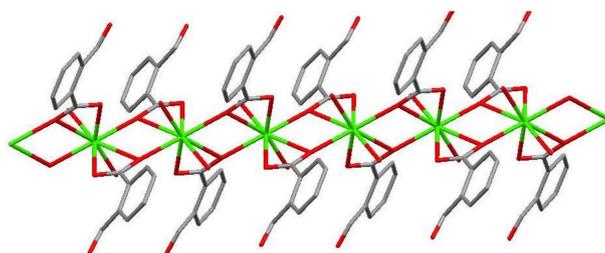


Figure 3. 1D chained structure of Ca(II) coordination polymer.

3.3. Catalytic Studies

The catalytic activity for the oxidation of benzyl alcohol was tested at 130 °C using the Ca(II) coordination polymer as catalyst and 99.999% pure O₂ as oxidant (Figure 4). First, the catalytic activity of Ca(II) coordination polymer catalyst was examined for the oxidation of benzyl alcohol at different reaction time. The reaction was conducted by heating Ca(II) coordination polymer catalyst (0.06 g) and benzyl alcohol (0.2 mmol) in THF (1.5 g) under 1 MPa O₂. Figure 5 shows the catalytic activity for the oxidation of benzyl alcohol over Ca(II) coordination polymer catalyst with THF as solvent at 130 °C under 1 MPa. As shown in Figure 5, the benzyl alcohol conversion increases with the increase of reaction time. The benzyl alcohol conversion reached to 90.4% at 130 °C within 5 h. Significant differences are observed in benzaldehyde selectivity over Ca(II) coordination polymer catalyst at 130 °C using 99.999% pure O₂ as the oxidant. Upon increasing the reaction time, there is a sharp decrease of the benzaldehyde selectivity over the Ca(II) coordination polymer catalyst. Maximum selectivity of 99% was obtained within 10 min over Ca(II) coordination polymer catalyst at 130 °C. However, the selectivity was 19.6% at 130 °C for 5 h. Then, the effect of the amount of the catalyst was studied to optimize the reaction conditions. The conversion of benzyl alcohol increases upon increasing the amount of the catalyst. The conversions of benzyl alcohol were 23.8%, 38.5%, 53.8%, and 90.9% when using 20 mg, 40 mg, 60 mg, and 80 mg Ca(II) coordination polymer catalyst at 130 °C for 3 h in THF under 1 MPa, respectively. However, the selectivities of benzaldehyde were 92.5%, 85.5%, 83.3%, and 12.5%, respectively. The good benzyl alcohol conversion (53.8%) and moderate benzaldehyde selectivity (83.3%) were achieved when the oxidation reaction was carried out at 130 °C for 3 h using 60 mg Ca(II) coordination polymer catalyst in THF under 1 MPa. Wang et al. [30] synthesized a poly(divinylbenzene-co-*N*-vinylimidazole) (PDVB-VI-*n*)-supported Au catalyst by using AuCl₃ as the precursor. Benzyl alcohol conversion and benzaldehyde selectivity was 97.3% and 10.5% at 90 °C for 16 h with 1 atm oxygen as the sole oxidant and water as the solvent over 1.9 Au/PDVB-VI-0.33. Zhang et al. [31] synthesized MoO₃/C-*N* hybrid materials via direct thermal treatment followed by calcination (600 °C for 2 h). The yield of oxidation of benzyl alcohol to benzaldehyde was 30% at 110 °C within 3 h using H₂O₂ as oxidant. Philip et al. [32] synthesized gold nanoparticle-decorated halloysite nanotubes (Au-Hal) by a deposition method. 3% Au-Hal-2 catalysts showed good benzyl alcohol conversion (79%) and high benzaldehyde selectivity (above 97%) in the benzyl alcohol oxidation with 10 bar of O₂ at 100 °C under magnetic stirring. Wang et al. [33] prepared palladium nanoparticles (PdNPs) supported on functional cross-linked mesoporous poly(ionic liquid)s (MPILs) (Pd@MPIL) through NaBH₄ reduction route. The obtained materials showed good benzyl alcohol (96%) and benzaldehyde selectivity (99%) by using O₂ as the oxidant and water as the sole solvent at low temperature (90 °C) with K₂CO₃ as additive. Based on the above results, although the activity of Ca(II) coordination polymer catalyst is still less than those of Au-Hal and Pd@MPIL, the catalyst of Ca(II) coordination polymer shows higher activity than 1.9 Au/PDVB-VI-0.33 and MoO₃/C-*N* hybrid materials.

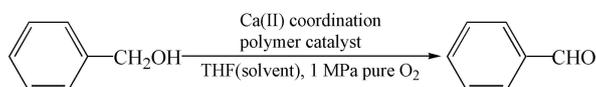


Figure 4. The conversion of benzyl alcohol oxidation.

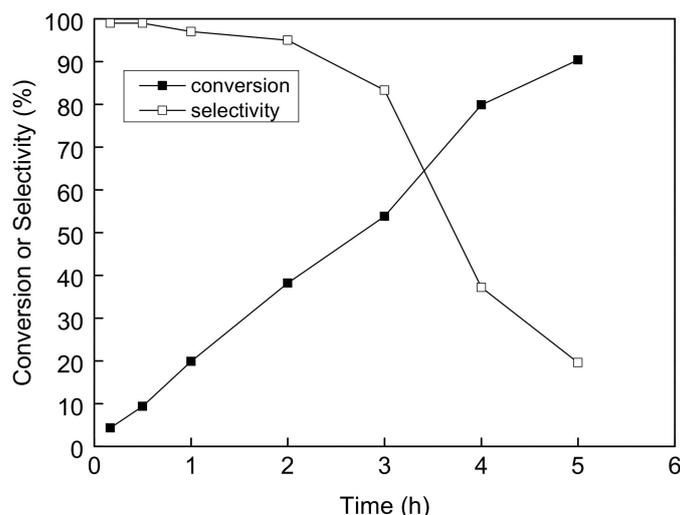


Figure 5. The conversion of benzyl alcohol and selectivity of the benzaldehyde for the benzyl alcohol oxidation over Ca(II) coordination polymer catalyst with THF as solvent at 130 °C under 1 MPa O₂.

The reusability of the Ca(II) coordination polymer catalyst was investigated in the oxidation of benzyl alcohol in THF. The results of reusability of the Ca(II) coordination polymer catalyst are given in Table 2. The benzyl alcohol conversion and benzaldehyde selectivity at 130 °C for 3 h were 53.8% and 83.3%, respectively. The Ca(II) coordination polymer catalyst was recovered by centrifugal separation. The recovered catalyst was washed twice with THF, dried at 100 °C under vacuum for 12 h, and reused. Benzyl alcohol conversions were 51.2%, 50.8%, and 48.6% respectively when the Ca(II) coordination polymer catalyst is used in three cycles at 130 °C within 3 h. The benzaldehyde selectivities were 78.5%, 67.7%, and 59.6% in the first, second, and third runs, respectively.

Table 2. Recyclability of Ca(II) coordination polymer catalyst in the oxidation of benzyl alcohol at 130 °C^a.

Entry	Solvent	Time (h)	Conversion (%) ^b	Selectivity (%) ^c
Fresh	THF	3	53.8	83.3
Run1 ^d	THF	3	51.2	78.5
Run2 ^d	THF	3	50.8	67.7
Run3 ^d	THF	3	48.6	59.6

^a Reaction conditions: benzyl alcohol (0.2 mmol), THF (1.5 g), and Ca(II) coordination polymer catalyst (0.06 g), 1 MPa O₂, 130 °C; ^b Conversion based on benzyl alcohol, and calculated by an external standard method;

^c The selectivity of benzaldehyde was calculated by an external standard method; ^d Run 1, Run 2, and Run 3 are the first, second, and third reuse of the Ca(II) coordination polymer catalyst, respectively.

Ca(II) coordination polymer, O₂ gas, N₂ gas, CaCl₂, Ca(NO₃)₂, and air gas were selected to demonstrate the catalysis of Ca(II) coordination polymer catalyst in the oxidation of benzyl alcohol. The results are summarized in Table 3. The benzyl alcohol conversion and benzaldehyde selectivity were 10.3% and 89.7% without any catalyst under 1 MPa O₂ (Table 3, entry 1). The benzyl alcohol conversions and benzaldehyde selectivities were 12.3%, 53.8%, 50.9%, and 17.9%, 83.3%, 37.2% over Ca(II) coordination polymer under 1 MPa N₂, O₂, and air, respectively. The benzyl alcohol conversions and benzaldehyde selectivities were 94.0%, 0.0 and 7.5%, 0.0% under 1 MPa O₂ (Table 3, entries 2 and 3), respectively. The above results show that both oxygen and Ca(II) coordination polymer are needed for the oxidation of benzyl alcohol.

Table 3. Effect of reaction conditions on the benzyl alcohol oxidation ^a.

Entry	Gas	Catalyst	Conversion (%) ^b	Selectivity (%) ^c
1	O ₂	-	10.3	89.7
2	O ₂	CaCl ₂	94.0	7.5
3	O ₂	Ca(NO ₃) ₂	0.0	0.0
4	N ₂	Ca(II) coordination polymer	12.3	17.9
5	O ₂	Ca(II) coordination polymer	53.8	83.3
6	Air	Ca(II) coordination polymer	50.9	37.2

^a Reaction conditions: benzyl alcohol (0.2 mmol), THF (1.5 g), and Ca(II) coordination polymer catalyst (0.06 g), 1 MPa O₂, 130 °C, 3 h; ^b Conversion based on benzyl alcohol, and calculated by an external standard method;

^c The selectivity of benzaldehyde was calculated by an external standard method.

4. Conclusions

A novel eight-coordinated Ca(II) coordination polymer with 2-carboxybenzaldehyde ligand has been synthesized and structural characterized. The Ca(II) coordination polymer exhibited relatively good catalytic activity in the benzyl alcohol oxidation reaction with benzyl alcohol conversion and moderate benzaldehyde selectivity.

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Author Contributions: Tai Xi-Shi and Liu Li-Li conceived and designed the experiments; Guo Qian-Qin and Liu Li-Li performed the experiments; Li Peng-Fei analyzed the data; Tai Xi-Shi wrote the paper.

Conflicts of Interest: The authors declare no conflict of interest.

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