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Synthesis of a novel L-tartaric acid derived homochiral nanoscale framework and its application in L-proline detection and acetalization catalysis

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Abstract: A novel homochiral nanoscale compound, $[Ca(L\text{-}C_4H_4O_6)(H_2O)_2]\cdot 2H_2O$ ($Ca(L\text{-}tart)(H_2O)_2$), which is derived from calcium ions and L-tartaric acid (L-tart =$C_4H_4O_6$), was synthesized under hydrothermal condition. It has been characterized by single crystal X-ray diffraction, SEM, XRD, FTIR and TG. The calcium atoms adopt a tetrahedron geometry and each atom coordinates with eight oxygen atoms. The compound forms a two-dimensional network structure in the solid state via hydrogen bonds. Its performance of L-proline detection was tested, which attained effective result for the porous framework. Meanwhile, the high activity was also shown in acetalization catalysis.

Keywords: L-Tartaric Acid, Inorganic-Organic Framework Compound, L-Proline Detection

1. Introduction

In the past decades, researchers have made notable work in the field of molecular inorganic-organic framework compounds, especially in terms of phosphonates and carboxylates.[1],[2] They were constituted of metal centers assembled by various functional organic ligands via an infinite, regular patterns, and form 1-, 2-, and 3-dimensional structures. The great interest has been attracted for the possible applications in areas such as separation,[3] catalysis[4] and hydrogen storage.[5] One of the particularly interesting hybrid frameworks related to those that have chiral properties.[6] The unique materials have potential application in enantioselective separation,[7] sensors,[8] catalysis[9],[10] and non-linear optics[11]. As we all known that the network of the coordination polymers were controlled by both the metal ions geometry and the nature of ligands.[12] So it was necessary to choose the desired polymers and appropriate ligands to obtain the intended structures and properties. The polycarboxylate ligands coordinating with metal ions should own a feature that they can act as precursors for various polynuclear cluster-based metal compounds for both discrete entities and multi-dimensional systems.[13]

L-tartaric acid, which was hydroxyl-containing polycarboxylate, was an versatile organic carboxylic acid.[14],[15] In recent years, the acid and its derivatives have been applied in hydrogels,[16],[17] chiral extractant,[18] asymmetric epoxidation[19] for its chiral feature. Various metal-tartrate compounds have been synthesized and researched. Xu et al. reported cobalt tartrate compound synthesized via hydrothermal reaction and researched the water chains in the framework.[20] Gübitz et al. reported copper compound of L-tartaric acid through hydrothermal reaction and applied it in the chiral separation of β-blockers and sympathomimetics.[21]

Herein, a novel chiral compound derived from calcium ions and L-tartaric acid, $[Ca(L\text{-}C_4H_4O_6)(H_2O)_2]\cdot 2H_2O$, which owns 2-dimensional chiral nanoscale framework, has been successfully synthesized. The structure of the compound was analyzed through the single crystal X-ray diffraction. Meanwhile, its properties in L-prolline detection was furtherly tested, which attained effective result. Further more, the highly activity was also shown in the acetalization catalysis.

2. Experimental Section

2.1. General Procedures

All reagents, calcium nitrate tetrahydrate [$Ca(NO_3)_2 \cdot 4H_2O$] (Beijing Chemical Reagent Company), L-(+)-tartaric acid [$L\text{-}C_4H_6O_6$] (99%,Alfa Aesar) and $LiOH \cdot H_2O$ (Guangdong Guanghua Sci-Tech Co., Ltd) were commercially available and used without further purification.

2.2. Synthesis of Ca(L-Tart)(H_2O)$_2$

$Ca(NO_3)_2 \cdot 4H_2O$ (0.56 mmol, 0.125 g), L-(+)tartaric acid (0.66 mmol, 0.099 g), and $LiOH \cdot H_2O$ (1.12 mmol, 0.047 g) were added to 10 mL deionized water in a 50 ml scintillation vial. The mixture was stirred until a clear solution was formed. The obtained resulting solution was sealed in a 20 ml Teflon-lined autoclave and put into an oven at 150 ^oC for 48 hours. Upon cooling during 12 hours, the crystals were washed with EtOH for three times and dried in air at 40 ^oC.

2.3. Detection Experiment

In this experiment, the calcium tartrate compound (3.9 mmol, 1 g) was added in 50 mL aqueous solution of 0.01 M L-proline. The mixture was filtered after stirring for 6 hours and then dried at 40 ^oC in the oven. The performance of detection was analyzed via FTIR and TGA.

2.4. Catalytic Acetalization Reactions

Generally, the properties of the compound in catalysis were examined for the acetalization in 25 mL round-bottom vial. The aldehydes were added in the mixed solution of 15 mL methanol and 15 mL dichloromethane, together with 20 mg (0.078 mmol) catalyst. The reaction mixture was stirred for 24 h at room temperature. Then the filtered liquid was analyzed by GC-MS, and nitrobenzene was added as an internal standard.

2.5. Characterization

The single crystal X-ray diffraction analysis and data collection were demonstrated on a Rigaku RAXIS-RAPID. And the basic information with regard to crystal parameters and structures was acquired from Diamond 3.1 and summarized in table 1 and table 2. The phase and structure of the samples were collected by X-ray powder diffraction (XRD, Rigaku DMAX-RB 12 KW) with Cu Kα radiation (λ=0.15406 nm). The morphology of the samples was characterized by scanning electron microscopy (SEM, ZEISS SUPRA55). The thermal characteristic of the samples was performed by thermogravimetric analysis (TG) using Netzsch STA449F3 instrument at a heating rate of 10 ^oC/min under a N_2 flow. Fourier transform Infrared spectras (FT-IR) were obtained on a Nicolet 6700 using the potassium bromide (KBr) pellet technique. The reaction products were analyzed via Gas Chromatography-Mass Spectrum (Agilent 7890A/5975C-GC/MSD), and nitrobenzene was added as an internal standard.

Table 1. *Crystal data and structure for Ca-tart*

Phase data	
Formula sum	$Ca_4\ O_{40}\ C_{16}\ H_8$
Formula weight	1000.53 g/mol
Crystal system	orthorhombic
Space-group	P 21 21 21 (19)
Cell parameters	a=9.229(2) Å b=9.6087(30) Å c=10.5827(22) Å
Cell ratio	a/b=0.9605 b/c=0.9080 c/a=1.1467
Cell volume	938.46(41) $Å^3$
Z	
Calc. density	1.77026 g/cm^3
Meas. density	
Melting point	
RAll	
RObs	
Pearson code	oP68
Formula type	NO2P4Q10
Wyckoff sequence	a17

Table 2. *Atomic parameters for Ca-L-tart.*

Atom	Ox.	Wyck.	Site	S.O.F.	x/a	y/b	z/c	U [$Å^2$]
CA1		4a	1		0.18639	0.81757	1.17719	0.0174
O1		4a	1		0.01439	0.76874	1.00959	0.0290
O2		4a	1		-0.04850	0.73695	0.80926	0.0252
O3		4a	1		0.27423	0.85763	0.95462	0.0214
O4		4a	1		0.16270	0.97363	0.71502	0.0219
O5		4a	1		0.46181	0.74112	0.71549	0.0245
O6		4a	1		0.44272	0.96775	0.67231	0.0248
C1		4a	1		0.04312	0.76129	0.89315	0.0181
C2		4a	1		0.20215	0.77919	0.85836	0.0168
H2		4a	1		0.24546	0.68607	0.85860	0.0800
C3		4a	1		0.22831	0.84015	0.72773	0.0188
H3		4a	1		0.18612	0.77748	0.66461	0.0800
C4		4a	1		0.39093	0.85096	0.70389	0.0168
O1W		4a	1		0.19505	0.56438	1.16892	0.0445
O2W		4a	1		0.22555	0.83698	1.41017	0.0316
O3W		4a	1		0.57193	0.91515	0.42630	0.0421
O4W		4a	1		0.42929	0.57609	0.43705	0.0544

3. Results and Discussion

3.1. Structure Characterization

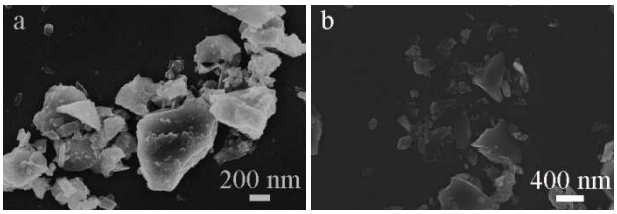


Figure 1. *The SEM of (a) fresh sample; (b) the sample after catalytic reaction.*

To investigate the structure of the novel compound, the scanning electron micrograph (SEM) and single crystal X-ray diffraction were analyzed. Figure 1 shows the SEM of the fresh sample, which was formed in nanoscale. And the unit of the compound, as demonstrated in Figure 2, which was obtained from Materials Studio 7.0, was consisted of four calcium atoms, four L-tartrate acid anions, eight consorted water molecules and eight uncoordinated water molecules. The calcium atoms lie in tetrahedron coordination environment and each atom coordinates with three different tartrate ligands eight oxygen atoms. Two of the independent tartrate anions complex with the metal centers via a hydroxyl oxygen atom and a carboxylate oxygen atom. Another two oxygen atoms of tartrate anions from neighboring dimer assemble through a carboxylate oxygen atom. The last two coordination sites were given to two aquo ligands. The distance between two metal ions was long enough that there was no interaction between them. What was more interesting , there exist pore structure in the 2D channeled framework which can absorb the water molecules in the channels.[22],[23]

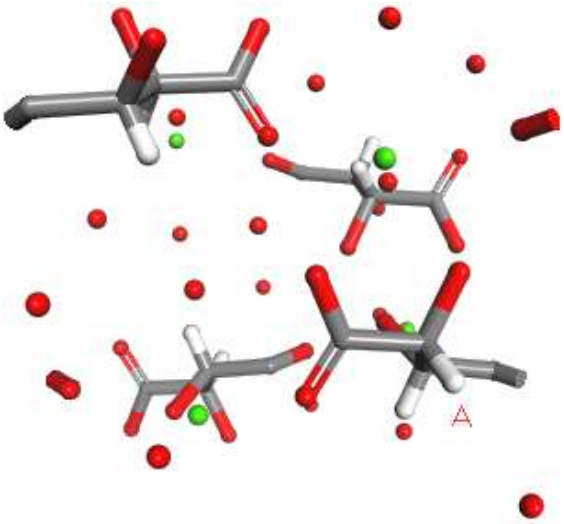


Figure 2. *The molecular structure for the Ca-L-tart compound.*

The crystal phases of the compounds were further confirmed by the X-ray diffraction (XRD). The simulated XRD was also achieved according to the single crystal data. As shown in figure 3, the XRD of as-prepared samples agrees well with the simulated result. The strong unexpected peak around 25 was result from the L-tartaric acid residing in the compound.

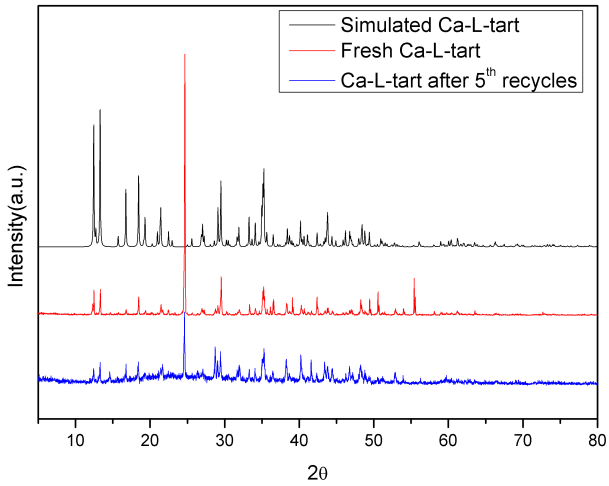
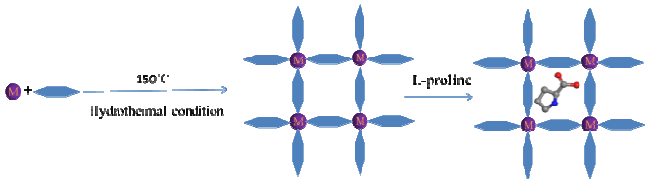


Figure 3. *The powder X-ray diffraction of the compound that simulated ,before and after catalytic reaction.*

3.2. The use of Ca-L-Tart for L-Proline Detection



Scheme 1. *Synthesis and detection of Ca-L-tart.*

Materials in nanoscale have great promise for medicine and biology in view of its properties, unique size and abilities that can be functionalized with recognizable biological elements.[24] The application of the porous compound comprised of metal and organic ligand in detection have been reported.[25] Herein, as shown in the scheme 1, the utilize of Ca-L-tart for L-proline detection , which was an important component of human proteins, was analyzed.

The recorded FTIR spectras were analyzed comparing with the standard spectra character of the functional groups. The strong peak at 3321 cm^{-1} for the O-H in the carboxyl group and the weak peak at 1408 cm^{-1} due to O-H deformation and C-O streching of L-tartaric acid has disppear because of the formation of the compound.[26] The band appears at 1589 cm^{-1} ascribed to protonated carboxylate groups indicates deprotonation upon reaction with Ca^{2+} in the compound, which was consistent with the analysis of the single crystal X-ray diffraction. Especially, the special band appears around 3000 cm^{-1} was attributed to the amino group in the L-proline, which confirmed the result of detection.

The TGA result for the compound was shown in Fig 4. The gradual weight loss from 80 to 190 ^{o}C was result from the liberation of the free water molecules. And the further weight loss, observed up to 330 ^{o}C was due to the dehydration of water molecules that coordinated with Calcium ions in the

compound.[27] Additional weight loss between 330 and 450 °C, followed by the final step between 620 and 750 °C, was attributed to the decomposition of the L-tartaric acid ligand and the formation of calcium oxide with amorphous character. The total weight loss of the initial calcium tartrate compound was 74.2%, which agrees well with the caculated value of 78.1%. Moreover, the weight loss of the compound after detection was 77.7%, which indicate the compound has absorb the L-proline. The decomposition of L-proline started at 200 °C, and the amount of detection was caculated to be 0.035g/g.

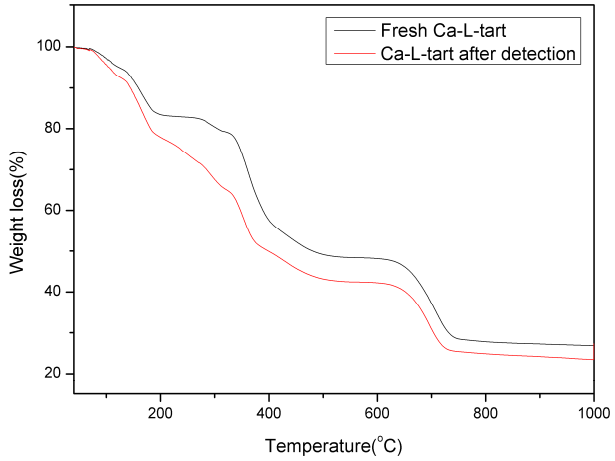


Figure 4. *The TG profile of the fresh sample and the sample after detection.*

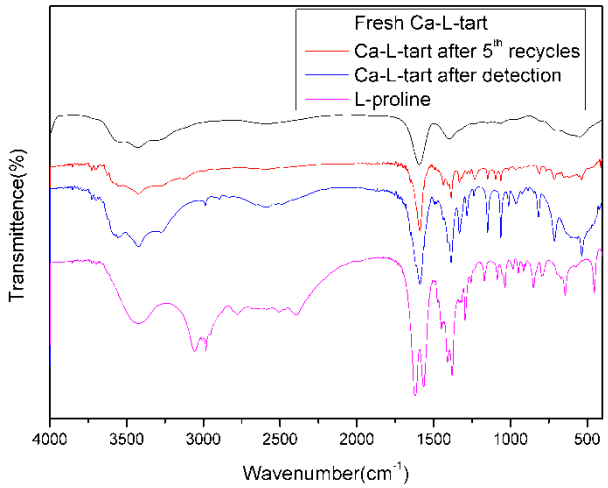
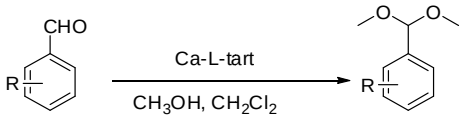


Figure 5. *The FTIR spectra of the fresh sample and the sample after catalytic reaction and detection.*

3.3. Catalytic Performance of the Catalyst In the Acetalization

The ability of the calcium tartrate compound was studied by catalyzing acetalization, since acetals were important intermediates in carbohydrate and synthetic chemistry as masked carbonyl derivatives.[28] The acetalization of methanol and aldehydes catalyzed by solid heterogeneous catalyst at home temperature has been reported in some literature.[29],[30] However, this compound which was inexpensive and easy to get offers effective catalysis with lowered catalyst loading. As shown in the table 3, benzaldehyde was converted to corresponding dimethyl acetal in good yield (entry 1). Electron-rich benzaldehyde resulted in relative low conversion, which ascribe to the higher electron-density around the benzylic carbon. Furthermore, 4-fluorobenzaldehyde was evaluated as electron-deficient aldehyde, which give better results.

Table 3. *Acetalization of several aldehydes with methanol using Ca-L-tart as solid heterogeneous catalyst.*[a]



Entry	Substrate	Time(h)	Conversion(%)[b]	Selectivity(%)[b]
1		24	84	>99
2		24	55	>99
3		24	72	>99

[a]*Reaction conditions: substrate (1.0 mmol), Ca-L-tart catalyst (0.078 mmol), methanol 15 mL and dichloromethane 15 mL, r.t.;* [b]*Determined by GC-MS.*

The catalyst was recovered by centrifugation, then washed with alcohol and dried at home temperature for the next cycle reaction. The conversion of the acetal product remained >80% after 5th recycles (Figure 6). Furthermore, the SEM and crystallinity of sample after 5th recycles have no change at all compared with the fresh one, as shown in Figure 3.

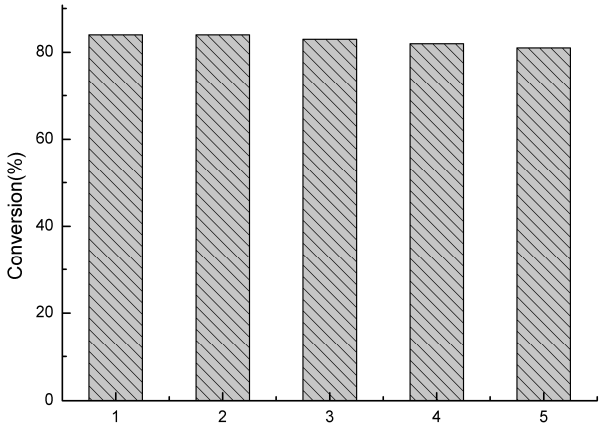


Figure 6. *Recycling test of Ca-L-tart.*

4. Conclusion

In summary, a novel calcium tartrate porous coordination

compound have been obtained via a simple strategy and the structure was discussed. Each calcium atom coordinated with three different tartrate ligands, which was unexpected complexity for the chiral character of the tartrate ligand. Nanoscale compound showed excellent ability in L-proline detection. Meanwhile, the catalytic activity of Ca-L-tart was also efficient in acetalization of methanol and aldehydes under mild temperature.

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