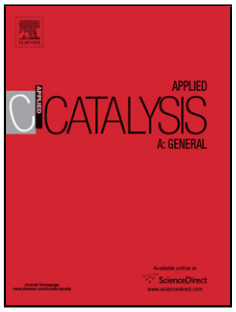


Zirconium coordination polymers based on tartaric and malic acids as catalysts for cyanosilylation reactions

Juan Amaro-Gahete, Dolores Esquivel, José R. Ruiz, César Jiménez-Sanchidrián, Francisco J. Romero-Salguero

PII:	S0926-860X(19)30345-X
DOI:	https://doi.org/10.1016/j.apcata.2019.117190
Article Number:	117190
Reference:	APCATA 117190
To appear in:	*Applied Catalysis A: General*
Received Date:	7 May 2019
Revised Date:	17 July 2019
Accepted Date:	4 August 2019

Please cite this article as: Amaro-Gahete J, Esquivel D, Ruiz JR, Jiménez-Sanchidrián C, Romero-Salguero FJ, Zirconium coordination polymers based on tartaric and malic acids as catalysts for cyanosilylation reactions, *Applied Catalysis A, General* (2019), doi: https://doi.org/10.1016/j.apcata.2019.117190

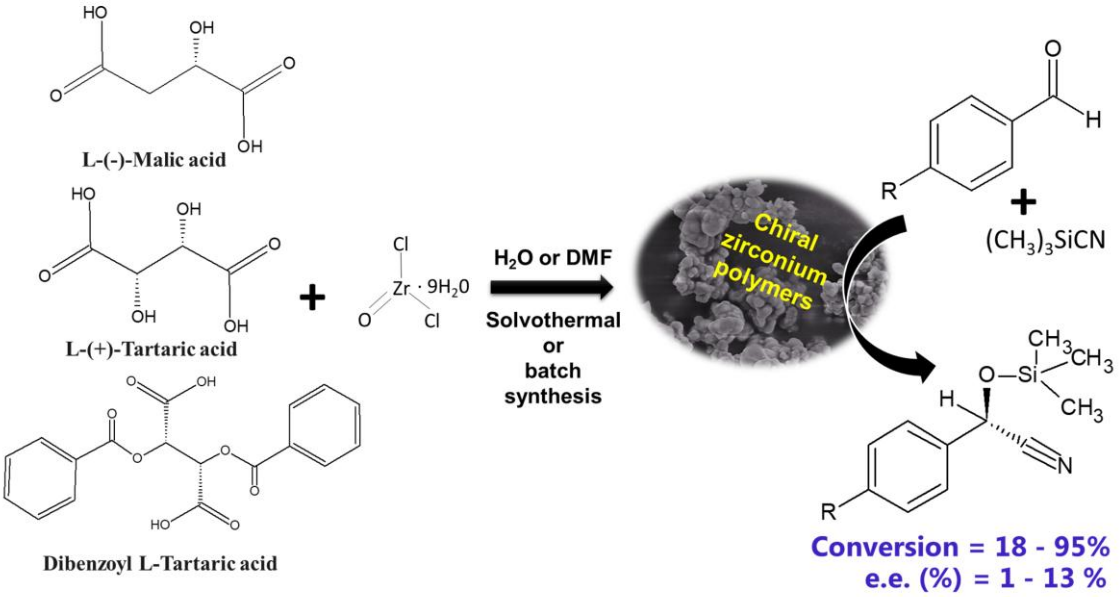
Zirconium coordination polymers based on tartaric and malic acids as catalysts for cyanosilylation reactions

Juan Amaro-Gahete, Dolores Esquivel, José R. Ruiz, César Jiménez-Sanchidrián and Francisco J. Romero-Salguero **

Departamento de Química Orgánica, Instituto Universitario de Investigación en Química Fina y Nanoquímica IUNAN, Facultad de Ciencias, Universidad de Córdoba, Campus de Rabanales, Edificio Marie Curie, E-14071 Córdoba, España

* Corresponding authors. Tel.: +34957218638; fax: +34957212066. E-mail address: qo2rosaf@uco.es (F.J.R.-S.); Tel.: +34957211050; fax: +34957212066. E-mail address: q12esmem@uco.es (D.E.)

Graphical abstract



Highlights

- Several coordination polymers containing Zr and L-tartaric acid, dibenzoyl-L-tartaric acid or L-malic acid were active in the cyanosilylation of benzaldehyde with TMSCN.
- Those polymers containing malic acid as ligand and a high Zr to malic acid ratio showed the highest catalytic activity.

- Enantiomeric excess of up to 12.6 % were obtained in Et_2O and low temperature (-10 ºC).
- Electron withdrawing groups in p-substituted benzaldehydes increased the conversion in the cyanosilylation reaction.

Abstract

The synthesis of chiral materials is a great challenge. This work describes the synthesis of Zr-based coordination polymers composed of chiral ligands derived from natural products. L-tartaric acid, dibenzoyl-L-tartaric acid and L-malic acid were selected as ligands from the chiral pool. Their reaction with zirconium oxychloride gave rise to several materials that were characterized by different techniques, such as XRD, Raman spectroscopy, ^{13}C MAS NMR, TGA and N_2 adsorption/desorption isotherms. Significant structural and textural properties have been observed depending on the ligand, the synthesis procedure and the metal to ligand ratio. These polymers were used for the first time as catalysts in the cyanosilylation of benzaldehyde with trimethylsilyl cyanide and their activity was compared with that of UiO-66. Different reaction parameters and reusability were studied for this asymmetric reaction. Some of the reported materials were very active in this reaction and provided a remarkable enantioselectivity depending on the reaction conditions.

KEYWORDS: Coordination polymers, Zr(IV) complexes, chiral linkers, cyanosilylation reaction, enantioselectivity, heterogenous catalysis.

1. Introduction

Coordination polymers are hybrid materials composed of organic linkers and metal nodes. [1, 2] Among different organic ligands used for the preparation of coordination polymers, malic and tartaric acids are promising linkers because they are readily abundant natural products and, besides two carboxylate groups, contains hydroxyl groups which can provide multiple coordination modes. In addition, both acids and their derivatives are simple and inexpensive chiral sources [3, 4].

Numerous coordination polymers and metal organic frameworks composed of malic and tartaric acids have been synthesized in the last years. Thus, for example, Williams et al. [5] reported two new indium tartrates, one of them with a microporous 3D framework with a channel size of ca. 6 Ǻ and Del Castillo et al. [6] described cadmium tartrates with open frameworks. Metal tartrates exhibit interesting applications such as antiferromagnetic coupling by manganese coordination polymers [3], photoluminescence by some rare-earth MOFs (La, Sm, Eu, Tb and Dy) [4] and ferroelectricity by cerium coordination polymers [7], among others. Metal malates of a variety of metal ions have also been synthesized [8]. For instance, the crystal structure of several chiral and achiral malates of Sr(II), Cu(II), Pb(II), Co(II), Ni(II), Mg(II), Zn(II) and Cd(II) have been reported in the last years [9-12].

Zirconium coordination polymers are particularly attractive because they generally exhibit a high stability due to the significant strength of Zr-O bonds. An example is UiO-66, which is a Zr-terephthalate based MOF, a versatile material for catalytic applications [13]. Both Lewis and Brönsted sites present in this material can act complementary to each other, making it very attractive for catalysis [14]. Even, the strength of the Lewis acid sites can be modulated changing the electronic character of groups bound to the linker [15]. Also, the important role of the accessibility of substrates to internal active sites was revealed by comparison of the catalytic activity of UiO-66 and UiO-67, the latter containing biphenyl-4,4'-dicarboxylate ligands [16]. Other Zr-based MOFs have been used as catalysts, i.e. a bimetallic Zr(Ti)-naphthalendicarboxylate MOFs [17], which was active in Lewis acid catalyzed reactions, such as Meerwein-Ponndorf-Verley and isomerization of α-pinene oxide, among others.

The first example of chiral catalysis with a MOF was reported by Kim et al. [18] This material was synthesized from a pyridyl derivative of tartaric acid and Zn(II). The enantiomeric excess in the transesterification of 2,4-dinitrophenyl acetate with 1-phenyl-2-propanol was 8%. Later, the coordination polymer Ni(L-asp)bipy$_{0.5}$, with L-asp = L-aspartate and bipy = 4,4'-dipyridyl, provided enantiomeric excess between +17% and -6% in the methanolysis of *cis*-2,3-epoxybutane [19]. A chiral Cu(II) coordination polymer based on binaphthyl units was essayed as catalyst in the cyanosilylation of benzaldehyde but it exhibited very low activity [20]. No results on the enantioselectivity of this process were provided.

The cyanosilylation of carbonyl compounds with TMSCN is an interesting organic reaction that gives rise to cyanohydrins, which are useful intermediates for the synthesis of a wide variety of compounds, such as α-hydroxyacids, α-hydroxyketones, β-hydroxyamines, α-aminonitriles and β-aminoalcohols, among others. A great number of different catalysts are active, including Lewis acids. In addition, the sp^2 carbon of the carbonyl group is transformed into a sp^3 stereogenic center and so the asymmetric cyanohydrins synthesis has been intensively pursued. Nevertheless, conversion and enantioselectivity are very sensible to the substrate, the catalyst and the reaction conditions [21]. Most homogeneous catalysts are based on privileged ligands as chiral building blocks, which usually work with coordinated expensive metals. Although most of these ligands are commercially available, their high cost prevents their general use in industry.

Even though several coordination polymers based on tartaric acid and malic acid has been reported (vide supra), to the best of our knowledge, materials containing them or very simple readily available derivatives have not been ever used as heterogeneous catalysts. Furthermore, the use of zirconium as metal node should provide Lewis acid sites and remarkable stability under reaction conditions. In addition, cyanohydrins have an asymmetric carbon atom and so the enantioselectivity in this process, which has hardly been studied for heterogeneous catalysts, can be assessed under different conditions.

Herein, we report the synthesis of zirconium coordination polymers with three different chiral organic linkers, i.e., tartaric acid, dibenzoyl tartaric acid and malic acid. After being characterized by different techniques, they have been tested as catalysts for the first time in cyanosilylation reactions. The activity and selectivity of these catalysts under different reaction conditions is reported. The influence of the ligand structure and the zirconium to ligand ratio has been described. Moreover, the stereoselectivity towards the chiral cyanohydrins has been determined.

2. Experimental

2.1. Reagents and materials

L-(+)-tartaric acid (≥ 99.5%), L-(-)-malic acid (≥ 99.5%), dibenzoyl-L-tartaric acid (98%), zirconium (IV) oxychloride octahydrate (99.5%) and N,N-dimethylformamide anhydrous (99.8%) were obtained from Sigma Aldrich. Formic acid pure (98%) was provided by PanReac AppliChem. For the catalytic activity tests, trimethylsilyl cyanide (98%) and benzaldehyde (99.5%) were supplied by Aldrich, whereas dodecane (≥ 99.5%) was provided by Fischer Scientific. All reactants and solvents were used as received, without further purification.

2.2. Synthesis of the catalysts

The synthesis of all materials was carried out either in an autoclave under autogenous pressure (A) or in a batch reactor under atmospheric pressure. The molar ratios of the Zr salt (Z) and linker precursor (tartaric acid (T), malic acid (M) or dibenzoyl-tartaric acid (DBT)) were 1:1 and 1:3, respectively. A summary of the nomenclature and reaction conditions are given in Table 1. Thus, Z_1T_1-110A was prepared by solvothermal synthesis using an autoclave under autogenous pressure (A) according to the following procedure. A mixture of 1 mmol of $ZrOCl_2 \cdot 9H_2O$ (0.322 g) (Z_1) and 1 mmol of tartaric acid (0.150 g) (T_1) in 10 mL of N,N-dimethylformamide (DMF) was heated in a teflon vessel at 110 ºC for 68 h. Later, the solid product was collected by membrane filtration and washed several times with DMF. To assure the complete removal of unreacted linker, the material was stirred in 25 mL of DMF for 24 h and then in ethanol for 24 h. Afterwards, the resulting material was dried under vacuum at 100 ºC for 24 h.

Alternatively, Z_1T_1-120 was synthesized in a batch reactor. For that, a solution containing 1 mmol of $ZrOCl_2 \cdot 9H_2O$ (0.322 g) (Z_1), 1 mmol of tartaric acid (0.150 g) (T_1) and 20 mL of DMF was transferred to a batch reactor at 120 ºC for 68 h. Then, the washing procedure was like the solvothermal synthesis. To increase the crystallinity of the materials synthesized in batch reactor, in some cases, formic acid (5 eq, 97.5µL) was added to the reaction mixture as a modulating agent (m).

Two batches of some materials were prepared to confirm the reproducibility in their synthesis and catalytic properties (see Scheme S1 in supplementary information).

Table 1 Nomenclature and reaction conditions for the synthesis of Zr-based coordination polymers.

Name	**Ligand (L)**	**Zr:L ratio**[a]	**Solvent**	**T (ºC)**	**Reactor**
Z_1T_1-110A	Tartaric acid	1:1	DMF	110	autoclave
Z_1T_1-120	Tartaric acid	1:1	DMF	120	batch
Z_1T_1-120m	Tartaric acid	1:1	DMF	120	batch
Z_1T_3-120	Tartaric acid	1:3	DMF	120	batch
Z_1T_3-120m	Tartaric acid	1:3	DMF	120	batch
Z_1DBT_1-110A	Dibenzoyl tartaric acid	1:1	DMF	110	autoclave
Z_1DBT_3-120	Dibenzoyl tartaric acid	1:3	DMF	120	batch
Z_1DBT_3-120m	Dibenzoyl tartaric acid	1:3	DMF	120	batch
Z_1M_1-110A	Malic acid	1:1	H_2O	110	autoclave
Z_1M_1-150A	Malic acid	1:1	H_2O	150	autoclave
Z_1M_1-180A	Malic acid	1:1	H_2O	180	autoclave
Z_1M_1-120	Malic acid	1:1	H_2O	120	batch
Z_1M_1-120m	Malic acid	1:1	H_2O	120	batch
Z_1M_3-120	Malic acid	1:3	H_2O	120	batch
Z_1M_3-120m	Malic acid	1:3	H_2O	120	batch

[a] Zr:L ratio in the synthesis medium; m: modulating agent.

2.3. Characterization of the catalysts

Powder X-ray diffraction (PXRD) patterns were recorded on a Bruker D8 DISCOVER A25 with Cu-Kα radiation of 0.15418 nm wavelength and a solid-state detector. The speed of the goniometer was 0.016 º / min and the sweep between 2º <2θ <70º. Nitrogen adsorption-desorption experiments were carried out using an Autosorb iQ/ASiQwin analyzer from Quantachrome Instruments at 77 K. Prior to measurements, the samples were outgassed at 90 ºC for 24 h. The specific surface area of each material was determined using the Brunauer-Emmett-Teller (BET) method over a relative pressure (P/P_0) range of 0.025 - 0.996. The thermogravimetric analysis was carried out to establish the stability of the coordination polymers as a function of temperature. The TGA records were obtained using a Mettler Toledo TGA/DSC instrument. The measurements were carried out in an O_2 atmosphere with a gas flow of 100 mL/min with a temperature range between 30 and 900 ºC and a heating ramp of 10 ºC/min. Raman spectra were acquired with a Renishaw Raman instrument (inVia Raman Microscope) by excitation with green laser light (532 nm) and a grating of 1800 lines/mm in a range 100-4000 cm^{-1}. A total of 15 scans per spectrum were performed to improve the signal-to-noise ratio. The ^{13}C CP/MAS NMR spectra were recorded at 100.61 MHz on a Bruker AVANCE 400 WB spectrometer at room temperature. An overall of 1000 free induction decays were accumulated. The excitation pulse and recycle time were 6 ms and 2 s, respectively. Chemical shifts were measured relative to a tetramethylsilane standard.

2.4. Catalytic activity

2.4.1. General procedure

The catalytic activity of the materials was studied in the cyanosilylation reaction [22]. The catalyst (12 mg) was pretreated at 120 ºC overnight under vacuum before the catalytic reaction and then added to a mixture of benzaldehyde (0.87 mmol), trimethylsilyl cyanide (2.6 mmol) and dodecane (0.39 mmol) as internal standard. The reaction was kept under nitrogen at different temperatures and reaction times. Samples collected at different times were analyzed by gas chromatography using a FID detector and VF-1MS capillary column (15 m x 0.25 mm ID). Benzaldehyde cyanohydrin was the only product identified. The enantioselectivity (% e.e.) was calculated by gas chromatography (VARIAN 450-GC) using a chiral capillary column (Restek Rtr-bDEXm).

For the cyanosilylation reaction of benzaldehyde and derivatives with TMSCN in presence of solvent, the molar ratios of reactants were kept, and 1 mL of solvent was added to the reaction mixture.

2.4.2. Hot filtration tests

The reactions were carried out as described previously, but alternatively after 1 or 3 h of reaction, the mixture was filtered off at room temperature using a syringe fitted with a 0.20 μm nylon membrane filter, to remove all catalyst particles. In each case, the clear solution obtained was transferred to a round-bottomed flask at room temperature under nitrogen atmosphere and stirred for further 17 h.

3. Results and discussion

3.1. Characterization of the catalysts

Different reaction conditions for the synthesis of Zr-coordination polymers based on chiral ligands were employed (see Experimental Section, Table 1). Zirconium malates were obtained in water at different temperatures. Unlike, zirconium tartrates could not be formed in water under the conditions studied and therefore DMF was used as solvent. This solvent was also chosen in the synthesis of zirconium dibenzoyltartrates due to the high insolubility of dibenzoyl tartaric acid in water. In some cases, the metal to ligand ratio was a determining parameter in the synthesis. For example, no precipitate was obtained in batch reactor with a Zr:DBT ratio of 1:1, being required a molar ratio of 1:3. In addition, in order to increase the crystallinity, a modulating agent (formic acid) was added in those synthesis performed in batch reactor.

After the synthesis, the stability of all coordination polymers was confirmed by solubility tests in different solvents such as water, ethanol, hexane and ethyl acetate.

The X-ray diffraction (XRD) patterns of some coordination polymers are depicted in Fig. 1. Under similar reaction conditions, only the material with malate as linkers exhibited crystallinity. All polymers based on tartaric acid, regardless of the metal to ligand ratio, showed a broad band at the interval $2\theta = 4 - 15^{\circ}$, which indicates poorly ordered materials (Fig. S1). Similar patterns were observed for those consisting of dibenzoyl tartaric acid (Fig. S2). Other Zr(IV) coordination polymers such as those based on 1,3,5-benzenetrisphosphonic acid and carboxylate-substituted derivatives have also been found to be poorly crystalline [23]. Unlike, malic acid led to amorphous materials when the metal:ligand ratio was 1:1 whereas crystalline materials were obtained with a metal:ligand ratio of 1:3 (Fig. S3). This difference of crystallinity for Zr-based coordination polymers could be related with the nature of the organic linkers. On one hand, the steric hindrance of the dibenzoyl groups could led to an amorphous structure and, on the other hand, the presence of two hydroxyl groups in the tartaric linker provides additional coordination modes that could affect the metal coordination and, therefore, their crystalline arrangement.

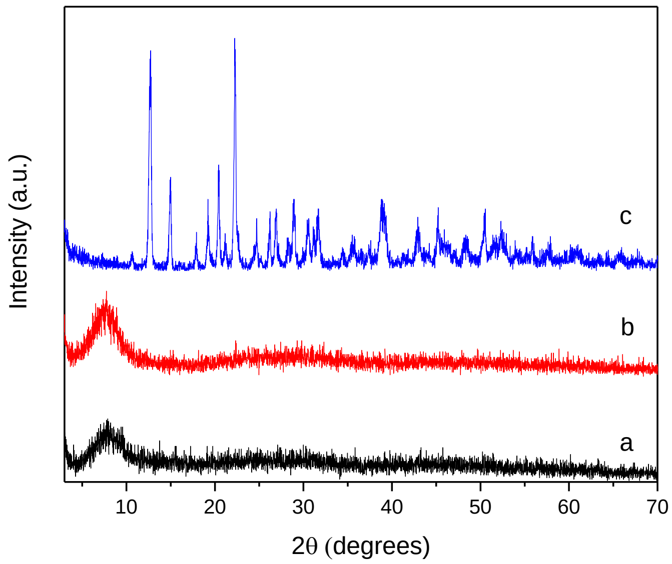


Fig. 1. X-ray diffraction patterns of Z_1T_3-120m (a), Z_1DBT_3-120m (b) and Z_1M_3-120m (c).

The adsorption-desorption isotherms for all samples, regardless of the synthesis conditions, were essentially type-IV with wide pore size distributions particularly in the mesopore range. For instance, adsorption-desorption isotherms and pore size distribution of Z_1M_1-110A, which has been used as catalyst (vide infra), are depicted in Fig. S4. Surface areas, pore volumes and pore radii are given for all coordination polymers in Table 2. All Zr-tartrate materials displayed a low specific surface area (below 20 m^2 g^{-1}), which slightly increased for Zr-dibenzoyl tartrates. Nevertheless, Zr-malates showed remarkable areas with up to 192 m^2 g^{-1}. For these coordination polymers, a slight decrease of the surface area was observed with the temperature of synthesis. However, the area dramatically decreased to ca. 30 m^2g^{-1} when the zirconium to malic acid molar ratio in the synthesis medium was 1:3. In addition, pore radii increased because the contribution of small pores in a more cross-linked structure is reduced.

Table 2 Physico-chemical properties of Zr-based coordination polymers

Name	**Zr:L ratio**[a]	**Zr/L ratio**[b]	**Weight loss (%)**	**S_{BET} (m^2/g)**	**Pore volume (cm^3/g)**	**Pore radius (Å)**
Z_1T_1-110A	1:1	0.8	64.7	7	0.016	43
Z_1T_1-120	1:1	1.1	57.4	19	0.033	38
Z_1T_1-120m	1:1	1.0	59.9	8	0.019	49
Z_1T_3-120	1:3	0.8	65.7	5	0.020	76

Z_1T_3-120m	1:3	1.0	61.9	8	0.016	41
Z_1DBT_1-110A	1:1	1.9	63.9	19	0.018	19
Z_1DBT_3-120	1:3	2.2	61.4	60	0.108	36
Z_1DBT_3-120m	1:3	2.0	63.2	26	0.049	38
Z_1M_1-110A	1:1	2.0	40.0	192	0.257	27
Z_1M_1-150A	1:1	2.4	41.9	121	0.207	32
Z_1M_1-180A	1:1	2.5	37.4	117	0.193	32
Z_1M_1-120	1:1	1.4	51.3	86	0.160	37
Z_1M_1-120m	1:1	1.4	50.8	190	0.146	15
Z_1M_3-120	1:3	0.8	59.9	28	0.120	87
Z_1M_3-120m	1:3	0.8	58.4	29	0.138	94

[a] Zr:L ratio in the synthesis medium; [b] Experimental Zr/L ratio calculated from TGA.

Thermogravimetric analysis was carried out to ascertain the stability and composition of the different materials (Figs. 2, S5, S6 and S7). Tartaric acid-based polymers displayed three weight losses. The first one up to 150 ºC is attributed to the removal of solvent molecules. The second loss between 250 and 350 ºC would correspond to the decomposition of the ligand molecules, i.e., tartaric acid. The decomposition of some fragments of the organic ligands in the form of carbonate ions bound to zirconium cations could be responsible for the third weight loss at ca. 550-650 ºC. Similar losses were observed for polymers with dibenzoyl tartaric acid, although the third loss occurred at somewhat lower temperature (ca. 450-500 ºC). In the case of malic acid-based polymers, some differences were observed depending on the metal to ligand ratio. Those polymers synthesized with a metal to ligand molar ratio of 1:1 exhibited three weight losses: up to 150 ºC, between 300 and 400 ºC and between 550 and 650 ºC. However, the second loss in these materials occurred in two stages. Nevertheless, more differences were observed for those solids obtained with a metal to ligand ratio of 1:3. The first loss was centered at ca. 200 ºC, clearly revealing a stronger interaction with solvent molecules in these materials. In addition, following the second loss, which was very steep, the weight remained constant.

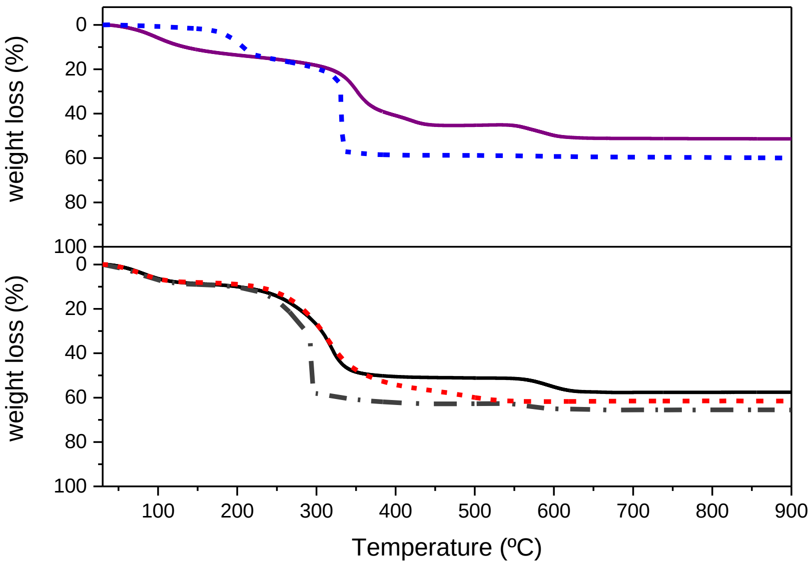


Fig. 2. Thermogravimetric curves for coordination polymers. Bottom: Z_1T_1-120 (solid line); Z_1T_3-120 (dotted-dashed line); Z_1DBT_3-120 (dashed line). Top: Z_1M_1-120 (solid line); Z_1M_3-120 (dashed line).

A rough estimate of the metal to ligand ratio can be obtained analyzing the TG curves of these materials, i.e. losses of organic ligands in relation to the remaining metal oxides [24]. The calculated values are given in Table 2. As can be seen, the metal to ligand ratios depended on several factors. In the case of zirconium tartrates, those values are close to 1, regardless of the relative amounts of Zr and tartaric acid present in the starting reaction mixture. This is the ratio for the most known zirconium metal organic framework, i.e. UiO-66 [24]. The metal to ligand ratio increased to ca. 2 for zirconium dibenzoyl tartrates. Interestingly, when malic acid was used as ligand, the metal to ligand ratio ranged from 0.8 to 2.5, depending on the relative amounts of the reactants, i.e. Zr and malic acid, and the reaction conditions.

When the metal to ligand ratio is compared for the three types of ligands under the same reaction conditions, an increase of the ratio is observed with the decrease in the number of coordinating functional groups of the ligands (-COOH and –OH). Consequently, the structure of the coordination polymers is more connected in the following order: Zr-tartrate ≥ Zr-malate ≥ Zr-dibenzoyl tartrate.

Raman spectra of the materials confirmed the presence of the corresponding linkers and so the formation of hybrid coordination polymers (Figs. 3, S8, S9 and S10).

All materials showed several bands in the range 2800 – 2975 cm^{-1} attributed to the C-H stretching of the chiral ligands. A signal centered at 1670 cm^{-1} can be assigned to the C=O stretching vibrations. Aromatic C-H stretching bands at 3072 and 3015 cm^{-1} were present in materials containing dibenzoyltartaric acid. Additionally, polymers based on tartaric acid showed a band at 3100 cm^{-1} indicating hydrogen bonding interaction between water molecules and carboxyl groups in the material [25]. Zr-O coordination was also confirmed in the polymers by the vibration modes at 663, 619 and 408 cm^{-1} ascribable to Zr-O stretching [26].

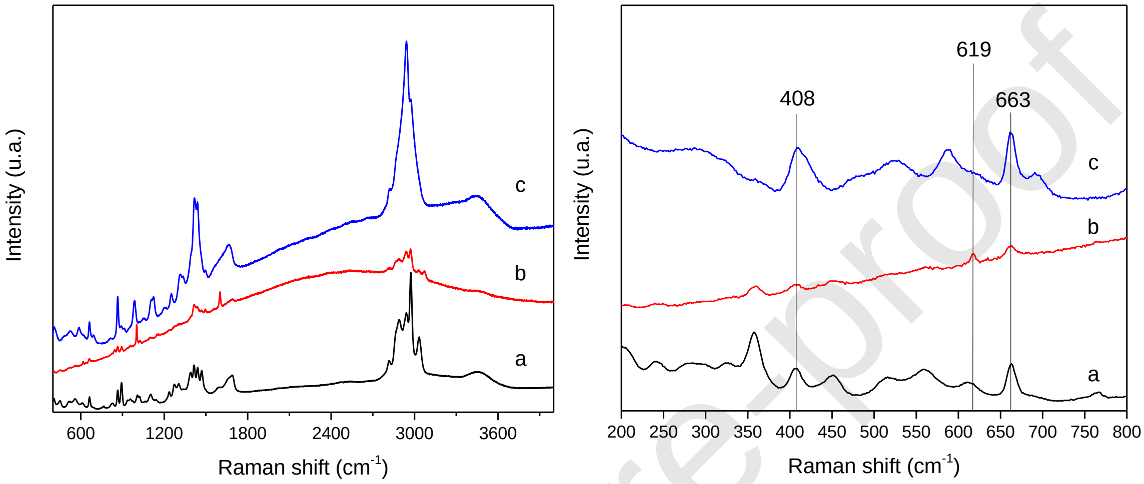


Fig. 3. Raman spectra of samples Z_1T_1-110A (a), Z_1DBT_1-110A (b) and Z_1M_1-110A (c).

In some cases, the linkers in coordination polymers can undergo chemical transformations. For example, upon heating, lithium L-malate undergoes topotactic dehydration to form a phase containing the unsaturated fumarate ligand, in which the original 3-D framework remains intact [27]. To assure that the ligands stay intact during the synthesis, ^{13}C NMR experiments were accomplished. The ^{13}C CP/MAS NMR spectra of Z_1M_1-110A, Z_1T_3-120m and Z_1DBT_1-110A without previous activation are shown in Fig. 4. Z_1M_1-110A and Z_1T_3-120m showed similar spectra with two sets of resonance peaks. A first set located in the range of 160-200 ppm is attributed to the carboxyl carbon atoms of the chiral ligands, which can be in different chemical environments. The second set at high field (30-80 ppm) is assigned to the Csp^3 of the organic linkers, being more deshielded the carbon atoms bearing hydroxyl groups. For Z_1DBT_1-110A, the ^{13}C NMR spectrum showed additional signals in the 120-140 ppm range which correspond to the aromatic rings of the benzoyl groups. The presence of signals associated to DMF molecules was present in all materials. These signals were absent after activation of the catalysts at 120 ºC overnight under vacuum (see experimental section and Fig. S11 in supplementary information).

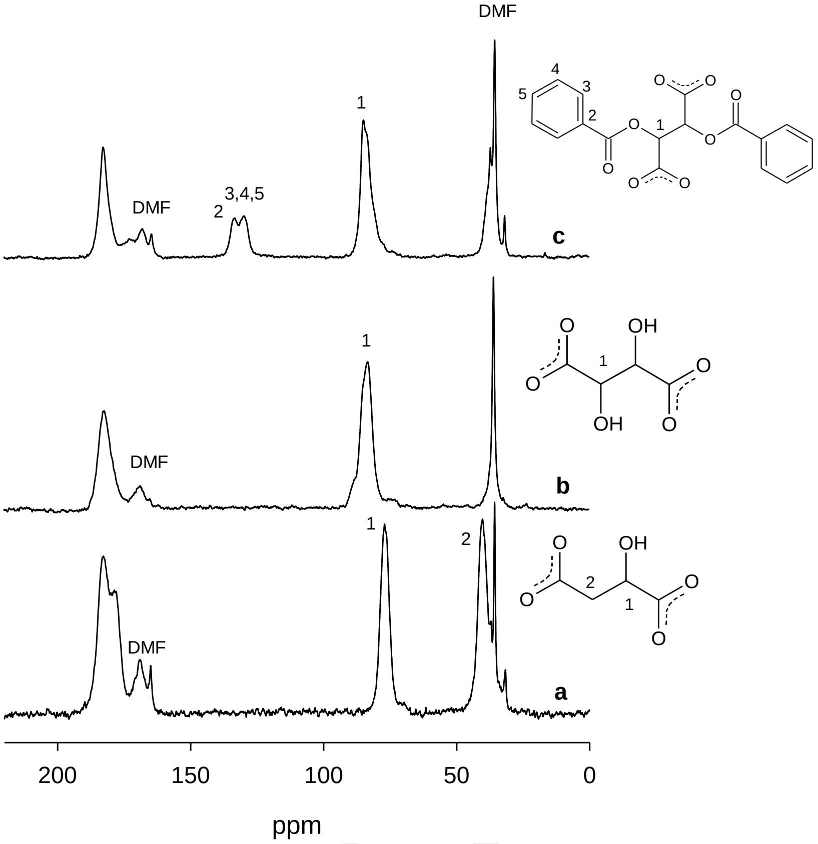


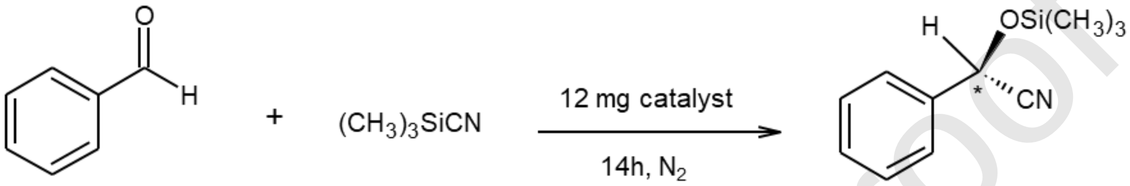
Fig. 4. Solid-state ^{13}C CP/MAS NMR spectra of Z_1M_1-110A (a), Z_1T_3-120m (b) and Z_1DBT_1-110A (c).

In order to prove that ligands do not undergo racemization under the synthesis conditions, vibrational circular dichroism measurements were undertaken. Unfortunately, they were not conclusive. Instead, degradation of the polymer followed by derivatization of the ligand and chiral GC analysis (Fig. S12 in supplementary information) demonstrated that the optical purity of the ligands remained intact during the synthesis procedure.

3.2. Catalytic activity

Solvent-free cyanosilylation of benzaldehyde with trimethylsilyl cyanide (TMSCN)

All coordination polymers were tested as catalysts for the cyanosilylation reaction of benzaldehyde with trimethylsilyl cyanide (TMSCN) (Scheme 1) under solvent-free conditions. In absence of any catalyst, the blank reaction gave a conversion of 18 % after 14h at room temperature (Fig. S13).



Scheme 1. Cyanosilylation of benzaldehyde with TMSCN.

Zr-tartrates exhibited relatively low activity as catalysts (Fig. 5). The maximum conversion obtained for such materials was 47%. Most of dibenzoyl tartrate polymers were inactive except for Z_1DBT_1-110A, which gave rise to a 67% conversion.

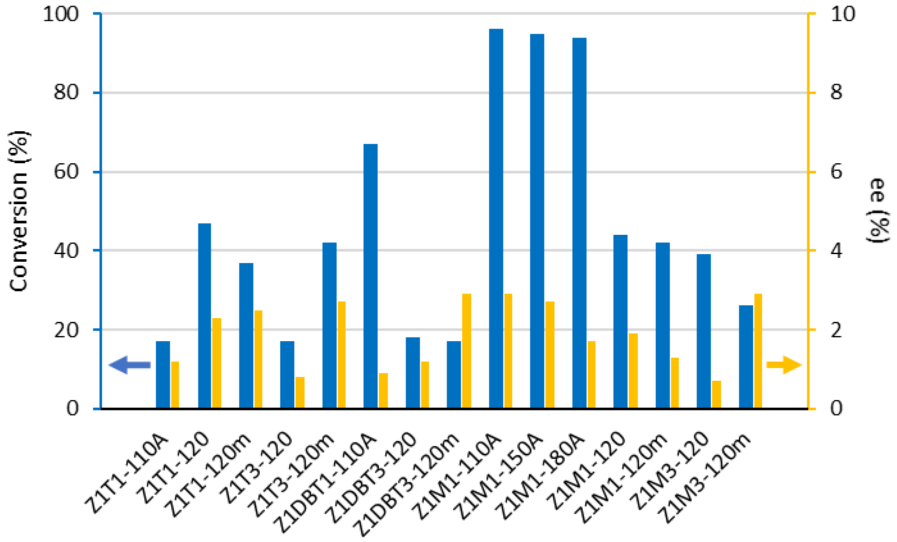


Fig. 5. Conversion (%) and ee (%) in the cyanosilylation of benzaldehyde with TMSCN at RT for 14 h.

However, the most active coordination polymers were those synthesized from malic acid. Some of them provided a conversion around 95%. For example, polymer Z_1M_1-110A gave a conversion and TON (turnover number) comparable to other heterogeneous catalysts (Table 3). Under the same conditions, the metal-organic framework UiO-66 was essayed, resulting in a conversion of 95%. In the case of Zr-malates, the metal to ligand ratio plays an important role in the catalytic activity. In fact, those materials with the highest activities have ratios about 2. The rest of Zr-malates with metal to ligand ratios between 1.4 and 0.8 gave conversions below 45%. In addition, the conversion decreased as the Zr/L ratio decreased. To compensate the lower content of Zr in sample Z_1M_3-120m compared to polymer Z_1M_1-110A, the catalyst weight for the latter was increased by 2.5 times, while maintaining the rest of conditions, and its catalytic activity remained very low, ca. 23%. This fact revealed the importance of the connectivity of the coordination polymer. Indeed, increasing the number of ligand molecules around Zr decreases the catalytic activity, thus corroborating the role of Zr cations as Lewis acid sites. If they are buried by ligands, they are no longer accessible to the reactants. Similarly, it has been reported that the catalytic activity of UiO-66 in the Fischer esterification increased when defects consisting of coordinatively unsaturated Zr ions with Lewis acid properties were present in its structure [14]. In particular, the activation of TMSCN by adsorption on Lewis acid sites (Zr ions) has been suggested for the cyanosilylation of benzaldehyde in sulfated-zirconia catalysts [28]. The metal-organic framework compound $Cu_3(BTC)_2(H_2O)_3 \cdot xH_2O$ (BTC= benzene 1,3,5-tricarboxylate) was tested as catalyst in the cyanosilylation of benzaldehyde [29]. Prior to its application it had to be dehydrated in high vacuum at 100 ºC in order to remove physically and chemically bound water molecules and so give Lewis acid Cu(II) sites. However, maximum yield was not higher than 57% even after 72 h. In addition, it was very sensitive to the reaction conditions.

Table 3 Activity of some heterogeneous catalysts reported in the literature.

Entry	Catalyst	Solvent	Yield (%)	TON	Ref.
1	Z_1M_1-110A	none	96	16.5	This work
2	Cu(II)-Arylhydrazone Coordination Polymers	MeOH	79.9	16	[30]
3	Cu(II) Mixed-ligand Coordination Polymers	none	95.2	47.6	[12]
4	Bu_2SnCl_2	none	97	9.7	[31]
5	primary amide-based cationic metal complexes	none	99	49.5	[32]
6	Cp–Zr–Binol@SBA-15	toluene	100	66.7	[33]
7	Eu^{3+}-MCM-41	none	90	137	[34]
8	$Cu_3(BTC)_2$	pentane	57	10.9	[29]
9	UiO-66-A	dichloromethane	96	9.6	[35]
10	UiO-68-V	1,2-dichloroethane	85	17	[36]
11	MIL-101 (Cr)	none	96	320	[37]

The three ligands used for the synthesis of the coordination polymers are chiral. Accordingly, the enantiomeric excess (e.e.) was determined in every reaction. These results are shown in Figure 5. In general, all materials provided a clear enantioselectivity but with e.e. values below 3%. Even so, it should be noted that, in the catalyst free reaction, enantioselectivity was not achieved, just obtaining the racemic mixture of the corresponding cyanohydrin. Those polymers composed of malic acid synthesized in autoclaves at different temperatures gave the highest conversion and enantioselectivity. Concerning these materials, a decrease in the e.e. value was observed as the synthesis temperature increased, which also corresponded with an increase in the metal to ligand ratio. Recent studies on rare-earth metal complexed to chiral pyrrolyl-substituted 1,2-diimino ligands in cyanosilylation reactions have reported similar yields but the products were racemic.[38]

To further investigate this reaction, Z_1M_1-110A, the most active polymer with higher enantiomeric excess (e.e.) among catalysts tested, was selected to perform additional studies on cyanosilylation reactions.

Effect of reaction temperature

In order to ascertain the effect of reaction temperature, particularly on enantioselectiviy, the cyanosilylation reaction was also carried out at 10 and -10 ºC. As observed in Table 4, the temperature clearly affected the enantioselectivity. The lower the temperature, the higher the e.e. value. Thus, at -10 ºC, the e.e. was ca. 6%, even though the yield was greatly reduced. Although this e.e. is low, it is significant because the active sites, i.e., Zr cations, are not directly attached to chiral centers but they are located in a chiral environment provided by chiral ligands. Analogous results were reported by Lin et al. [39] with coordination polymers consisting of 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl ligands (BINAP) and different lanthanides, which gave rise to e.e. below 5% in the cyanosilylation of aldehydes. Obviously, higher enantiomeric excess have been reported on catalysts based on transition metal complexes with chiral privileged ligands, such as those metal-organic frameworks [22] and periodic mesoporous organosilicas [40] containing homochiral vanadium-salen complexes, which yielded e.e. around 70% and 30%, respectively.

Table 4 Conversion and enantiomeric excess in the cyanosilylation reaction at different temperatures using Z_1M_1-110A as catalyst.

Temperature (ºC)	Time (h)	Conversion (%)	e.e. (%)
rt	14	96	2.9
10	20	95	5.1
-10	20	55	5.9

Solvent and promoter effects

Although previous studies have revealed that this type of reaction progresses very well under solvent-free conditions [41], additional experiments were performed in presence of different solvents to examine their role in the cyanosilylation reaction. As seen in Table 5, the presence of solvent in the reaction media produced a decrease in the conversion, from 96 % under solvent-free conditions to 18% when DMF was added. The polarity of the solvent clearly influenced on the cyanosilylation reaction. [42] Non-polar solvents, as hexane, did not affect the reaction rate. Unlike, the use of polar solvents such as DMF, CH_3CN and THF reduced the yield, which was lower than 25%. Unlike, the reactions in moderately polar solvents like CH_2Cl_2 and Et_2O gave higher conversions. This decrease in polar solvents can be probably due to the coordination ability of the solvent molecules to unsaturated Zr-sites.[37] Although the conversions in presence of solvents were greatly reduced, the ee values were higher in all cases, with 10.6 and 11.4 % ee in toluene and Et_2O, respectively. These results showed the important role of the solvent on the enantioselectivity of this type of reaction.

The enantioselective cyanohydrin formation has been a subject of study by numerous researchers. Not only the solvent has shown to have an important impact on asymmetric catalytic systems, but also the addition of “promoters”, such as $CH_3P(O)Ph_2$, Bu_3PO and Ph_3PO have been beneficial for the yields and enantioselectivies obtained.[43] Ph_3PO has been found to be a superior cocatalyst [44] and so, in order to evaluate this effect, additional catalytic experiments on the reaction of benzaldehyde with TMSCN under different solvents in the presence of Ph_3PO were carried out. The results obtained are listed in Table 4. In most cases, the reaction rates were enhanced by the addition of the promoter. In contrast, the enantioselectivities values did not show an increasing tendency in all solvents when the promotor was added. Only those reactions in CH_3CN and DMF increased twice the ee values.

In addition, those conditions providing higher conversions and enantiomeric excess were selected to perform the experiments at low temperature (-10 ºC) The cyanosilylation reaction of benzaldehyde in the presence of toluene and Ph_3PO at -10ºC gave a conversion of 15% and ee of 11.1%. Moreover, in Et_2O and without any added Ph_3PO, the reaction reached the highest ee, 12.6%. These results confirmed that the yield and enantiomeric excess on asymmetric catalytic systems are very sensitive to small changes in the reaction conditions.

Table 5 Z_1M_1-110A catalyzed cyanosilylation reaction of benzaldehyde under different conditions (solvents and promoter).

Solvent	Promoter	Conv. (%)	ee (%)
CH_2Cl_2	-	36	9.0
	Ph_3PO	84	7.1
THF	-	25	9.6
	Ph_3PO	71	6.3
CH_3CN	-	24	4.1
	Ph_3PO	74	9.2
Hexane	-	94	7.9
	Ph_3PO	89	8.4
DMF	-	18	3.9
	Ph_3PO	75	5.3
Toluene	-	44	10.6
	Ph_3PO	74	9.7
	Ph_3PO	15(*)	11.1(*)
Et_2O	-	78	11.4
	Ph_3PO	70	9.3
	-	19(*)	12.6(*)
Solvent free	-	96	2.9

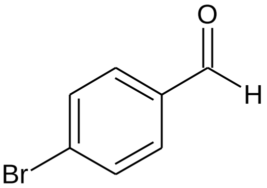
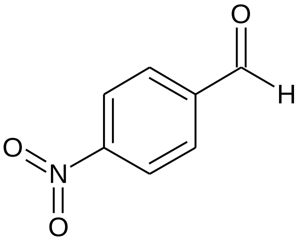
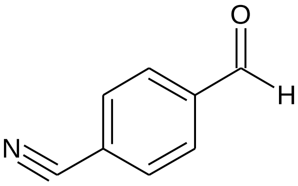
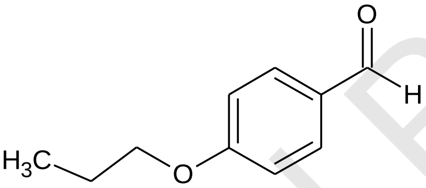
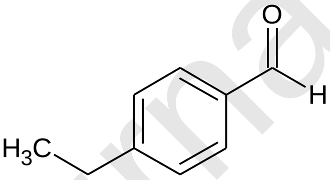
*The reaction was performed at -10ºC; Promoter, Ph_3PO, 0.2 equiv.

Scope of the reaction

In order to assess the scope of this catalytic system, tests were carried out using the catalyst Z_1M_1-110A to demonstrate its effectiveness in reactions with different p-substituted benzaldehydes. The experimental conditions were established considering the solubility of the different reactants. dichloromethane was selected because it dissolved all of the tested p-substituted benzaldehydes. In addition, the Ph_3PO promoter was added to the reaction mixture because it improved the catalytic results when using dichloromethane as solvent (vide supra).

The conversion and enantioselectivity results for the different substrates are shown in Table 6. It can be observed that the p-substituted benzaldehydes bearing electron withdrawing substituents such as nitro, cyano or bromo give riseto high conversion and ee. On the other hand, the p-substituted benzaldehydes with electro donating groups produced poorer yields in the catalytic process.[37]

Table 6 Catalytic cyanosilylation of p-substituted benzaldehydes after 14 h at room temperature in CH_2Cl_2 using 0.2 eq of Ph_3PO as promoter.

p-substituted benzaldehydes	**Conversion (%)**	**ee (%)**
p-bromobenzaldehyde 	88.7	8.4
p-nitrobenzaldehyde 	54.6	11.3
p-cyanobenzaldehyde 	>99	5.2
p-propoxybenzaldehyde 	31.1	n.a.[1]
p-ethylbenzaldehyde 	50.1	n.a.[1]

[1] not available; the enantiomeric reaction products could not be separated by chiral GC.

Heterogeneity tests

In order to check the heterogeneity of the cyanosilylation reaction, two hot filtration tests were undertaken with Z_1M_1-110A catalyst at different conversions (Fig. 6). After the removal of the catalyst, the reaction did not progress, thus revealing that the reaction occurred under heterogeneous conditions.[45] That was also indicative of the stability of these coordination polymers under the reaction conditions.

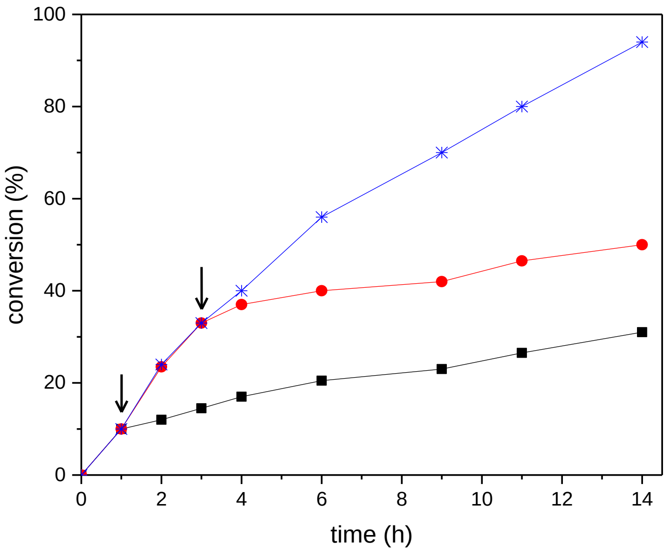


Fig. 6. Hot filtration test in the solvent-free cyanosilylation of benzaldehyde with TMSCN. Conversion vs time for the catalyzed reaction (*) and for the reaction after filtration of the catalyst at 1h (■) and 3 h (●).

4. Conclusions

Zirconium-based coordination polymers with different chiral ligands (L-tartaric acid, dibenzoyl-L-tartaric acid and L-malic acid) were synthesized under solvothermal conditions in batch reactor or autoclave. Textural and structural properties of the resultant polymers were directly related to the chiral ligand, the synthesis conditions and the metal:ligand ratio. Most of the resulting materials were amorphous except for some malic acid coordination polymers which showed high cristallinity. Zr-malates exhibited higher specific surface areas than Zr-tartrates and Zr-dibenzoyltartrates, although it strongly depended on the Zr to ligand ratio. Several characterization techniques showed that the organic linkers remained unaltered under the synthesis conditions. Several materials were active in the cyanosilylation reaction of benzaldehyde with TMSCN, particularly some coordination polymers containing malic acid as ligand, giving rise to conversions comparable to UiO-66. In general, a high Zr to malic acid ratio resulted in a higher catalytic activity. Furthermore, the use of Ph_3PO as promoter tended to increase the conversion whereas the activity in polar organic solvents decreased. Interestingly, enantiomeric excess of up to 12.6%, depending on the reaction conditions, has been observed. Different p-substituted benzaldehydes have also been used as substrates exhibiting moderate to good conversion toward the corresponding cyanosilylated product and variable enantioselectivity. Thus, these materials can be considered as promising green catalysts for Lewis acid-catalyzed organic processes.

Acknowledgments

The authors wish to acknowledge the financial support from Ramon Areces Foundation (Spain), Andalusian Regional Government (FQM-346 group), Spanish Ministry of Science, Innovation and Universities for an FPU teaching and research fellowship (FPU17/03981) and a project MAT2013-44463-R, Feder Funds, the technical staff from the Instituto Universitario de Investigación en Química Fina y Nanoquímica (IUNAN) and Servicio Central de Apoyo a la Investigación (SCAI).

References

[1] O.M. Yaghi, M. O'Keeffe, N.W. Ockwig, H.K. Chae, M. Eddaoudi, J. Kim, Reticular synthesis and the design of new materials, Nature, 423 (2003) 705-714.

[2] S. Kitagawa, R. Kitaura, S. Noro, Functional porous coordination polymers, Angew Chem Int Edit, 43 (2004) 2334-2375.

[3] J. Lu, H.T. Liu, D.Q. Wang, M.J. Niu, S.N. Wang, Two Novel Three-dimensional Networks Constructed by Mn or Cd Ion and Tartrate: Syntheses, Structures and Properties, J Chem Crystallogr, 41 (2011) 641-648.

[4] Z.G. Jiang, Y.K. Lv, J.W. Cheng, Y.L. Feng, Two types of rare earth-organic frameworks constructed by racemic tartaric acid, J Solid State Chem, 185 (2012) 253-263.

[5] A.S.F. Au-Yeung, H.H.Y. Sung, J.A.K. Cha, A.W.H. Siu, S.S.Y. Chui, I.D. Williams, Hydrothermal synthesis of indium tartrates: Structures of the chiral polymer [In(L-TAR)3-H2O] center dot 0.5H(2)O containing the tartrate trianion, and a microporous hybrid solid [In(OH)(D/L-TAR)(2-)] center dot 2H(2)O, Inorg Chem Commun, 9 (2006) 507-511.

[6] P. Vera-Cruz, R.A. Toscano, J. Balmaseda, M. Basterrechea, N. Nino, L.F. del Castillo, Synthesis and crystal structure of three new cadmium tartrates with open frameworks, Crystengcomm, 14 (2012) 8606-8614.

[7] J.L. Qi, S.L. Ni, Y.Q. Zheng, W. Xu, Syntheses, structural characterizations and ferroelectric properties of new Ce(III) coordination polymers via isomeric tartaric acid ligands, Solid State Sci, 28 (2014) 61-66.

[8] A. Beghidja, P. Rabu, G. Rogez, R. Welter, Synthesis, structure and magnetic properties of chiral and nonchiral transition-metal malates, Chem-Eur J, 12 (2006) 7627-7638.

[9] A. Ghosh, C.N.R. Rao, Chiral and achiral malate frameworks with different dimensionalities, Z Anorg Allg Chem, 634 (2008) 1115-1122.

[10] D.S. Raja, J.H. Luo, T.G. Chang, S.H. Lo, C.Y. Wu, C.H. Lin, Solvothermal synthesis, crystal structures and properties of two new magnesium coordination polymers of (L)-malic acid, Inorg Chem Commun, 32 (2013) 22-27.

[11] R.H. Zhang, Q.M. Hong, J.M. Yang, H.L. Zhang, G.M. Blackburnb, Z.H. Zhou, Syntheses, spectroscopies and structures of zinc complexes with malate, Inorg Chim Acta, 362 (2009) 2643-2649.

[12] X.P. Wang, Y.Q. Zhao, Z. Jaglicic, S.N. Wang, S.J. Lin, X.Y. Li, D. Sun, Controlled in situ reaction for the assembly of Cu(II) mixed-ligand coordination polymers: synthesis, structure, mechanistic insights, magnetism and catalysis, Dalton T, 44 (2015) 11013-11020.

[13] Y. Bai, Y.B. Dou, L.H. Xie, W. Rutledge, J.R. Li, H.C. Zhou, Zr-based metal-organic frameworks: design, synthesis, structure, and applications, Chem Soc Rev, 45 (2016) 2327-2367.

[14] C. Caratelli, J. Hajek, F.G. Cirujano, M. Waroquier, F.X.L.I. Xamena, V. Van Speybroeck, Nature of active sites on UiO-66 and beneficial influence of water in the catalysis of Fischer esterification, J Catal, 352 (2017) 401-414.

[15] M.N. Timofeeva, V.N. Panchenko, J.W. Jun, Z. Hasan, M.M. Matrosova, S.H. Jhung, Effects of linker substitution on catalytic properties of porous zirconium terephthalate UiO-66 in acetalization of benzaldehyde with methanol, Appl Catal a-Gen, 471 (2014) 91-97.

[16] U.S.F. Arrozi, H.W. Wijaya, A. Patah, Y. Permana, Efficient acetalization of benzaldehydes using UiO-66 and UiO-67: Substrates accessibility or Lewis acidity of zirconium, Appl Catal a-Gen, 506 (2015) 77-84.

[17] A.M. Rasero-Almansa, M. Iglesias, F. Sanchez, Synthesis of bimetallic Zr(Ti)-naphthalendicarboxylate MOFs and their properties as Lewis acid catalysis, Rsc Adv, 6 (2016) 106790-106797.

[18] J.S. Seo, D. Whang, H. Lee, S.I. Jun, J. Oh, Y.J. Jeon, K. Kim, A homochiral metal-organic porous material for enantioselective separation and catalysis, Nature, 404 (2000) 982-986.

[19] M.J. Ingleson, J.P. Barrio, J. Bacsa, C. Dickinson, H. Park, M.J. Rosseinsky, Generation of a solid Bronsted acid site in a chiral framework, Chem Commun, (2008) 1287-1289.

[20] W.W. Lestari, P. Lonnecke, H.C. Streit, F. Schleife, C. Wickleder, E. Hey-Hawkins, A chiral two-dimensional coordination polymer based on Cu-II and (S)-4,4 '-bis(4-carboxyphenyl)-2,2 '-bis(diphenylphosphinoyl)-1,1 '-binaphthyl: Synthesis, structure, and magnetic and optical properties, Inorg Chim Acta, 421 (2014) 392-398.

[21] R. Gregory, Vision science: Photons to phenomenology, Nature, 401 (1999) 213-214.

[22] A. Bhunia, S. Dey, J.M. Moreno, U. Diaz, P. Concepcion, K. Van Hecke, C. Janiak, P. Van Der Voort, A homochiral vanadium-salen based cadmium bpdc MOF with permanent porosity as an asymmetric catalyst in solvent-free cyanosilylation, Chem Commun, 52 (2016) 1401-1404.

[23] V. Luca, J.J. Tejada, D. Vega, G. Arrachart, C. Rey, Zirconium(IV)-Benzene Phosphonate Coordination Polymers: Lanthanide and Actinide Extraction and Thermal Properties, Inorg Chem, 55 (2016) 7928-7943.

[24] L. Valenzano, B. Civalleri, S. Chavan, S. Bordiga, M.H. Nilsen, S. Jakobsen, K.P. Lillerud, C. Lamberti, Disclosing the Complex Structure of UiO-66 Metal Organic Framework: A Synergic Combination of Experiment and Theory, Chem Mater, 23 (2011) 1700-1718.

[25] M. Rashidipour, Z. Derikvand, A. Shokrollahi, Z. Mohammadpour, A. Azadbakht, A 2D metal-organic coordination polymer of Cu(II) based on tartrate ligands; synthesis, characterization, spectroscopic, crystal structure, solution studies and electrochemical behavior, Arabian Journal of Chemistry, 10 (2017) S3167-S3175.

[26] S. Chavan, J.G. Vitillo, D. Gianolio, O. Zavorotynska, B. Civalleri, S. Jakobsen, M.H. Nilsen, L. Valenzano, C. Lamberti, K.P. Lillerud, S. Bordiga, H-2 storage in isostructural UiO-67 and UiO-66 MOFs, Phys Chem Chem Phys, 14 (2012) 1614-1626.

[27] H.H.M. Yeung, M. Kosa, J.M. Griffin, C.P. Grey, D.T. Major, A.K. Cheetham, Topotactic elimination of water across a C-C ligand bond in a dense 3-D metal-organic framework, Chem Commun, 50 (2014) 13292-13295.

[28] B. Thirupathi, M.K. Patil, B.M. Reddy, Activation of trimethylsilyl cyanide and mechanistic investigation for facile cyanosilylation by solid acid catalysts under mild and solvent-free conditions, Appl Catal a-Gen, 384 (2010) 147-153.

[29] K. Schlichte, T. Kratzke, S. Kaskel, Improved synthesis, thermal stability and catalytic properties of the metal-organic framework compound CU3(BTC)(2), Micropor Mesopor Mat, 73 (2004) 81-88.

[30] G.A.O. Tiago, K.T. Mahmudov, M.F.C.G. da Silva, A.P.C. Ribeiro, L.C. Branco, F.I. Zubkov, A.J.L. Pombeiro, Cyanosilylation of Aldehydes Catalyzed by Ag(I)- and Cu(II)-Arylhydrazone Coordination Polymers in Conventional and in Ionic Liquid Media, Catalysts, 9 (2019).

[31] J.K. Whitesell, R. Apodaca, Trimethylsilylcyanation of aldehydes and ketones catalyzed by diorganotin dichlorides, Tetrahedron Lett, 37 (1996) 2525-2528.

[32] D. Markad, S. Khullar, S.K. Mandal, Novel primary amide-based cationic metal complexes: green synthesis, crystal structures, Hirshfeld surface analysis and solvent-free cyanosilylation reaction, Dalton T, 48 (2019) 3743-3757.

[33] W. Xu, B. Yu, Y. Zhang, X. Chen, G.F. Zhang, Z.W. Gao, Single-site SBA-15 supported zirconium catalysts. Synthesis, characterization and toward cyanosilylation reaction, Appl Surf Sci, 325 (2015) 227-234.

[34] A. Procopio, G. Das, M. Nardi, M. Oliverio, L. Pasqua, A Mesoporous Er-III-MCM-41 Catalyst for the Cyanosilylation of Aldehydes and Ketones under Solvent-free Conditions, Chemsuschem, 1 (2008) 916-919.

[35] F.G. Xi, Y. Yang, H. Liu, H.F. Yao, E.Q. Gao, Different acidity and additive effects of zirconium metal-organic frameworks as catalysts for cyanosilylation, Rsc Adv, 5 (2015) 79216-79223.

[36] C.X. Tan, X. Han, Z.J. Li, Y. Liu, Y. Cui, Controlled Exchange of Achiral Linkers with Chiral Linkers in Zr-Based UiO-68 Metal-Organic Framework, J Am Chem Soc, 140 (2018) 16229-16236.

[37] Z.G. Zhang, J.W. Chen, Z.B. Bao, G.G. Chang, H.B. Xing, Q.L. Ren, Insight into the catalytic properties and applications of metal-organic frameworks in the cyanosilylation of aldehydes, Rsc Adv, 5 (2015) 79355-79360.

[38] W. Wang, X.J. Wang, S.L. Zhou, X.L. Xu, J. Du, L.J. Zhang, X.L. Mu, Y. Wei, X.C. Zhu, S.W. Wang, Syntheses, Structures, and Catalytic Activities of the Anionic Heterobimetallic Rare-Earth Metal Complexes Supported by Pyrrolyl-Substituted 1,2-Diimino Ligands, Inorg Chem, 57 (2018) 10390-10400.

[39] O.R. Evans, H.L. Ngo, W.B. Lin, Chiral porous solids based on lamellar lanthanide phosphonates, J Am Chem Soc, 123 (2001) 10395-10396.

[40] C. Baleizao, B. Gigante, D. Das, M. Alvaro, H. Garcia, A. Corma, Synthesis and catalytic activity of a chiral periodic mesoporous organosilica (ChiMO), Chem Commun, (2003) 1860-1861.

[41] A. Karmakar, G.M.D.M. Rubio, A. Paul, M.F.C.G. da Silva, K.T. Mahmudov, F.I. Guseinov, S.A.C. Carabineiro, A.J.L. Pombeiro, Lanthanide metal organic frameworks based on dicarboxyl-functionalized arylhydrazone of barbituric acid: syntheses, structures, luminescence and catalytic cyanosilylation of aldehydes, Dalton T, 46 (2017) 8649-8657.

[42] A.V. Gurbanov, K.T. Mahmudov, M. Sutradhar, A.C.G. da Silva, T.A. Mahmudov, F.I. Guseinov, F.I. Zubkov, A.M. Maharramov, A.J.L. Pombeiro, Copper(II) complexes with carboxylic- or sulfonic-functionalized arylhydrazones of acetoacetanilide and their application in cyanosilylation of aldehydes, J Organomet Chem, 834 (2017) 22-27.

[43] E.M. Vogl, H. Groger, M. Shibasaki, Towards perfect asymmetric catalysis: Additives and cocatalysts, Angew Chem Int Edit, 38 (1999) 1570-1577.

[44] D.H. Ryu, E.J. Corey, Highly enantioselective cyanosilylation of aldehydes catalyzed by a chiral oxazaborolidinium ion, J Am Chem Soc, 126 (2004) 8106-8107.

[45] J. Kim, S.N. Kim, H.G. Jang, G. Seo, W.S. Ahn, CO2 cycloaddition of styrene oxide over MOF catalysts, Appl Catal a-Gen, 453 (2013) 175-180.