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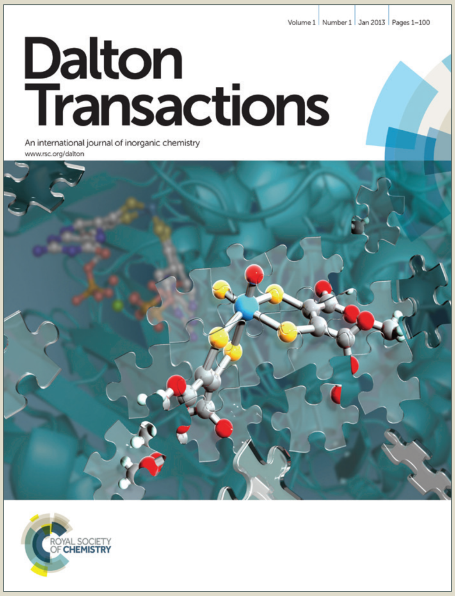

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Alkaline earth metal based metal-organic framework: Hydrothermal synthesis, X-ray structure and heterogeneously catalyzed Claisen–Schmidt reaction†

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†Electronic supplementary information (ESI) available: Table for hydrogen bonding interactions, ORTEP diagram of compound **1** and **2**, TG curve of compound **2**, In-situ PXRD of **1** and **2**, melting points, ^{1}H NMR, ^{13}C NMR, HRMS, IR and elemental analysis of final products of known compounds. CCDC numbers are 987109 and 987110 for compound **1** and **2**, respectively. For ESI and crystallographic data in CIF or other electronic format see DOI: xxxxxxxxxxx

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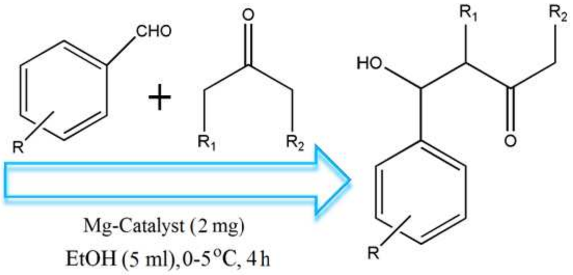

Hydrothermal treatment of chelidamic acid (H_3L) with magnesium and calcium nitrate affords MOFs. Two-dimensional $[Mg(HL)(H_2O)_2]_n$ upon dehydration demonstrates heterogeneous catalytic activity in Claisen–Schmidt reaction in environment friendly conditions.

Abstract

Two alkaline earth metal based carboxylate framework systems, $[Mg(HL)(H_2O)_2]_n$ (**1**) and $[Ca(H_2L)_2]_n$ (**2**) (H_3L = chelidamic acid) have been hydrothermally synthesized and characterized by single crystal X-ray diffraction measurement, IR, elemental analysis, and thermogravimetric analysis. Compound **1** is 2D framework structure consisting of two water molecules in its coordination site. Dehydrated species generated from compound **1** upon removal of its coordinated water molecules has been characterized by thermogravimetric analysis, IR, elemental analysis and variable temperature powder X-ray diffraction measurement. Both compound **1** and its dehydrated species catalyze Claisen–Schmidt reaction in heterogeneous condition, however, dehydrated variety catalyzes the reaction more efficiently in environment friendly conditions. Catalyst can be recovered easily and reused in successive cycles without any detectable loss of activity. Compound **2** has a 3D structure and thermally stable up to 540 °C, but inactive towards this catalytic reaction.

Keywords: Hydrothermal synthesis, metal-organic framework, heterogeneous catalysis, Claisen–Schmidt reaction

Introduction

Metal−organic frameworks (MOFs) or porous coordination polymers with well-defined channels or pores have been receiving intensive interest, not only by chemists but also researchers from fields beyond chemistry, because of their aesthetically appealing framework structures and potential applications as multifunctional materials. A lot of effort has been invested to rationally design MOF materials in the fields of gas adsorption and storage, catalysis, and magnetic materials.[1–3] The general approach of making these materials is usually the fabrication of metal ion building units and multidentate organic ligands in appropriate solvents under hydro(solvo)thermal conditions. Assembly of the building units that led to formation of MOF structures is controlled by many parameters, such as the metal coordination geometry, the Lewis acidity of the metal, the basicity of the ligands, and the number and type of donor atoms and their orientations. Among the different connecting ligands, aliphatic and aromatic carboxylic acids (mono-, di-, tri-, etc.) proved to be the most demanding candidates, and their use resulted in spawning of a large class of desired MOFs. Carboxylates exhibit versatile bridging modes. They can simply act as monodentate or bidentate ligand, often they can also have higher denticity.[4,5] By virtue of their different coordination bridging modes *viz.* syn–syn, syn–anti, and anti–anti, they are capable of tuning metal-metal magnetic interaction and surface properties.[5i] Besides, by using suitable bridging carboxylate ligands MOFs can be post-synthetically modified and functionalized.[6] Carboxylate based framework materials have a wide range of structural properties (from rigid to flexible) and they are amenable for developing desired properties by introducing appropriate ligands. It is well established that bifunctional dicarboxylates can bridge various metal ions, affording a lot of highly porous and catalytically active frameworks.[7,8] Pyridine-2,6-dicarboxylic acid is one such example which has been exploited extensively. This versatile N,O-chelator having various coordination motifs to form both discrete and interconnected metal assembled systems under appropriate experimental conditions.[9] From view point of coordination ability, 4-hydroxy derivative of dipicolinic acid i.e., 4-hydroxypyridine-2,6-dicarboxylic acid (chelidamic acid) being the combination of dipicolinate and hydroxy pyridine can potentially be more versatile than its parent acid.[10] However, literature shows this carboxylic acid has not been explored fully. So far as MOF is concern only few results have been published on this particular dicarboxylic acid.[10,11] Nevertheless, in most of the cases hydroxyl group remain non-coordinated.[11] In contrast to the huge number of MOFs that are built employing transition metal ions,[1–4] examples of alkaline earth metal analogue are scarce.[12,13]

In the course of our continuing investigation on catalytic uses of MOFs,[8,14] we have successfully employed alkaline earth metal-based MOFs to catalyze aldol reaction in heterogeneous condition in presence of triethylamine in THF medium.[8a,8b,8c] Recently, we have developed a barium-based MOF which successfully catalyzed aldol reaction under heterogeneous base-free condition.[8d] Further exploration of alkaline earth metal-based MOFs afforded two new systems, namely $[Mg(HL)(H_2O)_2]_n$ (**1**) and $[Ca(H_2L)_2]_n$ (**2**) (H_3L = chelidamic acid). Two dimensional framework compound **1**, undergoes dehydration easily to form its dehydrated species **1a**, which is capable of catalyzing Claisen–Schmidt reactions in ethanol medium and in absence of any external base. On the contrary compound **2** affords 3D structure, which shows high thermal stability, is inactive towards catalyzing the reaction.

Experimental

Materials

Chelidamic acid hydrate, cyclopentanone, acetophenone and substituted benzaldehydes were purchased from Aldrich. Solvents (analytical grade), magnesium nitrate hexahydrate, calcium nitrate tetrahydrate, lithium hydroxide monohydrate and other chemicals were purchased from Merck (India) Pvt. Ltd. Liquid aldehydes were distilled before use. Benzaldehyde was distilled before use and was kept over NaA molecular sieves to trap possible traces of benzoic acid.

Physical measurements

Elemental analysis was performed on a Vario-Micro V2.0.11 elemental (CHNSO) analyzer. Fourier transformed infrared spectra of KBr pellets were measured using a Perkin-Elmer RX I FT-IR spectrometer. PXRD was recorded with a Bruker D8 Advance X-ray powder diffractometer equipped with Cu-K_α radiation (λ = 1.54 Å). In situ temperature-resolved PXRD patterns were performed with the same devices equipped with a high-temperature chamber (Anton Paar HTK 16N) and TCU 2000N temperature controller unit using Cu-K_α radiation. The sample was loaded on a Pt plate and heated at a rate of 5 °Cmin^{-1} under a N_2 atmosphere. TG analysis was performed on a Perkin-Elmer (SINGAPORE) Pyris Diamond TGA unit. The heating rate was programmed at 5 °C min^{-1} with a protecting stream of N_2 flowing at a rate of 150 ml min^{-1}. The metal content of the sample was estimated on a Varian Techtron AA-ABQ atomic absorption spectrometer.

Synthesis of the compound 1

$[Mg(HL)(H_2O)_2]_n$ (**1**) was synthesized through hydrothermal route. The initial reaction mixture was prepared as follows: chelidamic acid hydrate (0.095 g) first dissolved in 5 ml of milliQ water and pH of the solution was adjusted to 8 by mixing lithium hydroxide. To this magnesium nitrate hexahydrate (0.256 g, 1 mmol) was added and the final mixture was stirred for half an hour. Compound **1** was obtained as colorless block crystals in a 20 ml capacity teflon-lined acid digestion bomb, at 160 °C for 3 days followed by slow cooling to room temperature. Yield was ca. 48% based on the metal. Anal. calcd. for $[Mg(HL)(H_2O)_2]_n$ (**1**); C = 34.82, H = 2.92, N= 5.80, O = 46.39, found C = 34.8, H = 2.9, N = 5.8, O = 46.4. Selected IR peaks (KBr disk, ν, cm^{-1}): 1639, 1602 [υ_{as} (CO_2^-)], 1511 [υ_s (CO_2^-)], 1441, 1404 [υ_s (C–O)], 3219-3571 s.br [υ_s (O–H)], and 3082 [υ_s (N–H)].

Synthesis of the compound 2

$[Ca(H_2L)_2]_n$ (**2**) was synthesized through hydrothermal route. The initial reaction mixture was prepared as follows: chelidamic acid hydrate (0.095 g) first added in 5 ml of milliQ water. To this calcium nitrate tetrahydrate (0.236 g, 1 mmol) was added and the final mixture was stirred for half an hour. A colorless solution was obtained in a 20 ml capacity teflon-lined acid digestion bomb, at 180 °C for 3 days followed by slow cooling to room temperature. The solution was kept for solvent evaporation at room temperature and compound **2** was obtained as colorless block crystals after 7 days. Yield was ca. 22% based on the metal. Anal. calcd. for $[Ca(H_2L)_2]_n$ (**2**); C = 41.59, H = 1.99, N = 6.93, O = 39.57 found C = 41.6, H = 1.9, N= 6.9, O = 39.6. Selected IR peaks (KBr disk, ν, cm^{-1}): 1719, 1602 [υ_{as} (CO_2^-)], 1476 [υ_s (CO_2^-)], 1404, 1378 [υ_s (C–O)], 3291 [υ_s (O–H)], and 3092 [υ_s (N–H)].

X-ray crystallography

X-ray diffraction data for **1** and **2** were collected at 296(2) K and 293(2) K, respectively, on a Bruker SMART APEX CCD X-ray diffractometer using graphite-monochromated MoKα radiation (λ = 0.71073Å). Determination of integrated intensities and cell refinement were performed with the SAINT[15] software package using a narrow-frame integration algorithm. An empirical absorption correction[16] (SADABS) was applied. The structure was solved by direct methods and refined using full-matrix least-squares technique against F^2 with anisotropic displacement parameters for non-hydrogen atoms with the programs SHELXS97 and SHELXL97.[17] Hydrogen atoms were placed at calculated positions using suitable riding models with isotropic displacement parameters derived from their carrier atoms. In the final difference Fourier maps there were no remarkable peaks except the ghost peaks surrounding the metal centers. A summary of crystal data and relevant refinement parameters for compound **1** and **2** are given in Table 1.

Catalytic reaction

The catalytic reactions were carried out in a glass batch reactor according to the following procedure. Ketone (3 mmol), ethanol (5 ml) and catalyst (2 mg) were taken in a round bottom flask. It was then placed in an ice-bath maintaining temperature 5–10 °C. To this solution aldehyde (2 mmol) was added and the reaction mixture was stirred for 4 h (Scheme 1). For isolation of products at the end of catalytic reaction, the catalyst was first separated out by centrifugation, filtered, and then finally concentrated in vacuum. The residue was purified by column chromatography over silica gel (mesh 60–120) using n-hexane/ethyl acetate mixture as eluent to get the desired product. The product was analyzed by ^{1}H NMR, ^{13}C NMR, HRMS, IR spectroscopy and elemental analysis, and the data were compared with those of authentic samples.

Results and discussion

X-ray structure of compound 1

Compound **1** crystallized in a space group $P2_1/c$ with $Z = 4$. The basic unit of compound **1** consists of Mg(II) center with distorted octahedral geometry. The basal plane of **1** is generated by three oxygen atoms from three carboxylato ligands (O2, O3, and O5) and one oxygen atom (O7) from water molecule, while remaining two axial positions of the octahedron are occupied by one oxygen atoms from carboxylate ligand (O1) and one oxygen atom (O6) from water molecule (Fig. 1a) (for ORTEP diagram see ESI; Figure S1). Selected bond distances and the bond angles are collated in Table 2. The Mg–O (carboxylate) bond lengths range from 2.0723(11) to 2.0945(11) Å which are in agreement with the Mg-O bond lengths observed in other magnesium carboxylate complexes.[8a,b] Each ligand coordinates to four alkaline earth metal centers through one phenolato oxygen atom (O2) and three carboxylate oxygen atoms (O1, O3, and O5) (Fig. 1b) to give rise a 2D net parallel to crystallographic *ac* plane (Fig. 2). Two oxygen atoms (O2 and O3), each from one phenolato group and one carboxylato group coordinate to a single metal center, whereas remaining carboxylato group bridged between two metal centers through its two oxygen atoms (Mg···O1–C1–O5···Mg) in a *syn-anti* fashion (Fig. 1b). To understand the structure of **1** further, a topological analysis was performed by reducing the multidimensional structure to a simple node-and-linker net. Topological analysis of **1** by TOPOS[18] revealed that this compound is binodal 4–c 2D net with the Schläfli symbol $\{4^4.6^2\}$ consisting of L^{3-} ligands and Mg(II) centers as four-coordinated nodes (Fig. 3). Additional reinforcement in the network structure is achieved by intramolecular and intermolecular hydrogen bonding among the carboxylate oxygen (O1, O3 and O4) atoms, phenolate oxygen atoms, nitrogen atoms and water molecules (See ESI; Table S1). Intermolecular hydrogen bonding interaction connects 2D layers along crystallographic *b* axis to produce a 3D supramolecular architecture.

X-ray structure of compound 2

Compound **2** crystallized in a space group *C2/c* with *Z* = 4. The basic unit of compound **2** consists of Ca(II) center with distorted octahedral geometry. The six coordination of the octahedron is satisfied by six oxygen atoms (O1, ^{b}O1, ^{c}O2, ^{d}O2, O3, ^{b}O3; b = (1-x, y, 1/2-z); c = (1-x, -y, 1-z); d = (x, -y, -1/2+z)) from six carboxylato ligands (Fig. 4a) (for ORTEP diagram see ESI; Figure S2). Selected bond distances and the bond angles are collated in Table 2. The Ca–O (carboxylate) bond distances range from 2.3020(17) to 2.3339(15) Å which are in agreement with the Ca-O bond lengths observed in other calcium carboxylate complexes.[13a–13c] Each ligand coordinates to three alkaline earth metal centers through three carboxylate oxygen atoms (O1, O2, and O3) (Fig. 4b) to give rise a 3D network (Fig. 5). One oxygen atom from one carboxylato group of a ligand coordinates to a single metal center, whereas remaining carboxylato group bridged two metal centers through its two oxygen atoms (Ca···O1–C6–O2···Ca) in a *syn-anti* fashion (Fig. 4b). Two Ca(II) centers are linked by two bridging bidentate carboxylate ligand to form a Ca_2 diad ($Ca_2C_2O_4$) with a Ca···Ca separation 5.034 Å (Fig. 4b). To get deeper insight into the structure of **2**, a topological analysis was performed by reducing the multidimensional structure to a simple node-and-linker net. Topological analysis of **2** by TOPOS[18] revealed that this compound is binodal 3,6-c 3D net with the Schläfli symbol $\{4^2.6\}2\{4^4.6^2.8^8.10\}$ consisting of one kind of three-coordinated node of H_2L^- ligands and a six-coordinated node of the Ca(II) centers (Fig. 6). Additional reinforcement in the network structure is achieved by intramolecular hydrogen bonding among the carboxylate oxygen atoms (O2 and O4), and nitrogen atoms (See ESI; Table S1).

Thermogravimetric analysis

The thermogravimetric analysis of **1** and **2** were performed using a powdered sample under nitrogen atmosphere. The TG measurement confirms that compound **1** is thermally stable up to ~100 °C (Fig. 7). TG curve indicates compound **1** starts to lose water molecules at ~100 °C and completes dehydration at around 210 °C. The mass loss of ~15% shown in the range 100–210 °C corresponds to the loss of two water molecules. Thereafter the TG curve remains flat up to ~340 °C, indicating no mass loss in this temperature range. On further heating, the TG curve shows a continuous mass loss indicating the decomposition of the compound.

TG measurement confirms that compound **2** is thermally stable up to ~540 °C, indicating good thermal stability of this MOF compound (See ESI; Fig. S3). The TG curve indicates that compound **2** starts to decompose at ~540 °C and completes decomposition at ~675 °C. There are only a few MOF compounds that are reported to be thermally stable above 500 °C.[19] Thermal stability of MOFs is usually explained in terms of the rigidity of the linkers, absence of solvent molecules in the network of the MOFs, strong bonds between the metal ions and the organic linkers, etc. Compound **2** satisfies all these requirements.

Powder X-ray diffraction measurements

In order to confirm the phase purity and structural integrity of the bulk materials, powder X-ray diffractions were measured for the compounds **1** and **2**. X-ray powder diffraction patterns of both the compounds were simulated using their single crystal data. Comparison of experimental and simulated PXRD patterns showed that all the major peaks of experimental PXRD of **1** and **2** match well with those of simulated ones, indicating their reasonable crystalline phase purity (See ESI; Fig. S4 and Fig. S5). Variable temperature PXRD patterns were also measured for compounds **1** and **2** using Anton Paar HTK 16N high-temperature chamber and TCU 2000N temperature controller unit mounting samples on a Pt plate in nitrogen atmosphere (See ESI; Fig. S4 and S5). PXRD patterns of **1** remained unaltered at 100°C and higher temperatures (up to 340°C) (See ESI; Fig. S4). Similarly PXRD patterns of **2** measured from ambient to higher temperature match well with the simulated one (See ESI; Fig. S5). Thus in-situ variable temperature PXRD measurement reveals that framework structure of **1** and **2** is stable enough up to 340 °C and 500 °C, respectively.

Dehydration and rehydration

Crystal structure analysis showed that **1** has two molecules of coordinated water per magnesium site. TG analysis clearly indicates that upon heating compound **1** loses its coordinated water molecules to produce a dehydrated product which is stable up to ~340 °C. The required amount of dehydrated product (**1a**) of compound **1** has been collected from the TG analyzer in several batches after heating up to 250 °C. Anal. calcd. for **1a**; C = 40.93, H = 1.47, N= 6.82, O = 38.95, found C = 40.9, H = 1.5, N = 6.8, O = 39.0. Selected IR peaks (KBr disk, ν, cm^{-1}): 1639, 1602 [υ_{as} (CO_2^-)], 1511 [υ_s (CO_2^-)], 1442, 1404 [υ_s (C–O)], and 3082 [υ_s (N–H)]. Dehydration can also be performed by heating compound **1** at 100 °C under vacuum (10^{-3} Torr) for 1 h. TG analysis, IR spectral analysis (Fig. 8), and elemental analysis of **1a** convincingly established that it is the dehydrated species of compound **1**. Upon exposure to humid atmosphere (relative humidity ~90%) or by simply immersing the sample in water, **1a** absorbs H_2O molecules and reverts to its original hydrated form. X-ray diffraction pattern of the rehydrated species and **1** are shown in Fig. 9. TG analysis, IR spectral analysis, and elemental analysis of the rehydrated compound corroborate the fact of rehydration (Fig. 7 and Fig. 8). We have tried to dehydrate compound **1** in controlled manner to perform single-crystal to single-crystal transformation, however, single crystallinity of **1** is lost upon dehydration. Further, single crystal of dehydrated product (**1a**) was not possible to come by through solution route.

Catalytic Claisen–Schmidt reactions

Environment friendly heterogeneous catalytic processes are increasingly receiving attention in the chemical industry. Designing of highly active solid Lewis acid or base catalysts which are capable of catalyzing C–C bond formation reactions is a challenge. The main drawbacks of the using acids or bases in homogeneous catalysis are separation difficulties, corrosion of the equipments and generation of large amount of wastes. In order to overcome these disadvantages several efforts have been made to adapt heterogeneous catalytic systems with controlled basic properties in order to increase efficacy of the process. MOFs are currently being investigated as heterogeneous catalysts for this type of acid-base catalytic reaction.[20] When the coordination sphere of the metallic nodes has one exchangeable position not compromised with the crystal structure of the MOF, then these metallic nodes can act as Lewis acid sites promoting organic reactions.[21] The aldol reaction, in which carbonyl group undergo nucleophilic attack by the same or a different type of carbonyl compound to give a β-hydroxy carbonyl compound, belong to the most general and versatile organic reactions to form C–C bonds. $Cu_3(btc)_2$ has been reported as a general catalyst for the synthesis of pyrimidine-chalcones through an aldol condensation under mild reaction conditions in toluene adding a few drops of concentrated sulfuric acid.[22] The Claisen–Schmidt reaction is the aldol condensation between an aromatic aldehyde and a ketone leading to a conjugated enone as the final product through formation of carbon-carbon bonds. The most studied example of the Claisen–Schmidt condensation is the reaction of benzaldehyde with acetophenone to form chalcones (1,3-diarylpropenones). Chalcone and its derivatives have gained increasing attention due to numerous pharmacological applications, for example, as anticancer and antihyperglycemic agents.[23] A high yield of chalcone was observed using 57 mol% of Fe(btc) as catalyst at 110 °C in toluene.[24] MIL-101 has been used as catalyst for the self-condensation of acetone to give mesityl oxide as the product.[25] The catalytic activity of UiO-66 and UiO-66(NH_2) was tested for the cross-aldol reaction between benzaldehyde and heptanal for the formation of jasminaldehyde under solvent free condition.[26] Among various magnesium compounds which are used as mediators or catalysts for several organic reactions,[27] magnesium oxide is a versatile catalyst for carbon–carbon bond formation reactions.[28] The magnesium oxide nano-particles also have been employed in catalytic aldol condensation reaction.[29] It was proposed that the surface -OH and O^{2-} of these oxide crystals are expected to trigger the carbon–carbon bond formation reactions**.**[29] However, little attentions have been paid in using magnesium carboxylates in C-C bond formation reactions due to their limited synthetic procedure and hygroscopic nature.[30] Recently two 3D porous magnesium carboxylate frameworks have been synthesized through hydrothermal route and their activity in heterogeneous aldol condensation reaction was tested in presence of triethylamine in THF medium.[8a,b] Magnesium pyridine-2,5-dicarboxylate framework on heating in controlled manner resulted void channels after removal of coordinated water molecules.[8b] This calcined MOF performed as an superior catalyst in aldol reaction between benzaldehyde and acetone or cyclohexanone than its parent compound. Under the same reaction condition, replacing acetone with *tert*-butylcycloheanone decreased the yield drastically indicating that the reaction seems occur inside the channels.[8b] Triethylamine was used in above mentioned catalytic reaction, which is to some extent corrosive and should preferably be avoided. In contrast, the catalytic activity of **1a** has been studied in Claisen–Schmidt reaction under heterogeneous base-free conditions and in ethanol medium (Scheme 1).

The performance of the catalytic reaction in ethanol medium was not satisfactory (Table 3). However, the yield of the reaction increased remarkably upon using the calcined species (**1a**) as catalyst (Table 3). Catalytic activity also enhanced in solvent free condition (Table 3). It may be realized that **1** loses the coordinated water molecules on heating, as a result, metal centers of the framework compound become coordinatively unsaturated. These open-metal sites interact better with the reactant molecules and give high yield of product. It is established that calcium based catalysts are active in aldol or aldol-type reaction.[31] However, compound **2** displayed no catalytic activity towards aldol reaction (Table 3). This inactive nature of **2** may be ascribed to non-availability of open-metal site in compound **2** and absence of any labile molecule in its coordination site. For **1**, it does not matter if the reaction is carried out in open atmosphere or in inert atmosphere (Table 3), same yield was obtained in both the cases. But in case of **1a**, a small change in the yield of the product was noticed between open atmosphere and inert atmosphere (Table 3). The yield obtained in inert atmosphere was higher than that of open atmosphere. In open atmosphere owing to absorption of water molecule from atmosphere deactivation of catalytic site may caused low yield of the products. In order to further explore the versatility of calcined species as a selective catalyst for Claisen–Schmidt reaction and the effect of substituents on the reaction, different types of aldehydes and ketones were used as substrates in ethanol medium and under inert atmosphere. As the chalcone and its derivatives are valuable products for pharmacological applications and those are obtained by the condensation of β-aldol products of benzaldehyde/substituted benzaldehyde and acetophenone,[23] we have focused our study on the synthesis of β-aldols derived from benzaldehyde/substituted benzaldehyde and acetophenone. Catalytic reactions were performed in presence of excess ketone for the effective use of aldehyde. The temperature of the medium was maintained in the range of 5–10 °C throughout the reaction. With increasing reaction temperature *β*-aldol product transformed to benzylidene ketone (Fig. 10). When the reaction was performed at 60 °C, benzylidene ketone was obtained as the sole product (Fig. 10 and Table 4). Generally, it is easier to get the condensed product than to get the *β*-aldol product. Therefore, we are interested to isolate the yield in *β*-aldol form. The results of Claisen–Schmidt reactions are summarized in Table 4. In all the above conditions aldehydes were converted to their respective *β*-aldols as sole product. In this study we noticed *β*-aldol products did not undergo further transformation to form unsaturated carbonyl compounds. Generally *β*-aldol product undergoes dehydration to give a conjugated enone in Claisen–Schmidt reaction.[32] Yield of the *β*-aldol product decreased from *p*-nitrobenzaldehyde to *m*-nitrobenzaldehyde through *o*-nitrobenzaldehyde. It may be realized that nitro substituent at *ortho* and *para* position affords both negative inductive effect and negative mesomeric effect which increases electrophilicity of >C=O group of nitrobenzaldehydes but substitution at *meta* position affords only the negative inductive effect. Between *p*-nitrobenzaldehyde and *o*-nitrobenzaldehyde, more steric crowding at *ortho* position may lead to lower conversion for *ortho* variety. Aldol-condensation reaction catalyzed by nonporous crystalline magnesium oxide showed 75% conversion for *p*-nitrobenzaldehyde and acetone in 24h in heterogeneous condition.[29] In case of chloro substituted benzaldehydes, yield of the *β*-aldol product decreased from *o*-chlorobenzaldehyde to *p*-chlorobenzaldehyde through *m*-chlorobenzaldehyde due to the decreasing effect of negative inductive effect. On the other hand presence of electron donating group in the ring, such as methyl, yield decreases significantly and demonstrated the lowest conversion. Interestingly in case of *p*-methoxy-benzaldehyde yield was still very good. Presumably methoxy group may interact with Mg^{2+} and facilitates the reaction.[33] Claisen–Schmidt reaction was also performed for cyclopentanone and cyclohexanone, however, the yield decreases from acetone to acetophenone to cyclopentanone to cyclohexanone.

We propose a mechanism for the magnesium MOF-mediated aldol condensation reaction on the basis of calcium MOF catalyzed heterogeneous hydrogenation reaction and zinc catalyzed aldol condensation reaction reported earlier.[33,34] Taking into account this type of mechanism, two different kinds of requirements are needed: (i) Lewis acidity, which favors the formation of the intermediate species and (ii) capability of the catalytically active alkaline-earth metal center to accommodate an external ligand to its coordination site which give rise to the metal complex intermediate species.[35] Magnesium has highest Lewis acidity in the series so it can easily fulfill the first requirement.[35] The second requirement is achieved by the removal of water molecules from the coordination site of compound **1**. Carbonylic oxygen possibly becomes coordinated to Lewis acidic magnesium in the intermediate stage. Subsequently, carbon–carbon bond formation takes place with concomitant coordination of the carbonyl group of the aldehyde or with noncoordinated aldehyde.[20,33]

To ascertain the catalysis was indeed heterogeneous, we performed hot filtration test. To test if metal was leached out from the solid catalyst during reaction, liquid phase of the reaction mixture was collected by filtration after ~40% completion of reaction and residual activity of the supernatant solution after separation of the catalyst was studied. The supernatant solution was kept in reaction condition for another 8 h and the composition of the solution was analyzed time to time. No progress of reaction was observed during this period, which excludes the presence of active species in solution. This result suggests that there was no leaching of Mg from the solid catalyst during reactions. Besides, Atomic absorption spectrometric analysis (sensitivity up to

0.001 ppm) of the supernatant solution of reaction mixture thus collected by filtration confirms the absence of magnesium ions in the liquid phase.

To check the stability of catalyst, we characterized the recovered material. After completion of catalytic reaction, solid catalyst was recovered by centrifugation, washed thoroughly with dichloromethane and dried. As 2 mg of solid catalyst is not enough to recover, reuse, and finally characterize, therefore, the catalyst was collected from different batches of same catalytic cycle and an average value of data are given here. The recovered catalyst was then subjected for X-ray powder diffraction analysis. Comparison of X-ray diffraction patterns (Fig. 9) of the pristine compound and recovered catalyst convincingly demonstrates that the structural integrity of the compound was retained after the reaction.

For the recycling study, the reactions were performed using *p*-nitrobenzaldehyde. After first cycle of reactions catalyst was recovered by centrifugation. The recovered catalyst was then washed several times with dichloromethane and activated under vacuum at 80 °C. The performance of the recycled catalyst in C–C coupling reactions up to five successive runs was studied (Table 4). The catalytic efficacy of the recovered catalyst remained almost the same in each run.

The catalytic efficacy of the compounds reported here are compared (Table 5) with the performance other alkaline earth metal based MOF catalysts reported previously which catalyzed Claisen–Schmidt reaction of *p*-nitrobenzaldehyde and acetone.[8a,8b,8c,8d,8g] Claisen–Schmidt reaction catalyzes by **1a** displayed much higher TON in comparison to other reported MOF catalysts. Advantages of our system are that the catalytic reaction was carried out in absence of any added base so there is no corrosion problem involved in the process. Reactants were converted to their respective product with high yield and 100% selectivity in short time duration which demonstrates that the surface of the catalyst is highly active. Reactions were performed ethanol medium which is relatively green than other solvents.

Conclusion

In summary, we have synthesized two new alkaline earth metal-organic framework (MOF), $[Mg(HL)(H_2O)_2]_n$ (**1**) and $[Ca(H_2L)_2]_n$ (**2**) (H_3L = chelidamic acid) and structurally characterized by single crystal X-ray diffraction analysis. Compound **2** have 3D structure and shows high thermal stability. Dehydrated compound (**1a**) catalyzes Claisen–Schmidt reaction more efficiently than the corresponding one in environment friendly conditions. Catalysts can be easily recovered by centrifugation after reaction, and can subsequently be used after washing. Recovered catalyst is showing no significant catalyst deactivation either due to leaching of active species or degradation of the structure. Further investigations regarding application of alkaline earth metal-based frameworks towards gas sorption and storage and application in other types of catalytic reactions are currently in progress in our laboratory.

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Legends to the Figures

Scheme 1 Claisen–Schmidt reaction catalyzed by compound **1a.**

Fig. 1 Segment of compound **1** showing local coordination environment of (a) magnesium (II), and (b) ligand.

Fig. 2 2D net of compound **1**(Mg(Magenta), O(Red), N(Blue), C(Gray)). Hydrogen atoms are omitted for clarity.

Fig. 3 Topological view of 2D net of **1**.

Fig. 4 Segment of compound **2** showing local coordination environment of (a) magnesium (II) ion, and (b) ligand.

Fig. 5 3D framework of **2**(Ca(Magenta), O(Red), N(Blue), C(Gray)). Hydrogen atoms are omitted for clarity.

Fig. 6 Topological view of 3D net of **2** (view along 001 plane).

Fig. 7 TGA curve of compound **1** and **1a**.

Fig. 8 IR spectra of compound **1** and **1a**.

Fig. 9 PXRD patterns of compound **1** and **1a**.

Fig. 10 Catalytic efficacy of **1a** at different temperature. Reaction conditions were the same as given in the footnote of Table 4.

Table 1 Crystal data and structure refinement parameters of compound **1** and **2**

Compound	**1**	**2**
Formula	$C_7H_7NO_7Mg$	$C_{14}H_8N_2O_{10}Ca$
Formula weight	241.45	404.30
Temperature (K)	296(2)	293(2)
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$C2/c$
a (Å)	4.7460(10)	10.1524(3)
b (Å)	21.0254(6)	19.9761(6)
c (Å)	8.6046(2)	7.4902(2)
β (°)	91.279(10)	94.091(2)
Volume (Å^3)	858.41(4)	1515.18(8)
Z	4	4
Calculated density (g/cm^3)	1.868	1.772
Absorption coefficient (mm^{-1})	0.232	0.480
F(000)	496	824
Intervals of reflection indices	$-6 \leq h \geq 6$, $-26 \leq k \geq 26$, $-11 \leq l \geq 11$	$-13 \leq h \geq 13$, $-25 \leq k \geq 25$, $-9 \leq l \geq 9$
Measured reflections	13772	12255
Reflections with [$I > 2\sigma (I)$]	1834	1391
Independent reflections	1898	1682

Final R indices [$I>2\sigma(I)$]	R_1=0.033, wR_2=0.088	R_1=0.039, wR_2=0.109
R indices (all data)	R_1=0.034, wR_2=0.089	R_1=0.049, wR_2=0.118
R_{int}	0.023	0.043
Goodness of fit on F^2	1.127	0.883
Largest diff. peak and hole (e. Å^{-3})	0.354, -0.504	0.632, -0.610

Table 2 Selected bond lengths (Ǻ) and angles (˚) for the compound **1** and **2**

Compound **1**		Compound **2**	
Bond lengths			
Mg1-O2	2.0931(11)	Ca1-O1	2.3020(17)
Mg1-O3	2.0789(10)	Ca1-O3	2.3331(17)
Mg1-O5	2.0945(11)	Ca1-^{b}O1	2.3020(17)
Mg1-O6	2.0723(11)	Ca1-^{b}O3	2.3331(17)
Mg1-O7	2.0838(13)	Ca1-^{c}O2	2.3339(15)
Mg1-^{a}O1	2.0910(11)	Ca1-^{d}O2	2.3339(15)
Bond angles			
O2-Mg1-O3	172.06(5)	O1-Ca1-O3	173.31(6)
O2-Mg1-O5	99.19(4)	O1-Ca1-^{b}O1	91.67(6)
O2-Mg1-O6	88.89(4)	O1-Ca1-^{b}O3	92.62(6)
O2-Mg1-O7	87.35(5)	O1-Ca1-^{c}O2	93.14(7)
^{a}O1-Mg1-O2	85.38(4)	O1-Ca1-^{d}O2	88.75(7)
O3-Mg1-O5	88.41(4)	^{b}O1-Ca1-O3	92.62(6)
O3-Mg1-O6	93.32(4)	O3-Ca1-^{b}O3	83.60(6)

O3-Mg1-O7	85.31(5)	^{c}O2-Ca1-O3	92.10(6)
^{a}O1-Mg1-O3	92.13(4)	^{d}O2-Ca1-O3	85.88(6)
O5-Mg1-O6	90.68(4)	^{b}O1-Ca1-^{b}O3	173.31(6)
O5-Mg1-O7	171.37(5)	^{b}O1-Ca1-^{c}O2	88.75(7)
^{a}O1-Mg1-O5	92.04(4)	^{b}O1-Ca1-^{d}O2	93.14(7)
O6-Mg1-O7	83.79(4)	^{c}O2-Ca1-^{b}O3	85.88(6)
^{a}O1-Mg1-O6	173.98(5)	^{d}O2-Ca1-^{b}O3	92.10(6)
^{a}O1-Mg1-O7	94.10(4)	^{c}O2-Ca1-^{d}O2	177.29(6)
O2-Mg1-O3	172.06(5)	O1-Ca1-O3	173.31(6)

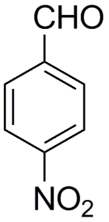
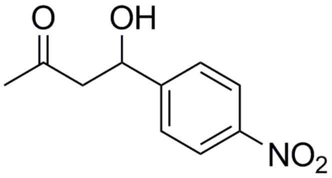
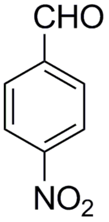
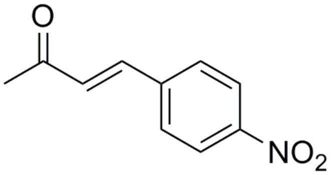
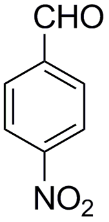
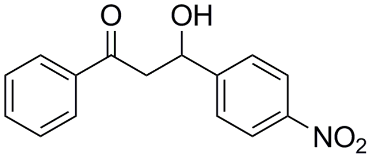
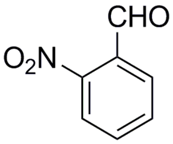
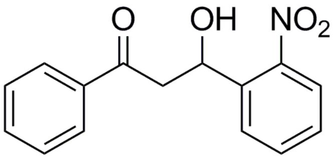
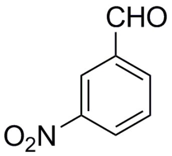
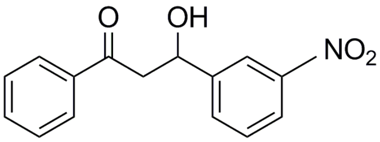
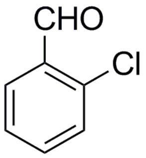
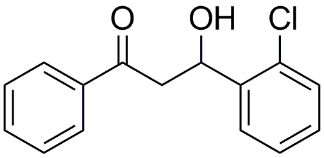
Symmetry codes: (a) –x, 1-y, 2-z; (b) 1-x, y, 1/2-z; (c) 1-x, -y, 1-z; (d) x, -y, -1/2+z

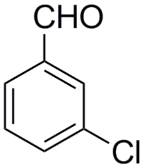
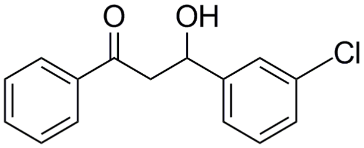
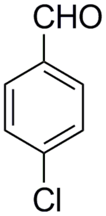
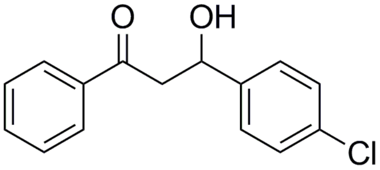
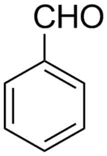
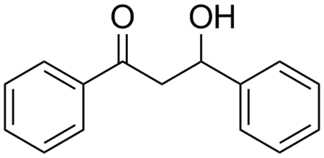
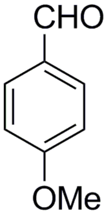
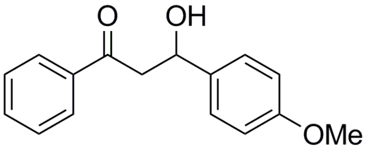
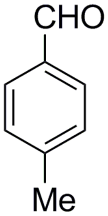
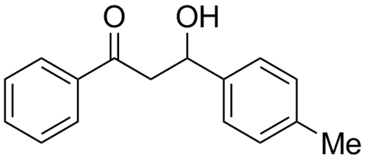
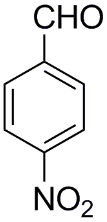
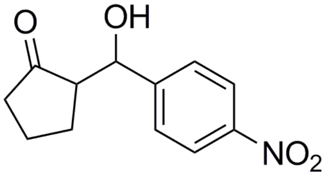
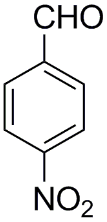
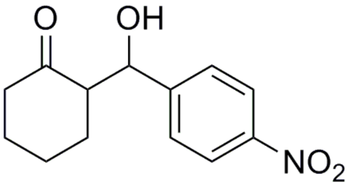
Table 3 Solvent effect in Claisen–Schmidt reaction[a] of *p*-nitrobenzaldehyde with acetone catalyzed by compound **1** and **1a**

Compound	Solvent	Product	Isolated yield (wt %)	Selectivity (wt %)
1	EtOH	β-aldol product	18[b]	100
1	EtOH-water (9:1)	β-aldol product	16[b]	100
1	EtOH	β-aldol product	18[c]	100
1	No solvent	β-aldol product	12[b]	100
2	EtOH	no product	-	-
1a	EtOH	β-aldol product	84[b]	100
1a	EtOH	β-aldol product	96[c]	100
1a	EtOH-water (9:1)	β-aldol product	68[c]	100
1a	No solvent	β-aldol product	48[c]	100

[a] Reaction conditions: *p*-nitrobenzaldehyde (2 mmol), acetone (3 mmol), catalyst (2 mg), solvent (5 ml), temperature (5–10 °C), Yields were isolated after 4 h of reaction. [b] Reactions were performed under open atmosphere. [c] Reactions were performed under inert atmosphere.

Table 4 Reactions[a] of various aromatic aldehydes and ketones catalyzed by compound **1** and **1a**

Entry	Ketone	Aldehyde	Major product	Isolated yield (wt %)	TON
1	Acetone			18[b] 96, 94[c]	43 240, 235[c]
2	Acetone			18[d] 96[d]	43 240
3	Acetophenone			16[b] 88,83[c]	39 220, 207[c]
4	Acetophenone			15[b] 82	36 205
5	Acetophenone			13[b] 72	31 180
6	Acetophenone			15[b] 83	36 207

7	Acetophenone			14[b] 77	34 192
8	Acetophenone			13[b] 70	31 175
9	Acetophenone			11[b] 58	26 145
10	Acetophenone			10[b] 54	24 135
11	Acetophenone			8[b] 44	19 110
12	Cyclopentanone			15[b] 80, 76[c]	36 200, 190[c]
13	Cyclohexanone			14[b] 74, 71[c]	34 185, 177[c]

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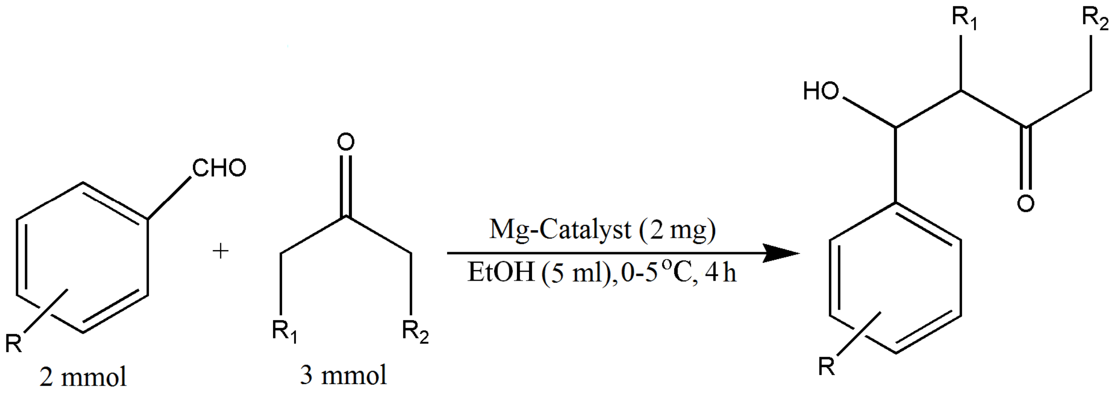
[a]Reaction conditions: Aldehyde (2 mmol), ketone (3 mmol), ethanol (5 ml), and catalyst (2 mg); temperature (5-10 °C). Yields were isolated after 4 h of reaction. [b]Catalytic activity of **1**. [c]Fifth cycle. Reactions were performed under inert atmosphere for **1a**. [d]Reaction was performed at 60 °C.

Table 5 Comparison of catalytic efficacy[a] of **1** and **1a** with other alkaline earth MOF based catalysts

Catalyst	Amount	Solvent	Temperature	Time	Yield[b] (wt %)	TON	Refs.
3D porous Mg-MOF[c]	5 mg	Dry THF	5-10 °C	6 h	94	41	8a
3D Ba-MOF[d]	5 mg	THF	5-10 °C	6 h	90	66	8c
3D porous Mg-MOF[e]	5 mg	Dry THF	5-10 °C	6 h	90	68	8b
3D Ba-MOF[f]	5 mg	THF : H_2O (3:1 (V/V))	0-5 °C	8 h	96	120	8d
2D Mg-MOF[g]	5 mg	THF : H_2O (3:1 (V/V))	5-10 °C	6 h	82	120	8g
1a	2 mg	EtOH	5-10 °C	4 h	96	240	This study
1	2 mg	EtOH	5-10 °C	4 h	18	43	This study

[a]Reaction conditions: *p*-nitrobenzaldehyde (2 mmol), acetone (3 mmol), solvent (5 ml), tryethylamine (2 mmol) except 8d, 8g and this study. [b]Selectivity = 100 % in all cases. [c]$\{[Mg_3(L)(OH)_3(H_2O)_2]\cdot H_2O\}_n$ (H_3L = 3,5-pyrazoledicarboxylic acid). [d]$[Ba(pdc)]_n$ (H_2pdc = pyridine-2,5-dicarboxylate). [e]$[Mg(Pdc)]_n$. [f]$[Ba(HL)H_2O]_n$. [g]$\{[Mg_2(HL)_2(H_2O)_4]\cdot H_2O\}_n$.



Scheme 1

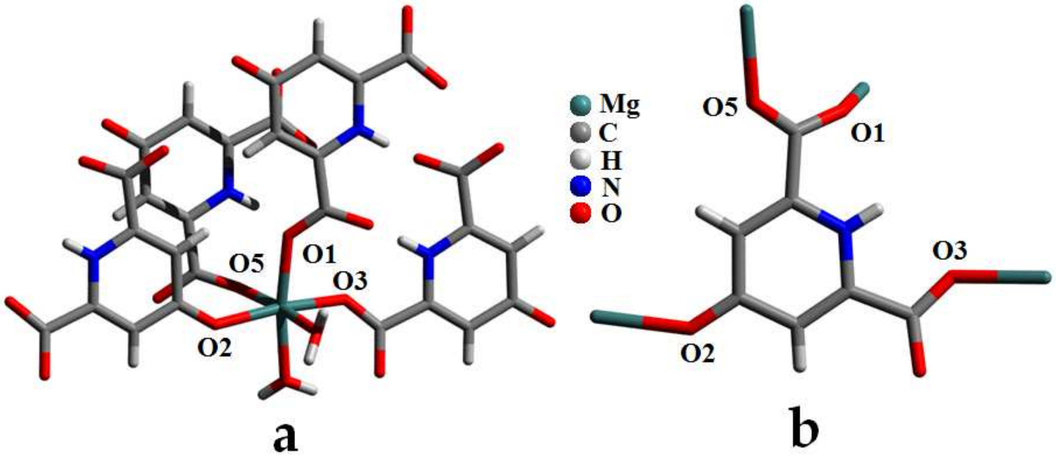


Fig. 1

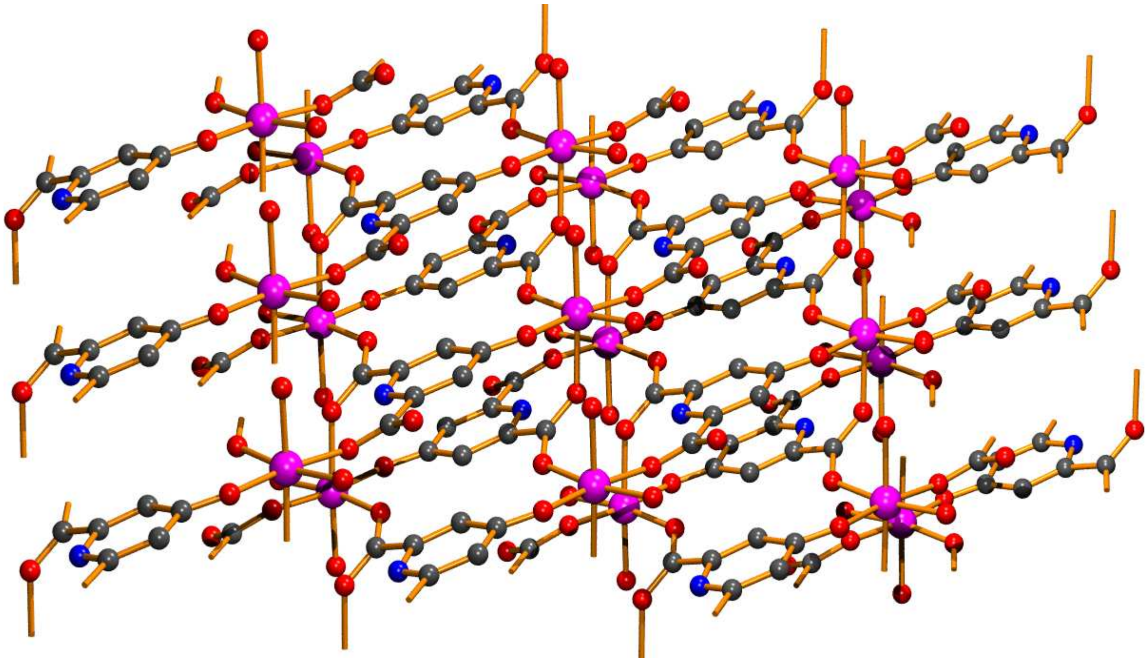


Fig. 2

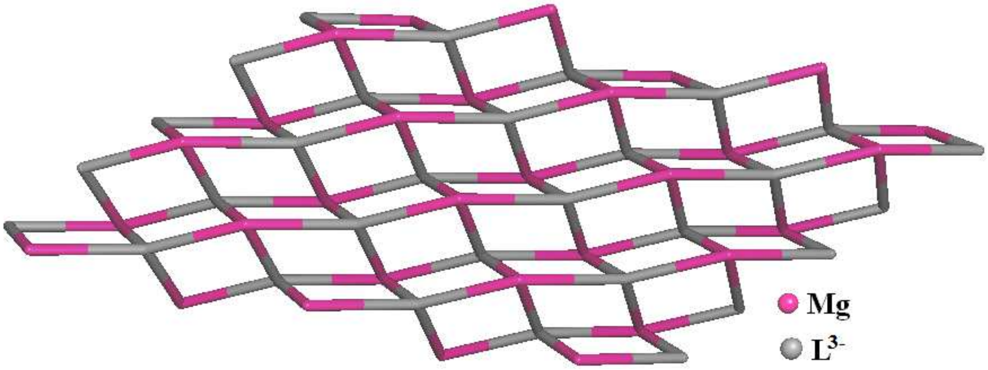


Fig. 3

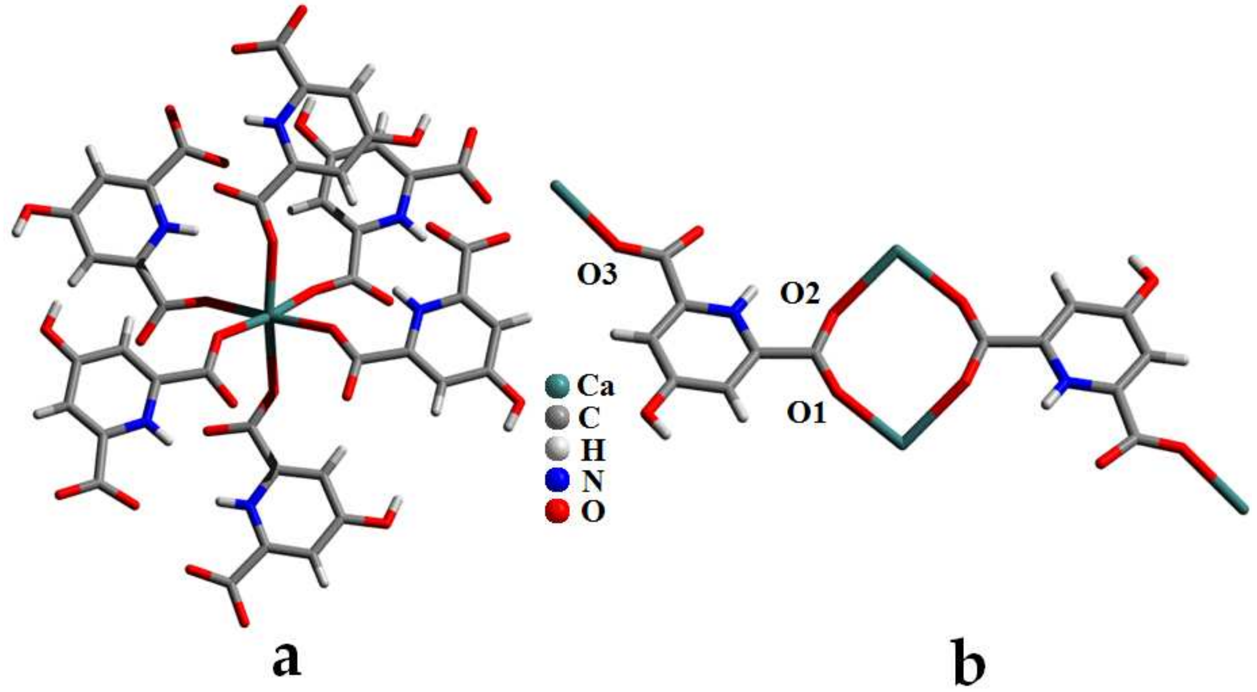


Fig. 4

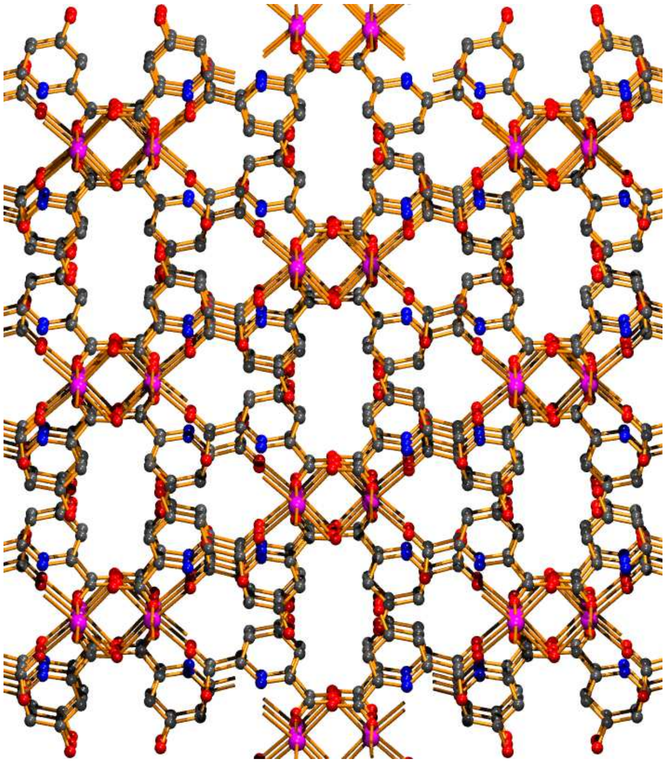


Fig. 5

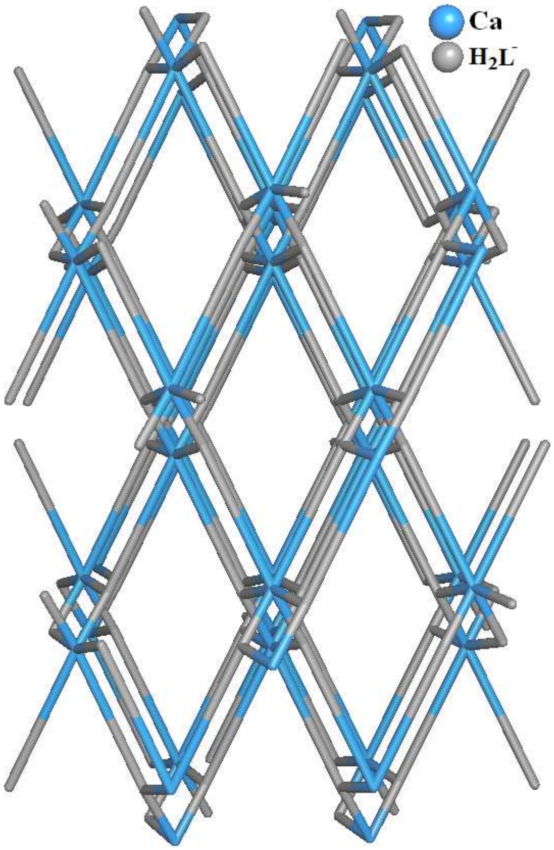


Fig. 6

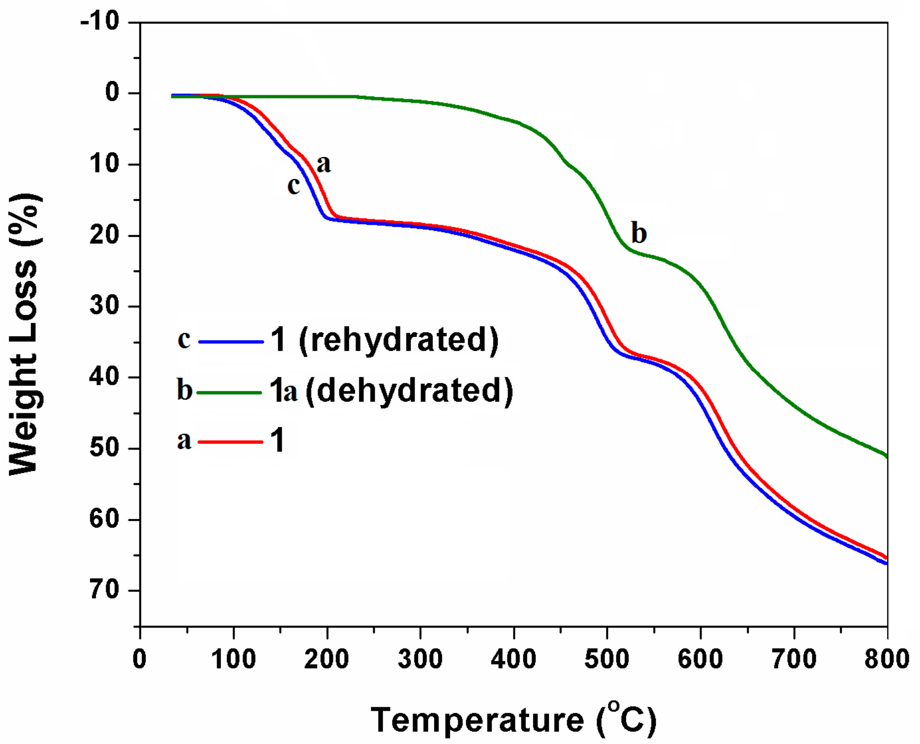

-10
0
10
20
30
40
50
60
70
Weight Loss (%)
0
100
200
300
400
500
600
700
800
Temperature (^{o}C)
a
c
b
c — 1 (rehydrated)
b — 1a (dehydrated)
a — 1

Fig. 7

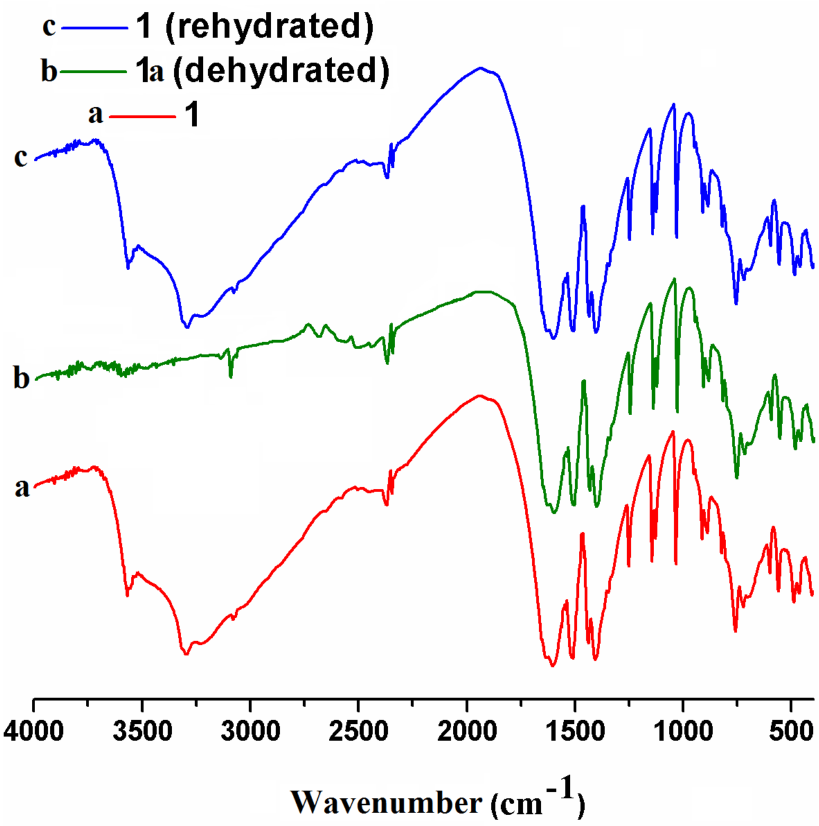

c 1 (rehydrated)
b 1a (dehydrated)
a 1
c
b
a
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm-1)

Fig. 8

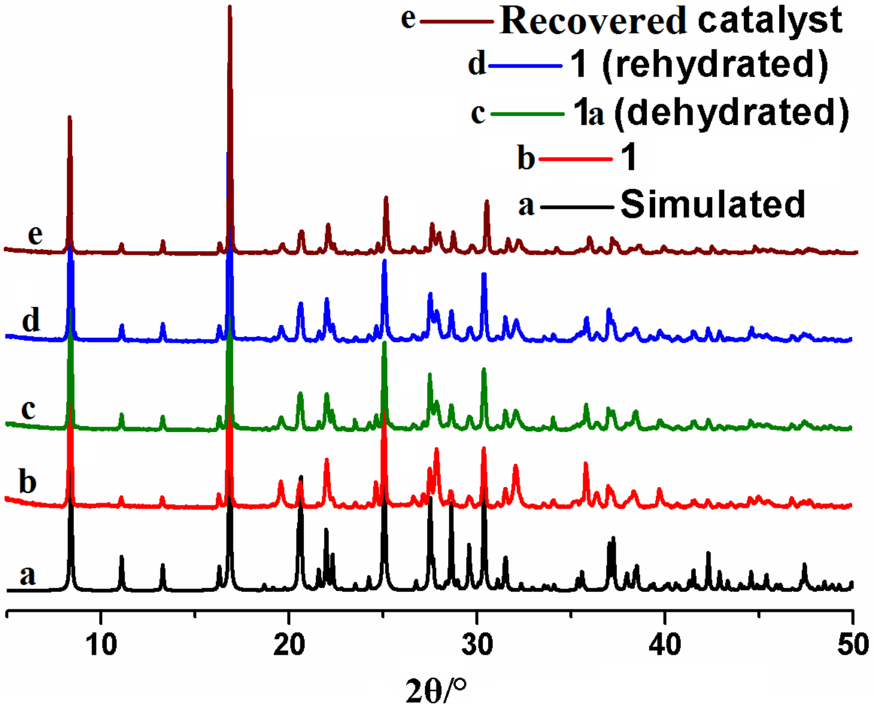

e Recovered catalyst
d 1 (rehydrated)
c 1a (dehydrated)
b 1
a Simulated
e
d
c
b
a
10
20
30
40
50
2θ/°

Fig. 9

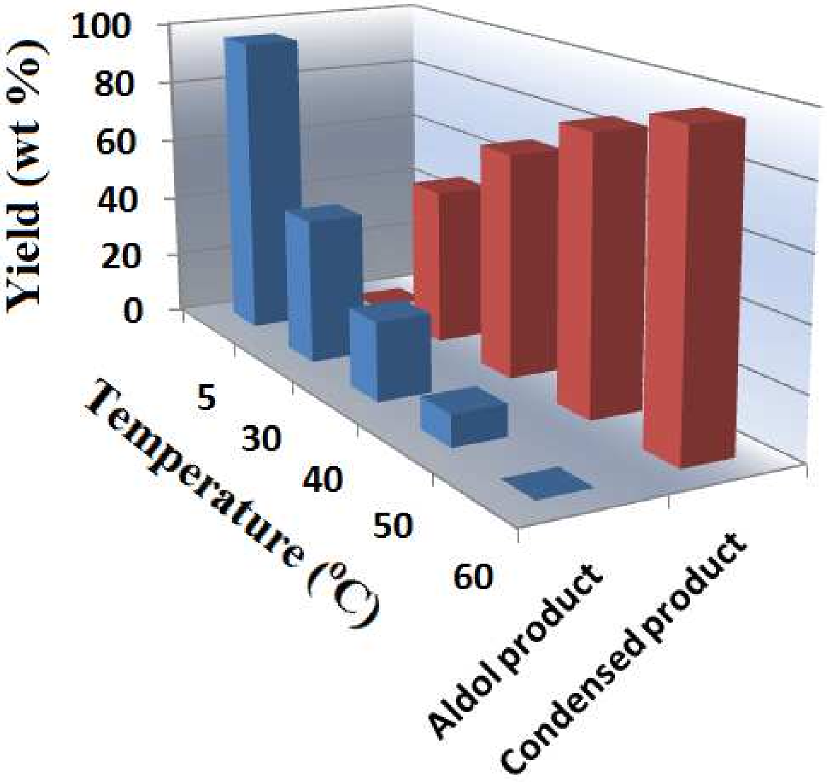

Yield (wt %)
100
80
60
40
20
0
Temperature (°C)
5
30
40
50
60
Aldol product
Condensed product

Fig. 10