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# Doubled-basic Sr-Amino containing MOF as highly stable heterogeneous catalyst

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## ABSTRACT

A novel metal-organic framework (MOF) based on strontium alkaline-earth metal and 2-amino-1,4-benzenedicarboxylic acid (NH<sub>2</sub>-bdc) has been developed. This material is formed by a linear succession of face-sharing strontium polyhedrons bridged by the organic ligand molecule to give a three-dimensional network with rhombohedral one-directional channels. This MOF is stable in polar organic solvents and up to 250 °C. The basic catalytic activity of both strontium metal nodes and amino groups of the ligand was tested in Knoevenagel condensation reactions. The influence of the temperature and reaction solvent over the catalytic performance of the MOF catalyst was demonstrated. The strontium/amino-containing MOF material evidenced a remarkable activity as compared to other conventional alkaline oxides typically used as reference basic solid catalysts. The novel MOF material proved a remarkable activity and structural stability during five consecutive catalytic runs with no evidence of activity loss at the best reaction conditions found in this study.

**KEYWORDS:** Strontium oxide, amino groups, metal-organic framework, basic catalysis, Knoevenagel condensation.

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## 1. INTRODUCTION

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Metal-Organic Framework (MOF) materials have emerged as a new class of porous crystalline hybrid metal-organic polymers built up from metallic ions or clusters connected through organic linkers by means of coordination chemistry. The topological richness, tunable pore size and the huge variety of possible combinations between metal ions and organic linkers make MOF materials excellent candidates for catalytic [1, 2] and electrocatalytic applications [3, 4]. Metal sites and/or specific functional groups from the organic linkers can act as active sites. Furthermore, post-synthetic routes can modify MOF materials in order to incorporate additional active species [5].

Terephthalic acid and its derivatives have been widely used for the synthesis of MOF materials due to their linear geometry, rigidity and multiple coordination modes of the carboxylate groups [6]. Likewise, transition metals have been extensively employed due to their variety of oxidation states [7], that could provide unsaturated open metal sites with acid and redox properties, able to directly interact with any substrate [8, 9, 10, 11]. In contrast, MOF materials based on s-block metals or rare-earth elements are not so frequent [12], although networks incorporating magnesium or calcium can also be very interesting as catalysts [13, 14, 15]. The use of alkaline-earth ions offers interesting advantages compared to the transition and lanthanide metal ions due to their relatively larger radius and lower weight, being also more abundant and non-toxic [16, 17, 18].

The assembly of alkaline-earth metals in a MOF scaffold is rather challenging, taking into account that alkaline-earth metal oxides are classic solid bases. Besides, MOFs can have different types of basic sites in both metal nodes and organic ligands, leading to design a range of base catalysts with targeted features. Moreover, these sites are plentiful, site isolated, and periodically organized in the crystalline material. As a result, MOFs provide the opportunity of developing new solid bases with characteristic features that are unachievable by traditional porous materials [19]. In this sense, MOFs with basic functionalities are able to catalyze an assortment of organic reactions including Aldol-condensation [20], Knoevenagel condensation [21, 22] and other reactions of interest in fine chemistry [23].

Knoevenagel condensation between a carbonyl compound and a molecule containing an activated methylene group have been traditionally used as a test reaction to evaluate the catalytic behavior of basic catalysts. This is a two-step reaction with a first nucleophilic addition of active methylene group to carbonyl group and following dehydration to

produce an  $\alpha,\beta$ -conjugated enone [24]. Some heterogeneous catalysts used so far for Knoevenagel condensation are zeolites [25, 26], alkali earth oxide supported on alumina [27], magnesium oxide [28] and amino based MOFs [29]. Some examples of amino-containing MOF materials evaluated as basic catalysts for Knoevenagel condensation have been IRMOF-3, MIL-101(Al)-NH<sub>2</sub> and MIL-53(Al)-NH<sub>2</sub> [29, 30, 31]. All these MOF materials were catalytically active due to the non-coordinated primary amines as Brønsted-basic sites.

Therefore, a new MOF with a crystalline 3D structure based on strontium and 2-amino-1,4-benzenedicarboxylate organic ligand (NH<sub>2</sub>-bdc) was synthesized in this work. This material provides alkaline-earth metal oxides and amino groups, both as basic active sites. The catalytic activity and stability in Knoevenagel condensation reactions were evaluated under different conditions. The catalytic performance of the new material was compared to other reference solid base catalysts reported in the literature.

## 2. EXPERIMENTAL

### 2.1. Synthesis of Sr(NH<sub>2</sub>-bdc)

All analytical reagents were commercial products and they were used without further purification. In a typical synthesis, 27.2 mg (0.150 mmol) of 2-amino-1,4-benzenedicarboxylic acid and 63.5 mg (0.300 mmol) of strontium (II) nitrate were dissolved in a mixture of N,N-dimethylformamide (15 mL) and water (1 mL). The solution was added to a 20 mL scintillation vial and placed in a preheated oven at 90 °C for 72 hours. Then, yellowish crystals were isolated by decanting the mother liquor and washed with DMF. The size of crystals was suitable for single X-ray diffraction (section S1). The synthesis yield was ca. 66% based on the linker content. IR = 3467 (w), 3337 (w), 1643 (m), 1554 (s), 1490 (m), 1377 (m), 1251 (m), 1107 (w), 837 (m), 809 (w), 775 (m), 667 (w) cm<sup>-1</sup>. C, H, N analysis (%): calc. C 36.99, H 3.27, N 7.26; found C 33.57, H 3.10, N 6.61.

Other catalytic materials used in this work for comparison purposes, such as BaO, SrO and BETA zeolite, were obtained from Sigma-Aldrich Química S.L. and Zeolyst International, respectively. BETA zeolite was ion-exchanged with sodium in our laboratory following the procedure reported by Seung-Tae et al. [32]. Additionally, an IRMOF-3 material was synthesized according to the method described in literature [33].

## 2.2. Characterization techniques

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The crystalline structure of Sr(NH<sub>2</sub>-bdc) was determined by single crystal X-ray diffraction. For this purpose, suitable crystals of Sr(NH<sub>2</sub>-bdc) were mounted on a glass fiber and used for data collection using MoK $\alpha$  radiation ( $\lambda = 0.71073$  Å) on a Bruker D8 Venture diffractometer equipped with CMOS Photon100 detector at 100(2) K by applying the  $\omega$ -scan method. The crystal of Sr(NH<sub>2</sub>-bdc) is a two-component nonmerohedral twin (0.59:0.41). The twin law describes a rotation of 180° around the [1 0 0] direction, given by the matrix (1 0 0 0 -1 0 0 0 -1). Absorption correction was applied using TWINABS [34]. The structure was solved by direct methods and refined with full-matrix least-squares calculations on F<sup>2</sup> using the program SHELXL [35] and Olex2 as graphical interface [36]. Anisotropic temperature factors were assigned to all atoms except for hydrogen atoms, which are riding their parent atoms with an isotropic temperature factor arbitrarily chosen as 1.2 times that of the respective parent. The structure exhibits disorder of the coordinated DMF molecule, which was successfully refined using a two-site model with a 0.50:0.50 occupancy ratio. Moreover, the NH<sub>2</sub>-bdc ligands reside on crystallographically imposed inversion centers and therefore their NH<sub>2</sub>-groups are equally disordered over two positions. Final R (F), wR (F<sup>2</sup>) as well as goodness of fit agreement factors and details on the data collection and analysis can be found in Table S1. Selected bond lengths and angles are given in Table S2. Powder X-ray diffraction (XRD) patterns were obtained from a PHILIPS X'PERT diffractometer using CuK $\alpha$  radiation (1.54056 Å). The data were recorded from 5 to 50° (2 $\theta$ ) with a resolution of 0.01°. Fourier transform-infrared spectra (FT-IR) on powdered samples were carried out on a Varian 3100 Excalibur Series spectrometer with a resolution of 4 cm<sup>-1</sup> and 64 scans coupled to an MKII Golden Gate Single Reflection ATR system to acquire spectra in Attenuated Total Reflectance mode. Nitrogen adsorption–desorption isotherms at –196 °C were measured using an AutoSorb equipment (Quantachrome Instruments). Samples were previously evacuated *in situ* under high vacuum (<10<sup>-7</sup> bar) for 8 h at 150 °C. The surface area was calculated by using the Brunauer–Emmett–Teller (BET) model [37]. The pore volume and diameter were estimated by non-local DFT calculations, assuming a kernel model of N<sub>2</sub> at -196 °C on carbon (cylindrical pores, NLDFE equilibrium model) [38]. Simultaneous thermogravimetry and derivative thermogravimetry analyses (TGA/DTG) were carried out under air flow (100 mL min<sup>-1</sup>) at a heating rate of 5 °C/min up to 900 °C, using a Mettler Toledo TGA/DSC1 thermobalance. Elemental analyses

were carried out using an analyzer type Flash 2000 (Thermo Fisher Scientific), equipped with a thermal conductivity detector (TCD). Carbon, nitrogen and hydrogen are determined by an oxidation/reduction reactor at a temperature of 900 °C. Oxygen determination is achieved through an Oxygen-specific pyrolysis reactor heated at 1060 °C.

### 2.3. Catalytic Knoevenagel condensation reaction

The basic catalytic activity of the  $\text{Sr}(\text{NH}_2\text{-bdc})$  material was assessed in the Knoevenagel condensation of benzaldehyde (BZ) with ethyl cyanoacetate (EC) to produce ethyl trans- $\alpha$ -cyanocinnamate (ETCN). All the experiments were carried out in a round bottom flask (50 mL) placed in a silicone bath under nitrogen atmosphere. Typically, 5 mmol of ethyl cyanoacetate (EC) as methylene compound, 10 mL of solvent and catalyst (5 mmol of metal) were added at room temperature. Thereafter, the mixture was heated up to the reaction temperature. Once the desired temperature was achieved, 5 mmol of benzaldehyde (BZ) was added. The influence of reaction solvent and temperature was explored according to previous studies [39]. A stirring speed of 1000 rpm was fixed in order to avoid mass transfer limitations. Aliquots were withdrawn at selected reaction times ranging from 0 to 4 h. Reactant and product concentrations were quantified by gas chromatography, using a GC-3900 Varian chromatograph equipped with a DB-5MS Ultra Inert capillary column (30 m  $\times$  0.25 mm, film thickness 0.25  $\mu\text{m}$ ) and a flame ionization detector (FID). Dodecane was used as an internal standard.

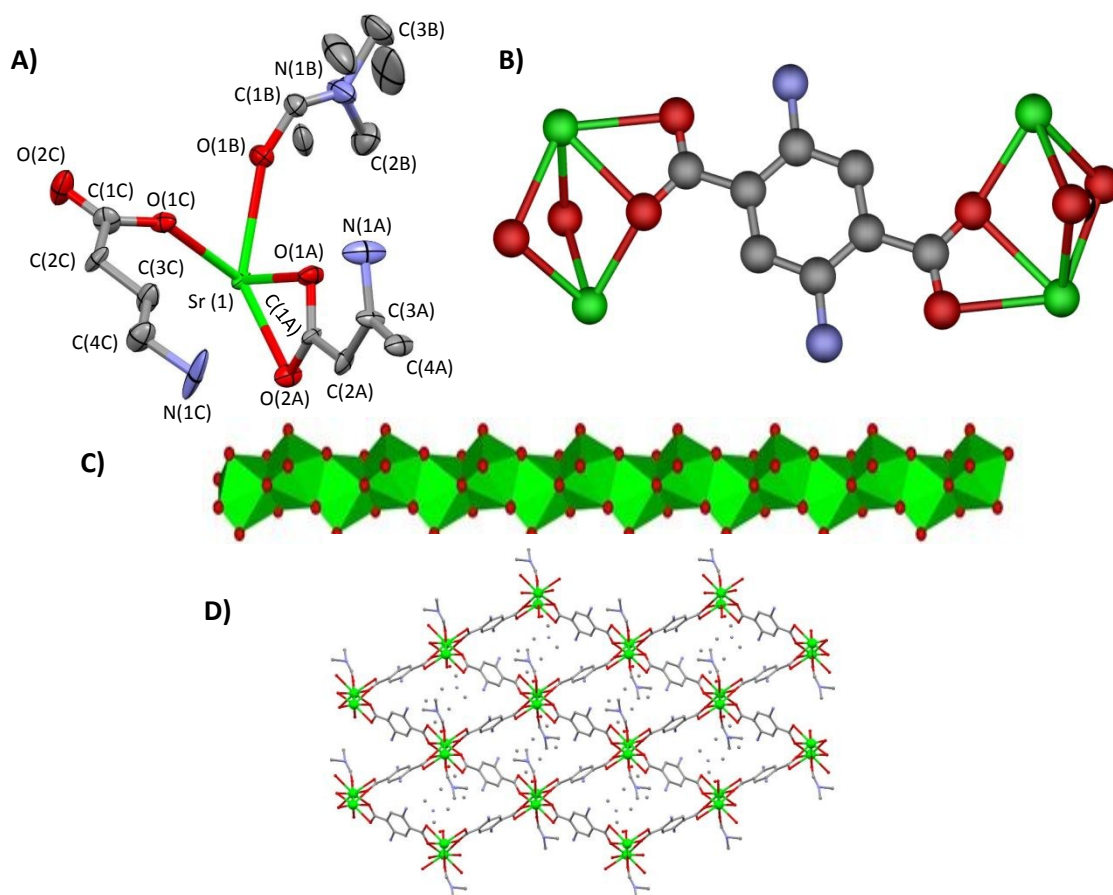
## 3. RESULTS AND DISCUSSION

### 3.1. Structural characterization of $\text{Sr}(\text{NH}_2\text{-bdc})$ material

The crystalline structure of the new material  $\text{Sr}(\text{NH}_2\text{-bdc})$  was elucidated by the single crystal XRD technique. The asymmetric unit comprises a strontium ion linked to two halves of  $\text{NH}_2\text{-bdc}^{2-}$  ligand and one DMF solvent molecule (Figure 1A). The  $\text{NH}_2\text{-bdc}^{2-}$  ligand is connected to four different strontium ions (Figure 1B). The coordination geometry of strontium ion can be described as a biaugmented triangular prism, a Johnson solid (J50) with a distorted  $\text{C}_{2v}$  symmetry with eleven faces: one quadrilateral face and ten triangular faces, as well as eight vertex and seventeen edges. Similar coordination geometry for calcium and strontium ions has been previously described in literature [40]. The metallic secondary building unit is composed by lineal chains along [100] direction

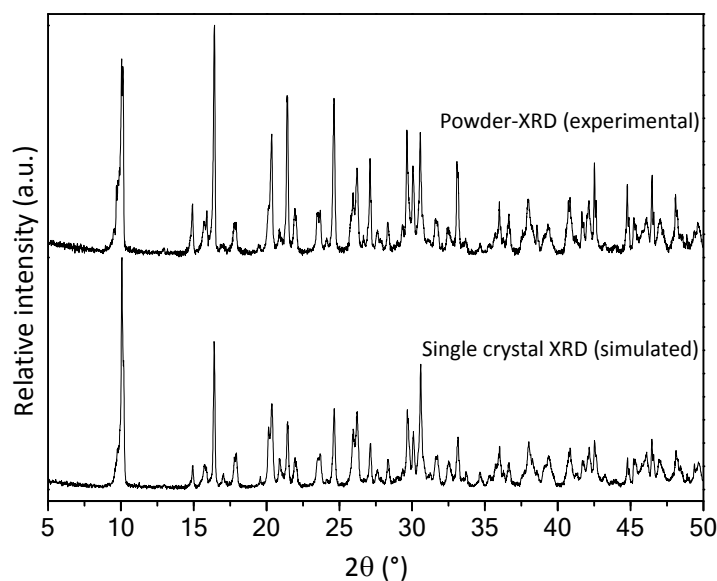


comprised by a succession of face-sharing strontium polyhedrons (Figure 1C), which are bridges by  $\text{NH}_2\text{-bdc}^{2-}$  linkers, giving rise a three-dimensional network, with rhombohedral one-directional channels along the  $b$  axis, fully occupied with coordinated DMF molecules (Figure 1D). More details of the structural unit of  $\text{Sr}(\text{NH}_2\text{-bdc})$  material were included in Tables S1 and S2.



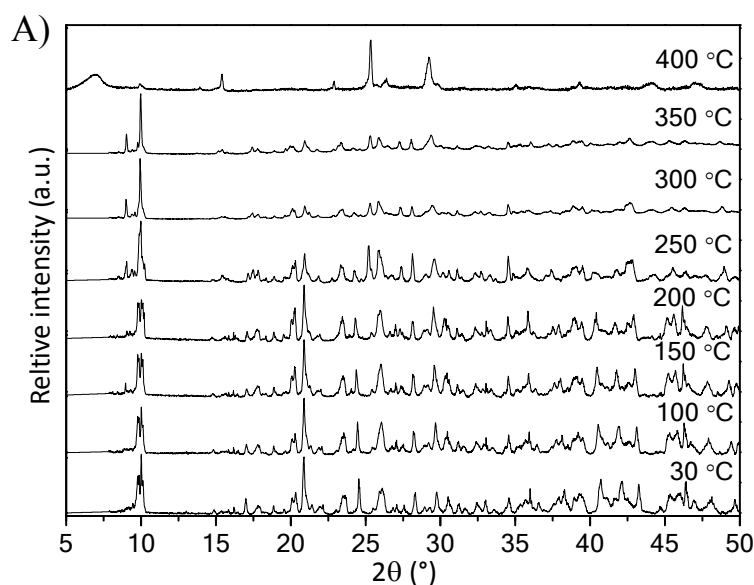
**Figure 1.** (A) Asymmetric unit of  $\text{Sr}(\text{NH}_2\text{-bdc})$  structure; (B)  $\text{NH}_2\text{-bdc}^{2-}$  ligand coordination; (C) Metallic secondary building unit of  $\text{Sr}(\text{NH}_2\text{-bdc})$ ; (D) View down the  $b$  axis of the channels in  $\text{Sr}(\text{NH}_2\text{-bdc})$  structure. Sr: green, C: grey, N: blue, and O: red. Hydrogen atoms are omitted for clarity.

In order to confirm the purity of the crystalline phase in the bulk sample, the experimental powder X-ray diffraction pattern of the new material was compared to the simulated one obtained from its crystallographic data (Figure 2). As observed, the location and intensity of main reflections match quite well in both patterns, endorsing the crystalline structure resolved by single crystal XRD.

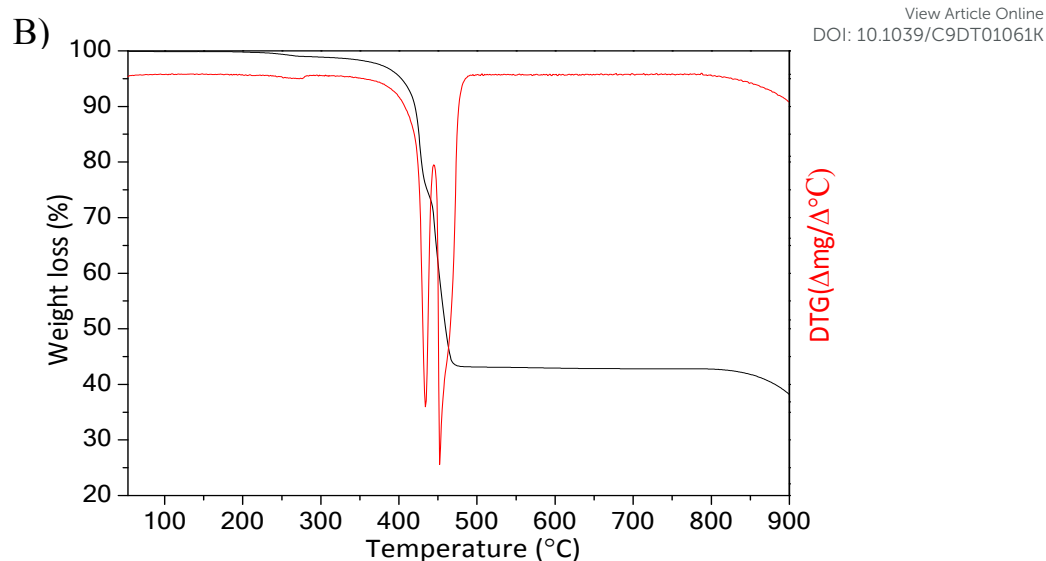


**Figure 2.** XRD patterns of powder and single crystal  $\text{Sr}(\text{NH}_2\text{-bdc})$  material

The thermal stability of the crystalline  $\text{Sr}(\text{NH}_2\text{-bdc})$  material was evaluated from *in-situ* powder XRD measurements at different temperatures in inert atmosphere and also using TG/DTG analyses in air atmosphere, as shown in Figure 3. The *in-situ* XRD patterns at different temperatures indicate the presence of the main diffraction reflections of the structure until 350 °C, although a significant decay of crystallinity was observed from 250 °C. The TG/DTG analyses display a strong weight loss at ca. 375-460 °C, caused by the organic linker decomposition. Thus, the  $\text{Sr}(\text{NH}_2\text{-bdc})$  material is thermally stable up to 250 °C with no evidence of structural damage, but above this temperature the loss of crystallinity is clear.



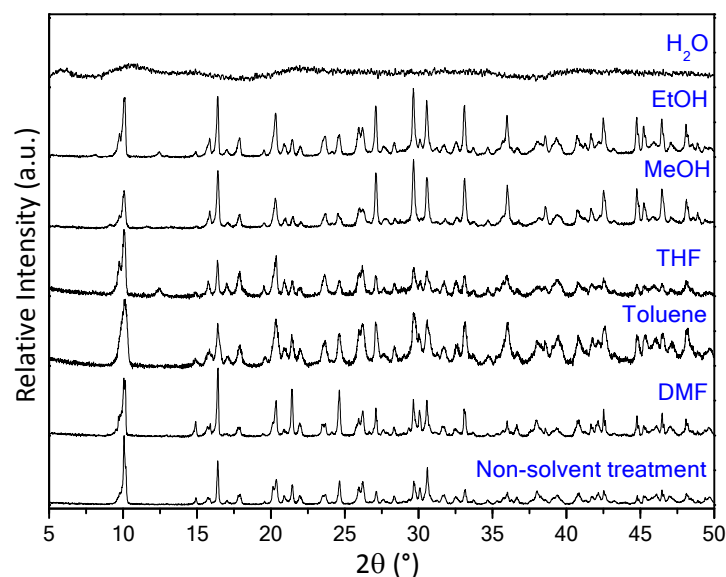




**Figure 3.** *In-situ* XRD patterns at different temperatures (a) and TG/DTG analyses (b) of  $\text{Sr}(\text{NH}_2\text{-bdc})$  material.

Nitrogen adsorption/desorption at 77 K of  $\text{Sr}(\text{NH}_2\text{-bdc})$  material shows a type-IV isotherm (Figure S3), typical of nonporous or macroporous materials, according to the IUPAC classification [41]. The low porosity suggests a strong interaction of coordinated solvent molecules, which are not evacuated after the degasification treatment, occupying a significant volume of the voids. The profiles of TG/DTG analyses seem to confirm that these solvent molecules strongly linked to the crystalline framework are released just before the organic ligand decomposition.

The structural stability of MOF materials in different chemical media is also a crucial issue for their application as heterogeneous catalysts. Thus, the chemical stability of  $\text{Sr}(\text{NH}_2\text{-bdc})$  material was tested in several solvents of different polarities, ranging the polar indexes from 2.3 (toluene) to 10.2 (water). Figure 4 shows the powder XRD patterns after dispersing the material in the corresponding solvent for 24 h at room temperature and subsequent drying. It was observed that the crystalline structure of  $\text{Sr}(\text{NH}_2\text{-bdc})$  collapsed in water. However, it was maintained for all the other organic solvents, keeping the typical diffraction peaks of the characteristic crystalline framework.



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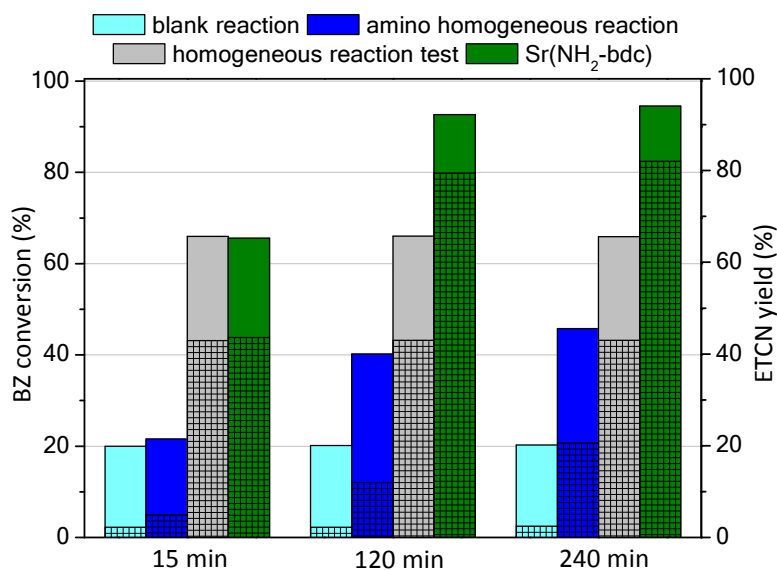
**Figure 4.** Powder XRD patterns of the  $\text{Sr}(\text{NH}_2\text{-bdc})$  material after suspension in different solvents.

The remarkable structural stability of  $\text{Sr}(\text{NH}_2\text{-bdc})$  material can be rationally explained by the ionic nature and high charge density of alkaline-earth metal ions that make the M–O bonding interactions much stronger [42]. Moreover, the large ionic size of the alkaline-earth metals allows a higher coordination number ranging from six to ten that leads to a higher connectivity of the alkaline-earth metal nodes of the framework, and consequently an improved stability. These two effects have been already reported in literature for other MOF materials based on alkaline-earth metal ions [43].

### 3.2. Catalytic activity of $\text{Sr}(\text{NH}_2\text{-bdc})$ material

Figure 5 shows the catalytic activity of  $\text{Sr}(\text{NH}_2\text{-bdc})$  in terms of benzaldehyde (BZ) conversion and ETCN product yields in Knoevenagel condensation of benzaldehyde and ethyl cyanoacetate (EC) using DMF as solvent, at 80°C, equimolar ratio of BZ/EC, and catalyst concentration of 5 mmol of strontium. Additionally, several experiments were included: i) blank reaction, in absence of  $\text{Sr}(\text{NH}_2\text{-bdc})$ ; ii) amino homogeneous reaction, in absence of  $\text{Sr}(\text{NH}_2\text{-bdc})$  but 2-amino-1,4-benzenedicarboxylic acid as basic organic ligand; and iii) homogeneous reaction test, in presence of  $\text{Sr}(\text{NH}_2\text{-bdc})$  for the first 15 min and later removal by hot filtration. The catalytic activity of the heterogeneous  $\text{Sr}(\text{NH}_2\text{-bdc})$  catalyst is clearly evidenced taking into account the results of the additional experiments. The BZ conversion of  $\text{Sr}(\text{NH}_2\text{-bdc})$  is 66% after 15 min, and 94% after 240

min, which are much higher than the values observed by the blank reaction. The amino homogeneous reaction test shows a certain activity but significantly lower than that obtained by the heterogeneous  $\text{Sr}(\text{NH}_2\text{-bdc})$  catalyst. This fact clearly proves the important benefit of  $\text{Sr}(\text{NH}_2\text{-bdc})$  material with double basic sites, alkaline-earth metal oxides and amine groups. Note that concentration of the amino-organic ligand was equivalent in both experiments (heterogeneous and amino homogeneous reaction tests). Moreover, the  $\text{Sr}(\text{NH}_2\text{-bdc})$  material evidenced a higher selectivity to ethyl trans- $\alpha$ -cyanocinnamate (ETCN) than that displayed by the amino homogeneous organic ligand.  $^1\text{H}$  and  $^{13}\text{C}$  NMR analyses confirmed the formation of ETCN product for Knoevenagel condensation of benzaldehyde and ethyl cyanoacetate with  $\text{Sr}(\text{NH}_2\text{-bdc})$  catalyst (Figure S4a and S4b, respectively). The homogeneous reaction test, which was performed in order to assess the potential activity of species leached-off by  $\text{Sr}(\text{NH}_2\text{-bdc})$  following the procedure used in literature [44], shows no further conversion of BZ after removing the  $\text{Sr}(\text{NH}_2\text{-bdc})$  solid material (at 15 minutes). This fact indicates that there is not contribution of homogeneous active species. The absence of strontium in the liquid phase of reaction (measured by ICP-OES analysis) confirmed this hypothesis.

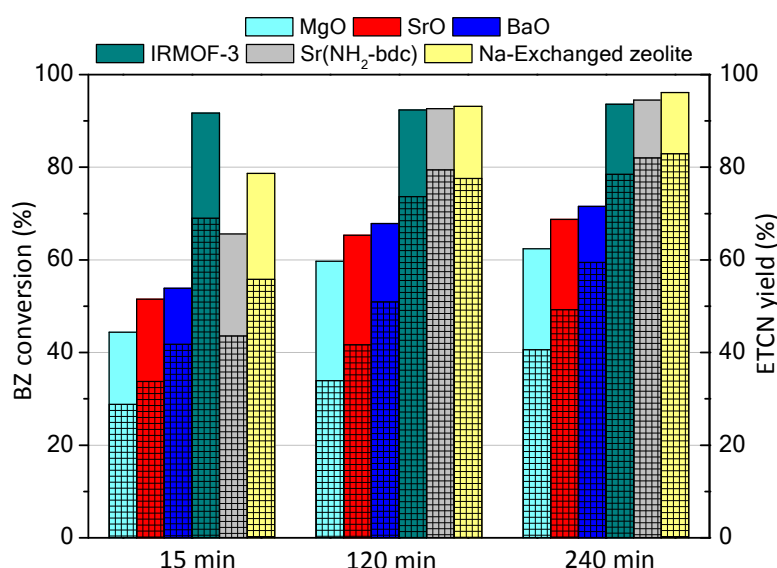


**Figure 5.** Catalytic activity of  $\text{Sr}(\text{NH}_2\text{-bdc})$  material, blank and homogeneous experiments for Knoevenagel condensation of benzaldehyde and ethyl cyanoacetate. Normal columns, benzaldehyde (BZ) conversion (left vertical axis); filled columns, ethyl trans- $\alpha$ -cyanocinnamate (ETCN) product yield (right vertical axis).

### 3.3 Catalytic activity of $\text{Sr}(\text{NH}_2\text{-bdc})$ material versus other solid catalysts

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The catalytic performance of  $\text{Sr}(\text{NH}_2\text{-bdc})$  was compared to different basic materials such as another  $\text{NH}_2$  containing-MOF material (IRMOF-3;  $\text{Zn-NH}_2\text{-bdc}$ ), alkaline-earth metal oxides ( $\text{MgO}$ ,  $\text{SrO}$  and  $\text{BaO}$ ) and Na-exchanged BETA zeolite. These catalytic experiments were carried out at  $80^\circ\text{C}$ , equimolar ratio of benzaldehyde/ethyl cyanoacetate and DMF as solvent. The catalyst loading of IRMOF-3, metal oxides and Na-exchanged BETA zeolite was set to amounts corresponding to the same concentration of  $\text{NH}_2\text{-bdc}$  (IRMOF-3) and alkaline-earth metal content (metal oxides and Na-Exchanged zeolite) which were 0.25 mmol of  $\text{NH}_2\text{-bdc}$  ligand and 5 mmol of alkaline-earth metal. Figure 6 shows the BZ conversion and ETCN product yield for all tested materials.



**Figure 6.** Catalytic activity of different catalysts for the Knoevenagel condensation of benzaldehyde and ethyl cyanoacetate. Normal columns, benzaldehyde conversion; filled columns, ETCN product yield.

The alkali-earth oxides ( $\text{MgO}$ ,  $\text{SrO}$ ,  $\text{BaO}$ ) were significantly less active than the  $\text{Sr}(\text{NH}_2\text{-bdc})$ . The increasing basicity of the alkaline-earth metal oxides with its atomic weight leads to a slight enhanced of its catalytic performance. It can be seen that the  $\text{Sr}(\text{NH}_2\text{-bdc})$  material, with both strontium metal oxide and amine basic sites, allows increasing significantly the catalytic activity of the  $\text{SrO}$  as itself. Likewise, the ETCN selectivity of  $\text{Sr}(\text{NH}_2\text{-bdc})$  material is slightly higher than that obtained by the  $\text{SrO}$ . Regarding the amino-containing IRMOF-3 material ( $\text{Zn-NH}_2\text{-bdc}$ ), a very good catalytic activity, particularly at shorter reaction times, was observed. However, according to the

powder DRX patterns, the IRMOF-3 material clearly evidenced signs of structural collapse with a significant loss of crystallinity after reaction. In contrast, the Sr(NH<sub>2</sub>-bdc) material kept its crystalline structure unchanged (Figure S5). These results indicate that Sr(NH<sub>2</sub>-bdc) material is chemically more stable than IRMOF-3 under the operation conditions of Knoevenagel condensation reaction. Additionally, FT-IR spectra of the Sr(NH<sub>2</sub>-bdc) material before and after reaction revealed the characteristic bands of functional organic groups of Sr(NH<sub>2</sub>-bdc) material (Figure S6). This fact also proves the chemical stability of this material for Knoevenagel condensation reactions. Finally, the Sr(NH<sub>2</sub>-bdc) material showed a similar catalytic performance than Na-exchanged BETA zeolite after 4 hours of reaction, with BZ conversions and ETCN yields above 90 and 80%, respectively.

### 3.4. Influence of substrates and reaction conditions on the catalytic performance of Sr(NH<sub>2</sub>-bdc)

Table 1 displays the catalytic performance of Sr(NH<sub>2</sub>-bdc) for Knoevenagel condensation reactions using different substrates, solvents and temperatures. Concerning the substrates, 4-methylbenzaldehyde and 4-nitrobenzaldehyde were used instead of benzaldehyde (entries 1-3). The 4-nitrobenzaldehyde exhibited the highest conversion of all the tested carbonyl compounds with a remarkable conversion of 91% at 15 minutes. 4-methylbenzaldehyde showed the lowest conversion with values of 61 and 84 % at 15min and 120 min, respectively. The largest conversion for 4-nitrobenzaldehyde is attributed to the strong electron withdrawing effect of the nitro substituent. This fact favors the nucleophilic attack at the carbonyl group of benzaldehyde molecule by the methylene group [45]. This behavior has been also reported in literature by other amino-containing MOF materials [39]. Additionally, malononitrile was studied instead of ethyl cyanoacetate as active methylene molecule (entry 4). When using malononitrile, a clear acceleration of the aldehyde conversion was observed, being complete not only at 120 min but also at 90 min (result not shown). These results are due to the higher reactivity of the methylene group as its acid strength is increased, being higher for malononitrile (pK<sub>a</sub> ≈ 11) as compared to ethyl cyanoacetate (pK<sub>a</sub> ≈ 13) [39, 45].

The effect of the solvent polarity was assessed for solvents with different dielectric constants: DMF (36.7), methanol (32.7), ethanol (24.3), THF (7.6) and toluene (2.4). The results (Table 1, entries 5-9) evidenced a clear relationship between the BZ conversion

and the solvent polarity. The high polarity of DMF, methanol and ethanol led to higher conversions. This fact is due to the ability of polar solvents to produce protonated forms of the amino groups of the MOF linker, which favors the formation of bezaldimine intermediates by a proton transfer mechanism. The higher conversion achieved by methanol despite of having a lower polarity than DMF, is related to the amphiprotic character of methanol [29], which induces the electrophilic polarization of the carbonyl group of benzaldehyde, and consequently increasing the reaction rate [46, 47]. In contrast, toluene, as less polar solvent showed the lowest BZ conversion and ETCN yield.

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**Table 1.** Catalytic activity of Sr(NH<sub>2</sub>-bdc) at different reaction conditions.

Variable	Nº	Value	Conv. (%) 15 min	Yield. (%) 15 min	Conv. (%) 120 min	Yield. (%) 120 min
<b>SUBSTRATE <sup>a</sup></b>	1	4-methylbenzaldehyde	61	37	84	77
	2	benzaldehyde	66	44	93	80
	3	4-nitrobenzaldehyde	91	63	100	89
	4	malononitrile	83	57	100	87
<b>SOLVENT <sup>b</sup></b>	5	MeOH	71	54	96	84
	6	DMF	66	44	93	80
	7	EtOH	49	23	65	47
	8	THF	39	5	54	10
	9	Toluene	33	2	47	8
<b>TEMPERATURE (°C) <sup>c</sup></b>	10	100	80	64	100	88
	11	80	71	54	96	84
	12	60	63	49	87	79
	13	40	52	34	80	74
	14	25	38	22	72	60

Rest of reaction conditions:

<sup>a</sup> Temperature: 80 °C, [Sr] = 5 mmol, DMF as solvent.

<sup>b</sup> Temperature: 80 °C, [Sr] = 5 mmol, substrate: benzaldehyde.

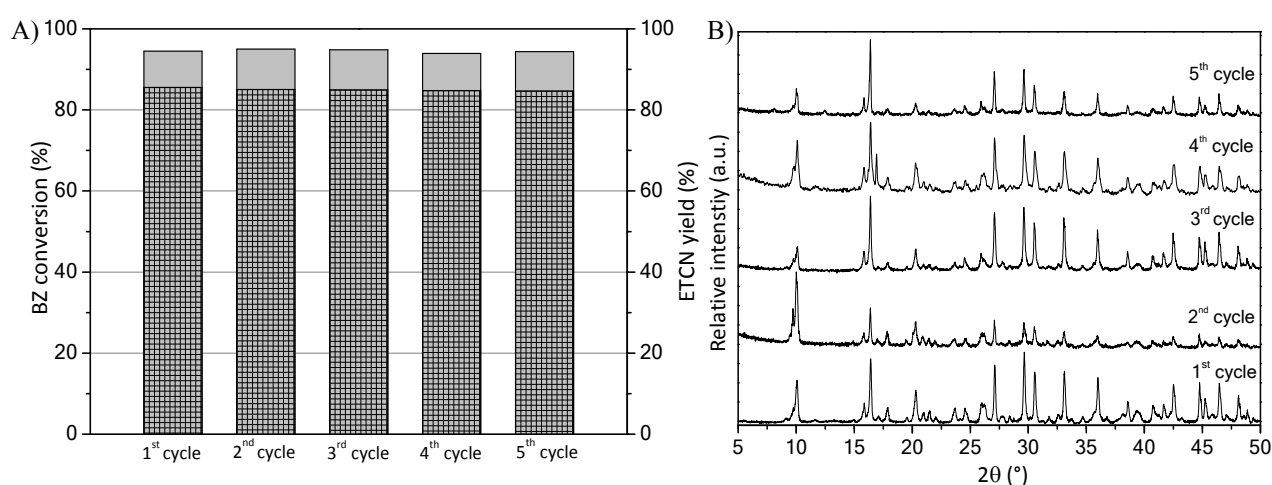
<sup>c</sup> [Sr] = 5 mmol, MeOH as solvent, substrate: benzaldehyde.



Finally, the influence of the reaction temperature was evaluated in the interval of 25-100 °C using methanol as solvent, catalyst concentration of 5 mmol of strontium and equimolar ratio between benzaldehyde and ethyl cyanoacetate (Table 1, entries 10-14). The effect of temperature is quite relevant in the activity of Sr(NH<sub>2</sub>-bdc), increasing the BZ conversion and the ETCN product yield. This effect is particularly noticeable at early reaction times (15 min). Remarkable results of BZ conversion (96%) and ETCN yield (84%) were achieved at 80°C after 120 min of reaction (entry 11). The increase of temperature up to 100°C did not significantly enhance the BZ conversion and the ETCN product yield (entry 10).

### 3.5 Catalyst reusability and stability

The reusability of Sr(NH<sub>2</sub>-bdc) catalyst was also studied at 80 °C, catalyst concentration of 5 mmol of strontium, benzaldehyde/ethyl cyanoacetate equimolar ratio and methanol as solvent. The results of BZ conversion and ETCN yield for five consecutive catalytic runs are shown in Figure 7A. As observed, the values of BZ conversion and ETCN yield remain practically constant (around 94% and 84%, respectively). Interestingly, the solid recovery after each reaction was almost total (above 97% in all the cases). Moreover, the characteristic crystalline phase of the Sr-(NH<sub>2</sub>-bdc) material is maintained along the successive cycles, as it can be attested from the X-ray diffraction patterns of fresh and recovered Sr(NH<sub>2</sub>-bdc) catalyst after the different cycles (Figure 7B). These results indicate the excellent stability of the catalyst under the studied reaction conditions.



**Figure 7.** (A) Catalytic performance of Sr(NH<sub>2</sub>-bdc) in several Knoevenagel condensation reaction cycles. Normal columns, benzaldehyde conversion; fill columns,

ETCN product yield; and (B) X-ray diffraction patterns of fresh and recovered  $\text{Sr}(\text{NH}_2\text{-bdc})$  catalyst after different cycles.

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#### 4. CONCLUSIONS

A novel metal-organic framework, named  $\text{Sr}(\text{NH}_2\text{-bdc})$  has been synthesized and characterized by different physico-chemical techniques. This material, based on the linkage of 2-aminobenedicarboxylate ( $\text{NH}_2\text{-bdc}^{2-}$ ) with strontium ions, exhibits a 3D crystallographic structure with 1-D secondary building lineal chains of face-sharing strontium polyhedrons in the [100] direction. This material provides strong basic catalytic properties with the presence of strontium metal oxides and amino containing groups. This material showed an excellent thermal and chemical stability. The catalytic performance of  $\text{Sr}(\text{NH}_2\text{-bdc})$  for Knoevenagel condensation reactions is significantly better than those of alkaline-earth oxides, typically used in basic-catalyzed reactions. These results evidence the important catalytic role of strontium metal sites and amino-containing ligand in a crystalline MOF network. In addition, this material showed a better stability than IRMOF-3 as well-known amino-containing MOF material. The catalytic activity of  $\text{Sr}(\text{NH}_2\text{-bdc})$  material increases for benzaldehyde derivatives containing electron withdrawing groups and activated methylene compounds of higher acid strength for favoring the nucleophilic addition. The polarity of the solvent and the reaction temperature also play an important role in the catalytic performance. Remarkable results of benzaldehyde conversion (96%) and ethyl trans- $\alpha$ -cyanocinnamate product yield (84%) were achieved after 120 min of reaction using 80°C for condensation of benzaldehyde and ethyl cyanoacetate. Moreover, the  $\text{Sr}(\text{NH}_2\text{-bdc})$  exhibited a notable structural stability without loss of the crystalline phase and also maintaining its catalytic activity under the optimal conditions during five consecutive catalytic runs.

#### Conflicts of interest

There are no conflicts of interest to declare.

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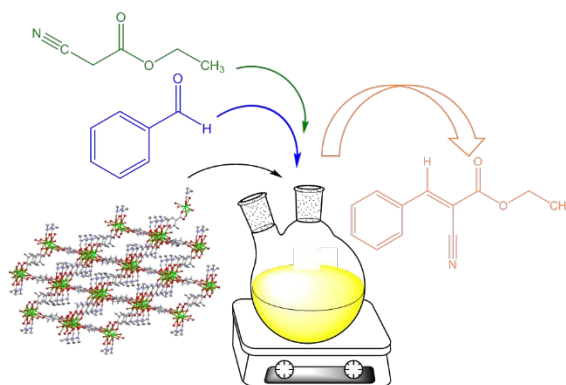
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## Table of Contents

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**Sr(NH<sub>2</sub>-bdc)** is new strontium-based MOF material that exhibits high activity in the Knoevenagel condensation which can be facilely separated and be reused without significant degradation.