



Editor's choice paper

Two-dimensional rhombus grid coordination polymer showing heterogeneous catalytic activities

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ABSTRACT

A coordination polymer, $\{[\text{Cd}(\text{L})_2(\text{DMF})_2] \cdot (\text{ClO}_4)_2 \cdot (2\text{DMF})\}_n$ (**1**) ($\text{L} = \text{bis}-(4\text{-imidazol-1-yl-phenyl})\text{-diazene}$) has been synthesized at room temperature. The polymer forms a two-dimensional (2D) rhombus-grid sheet structure. These 2D sheets are stacked in *ABAB*... mode with an inter-planar spacing of 3.729 Å. Each Cd(II) ion is equatorially bonded to four imidazole N atoms belong to four different ligand units while O atoms from two DMF molecules occupy the axial sites. Two ClO_4^- counter anions as well as two DMF molecules occupy the void space in each rhombus grid. This compound catalyzes cyanosilylation reactions of aromatic aldehydes in dichloromethane under mild conditions in heterogeneous fashion. On heating **1** at 120 °C for 4 h, all DMF molecules are lost and the ClO_4^- anions move out of the void space to occupy the axial sites on the metal to yield, de-solvated $\{[\text{Cd}(\text{L})_2(\text{ClO}_4)_2]\}_n$ (**1**) without losing crystallinity. De-solvated **1** exhibits heterogeneous catalytic activity in several Knoevenagel condensation reactions at RT.

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1. Introduction

Porous coordination polymers can be synthesized from metal ions and organic multi-dentate ligands under mild conditions. These materials have certain desirable properties such as large surface area, different pore volumes and their distribution, size and shape of pores, etc., that can be controlled via ligand design as well as choice of metal ion(s) [1–5]. A few coordination polymers have been used as heterogeneous catalysts [6–9]. For use in heterogeneous catalysis, the organic groups can be designed to have guest-accessible functional sites [10] where reactants can bind via various non-covalent interactions leading to their activation. Alternatively, labile solvent molecules bound to metal ions, can be removed by heating to make the metal ions as Lewis acid sites [11]. Heterogeneous catalysis is playing an increasingly important role [12,13] in small-scale chemical manufacturing, often with the result of a major reduction in waste. While enhancement in catalytic performance, be it in terms of activity and/or selectivity, is clearly desirable, the principal motive for heterogenization is to facilitate separation, recovery and re-use of the catalyst. It is often found that catalytic activity of metal complexes immobilized on a solid support such as oxide or zeolite, deteriorate [14,15] on exposure to moisture or heat leading to loss of catalytic activity. A number of coordination polymers also suffer from degradation of the porous structure upon removal of the lattice solvent molecules

by heating. However, a robust structure can withstand the heat treatment with minimum damage to afford a porous material that may act as a catalyst.

Cyanosilylation reactions provide a convenient route to cyanohydrins. Cyanohydrins are versatile intermediates in organic synthesis [16]. While cyanosilylation reactions have been extensively studied in homogeneous media, only few studies have employed heterogeneous catalysts [17,18]. Recently, Long et al. have used the coordination polymer, $\text{Mn}_3[(\text{Mn}_4\text{Cl})_3(\text{bt})_8(\text{CH}_3\text{OH})_{10}]_2$ as a catalyst for cyanosilylation reactions. It is proposed that the Mn(II) ions exposed on the surface of the framework act as Lewis acid sites [11]. Besides, Cu(II)- [19], Cd(II)- [20] and Sm(III)-based [21] MOFs have also been used as active catalysts for cyanosilylation of aldehydes.

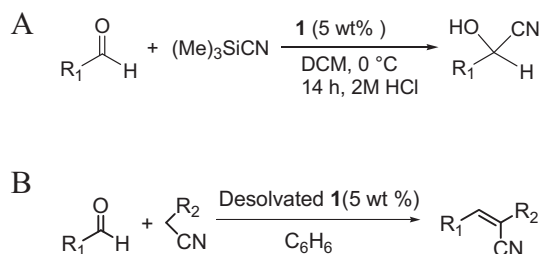
In an earlier report, we have discussed [22] room temperature synthesis of the coordination polymer, $\{[\text{Cd}(\text{L})_2(\text{DMF})_2] \cdot (\text{ClO}_4)_2 \cdot 2\text{DMF}\}_n$ (**1**) by reacting $\text{Cd}(\text{ClO}_4)_2$ with the ligand, *bis*-(4-imidazol-1-yl-phenyl)-diazene (L). Compound **1** catalyzes a number of cyanosilylation reactions while the fully de-solvated **1** obtained upon heating of **1** catalyzes several Knoevenagel condensation reactions at RT (Scheme 1).

2. Experimental

2.1. Materials

The metal salts were obtained from Aldrich and used as received. All other chemicals were procured from Aldrich and S. D. Fine Chemicals, India. All solvents were purified prior to use.

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Scheme 1. Cyanosilylation (A) and Knoevenagel (B) reactions of aromatic aldehydes.

2.2. Preparation of the ligand

The ligand *bis*-(4-imidazol-1-yl-phenyl)-diazene was prepared in two steps as described earlier [22].

2.3. Preparation of $\{[\text{Cd}(\text{L})_2(\text{DMF})_2] \cdot (\text{ClO}_4)_2 \cdot (2\text{DMF})\}_n$ (**1**)

A hot DMF solution (3 ml) of ligand **L** (50 mg, 0.16 mmol) was added to MeOH/H₂O mixed solution (1:1, 2 ml) of Cd(ClO₄)₂·xH₂O (49 mg, 0.16 mmol). On slow evaporation of the filtrate at RT, orange crystals were obtained in ~80% yield. Calc. for C₄₈H₅₆CdCl₂N₁₆O₁₂: C, 46.78; H, 4.58; N, 18.18%. Found: C, 46.82; H, 4.62; N, 18.12%.

2.4. Preparation of de-solvated **1** $\{[\text{Cd}(\text{L})_2(\text{ClO}_4)_2]\}_n$

Crystals of **1** was heated at 120 °C (heating rate of 5 °C/min.) for 4 h under vacuum to obtain de-solvated **1**. Calc. for C₃₆H₂₈CdCl₂N₁₂O₈: C, 46.78; H, 4.58; N, 18.18%. Found: C, 46.82; H, 4.62; N, 18.12%.

Caution! Perchlorate salts can form explosive mixture when added to organic compounds and hence should be handled with extreme caution and in small (<100 mg) quantities.

2.5. General procedure for cyanosilylation reactions

A solution of an aromatic aldehyde (1.32 mmol) and trimethylsilyl cyanide (2.64 mmol) in DCM (10 mL) is stirred for 5 min and then catalyst **1** (5 wt%) is added at 0 °C. The suspension is stirred under ice-cold condition for 45 min and progress of the reaction is monitored by TLC. Once the reaction is complete, the catalyst is removed by filtration, washed with DCM and recovered for reuse. After evaporation of solvent from the filtrate in a rotary evaporator, the crude solid obtained is recrystallized with EtOAc/hexane mixture.

2.6. General procedure for Knoevenagel condensation

The catalytic reactions are carried out in benzene. In a typical reaction, a solution (10 ml) containing an aromatic aldehyde and malononitrile (1:1 molar ratio) is stirred for 5 min and then 5 wt% of de-solvated **1** is added. The suspension is allowed to stir at room temperature under nitrogen atmosphere. The progress of reaction is monitored by TLC. On completion of the reaction, the catalyst is removed by filtration, washed with MeOH followed by benzene and air-dried. The filtrate is evaporated to dryness under reduced pressure and the residue is recrystallized from EtOAc:hexane (1:10) mixture to get the pure products.

2.7. Physical measurements

Spectroscopic data were collected as follows: IR spectra (KBr disk, 400–4000 cm⁻¹) Perkin Elmer Model 1320 spectrometer; X-ray powder patterns (Cu K_α radiation, 3°/min scan rate, 293 K) Philips PW100 diffractometer; thermogravimetric analysis (TGA)

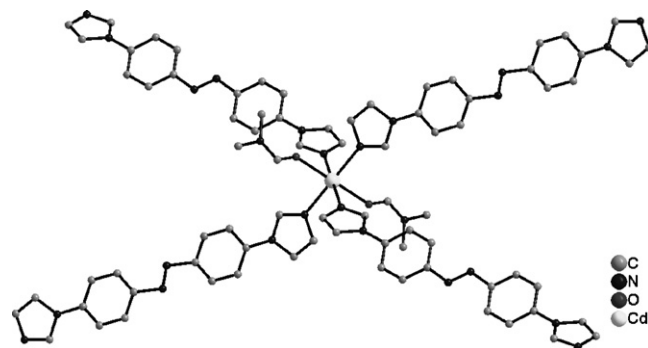


Fig. 1. A perspective view of metal coordination environment in **1**.

(5 °C/min heating rate under a nitrogen atmosphere) Mettler Toledo Star System; ¹H NMR (500 MHz, CDCl₃ and DMSO *d*₆, TMS) JEOL JNM-LA500 FT instrument. Microanalyses data for the compounds were obtained from CDRI, Lucknow.

2.8. X-ray structural studies

Single-crystal X-ray data were collected at 100 K on a Bruker SMART APEX CCD diffractometer using graphite-monochromatized MoK_α radiation (λ, 0.71069 Å) on **1** and de-solvated **1** as described earlier [22]. Crystals of de-solvated **1** were not of good quality as several cracks developed on heating. Nevertheless, a data could be collected and an approximate structure could be obtained.

3. Results and discussion

3.1. Structural description

Compound $\{[\text{CdL}_2(\text{DMF})_2] \cdot (\text{ClO}_4)_2 \cdot (2\text{DMF})\}_n$ (**1**) once isolated, is found to be air-stable and slightly soluble in DMSO but insoluble in other common organic solvents or water.

The X-ray crystallographic analysis of **1** reveals that each Cd(II) ion is octahedrally coordinated where equatorial coordination comes from imidazole N from four different ligand units. Two O from two DMF molecules occupy the axial positions. All Cd–N and Cd–O bond distances are found to be normal compared to literature values [23]. The overall structure looks like a 2D layer consisting of rhombus grids with two DMF and two ClO₄⁻ ions occupy the void spaces (Fig. 1). These 2D layers are stacked in ABAB... fashion (Fig. 2) with an inter-planar spacing of ~3.729 Å. A Cd(II) ion in one grid is situated approximately in the middle of the void of the grid below/above with the Cd...Cd separation of ~9.233 Å.

An intricate array of C–H...O and C–H...π interactions involving DMF, phenyl and/or imidazole rings and ClO₄⁻ anions stabilize the overall 3D structure of **1**. It has been shown earlier [22] that careful heating of crystals of **1** affords de-solvated **1** in single-crystal to single-crystal fashion. The structure of de-solvated **1** shows that all DMF molecules are lost and the ClO₄⁻ anions have moved to occupy the axial positions on the Cd(II) ion creating a large void space in the structure (Fig. 3).

In the IR spectrum [24] of **1**, C=O stretching vibration of DMF appears at 1670 cm⁻¹ while N=N stretching vibrations appear in the range, 1602–1515 cm⁻¹ and the ionic ClO₄⁻ gives a broad band centering around 1120 cm⁻¹. In de-solvated **1**, the peak at 1670 cm⁻¹ disappears suggesting absence of DMF molecules. The broad band at 1120 cm⁻¹ splits into two due to coordination of ClO₄⁻ anions to Cd(II) centers [25].

Thermal analysis of **1** shows ~23.4% of weight loss in the temperature range, 70–150 °C corresponding to loss of both lattice and coordinated DMF molecules (calc. 23.7%). The de-solvated frame-

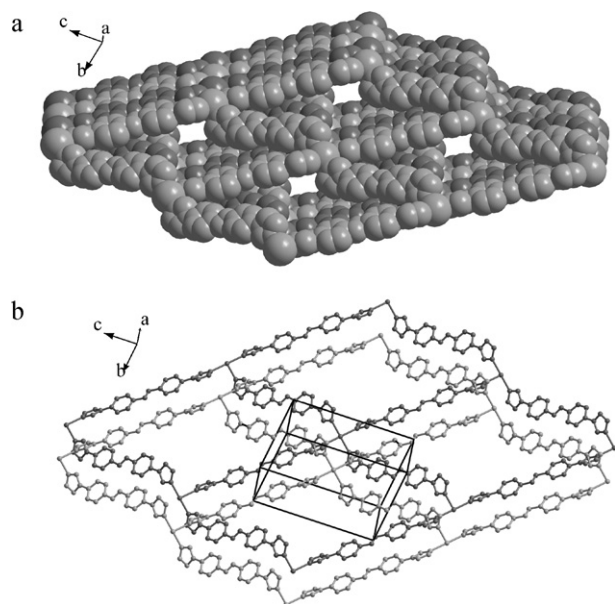


Fig. 2. A view of **1** (top) showing ABAB... stacking mode of grid layers (CPK model). 2D rhombus grid networks of **1** (bottom) with cell edges (guest molecules are removed for clarity).

Table 1
Cyanosilylation reactions catalyzed by **1**.

Entry	R ₁	Time (h)	Yield (%)
1	Ph	14	92
2	4-NO ₂ Ph	14	80
3	4-BrPh	14	72
4	4-MePh	14	40
5	Naphthyl	14	6

work is stable up to $\sim 300^\circ\text{C}$ [24]. Thermal analysis of de-solvated **1** indicates that the framework starts to decompose only after 350°C . Variable temperature PXRD data show that upon heating, the crystalline nature of framework is maintained even at high temperature (Fig. S13).

3.2. Cyanosilylation reactions

Compound **1** is assessed for its activity in the cyanosilylation reactions of different aromatic aldehydes with trimethylsilyl cyanide to form cyanohydrins as the principal product (Table 1) after work-up. The reactions are carried out using 5 wt% of **1** in DCM. With a substrate like benzaldehyde, 4-nitrobenzaldehyde, 4-bromobenzaldehyde or *p*-tolualdehyde, the yield is moderate (Fig. 4). When 1-naphthaldehyde is used as the substrate, the yield is very poor suggesting that the aldehyde here is not accommodated as per the transition-state geometry requirement for driving the reaction to the product. Compound **1** is stirred with benzaldehyde

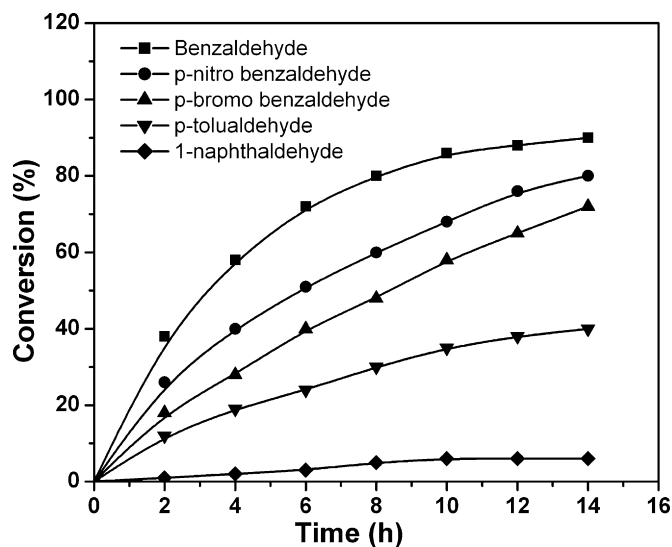


Fig. 4. Time conversion plot for the cyanosilylation reactions of different aromatic aldehydes catalyzed by **1**.

in DCM for 10 h at RT, the solid is collected by filtration, dried in air and is subjected to IR study. The IR spectrum shows absence of C=O stretching vibrations corresponding to DMF and C=O stretching vibration of benzaldehyde undergoes a red-shift by $\sim 12\text{ cm}^{-1}$ suggesting that the benzaldehyde interacts with the Cd(II) ion (Figs. S7 and 8). Also, the broad band around $1100\text{--}1080\text{ cm}^{-1}$ suggests the presence of ionic perchlorate in the lattice.

When one uses a solid catalyst, a crucial issue is the possibility that some of active sites can migrate to the liquid phase and that these leached species become responsible for the catalytic activity to a significant extent. In order to determine if leaching is a problem for the cyanosilylation reaction, the whole suspension is filtered after 1 h ($\sim 16\%$ conversion) to remove the catalyst **1**. The filtrate does not afford further conversion (Fig. 5, dotted line). This procedure is repeated with another batch and the suspension is filtered after 5 h ($\sim 60\%$ conversion) and obtained the same result with the filtrate (Fig. 5, dashed line). Thus, there is no active species leached into the liquid phase and the conversion is only possible with the solid catalyst (**1**).

3.3. Knoevenagel condensation

Knoevenagel condensation reactions are well known organic reactions largely employed in order to form C–C bonds for the synthesis of important derivatives for various applications [26,27]. Base catalyzed Knoevenagel condensation reactions have been extensively studied in homogeneous systems [28] but very few studies have employed heterogeneous catalyst [10,29–32]. To date, heterogeneous catalytic studies have shown either low activity or have been prepared in a complex way. Since all DMF molecules

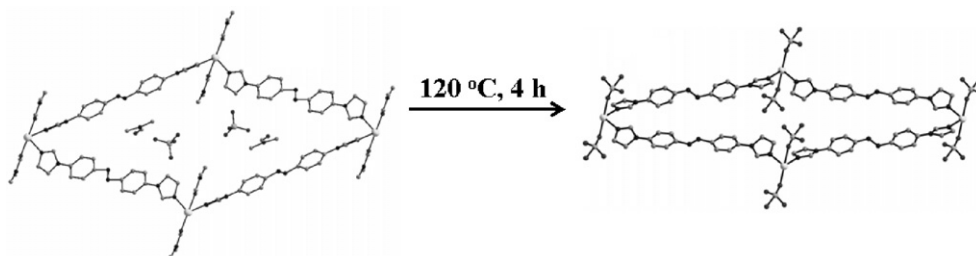


Fig. 3. A representation of the formation of de-solvated **1** from **1**.

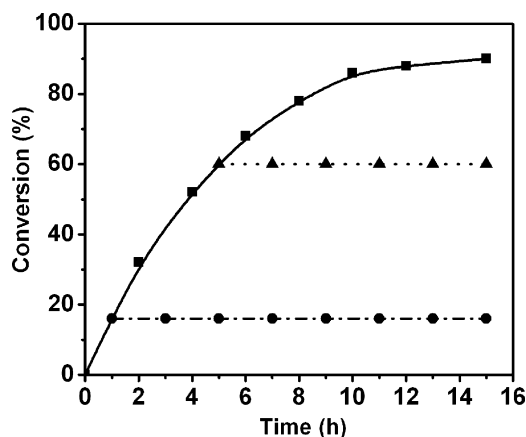


Fig. 5. Evidence of heterogeneous nature of catalysis in cyanosilylation reaction of benzaldehyde. (■) Continuous reaction; (●) catalyst was removed after 1 h; (▲) catalyst was removed after 5 h.

are lost upon heating with concomitant movement of the ClO_4^- anions, which now occupy the axial positions on the Cd(II) center, the MOF becomes more accessible by reagents. As a first batch of catalytic reactions, several Knoevenagel condensation reactions have been carried out with de-solvated **1** (Table 2). We have synthesized compounds derived from benzylidene malononitrile (BMN) as they have been found to be inhibitors for the protein tyrosine kinase [33,34].

In each case, 5% by weight of de-solvated **1** is used as the catalyst. The reactions proceed at various speeds depending upon the structure of the substrate as well as nature of the solvent (Table 2). Once a reaction is over as monitored by TLC, the reaction mixture is filtered to recover the catalyst and the filtrate is evaporated to dryness under reduced pressure and finally the resulting residue recrystallized with ethylacetate:hexane mixture (1:10) to get the pure product. The recovered catalyst obtained is washed with methanol followed by benzene, air-dried and re-used without observing any loss of catalytic activity. We have carried out each reaction at least five times to probe the reusability of the catalyst. The X-ray powder pattern of the dried catalyst, recovered from the reaction mixture after it is used for five times, is found to be almost same with respect to the pattern (Fig. 6) obtained with de-solvated **1** taken before the first run.

We have carried out the catalytic reactions in different solvents such as MeOH, MeCN, benzene and MeOH:H₂O (1:1). Each reaction is faster in benzene compared to other solvents. Also, it is found that $\text{Cd}(\text{ClO}_4)_2 \cdot x\text{H}_2\text{O}$ dissolved in MeOH/MeCN or suspended in benzene can only poorly promote some Knoevenagel condensation reactions (yield ~20%) in 24 h. Under the same condition, the ligand as well as CdO does not promote the reaction at all, even after 24 h. De-solvated **1** is stirred separately in MeOH/MeCN/benzene for 2 days and the filtrate collected. In none of the cases, the filtrate can catalyze any of the above reactions suggesting no leaching of Cd(II) from de-solvated **1**.

Table 2
Knoevenagel condensation reactions catalyzed by de-solvated **1**.

Entry	R ₁	R ₂	Time (min)	Yield (%)
1	C ₆ H ₅	CN	30	93
2	4-NO ₂ -C ₆ H ₄	CN	20	92
3	4-CH ₃ -C ₆ H ₄	CN	60	78
4	4-Br-C ₆ H ₄	CN	60	86
5	4-OCH ₃ -C ₆ H ₄	CN	120	62
6	4-F-C ₆ H ₄	CN	60	70
7	1-Naphthyl	CN	120	6

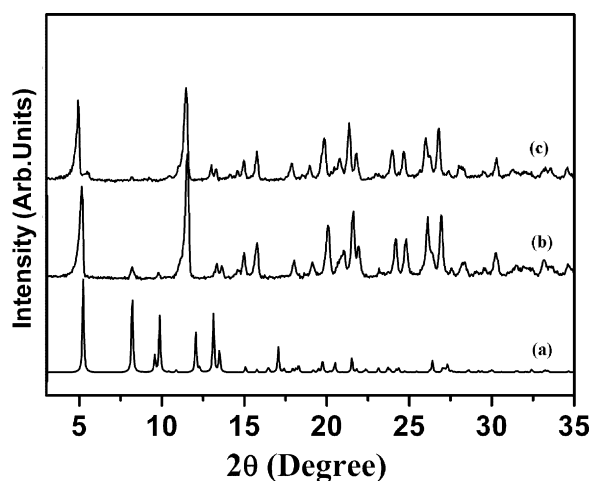


Fig. 6. X-ray powder diffraction (PXRD) patterns of (a) simulated pattern from crystal data of **1** (black) (b) de-solvated **1** and (c) de-solvated **1** after 5 catalytic runs.

Heterogeneous nature of the catalyst is probed for the Knoevenagel condensation reaction between benzaldehyde and malononitrile as the rate is moderate and the progress of the reaction can be easily monitored by GC-MS and ¹H NMR. The result is shown graphically in Fig. 7. Here, the solid line shows the progress of the reaction, which is completed in about 30 min. In a control experiment, the whole suspension is filtered after 10 min (62% conversion) to remove de-solvated **1**. The filtrate does not afford further conversion (Fig. 7, dotted line). We repeated the above procedure with another batch and filtered the suspension after 5 min (32% conversion) and obtained the same result with the filtrate (Fig. 7, dashed line). These results clearly show that the reaction is heterogeneous by nature and catalytically active species are not eluted at all under the reaction conditions.

To probe possible mechanism for substrate activation, de-solvated **1** is stirred with malononitrile in benzene for 8 h at room temperature and the solid collected by filtration, washed with benzene and air dried. The IR spectrum of the solid shows the C≡N stretching frequency at 2237 cm⁻¹ that is red-shifted by ~35 cm⁻¹ and also a doublet at 2110 cm⁻¹, which may be attributed to the hydrogen bonding interaction between methylenic H atom of malononitrile and O atom of metal bound ClO_4^- anion. Similar observations are reported in the literature [10]. The Cl-O stretching

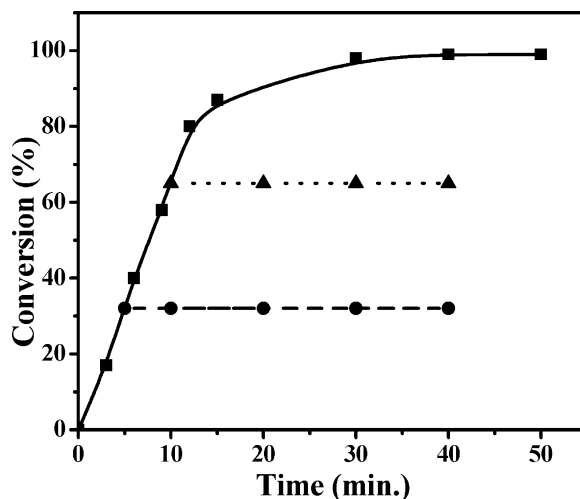


Fig. 7. Evidence of heterogeneous nature of catalysis in the Knoevenagel condensation of benzaldehyde with malononitrile. (■) Continuous reaction; (●) catalyst was removed after 5 min; (▲) catalyst was removed after 10 min.

of ClO_4^- anions shows a sharp doublet at $\sim 1100\text{ cm}^{-1}$. No change in $\text{N}=\text{N}$ stretching frequency is observed. It is, therefore, proposed that malononitrile interacts with the O atom(s) of metal bound ClO_4^- at the surface of the catalyst via H-bonding. On the other hand, IR spectrum of de-solvated **1** taken after treatment with ethyl cyanoacetate neither shows any shift of $\text{C}\equiv\text{N}$ stretching vibration nor a doublet as above. Besides, no change in the ClO_4^- stretching is observed indicating that ethyl cyanoacetate does not approach the O atom of metal bound ClO_4^- anions due to the bulkier ethyl group. Hence, when ethyl cyanoacetate is taken in place of malononitrile, no Knoevenagel condensation reaction takes place.

4. Conclusion

In conclusion, we have shown that the ligand, *bis*-(4-imidazol-1-yl-phenyl)-diazene (**L**) having two imidazole units at two ends, forms a non-interpenetrated rhombus grid network with two DMF molecules and two ClO_4^- anions occupying the void space. Two of the metal coordination sites are occupied by DMF molecules. This compound shows heterogeneous catalytic activity as a Lewis acid in cyanosilylation reactions of aromatic aldehydes. Upon heating, metal bound DMF molecules can be removed cleanly and the two ClO_4^- anions move to occupy these sites leaving the voids empty. This compound catalyzes Knoevenagel condensation reactions in a heterogeneous fashion. In both the cases, the catalyst can be reused without losing activity.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.molcata.2011.04.016](https://doi.org/10.1016/j.molcata.2011.04.016).

References

- [1] S. Kitagawa, R. Kitaura, S. Noro, *Angew. Chem., Int. Ed.* 43 (2004) 2334.
- [2] S. Xiang, W. Zhou, Z. Zhang, M.A. Green, Y. Liu, B. Chen, *Angew. Chem., Int. Ed.* 49 (2010) 4615.
- [3] M. Eddaoudi, D.B. Moler, H.L. Li, B.L. Chen, T.M. Reineke, M. O'Keeffe, O.M. Yaghi, *Acc. Chem. Res.* 34 (2001) 319.
- [4] M.C. Das, P.K. Bharadwaj, *J. Am. Chem. Soc.* 131 (2009) 10942.
- [5] M.C. Das, P.K. Bharadwaj, *Chem. Eur. J.* 16 (2010) 5070.
- [6] A. Corma, H. Garcia, F.X. Llabres i Xamena, *Chem. Rev.* 110 (2010) 4606.
- [7] L. Ma, J.M. Falkowski, C. Abney, W. Lin, *Nat. Chem.* 2 (2010) 838.
- [8] K.K. Tanabe, S.M. Cohen, *Angew. Chem., Int. Ed.* 48 (2009) 1.
- [9] D.N. Dybtsev, A.L. Nuzhdin, H. Chung, K.P. Bryliakov, E.P. Talsi, V.P. Fedin, K. Kim, *Angew. Chem., Int. Ed.* 45 (2006) 916.
- [10] S. Hasegawa, S. Horike, R. Matsuda, S. Furukawa, K. Mochizuki, Y. Kinoshita, S. Kitagawa, *J. Am. Chem. Soc.* 129 (2007) 2607.
- [11] S. Horike, M. Dincă, K. Tamaki, J.R.J. Long, *J. Am. Chem. Soc.* 130 (2008) 5854.
- [12] M. Haruta, *Nature* 437 (2005) 1098.
- [13] M. Haruta, S. Tsubota, T. Kobayashi, H. Kageyama, M.J. Genet, B.J. Delmon, *J. Catal.* 144 (1993) 175.
- [14] Y. Nishihata, J. Mizuki, T. Akao, H. Tanaka, M. Uenishi, M. Kimura, T. Okamoto, N. Hamada, *Nature* 418 (2002) 164.
- [15] M.S. Chen, D.W. Goodman, *Science* 306 (2004) 252.
- [16] W.P. Weber, *Silicon Reagents for Organic Synthesis*, Springer, Berlin, 1983 (and references cited therein).
- [17] D. Dang, P. Wu, C. He, Z. Xie, C. Duan, *J. Am. Chem. Soc.* 132 (2010) 14321.
- [18] P. Phuengphai, S. Youngme, P. Gamez, J. Reedijk, *Dalton Trans.* 39 (2010) 7936.
- [19] K. Schlichte, T. Kratzke, S. Kaskel, *Micropor. Mesopor. Mater.* 73 (2004) 81.
- [20] M. Fujita, Y.J. Kwon, S. Washizu, K. Ogura, *J. Am. Chem. Soc.* 116 (1994) 1151.
- [21] O.R. Evans, H.L. Ngo, W. Lin, *J. Am. Chem. Soc.* 123 (2001) 10395.
- [22] M.K. Sharma, P.K. Bharadwaj, *Inorg. Chem.* 50 (2011) 1889.
- [23] S. Neogi, M.K. Sharma, M.C. Das, P.K. Bharadwaj, *Polyhedron* 28 (2009) 3923.
- [24] See supporting information.
- [25] A.E. Wickenden, R.A. Krause, *Inorg. Chem.* 4 (1965) 404.
- [26] L.F. Tietze, U. Beifuss, *Comprehensive Organic Synthesis*, vol. 2, Pergamon, New York, 1991, p. 341.
- [27] D. Michaud, F. Texier-Boullet, J. Hamelin, *Tetrahedron Lett.* 43 (1997) 7563.
- [28] H. Pines, M.M. Stalick, *Base-Catalyzed Reactions of Hydrocarbons and Related Compounds*, Academic Press, New York, 1977, 234 pp.
- [29] D.-Y. Hong, K.H. Young, C. Serre, G. Férey, J.S. Chang, *Adv. Funct. Mater.* 19 (2009) 1537.
- [30] J. Gascon, U. Aktay, M.D. Hernandez-Alonso, G.P.M. Van Klink, F. Kapteijn, *J. Catal.* 261 (2009) 75.
- [31] Q.-R. Fang, D.-Q. Yuan, J. Sculley, J.-R. Li, Z.-B. Han, H.-C. Zhou, *Inorg. Chem.* 49 (2010) 11637.
- [32] Y.K. Wang, D.-Y. Hong, J.-S. Chang, S.H. Jhung, Y.-K. Seo, J. Kim, A. Vimont, M. Daturi, C. Serre, G. Férey, *Angew. Chem., Int. Ed.* 47 (2008) 4144.
- [33] P. Yaish, A. Gazit, C. Gilon, A. Levitzki, *Science* 242 (1988) 933.
- [34] A. Gazit, P. Yaish, C. Gilon, A. Levitzki, *J. Med. Chem.* 32 (1989) 2344.