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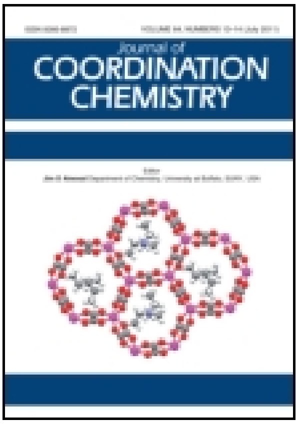

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Synthesis, structure, and base-catalytic performance of a laminar zinc phosphite-phosphate

Zhiyong Fu [a] , Jie Zhang [a] , Yi Tan [a] , Desheng Song [a] , Changchun Liu [a] & Jiaqi Wu [a]

[a] Key lab for fuel cell technology of Guangdong Province , School of Chemistry and Chemical Engineering, South China University of Technology , Guangzhou 510640, China

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Synthesis, structure, and base-catalytic performance of a laminar zinc phosphite-phosphate

ZHIYONG FU*, JIE ZHANG, YI TAN, DESHENG SONG,
CHANGCHUN LIU and JIAQI WU

Key lab for fuel cell technology of Guangdong Province, School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510640, China

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A two-dimensional zinc phosphite-phosphate $[C_3H_6(OH)NH_3][Zn_2(HPO_3)(PO_4)]$ (**1**) was hydrothermally synthesized with 2-hydroxypropylammonium cation as the structure-directing agent. This compound has been characterized by single-crystal X-ray diffraction, IR spectroscopy, and powder X-ray diffraction (XRD). Its microporous framework is constructed by ZnO_4, PO_4, and HPO_3 tetrahedral building blocks with 3, 4, and 6-ring channels. With **1** as base catalytic support, the Knoevenagel condensation reaction of benzaldehyde and ethyl cyanoacetate gives a yield of 59%.

Keywords: Zinc phosphite-phosphate; Layered compound; Inorganic microporous framework; Solid base catalyst; Structure and characterization

1. Introduction

Zeolite materials are popular catalytic supports for many important industrial processes [1]. Since the 1980s, zeolite-like connections of MO_4 and PO_4 tetrahedral building units attract considerable interest, extending research to the field of metal phosphates [2]. In the past decades, various inorganic frameworks based on metal phosphate and metal phosphite have been synthesized and characterized with structural motifs of one-dimensional chains [3], two-dimensional layers [4] and three-dimensional open structures [5]. Microporous channels, such as 3, 4, 6, and 8-ring structures, are usually found in these materials [6]. By the strategy of making interrupted structural units with terminal P–O groups, the pore size of the network can be enlarged to 24 tetrahedra for zinc phosphate [7] and zinc phosphite [8]. The connected modes of ligand are important for the final structure of an open framework. The inorganic phosphite ligand coordinates with zinc and iron in an M-O-P fashion [9, 10], while the organic phosphite ligand can form a Fe–P bond to create functional phosphite materials [11]. Phosphate derivatives with organic pendants enrich the structural features of this species. Mononuclear $(NH_4)[Zn(HPMIDA)(H_2O)_2]$ [12] and dimeric $[Zn_2(2\text{-pmOpe})_2Cl_4]$ [13] with N,O-bridging ligands display interesting supramolecular assemblies. However,

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*Corresponding author. Email: zyfu@scut.edu.cn

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by comparison with structural variety, few reports have focused on understanding the properties and potential use of metal phosphate species. Recently, industrial need of basic solids initiated research for zeolites with basic properties [14]. The replacement of liquid bases by solid catalysts can improve atom efficiency of reactions and simplify the separation processes [15]. Base functionalized zeolitic frameworks have been widely explored and used successfully [16]. Their basic nature helps the reaction. In this paper, a new example of metal phosphate species as base solid support is presented, showing efficient catalysis. A new laminar zinc phosphite-phosphate $[C_3H_6(OH)NH_3][Zn_2(HPO_3)(PO_4)]$ (**1**) is synthesized and characterized as containing a porous network. Linkages between ZnO_4, HPO_3 and PO_4 building units generate three kinds of cavities, 3, 4, and 6-ring channels, respectively. Compound **1** has been studied as a catalyst in a base catalyzed Knoevenagel condensation reaction of benzaldehyde and ethyl cyanoacetate. Experimental data indicate that it gives a high yield for the condensation products.

2. Experimental

2.1. *Synthesis and characterization*

Synthesis of **1**: a mixture of ZnO (2 mmol, 0.164 g), H_3PO_3 (3 mmol, 0.25 g), 1-amino-2-propanol (5 mmol, 0.4 mL), iminodiacetic acid (1 mmol, 0.133 g), H_2O (4 mL) and ethylene glycol (2 mL) was sealed in a 23 mL Teflon-lined bomb at 170°C for 72 h and then cooled to room temperature at a rate of 10.4°C/h. Colorless plate crystals were obtained in 55% yield (based on ZnO).

The infrared spectrum (KBr pellet) was recorded on a Bruker Tensor 27 infrared spectrophotometer from 4000–400 cm^{-1}. Powder X-ray diffraction (XRD) patterns were recorded on a Shimadzu XD-3A X-ray diffractometer with Cu-Kα radiation ($\lambda = 1.5406$ Å) and the recording speed was 2°/min over the 2θ range of 5–60° at room temperature.

2.2. *Single-crystal X-ray diffraction*

Suitable crystal of **1** (colorless block, $0.15 \times 0.15 \times 0.13\ mm^3$) was selected and mounted on a glass fibre. The measurement was made on a Rigaku R-AXIS SPIDER IP diffractometer with graphite-monochromated Mo-Kα radiation. Data were collected at 25°C using the ω and φ scans to a maximum θ value of 25.34°. The data were refined by full-matrix least-squares on F^2 with SHELXTL-97 and the structure was solved by direct methods SHELXS-97 [17]. All non-hydrogen atoms were refined anisotropically. Hydrogens of the hydroxyl were located in a difference map and refined with distance restraints of O–H = 0.82(3) Å. Other hydrogens were positioned geometrically and refined using a riding model with C–H = 0.93–0.97 Å. C1 of 2-hydroxypropylammonium cation exhibited disorder at two positions with a ratio of 7 : 3. Crystallographic data for **1** are summarized in table 1. Selected bond lengths and angles are listed in table 2.

Table 1. Crystallographic summary for **1**.

Chemical formula	$C_3H_{11}NO_8P_2Zn_2$
Formula weight	381.81
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions (Å, °)	
a	5.3018(11)
b	8.9343(18)
c	12.686(3)
α	74.35(3)
β	88.54(4)
γ	73.94(3)
V (Å^3), Z	555.25(24), 2
$F(000)$	380
Data/restraints/parameters	2001/3/148
Goodness-of-fit on F^2	1.049
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0463$, $wR_2 = 0.1312$
R indices (all data)	$R_1 = 0.0490$, $wR_2 = 0.1420$

$R_1 = \Sigma||F_o - F_c||/\Sigma|F_o|$; $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$

Table 2. Selected bond lengths (Å) and angles (°) for **1**.

Zn(1)–O(4a)	1.913(3)	O(7)–Zn(2b)	1.912(4)
Zn(1)–O(3b)	1.922(4)	O(3)–Zn(1d)	1.922(4)
Zn(1)–O(5)	1.963(4)	O(2)–Zn(2c)	1.904(3)
Zn(1)–O(1)	2.023(3)	O(4)–Zn(1a)	1.913(3)
Zn(2)–O(2c)	1.904(3)	O(3)–P(2)	1.524(3)
Zn(2)–O(7d)	1.912(4)	O(4)–P(2)	1.527(3)
Zn(2)–O(6)	1.952(4)	Zn(2)–O(1)	1.983(3)
O(5)–P(1)	1.511(4)	O(1)–P(2)	1.559(4)
O(6)–P(1)	1.516(4)	O(2)–P(2)	1.514(4)
O(7)–P(1)	1.507(4)		
O(4a)–Zn(1)–O(3b)	116.45(16)	O(7d)–Zn(2)–O(1)	109.54(16)
O(4a)–Zn(1)–O(5)	102.35(16)	O(6)–Zn(2)–O(1)	106.14(15)
O(3b)–Zn(1)–O(5)	115.73(16)	P(2)–O(1)–Zn(2)	125.8(2)
O(4a)–Zn(1)–O(1)	112.83(15)	P(2)–O(1)–Zn(1)	116.02(19)
O(3b)–Zn(1)–O(1)	109.37(15)	Zn(2)–O(1)–Zn(1)	115.88(17)
O(5)–Zn(1)–O(1)	98.68(15)	P(2)–O(2)–Zn(2c)	152.1(2)
O(2c)–Zn(2)–O(7d)	110.08(16)	P(2)–O(3)–Zn(1d)	144.9(3)
O(2c)–Zn(2)–O(6)	106.61(16)	P(2)–O(4)–Zn(1a)	138.2(2)
O(7d)–Zn(2)–O(6)	104.74(17)	P(1)–O(5)–Zn(1)	126.8(2)
O(2c)–Zn(2)–O(1)	118.71(16)	P(1)–O(6)–Zn(2)	128.1(2)
P(1)–O(7)–Zn(2b)	136.2(2)		

Symmetry transformations used to generate equivalent atoms: a: $1-x$, $-y$, $1-z$; b: $-1+x$, y, z; c: $1-x$, $1-y$, $1-z$; d:$1+x$, y, z.

3. Results and discussion

3.1. *Description of crystal structure*

Compound **1** is synthesized with H_3PO_3 as the phosphorus source. X-ray crystal diffraction analysis reveals that there are three different tetrahedral building units ZnO_4, PO_4, and HPO_3 existing in the inorganic framework. Some molecules of H_3PO_3 are oxidized to PO_4^{3-} in the hydrothermal process [18]. Compound **1** exhibits a

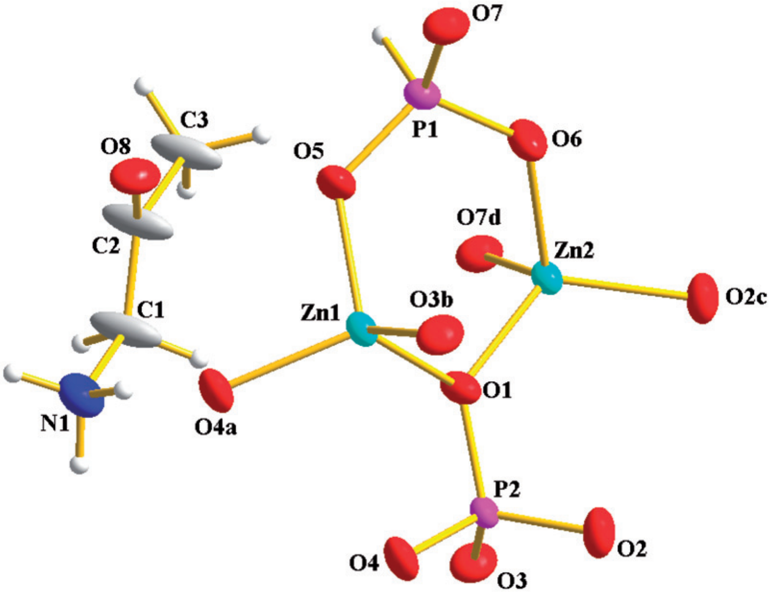


Figure 1. The asymmetric unit of **1** (ellipsoids at 50% probability).

two-dimensional layered network, as shown in figure 1. The asymmetric unit of **1** contains two Zn^{2+}, one HPO_3^{2-}, and one PO_4^{3-} with a 2-hydroxypropylammonium cation as the templating agent. The zinc ions have the same tetrahedral coordination geometry as $Zn_3PO_4(HPO_4)_3 \cdot C_6N_3H_{18}$ (FJ-11) [19]. Zn1 is coordinated with four oxygens of one HPO_3^{2-} and three PO_4^{3-}, whereas Zn2 is surrounded by four oxygens from two HPO_3^{2-} and two PO_4^{3-}. Zn–O bond distances range from 1.904(3)–2.023(3) Å (table 2). The bond angles of O–Zn–O vary from 98.68(15)–118.71(16)°, indicating distorted coordination spheres. These geometrical parameters are in agreement with previous report for the related zinc phosphite $Zn_3(HPO_3)_4 \cdot Ni(en)_2(H_2O)_2$ [20]. P1 and P2 have pseudo-tetrahedral and tetrahedral connections, respectively. The P–O bonds average a distance of 1.523 Å. The ZnO_4, PO_4, and HPO_3 tetrahedra via vertex sharing mode afford 3, 4 and 6-ring building units (figure 2). Assembly of these units finally gives a zinc phosphite-phosphate layer. By comparison with related layer structure built by an 8-membered ring in $(C_6H_{17}N_3)[Zn_4(PO_4)_2(HPO_3)_2]$ [21], **1** has a 6-membered ring unit. The difference is due to a tri-coordinated oxygen (phosphate) in **1** that links two zincs, whereas in $(C_6H_{17}N_3)[Zn_4(PO_4)_2(HPO_3)_2$ the phosphate ligand links through two different O donors with adjacent zinc centers. The 2-hydroxypropylammonium template ions locate at the space between the orderly separation inorganic layers (figure 3) and form hydrogen bonds with oxygens of the host framework $(O \cdots N = 2.96\,Å)$.

3.2. *IR and XRPD data*

IR spectrum of **1** shows a broad band centered at 3421 cm^{-1} due to the –OH stretching vibration of 2-hydroxypropylammonium. Bands in the 3120–3300 cm^{-1} region are

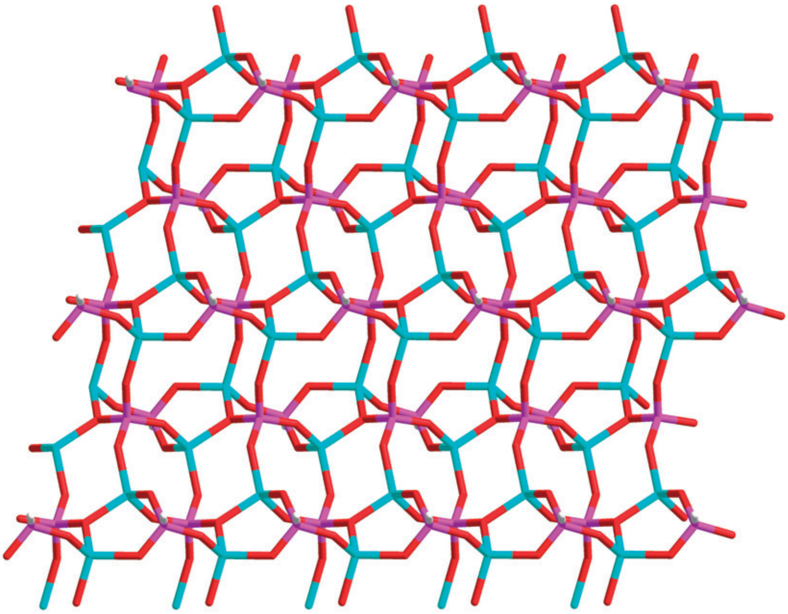


Figure 2. The zinc phosphite–phosphate layer with 3-, 4- and 6-ring channels.

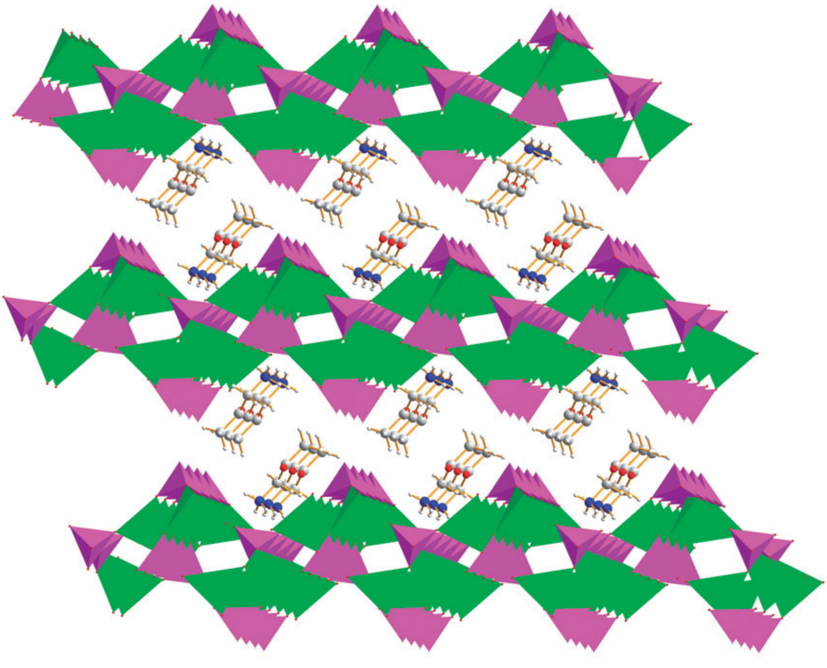


Figure 3. The arrangement of the layers and the organic cations in the structure of **1**.

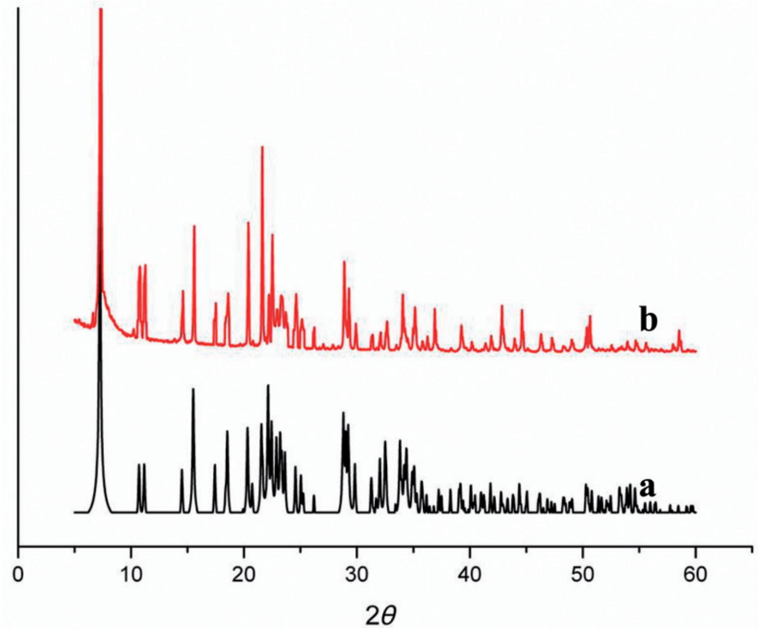


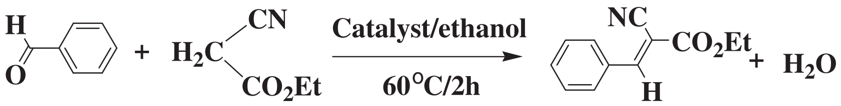
Figure 4. The powder X-ray diffraction patterns of **1**: (a) simulated and (b) experimental.

related to N–H vibrations. The C–H stretch appears at 3000 cm^{-1} and 2390 cm^{-1} is the P–H stretching vibration. The CH_2 and CH_3 bends are observed at 1400 cm^{-1}.

X-ray powder diffraction (XRPD) patterns of **1** are shown in figure 4. Phase purity of the bulk samples is confirmed by comparison of the observed and simulated XRPD patterns.

3.3. *Basic catalytic behavior*

Knoevenagel condensations between aldehydes and substrates containing active methylene groups are important for industrial syntheses of drugs. The use of heterogeneous catalysts for these reactions eliminates the possibility of side reactions, giving better selectivity and more yield [22]. They also avoid the separation process for homogeneous catalysts. With **1** $[C_3H_6(OH)NH_3][Zn_2(HPO_3)(PO_4)]$ as solid catalytic support, the Knoevenagel condensation of benzaldehyde and ethyl cyanoacetate is carried out in ethanol at 333 K (scheme 1). In a typical run, 0.1 mmol of zinc phosphite-phosphate was added to a solution of 20 mmol benzaldehyde and 20 mmol ethyl cyanoacetate in 5 mL of ethanol. The mixture was then stirred vigorously at 333 K for 2 hours. At the end of the reaction, the catalyst was removed by filtration. Solvent ethanol was removed by vacuum distillation. The amount of condensation product was determined using a gas chromatograph GC/MS Trance DSQ system (gas chromatograph coupled to a mass spectrometer; carrier gas—nitrogen; flow, 1 mL min^{-1}; oven, 70–280°C; injector, 100°C; detector, 280°C). Figure 5 shows that the yield of the condensation product ethyl (E)-α-cyanocinnamate is about 59% with **1** as solid catalyst. By comparison, no condensation



Scheme 1. Knoevenagel condensation of benzaldehyde and ethyl cyanoacetate with **1** as solid catalytic support.

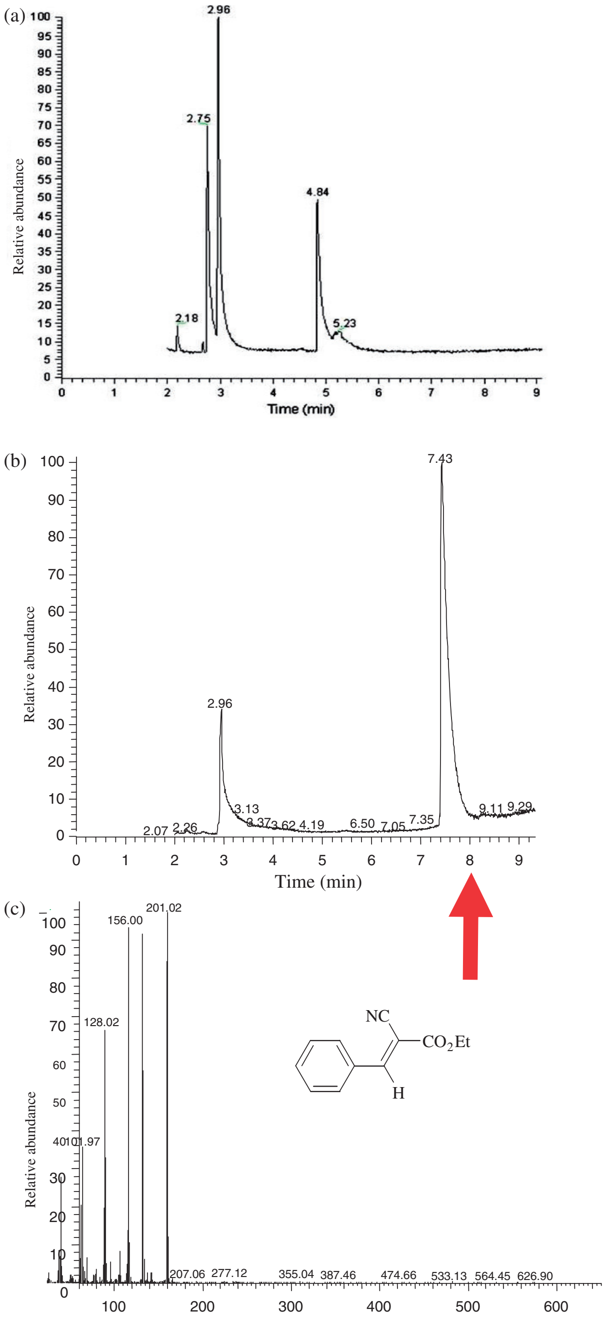


Figure 5. GC-MS spectrum of reaction mixture: (a) blank (without catalyst); (b) with **1** as solid catalytic support; and (c) MS spectrum of the condensation product.

product is observed without the solid catalyst. In contrast to analogous base catalysts, the catalytic activity of **1** is about 40% higher than that of $NaLaCa_3(PO_4)OH$ and $NaLaSr_3(PO_4)_3OH$ [22], and it is about 30% lower than that of methylammonium FAU zeolite [23].

4. Conclusions

A laminar zinc phosphite-phosphate is synthesized and characterized. Its structure contains ZnO_4, HPO_3 and PO_4 building units and 3, 4, and 6-ring channels. The performance of this new zeolite-like material is tested by a Knoevenagel condensation of benzaldehyde and ethyl cyanoacetate. It is a useful solid catalyst and gives high catalytic activity compared with the blank. The test of base catalytic behavior of zeolite materials is interesting for it may produce useful solid catalysts for industrial applications.

Supplementary material

CCDC 829479 contains the supplementary crystallographic data of **1**. The data can be obtained free of charge from The Cambridge Crystallographic Data center via www.ccdc.cam.ac.uk/data_request/cif, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (+44) 1223-336-033.

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