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ARTICLE

Two Organic-Inorganic Hybrid Polyoxovanadates as Reusable Catalysts for Knoevenagel Condensation

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Two novel organic-inorganic hybrid polyoxovanadates, i.e., $[Ni(1\text{-mIM})_4(H_2O)_2][Ni(H_2O)_5]_2V_{10}O_{28}\cdot 5.5H_2O$ (compound **1**) and $[V(O)(1\text{-vIM})_4]_2V_4O_{12}\cdot H_2O$ (compound **2**) (1-mIM = 1-methylimidazole; 1-vIM = 1-vinylimidazole) were synthesized under routine conditions. The two polyoxovanadates hybrids were further unequivocally characterized by usual physicochemical techniques, such as single crystal X-ray diffraction (SCXRD), fourier transform infrared spectroscopy (FT-IR), powder X-ray diffraction (PXRD), thermogravimetric analyses (TG) and elemental analyses. SCXRD analyses demonstrate that the three Ni^{2+} atoms of compound **1** present the distorted octahedral geometry, and one of Ni^{2+} atoms is coordinated with four 1-mIM molecules and two coordinated water molecules, exhibiting a $[NiN_4O_2]$ binding set. On the other hand, the other two Ni^{2+} atoms are coordinated with five water molecules and one decavanadates polyanion, presenting a $[NiO_6]$ coordination environment. The structure of **2** exhibits the central $[V_4O_{12}]^{4-}$ unit attached on opposite sides of two $[V(O)(1\text{-vIM})_4]_2$ groups, in which the V center displays a distorted octahedron configuration. More importantly, two organic-inorganic hybrid polyoxovanadates further were studied in the Knoevenagel condensation, and found to display efficient heterogeneous catalytic activities (yield up to 99%) and the catalytic performance of the compound **1** did not decrease after three runs catalytic cycle.

Introduction

Polyoxometalates (POMs) are early transition-metal-oxygen clusters with well-defined structure and high anionic charge, and their unique physical and chemical functionalities can be precisely tuned by choosing corresponding Mo, W, V, Nb and Ta, etc, elements, and therefore they are of increasing interest in wide fields including catalysis, medical science and materials science, etc.[1-2] In the territory of POMs chemistry, polyoxovanadates (POVs) are of great importance due to their attractive magnetic and electronic performance, along with their long-promised potential as oxidative catalysts.[3-4] As for pure POVs, they have been generally applied in the field of oxidation catalysis due to vanadium has strong reversible redox properties.[5-6] In addition, it is generally accepted that the combination of transition-metal complexes with Lewis bases ligands and POVs anions play a key role in the synthesis process, which affect not only the diversity of POVs structure, but also their catalytic activities in the oxidative and acid-base reactions.[7] Recently, some transition-metal POVs hybrids have been investigated in the catalytic oxidation systems of organic compounds with molecular oxygen or *tert*-butyl hydroperoxide as the oxidant.[8-10] However, as reported to date, these transition-metal polyoxovanadates hybrids involved with base catalytic reactions are rather rare. Consequently, the development of constructing highly effective transition-metal POVs hybrids catalysts for such transformation remains an attractive research field.

Knoevenagel condensation of aromatic carbonyl compounds with active methylene derivatives, as one of the significant reactions for carbon-carbon double bonds formation, has been widely applied in the production of pharmaceutical intermediates and fine chemicals.[11-12] In the last few years, the application of Knoevenagel condensation ranged from polymers to pharmaceutical industry have been widely reported.[13-14] Recently, a large variety of catalysts have been proven to significantly improve Knoevenagel condensation, such as zinc(II) organic-inorganic hybrid $[Zn(L)(H_2O)_2]_n\cdot n(DMF)$ (L = 5-acetamidoisophthalate; DMF = N-methylformamide),[15] $[Zn_2(TCA)(BIB)_{2.5}](NO_3)$ (H_3TCA = tricarboxytriphenyl amine, BIB = 1,3-bis(imidazol-1-ylmethyl)benzene)[16] and some Ni coordination supramolecular complexes[17], etc. Thereby, the development of suitable catalysts for Knoevenagel condensation is still an increasing demand.

Owing to facile tunability at atom level, polyoxometalates might be ideal catalysts for Knoevenagel condensation. Mizuno reported highly negatively charged γ-Keggin germanodecatungstate and $TBA_8[\alpha\text{-}Si_2W_{18}O_{62}]\cdot 3H_2O$ as efficient Knoevenagel condensation catalysts, however, these POMs catalysts are homogeneous in the case.[18-19] Compared with homogeneous catalysts, the heterogeneous catalysts mainly provided significant advantages, such as succinctly recovery, efficient recyclability, least possible

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contamination by the reaction medium and superior stability. Importantly, few POVs demonstrated as fine catalysts for Knoevenagel condensation are rare, and thus developing synthetic methods of transition-metal POVs hybrids for the condensation with mild and green methodologies is highly desirable.

In the present study, and in continuation to develop our investigation in the base catalytic field of POVs, we controllably synthesized two organic-inorganic polyoxovanadates hybrids $[Ni(1\text{-}mIM)_4(H_2O)_2][Ni(H_2O)_5]_2V_{10}O_{28}\cdot 5.5H_2O$ (compound **1**) and $[V(O)(1\text{-}vIM)_4]_2V_4O_{12}\cdot H_2O$ (compound **2**) by controlling different solvents, base environment and amount of transition metal salts. The new organic-inorganic polyoxovanadate hybrids as highly efficient heterogeneous catalysts were further used in the Knoevenagel condensation of various aromatic aldehydes with malononitrile under solvent-free conditions.

Results and discussion

Syntheses

In the structure database of organic-inorganic hybrid vanadates, there exist a host of fascinating structures. In continuation to explore and develop the formation of the various architectures of hybrid vanadates with potential applications, we chose the simple vanadium source V_2O_5 or $VO(acac)_2$ as the precursors along with 1-mIM to react with $NiCl_2\cdot 6H_2O$. At first, water was used as eco-friendly solvent in the synthetic procedure, compound **1** was obtained with 1-mIM as the ligand. When we used 1-vIM only to replace water as the solvent and ligand, remaining V_2O_5 as the vanadium source, to react with $NiCl_2\cdot 6H_2O$, no crystal was obtained due to the poor solubility of these materials. Then, we further used $VO(acac)_2$ instead of the $NiCl_2\cdot 6H_2O$ to enhance the vanadium species solubility, compound **2** was obtained fortunately.

Structure Analysis of Compound (1) $[Ni(1\text{-}mIM)_4(H_2O)_2][Ni(H_2O)_5]_2[V_{10}O_{28}]\cdot 5.5H_2O$

As presented in Fig. 1, the result of SCXRD analysis reveals that compound **1** contains a typical $[V_{10}O_{28}]^{6-}$polyanion, two five water-coordinated $[Ni(H_2O)_5]^{2+}$ along with a six-coordinated $[Ni(1\text{-}mIM)_4(H_2O)_2]^{2+}$ counteraction part, and the two terminal oxygen atoms of $[V_{10}O_{28}]^{6-}$ polyanion are coordinated with the two five water-coordinated Ni^{2+} cations to form the $(Ni(H_2O)_5)_2[V_{10}O_{28}]^{2-}$ unit. The $[V_{10}O_{28}]^{6-}$ of **1** has a crystallographic inversion center on the midpoint of the O12 and O12A and is made up of an ten distorted VO_6 octahedron including with highly condensed ten vanadium atoms and twenty-eight different types of oxygen atoms. The bond distances and bond angles of the $[V_{10}O_{28}]^{6-}$ anion (Table S1) are similar with those of reported $[V_{10}O_{28}]^{6-}$ units.[20-22] For the $[V_{10}O_{28}]^{6-}$ cluster in **1**, the terminal oxygen atom O2 and O2A form the bridges to two outer-shell $[Ni(H_2O)_5]^{2+}$ cations. Additionally, the bond distance (V4-O2) is 1.642(6) Å, which is usual for the vanadyl oxygen double bonds, however, the bond length (Ni2-O2) is 2.076(6) Å, which is longer than that of V=O bonds as a result of being the relatively weak coordination bonds.

In addition, the supramolecular structure of **1** was stabilized by intermolecular electrostatic interactions and strong hydrogen-bonding interactions between $[Ni(H_2O)_5]^{2+}$ cations and $[V_{10}O_{28}]^{6-}$ anions, i.e. the $\{[Ni(H_2O)_5]_2[V_{10}O_{28}]\}^{2-}$ subunits in **1** are all connected to the adjacent one through various intermolecular O-H···O hydrogen-bonding actions [O3···O8 (-x+1/2, -y+1/2, -z+2): 2.741(7) Å; O10··· O4 (-x-1, -y, -z): 2.713(7) Å; O5···O11(-x+1/2, -y+1/2, -z+2): 2.720(6) Å] (Table S2) forming a 2D network along the *ab* plane (Fig. 2).

Structure Analysis of Compound (2) $[V(O)(1\text{-}vIM)_4]_2V_4O_{12}\cdot H_2O$

SCXRD analysis displayed that the asymmetric unit of compound **2** comprises one VO^{2+} cation, one $V_2O_6^{2-}$ anion and four 1-vIM N-ligands (Fig. 3). The V atom of VO^{2+} unit is six-coordinated and exhibited in a distorted VN_4O_2 octahedral geometry, and the V coordination sphere is completed by four nitrogen atoms (N1, N3, N5 and N7) from 1-vIM N-ligands, one bridging oxygen atom (O1) from VO_4 tetrahedron and one terminal oxygen atom (O7) (Fig. 4: Top).

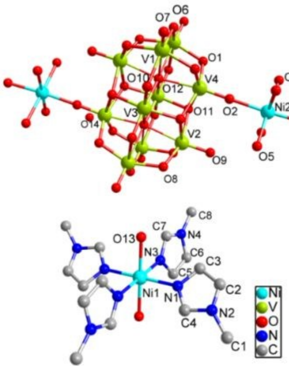

Fig. 1 The crystal structure of compound 1.

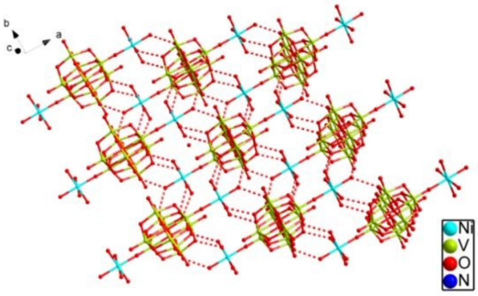

Fig. 2 The crystal structure of compound 1.

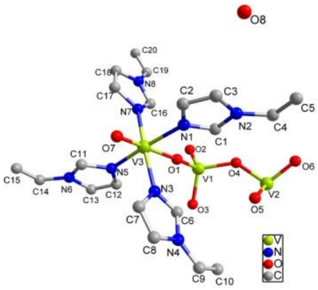

Fig. 3 The crystal structure of compound 2.

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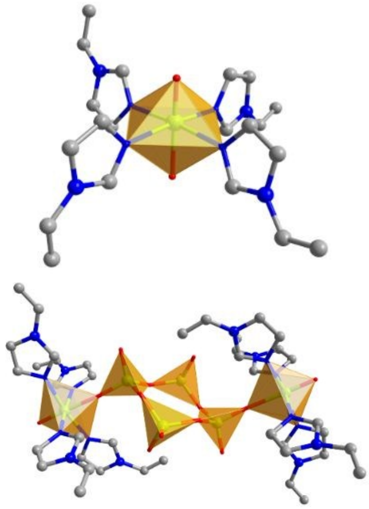

Fig. 4 Top: The coordination environment of V3 atom; Bottom: The polyhedral schematic diagram of compound 2.

In the asymmetric $V_2O_6^{2-}$ cluster of **2**, both V1 and V2 atoms possess a distorted tetrahedral geometry. The tetrahedron of V(1)O_4 is occupied by one terminal oxygen (O2) and three bridging oxygen (two oxygen atoms (O3, O4) from the two adjacent VO_4 tetrahedrons and one (O1) from the VN_4O_2 octahedron. The V2 atom possesses a distorted V(2)O_4 tetrahedron and coordinated by two terminal oxygen (O5, O6), two bridging oxygen (O3, O4) from the two adjacent VO_4 tetrahedrons. In addition, the adjacent VO_4 tetrahedrons are further linked by the corner-sharing oxygen atoms and formed an intact $V_4O_{12}^{4-}$ anion cluster. In the $V_4O_{12}^{4-}$ anion, the V-O and V=O bond lengths are comparable with those of reported $V_4O_{12}^{4-}$ inorganic-organic hybrid vanadates.[23-26] As showed the Fig. 4 bottom, it was obvious that the $V_4O_{12}^{4-}$ subunit coordinate with two VN_4O_2 octahedrons by the terminal oxygen atoms on the either side of the $V_4O_{12}^{4-}$ unit and formed the final $V_2N_4O_2V_4O_{12}$ skeleton. Additionally, strong intermolecular hydrogen bonds exist in the supramolecular structure of compound **2** due to the lattice water molecules with the distances of 2.815(10) Å and 2.906(11) Å corresponding to O8⋯O2 (-x+3/2, y-1/2, -z+1/2) and O8⋯O5 (x-1/2, -y+3/2, z-1/2) (Table S2), respectively, which further stabilize the supramolecular structure of **2** (Fig. 5).

Bond Valence Sum (BVS) calculations of compound 2 show the oxidation states of six V atoms are mixed-valence V^{IV}/V^{V}(four vanadium atoms in the $V_4O_{12}^{4-}$ unit are V^{V} and the rest two are V^{IV}), which also be similar with the reported compounds (Table S3).[5]

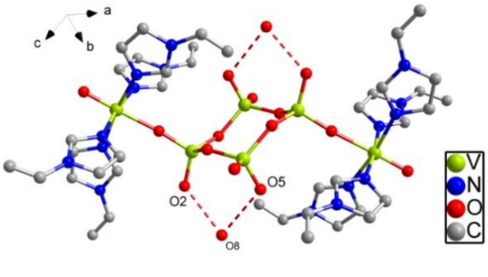

Fig. 5 The hydrogen bonds interaction of compound **2**.

IR analysis

In generally, the IR can afford some valuable information for investigation of polyoxovanadates. Especially, the 400-1000 cm^{-1} region is worthy of carefully discriminating, in where M-O_t (terminal oxygen atoms) and M-O_b (bridging oxygen atoms) that can be found. The stretching bands of V=O_t in **1** appear at 964 cm^{-1}, 942 cm^{-1} for **2**. Absorption bands at 836, 742 and 665 cm^{-1} for compound **1** (Fig. S1), and 879, 763 and 642 cm^{-1} for compound **2** (Fig. S2) can be attributable to the V–O–V or Ni–O–V stretching vibrations.[27] The apparent stretch absorption bands from 1650 cm^{-1} to 1510 cm^{-1} region are assigned to C=C and C=N (1-methylimidazole/1-ethylimidazole ligands).[28] Moreover, absorption bands of coordinated water in the compounds **1-2** could be positioned at around 3300–3500 cm^{-1}.[29]

PXRD analysis

To investigate the repeatability and purity of the two organic-inorganic hybrid polyoxovanadates, the obtained compounds **1-2** were ground to suitable powder for PXRD analysis. The results of PXRD detection endorsed us to acknowledge that the two synthesized samples were single phase materials, respectively. As shown in Fig. S3-4. These peaks positions of the simulated PXRD patterns of compounds **1**-**2** were in well agreement with those of as-synthesized PXRD patterns, which revealed that the phase purity of compounds **1**-**2**.

Thermogravimetric analyses

Compounds **1**-**2** were investigated by TG analysis, which was carried out in a flowing N_2 atmosphere with a heating rate of 5 °C min^{-1} from 30 to 800 °C (Fig. S5-6). For **1**, the TG curve shows two-step weight losses. The first-step weight losses of 11.42 % at 85–271 °C is related to the loss of coordinated water molecules and free water molecules. Then, there is sharp weight loss to 800 °C, which means that the compound's skeleton begins to collapse. For **2**, the skeleton of compound **2** begins to collapse at the start of heating, indicating poor thermal stability.

Knoevenagel Condensation Reaction

Initially, benzaldedyde and malononitrile were used as model substrates to investigate the catalytic performance of the two catalysts (Scheme 1). In a model experiment, benzaldedyde (0.5 mmol) and malononitrile (0.8 mmol) along with the compound **1** (0.1 mol%) were mixed uniformly without solvent in a flask and reacted at 40 °C for 1 h, achieving only a product 2-benzylidenemalononitrile in 99% yield (Fig. 6g). Whereas, the blank experiment indicates that only trace conversion was achieved in the absence of catalysts (Fig. 6a). To evaluate the catalytic performance of cations and anion of Ni-POVs on the Knoevenagel conversion, a series of designed experiments were carried out. The results presented that poor yields of 2-benzylidenemalononitrile was achieved with $NiCl_2 \cdot 6H_2O$ (Fig. 6b). Although 1-methylimidazole as homogeneous catalyst can produce 2-benzylidenemalononitrile (Fig. 6e), the yield (34.6%) is much lower than those of compounds **1-2**. When the Knoevenagel reaction was completed using the mixture of $NiCl_2 \cdot 6H_2O$, V_2O_5 and 1-methylimidazole as catalyst under the same conditions, the yield was 47% (Fig. 6d). Those control experiments obviously suggested that compound **1** played an important role in the Knoevenagel

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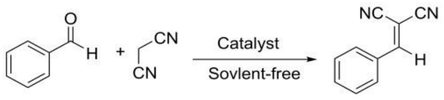
condensation. Indeed, catalytic performance of compound **1** in the Knoevenagel condensation was superior to many reported heterogeneous catalysts, i.e. Ni-induced fabrication of ZIF-8 nanoframes,[30] interface-active ZIF-8,[31] etc.

Additionally, the catalytic recycle of the catalyst was further investigated and compound **1** was simply filtrated after the reaction was completed and then washed by methanol; the recovered compound **1** can be used for the successive three runs recycles. Remarkably, the catalytic performance of compound **1** was kept at high level even after three recycles [Yields of products: 99% (First run), 97% (Second run), 98 % (Third run)] (Fig. 7) in the Knoevenagel condensation. Importantly, the recovered compound **1** remained its structural integrity after three runs recycles and they were confirmed by the PXRD patterns (Fig. 8).



Scheme 1. Knoevenagel condensation of benzaldedyde and malononitrile.

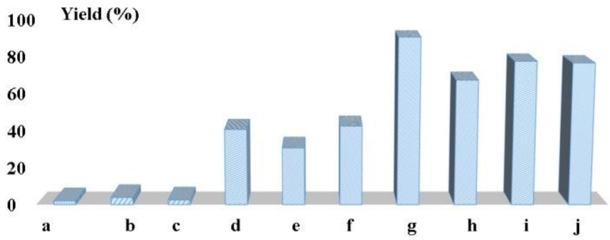


Fig. 6 Knoevenagel condensation of benzaldehyde with malononitrile with different catalysts. Reaction conditions: benzaldehyde (0.5 mmol), malononitrile (0.8 mmol), catalysts (0.1 mol%), 40 °C, 1 h; (a) Blank; (b) $NiCl_2{\cdot}6H_2O$; (c) V_2O_5; (d) $NiCl_2{\cdot}6H_2O$ and 1-mIM; (e) 1-mIM; (f) $NiCl_2{\cdot}6H_2O$,V_2O_5 and 1-mIM; (g) compound **1**; (h) compound **1** (0.1 mol%) (h) compound **1** (0.05 mol%); (h) compound **1** (0.075 mol%); (h) compound **2**.

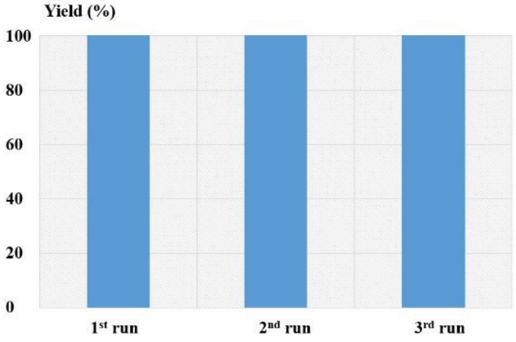


Fig. 7 The reaction results of Knoevenagel condensation catalyzed by compound **1** in recycle experiments. Reaction conditions: benzaldehyde (0.5 mmol), malononitrile (0.8 mmol), compound **1** (0.1 mol%), 40 °C, 1 h.

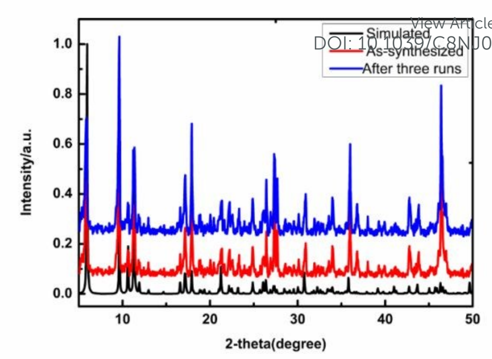
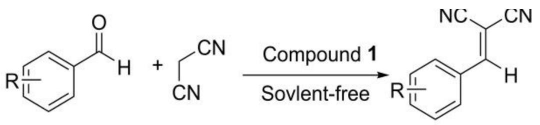
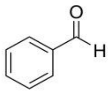
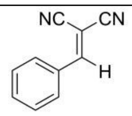
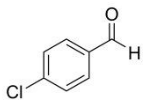
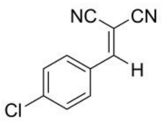


Fig. 8 The PXRD patterns of compound **1** after three runs recycles

In the case, to explore the substrate scope and generality of aromatic aldehyde, various substituted benzaldehyde derivatives were expanded under optimal conditions and the corresponding results were shown in Table 1. First, various functional groups with bearing electron-withdrawing groups and on the *para*-position of the benzaldehyde were scanned (-Cl, -Br, -NO_2). Para-chloro-, bromo- or nitro- substituted benzaldehyde lead to the desired products (Table 1, entries 2-4) in similar yield as that of entry 1. The yields with halogen on the para-position of benzaldehyde are slightly decreased from 96.4 to 98.3% by changing from methyl- to methoxyl- (Table 1, entries 5-6). In addition, sterically hindered 2-bromobenzaldehyde also gives the 96.2% yield (Table 1, entry 7). Based on the above results, it was obvious that highly selective and efficient Knoevenagel condensation of various substituted aldehydes can be realized by applying $[Ni(1\text{-}mIM)_4(H_2O)_2][Ni(H_2O)_5]_2V_{10}O_{28}{\cdot}5.5H_2O$ as catalyst and the results were similar with those of in the reported literature.[32]

Table 1. Compound **1**-Catalyzed Knoevenagel Condensation [a]



Entry	Substrates	Products	Yield[b](%)
1			>99
2			>99

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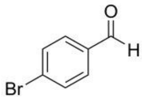
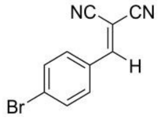
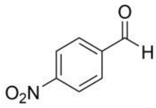
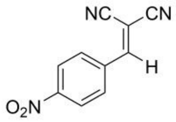
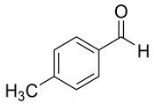
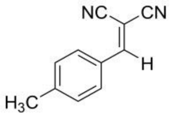
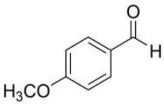
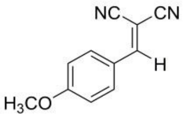
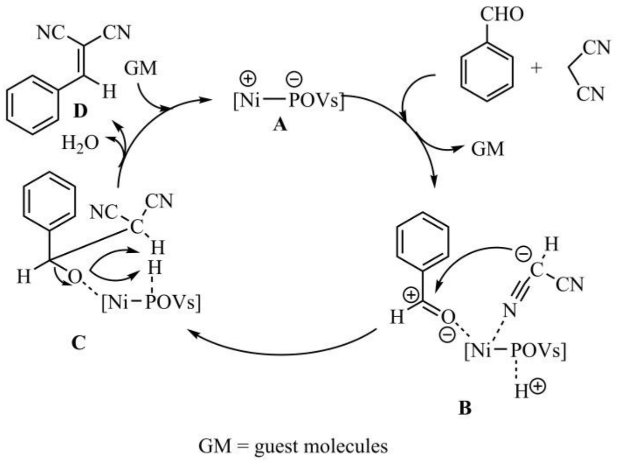
3			>99
4			>99
5			98.3
6			96.4
7			96.2

[a] Reaction performed at 40 °C under solvent-free conditions, 0.5 mmol aldehyde, 0.8mmol malononitrile, 0.1 mol% compound **1**, 1h; [b] Yield of products were determined by GC.

Table 2.Crystallographic data for compounds **1** and **2**

	Compound **1**	Compound **2**
Formula	$C_{16}H_{57}N_8Ni_3O_{45.5}V_{10}$	$C_{40}H_{50}N_{16}O_{15}V_6$
M_r	1775.22	1300.60
Crystal system	Monoclinic	Monoclinic
Space group	*C2/m*	*P2(1)/n*
Temperature	298(2) K	298(2) K
a (Å)	19.5903(17)	14.4908(13)
b (Å)	9.3317(8)	12.5546(12)
c (Å)	15.8463(12)	15.4384(14)
α (deg)	90	90
β (deg)	110.430(2)	106.662(2)
γ (deg)	90	90
V (Å^3)	2714.7(4)	2690.7(4)
Z	2	2
$D_{calc.}$(g cm^{-3})	2.172	1.077
F(000)	1744	1320
$R_1[I>2\sigma(I)]$	0.0713	0.0448
$wR_2[I>2\sigma(I)]$	0.1905	0.1050
R_1(all data)	0.0908	0.0869
wR_2(all data)	0.2063	0.1267
GOOF	0.993	1.008
CCDC No.	1875917	1875916



Scheme 2. A proposed plausible mechanism for the reaction of benzaldehyde with malononitrile

Although the detailed mechanism of this Knoevenagel condensation catalyzed by Ni-POVs remains to be elucidated, a tentative mechanism on the basis of reported work is proposed and presented in Scheme 2.[17, 33] In our coordination Ni-POVs, first, dissociation of coordinated water molecules or imidazole molecules of Ni-POVs occurs under reaction conditions**,** the carbonyl group of benzaldehyde interacts with the active nickel center, achieving a polarization of the carbonyl group and improving the electrophilic property of the carboxylic carbon atom, which was favored the nucleophilic attack from the malononitrile. Meanwhile, the interaction of nitrogen atom of cyano group with nickel increases the acidity of the methylene group, which increases the deprotonation of methylene group of malononitrile. As a consequence, the basic sites (carboxylate-O) can abstract the proton from the methylenic group to generate the corresponding nucleophilic species and the species further attacks the carbonyl group of benzaldehyde, and forms the C−C bond via aldol condensation. Next, aldol condensation intermediate is dehydrated to form the Knoevenagel products **D** and reacts with guest molecules to form **A** again.[34]

Experimental

Materials and reagents

V_2O_5, $VO(acac)_2$, 1-vinylimidazole, 1-methylimidazole, 25 % tetramethylammonium hydroxide, 25 % tetraethylammonium hydroxide, nickel(II) chloride hexahydrate and other solvents and reagents purchased from Aladdin Co., Ltd.

The FT-IR spectra of compounds **1-2** were recorded on Nicolet 170 SXFT/IR spectrometer in the range 4000–400 cm^{-1}. PXRD data was obtained by using a Rigaku D/max-2550 diffractometer with Cu-Kα radiation. After the each catalytic reaction was completed, the result of product was evaluated by GC (Shimadzu GC-2014C) and GC-MS (Agilent 7890A-5975C) using naphthalene as internal standard substrate. The elemental analyses measurements were done on Perkin-Elmer 240C elemental analyzer. ^1H and ^{13}C NMR spectra were measured on Bruker 500 MHz spectrometer by using tetramethylsilane (TMS) as the internal standard.

Synthesis

Synthesis of $[Ni(1\text{-}mIM)_4(H_2O)_2][Ni(H_2O)_5]_2V_{10}O_{28}\cdot 5.5H_2O$ (1):V_2O_5 (2.75 mmol, 500mg) and 25 wt% tetraethylammonium hydroxide (100 mg) were slowly added to 20 mL water in a clean beaker. The above solution was stirred intensely at 25 °C for 60 min, and to this were added nickel(II) chloride hexahydrate (119 mg, 0.5 mmol), 1-mIM (300 mg, 3.65 mmol), respectively. The reaction mixture of earthy yellow was stirred for another 24h and followed to heat at 50 °C for 40 min. Finally, the resulting mixture was filtrated and the resulted filtrate stood for seven days, yellow crystals, suitable for X-ray diffraction, were obtained. Yield: 60.8%. Anal. Calcd. (found) for $C_{16}H_{57}N_8Ni_3O_{45.5}V_{10}$: C, 10.83 (10.93); H, 3.24 (3.02); N, 6.31 (6.52). FT-IR spectrum, ν (cm^{-1}): 3338 (s), 3147 (w), 2926 (w), 1637 (s), 1531 (s),1384 (s), 1244 (w), 1114 (w),1098 (w), 964 (s), 836 (s),742 (s), 665 (w),598 (s), 453 (w).

Synthesis of $[V(O)(1\text{-}vIM)_4]_2V_4O_{12}\cdot H_2O$ (2):V_2O_5 (2.75 mmol, 500mg) and 25 wt% tetramethylammonium hydroxide (100 mg) were added to 3 mL 1-vinylimidazole. The resulting mixture of earthy yellow was stirred at ambient temperature for 1 h, next vanadiumoxyacetylacetonate (67 mg, 0.25 mmol) was added. The obtained mixture was stirred for another 24h and then heated at 50 °C for 40 min. After the reaction was completed, the mixture was filtrated and the resulted filtrate stood for seven days, green crystals suitable for X-ray diffraction were achieved. Yield: 56.5%. Anal. Calcd. (found) for $C_{40}H_{50}N_{16}O_{15}V_6$: C, 36.94 (36.82); H, 3.88 (4.01); N, 17.23 (17.12). FT-IR spectrum, ν (cm^{-1}): 3421 (O-H, s), 3115 (m), 2929 (w), 1639 (s), 1504(s), 1389 (s), 1224(m), 1096 (s), 942 (s), 879 (w), 763(s), 642(m), 591(m), 508 (m).

Characterization of the Ni-POVs crystals

SCXRD data for two organic-inorganic polyoxovanadates compounds **1** and **2** were performed on a Bruker-AXS CCD diffractometer equipped with a graphite-monochromated Mo-Ka radiation (λ = 0.71073 Å) at 298 K. All absorption corrections were applied using multi-scan technique. The crystal structures of compounds **1**-**2** were solved by the direct method and refined through full-matrix least-squares techniques method on F^2 using the SHELXTL 97 crystallographic software package. The crystallographic data for compounds **1**-**2** are summarized in Table 2.

Catalytic Knoevenagel condensation of aromatic aldehydes and malononitrile by organic-inorganic polyoxovanadates

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The catalytic reaction was conducted in a 10 mL reaction tube using aromatic malononitrile (0.8 mmol), aldehydes (0.5 mmol) and catalyst (0.1 mol%). The reaction mixture was slowly heated to 40 °C in a Wattecs Parallel Reactor for 1 h. When the reaction was finished, catalyst was simply retrieved by filtration, washed with methanol (ca. 3 * 5 mL), and the reaction mixtures were analyzed using an Shimadzu 2014C GC equipped with a flame ionization detector. All the products were analyzed over Bruker 500 MHz spectrometer.

Conclusions

In summary, we report the facile synthesis of two new organic-inorganic hybrid polyoxovanadate, by employing various solvent, imidazole ligand and base environment, etc. These Ni-POVs with highly catalytic active centers show distinctive coordination environments with organic ligands. Importantly, compound **1** demonstrated efficient catalytic activities (up to yield 99%) in the Knoevenagel condensation under solvent-free conditions, especially, the novel catalyst was heterogeneous and can be simply recovered and recycled without losing its catalytic activity. Work is underway to explore the synthesis of catalytic active new organic-inorganic polyoxovanadates and expand this approach to other potential catalytic reactions for these catalysts.

Conflicts of interest

There are no conflicts to declare.

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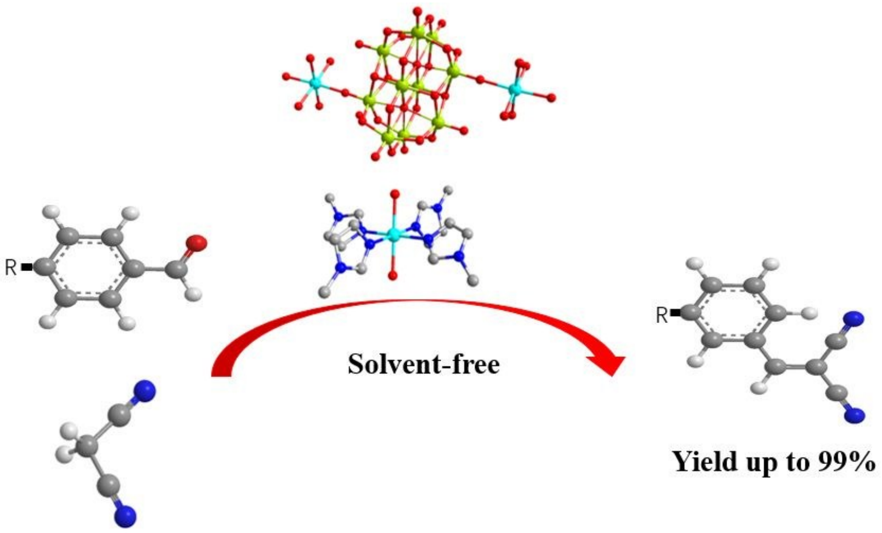
Graphic Abstract



Two organic-inorganic hybrid polyoxovanadates as heterogeneous catalyst have been controllable synthesized and fully characterized. Importantly, compound **1** can effectively catalyze Knoevenagel condensation reaction (yields up to 99%) under solvent-free and mild conditions in heterogeneous system and its activity is basically maintained after three cycles.