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A novel silver(1)-Keggin-polyoxometalate inorganic–organic hybrid: a Lewis acid catalyst for cyanosilylation reaction[†]

Tuo-Ping Hu,^{ab} Ya-Qin Zhao,^a Kai Mei,^a Shu-Jie Lin,^a Xing-Po Wang^a and Di Sun^{*a}

A novel polyoxometalate (POM) hybrid material based on a Keggin polyanion and silver(i)–organic sheet, namely, $[Ag_4(apym)_4(SiW_{12}O_{40})]_n$ (1), where apym = 2-aminopyrimidine, has been synthesized under hydrothermal conditions and characterized by elemental analysis, IR spectroscopy, thermal gravimetric analysis, powder X-ray diffraction and single-crystal X-ray diffraction. In the structure of 1, polyanions link 2D 3-connected $4\cdot8^2$ -fes Ag^l–organic sheets to generate a 3D complicated framework. Moreover, the catalytic performance of 1 towards the cyanosilylation of carbonyl compounds has been tested under mild conditions, showing a high turnover number and turnover frequency.

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Introduction

As a large family of inorganic materials, polyoxometalates (POMs) are anionic metal oxide clusters of early transition metals such as Mo, W, V, and Nb in their highest oxidation states.1 POMs are excellent candidates for secondary building units (SBUs) because of their several significant characteristics including high stability and ease of functionalization.² Hybrid inorganic-organic POMs constructed from inorganic POM building blocks with various organic and/or transition metal complex moieties can bring novel structural motifs and functionalities into one entity.³⁻⁸ So, the design and development of functional POM-based hybrids is a hot research field aiming at potential applications in areas like biology, materials chemistry, catalysis, medicine, electronics, photocatalysis, electrochemistry, and so on,⁹ which, in turn, makes the deliberate assembly strategies for the synthesis of new POM-based hybrids come forth. Many POM-based hybrids with variable dimensionalities and topologies have been constructed under hydrothermal conditions.¹⁰ The silver ion could exhibit versatile coordination numbers (2-8) in the construction of interesting motifs.¹¹ When a low coordination number of the Ag atom is incorporated, it exhibits unsaturated coordination sites, which may act as Lewis acid sites to catalyze chemical reactions. The combination of two species into one hybrid may bring a new structure as well as functionalities such as enhanced chemical catalysis performance. As a very simple but versatile ligand, 2-aminopyrimidine (apym) has found its niche in silver(1) coordination chemistry,¹² but to date, incorporation of silver(1)-apym motifs into POMs has not been achieved.

Until now, the systematic synthesis and utilization of satisfying POM catalysts has been a crucial challenge for chemists because of some inherent drawbacks of these materials, like high solubility in aqueous solution, small specific surface area and low stability under catalytic conditions.¹³ These drawbacks widely reduce the catalytic efficiency and recovery rate as well as restrict their applications. On the other hand, the characteristics of nanosized space and functional surface of metal-organic frameworks (MOFs) make them to be effective host materials.14,15 Especially the internal restricted and functionalized channels of MOFs provide a distinct chemical environment to capture molecules and facilitate catalytic reactions.16 Hence, utilizing POMs to construct MOFs is intriguing and has been reported in succession.^{17,18} Nevertheless, there are only a few articles reported on the use of Keggin polyoxoanions as templates to direct the construction of catalytic MOFs.19

Based on the above consideration and our previous works, in this study, we achieved the goal of obtaining a Keggin-POM based organic–inorganic hybrid material, $[Ag_4(apym)_4(SiW_{12}O_{40})]_n$ (1, apym = 2-aminopyrimidine) constructed from a Keggin polyoxoanion and Ag(i)-apym motifs. This novel silver(i)-Keggin-POM inorganic–organic hybrid exhibits high catalytic efficiency for the cyanosilylation of carbonyl compounds.

^a Key Lab of Colloid and Interface Chemistry, Ministry of Education, School of Chemistry and Chemical Engineering, Shandong University, Jinan, 250100, PR China. E-mail: dsun@sdu.edu.cn

^b Department of Chemistry, North University of China, Taiyuan, Shanxi 030051, People's Republic of China

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Results and discussion

Crystal structure description

The single crystal X-ray study reveals that 1 crystallizes in the monoclinic space group *Pn*. The structure of 1 is a 3D framework constructed by 2D silver(I)–organic sheets and SiW₁₂O₄₀^{4–} building blocks. The asymmetric unit of 1 is composed of four Ag(I) ions, four apym ligands, and one SiW₁₂O₄₀^{4–} anion. As shown in Fig. 1a, Ag1, Ag3 and Ag4 atoms are all four-coordinated by two nitrogen atoms from two different apym ligands and two oxygen atoms from two different SiW₁₂O₄₀^{4–} anions, showing a distorted AgN₂O₂ tetrahedral coordination geometry. The Ag2 atom binds to two nitrogen atoms from two different SiW₁₂O₄₀^{4–} anions from three different SiW₁₂O₄₀^{4–} anions, displaying a five-coordinated AgN₂O₃ distorted square pyramidal geometry with a τ_5 parameter of 0.198 ($\tau_5 =$ Addison parameter, $\tau_5 = 0$ for an ideal square pyramid and $\tau_5 = 1$



Fig. 1 (a) Polyhedral and ball-and-stick representation of the coordination environments of Ag atoms in **1**. (b) Coordination mode of apym found in **1**. (c) Polyhedral representation of the octadentate $\text{SiW}_{12}\text{O}_{40}^{4-}$ anion in **1**. (d) 3-Connected (4.8²)-**fes** 2D Ag-apym sheet. (e) Polyhedral and ball-and-stick representation of the 3D framework of **1** (colour code: purple = Ag, red = O, blue = N, gray = C).

for an ideal trigonal bipyramid).²⁰ The coordination mode of the apym ligand in compound 1 is uniform μ_2 -N¹:N¹ (Fig. 1b) (Ag-N: 2.15(4)-2.24(4) Å). The Keggin-type $SiW_{12}O_{40}^{4-}$ anion acts as an octadentate inorganic ligand that coordinates to eight Ag(I) ions completely with Ag-O bond distances ranging from 2.57(4)-2.88(2) Å (Fig. 1c). A better insight into the structural nature of 1 can be achieved by the application of topological analysis; that is, simplifying the structure into node and linker nets. According to the simplification principle, each Ag(1) atom can be considered as a 3-connected node, while coordinated apym ligands and μ_2 -O atoms serve as linkers. Therefore, the Ag-apym motifs can be described as 2D 3-connected fes $(4 \cdot 8^2)$ sheets, as illustrated in the Fig. 1d. On account of the oxygen atoms which bond to the Ag(1)atom from $SiW_{12}O_{40}^{4-}$ anions, $SiW_{12}O_{40}^{4-}$ anions, Ag(1)atoms, and organic apym ligands finally form a complicated 3D network (Fig. 1e).

Catalytic activity

To evaluate the catalytic activity of compound 1, we used the cyanosilylation of carbonyl compounds catalyzed by Lewis acids as a test reaction. The reaction of carbonyls with trimethylsilyl cyanide (TMSCN) in the presence of a catalyst produces the corresponding cyanohydrin trimethylsilyl ethers, which are industrially valuable and important intermediates in the synthesis of cyanohydrins, α -hydroxy acids, β -amino alcohols and other biological compounds.²¹ Before the catalytic test, compound 1 was activated at 50 °C under vacuum for 20 min. The cyanosilylation was carried out in the presence of 1 with a 1:2 molar ratio of the selected carbonyls and TMSCN for 4 h at room temperature under nitrogen. The conversions were calculated based on ¹H NMR spectroscopy (see the ESI[†]). In the course of studies of the catalytic properties of 1, we found that 1 with 0.1 mol% loading is an active and selective catalyst for cyanosilylation of various types of carbonyl compounds (Table 1). The reaction of benzaldehyde with TMSCN proceeds with high conversion and the corresponding product is obtained in up to 96.2% yield, in a short reaction time (4 h) and under mild conditions. This high conversion indicates that 1 is a quite efficient catalyst for this reaction. For ketones, the activity is much lower due to the low reactivity of ketones compared with aldehydes.

The plot of yield *versus* time for the cyanosilylation reaction of benzaldehyde and TMSCN with different loadings of compound 1 is presented in Fig. 2. With the extension of reaction time from 1 h to 6 h, an obvious increase in conversion was detected in the presence of 0.1 mol% loading of 1 (entries 1–5, Table 2). The same experimental phenomenon was obtained when the loading of catalyst 1 was 1 mol% (entries 7–12, Table 2). The 0.5 mol% loading of 1 was also tested, giving a conversion of 93.4% (entry 6, Table 2).

Furthermore, when the reaction was performed with 0.1 mol% of the catalyst, the turnover number (TON) can reach up to 565 for the cyanosilylation of benzaldehyde in 1 h, and the corresponding turnover frequency (TOF) is 565 h^{-1} , which



^{*a*} Reaction conditions: aldehyde/ketone, 0.5 mmol; TMSCN, 1 mmol; catalyst 1, 5×10^{-4} mmol (0.1%, based on the formula weight of 1); at room temperature under N₂ for 4 h.

is much higher than those of several previously reported MOFs (see Table S2 in the ESI⁺).^{22–26} Under other similar reaction conditions, the respective TONs for 2 h, 3 h, 4 h, and 6 h are 735, 909, 962, and 999. Additionally, upon raising the catalyst amount from 0.1 to 0.5 mol%, the TON was 187 under 2 h of reaction time. Finally, as shown in Table 2, the TONs of 1 mol% loading for compound 1 were 11, 45, 97, 97, 99, and 99 with increasing reaction time, respectively.

A series of experiments such hot filtration test and inductively coupled plasma (ICP) analysis were performed to verify the heterogeneous nature of catalyst 1. When the catalytic reaction was stopped after 0.5 hour (benzaldehyde as substrate), the supernatant obtained by high-speed centrifugation, then filtration through a regular filter paper did not afford any additional product by further reaction for another 1 hour. ICP analysis of the supernatants gave only trace



Fig. 2 Plots of cyanohydrin conversion vs. time for the cyanosilylation reaction of benzaldehyde with TMSCN at 0.1 mol% loading of 1 (blue) and at 1 mol% loading of 1 (red).

amounts of residual Ag and W atoms (~0.007% and ~0.005%, respectively), which may come from some unknown silver or W species or nanoparticles that are difficult to remove by filtration. These results clearly prove that the cyanosilylation reaction could mainly proceed in a heterogeneous manner and the catalytic effect from leached active species in the solution, if any, was insignificant.

We also checked the stability and recyclability of 1 in cyanosilylation reaction. Benzaldehyde is still selected as the reaction substrate (1% loading, 30 min). The PXRD of recovered catalyst 1 confirmed the structural integrity of 1 after 2 h of catalytic reaction (Fig. S1 in the ESI†), thus verifying the excellent stability of 1 during the cyanosilylation reaction. Also importantly, for 1, the recycling experiments (1% loading, 30 min) presented in Fig. S5† suggest a decrease in activity from 97% to 85% during the first cycle, but the following four cycles only show a very slight decrease in activity from 85% to 78%. However, if the reaction time was elongated to 2 h, the yield could recover to 83%.

Experimental

Methods

All chemicals and solvents used in the syntheses were of analytical grade and used without further purification. IR spectra were recorded on a Nicolet AVATAT FT-IR360 spectrometer as KBr pellets in the frequency range of 4000–400 cm⁻¹. Elemental analyses (C, H, N contents) were carried out on a Vario EL III analyzer. Elemental analyses of Si, W, and Ag were performed by a Leaman inductively coupled plasma (ICP) spectrometer. Powder X-ray diffraction (PXRD) data were collected on a Philips X'Pert Pro MPD X-ray diffractometer with MoK_{α} radiation equipped with an X'Celerator detector. Thermogravimetric analyses (TGA) were performed on a Netzsch STA 449C thermal analyzer from room temperature

Entry	Catalyst (%mol)	Time	Conversion (%)	TON	TOF (h^{-1})
1	0.1	1 h	56.5	565	565
2	0.1	2 h	73.5	735	368
3	0.1	3 h	90.9	909	303
4	0.1	4 h	96.2	962	241
5	0.1	6 h	99.9	999	167
6	0.5	2 h	93.4	187	93
7	1	5 min	11.5	11	132
8	1	10 min	45.0	45	270
9	1	30 min	97.1	97	194
10	1	1 h	97.1	97	97
11	1	2 h	99.0	99	50
12	1	3 h	99.0	99	33

TON = %conversion (mmol of substrate/mmol of catalyst); TOF = %conversion (mmol of substrate/mmol of catalyst per hour).

to 800 °C under nitrogen atmosphere at a heating rate of 10 °C min⁻¹. ¹H NMR spectra were measured on a Bruker AVANCE-300 NMR Spectrometer.

Synthesis of $[Ag_4(apym)_4(SiW_{12}O_{40})]_n$ (1)

A mixture of AgNO₃ (27.2 mg, 0.16 mmol), apym (4.75 mg, 0.05 mmol), $H_4SiW_{12}O_{40}$ (60 mg, 0.021 mmol) and 5 mL of H_2O was adjusted to pH = 5.0 with 3d 1 M NaOH and stirred for 10 min at room temperature. The resulting mixture was sealed in a 25 mL Teflon-lined high pressure bomb, then heated to 120 °C for 10 hours and kept at 120 °C for 50 hours, then slowly cooled to 30 °C for 13 hours. Yellow block crystals of 1 were isolated by filtration, washed with alcohol, and dried in air. Elemental analysis calcd (%) for 1 ($C_{16}H_{20}Ag_4N_{12}O_{40}SiW_{12}$): C, 5.21; H, 0.55; N, 4.56; Si, 0.76; W, 59.85; Ag, 11.71. Found: C, 5.15; H, 0.62; N, 4.46; Si, 0.67; W, 59.75; Ag, 11.68. Selected IR peaks (cm⁻¹): 3438(w), 3334(w), 1626(m), 1580(m), 1478(w), 924(s), 784(s), 526(w).

X-ray crystallography

Single crystals of compound 1 with appropriate dimensions were analyzed under an optical microscope and quickly coated with high vacuum grease (Dow Corning Corporation) before being mounted on a glass fiber for data collection. Data for them were collected on a Bruker Apex II CCD diffractometer with a graphite-monochromated Mo Ka radiation source ($\lambda = 0.71073$ Å). Cell parameters were retrieved using SMART software and refined with SAINT on all observed reflections.²⁷ Data reduction was performed with the SAINT software and corrected for Lorentz and polarization effects. Absorption corrections were applied with the program SADABS.²⁷ In all cases, the highest possible space group was chosen. All structures were solved by direct methods using SHELXS-97 (ref. 28) and refined on F^2 by full-matrix leastsquares procedures with SHELXL-97.29 Atoms were located from iterative examination of difference F-maps following least squares refinements of the earlier models. Hydrogen

Table 3	Crystal	data for	compound	1

Empirical formula	$C_{16}H_{20}Ag_4N_{12}O_{40}SiW_{12}$
Formula weight	3686.21
Temperature/K	298(2)
Crystal system	Monoclinic
Space group	Pn
a/Å	12.476(4)
<i>b</i> /Å	12.003(4)
c/Å	17.582(5)
$\alpha / ^{\circ}$	90
β/°	94.066(4)
γ/°	90
Volume/Å ³	2626.4(13)
Ζ	2
$\rho_{\rm calc}/{\rm mg~mm}^{-3}$	4.661
μ/mm^{-1}	27.740
<i>F</i> (000)	3220.0
2θ range for data	3.394 to 50°
collection	
Index ranges	$-13 \le h \le 14, -7 \le k \le 14, -15 \le l \le$
	20
Reflections collected	11 357
Independent reflections	7563 [R(int) = 0.0476]
Data/restraints/parameters	7563/206/797
Goodness-of-fit on F^2	0.959
Final <i>R</i> indexes $[I \ge 2\sigma(I)]$	$R_1 = 0.0561, wR_2 = 0.1464$
Final <i>R</i> indexes [all data]	$R_1 = 0.0579, wR_2 = 0.1487$

atoms were placed in calculated positions and included as riding atoms with isotropic displacement parameters 1.2–1.5 times U_{eq} of the attached C atoms. All structures were examined using the Addsym subroutine of PLATON³⁰ to assure that no additional symmetry could be applied to the models. Crystal data for compound **1** is given in Table 3. Selected bond lengths and angles are collated in Table S1 (ESI).†

Catalytic studies

In a typical experiment, to a Schlenk tube was added a mixture of aldehyde and $(CH_3)_3SiCN$ (TMSCN), and then solid MOF-catalyst 1 was rapidly added into the reactor. The cyanosilylation reactions of aldehydes were carried out at room temperature under N₂ atmosphere, and aliquots were taken and analyzed by ¹H NMR spectroscopy at given time intervals to evaluate the yield of aldehydes or ketones.

Conclusions

In this work, we have successfully constructed one POMsupported hybrid material based on a Keggin and silver(1)apym framework under hydrothermal condition. Compound 1 shows a fascinating 3D framework incorporating 2D 3-connected fes $(4\cdot8^2)$ [Ag(apym)]_n sheets. In the presence of 1, the cyanosilylation of several structurally diverse aldehydes and ketones with TMSCN selectively proceeded to produce the corresponding cyanohydrin trimethylsilyl ethers. Especially, the catalytic performance for aldehydes was very considerable; for example, TON = 565 and TOF = 565 h⁻¹ were observed for benzaldehyde. In consequence, this approach provides a new strategy for the design of a highly efficient catalyst for Lewis acid-catalyzed reactions.

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