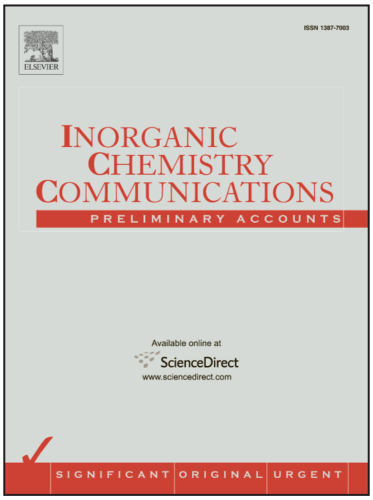

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Two polyoxoniobates-based ionic crystals as Lewis base catalysts for cyanosilylation

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Abstract: Two transition-metal containing heteropolyniobates, $H[Ni(en)_3]_5[VNb_{12}O_{40}(VO)_2]\cdot 15H_2O$ (**1**) and $H_3[Cu(en)_2]_4[VNb_{12}O_{40}(VO)_2]\cdot 13H_2O$ (**2**) (en = ethylenediamine), based on dicapped vanadium keggin polyoxoniobates have been synthesized by using ethylene glycol and water as a mixed solvent and characterized by various means. Due to the synergy between polyoxoniobate anions and transition-metal chelates, **1** and **2** showed remarkable catalytic performance for cyanosilylation of various aldehydes and ketones, giving the corresponding cyanohydrin trimethylsilyl ethers with high yields in short time. In particular, with 0.1 mol% loading of **1**, the turnover frequency (515.5 h^{-1}) for the cyanosilylation of benzaldehyde was higher than those of previously reported heterogeneous polyoxometalates catalysts.

Keywords: Catalysts, Cyanosilylation, Lewis base, Polyoxometalates, Polyoxoniobates.

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The cyanosilylation reaction of carbonyl compounds is one of the most effective methods for synthesizing cyanohydrins [1, 2], which are a class of organic synthesis intermediates having a wide range of value in the organic chemical, medicine, pesticide, pigment and perfume due to their multi-functional structures [3-7]. At present, there are many catalysts for catalyzing this reaction, such as some transition metal-containing compounds and chiral organic catalysts [8]. The Lewis acid, such as lanthanide complexes [9,10], metal-organic frameworks (MOFs) [11,12] and transition-metal complexes [13-15], or Lewis base, such as some organic base compounds [16, 17], have been usually applied as catalysts in this reaction. Recently, some polyoxotungstates and polyoxomolybdates containing transition-metal (TM) or rare-earth (RE) ions have been reported to catalyze this reaction with high efficiency, stability and recyclability. In these polyoxometalates (POMs), TM or RE cations can activate the carbonyl group in the carbonyl compounds, and the POMs anions having the oxygen-enriched surfaces of negative charge can interact with the cyano groups in the trimethylsilyl cyanide (TMSCN) [18-21].

As a subset of POMs, polyoxoniobates (PONs) possess higher negative charge than other POMs (Mo^{VI} or W^{VI}) by comparison of their “charge-density” as: charge-density (charge/atom) = (anionic charge of the POM)/(number of non-hydrogen atoms of the POM) [22, 23]. Therefore, PONs have stronger Lewis basicity than other POMs of the same structure, and have been applied in the field of base catalysis and nuclear waste processing [22, 24-27]. However, PONs catalysts for cyanosilylation reaction have been unreported as far as we know. Developing novel PONs with efficient catalytic activity for the cyanosilylation is a significant and challenge task, owing to the synthesis of PONs requires specific alkaline conditions [28].

On the other hand, introducing suitable TM complexes into PONs is one of the effective ways to construct novel multi-functional PONs. Since Flynn et al. synthesized the TM(en)-decorated isopolyniobates (IPONs) for the first time in 1969 [29, 30], a series of TM-containing IPONs based on $[Nb_6O_{19}]^{8-}$ [31-35] and $[Nb_{10}O_{28}]^{6-}$ [36-38] have been reported. Simultaneously, the synthesis of heteropolyniobates (HPONs) modified by TM has also been extensive concerned, after Nyman et al. obtained the first Keggin-type HPON $K_{12}[Ti_2O_2][SiNb_{12}O_{40}]\cdot22H_2O$ in 2002 [39]. Especially, in 2011, Hu's group synthesized the first polyoxovanadoniobate cluster $\{VNb_{12}O_{40}(VO)_2[Cu(en)_2]\}$, which was a decorated α-Keggin core with one vanadium atom as the heteroatomic center and two other vanadium atoms capping two opposite pits [40]. Several similar Keggin polyoxovanadoniobates modified by copper complexes were subsequently reported [41-43]. But these compounds can only be synthesized with low yields, and there is a lack of a general synthesis approach to obtain polyoxovanadoniobates containing different TM ions. In this work, by using ethylene glycol and water as a mixed solvent, we successfully introduced Ni^{II} and Cu^{II} into the polyoxovanadoniobates under simple solvothermal method and obtained $H[Ni(en)_3]_5[VNb_{12}O_{40}(VO)_2]\cdot15H_2O$ (**1**) and $H_3[Cu(en)_2]_4[VNb_{12}O_{40}(VO)_2]\cdot13H_2O$ (**2**) in high yields. More importantly, **1** and **2** were found to be effectively heterogeneous catalysts for cyanosilylation reaction.

Solvothermal treatment of a mixture of en, $NiCl_2\cdot6H_2O$, $K_7HNb_6O_{19}\cdot13H_2O$ and $NaVO_3$ gave rise to **1** in the presence of ethylene glycol and deionized water at 110°C. **2** was prepared by the similar synthetic procedure with only difference that replacing $NiCl_2\cdot6H_2O$ with $Cu(NO_3)_2\cdot3H_2O$. Parallel experiments have shown that ratio of reagents and the temperature of reaction played important roles in synthesis of **1** and **2**. Notably, the presence of ethylene glycol was crucial during the course of the reaction, because **1** and **2** could not be obtained if methanol, ethanol and acetonitrile were used to replace it or in the absence of it. In short, it was easy to obtain containing Cu^{II} and Ni^{II} polyoxovanadoniobates based on $\{VNb_{12}O_{40}(VO)_2\}$ building block in high yields by this method.

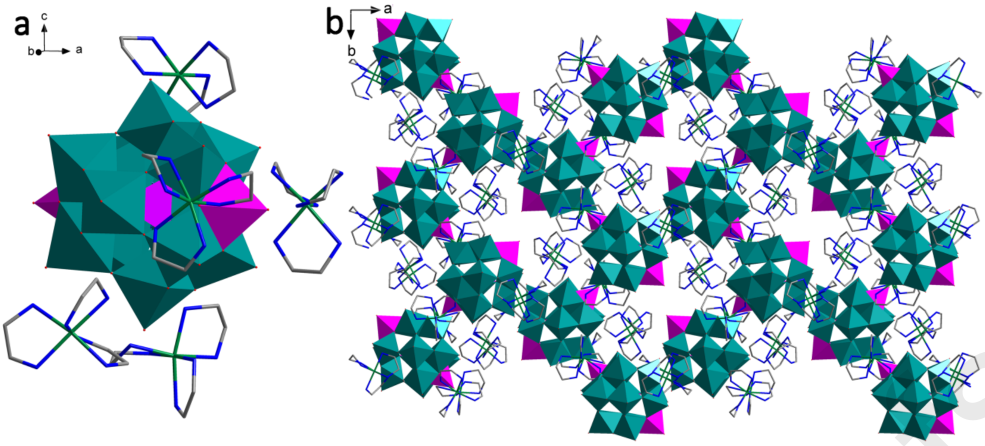


Fig. 1 Polyhedeal and wires-or-sticks representation of $[VNb_{12}O_{40}(VO)_2]^{11-}$ and $[Ni(en)_3]^{2+}$ in a unit of **1** (a) and the 3D framework of **1** (b) (H atoms and water molecules are omitted for clarity). Colour code: Nb, teal; V, pink; Ni, green; O, red; N, blue; C, gray-50%.

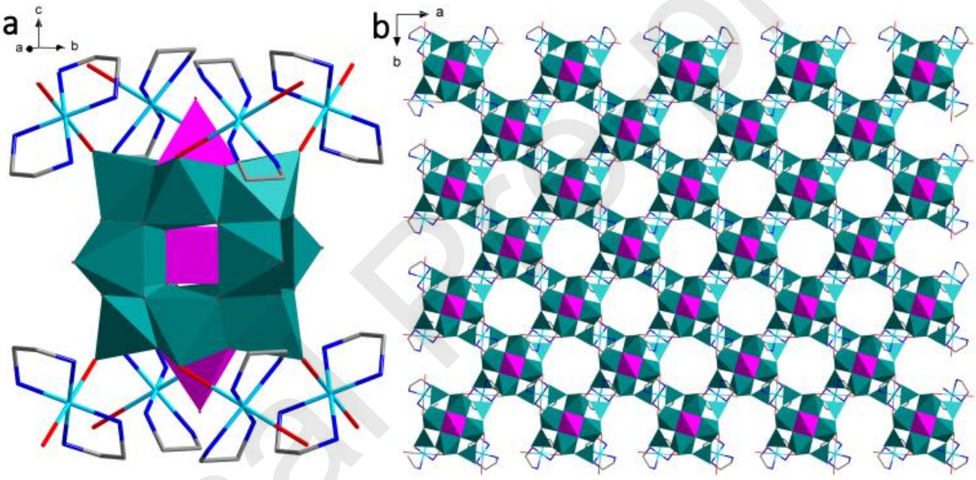


Fig. 2 Polyhedeal and wires-or-sticks representation of $[VNb_{12}O_{40}(VO)_2]^{11-}$ and $[Cu(en)_2]^{2+}$ in a unit of **2** (a) and the 3D framework of **2** (b) (H atoms and water molecules are omitted for clarity). Colour code: Nb, teal; V, pink; Cu, sky-blue; O, red; N, blue; C, gray-50%.

Single-crystal X-ray diffraction analysis reveals that **1** and **2** crystallize in orthorhombic $Pna2_1$ space group and tetragonal $I4/m$ space group, respectively. The PONs anions of **1** and **2** are both keggin-type $\{VNb_{12}O_{40}\}$ with two capped $[VO]^{2+}$. The capped V is in the centre of a pyramid consisting of five oxygen atoms, one of which is terminal and the other four are bridging oxygens from Nb-O-Nb. The central V is surrounded by four oxygen atoms, and the V-O bond length distances in the range of 1.689-1.707 Å for **1** and 1.688 Å for **2**, respectively. In **1**, each polyoxoniobate anion is surrounded by five octahedral configuration $[Ni(en)_3]^{2+}$, and the Ni-N bond length distances are in the range of 2.047-2.168 Å (Fig. 1a). There are N-H···O and C-H···O interactions between ethylenediamine coordinated with nickel and oxygens of PONs anions. $[Ni(en)_3]^{2+}$ and $[VNb_{12}O_{40}(VO)_2]^{11-}$ are connected into a supramolecular structure through electrostatic attraction and hydrogen bonding interactions (Fig. 1b). In **2**, each polyoxoniobate anion is coordinated by eight planar quadrilateral $[Cu(en)_2]^{2+}$ with Cu···O distances of 2.807 Å (Fig. 2a). Each $[Cu(en)_2]^{2+}$ as a bridging group interacts with the terminal oxygen of NbO_6 octahedron from the adjacent two PONs anions $[VNb_{12}O_{40}(VO)_2]^{11-}$ to form a three-dimensional network structure (Fig. 2b). The Cu-N bond length distances are in the range of 1.993-2.043 Å in $[Cu(en)_2]^{2+}$.

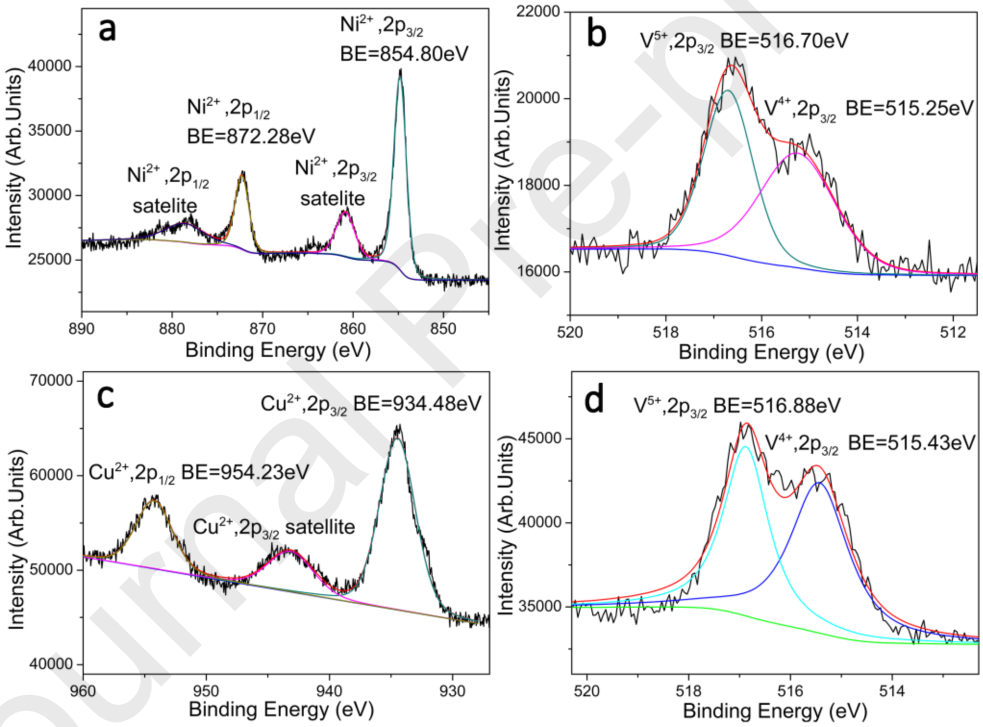


Fig. 3 The XPS spectra for Ni2p (a) and V2p (b) in **1,** and Cu2p (c) and V2p (d) in **2**.

In the XPS spectrum of **1**, the peaks at 872.28 eV and 854.80 eV can be attributable to Ni^{2+} $2p_{1/2}$ and Ni^{2+} $2p_{3/2}$, respectively (Fig. 3a) [44, 45]. Two chemically distinct vanadium ions are clearly shown in the $V2p_{3/2}$ region by the two peaks at 515.25 eV (V^{4+} $2p_{3/2}$) and 516.70 eV (V^{5+} $2p_{3/2}$), respectively (Fig. 3b) [46, 47]. The bond-valence sum (BVS) calculation [48] further indicates that the central vanadium is in +5 oxidation state (4.507 for V3), and the two capped vanadium ions are in +4 oxidation state (3.628 For V1 and V2). For **2**, XPS analysis reveals that copper is in +2 oxidation states (Fig. 3c) [49]. The two peaks at 515.43 eV and 516.88 eV in the V2p$_{3/2}$ region are attributed to V^{4+} 2p$_{3/2}$ and V^{5+} 2p$_{3/2}$ (Fig. 3d), respectively, which is consistent with the BVS values of the center V$^{\mathrm{V}}$ (4.640 for V1) and the capped V$^{\mathrm{IV}}$ (3.679 for V2).

As an important intermediate for organic synthesis, cyanohydrins can be used to prepare some chiral compounds by functional group conversion, which is important in natural products and chemical pharmaceutics. At present, the addition reaction of trimethylsilyl cyanide (TMSCN) with aldehydes and ketones has attracted extensive attention as a major chemical synthesis method for cyanohydrins. **1** and **2**, composed by transition-metal chelates and nucleophilic PONs anions, are supposed to increase the reaction rate of cyanosilylation reaction.

Firstly, we selected the cyanosilylation of benzaldehyde as a model reaction to evaluate the catalytic activities of **1** and **2**. The cyanosilylation reaction was performed at the following conditions: 1.25 mmol TMSCN, 0.5 mmol benzaldehyde, catalyst **1** or **2** with different loadings, at 25°C under nitrogen atmosphere (Table 1). As shown in entries 1 and 4 in Table 1, **1** and **2** showed high catalytic activities for cyanosilylation of benzaldehyde, but compared to **1** (reaction time: 2h), **2** required longer reaction time (2.5h) to achieve 99.01% conversion. Further, we carried out the contrast reactions to investigate the difference for catalytic nature of **1** and **2** (Fig. 4). The PONs-free complexes $[Ni(en)_3](O_2C_2H_3)_2$ and $[Cu(en)_2](NO_3)_2$ showed very limited catalytic activity (23.31% and 8.22% in Fig. 4), which confirmed that the catalytic effect of **1** and **2** were mainly caused by the Lewis basicity of the PONs anions. The relatively higher catalytic performance of **1** than **2** (Fig. 4 and Entries 1 and 5 in Table 1) may be due to the difference in their cationic complexes. As shown in Table 1 and Figure S7, the catalytic activities of **1** and **2** increased with an increase of loading for this reaction. With 0.1 mol% of **1**, the turnover frequency (TOF) reached 515.5 h^{-1} (Entry 3 of Table 1), which is higher than those of previously reported heterogeneous POMs catalysts (listed in Table S2) [18-21].

Table 1. The parameters of the cyanosilylation reaction between benzaldehyde and TMSCN with **1** and **2** as the catalysts.

Entry	Catalyst (mol%)	Time (h)	Conversion (%)	TON	TOF (h^{-1})
1	**1** (1)	2	99.01	99.0	49.5
2	**1** (0.5)	1	68.03	136.1	136.1
3	**1** (0.1)	1	51.55	515.5	515.5
4	**2** (1)	2.5	99.01	99.0	39.6
5	**2** (1)	2	86.96	87.0	43.5
6	**2** (0.5)	1	28.01	56.0	56.0
7	**2** (0.1)	1	5.27	52.7	52.7

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

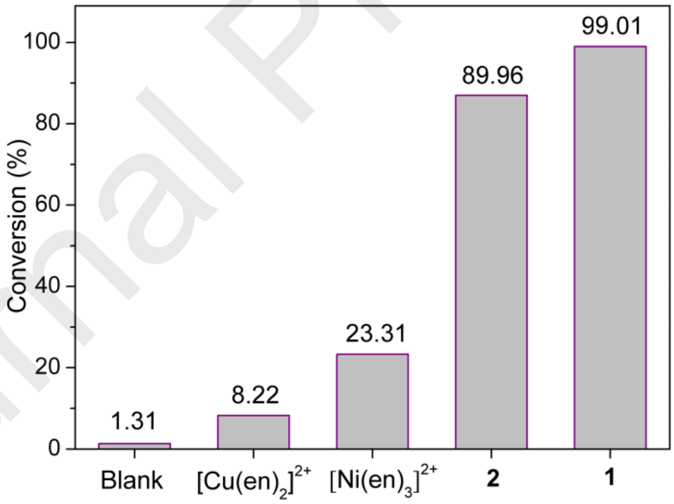
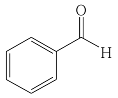
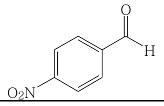
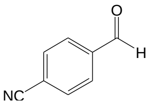
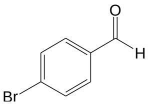
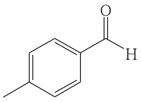
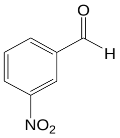
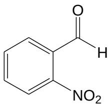
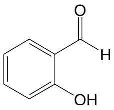
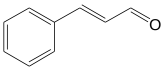
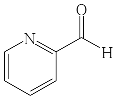
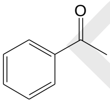
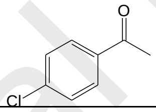


Fig. 4 Catalytic cyanosilylation of benzaldehyde in the presence different catalysts, $[Cu(en)_2]^{2+}$ = $[Cu(en)_2](NO_3)_2$, $[Ni(en)_3]^{2+}$ = $[Ni(en)_3](O_2C_2H_3)_2$, Reaction conditions: benzaldehyde 0.5 mmol, TMSCN 1.25 mmol, catalysts 1 mol% for **1** and **2**, catalysts 4 mol% for $[Cu(en)_2]^{2+}$ and 5 mol% for $[Ni(en)_3]^{2+}$, without solvent, at room temperature (25°C) under N_2 for 2 h.

Cyanosilylation of various aldehydes and ketones has been carried out in the presence of 1 mol% **1** at room temperature (25°C) under N_2 conditions (Table. 2). The benzaldehyde derivatives with electron-withdrawing substituents, such as nitro- (99.01%, Entry 2), cyano- (99.01%, Entry 3) and bromo- (97.09%, Entry 4), showed higher reactive activities than that with electron-donating substituents such as methyl- (81.30%, Entry 5). This may be because the carbonyl carbon atom of benzaldehyde derivatives with stronger electropositive nature can be easily attacked by nucleophilic cyano- in TMSCN. The electropositive nature of carbonyl carbon atom with electron-withdrawing substituents is enhanced, so the reaction rate is increased. The nitro-substituted in benzaldehydes at different positions exhibited different reactive activity owing to the steric hindrance effect, which are para- (99.01%, Entry 2), meta- (94.34%, Entry 6) and ortho- (72.46%, Entry 7). When a substituent is attached to the ortho- of benzaldehydes, the cyano- in TMSCN can only attack the carbonyl carbon atom of substrate from other side, leading to poor conversion. The poor reactivity of 2-hydroxybenzaldehyde further indicated the effect of steric hindrance to reactive activity (Entry 8). By comparing Entries 1 and 9, the reactive activity of cinnamaldehyde and benzaldehyde is similar. It is worth mentioning that 2-pyridinecarboxaldehyde almost quantitatively afforded corresponding product within 30 minutes (Entry 10), which was much faster than the reaction rate of other substrates. **1** can also catalyze the cyanosilylation reactions of ketones but with significantly lower activity due to the low reactivity of ketones compared with aldehydes (Entries 11, 12).

Table 2. Results for the catalytic cyanosilylation of aldehydes/ketones in the presence of **1**.

Entry	Aldehyde/Ketone	Time (min)	Yield (%)
1		80	89.29
2		80	99.01

3		80	99.01
4		80	97.09
5		80	81.30
6		80	94.34
7		80	72.46
8		80	70.92
9		80	87.72
10		30	98.04
11		300	26.47
12		300	31.03

[a] Reaction conditions: aldehydes/ketones 0.5 mmol, TMSCN 1.25 mmol, catalyst **1** 1 mol%, without solvent, at room temperature (25°C) under N_2. [b] The conversions were determined by ^1H-NMR spectroscopy.

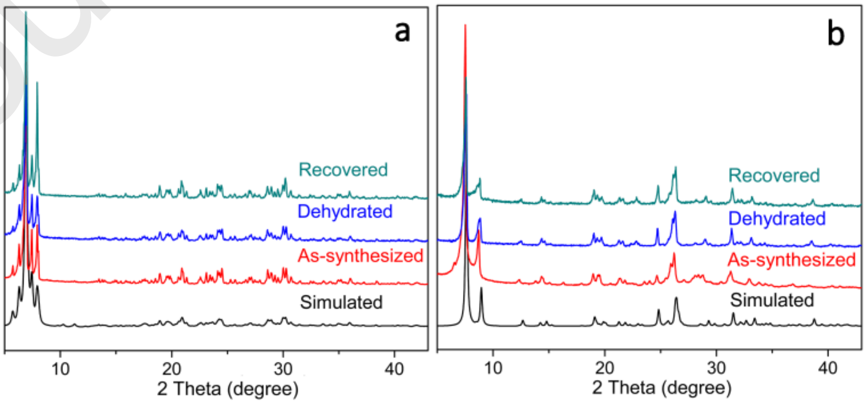


Fig. 5 PXRD patterns of the simulated (black), as-synthesized sample (red), dehydrated sample at 100°C for 0.5 hours (blue) and recovered sample from the catalytic reaction (green)

for **1** (a) and **2** (b).

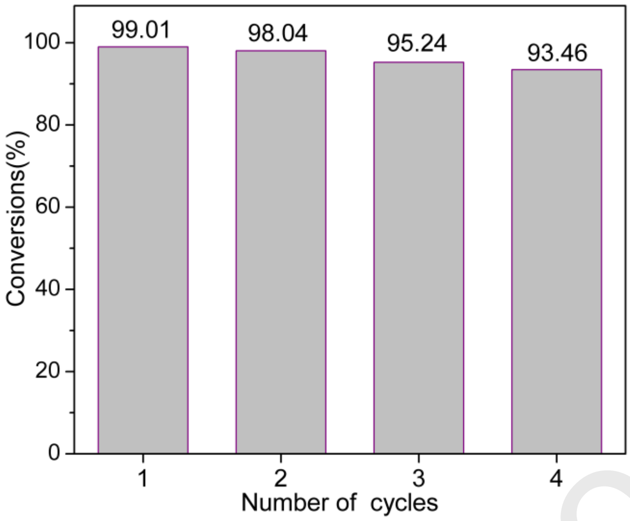
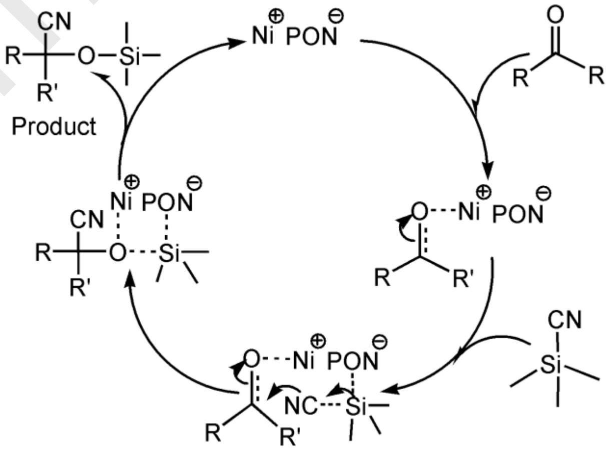


Fig. 6 The comparison of 3 cycles for cyanosilylation reaction (benzaldehyde and TMSCN) with **1** as catalyst (reaction time: 2 hours).

After the catalytic reaction, catalysts **1** and **2** can be recovered by simply centrifugation and purified by washing with ethanol and deionized water. The purified catalysts were activated by dehydration at 100°C for 0.5 hours for the next catalytic reaction. The IR spectra (Fig. S5) and PXRD pattern (Fig. 5) of the recovered catalysts were identical to those of the fresh catalysts. The catalytic effect of cyanosilylation reaction (benzaldehyde and TMSCN) with **1** as catalyst is not significantly reduced after three cycles (Fig. 6).



Scheme 1. Proposed mechanism for the **1-**catalysed cyanosilylation of carbonyl compounds.

On the basis of the above experiment results and the reported mechanisms for cyanosilylation form the literature [18-20, 50], we proposed the possible catalytic mechanism with the title compounds. As shown in Scheme 1, TM cations such as Ni^{2+} chelated in PONs can activate the carbonyl group in the carbonyl compounds, and the PONs anions having the nucleophilic oxygen-enriched surfaces can interact with the cyano groups in the TMSCN. The next step is the nucleophilic addition to activated carbonyl compounds with the nucleophile TMSCN to form the corresponding product, and meanwhile the catalyst is regenerated.

In summary, a simple synthetic method to produce transition-metal containing polyoxovanadoniobates in high yields was developed by using ethylene glycol and water as a mixed solvent. Due to the coexistence of the highly negative charged PONs anions and the transition-metal chelates, **1** and **2** showed excellent catalytic effect for cyanosilylation of various aldehydes and ketones, giving the corresponding cyanohydrin trimethylsilyl ethers with high yields in short time. This work provides inspiration for the synthesis of highly active PONs by synergizing the functions of multiple moieties.

Acknowledgements

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Research highlights

1. A simple synthetic method to produce transition-metal containing keggin polyoxovanadoniobates (**1** and **2**) in high yields was developed.

2. The addition of ethylene glycol played an important role in the synthesis of the title compounds.

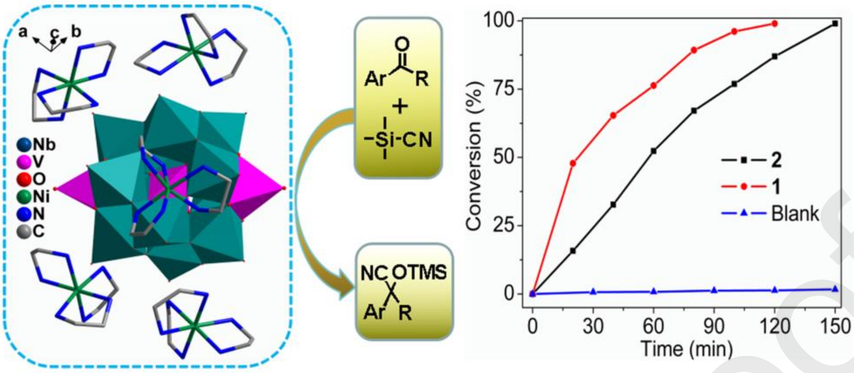
3. The title compounds exhibited excellent catalytic activity toward cyanosilylation reaction.

4. With 0.1 mol% loading of catalyst **1,** the turnover frequency (TOF) for the cyanosilylation of benzaldehyde reached 515.5 h^{-1} under mild condition.

Competing Interests

The authors declare that they have no known competing financial interests or personal relationships which have, or could be perceived to have, influenced the work reported in this article.

Graphical Abstract



Two transition-metal containing heteropolyniobates, $H[Ni(en)_3]_5[VNb_{12}O_{40}(VO)_2]\cdot15H_2O$ (**1**) and $H_3[Cu(en)_2]_4[VNb_{12}O_{40}(VO)_2]\cdot13H_2O$ (**2**) were synthesized in high yields. **1** and **2** exhibited excellent catalytic activity toward cyanosilylation reaction.