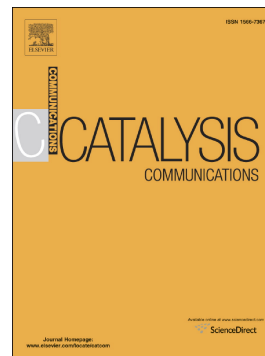


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Monosubstituted Keggin as heterogeneous catalysts for solvent-free cyanosilylation of aldehydes and ketones

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Abstract

Any successful catalyst should have a dedicated synthesizing route considering their high yields, time-efficient, and do not require any highly toxic chemicals. In this regard, two nano-sized monosubstituted polyoxometalates (POMs) with the well-known Keggin structure were synthesized and characterized: $(TBA)_5[Zr(OH)PW_{11}O_{39}] \cdot 22H_2O$ (**TBA-ZrPW₁₁**) and $(TBA)_5[Zr(OH)SiW_{11}O_{39}] \cdot 17H_2O$ (**TBA-ZrSiW₁₁**) (TBA⁺: tetrabutylammonium). Thus, the catalytic activities of both catalysts were tested in the cyanosilylation reaction without any solvents of various aldehydes and ketones with trimethylsilyl cyanide (TMSCN) over two heterogeneous catalysts. Finally, the recyclability and heterogeneity of these POM-based catalysts were also checked, showing that they remain active at least after three recycling procedures.

Keywords: Zirconium substituted Keggin, Heterogeneous Catalyst, Solvent-free, Cyanosilylation, TMSCN.

1. Introduction

The cyanosilylation reaction (CYSR) is a crucial C-C bond-forming process that opened the door to many molecules, including a variety of biological substances and poly-functionalized building blocks [1,2]. Numerous α -hydroxy compounds can be made from cyanohydrin, a well-known synthetic intermediate, by utilising trimethylsilyl cyanide (TMSCN) in the presence of heterogeneous and homogeneous catalysts, such as Lewis acid and base catalyst [3–8]. The use of TMSCN as a cyanide (CN) source is more common than other approaches because it avoids the poisonous and unstable hydrogen cyanide (HCN) used in the production of cyanohydrins. For this kind, it is crucial that current research focus on creating a powerful, clean, and safe approach that can effectively catalyse CYSR [9]. Despite the large number of articles that have been published in this area, some of which have drawbacks and limits, cyanohydrin synthesis still needs to be presented and promoted. As a result, much emphasis is being paid to finding an efficient heterogeneous catalytic system for the CYSR of carbonyl compound and TMSCN under solvent-free conditions.

Polyoxometalates (POMs), as unique metal-oxide clusters, consist of early transition metals in their highest oxidation state. They benefit from the alterable physicochemical properties, which can be adjusted in different reaction conditions or applications [10,11]. Therefore, POMs can be applied in various fields such as magnetism [12], medicine [13], catalysis [14,15] analytical chemistry [16,17]. Also, their application in catalysis [18] is still the most prominent due to their existing features, such as tunable redox potential, high thermal stability, oxidation resistance, and sensitivity to light and electricity. It is important to note that POMs can be applied as both acid and base catalysts because of their available protons (Brønsted acids) as well as their oxygen-rich surface (Lewis base (nucleophile)) [19]. POMs are also well known as Lewis acid catalysts due to the unoccupied metallic orbitals that can accept pair electrons of target organic components. In this regard, POMs can be substituted by metals with stronger Lewis acidities, including lanthanoids or transition metals like zirconium. In this form, both acidic protons and Lewis acid sites of metal ions are categorized as active sites in catalytic reactions.

Early research on POMs was performed to study their properties in homogeneous forms. To improve their feasibility in real-world applications, heterogenized POMs must be prepared from the standpoint of sustainable development. While homogeneous POMs as catalysts have higher activity, their heterogeneous form can separate easily and increase the stability of POMs from being dissociated under low concentration and higher pH values. Generally, catalyst stability affects the catalyst's activity and recyclability, which is one of the biggest concerns. Although POMs are thermally stable, they begin to disintegrate in solution, so this hugely affects their applications in solution. Therefore, heterogeneous approaches have been widely employed, such as immobilizing POMs on solid supports or covering POMs with specific cations.

Keggin, as the well-known form of POMs, has been used in several catalytic reactions due to its excellent structural stability while accepting or donating electrons. Keggin, which contains tungsten addenda atoms (rather than molybdenum), shows higher Brønsted acidity. Lacunary POMs, known as multidentate inorganic ligands with the deliberately vacant site(s) and higher negative charge, can efficiently react with heteroatoms and lead to a wide range of POM subclasses. Zirconium-containing POMs constitute an essential class of bimetallic compounds that have attracted much attention due to the discovery of their bioactivity. Despite their exciting chemistry, zirconium-containing POMs are not well explored compared with other transition metal counterparts [20,21].

Regarding our efforts to study the synthesis and application of zirconium substituted POMs catalysts in organic reactions [22–25] and our extensive research in heterocyclic-chemistry [26–30] herein, we present two nano-sized mono substituted Keggin with heterogeneous zirconium catalysts $(\text{TBA})_4[\text{Zr}(\text{OH})\text{PW}_{11}\text{O}_{39}] \cdot 22\text{H}_2\text{O}$ (**TBA-ZrPW₁₁**) and $(\text{TBA})_5[\text{Zr}(\text{OH})\text{SiW}_{11}\text{O}_{39}] \cdot 17\text{H}_2\text{O}$ (**TBA-ZrSiW₁₁**) for promoting the CYSR of the aldehydes and ketones without any solvents. It is expected that the above catalysts show better catalytic activity due to the presence of Zr^{4+} Lewis acid as well as several oxygen atoms on the structure of the mono lacunary Keggin, which can act simultaneously as Lewis acid/base (Figure 1).

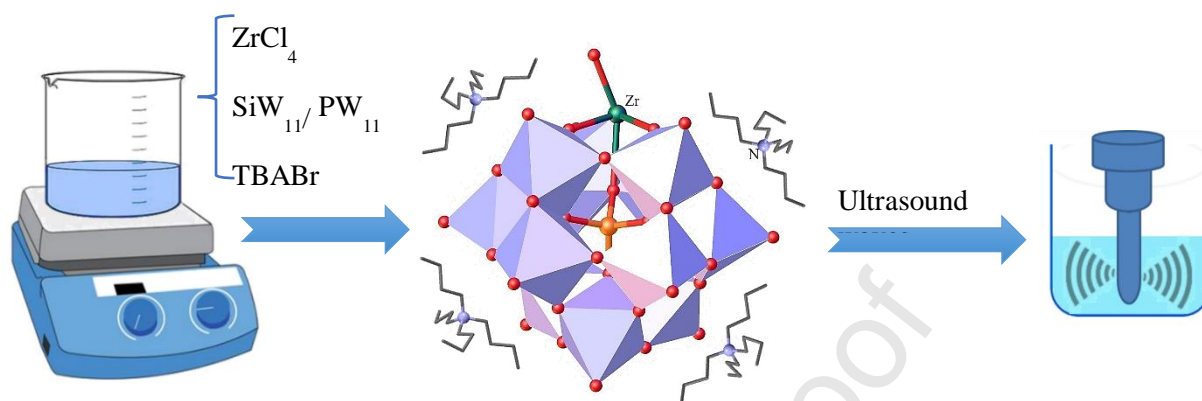


Figure 1. Preparatory route for nano-sized catalysts.

2. Experimental

2.1. Materials

All the chemicals used in this work were obtained from Sigma-Aldrich (St. Louis, MO, USA; www.sigmaaldrich.com) and Merck (Darmstadt, Germany; www.merckmillipore.com) and were at least of analytical reagent quality. They were used without additional purification. TMSCN, chloroform, methanol, toluene and tetrahydrofuran (THF) were utilized in the CYSR experiment along with aromatic aldehydes and ketones.

2.2 Instrumentations

FT-IR spectra were recorded using Bruker Tensor 27 FT-IR spectrometer (400-4000 cm^{-1} region). Additionally, a Thermo Nicolet/AVATAR 370 Fourier transform spectrophotometer was chosen to measure the 4000-400 cm^{-1} infrared spectra of catalysts using KBr discs. Elemental analysis (CHN) data of compounds was collected using a Thermo Finnigan Flash EA 1112 micro analyzer. Inductively coupled plasma was applied to measure the metal content (ICP-OES spectrometer model 76004555).

2.2. Preparation of catalysts

The $K_7[PW_{11}O_{39}] \cdot xH_2O$ (PW_{11}) and $K_8[SiW_{11}O_{39}] \cdot xH_2O$ (SiW_{11}) were synthesized in the following way [31], and FT-IR and elemental analysis were employed to identify them. Then, heterogeneous catalysts were synthesized by the above mono-lacunary Kegging.

2.2.1. Synthesis of $(TBA)_4[Zr(OH)PW_{11}O_{39}] \cdot 22H_2O$ (TBA-ZrPW₁₁)

First, an aqueous PW_{11} solution (0.67 mmol, 8 mL) was produced, and then an aqueous $ZrCl_4$ solution (0.73 mmol, 1 mL) was added dropwise to it while being agitated for 15 minutes. The aforementioned solution was then added to a TBABr solution (6 mmol, 7 mL) made in hot water. After 30 minutes of stirring, the mixture yielded a white precipitate, which was filtered and washed twice with H_2O .

2.2.2. Synthesis of $(TBA)_5[Zr(OH)SiW_{11}O_{39}] \cdot 17H_2O$ (TBA-ZrSiW₁₁)

TBA-ZrSiW₁₁ was prepared similarly to **TBA-ZrPW₁₁**, except that SiW_{11} (0.67 mmol, 8 mL) was used instead of PW_{11} . The obtained white precipitate was collected by filtration and washed twice with H_2O .

2.2.3. Synthesis of nano-sized TBA-ZrPW₁₁ and TBA-ZrSiW₁₁

The TBA-ZrPW₁₁ (or TBA-ZrSiW₁₁) (0.33 g) solution in ethanol (10 mL) and water (15 mL) was sonicated (150 W). The nano-sized catalysts were separated by centrifugation after 10 minutes and rinsed with 3–5 mL of water in a vacuum.

2.3. Typical method for the cyanosilylation of carbonyl compounds

In order to make the mixture, ketone or aldehyde (1 mmol), TMSCN (2 mmol, 250 L), and 1.5 mol% of TBA-ZrPW₁₁ or TBA-ZrSiW₁₁ were poured in a tube, placed in an oil bath, and heated at 50 °C under solvent free (S.F.) conditions. Thereafter, filtration was used to isolate the catalysts, and the residue was evaporated. Pure product was finally obtained after dissolving it in chloroform.

2.4. Characterization data

Spectroscopic data for catalysts:

TBA-ZrPW₁₁: Yield: 54 %; Anal. Calcd. for C₆₄H₁₈₉N₄O₆₂PW₁₁Zr: C, 18.51; W, 48.71; Zr, 2.20; N, 1.35; P, 0.75; H, 4.59%. Found: C, 18.17; W, 45.21; Zr, 2.35; N, 2.01; P, 0.64; H, 6.11%. FT-IR (KBr pellet, cm⁻¹): 3442, 2961, 2933, 2873, 1631, 1483, 1380, 1152, 1107, 1062, 959, 888, 816, 767, 686, 515, 498. ¹H NMR (*d*₆-DMSO, 300 MHz) δ : 0.93–0.98 (t, TBA-CH₃), 1.29–1.41 (h, TBA-CH₂), 1.55–1.65 (dq, TBA-CH₂), 3.17–3.23 (m, TBA-CH₂). ¹³C NMR (*d*₆-DMSO, 300 MHz) δ : 14.04, 19.70, 23.58, 57.99 (all singlets). ³¹P NMR (*d*₆-DMSO, 300 MHz) δ : -13.82 (s, P).

TBA-ZrSiW₁₁: Yield: 60%; Anal. Calcd. for C₈₀H₁₈₀N₅O₅₇SiW₁₁Zr: C, 22.52; W, 47.41; Zr, 2.14; N, 1.64; Si, 0.66; H, 4.25%. Found: C, 23.86; W, 44.92; Zr, 1.95; N, 2.13; Si, 0.52; H, 5.01%. FT-IR (KBr pellet, cm⁻¹): 3445, 2961, 2933, 2873, 1633, 1483, 1380, 1151, 1001, 961, 908, 799, 669, 525. ¹H NMR (*d*₆-DMSO, 300 MHz) δ : 0.93–0.98 (t, TBA-CH₃), 1.28–1.40 (h, TBA-CH₂), 1.54–1.65 (pd, TBA-CH₂), 3.17–3.22 (m, TBA-CH₂). ¹³C NMR (*d*₆-DMSO, 300 MHz) δ : 14.03, 19.70, 23.57, 57.98 (all singlets).

Nano-TBA-ZrPW₁₁: FT-IR (KBr pellet, cm⁻¹): 3445, 2961, 2929, 2873, 1633, 1484, 1380, 1151, 1049, 1059, 957, 887, 816, 767, 515

Nano-TBA-ZrSiW₁₁: FT-IR (KBr pellet, cm⁻¹): 3415, 2960, 2937, 2872, 1631, 1484, 1381, 1152, 1001, 959, 908, 799, 526.

3. Results and discussion

3.1. Synthesis and characterization of catalysts

Two heterogeneous nanocatalysts, **TBA-ZrPW₁₁** and **TBA-ZrSiW₁₁** of this study, were obtained by top-down approach with the ultrasonic method, and the average particle size of catalysts is less than 100 nm upon 10 minutes of sonication. Also, the SEM images showed that the morphologies of nanocatalysts **TBA-ZrPW₁₁** and **TBA-ZrSiW₁₁** are hexagonal-like and cubic-like (Figure 2). Furthermore, the presence of O, C, Zr, and W in the nanocatalysts is confirmed by the EDS spectrum (Figure 2). According to similar works, cationic alkyl chains can be placed around POMs [32,33]. Here, the presence of TBA⁺ in both catalysts confirm by ¹H NMR and ¹³C NMR spectra (Figure 3), in which three separated ¹H NMR peaks are around 1.33, 1.57, and 3.18 ppm assigned to the CH₂ and a peak at 0.94 ppm assigned to CH₃ group. Also, the ³¹P NMR spectrum of **TBA-ZrPW₁₁**, dissolved in D₂O, was in the normal range of diamagnetic polyoxotungstates and showed one peak at -13.82 ppm (Fig. S1).

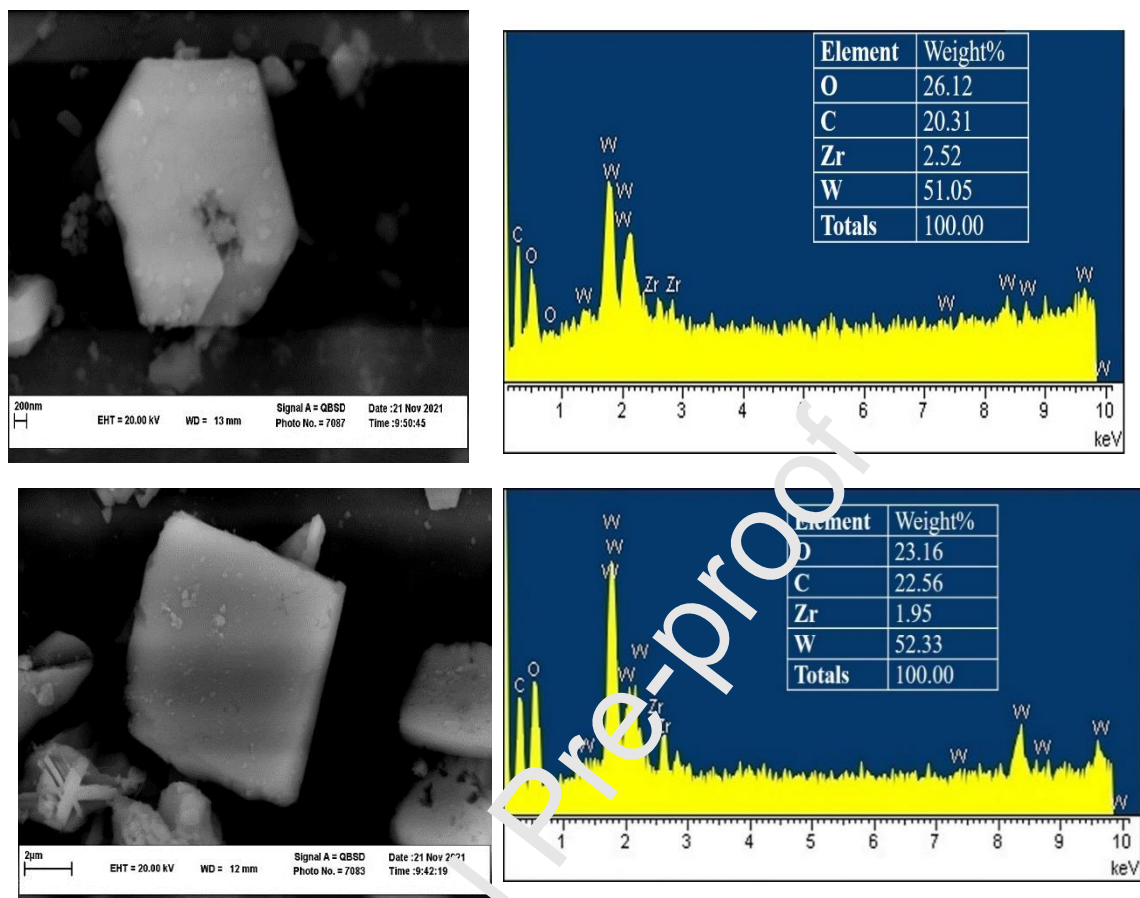


Figure 2. SEM image and EDS spectrum of (up) TBA-ZrPW₁₁ and (down) TBA-ZrSiW₁₁ nanocatalysts.

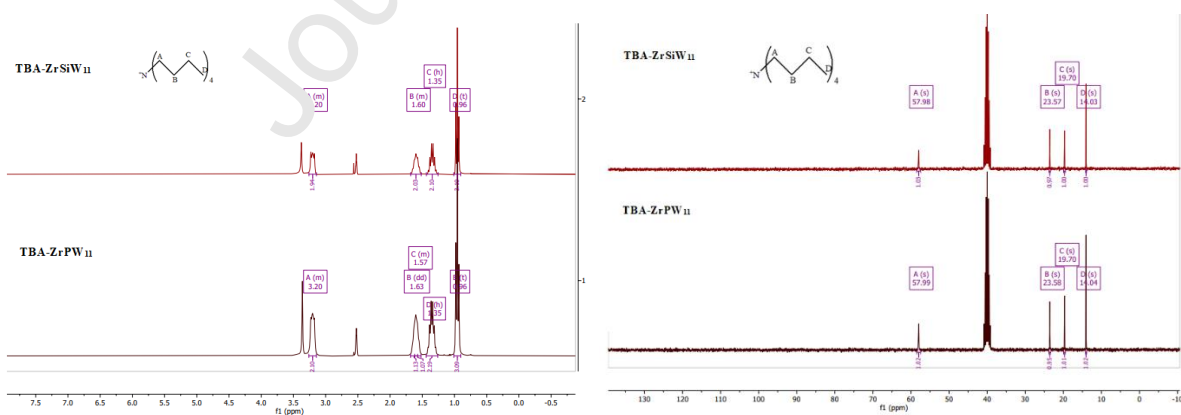


Figure 3. ¹H NMR (left) and ¹³C NMR (right) spectra for TBA-ZrPW₁₁ and TBA-ZrSiW₁₁.

Metal-oxygen stretching vibrations (often recognizable as distinct bands between 400 and 1000 cm^{-1}) can be found in the IR spectra of POMs. In Table S1 and Figure 4, we see the distinctive strong bands for X-O, W-O_t, W-O_b, and W-O_c stretching vibrations of nanocatalysts, which can verify the precise structures of the final catalysts. In addition, the C-H stretching vibrations of TBA were attributed to absorptions in the region of 2873-2961 cm^{-1} .

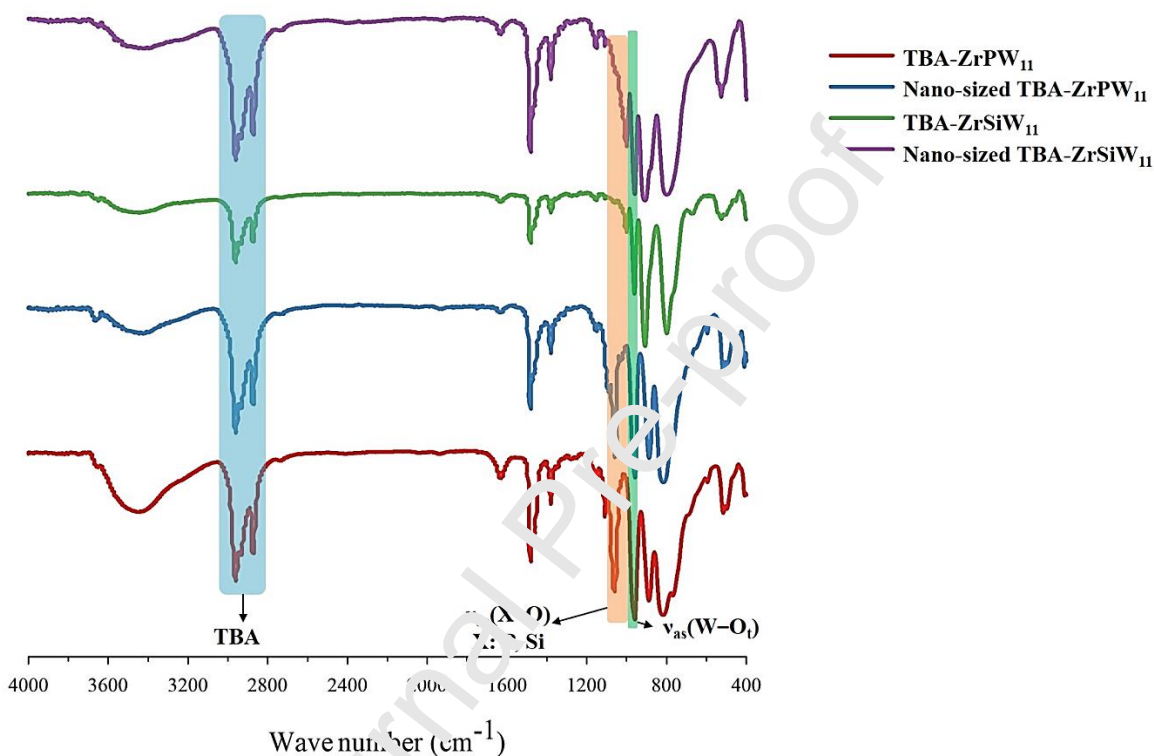


Figure 4. FTIR spectra of TBA-ZrPW₁₁ and TBA-ZrSiW₁₁ heterogeneous and nano-catalysts.

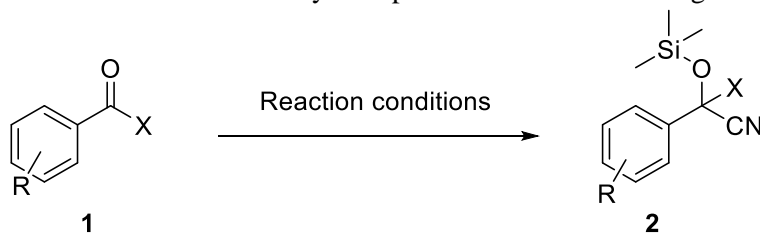
3.2. Catalytic Activity

Taking benefit of insolubility in several organic solvents of the TBA-ZrPW₁₁ and TBA-ZrSiW₁₁, the activity of them were tested for the CYSR of diverse aldehydes under S.F. conditions. First, benzaldehyde (BA) and TMSCN were taken as substrates and two POMs, TBA-ZrPW₁₁ and TBA-ZrSiW₁₁ as catalysts, and various reaction conditions such as catalyst amount, temperature and solvent were optimized.

For this purpose, a combination of BA (1.0 mmol), TMSCN (2 mmol), and POMs (1.5 mol%) was placed in a tube and stirred at 50 °C, under S.F. condition, for the appropriate time. After this time, the desired product was isolated. Then, the CYSR using various solvents including,

CHCl_3 , methanol, toluene, THF and without any solvents was carried out. As evident, S.F. conditions demonstrate higher activity, leading to a product in 97% or 75% yields for **TBA-ZrPW₁₁** and **TBA-ZrSiW₁₁**, respectively (Table S2, entries 3 and 4). Next, using other solvents was not appropriate as it caused the production of low-yield products in the range of 35-80% (Table S2, entries 10-13). For optimization of the catalyst loading, the catalyst amount was changed from 0.5 to 2.5 mol%, and significant enrichment of yield was observed from 45 to 97% for **TBA-ZrPW₁₁** or from 30 to 75% for **TBA-ZrSiW₁₁** (Table S2, entries 6-9). However, the extra increase did not improve the yields (for both catalysts). Therefore, the best catalyst amount was achieved as 1.5 mol%. Next, the CYSR was carried out at various temperatures. As tabulated, only 30% or 25% of the product were achieved at r.t. (Table S2, entries 1 and 2), using **TBA-ZrPW₁₁** or **TBA-ZrSiW₁₁** catalyst, respectively, in contrast, by increasing the temperature of the reaction from r.t. to 50 °C, the corresponding product was attained in an excellent yield for **TBA-ZrPW₁₁** but by increasing to 70 °C, the yield of the product did not improve (Table S2, entry 14). Finally, a blank test using BA and TMSCN without any solvent and catalyst at 50 °C was performed and resulted 15% of the final product yield after three h (Table S2, entry 5). Accordingly, the most satisfactory conditions for the CYSR of carbonyl compounds and TMSCN is applying 1.5 mol% of **TBA-ZrPW₁₁** as the best catalyst at 50 °C in S.F. condition.

The best catalyst, **TBA-ZrPW₁₁**, was then put to the test by seeing how well it catalyzed the addition of various substitutes to ketones and aldehydes. Table 1 shows that the aldehydes containing electron-withdrawing groups, such as -Cl, -Br, and -NO₂, have the best activity and yields, and that the *para* position played a crucial role in accelerating the reaction to the *ortho* and meta positions (Table 1, entries 1-4 and 7-9). In contrast, aldehydes containing electron-donating groups, such as -Me and -OMe, show lower yields and longer reaction durations (Table 1, entries 5 and 6). Also, the yields for the equivalent cyanohydrins (Table 1, entries 10-13) made from aromatic ketones with electron-withdrawing groups are higher than those made from ketones with electron-donor substituents. When compared to ketones, however, aldehydes clearly shine in terms of their reactivity. These results are consistent with the expected impact of the substituent on the electrophilic location of the carbonyl groups vulnerable to attack by the -CN group of TMSCN.

Table 1. CYSR of diverse substituted carbonyl compounds and TMSCN using **TBA-ZrPW₁₁** catalyst.^a

Entry	R	X	Products	Yield ^b (%)	Time (h:min)
1	H	H	2a	97	01:00
2	<i>p</i> -NO ₂	H	2b	97	00:50
3	<i>m</i> -NO ₂	H	2c	90	01:15
4	<i>o</i> -NO ₂	H	2d	92	01:05
5	<i>p</i> -Me	H	2e	80	01:35
6	<i>p</i> -OMe	H	2f	85	01:25
7	<i>p</i> -OH	H	2g	90	01:05
8	<i>p</i> -Cl	H	2h	86	01:25
9	<i>p</i> -Br	H	2i	88	01:15
10	H	Me	2j	92	01:30
11	<i>p</i> -NO ₂	Me	2k	95	01:15
12	<i>p</i> -Me	Me	2l	84	02:00
13	<i>p</i> -OMe	Me	2m	89	01:50

^a Reaction conditions: aldehyde (1 mmol), TMSCN (2 mmol), 1.5 mol% of **TBA-ZrPW₁₁** at 50 °C.

^b Isolated yields.

The reusability of the **TBA-ZrPW₁₁** and **TBA-ZrSiW₁₁** was also studied. After the reaction cycle was complete, both catalysts were filtered out, washed with ethanol, and dried. Reusing **TBA-ZrPW₁₁** and **TBA-ZrSiW₁₁** catalysts for three reaction runs showed no discernible loss in activity (Figure S2).

Moreover, after 30 minutes, both the **TBA-ZrPW₁₁** and **TBA-ZrSiW₁₁** catalysts were isolated from the reaction, allowing for an examination of the heterogeneity and leaching of these catalysts. They continued the reaction for another 30 minutes in the identical conditions but without the catalyst. Since no increase in yield was observed after either **TBA-ZrPW₁₁** or **TBA-ZrSiW₁₁** catalyst was removed from the mixture, their heterogeneous character is confirmed. Moreover, to check the structural integrity of **TBA-ZrPW₁₁** and **TBA-ZrSiW₁₁**, FTIR analyses of recycled catalysts was performed and compared with those of fresh catalysts. It was found that no historic changes were detected in their spectra (Figure S3). These results support that the

structure of the **TBA-ZrPW₁₁** catalyst was well preserved and that the **TBA-ZrSiW₁₁** catalyst underwent a series of reactions, as expected from the reaction results.

With the goal of gauging the study's usefulness, we evaluated the catalytic activity of **TBA-ZrPW₁₁** towards the CYSR of BA with TMSCN to that of previous literature (Table S3). Results reveal that TBA-ZrPW₁₁ is more effective than **TBA-ZrSiW₁₁** and other reported catalysts in a shorter amount of time under S.F. settings (Yield of 96%, in S.F. at 50 °C after one hour, Table S3, entry 6).

The CYSR mechanism should be comparable to other metal complexes catalyzed systems proposed, which a possible CYSR mechanism is proposed and illustrated in Figure S4 [3]. First, the catalytic transformation possibly can be activation of the carbonyl group in BA (**I**) by the metal center in catalyst, towards the nucleophilic attack of CN group (**II**), also with the migration of the silyl group to oxygen (**III**), carbon-carbon bond and then cyanohydrin (**IV**) is formed.

4. Concluding remarks

In summarize, this work investigated the catalytic behavior of two nano-sized heterogeneous catalysts; **TBA-ZrPW₁₁** and **TBA-ZrSiW₁₁**. Both catalysts were synthesized by a rapid ultrasonic method and characterized by various spectral techniques. When cationic alkyls (**TBA⁺**) are present on the surface of POMs, they create hydrophobic and polar structures that can trap organic reactants on the catalysts' surfaces, hence enhancing their catalytic efficiency. Even though both catalysts were heterogeneous, **TBA-ZrPW₁₁** demonstrated greater catalytic activity toward the CYSR under S.F. conditions (97%). Since the P center is more Lewis acidic than the Si center and occupies a more advantageous position in the POM structure, **TBA-ZrPW₁₁** is more energetic than **TBA-ZrSiW₁₁**. Finally, the as-mentioned catalyst showed remained activity at least after three recycling procedures.

Acknowledgments

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References

- [1] R.J.H. Gregory, Cyanohydrins in Nature and the Laboratory: Biology, Preparations, and Synthetic Applications, *Chem. Rev.* 99 (1999) 3649–3682. <https://doi.org/10.1021/cr9902906>.
- [2] J.-M. Brunel, I.P. Holmes, Chemically Catalyzed Asymmetric Cyanohydrin Syntheses, *Angew. Chem. Int. Ed.* 43 (2004) 2752–2778. <https://doi.org/10.1002/anie.200300604>.
- [3] N. Kurono, T. Ohkuma, Catalytic Asymmetric Cyanation Reactions, *ACS Catal.* 6 (2016) 989–1023. <https://doi.org/10.1021/acscatal.5b02184>.
- [4] A.G. Mahmoud, K.T. Mahmudov, M.F.C. Guedes da Silva, A.J.L. Pombeiro, Reaction of sodium 2-(2-(2,4-dioxopentan-3-ylidene)hydrazinyl) benzenesulfonate with ethylenediamine on Cu(II) and Ni(II) centres: efficient Cu(II) homogeneous catalysts for cyanosilylation of aldehydes, *RSC Adv.* 6 (2016) 54263–54269. <https://doi.org/10.1039/C6RA12274D>.
- [5] Z. Ma, A. V. Gurbanov, M. Sutradhar, M.N. Kopylovich, K.T. Mahmudov, A.M. Maharramov, F.I. Guseinov, F.I. Zubkov, A.J.L. Pombeiro, Effective cyanosilylation of aldehydes with copper(II)-based polymeric catalysts, *Mol. Catal.* 428 (2017) 17–23. <https://doi.org/10.1016/j.molcata.2016.11.036>.
- [6] A. V. Gurbanov, K.T. Mahmudov, M. Sutradhar, F.C. Guedes da Silva, T.A. Mahmudov, F.I. Guseinov, F.I. Zubkov, A.M. Maharramov, A.J.L. Pombeiro, Copper(II) complexes with carboxylic- or sulfonic-functionalized arylhydrazones of acetoacetanilide and their application in cyanosilylation of aldehydes, *J. Organomet. Chem.* 834 (2017) 22–27. <https://doi.org/10.1016/j.jorganchem.2017.02.006>.
- [7] A. Karmakar, S. Hazra, M.F.C. Guedes da Silva, A.J.L. Pombeiro, Synthesis, structure and catalytic application of lead(II) complexes in cyanosilylation reactions, *Dalt. Trans.* 44 (2015) 268–280. <https://doi.org/10.1039/C4DT02316A>.
- [8] Y. Jia, S. Zhao, Y.-F. Song, The application of spontaneous flocculation for the preparation of lanthanide-containing polyoxometalates intercalated layered double hydroxides: highly efficient heterogeneous catalysts for cyanosilylation, *Appl. Catal. A*

- Gen. 487 (2014) 172–180. <https://doi.org/10.1016/j.apcata.2014.09.005>.
- [9] M.-A. Lacour, N.J. Rahier, M. Taillefer, Mild and Efficient Trimethylsilylcyanation of Ketones Catalysed by PNP Chloride, *Chem. - A Eur. J.* 17 (2011) 12276–12279. <https://doi.org/10.1002/chem.201101195>.
- [10] M. Mirzaei, H. Eshtiagh-Hosseini, M. Alipour, A. Frontera, Recent developments in the crystal engineering of diverse coordination modes (0–12) for Keggin-type polyoxometalates in hybrid inorganic–organic architectures, *Coord. Chem. Rev.* 275 (2014) 1–18. <https://doi.org/10.1016/j.ccr.2014.03.012>.
- [11] S. Taleghani, M. Mirzaei, H. Eshtiagh-Hosseini, A. Frontera, Tuning the topology of hybrid inorganic–organic materials based on the study of flexible ligands and negative charge of polyoxometalates: A crystal engineering perspective, *Coord. Chem. Rev.* 309 (2016) 84–106. <https://doi.org/10.1016/j.ccr.2015.10.004>.
- [12] M. Babaei Zarch, M. Mirzaei, M. Bazargan, S.K. Gupta, F. Meyer, J.T. Mague, Single-molecule magnets within polyoxometalate-based frameworks, *Dalt. Trans.* 50 (2021) 15047–15056. <https://doi.org/10.1039/L1DT01708J>.
- [13] M. Arefian, M. Mirzaei, H. Eshtiagh-Hosseini, A. Frontera, A survey of the different roles of polyoxometalates in their interaction with amino acids, peptides and proteins, *Dalt. Trans.* 46 (2017) 6812–6822. <https://doi.org/10.1039/C7DT00894E>.
- [14] M. Arab Fashapoyeh, M. Mirzaei, H. Eshtiagh-Hosseini, A. Rajagopal, M. Lechner, R. Liu, C. Streb, Photochemical and electrochemical hydrogen evolution reactivity of lanthanide-functionalized polyoxotungstates, *Chem. Commun.* 54 (2018) 10427–10430. <https://doi.org/10.1039/C8CC06334F>.
- [15] M.M. Heravi, M. Mirzaei, S.Y.S. Beheshtiha, V. Zadsirjan, F. Mashayekh Ameli, M. Bazargan, $H_5BW_{12}O_{40}$ as a green and efficient homogeneous but recyclable catalyst in the synthesis of 4 H -Pyrans via multicomponent reaction, *Appl. Organomet. Chem.* 32 (2018) e4479. <https://doi.org/10.1002/aoc.4479>.
- [16] S. Derakhshanrad, M. Mirzaei, C. Streb, A. Amiri, C. Ritchie, Polyoxometalate-Based Frameworks as Adsorbents for Drug of Abuse Extraction from Hair Samples, *Inorg.*

- Chem. 60 (2021) 1472–1479. <https://doi.org/10.1021/acs.inorgchem.0c02769>.
- [17] M. Akbari, M. Mirzaei, A. Amiri, Synergistic effect of lacunary polyoxotungstates and carbon nanotubes for extraction of organophosphorus pesticides, *Microchem. J.* 170 (2021) 106665. <https://doi.org/10.1016/j.microc.2021.106665>.
- [18] N. Lotfian, M.M. Heravi, M. Mirzaei, B. Heidari, Applications of inorganic-organic hybrid architectures based on polyoxometalates in catalyzed and photocatalyzed chemical transformations, *Appl. Organomet. Chem.* 33 (2019) e4808. <https://doi.org/10.1002/aoc.4808>.
- [19] S. Herrmann, C. Ritchie, C. Streb, Polyoxometalate – conductive polymer composites for energy conversion, energy storage and nanostructured sensors, *Dalton Trans.* 44 (2015) 7092–7104. <https://doi.org/10.1039/C4DT03763D>.
- [20] N. V. Maksimchuk, V.Y. Evtushok, O. V. Zabolinaeva, G.M. Maksimov, I.D. Ivanchikova, Y.A. Chesalov, I. V. Eltsov, P.A. Abanov, T.S. Glazneva, V. V. Yanshole, O.A. Kholdeeva, R.J. Errington, A. Sol-Daura, J.M. Poblet, J.J. Carbó, Activation of H₂O₂ over Zr(IV). Insights from Model Studies on Zr-Monosubstituted Lindqvist Tungstates, *ACS Catal.* 11 (2021) 10589–10603. <https://doi.org/10.1021/acscatal.1c02485>.
- [21] H. Aoto, K. Matsui, Y. Sakai, T. Kuchizi, H. Sekiya, H. Osada, T. Yoshida, S. Matsunaga, K. Nomiya, Zirconium(IV)- and hafnium(IV)-containing polyoxometalates as oxidation precatalysts: Homogeneous catalytic epoxidation of cyclooctene by hydrogen peroxide, *J. Mol. Catal. A Chem.* 394 (2014) 224–231. <https://doi.org/10.1016/j.molcata.2014.07.020>.
- [22] S. Sadjadi, M. Akbari, B. Léger, E. Monflier, M.M. Heravi, Eggplant-Derived Biochar-Halloysite Nanocomposite as Supports of Pd Nanoparticles for the Catalytic Hydrogenation of Nitroarenes in the Presence of Cyclodextrin, *ACS Sustain. Chem. Eng.* 7 (2019) 6720–6731. <https://doi.org/10.1021/acssuschemeng.8b05992>.
- [23] S. Sadjadi, G. Lazzara, M. Malmir, M.M. Heravi, Pd nanoparticles immobilized on the poly-dopamine decorated halloysite nanotubes hybridized with N-doped porous carbon monolayer: A versatile catalyst for promoting Pd catalyzed reactions, *J. Catal.* 366 (2018) 245–257. <https://doi.org/10.1016/j.jcat.2018.08.013>.

- [24] S. Sadjadi, M. Malmir, G. Lazzara, G. Cavallaro, M.M. Heravi, Preparation of palladated porous nitrogen-doped carbon using halloysite as porogen: disclosing its utility as a hydrogenation catalyst, *Sci. Rep.* 10 (2020) 2039. <https://doi.org/10.1038/s41598-020-59003-5>.
- [25] M. Heravi, M. Daraie, A Novel and Efficient Five-Component Synthesis of Pyrazole Based Pyrido[2,3-d]pyrimidine-diones in Water: A Triply Green Synthesis, *Molecules*. 21 (2016) 441. <https://doi.org/10.3390/molecules21040441>.
- [26] M.M. Heravi, L. Mohammadkhani, Synthesis of various 1,4-heterocycles using the four-component Ugi reaction, *Adv. Heterocycl. Chem.* 131 (2020) 351–403. <https://doi.org/10.1016/bs.aihch.2019.04.001>.
- [27] M.M. Heravi, B. Talaei, Diketene as Privileged Synthons in the Syntheses of Heterocycles Part 1, *Heterocycl. Chem.* 122 (2017) 43–114. <https://doi.org/10.1016/bs.aihch.2016.10.003>
- [28] M.M. Heravi, B. Talaei, Ketenes as Privileged Synthons in the Synthesis of Heterocyclic Compounds Part 3, *Heterocycl. Chem.* 118 (2016) 195–291. <https://doi.org/10.1016/bs.aihch.2015.10.007>.
- [29] M.M. Heravi, V. Fathi Varsani, Recent Advances in Application of Amino Acids: Key Building Blocks in Design and Syntheses of Heterocyclic Compounds, *Adv. Heterocycl. Chem.* (2015) 77–145. <https://doi.org/10.1016/bs.aihch.2015.02.002>.
- [30] M.M. Heravi, T. Alishiri, Dimethyl Acetylenedicarboxylate as a Building Block in Heterocyclic Synthesis, *Adv. Heterocycl. Chem.* 113 (2014) 1–66. <https://doi.org/10.1016/B978-0-12-800170-7.00001-8>.
- [31] A. Tézé, M. Michelon, G. Hervé, Syntheses and Structures of the Tungstoborate Anions, *Inorg. Chem.* 36 (1997) 505–509. <https://doi.org/10.1021/ic961051t>.
- [32] A. Nisar, J. Zhuang, X. Wang, Cluster-Based Self-Assembly: Reversible Formation of Polyoxometalate Nanocones and Nanotubes, *Chem. Mater.* 21 (2009) 3745–3751. <https://doi.org/10.1021/cm901305r>.
- [33] Y.-M. Nie, S.-H. Li, M.-Y. Lin, J. Yan, A micro-environment tuning approach for

enhancing the catalytic capabilities of lanthanide containing polyoxometalate in the cyanosilylation of ketones, *Chem. Commun.* 56 (2020) 3809–3812. <https://doi.org/10.1039/D0CC01216E>.

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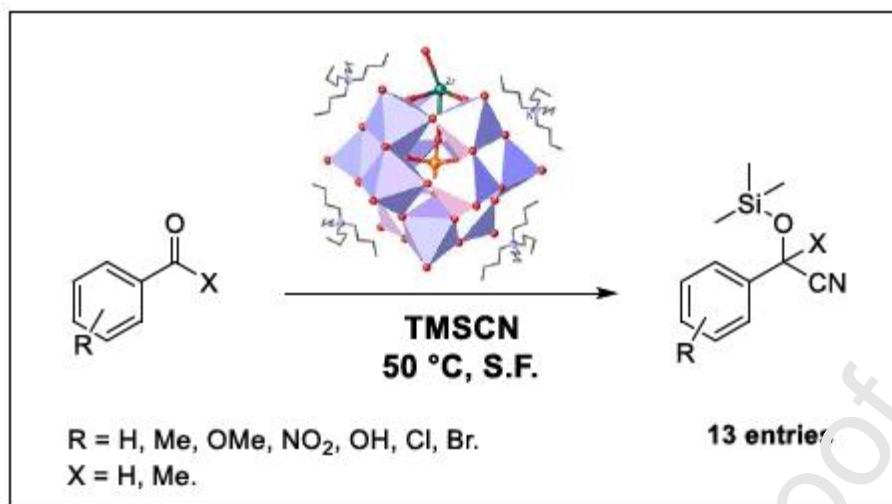
Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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Graphical Abstract



Highlight

- Two lacunary Keggin type polyoxometalates (POM) were synthesized and characterized.
- Both POMs were used as catalysts in the solvent-free cyanosilylation reaction.
- Both catalysts were recycled up to 3 runs with slight loss of activities.
- TBA-ZrPW₁₁ is more effective than TBA-ZrSiW₁₁, due to the presence of P center.

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