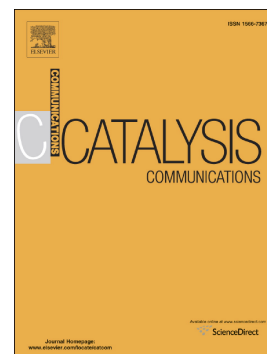


Accepted Manuscript

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PII: S1566-7367(18)30029-3
DOI: doi:[10.1016/j.catcom.2018.01.023](https://doi.org/10.1016/j.catcom.2018.01.023)
Reference: CATCOM 5302
To appear in: *Catalysis Communications*
Received date: 4 December 2017
Revised date: 10 January 2018
Accepted date: 18 January 2018

Please cite this article as: Abdulmohsen Al-Shehri, Katabathini Narasimharao , Influence of polyoxometalate structure in ammoxidation of 2-methylpyrazine. The address for the corresponding author was captured as affiliation for all authors. Please check if appropriate. Catcom(2018), doi:[10.1016/j.catcom.2018.01.023](https://doi.org/10.1016/j.catcom.2018.01.023)

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Influence of polyoxometalate structure in ammoxidation of 2-methylpyrazine

Abdulmohsen Al-Shehri, Katabathini Narasimharao*

Department of Chemistry, Faculty of Science, King Abdulaziz University
P. O. Box 80203, Jeddah 21589, Kingdom of Saudi Arabia

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Abstract

Keggin, Wells-Dawson and Preyssler structured polyoxometalates (POMs) were synthesized by different methodologies. The POMs were used as catalysts for ammoxidation of 2-methylpyrazine. The structural properties of POMs were determined by XRD, SEM, DRIFT, DRUV-*vis*, H₂-TPR, NH₃-TPD and N₂-physisorption. Preyssler POM sample showed highest 2-methylpyrazine conversion (69%) and 2-cyanopyrazine selectivity (98%) at 380 °C. Superior performance of Preyssler POM could be attributed to its redox behavior and relatively strong acid sites. Large number of ammonium ions in the secondary structure of Preyssler POM could also enhance the transformation of oxygenated 2-methylpyrazine species into 2-cyanopyrazine. A correlation between the amount of ammonium content of POMs and their catalytic ammoxidation activity was obtained.

Keywords: Polyoxometalates; Keggin; Wells-Dawson; Preyssler; Ammoxidation; 2-methylpyrazine

*Corresponding author, Fax: +966-26952292; Tel: +966-538638994; E-mail: nkatabathini@kau.edu.sa

1. Introduction

The polyoxometalates (POMs) possessed unique properties such as acid, base and redox properties which render them as potential alternative catalysts to corrosive mineral acids and other homogeneous reagents [1]. POMs with different structures are reported in the literature; for instance, Keggin, Wells-Dawson, Anderson, Lindqvist and Preyssler type POMs [2]. Among many POMs, Keggin compounds were widely utilized as heterogeneous catalysts in different reactions [3]. Recently, other POMs majorly Wells-Dawson [4] and Preyssler [5] POMs were also attracted considerable interest in catalysis. In POMs, the three-dimensional arrangement of anions is usually called primary structure and counter cations, water of crystallization and any additional molecules is known to be the secondary structure [2]. In proton form, the acidic strength of POMs is higher than the mineral acids; this is mainly due to large number of oxygen atoms in anions (40, 62 and 110 in Keggin, Wells-Dawson and Preyssler respectively) [3].

Catalytic ammoxidation of 2-methylpyrazine to 2-cyanopyrazine is a crucial step in synthesis of 2-amidopyrazine, famously termed as pyrazinamide, an effective anti-Tuberculosis drug. The conventional multi-step synthesis process is unacceptable both economically as well as environmentally due to multi-step synthesis and generates number of byproducts [6]. It was previously observed that ammonium salt of Keggin POM showed good performance in ammoxidation reaction [7, 8]. However, thermal and hydrolytic stability of POMs is important and related to their primary and secondary structures [9]. In addition, the nature and number of counter cations as well as the central and poly atoms play an important role over the physico-chemical and catalytic properties of POM materials. It was previously reported that the rate of ammoxidation is controlled

by acidity and redox properties of catalyst [10]. Keggin, Wells-Dawson and Preyssler structured ammonium tungstophosphates were synthesized and the materials were used as catalysts for vapor phase ammoxidation of 2-methylpyrazine. A wide variety of characterization techniques were used to study structural properties of the synthesized samples and the performance of catalysts in ammoxidation of 2-methylpyrazine is correlated with their structural properties. To best of our knowledge, this is the first attempt to study the influence of structure of POM on the ammoxidation functionality.

2. Experimental

2.1. Synthesis of POMs

(i) **Keggin POM:** $[(\text{NH}_4)_3\text{PW}_{12}\text{O}_{40}]$ was synthesized using stoichiometric amounts of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ and NH_4Cl by an ion exchange technique [11].

(ii) **Wells-Dawson POM:** $[(\text{NH}_4)_6\text{P}_2\text{W}_{18}\text{O}_{62}]$ was prepared as per the procedure reported by Briand et al [12].

(iii) **Preyssler POM:** $(\text{NH}_4)_{13}[\text{NaP}_5\text{W}_{30}\text{O}_{110}]$ was produced by following the procedure reported by Creaser et al [13]. The POM samples were calcined at $400\text{ }^\circ\text{C}$ for 4h under the flow of air.

2.2. Characterization

Powder X-ray diffraction measurements of the samples were conducted using Bruker diffractometer. DRIFT analysis of POM materials was performed on a Bruker D70 spectrometer. Scanning Electron Microscopy (SEM) measurements were carried out using a JEOL JSM840A instrument. The DRUV-*vis* spectra of the samples were collected using a Thermo-Scientific evolution spectrophotometer. The textural properties of samples were determined from N_2 -physisorption analysis using NOVA 3200e sorption

system. H₂-TPR, temperature programmed decomposition and NH₃-TPD analyses were performed using Quantachrome CHEMBET-3000 instrument. The detailed preparation procedures and characterization techniques are provided in the supplementary information.

2.3. Catalytic ammoxidation of 2-methylpyrazine

The vapor phase ammoxidation of 2-methylpyrazine was performed in a fixed bed catalytic reactor. Prior to the activity tests, the POMs were treated with ammonia for 2 h at 300 °C. The 2-methylpyrazine diluted with water, ammonia and air was used as the feed (molar ratio of 2-methylpyrazine: H₂O:NH₃: air=1:13:7:38). The reaction was carried out at a different temperatures. The liquid products were collected by condensation and the samples were analyzed by GC with SE-30 column and a flame ionization detector.

3. Results and discussion

3.1. Powder X-ray diffraction (XRD)

Fig. 1 presents the XRD patterns of synthesized POM samples. The diffraction peaks of Keggin sample is matched with the cubic structure of [NH₄]₃PW₁₂O₄₀. 4H₂O salt as reported in the literature [14] and absence of other diffraction peaks indicate the presence of pure crystalline Keggin POM. The Wells-Dawson sample showed the major XRD reflections of [NH₄]₆H₆[P₂O₂(W₂O₇)₉].7H₂O phase as represented in JCPDS 04-0443. Interestingly, this sample exhibited the reflections due to Keggin POM [JCPDS 50-0305] and NH₄Cl [JCPDS 01-0674] phases, which represent residue of the Wells-Dawson POM synthesis. However, the intensity of the reflections due to Keggin POM and NH₄Cl are weak and the synthesized sample majorly possessed Wells-Dawson

structured POM. A very similar results were previously reported by Arendt et al [15]. The volume percentage of the Wells-Dawson phase (87%) of calcined sample was estimated with the formula proposed by Toraya et al [16]. Powder XRD pattern of Preyssler sample showed diffraction peaks at $2\theta = 6.6^\circ, 8.8^\circ, 12^\circ, 13.6^\circ, 17.6^\circ, 25.5^\circ$ and 33.7° . The observed diffraction peaks for this sample are in accordance with reported for Preyssler POM [17].

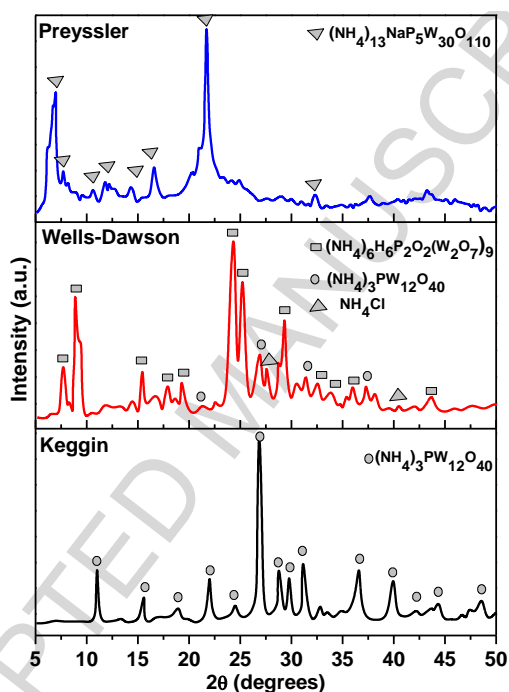


Fig.1: Powder X-ray diffraction patterns of the samples

3.2. DRIFT analysis

The DRIFT spectrum (Fig. S1) of the Keggin structured POM shows characteristic bands at $1075\text{ cm}^{-1}, 983\text{ cm}^{-1}, 885\text{ cm}^{-1}$ and 798 cm^{-1} corresponding to (P-O_d), (W-O_a), (W-O_b-W) and (W-O_c-W) functional groups [18]. As shown in Fig. 2, the DRIFT spectrum of $[\text{NH}_4]_6\text{P}_2\text{W}_{18}\text{O}_{62}$ sample showed strong vibration bands at $1090\text{ cm}^{-1}, 962\text{ cm}^{-1}, 914$ and 780 cm^{-1} attributed to asymmetric stretching vibration of the PO₄ tetrahedron, terminal W=O and W-O-W bonds, in agreement to the Wells-Dawson POM

spectrum reported in the literature [19]. The Preyssler POM showed characteristic peaks corresponding to P-O stretching at 1163, 1079 and 1022 cm^{-1} , and two bands corresponding to W-O-W bonding at 941 and 913 cm^{-1} ; a band at 757 cm^{-1} attributed to W=O; and another band at 536 cm^{-1} related to P-O bending. The observed peaks are in quite accordance with the literature report [20]. The DRIFT pattern of Preyssler POM is different from Keggin and Wells-Dawson POMs, because its structural arrangement contained of five $[\text{PW}_6\text{O}_{22}]$ entities, which are resulted from $[\text{PW}_{12}\text{O}_{40}]^{3-}$ ions by elimination of two sets of three corner-sharing WO_6 octahedron [21]. In addition to the characteristic bands of three POM structures, the DRIFT spectra of POM samples exhibited two sharp IR bands at 1615 cm^{-1} and 1410 cm^{-1} due to N-H stretching and O-H bending vibrations of NH_4 and H_2O moieties [7].

3.3. DRUV-*vis* analysis

DRUV-*vis* spectra of POMs are shown in Fig. S2. Appearance of multiple absorption peaks in the UV-*vis* spectra of POMs is due to different structural oxygen atoms presented in their structure [22]. Keggin POM showed DRUV-*vis* bands at 255 nm and 320 nm. On other hand, the spectra of Wells-Dawson and Preyssler-POMs exhibited absorption bands in the region of 220-550 nm. The peaks at lower wavelengths are associated with ligand-metal charge transfer from O atoms to W(VI) species in the POM structures. The position of the peak is at 320 nm for Keggin POM, which is corresponding to W-O-W bonding and this peak is shifted towards higher wavelengths in case of Wells-Dawson and Preyssler POMs [430 nm: Wells-Dawson, 460 nm: Preyssler]. The broadening of the peak could be related to increase in the number of the counter cations in the POM structure [23].

3.4. Textural properties

Fig. 2 represents the N₂ adsorption-desorption isotherms for POM materials. The three POM samples exhibited type-IV isotherms, which are characteristic of mesoporous powders. However, an increase of adsorption at very low pressure was observed in all the three samples, indicating that the samples also possessed micropores along with the mesopores. Okamoto et al [24] and Inumaru [25] synthesized [NH₄]₃PW₁₂O₄₀ by neutralizing the phosphotungstic acid with different ammonium sources and observed a surface area between 90-130 m² g⁻¹. It was also previously reported that ammonium salt of Keggin POM is microporous and/or mesoporous and the porosity of the material is derived from aggregation of nanometer size crystallites of POMs [26].

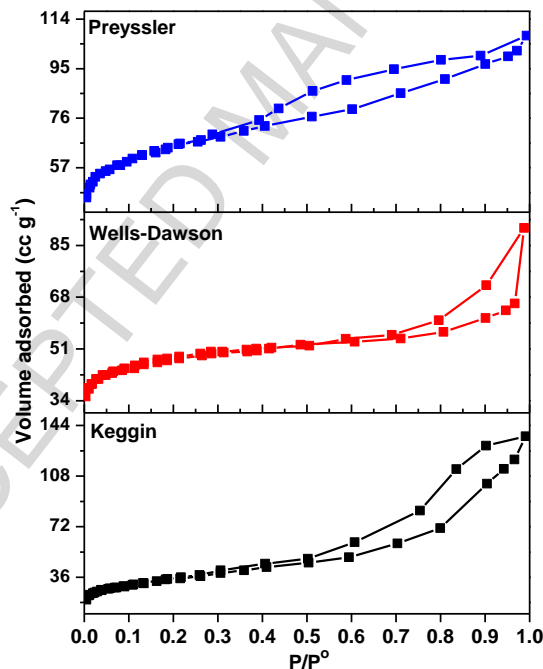


Fig. 2: N₂ adsorption-desorption isotherms of POM samples

To investigate the particles aggregation in samples, FE-SEM analysis was performed (Fig S3). It can be seen that Keggin POM exhibited aggregates of spherical shape with size in the range of 1.0-0.5 μm. In contrast, Wells-Dawson and Preyssler

POM samples form tightly packed aggregates of non-uniform particles having average sizes about 0.5-0.25 μm . As expected, the three samples possessed different hysteresis loops. Keggin and Wells-Dawson structured POMs showed H2 type hysteresis loop, which reveals that the synthesized POM materials have bottle neck shaped pores [27]. Presence of H4 type hysteresis, which is associated with narrow pores is clearly observed in Well-Dawson POM. The pore diameter, pore volume and BET surface area of the POM samples are determined from the N_2 -physisorption measurements. The surface area of Keggin POM ($175 \text{ m}^2\text{g}^{-1}$) is significantly higher than those of both Preyssler ($26 \text{ m}^2\text{g}^{-1}$) and Wells-Dawson ($14 \text{ m}^2\text{g}^{-1}$) structured POMs. The average pore diameter of Wells-Dawson POM is the highest (35 \AA) than other two POM samples [Keggin: 24 \AA and Preyssler: 20 \AA]. The pore volume is the highest for Wells-Dawson structured POM, $0.113 \text{ cm}^3\text{g}^{-1}$, while Keggin and Preyssler structured POMs showed pore volumes $0.062 \text{ cm}^3\text{g}^{-1}$, $0.046 \text{ cm}^3\text{g}^{-1}$ respectively.

3.5. Catalytic ammoxidation of 2-methylpyrazine

Influence of reaction temperature on 2-methylpyrazine conversion and 2-cynaopyrazine selectivity over three POM samples is presented in Fig. 3. All the POM samples exhibited rise in 2-methylpyrazine conversion with increase of reaction temperature from 360 to 400°C . Comparison of 2-methylpyrazine conversion and 2-cyanopyrazine selectivity of the POMs samples reveals that Preyssler POM showed superior performance than other two POMs under the identical reaction conditions. The Preyssler POM offered a maximum conversion of 85% with 2-cyanopyrazine selectivity of 96% , while Keggin structured POM is less active compared to Preyssler and Wells-Dawson POM samples, demonstrated a maximum conversion of 66% with selectivity

towards 2-cyanopyrazine of 82% at a reaction temperature of 400 °C. The major byproduct observed is the pyrazine and the formation of CO_x is negligible in all POM catalysts. It is clear from the results that the selectivity to 2-cyanopyrazine decreased with increase of reaction temperature from 360 °C to 400 °C in all the POM materials, however the extent of decrease is small (from 98% to 96%) in Preyssler POM.

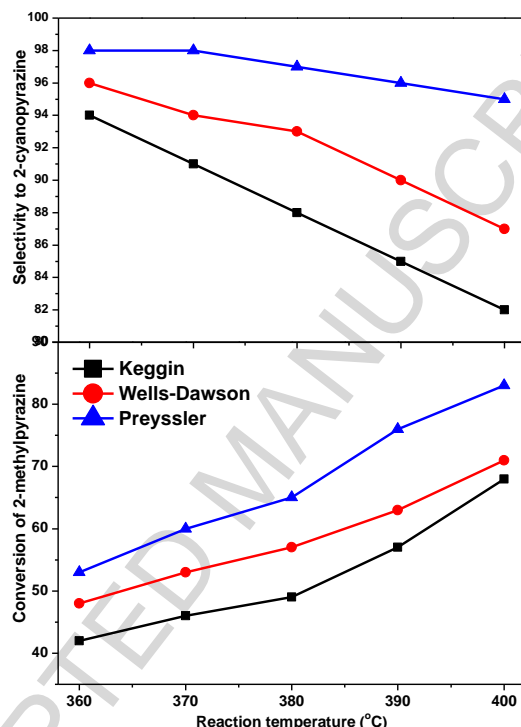


Fig. 3: Influence of reaction temperature on 2-methylpyrazine conversion and 2-cyanopyrazine selectivity

The variations in 2-methylpyrazine conversion and 2-cyanopyrazine selectivity with reaction time also studied. The reaction of the POM samples was investigated under previously optimized feed composition (2-methylpyrazine, water, oxygen and ammonia = 1:13:7:38) and at the reaction temperature of 380 °C. The ammoxidation activity of POM samples after 10 h is presented in Table S1. The results indicating that Preyssler POM exhibited superior performance that it offered higher rate of reaction. The reaction was continued for 24 h to perform the time on stream analysis and the results are

presented in Fig. S4. The Preyssler POM has exhibited higher stability than other two POM samples. The 2-methylpyrazine conversion and 2-cyanopyrazine selectivity have not changed significantly over 24 h and the POMs are resistant to deactivation.

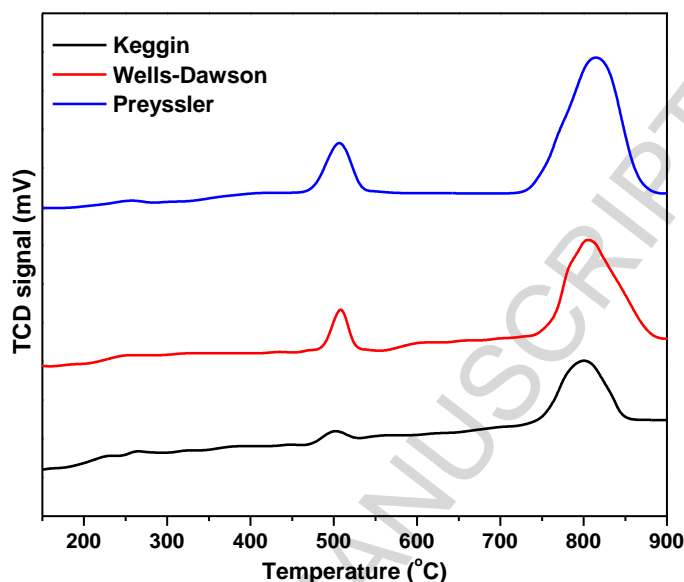


Fig. 4: H₂-TPR patterns for POM samples

It is well known that rate of ammoxidation is controlled by acidity and redox properties of catalyst. The redox properties and strength of acid sites of the samples were determined by H₂-TPR and potentiometric titration of samples with *n*-butyl amine respectively. The H₂-TPR patterns of POM samples are shown in Fig. 4. From the H₂-TPR results, it can be understood that the synthesized three POM samples exhibited two reduction peaks around 500-515 °C and 790-800 °C. The first reduction peak for the three samples can be attributed to the reduction of W⁶⁺ to a lower valence state W⁵⁺ and/or W⁴⁺ [28]. Since, the POM structures starts to decompose to WO₃ and P₂O₅ (below 500 °C) as it observed in the temperature programmed decomposition patterns. The reduction peak in the 515 °C represent not only the reduction of octahedrally coordinated W⁶⁺ in the POM structure, but also the reduction of WO₃ formed by the decomposition of POM in the

reductive environment. The reduction of W^{4+} to lower oxidation states could have happened at higher temperature (790-800 °C) [29].

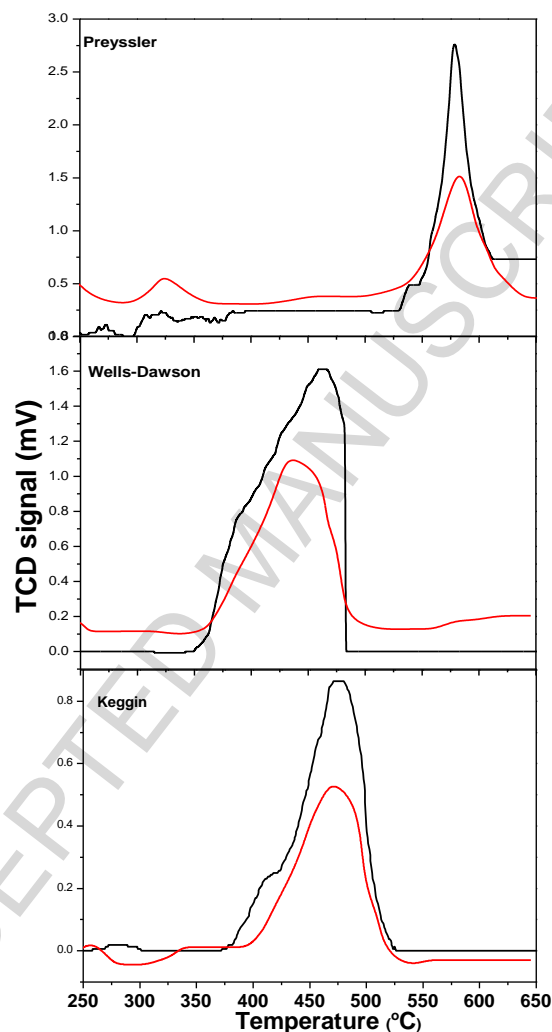


Fig.5: NH_3 -TPD patterns of POM samples

Bondareva et al [32] proposed the ammoxidation mechanism that 2-methylpyrazine transforms into oxygen containing intermediate complexes (aldehyde and asymmetric carboxylate) by interacting with oxygen and Lewis acid sites of catalyst. It is known that ammonia could partially reduce the catalyst and it also compete with the

oxygen to adsorb on the surface of catalyst. Due to the competitive adsorption, ammonia blocks some active sites and this is beneficial for the formation of nitrile, ammonia arrests undesirable total oxidation of 2-methylpyrazine. Among the studied POMs, Preyssler POM possessed more number of redox sites and ammonium cations in the secondary structure. This is the main reason for the superior performance of Preyssler POM. Centi et al [33] and Martin et al [34] reported that presence of NH_4^+ ions influences the catalyst acid-base properties and the reaction of oxygenated species with NH_4^+ ions proceeds fast to form nitrile and water [35]. The NH_3 -TPD profiles of the POM samples are shown in Fig. 5. Along with NH_3 -TPD experiments, decomposition behavior of three POM samples under neutral atmosphere also studied by the same procedure except saturation of sample with ammonia at the beginning. The decomposition patterns of POM samples are represented by red lines in Fig. 5. The Keggin and Wells-Dawson samples showed main desorption peak between 350 and 530 °C, however the Preyssler POM showed peak in between 525 and 600 °C. The NH_3 -TPD samples clearly revealed that the Preyssler POM has the highest ammonium content among the POM samples [Keggin: 3.84 mmol g^{-1} , Wells-Dawson: 7.59 mmol g^{-1} , Preyssler: $18.16 \text{ mmol g}^{-1}$]. The observed ammonium content include the ammonia adsorbed at the acid sites of the POMs and evolved ammonia due to the decomposition of the ammonium salts. It is known that POM samples generally possesses Lewis and Brønsted acid sites [1]. It has been reported that desorption peak at lower temperature is due to the ammonia adsorption over Lewis acid sites, while desorption peak at higher temperature attributed to the ammonia adsorption on Brønsted acid sites [23].

Pizzio et al [30] interpreted the potentiometric titrations results that initial electrode potential (E_i) could be considered as the acid strength of surface sites and the range, where the plateau is reached as the total number of acid sites. The acid strength of sample can be considered as very strong when $E_i > 100$ mV, strong if $0 < E_i < 100$ mV, weak when $-100 < E_i < 0$ mV, and very weak site if $E_i < -100$ mV [31]. The acidic strengths of Keggin, Wells-Dawson and Preyssler POM catalysts are found to be strong (Fig. S5). The Preyssler POM showed high measured electrode potential implying the presence of stronger acid sites than other two POMs.

A comparison among the ammonia content of POM, 2-methylpyrazine conversion and 2-cyanopyrazine selectivity has been obtained (Fig. 6). The Preyssler POM possessed much more ammonia content than other two POMs and offered highest 2-methylpyrazine conversion and 2-cyanopyrazine selectivity. A good correlation among them indicates that presence of more number of ammonium cations helps to obtain better 2-methylpyrazine conversion and selectivity to 2-cyanopyrazine.

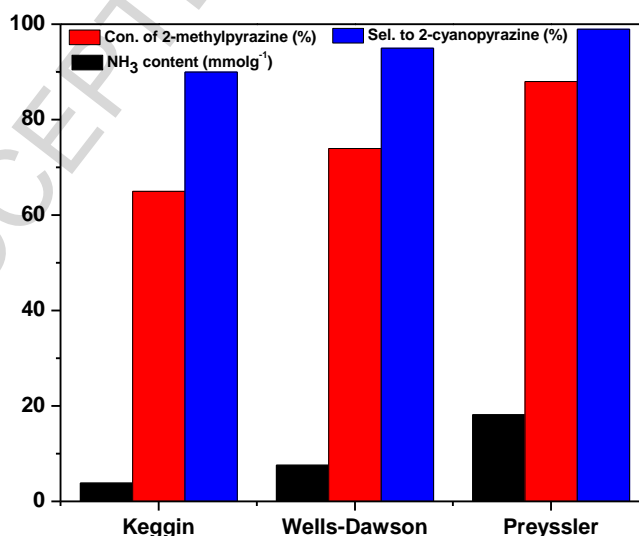


Fig. 6: Comparison of ammonia content of POM with ammoxidation activity; molar ratio of 2-methylpyrazine: H₂O:NH₃: air=1:13:7:38; reaction temperature: 400 °C; reaction time: 2h; catalyst weight: 1.0g

Conclusions

Three different ammonium tungstophosphate POM samples with Keggin, Wells-Dawson and Preyssler structures were successfully synthesized by different preparation methods. The XRD, DRIFT, DRUV-*vis*, SEM, NH₃-TPD and N₂-physisorption techniques were used to determine the physico-chemical properties of the samples. The POM samples were used as catalysts for 2-methylpyrazine ammoxidation to produce 2-cyanopyrazine in the range of 360-400 °C. The catalytic activity results revealed that Preyssler POM sample is efficient among the three samples, and it offered 69% of 2-methylpyrazine conversion with 98% selectivity to 2-cyanopyrazine at 380 °C. The superior catalytic performance of Preyssler POM is mainly due to the fact that this sample possessed superior redox property, relatively strong acid sites and large number of ammonium cations in its secondary structure, which enhanced the transformation of oxygenated 2-methylpyrazine species into 2-cyanopyrazine. For the first time, a correlation was deduced between the amount of ammonium content of the POM samples and their catalytic ammoxidation activity.

Acknowledgements

This work was supported by the Deanship of Scientific Research (DSR), King Abdulaziz University, Jeddah under grant No. (D-80-130-1438). The authors, therefore, gratefully acknowledge the DSR technical and financial support.

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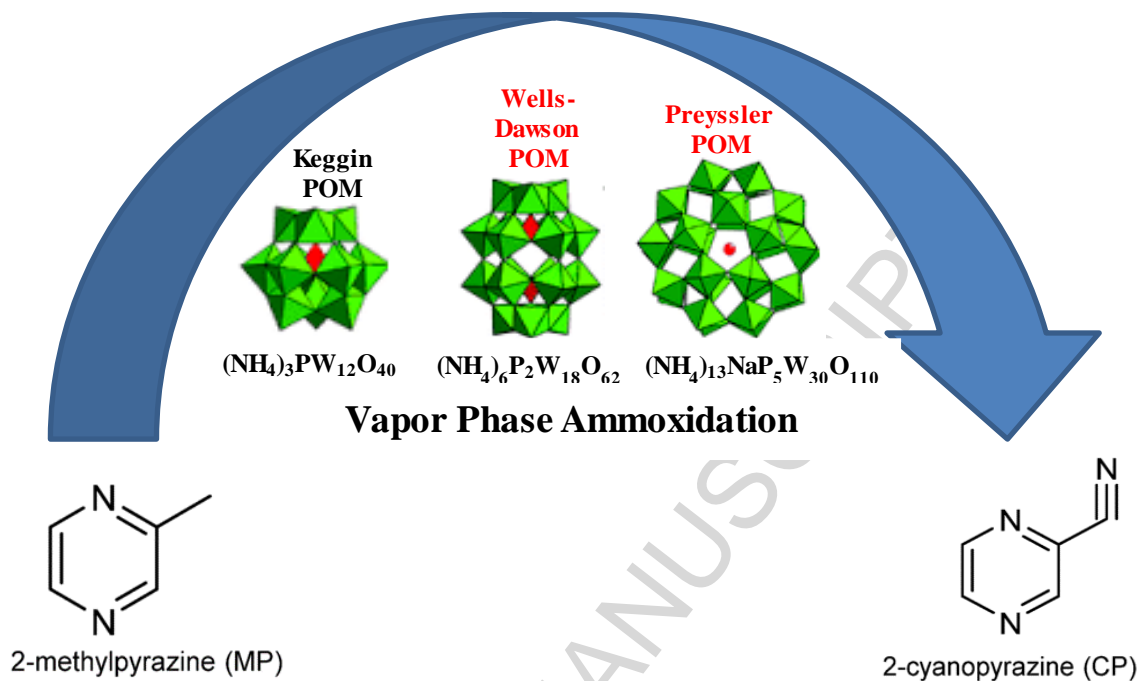
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Graphical Abstract



Highlights

- Keggin, Wells-Dawson & Preyssler structured tungstophosphates are synthesized.
- Synthesized POMs are tested for vapor phase ammoxidation of 2-methylpyrazine.
- Preyssler POM offered the best ammoxidation performance.
- Presence of more NH_4^+ ions in Preyssler POM is responsible for high activity.
- First report on correlation of between POM structure and ammoxidation activity.

ACCEPTED MANUSCRIPT