Supporting Information

Low temperature activation of methane over zinc-exchanged Heteropolyacid as an entry to selective oxidation to methanol and acetic acid

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Materials and synthesis: Phosphotungstic acid $H_3PW_{12}O_{40}.xH_2O$ utilized in this study was obtained from Aldrich and used without further purification. A zinc salt of phosphotungstic acid was synthesized as described previously[27]. Phosphotungstic acid was dissolved in de-ionized water and titrated with an ethanolic solution of zinc acetate (Aldrich) followed by slow filtration through commercial filter paper (Whatman No. 41, ash less, pore size 20um). Then the filter paper was thoroughly washed with water and ethanol alternatively in order to remove the complexes, which did not attach onto the surface of the filter paper. Then the filter paper was dried with airflow. The as prepared Zn-exchanged HPA/paper was calcined for 6 h at 450 °C in air with heating rate 10°C/min. The resulting green powder was obtained with yield of 0.6g. Elemental analysis (W 75.70, P 0.81, Zn 1.72%) corresponds to approximate formula of $Zn_{1.4}H_{0.6}PW_{12}O_{40}$. Silica supported Zn-HPW catalyst was prepared by the wet impregnation method. A mixture of heteropolyacid dispersed in water and silica (surface area: 200 $m^2.g^{-1}$) was stirred vigorously until evaporation of all the solvent at room temperature. The resultant Zn-HPW/SiO_2 (containing 20 wt% of Zn-HPW) was collected and ground in the mortar. This material was then treated under high vacuum (10^{-6} Torr) for 2 h at 200°C (sample colour changed to dark grey). High purity gases (methane 99.9995%, argon 99.9999%) were purchased from Specialty Gases Center of Abdullah Hashim Industrial Gases & Equipment Co. Ltd. (Saudi Arabia).

NMR experiments: For all the experiments, ZnHPW/SiO_2 powder (0.1 g) was placed into a glass tube (10 mL), and evacuated ($> 10^{-5}$ torr at 200 °C for 2 h). The gas feed, for **A**, $^{13}CH_4$ (0.5 mmol), was introduced at room temperature and condensed by cooling using liquid N_2; the tube was then sealed. Cooling with liquid N_2 condensed the gas phase. Then the unreacted gases were removed by warming up *in vacuo* in a glove box under a dry argon atmosphere. The solid content of the ampule were transferred to a 4 mm NMR rotor. Similar experiments were conducted for combination of 0.5 mmol $^{13}CH_4$ + 0.5 mmol O_2 (heated to 250 °C) (**B**) and 0.5 mmol $^{13}CH_4$ + 0.5 mmol $^{13}CO_2$ (heated to 300 °C) (**C**).

Catalytic Testing: The catalytic tests were performed in a fixed-bed continuous flow dynamic reactor operated at atmospheric pressure. In a typical experiment, 200 mg of material was loaded into the reactor and the total feed flow rate of reaction mixture was 20 mL/min. The purity of gases was greater than 99.99% and the gases were dehydrated and purified with suitable filters. A tube placed in the outlet side of the dynamic reactor was used to constantly feed a sample of the outlet gas to the Gas chromatogram (GC) (equipped with TCD and FID detectors) and a quadrupole mass spectrometer (MS). The sample was then pretreated in a flow of 50 mL/min of helium for 30 min. The temperature was raised to 200 °C at 20 °C/min and held for 1 h in the flow of helium. The sample was then cooled back down to 50 °C and held for 30 min. This pretreatment was used to clean the catalyst surface and remove any air or water vapours from the reactor tube. After the pretreatment, the sample was exposed to a 20 mL/min flow of the experimental gas. The sample was exposed to the experimental gas flow and the temperature was increased from 25 to 500 °C at a rate of 5 °C/min. The following m/z values were chosen to monitor the possible oxygenated products: 32 m/z for methanol and 60 m/z for acetic acid.

Characterization:

Infrared (IR) spectra of the heteropolyacids were collected on a Thermo-Nicolet Fourier transformed infrared spectrometer using Diffuse Reflectance technique.

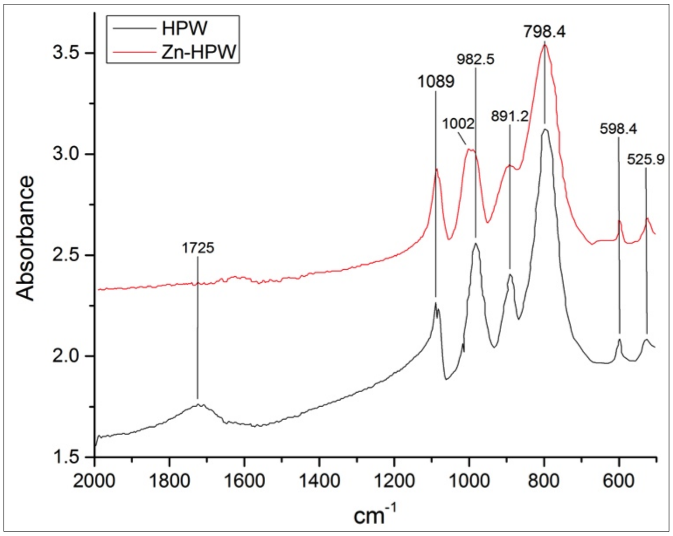

Fig. S1: FTIR spectrum of HPW and Zn-HPW

One dimensional ^{1}H MAS, ^{13}C CP/MAS and ^{31}P CP/MAS solid state NMR spectra were recorded on Bruker AVANCE III spectrometers operating at 400 MHz resonance frequencies for 1H with a conventional double resonance 4 mm CP/MAS probe at a spinning frequency of 10 KHz. The samples were packed into rotors under inert atmosphere inside glove boxes. Dry nitrogen gas was utilized for sample spinning to prevent degradation of the samples. NMR chemical shifts are reported with respect to the external references TMS and adamantine for ^{1}H and ^{13}C, and from $Na_2HPO_4.2H2O$ (6.6 ppm) for ^{31}P spectra. For ^{13}C and ^{31}P CP/MAS NMR experiments, the following sequence was used: 90° pulse on the proton (pulse length 2.4 s), then a cross-polarization was achieved using a linear ramp of rf field amplitude on the ^{1}H channel, with a contact time of 2 ms and ^{1}H rf field strength. For ^{31}P channel, the rf field strength was chosen for optimum transfer efficiency. And finally acquisition of the ^{13}C and ^{31}P NMR signal under SPINAL-64 proton decoupling at a RF field of 100 KHz. The delay between the scans was set to 4 s to allow the complete relaxation of the ^{1}H nuclei and the number of scans ranged between 1000-10000 for ^{13}C, 500-5000 for ^{31}P and was 32 for ^{1}H. An exponential apodization function corresponding to a line broadening of 80 Hz was applied prior to Fourier transformation.

Two-dimensional ^{1}H-^{13}C heteronuclear correlation (HETCOR) solid-state NMR spectroscopy experiments were conducted on a Bruker AVANCE III-400 spectrometer using a 4 mm MAS probe. The experiments were performed according to the following scheme: 90° proton pulse, t_1 evolution period, cross-polarization (CP) to carbon spins, and detection of carbon magnetization under TPPM decoupling. For the cross-polarization step, a ramped radio frequency (RF) field centered at 80 kHz was applied to the protons, while the carbon RF field was matched to obtain optimal signal. A total of 32 t_1 increments with 5000 scans each were collected. The sample spinning frequency was 8.5 kHz, and the contact time for the cross-polarization step was set to 0.2 ms, which allowed the selective observation of the spatially close attached C-H pairs. Using longer contact times (5 ms), we found that is possible to observe extra correlation peaks, which arise from longer-range dipolar interactions (e.g., to non-bonded protons). During acquisition, the proton decoupling field strength was also set to 80 kHz. Quadrature detection in $\omega 1$ was achieved using the TPPI method

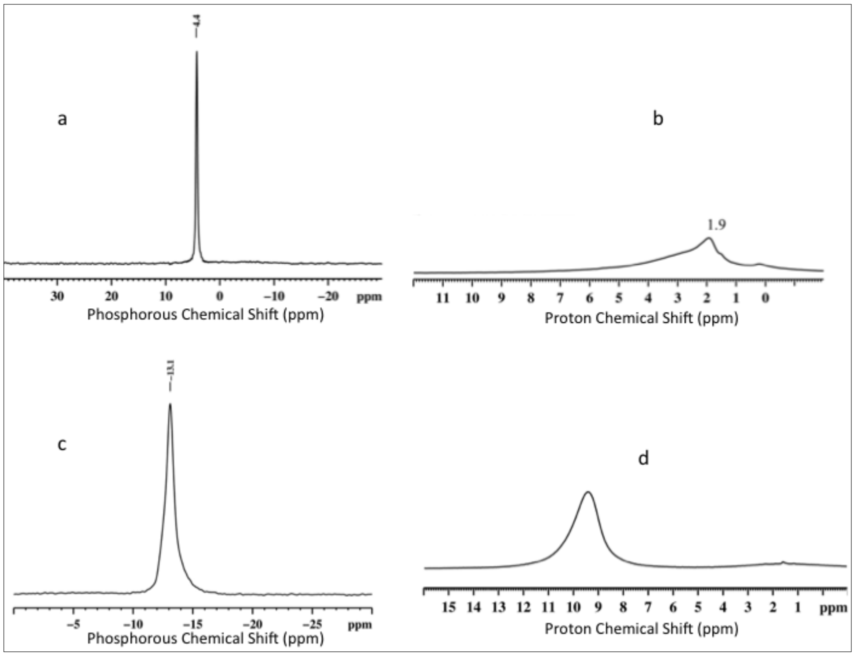

Fig. S2: ^{1}H and ^{31}P NMR spectrum of Zn-HPW (a, b) and HPW (c, d)

Surface area measurements (BET) were performed on a Micromeritics ASAP 2040 using dinitrogen (99.9995%) adsorption-desorption at 77 K. Surface areas were determined after outgassing at temperature of 300 °C.

Significant increase in surface area is observed for Zn substituted heteropolyacid over the parents HPA. Parent et al[38] have explained the larger surface area of other cation substituted heteropoly salts by the rotation and translation of the Keggin anion, so that the barriers between the interstitial voids present in the parents acid are partially removed allowing the formation of channels between the anions and the counter cations.[39] Also, possibly, the use of filter paper as a template favours the formation of Zn-HPW with smaller particle size)

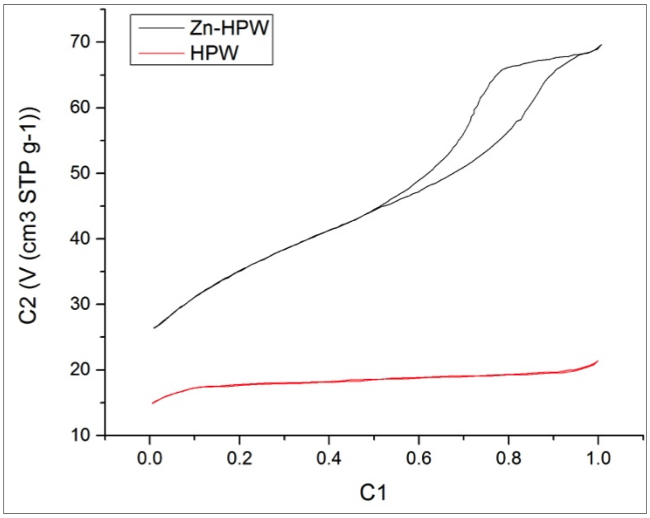

Fig. S3a: Adsorption-desorption isotherms for nitrogen on HPW and Zn-HPW

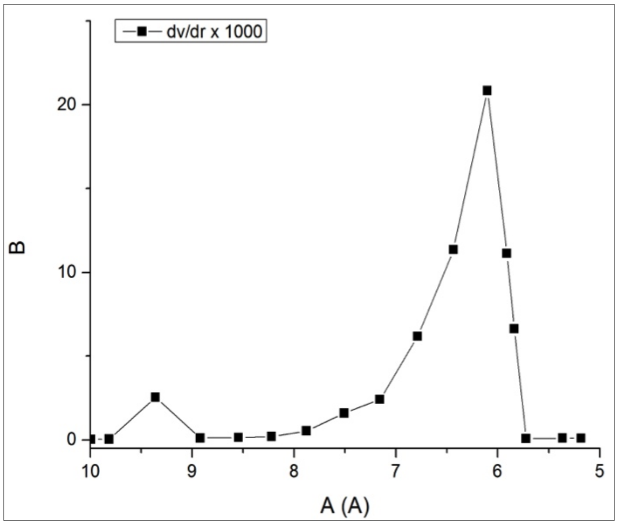

Fig.S3b: Micropore volume distribution for Zn-HPW

Thermal gravimetric analysis (TGA) and Differential Scanning Calorimetry (DSC) of the sample was conducted using a Metller Toledo Instruments with helium (99.9999%) flowing at 100 mL/min. The temperature program was a simple linear ramp from 25 °C to 800 °C for at a rate of 5 °C/min. Approximately 20 mg and 30 mg of sample was used for HPW and Zn-HPW, respectively.

During thermal gravimetric analysis, weight loss was observed in two stages for HPW. The first showing removal of water to yield 5-hydrate, the second corresponding to the formation of anhydrous acid by removal of protonic water (evolved by extraction of a oxygen atom from kegging anion by two protons) and thus decomposing of kegging structure. Final weight loss in the high-temperature region was attributed to loss of phosphorous, which presumably occurs through the sublimation of P_2O_5. In comparison, Zn-HPW exhibits higher thermal stability. It has practically no physisorbed water molecules and the loss of protonic water occurs at about 500 °C. Higher thermal stability can be associated with the partial substation of protons by larger divalent cations of zinc. This larger cation can coordinate to more oxygen atoms on the periphery of Keggin structure consequently causing atoms in the anions to have small mobility, meaning more stable crystal. [40,41]

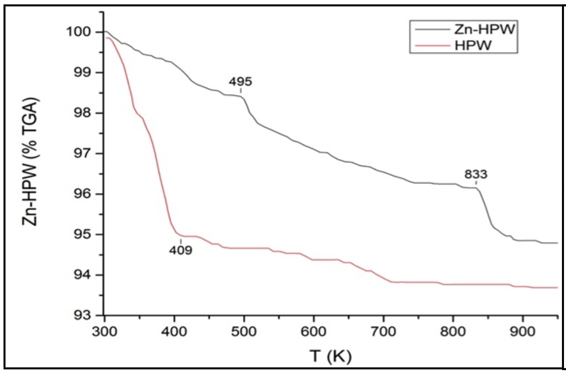

Fig. S4a: TGA curves of HPW and Zn-HPW

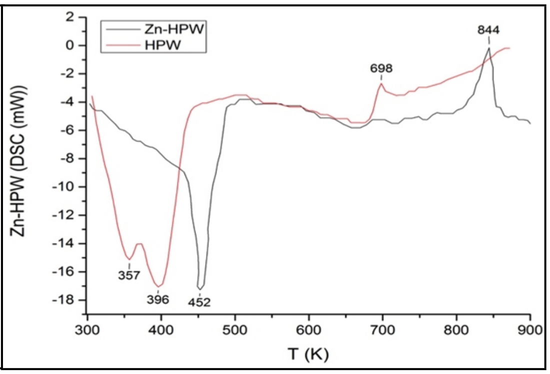

Fig.S4b: DSC curves of HPW and Zn-HPW

Table S1 below summarizes the results from thermal gravimetric analysis and dinitrogen adsorption.

Sample	Physisorbed + hydration (per kegging unit)[a]	Protonic water (per kegging unit)[b]	DTA transition (exotherm) °C	Protons (per kegging unit)[c]	BET surface area (m^2/g)
HPW	19.8	1.4	200-250	2.8	8
Zn-HPW	0	0.3	480-550	0.6	65

a. Water evolved at low temperature (less than 200 °C)

b. Water loss from decomposition of Keggin Unit

c. Protons per Keggin unit calculated as 2 times the amount of evolved protonic water

The acidity of the supported HPW materials was tested with the amine TPD technique. 50 mg of sample was pretreated at 300 °C in a flow of He for 1 h. After the pretreatment, the sample was cooled in He to room temperature and then a He stream saturated with isopropylamine (bubbler in ice bath at 0 °C) was flowed over the sample. After removing the excess of isopropylamine by flowing He, the sample was heated to 500 °C at a heating rate of 5 °C/min. Mass 41, was monitored to determine the evolution of isopropylamine.

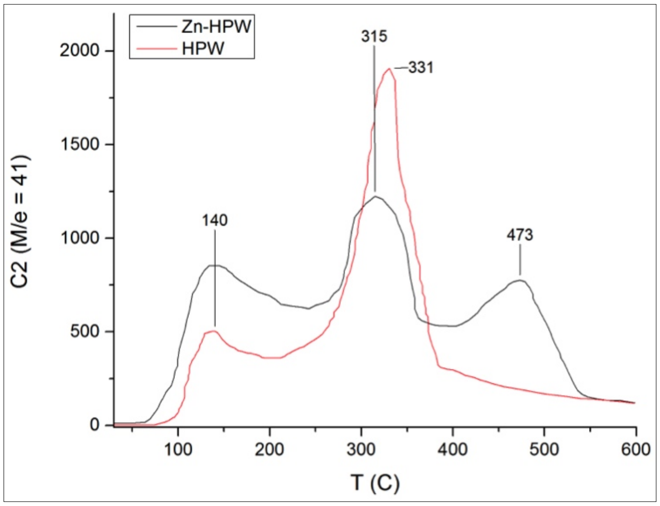

Fig. S5: Evolution of the m/e = 41 signal during TPD of isopropylamine from supported HPW and Zn-HPW

Powder X-ray diffraction experiments were conducted on a Bruker XYZ diffractometer using CuKa radiation at a wavelength of 0.154060 nm. A scan rate of one degree per minute with a step size of 0.0300 degrees was used for data collection.

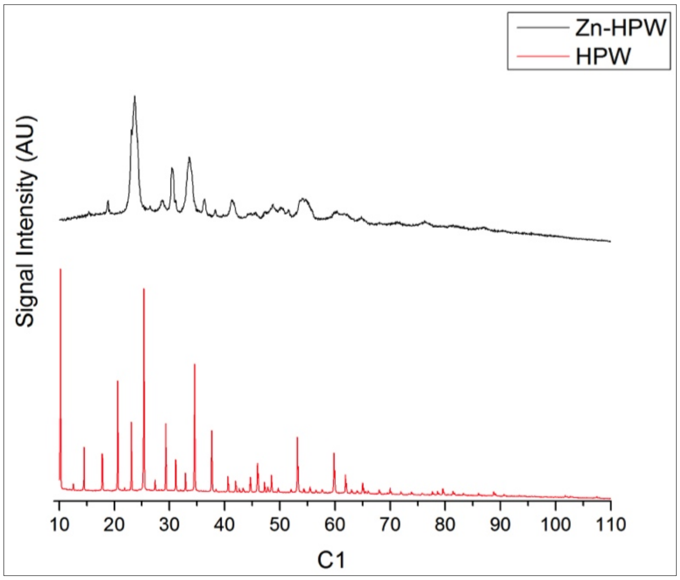

Fig. S6: XRD curves for HPW and Zn-HPW

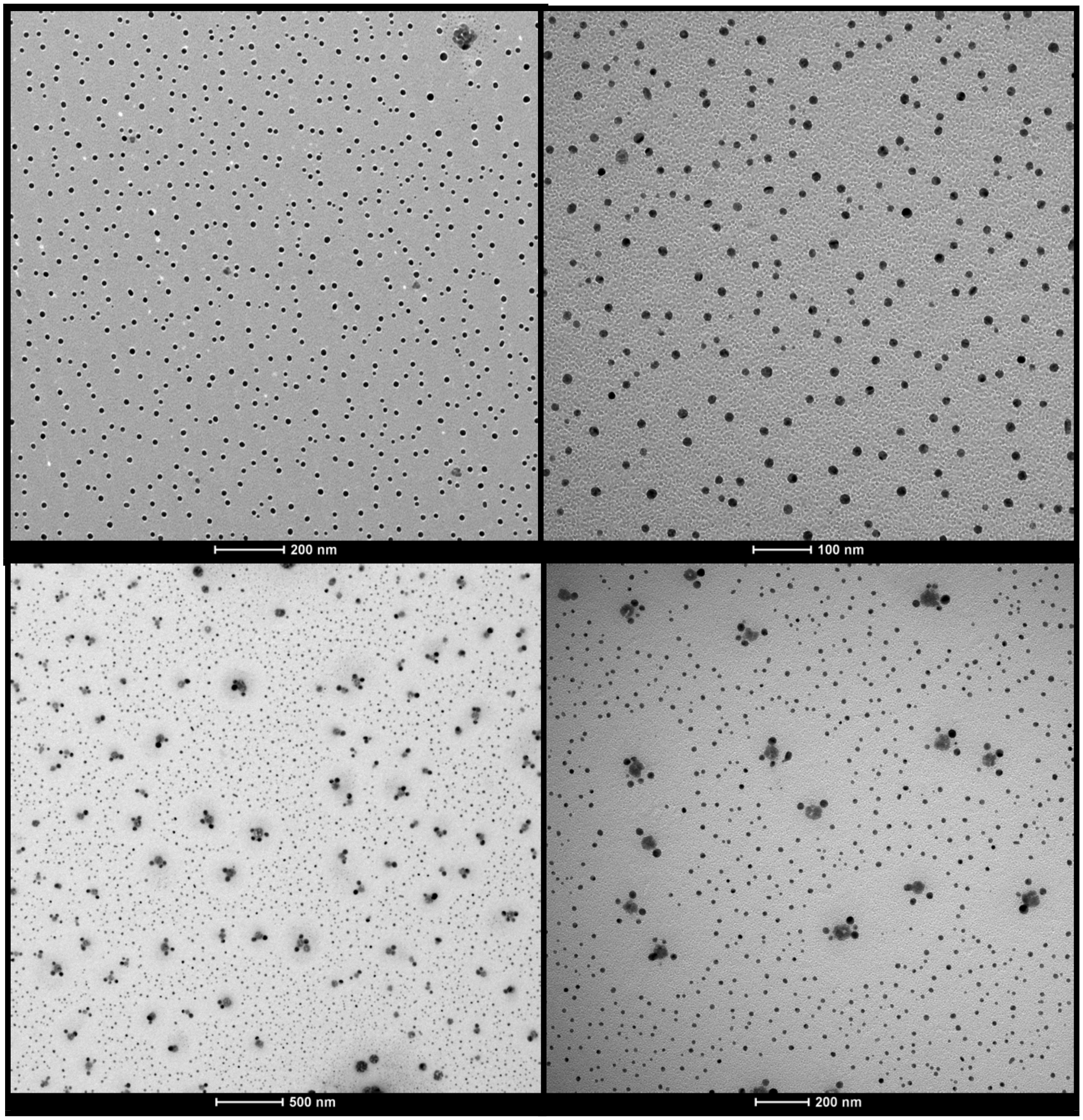

Fig. S7: TEM images for Zn-HPW