Electronic Supplementary Information

Polyoxotungstate ($[PW_{11}O_{39}]^{7-}$) Immobilized on Mesoporous Polymer for Selective Liquid-Phase Oxidation of Alcohols using H_2O_2

Sathyapal R. Churipard, [a,b] Kempanna S. Kanakikodi, [a,b] Jyoti Roy Choudhuri, [c] and Sanjeev P. Maradur, [a]*

[a] *Materials Science and Catalysis Division, Poornaprajna Institute of Scientific, Research (PPISR), Bidalur Post, Devanahalli, Bangalore-562164, Karnataka State, India.*

[b] *Graduate studies, Manipal Academy of Higher Education, Manipal - 576104, Karnataka, India.*

[c] *BMS Institute of Technology and Management, Doddaballapur Main Road, Avalahalli, Yelahanka, Bangalore, Karnataka – 560064.*

**** Corresponding author***

Tel: +91(080)27408552; Fax: +91 23619034.

E-mail: sanjeevpm@poornaprajna.org

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1. Synthesis of tetranuclear peroxotungstate complex (PW_4)

Tetranuclear peroxotungstate complex $[PO_4\{WO(O_2)_2\}_4]^{3-}$ was synthesized according to the previously reported procedure of Venturello *et. al.* [1] In a typical synthesis, 2.5g of tungstic acid was suspended in 7ml 30% H_2O_2 in a 100ml RB flask fitted with a reflux condenser and a stirrer. This solution was stirred at 60°C until a pale yellow coloured solution was obtained. The solution was cooled to room temperature and filtered, then 0.62ml 40% H_3PO_4 was added to it. The whole mixture was diluted to 30 ml with distilled water. To the resultant solution, 2.09 g of methyltrioctylammonium chloride in 40 ml dichloromethane was added dropwise over about two mins. Stirring was continued for an additional 15 min. The organic phase was separated and dried over Na_2SO_4, filtered, and gently evaporated on a rotary evaporator under reduced pressure at 40-50 °C water bath to give quaternary ammonium salt of tetranuclear peroxotungstate complex in the form of a colorless syrup. This complex is designated as PW_4 complex.

2.Tables

Table S1: Physicochemical properties of various catalysts synthesized

Sample	S_{BET} (m^2 g^{-1})	V_t (ccg^{-1}) [a]	Pore size (nm) [a]	Tungsten loading (mmol/g) [b]
Recycled PW_{11}/MP (80:20) [c]	148	0.44	13.9	0.1203
PW_{11}/Amberlite	15	0.17	-	0.7610
PW_{11}/KIT -6	444	0.88	8.1	0.0770
Reaction mixture	-	-	-	ND

[a] By BJH method.

[b] Measured by ICP-OES analysis

[c] Five times recycled catalyst

ND - Not detected

Table S2: Adsorption of benzyl alcohol on PW_{11}/MP catalysts

Catalyst	Adsorption capacity (w/w)
PW_{11}/MP (90:10)	4.2 times
PW_{11}/MP (80:20)	2.2 times
PW_{11}/MP (70:30)	1.7 times

For the adsorption experiment, a known weight of benzyl alcohol is taken in a glass vial and polyoxotungstate supported mesoporous polymer was added to the vial with occasional shaking until the benzyl alcohol was completely adsorbed on to polymer to form a hard gel. The mass of vial before and after the addition of polymer was noted to calculate the weight of the polymer. The adsorption capacity of PDVB polymer is calculated using the following formula:

$$\textbf{Adsorption capacity (wt \%)} = \frac{weight\ of\ the\ benzyl\ alcohol\ (g)}{weight\ of\ catalyst\ (g)} \times 100$$

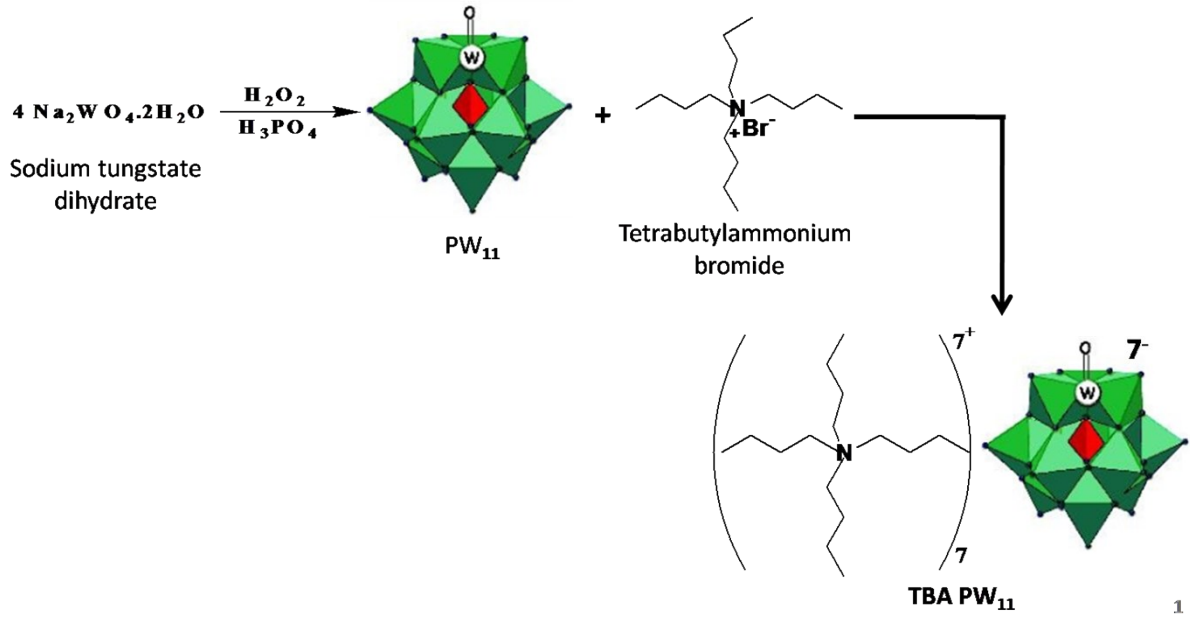
Table S3: Oxidation of benzyl alcohol using identical amount of tungsten.

Catalyst	Tungsten taken (mmol)	H_2O_2/ BzOH	Benzyl alcohol con. (wt%)	Benzaldehyde selec. (wt%)
PW_{11}/MP (90:10)	0.0281	1:1	72.3	80.1
PW_{11}/MP (80:20)	0.0281	1:1	87.9	81.6
PW_{11}/MP (70:30)	0.0281	1:1	73.5	81.2

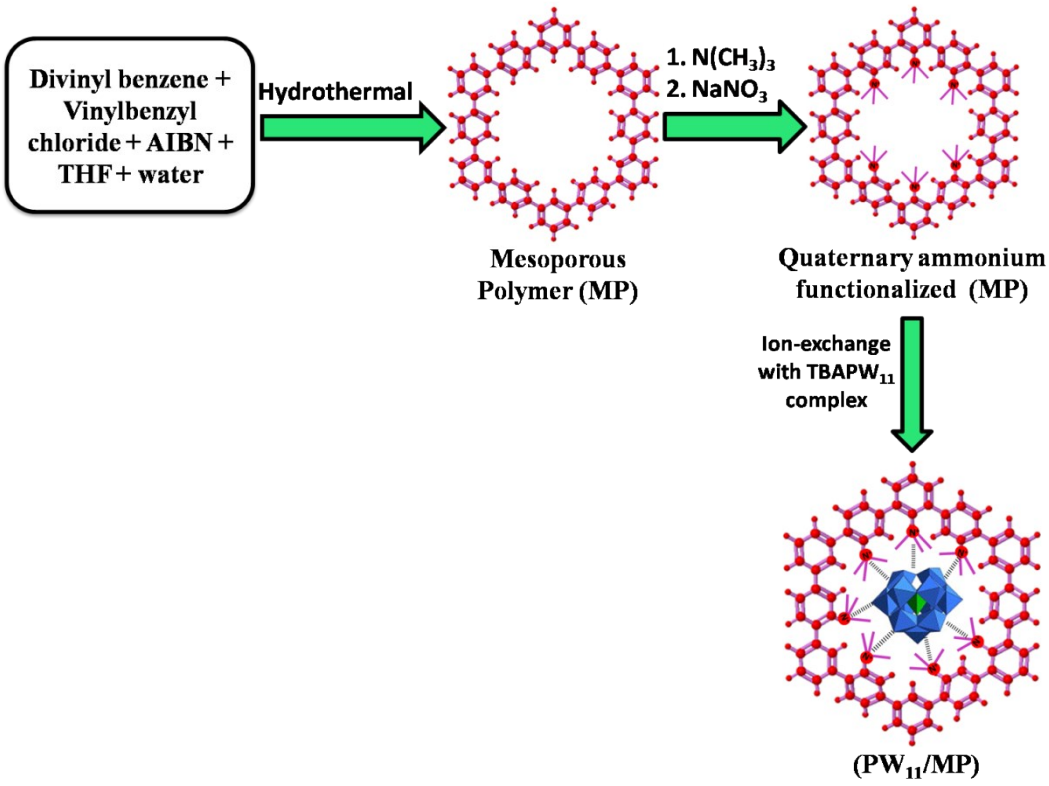
Reaction conditions:
Benzyl alcohol = 20 mmol, H_2O_2 = 20 mmol, catalyst = 10 wt% in case of PW_{11}/MP 80:20, reaction temperature = 90°C, reaction time = 6h.

3. Schemes

Scheme S1: Preparation of polyoxotungstate complex ($TBAPW_{11}$)



Scheme S2: Synthesis of mesoporous polymer and immobilization of polyoxotungste



4. Figures

Figure S1: FTIR spectrum of PW_{11}/MP (80:20) from which spectrum of MP (80:20) in NO_3 form is subtracted

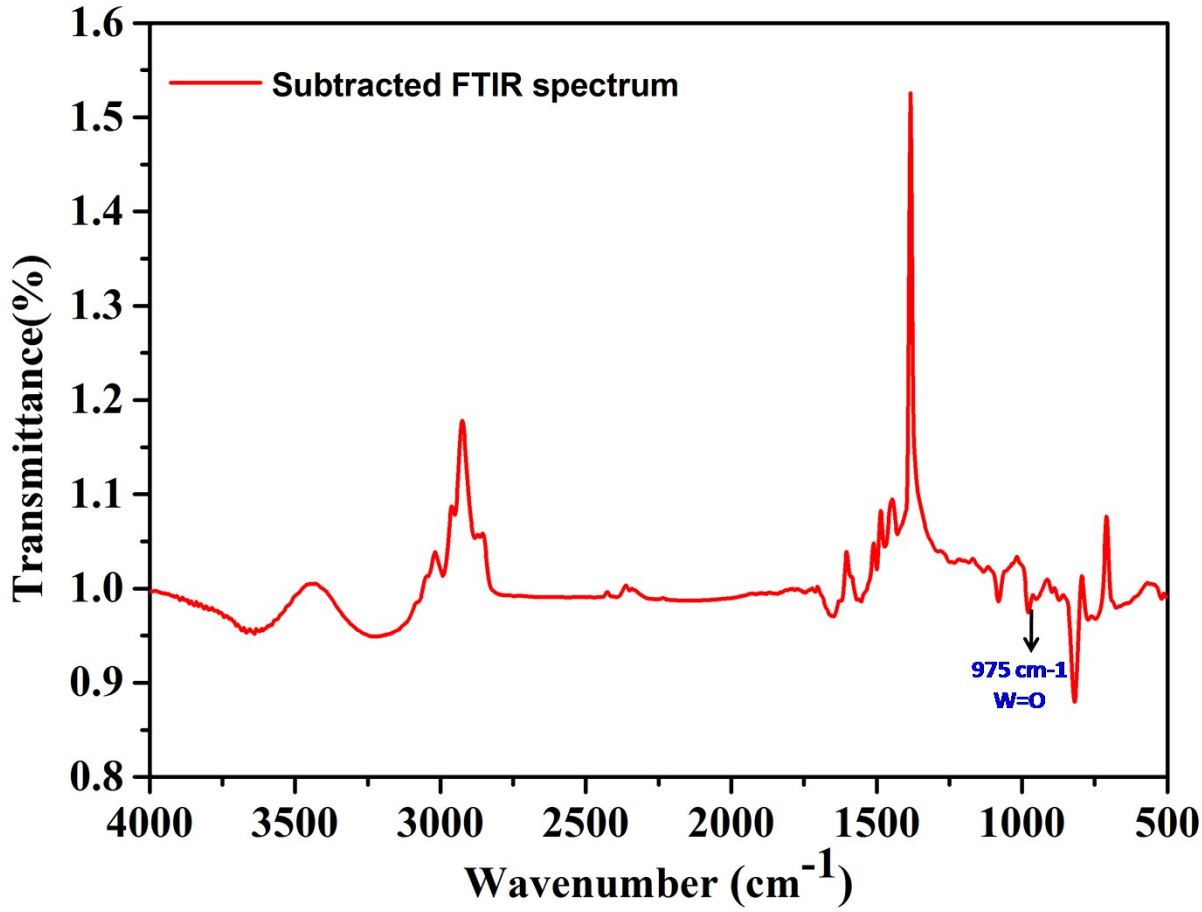


Figure S2: Comparitive FTIR spectrum of MP (80:20) NO_3 form with PW_{11}/MP (80:20)

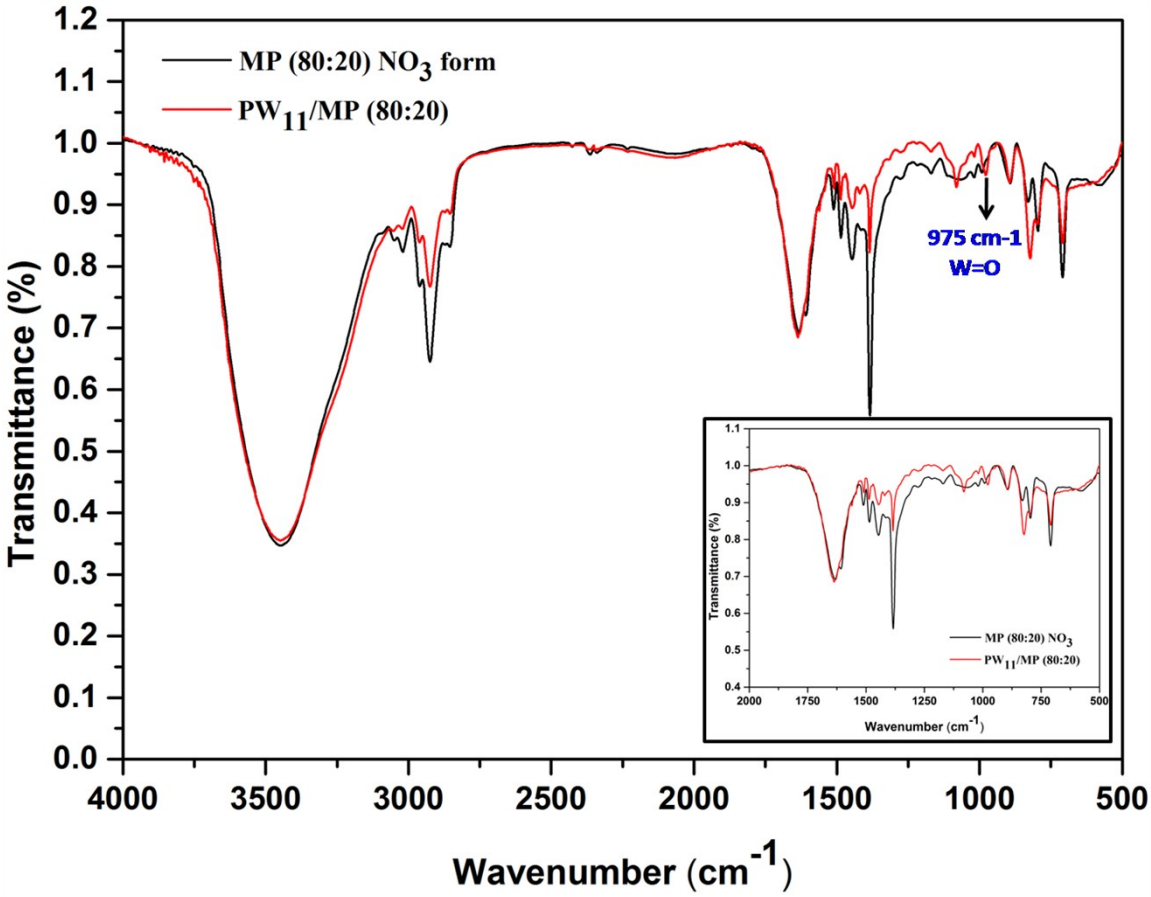


Figure S3: FTIR spectrum of tetranuclear peroxotungstate complex (PW_4)

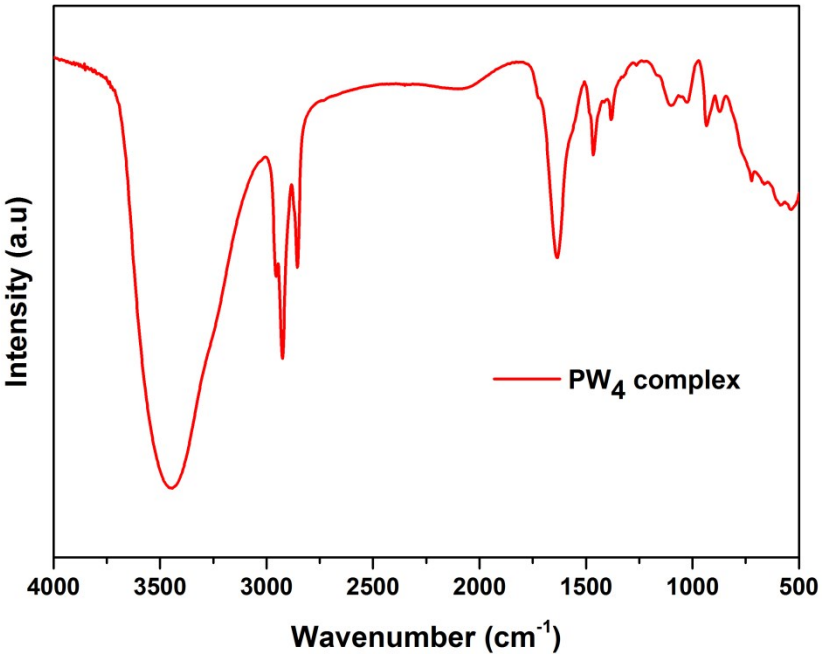


Figure S4: Thermogravimetric analysis plot of MP (80:20) and PW_{11}/MP (80:20) catalyst

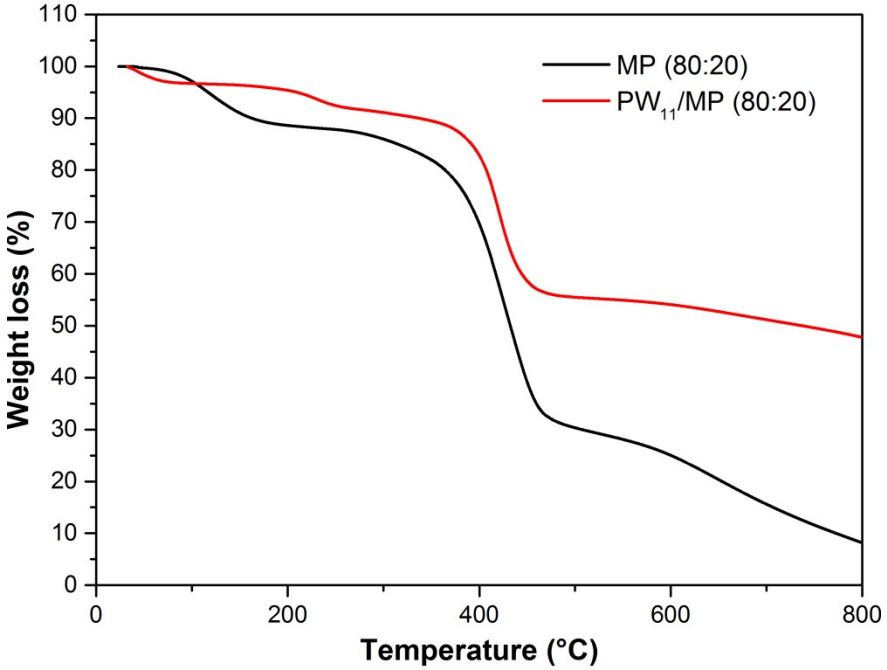


Figure S5: Nitrogen adsorption-desorption isotherm of MP and PW_{11}/MP catalysts

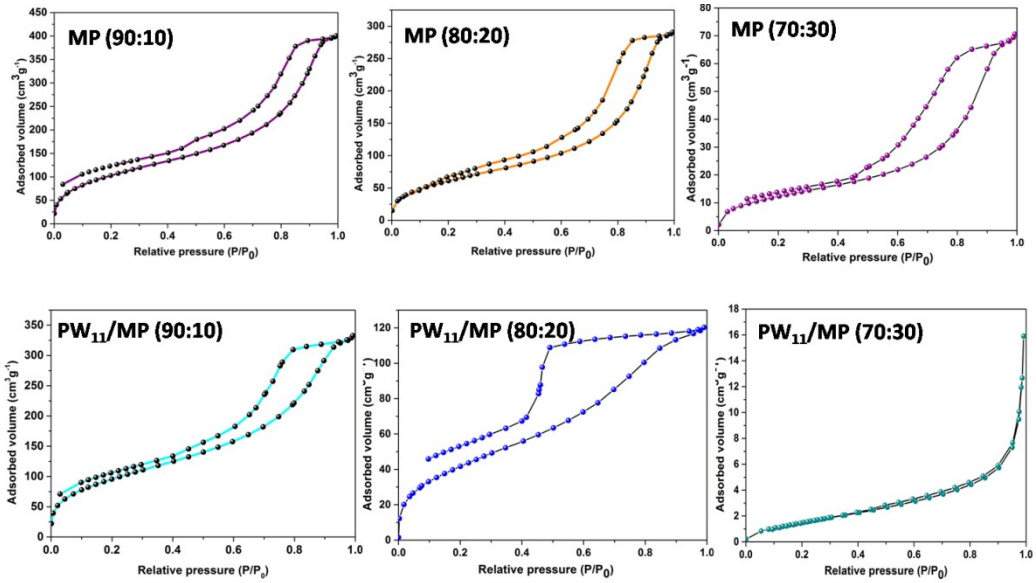


Figure S6: Pore size distribution of MP and PW_{11}/MP polymers

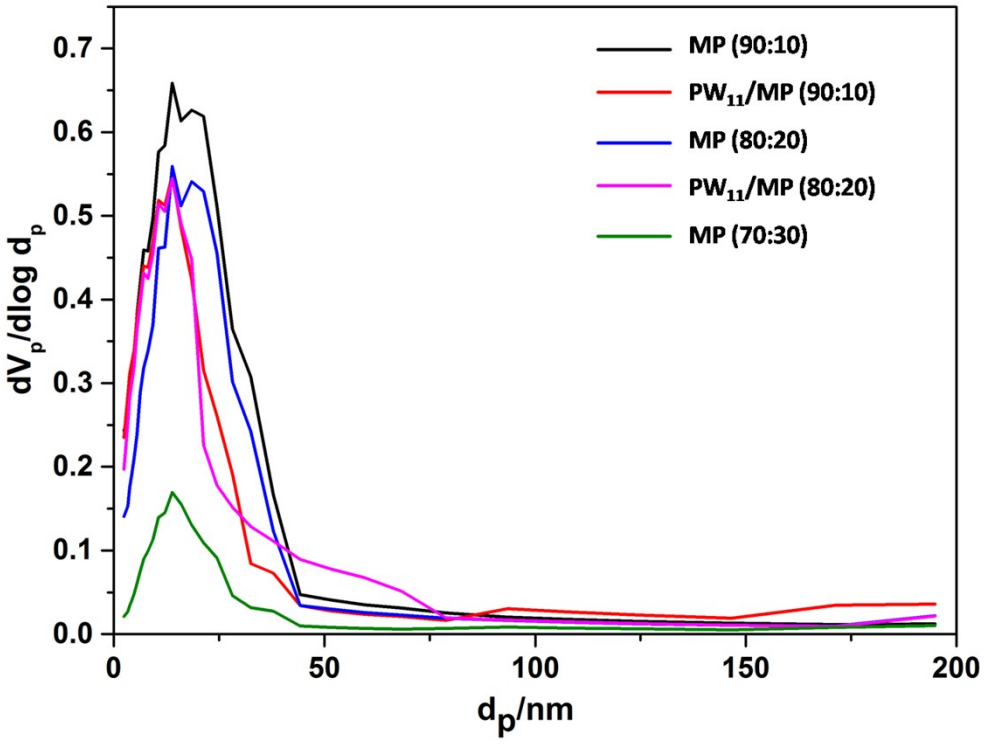


Figure S7: ^{31}P NMR spectrum of tetranuclear peroxotungstate (PW_4) complex

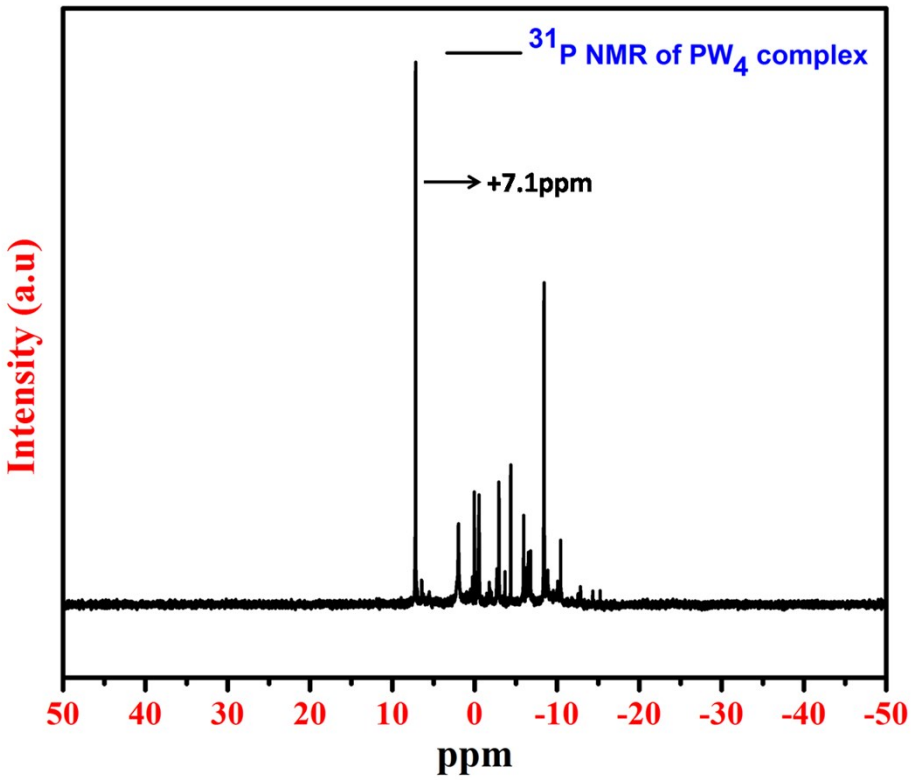
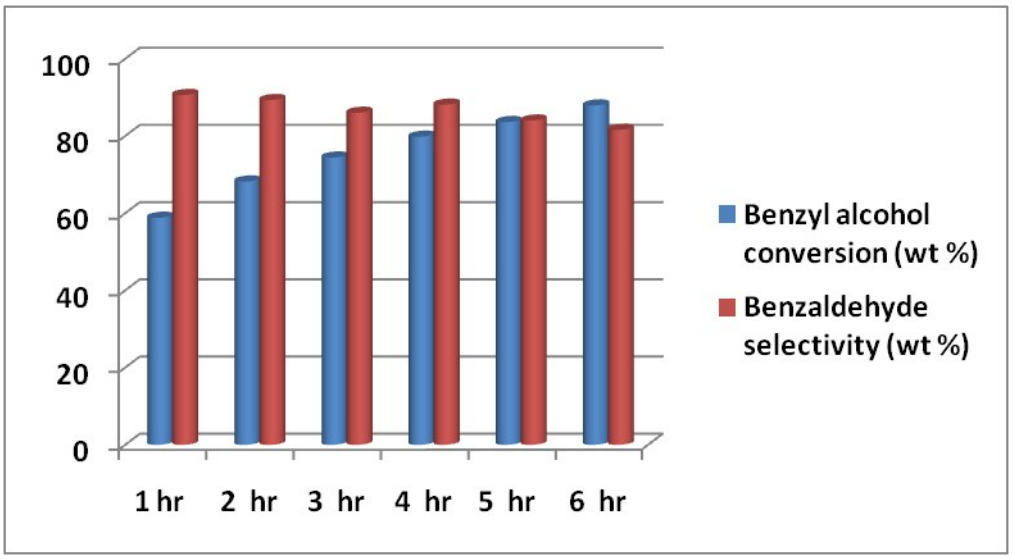


Figure S8: Effect of reaction time



Reaction conditions: Benzyl alcohol = 20 mmol, H_2O_2 = 20mmol, catalyst = PW_{11}/MP (80:20) 10 wt% w.r.t benzyl alcohol, reaction temperature = 90°C

4. Reference

1. C. Venturello and R. D'Aloisio, *The Journal of organic chemistry*, 1988, 53, 1553-1557.