

Preparation, characterization and catalytic application of some polyoxometalates with Keggin, Wells-Dawson, and Preyssler structures

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Dibutylphthalate has been prepared via esterification reaction in the presence of some solid acidic catalysts. Transition metal polyoxometalates with Keggin ($K_3[PMo_6W_6O_{40}]$, $K_3[PMo_{12}O_{40}]$, $K_4[SiMo_{12}O_{40}]$, $K_4[SiW_{12}O_{40}]$, $Na_7[PW_{11}O_{39}]$), Wells-Dawson ($K_6[P_2W_{18}O_{62}]$), and Preyssler structures ($K_{14}[NaP_5W_{30}O_{110}]$) have been synthesized and characterized. The reactivity of these catalysts has been studied for the preparation of dibutylphthalate by esterification reaction of phthalic anhydride and 1-butanol. Among the various acidic catalyst used, $K_3[PMo_6W_6O_{40}]$ showed the best reactivity and efficiency compared to other catalysts.

Keywords: Catalysts, Solid catalysts, Polyoxometalates, Keggin structure, Wells-Dawson structure, Preyssler structure, Esterification, Dibutylphthalate

In the past decades, the environmental impact of chemicals has been fully recognized as a global issue. As a consequence, more stringent legislation, which promotes preservation and protection of the quality of the environment for future generations has become of concern. To overcome the problem at the source, the chemical industry must develop cleaner chemical processes or materials by the design of innovative and environmentally benign chemical reactions. Green chemistry offers the tools for this approach. In the other words, green chemistry is the chemical products and processes that reduce or eliminate the use and generation of hazardous substances¹.

The drive to develop green processes has led to the development of solid acid catalysts. These materials can replace the corrosive liquid acids currently used in many industries. A variety of materials have been used as solid acid catalysts such as clays, zeolites,

sulfated metal oxides and polyoxometalates (POMs)^{2,3}. Each of these materials offers unique properties that can influence the catalytic activity. Among these solid acids, polyoxometalates (POMs) represent a well known class of structurally well-defined clusters with an enormous variation in size, metal-oxygen frame work topology, composition and function. The preparation of POMs is based on the programmed self-assembly of metal oxide building blocks⁴⁻⁶. In recent years, POMs have been widely used in a variety of acid catalyzed reactions for both homogeneous and heterogeneous reactions due to their high acid strength and high thermal stability such as esterification, etherification, oxidation, Friedel-Crafts alkylation, hydration of olefin, and polymerization of tetrahydrofuran⁷⁻²¹. Many POMs have been used as building blocks to construct a variety of organic-inorganic solid state hybrid materials^{22,23}.

In the present study, preparation of some polyoxometalate compounds containing molybdenum and tungsten as green catalysts, with Keggin, Wells-Dawson and Preyssler structures have been investigated. In addition, catalytic application of the prepared polyoxometalate compounds in the esterification reaction of phthalic anhydride with 1-butanol has been studied. The effects of catalyst amount, various solvents and the reaction time have also been investigated in the formation of dibutylphthalate.

Experimental

All solvents and materials were of analytical grade, commercially available and used without further purification. Infrared spectra were recorded as KBr disks on a Tensor 27 Bruker spectrophotometer. The electronic spectra were obtained with a Cary 100 Bio UV-vis spectrophotometer. The NMR spectra were recorded on a Bruker spectrometer at 300 MHz ($CDCl_3$ solution). Elemental analysis was performed on a Perkin-Elmer 2400 CHN elemental analyzer. Mass spectra were recorded on an Agilent technologies 5973 network mass selective detector (MSD), operating at an ionization potential of 70 eV.

Polyoxometalates with Keggin structure were prepared as follows: For the preparation of

$K_3[PMo_6W_6O_{40}]$, sodium tungstate (0.05 mol), sodium molybdate (0.05 mol), and sodium dihydrogen phosphate (0.02 mol) were dissolved in deionized water (60 mL). The solution was kept at 80 °C for 3 h with agitation and then concentrated to 30 mL. Subsequently, hydrochloric acid 24 % (30 mL) was added, while the solution color was yellow. On extraction with diethyl ether at room temperature, crystals were obtained. The product was characterized by IR and UV-vis spectroscopies.

$K_3[PMo_{12}O_{40}]$ was prepared by the reaction between disodium hydrogen phosphate (0.01 mol) and a solution of sodium molybdate (0.04 mol) in water (30 mL). The solution was stirred while it was heated to boiling point. Then, hydrochloric acid 37 % (8 mL) was added. The purification procedure was done by extraction with diethyl ether in two stages.

For the preparation of $Na_7[PW_{11}O_{39}]$, sodium tungstate (0.07 mol) and disodium hydrogen phosphate (0.01 mol) were dissolved in water (50 mL). The solution was heated to 80 °C and titrated exactly with conc. nitric acid with vigorous stirring to pH 4.8. The volume was reduced to half by evaporation when the polyoxometalate separated in a dense lower layer on liquid-liquid extraction with acetone. The extraction was repeated until the acetone extract shows no nitric ions (ferrous sulfate test). The solid sodium salt was obtained as the hydrate by evaporation to dryness of the acetone extracts.

$K_4[SiMo_{12}O_{40}]$ was synthesized by the addition of sodium silicate (0.5 mL) to a solution of sodium molybdate (0.02 mol) in water (10 mL). The solution was stirred and heated to boiling point. Consequently, hydrochloric acid (4 mL) and diethyl ether (10 mL) was added. After 7 days, colorless cubic crystals were obtained by vaporization of solvent in room temperature.

The experimental procedure for preparation of $K_4[SiW_{12}O_{40}]$ was similar to that of $K_4[SiMo_{12}O_{40}]$ with a replacement of the sodium tungstate (0.02 mol) by sodium molybdate (0.02 mol).

It is to be noted that some Keggin salt such as $K_3[PMo_6W_6O_{40}]$, $K_3[PMo_{12}O_{40}]$, $K_4[SiMo_{12}O_{40}]$ and $K_4[SiW_{12}O_{40}]$ were prepared by passing an aqueous acidic solution through a column of ion-resin.

Polyoxometalate with Wells-Dawson structure, $K_6[P_2W_{18}O_{62}]$, was prepared as follows: phosphoric acid (2 mL) was added to a solution of sodium tungstate (0.01 mol) in water (30 mL). The solution was refluxed for 8 h. The salt was precipitated by

adding potassium chloride (1 g), purified by recrystallization and cooled overnight to 5 °C. The product was filtered, washed and then vacuum-dried for 8 h.

Polyoxometalate with Preyssler structure, $K_{14}[NaP_5W_{30}O_{110}]$, was synthesized by dissolving sodium tungstate (0.01 mol) in water (30 mL). The solution was added to phosphoric acid 85 % (3 mL). In the next step, the mixture was sealed into a Teflon bottle at 120 °C for 18 h. Then, a solution of potassium chloride (1 g) was added into the above mixture to form the precipitate. The precipitate was obtained by filtration and washed successively with an aqueous solution of potassium acetate (2 M) and methanol. The white precipitate was dried and recrystallized twice to obtain the potassium salt of Preyssler type POM.

The esterification reaction of phthalic anhydride with 1-butanol was carried out in a round-bottom flask equipped with a magnetic stirrer, reflux condenser and Dean-Stark trap. All the catalysts were dried prior to use. The temperature was maintained with an oil bath. To prepare dibutylphthalate ester, phthalic anhydride (0.1 mol), 1-butanol (0.2 mol) and POMs were added to the solvent (15 mL) and the mixture was refluxed. The water formed in the reaction was removed by azeotropic distillation with the solvent, and then the solvent was sent back to the reaction vessel. After completion of reaction, the catalyst was extracted from the reaction mixture with an aqueous solution of sodium carbonate. The reaction mixture was distilled under reduced pressure for initially removing excess alcohol and then continued to obtain the main product. The formation of ester was monitored by TLC, IR, 1H NMR, mass spectroscopy and CHN analysis. The reaction conversions were calculated from the amount of collected water in the Dean-Stark trap.

The spectra data (IR, 1H NMR) and physical data for dibutylphthalate ester are presented as, IR (KBr, cm^{-1}): 3071 (C–H aromatic), 2960 (C–H aliphatic), 1728 (C=O ester), 1599, and 1465 (C=C aromatic), 1285 (C–O ester), 743 (bending vibration, C–H aromatic); 1H NMR ($CDCl_3$, 300 MHz, δ ppm): 7.40-7.70 (m, 4H, aromatic ring), 4.25-4.29 (t, $J=6.6$, 4H, $2CH_2$ aliphatic), 1.63-1.72 (m, 4H, $2CH_2$ aliphatic), 1.30-1.46 (m, 4H, $2CH_2$ aliphatic), 0.89-0.98 (t, $J=7.35$, 6H, $2CH_3$ aliphatic). MS, (m/z , %): 278 (10.5), 223 (52.6), 149(100), 76(15.7), 56(36.8), 41(57.8). Anal.(%): Calcd for $C_{16}H_{22}O_4$: C, 69.06; H, 7.91. Found: C, 69; H, 8.

Results and discussion

The FT-IR and UV-visible spectra of 7 POMs compound were recorded (Figs 1-3). The $[XM_{12}O_{40}]^{n-}$ structure (Keggin structure), where X is the heteroatom and M is the d^0 metal consists of one XO_4 tetrahedron surrounded by four M_3O_{13} sets formed by three edge-sharing octahedral. The M_3O_{13} sets are linked together through oxygen atoms. Thus, there are four kinds of oxygen atoms in $[XM_{12}O_{40}]^{n-}$, four $X-O_a$ in which one oxygen atom connects with heteroatom (X), 12 $M-O_b-M$ oxygen-bridges (corner-sharing oxygen-bridge between different M_3O_{13} sets), 12 $M-O_c-M$ oxygen bridges (edge-sharing oxygen-bridge within M_3O_{13} sets) and 12 $M=O_d$ terminal oxygen atoms. For example, in the IR spectrum of $K_3[PMo_6W_6O_{40}]$, there are four characteristic bands (ν_{as} , cm^{-1}): 1072 (X-O); 973 (M=O_d); 878 (M-O_b-M) and 789 (M-O_c-M) (Fig. 1). In the Keggin structure, intense absorption bands at 220 and 270 nm are due to charge-transfer of the terminal oxygen and bridge-oxygen to metal atoms, respectively.

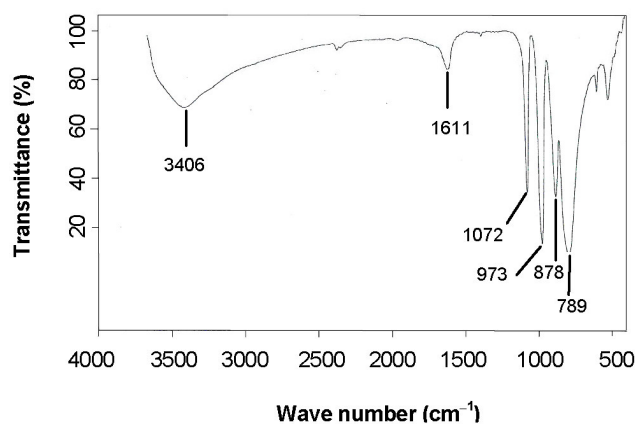


Fig. 1—IR spectra of $K_3[PMo_6W_6O_{40}]$ with Keggin structure.

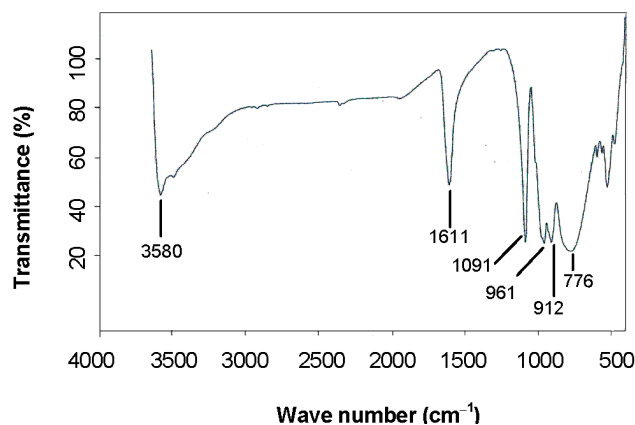


Fig. 2—IR spectra of $K_6[P_2W_{18}O_{62}]$ with Wells-Dawson structure.

In the IR spectrum of $K_6[P_2W_{18}O_{62}]$ ($[X_2M_{18}O_{62}]^{n-}$, Wells-Dawson structure), there are four characteristic bands (ν_{as} , cm^{-1}): 1091(X-O); 961 (M = O_d); 912 (M-O_b-M); 776 (M-O_c-M) (Fig. 2). In the UV spectrum of $K_6[P_2W_{18}O_{62}]$, there are two characteristic bands, 203 nm (O_d to metal charge transfer) and 250 nm O_b/O_c to metal charge transfer.

The Preyssler anion $[NaP_5W_{30}O_{110}]^{14-}$, consists of a cyclic assembly of five PW_6O_{22} units, each derived from the Keggin anion, $[PW_{12}O_{40}]^{3-}$, by removal of two sets of three corner-shared WO_6 octahedral. The IR spectrum of $K_{14}[NaP_5W_{30}O_{110}]$, displayed vibrations (ν_{as} , cm^{-1}) at 1165, 1082, 1021 (X-O); 788 (M=O_d); 940 and 983 (M-O_b-M). In the UV spectrum of $K_{14}[NaP_5W_{30}O_{110}]$, there are two characteristic bands, 201 nm, O_d to metal charge transfer and 278 nm O_b/O_c to metal charge transfer. The UV-vis spectra of $K_{14}[NaP_5W_{30}O_{110}]$ with Preyssler structure is shown in Fig. 3.

Esterification of phthalic anhydride by alcohol takes place in two stages. The first stage is so rapid that it can be carried out in the absence of catalyst. However, esterification of the second carboxylic group is very slow and needs to be facilitated by acid catalyst. Also, the resulting water must be removed from the reaction mixture (Scheme 1).

In this work, the effects of three variable factors, namely, amount of catalyst, reaction time and solvent type on the percentage conversion for the reaction of phthalic anhydride with 1-butanol has been studied.

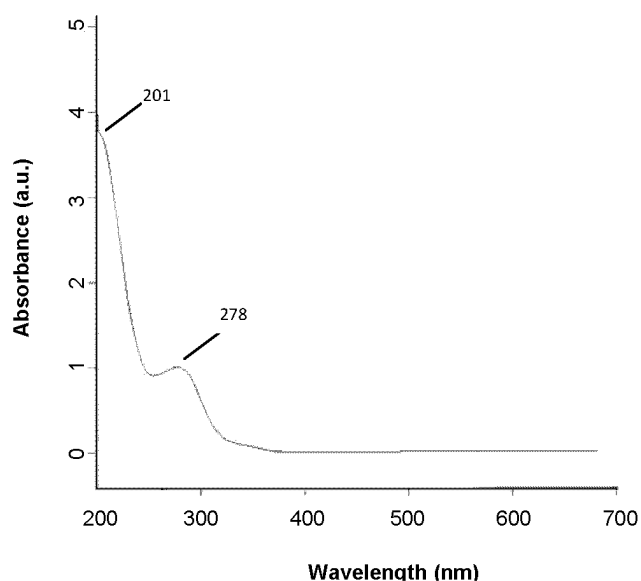
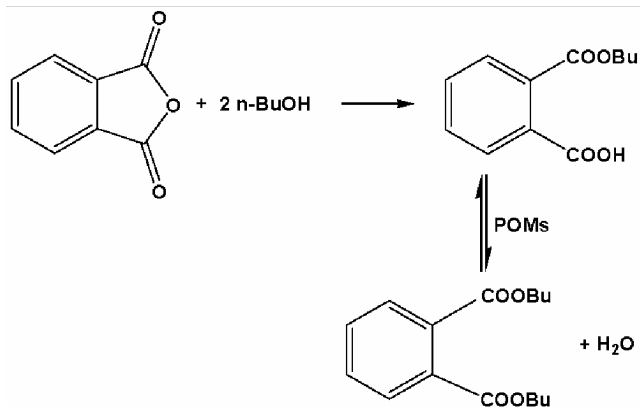


Fig. 3—UV-vis spectra of $K_{14}[NaP_5W_{30}O_{110}]$ with Preyssler structure.



Scheme 1

The reaction time and amount of catalyst were varied in the range of 2-6 h and 0.1-0.9 g, respectively. Furthermore, the reaction was carried out in toluene and xylene as solvent. Increasing the amount of catalyst (>0.7 g) and reaction time (>5 h) did not show any remarkable effect on the reaction conversion. It is to be noted that the effect of solvent should not be ignored. Esterification yields in xylene as solvent in the present work are higher than that in toluene due to the higher boiling point and influence of refluxing temperature and consequently higher reaction rate.

Among the investigated catalysts, $K_3[PMo_6W_6O_{40}]$ with Keggin structure with amount of 0.7 g and the reaction time of 5 h in xylene solvent showed the best reactivity and efficiency (97 %), while the lowest conversion percent using $K_{14}[NaP_5W_{30}O_{110}]$ catalyst is 20 % in toluene solvent (Table 1). Also, results clearly demonstrated that $K_3[PMo_6W_6O_{40}]$ was a better catalytic system when compared to conventional acid catalysts such as H_2SO_4 . The conversion percent depends on the acidity of catalysts. The relation between efficiency of catalysts and pH are given in Table 1.

Polyoxometalates have several advantages over liquid acid catalysts, including that of being noncorrosive and environmentally benign. Thus, they present fewer disposal problems and are more economically and environmentally attractive. The present study shows that changes in the central and addenda atoms of the POM cluster and the presence of vicinal POM clusters lead to changes in the deprotonation energy (DPE) of the POM cluster and activation barriers. The direct interaction between the POM protons with other POM clusters and reactants decreased the negative charge of the oxide shell of the

Table 1—Comparison of pH with efficiency of various polyoxometalates as catalyst under different solvent in esterification. [Amt. of catalyst: 0.7 g; time: 5 h]

Structure	Comp.	Conv. (%)		pH
		Toluene	Xylene	
Keggin	$K_3[PMo_6W_6O_{40}]$	85	97	3.72
	$K_3[PMo_{12}O_{40}]$	39	37	4.83
	$K_4[SiMo_{12}O_{40}]$	42	44	4.50
	$K_4[SiW_{12}O_{40}]$	40	41	4.80
	$Na_7[PW_{11}O_{39}]$	30	42	5.28
Wells-Dawson	$K_6[P_2W_{18}O_{62}]$	45	64	5.04
Preyssler	$K_{14}[NaP_5W_{30}O_{110}]$	20	27	5.35

POM. In addition, it decreased the DPE and increased the acidic strength. Generally, it is well known that by changing the central atom of POM from a high valent to a low valent element and replacing the tungsten addenda atom with other atoms, its acidity decreases. This is due to the increase of negative charge of POM²⁴. Esterification reactions of phthalic anhydride by 1-butanol catalyzed by various POMs compounds have been investigated in the present study. Our results show that esterification yield depends on several factors, such as reaction time, amount of catalyst and type of solvent. When the amount of catalyst and the reaction time was increased, initially there was an increase in conversion percent which reached a plateau subsequently. The highest conversion percent using 0.7 g of $K_3[PMo_6W_6O_{40}]$ catalyst for a duration of 5 h in xylene solvent was 97 %, while the lowest conversion percent using $K_{14}[NaP_5W_{30}O_{110}]$ catalyst was 20 % in toluene as solvent.

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