

Acylation of aromatic compounds by acid anhydrides using Preyssler's anion $[\text{NaP}_5\text{W}_{30}\text{O}_{110}]^{14-}$ and heteropolyacids as green catalysts

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The Preyssler, Wells-Dowson and Keggin heteropolyacids are efficient and eco-friendly solid acid catalysts for the acylation of electron-rich aromatic compounds with acid anhydrides. The performance of different forms of heteropolyacids was compared. In all the cases, the best results were obtained using the Preyssler heteropolyacid as the catalyst. In the presence of 25 mol% (with respect to H^+ equivalency) Preyssler catalyst, highly *para*-selective acetylation of anisole occurs using two equivalents of acetic anhydride, in 15 min at room temperature. The isolated yield of the *p*-methoxyacetophenone product is 98%.

Keywords: Acylation, Preyssler, Anhydride, Heteropolyacids, Catalyst, Aromatic compounds.

INTRODUCTION

Acylation of aromatic compounds is a widely used reaction for the production of fine chemicals¹. In the last decades, considerable effort has been made to develop solid acid catalysts such as zeolites, clays, Nafion H², and silica sulfuric acid³ as heterogeneous catalysts of Friedel-Crafts acylation⁴. Of these catalysts, the zeolites are the most studied². Polyoxometalates (POMs) are discrete molecular structures composed of metal cations bridged by oxide anions. They are not multi-metal species with metal-metal bonding, one conventional definition of "clusters", but rather they are clusters in the generic sense of the word. Catalysis by heteropolyacids (HPAs) and related compounds is a field of growing importance, attracting attention worldwide in which many novel and exciting developments are taking place, both in the areas of research and technology. Heteropolyacids belong to the family of polyoxometalates that incorporate anions (heteropolyanions) having metal-oxygen as the basic structural unit⁵. The octahedra are linked together to form the extremely stable and compact skeleton of the heteropolyanions. Heteropolyacids (HPAs) are promising solid acid catalysts for aromatic acylation. HPAs are Brønsted acids composed of heteropolyanions and protons as the counter-cations. For Friedel-Crafts chemistry, present industrial practice uses acyl chlorides or acid anhydrides as acylating agents and requires a stoichiometric amount of soluble Lewis acids (for example, AlCl_3) or strong mineral acids (for example, HF or H_2SO_4) as catalysts. This practice results in corrosion problems and substantial amounts of waste². Therefore, the development of new solid acid catalysts that are inexpensive and effective with non-polluting carboxylic acids and anhydrides is desirable. The acylation of methoxybenzene with acetic anhydride using a zeolite catalyst has been commercialized by Rhodia². The strong Brønsted sites on the heteropolyacids are able to generate acylium ions which are the active intermediates in the acylation of aromatic substrates through the electrophilic attack at the π -electron system of the substrate. A Weyland type transition state is suggested as an intermediate in the formation of aromatic ketones^{6,7}. The use of carboxylic acids and acid

anhydrides are advantageous alternatives to halogenated agents when more efficient acid catalysts are available. On the other hand, the mobile protons in the cages of heteropolyacids and the homogeneous micropore structure render such catalysts highly regioselectivity and active in many chemical reactions, making them promising substitutes for the traditional polluting inorganic acids and metal halides. We have recently used the Preyssler type heteropolyacid, $\text{H}_{14}[\text{NaP}_5\text{W}_{30}\text{O}_{110}]$ as a catalyst for the acetylation of *p*-aminophenol⁸, the synthesis of aspirin⁹ and the synthesis of propranolol¹⁰. In this work we evaluate sodium-30 tungstopentaphosphate, the so-called Preyssler's anion, as catalyst for selective Friedel-Crafts acylation. The performance of the Preyssler catalyst in three forms-pure, mixed addenda and silica-supported was compared to a classical catalyst, sulfuric acid. We find that Preyssler's anion is a green and recyclable catalyst, and is a more effective catalyst than sulfuric acid when used in an organic solvent at different reaction temperatures. Under both homogeneous and heterogeneous catalysis, the results show that the performance of this catalyst is excellent. The effects of various parameters such as catalyst type, reaction time, temperature, molar ratio and solvent type were studied to identify optimum reaction conditions. All of the different forms of this catalyst are easily recovered, and recycled with retention of their initial structure and activity.

EXPERIMENTAL SECTION

Materials

Acetic and propionic anhydrides, aromatic compounds, sodium tungstate dihydrate, molybdotungstate, orthophosphoric acid, potassium chloride, $\text{H}_3[\text{PMo}_{12}\text{O}_{40}]$, $\text{H}_3[\text{PW}_{12}\text{O}_{40}]$, $\text{H}_4[\text{SiW}_{12}\text{O}_{40}]$, $\text{H}_4[\text{SiMo}_{12}\text{O}_{40}]$, and the various solvents and silica gel were obtained from commercial sources. A standard sample of *p*-methoxyacetophenone (> 99% purity, Aldrich Chemical) was used as the reference standard.

Instruments

The IR spectra were obtained with a Buck 500 scientific spectrometer. $^1\text{H-NMR}$ spectra were recorded on a FT NMR Bruker 100 MHz Aspect 3000 spectrometer. The GC analysis was performed on a Pu 4500 gas chromatograph with FID detector.

Catalyst Preparation

Preyssler catalyst, $\text{H}_{14}[\text{NaP}_5\text{W}_{30}\text{O}_{110}]$ was prepared by a passage of the solution of the potassium salt (30 mL) in water (30 mL) through a column (50 cm \times 1 cm) of Dowex 50w \times 8 in the H^+ form. The eluent was evaporated to dryness under vacuum^{11, 12}. Molybdenum-substituted Preyssler heteropolyanion, $\text{H}_{14}[\text{NaP}_5\text{W}_{29}\text{MoO}_{110}]$, was prepared by the dissolution of 2.8 g (0.849 mol) of $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ and 2.0 g (0.008 mol) of $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ in 35 mL water. The solution was stirred at 60°C for 30 min. The resulting solution was cooled to room temperature, and to this solution 25 mL of concentrated phosphoric acid was added. The resulting yellow solution was refluxed for 18 h. The solution was cooled to room temperature, diluted with water (20 mL), and while stirring 10 g of solid KCl were added. The mixture was stirred and then evaporated to dryness. The residue was dissolved in water (30 mL) at 45 °C. Upon cooling to room temperature, yellow crystals formed. The crystals were collected by filtration, and the crystals were dried at 120–140°C, then, they were powdered and stored. The acidic form of the molybdenum-substituted heteropolyacid was obtained as described above for $\text{H}_{14}[\text{NaP}_5\text{W}_{30}\text{O}_{110}]$. Supported heteropolyacid catalyst was synthesized, according to our previous report⁹, by impregnating powdered SiO_2 with an aqueous solution of $\text{H}_{14}[\text{NaP}_5\text{W}_{29}\text{MoO}_{110}]$. After stirring the mixture, the solvent was evaporated. The residue was dried at 120°C and was calcined at 250°C (5 h) in a furnace prior to use. Silica-supported Preyssler $\text{H}_{14}[\text{NaP}_5\text{W}_{30}\text{O}_{110}]/\text{SiO}_2$ catalysts were prepared by impregnating Aerosil 300 silica with a methanol solution of $\text{H}_{14}[\text{NaP}_5\text{W}_{30}\text{O}_{110}]/\text{SiO}_2$ ¹³.

Catalytic acylation reaction: general procedure

General experimental procedure: A mixture of the aromatic compound (1 mmol), acetic anhydride (2 mmol) and heteropolyacid (0.1 g, 0.25 mmol of H^+) was heated with stirring at 80°C for 15–180 minutes. The progress of the reaction was followed by TLC. An aliquot from the reaction mixture (approximately 0.1 mL) was injected into the GC at an initial temperature of 50 °C for 1 min, followed by increasing the temperature at the rate of 10°C min^{-1} to the final temperature of 200°C, held for 20 min. Each analysis was carried out in triplicate to ensure reproducibility. On completion of the reaction, saturated sodium carbonate (20 mL) was added to the reaction mixture. The product was extracted with Et_2O (3 \times 10 mL). The catalyst is filtered off using a Buechner funnel (O = 6.0 cm) and washed with 20 mL dichloromethane. The filtrate is concentrated on a rotary evaporator. The organic layer was separated, and dried over anhydrous MgSO_4 . Evaporation of the solvent afforded the crude product, which was purified by column chromatography to afford *p*-methoxyacetophenone.

Analytcs

Reaction monitoring

TLC is not sensitive enough for reaction monitoring in this case. After 1.5 hours reaction time the TLC shows complete anisole conversion, while the GC analysis of the crude product detects anisole even after 4 hours of the reaction time (Table 1).

TLC

TLC conditions:

adsorbent: Macherey and Nagel Polygram SilG/UV plates, 0.2 mm

elution solvent: *n*-heptane/ethyl acetate 9:1

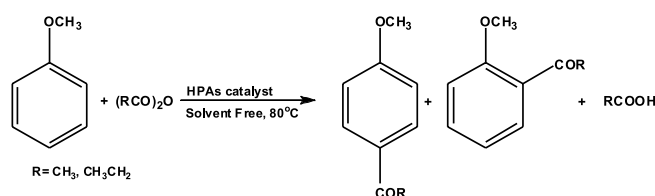
Dry the TLC after the first development and place it for a second development again into the eluent chamber to detect the side product *ortho*-methoxyacetophenone (Table 1).

Table 1. TLC conditions in the acylation of anisole

Rf	Substance
0.84	anisole
0.42	<i>para</i> -methoxyacetophenone
0.47	<i>ortho</i> -methoxyacetophenone

RESULTS AND DISCUSSION

The highly selective acylation of methoxybenzene with acetic anhydride at 80°C (Scheme 1) was carried out for the first time using the inexpensive, recyclable, and easily prepared Preyssler's anion as a catalyst.



Scheme 1. Acylation of methoxybenzene with acetic anhydride

The performance of this polyanion in different forms was compared with the Keggin-type catalysts $\text{H}_4[\text{SiMo}_{12}\text{O}_{40}]$, $\text{H}_4[\text{SiW}_{12}\text{O}_{40}]$, $\text{H}_3[\text{PW}_{12}\text{O}_{40}]$ and $\text{H}_3[\text{PMo}_{12}\text{O}_{40}]$.

A GC chromatogram of the liquid product from the reaction of methoxybenzene with acetic anhydride over Preyssler catalyst is presented in Fig. 1. The first two peaks correspond to the reactants, methoxybenzene (anisole) and acetic anhydride, respectively. The rest of the peaks are the products of the reaction. The major product was identified as *p*-methoxyacetophenone (46 – 98% yield), as expected. However, since only a single peak was observed in the chromatogram which related to *p*-methoxyacetophenone, it was then concluded that only *para* isomer was formed from the reaction, hence the selectivity of the *para* isomer is 100%. The results showed the shape selective characteristic of heteropolyacids catalysts towards *para* isomer rather than other isomers due to its smaller molecular sizes compared to its counterpart *ortho* or *meta* isomers. Among the products, acetic acid is the main side product obtained in high yield from the reaction and the acylation of anisole with acetic anhydride using heteropolyacids as catalysts. Since acetic acid can also be the source of acyl, it may influence the reaction products (Fig. 1).

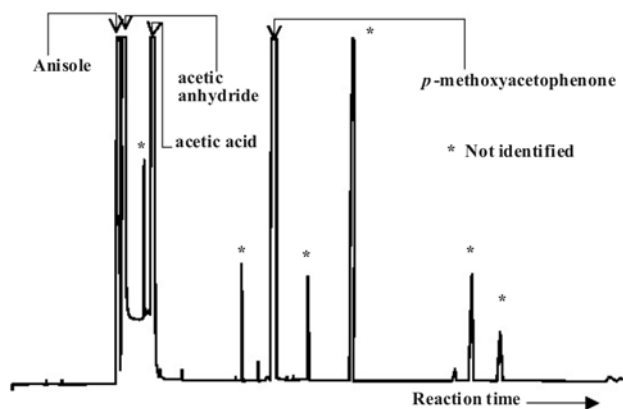
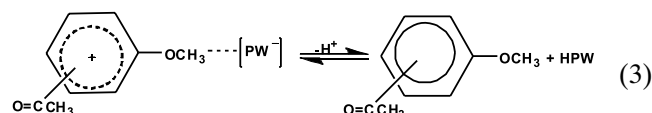
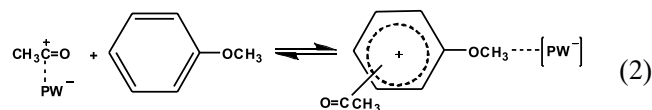
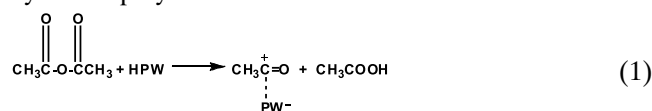
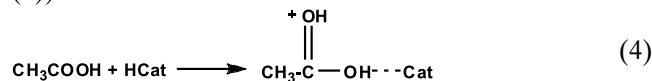


Figure 1. GC chromatogram of the acylation products catalysed by Preyssler heteropolyacid

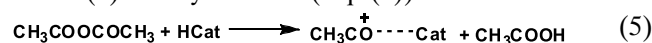
Anisole (methoxybenzene) is an *ortho/para* directing substrate for electrophilic substitution reactions, presenting a relatively high susceptibility to such reactions by means of the release of electron density from the methoxyoxygen atom to the aromatic ring, constituting itself in a very feasible substrate for the synthesis of substituted ketones. The possible pathways for the production of methoxyacetophenones in the Friedel-Crafts acylation of anisole (methoxybenzene) with acetic anhydride catalysed by heteropolyacids are shown below:



Ma et al.¹⁴ have pointed out the influence of the nature of the acylating agents, the character of the aromatic substrate and the nature of the active sites of the catalyst on the reaction mechanism. Accordingly, two types of charged electrophiles are responsible for the attack at the aromatic substrate: (1) a protonated carboxylic acid (Eq. (4)):



and (2) an acylium ion (Eq. (5)):



A low conversion of nearly 5% was found when acetic acid was used as an acylating agent, corroborating the assumptions that acylium ions are hardly formed from acetic acid and that *p*-MAP is formed by direct C-acylation of anisole (methoxybenzene) with acylium ions.

The product of methoxybenzene acylation in the presence of Preyssler, $\text{H}_{14}[\text{NaP}_5\text{W}_{30}\text{O}_{110}]/\text{SiO}_2$ (50%) was *p*-methoxyacetophenone isomer and it was identified and purified by column chromatography to afford *p*-methoxyacetophenone as a colorless crystalline solid (1.42 g, 91%), (mp = 35.6–37.5 °C), having >99% purity

by ^1H NMR, ^{13}C NMR, GC-IR and GC analysis, (Tables 2, 3, 4, entry 1).

The IR spectrum of synthetic *o*-methoxyacetophenone was identified an authentic sample and the yield of *o*-methoxyacetophenone isomer with use of Preyssler's catalyst was <1% (Table 2, entry 1).

The results (Table 2) show that Preyssler catalyst is better with respect to yield and to reaction. In all cases, the Preyssler heteropolyacids show higher activity compared with the Keggin-type heteropolyacids, zeolite, $\text{Hf}[\text{N}(\text{SO}_2\text{C}_8\text{F}_{17})_2]_4$ ¹³, $\text{Yb}(\text{OTf})_3$ ¹³ and H_2SO_4 (Table 2, entries 19–22). The yields of acylated products using other aromatic substrates are given in Table 4. In the presence of $\text{H}_{14}\text{-P}_5$, $\text{H}_{14}[\text{NaP}_5\text{W}_{30}\text{O}_{110}]$, methoxybenzene was converted to *p*-methoxyacetophenone with acetic anhydride in 98% yield with 100% regioselectivity at room temperature in 15 minutes (Table 2, entry 1). $\text{H}_{14}[\text{NaP}_5\text{W}_{29}\text{MoO}_{110}]$, $\text{H}_{14}\text{-P}_5\text{Mo}$ has good activity similar of Preyssler catalyst, 97% (Table 2, entry 2). It gives a 97% yield of *p*-methoxyacetophenone with 100% regioselectivity at room temperature in 15 minutes (Table 2, entry 2). The catalytic activity of Keggin heteropolyacids such as $\text{H}_4[\text{SiMo}_{12}\text{O}_{40}]$, $\text{H}_4[\text{SiW}_{12}\text{O}_{40}]$, $\text{H}_3[\text{PW}_{12}\text{O}_{40}]$ and $\text{H}_3[\text{PMo}_{12}\text{O}_{40}]$, was lower than Preyssler's anion. They give the yields of 58%, 70%, 96% and 61%, respectively, with 90–95% regioselectivity (Table 2, entries 3–6). The selective synthesis of the *p*-methoxybenzene isomer reflects the shape-regioselective characteristic of Preyssler catalyst. Using the silica-supported Preyssler's catalyst, the yield of *p*-methoxyacetophenone increased from 83% to 91% with an increase in catalyst loading from 10% to 50% (Table 2, entries 9–13). The results given in (Table 2, entries 9–18) show that Preyssler and Keggin heteropolyacid homogeneous catalysts with loadings of 10% to 50% are better with respect to the yield and to the reaction time.

In this reaction, the surface area of heteropolyacid bulk acids is typically, 1–10 m² g⁻¹ and their porosity is <0.1 cm³ g⁻¹. Because of this, for Friedel-Crafts reactions, supported heteropoly acids are usually preferred. But supported heteropolyacid catalysts have much greater number of surface acid sites than the bulk acids, hence they are more important for applications⁵. The acidity and catalytic activity of supported heteropolyacids depend on the type of the carrier, the HPA loading, conditions of pre-treatment, etc. Acidic or neutral substances such as SiO_2 , the most often used being SiO_2 . At low loadings, $\text{H}_3[\text{PW}_{12}\text{O}_{40}]$ form finely dispersed species on the SiO_2 surface; HPA crystal phase on silica (200–300 m² g⁻¹) is developed at an HPA loading above 20 wt.%. The model reaction was examined under solvent-free conditions at 80°C, and using *n*-hexane, nitromethane, acetonitrile, diethyl ether, chloroform and dichloromethane as solvents (Table 3). Reaction under solvent-free conditions, an approach that is gaining popularity as it eliminates the use of volatile organic solvents, afforded the highest yield (98%) after a 15 min reaction time. Moreover, shorter reaction times were used under solvent-free conditions compared to in-solvent conditions. The reaction temperature is not the reason for this differences (Table 3, entry 2). The pK_a of HPAs, which depends on the solvent, may account for the differences in yields. The yields from the

Table 2. Comparison of the results for the acylation of methoxybenzene with Preyssler's and other catalysts

Run	Catalyst ^b	Temp (°C)	Time (min)	Yield(%) ^{a,c} <i>p</i> -MOAP	^{d,e} Yield (%) <i>p</i> -MOAP	^f Yield(%) <i>o</i> -MOAP
1	H ₁₄ [NaP ₅ W ₃₀ O ₁₁₀]	80	15	^a 98(98, 97, 97) ^c	98 ^d , 98 ^e	<1%
2	H ₁₄ [NaP ₅ W ₂₉ MoO ₁₁₀]	80	15	^a 97(97, 96, 96) ^c	98 ^d , 98 ^e	<1%
3	H ₃ [PMo ₁₂ O ₄₀]	70	75	^a 61(60, 59, 58) ^c	69 ^d , 70 ^e	2.1
4	H ₃ [PW ₁₂ O ₄₀]	90	75	^a 96(96, 95, 93) ^c	97 ^d , 97.5 ^e	<1%
5	H ₄ [SiW ₁₂ O ₄₀]	70	75	^a 70(69, 67, 66) ^c	74 ^d , 74.4 ^e	1.5
6	H ₄ [SiMo ₁₂ O ₄₀]	80	75	^a 58(57, 56, 54) ^c	66 ^d , 66.8 ^e	1.9
7	HNa ₂ [PW ₁₂ O ₄₀]	85	75	^a 46(45, 43, 41) ^c	53 ^d , 53.5 ^e	2.4
8	H ₆ [P ₂ W ₁₈ O ₆₂]	85	75	^a 72(72, 70, 69) ^c	76.5 ^d , 77.3 ^e	<1%
9	H ₁₄ [NaP ₅ W ₃₀ O ₁₁₀]/SiO ₂ (10%)	80	65	^a 83(81, 80, 78) ^c	85 ^d , 85.8 ^e	2.9
10	H ₁₄ [NaP ₅ W ₃₀ O ₁₁₀]/SiO ₂ (20%)	80	65	^a 85(84, 83, 82) ^c	86 ^d , 86 ^e	2.6
11	H ₁₄ [NaP ₅ W ₃₀ O ₁₁₀]/SiO ₂ (30%)	80	65	^a 86(85, 84, 81) ^c	89 ^d , 89.6 ^e	2.1
12	H ₁₄ [NaP ₅ W ₃₀ O ₁₁₀]/SiO ₂ (40%)	80	65	^a 89(87, 86, 84) ^c	94 ^d , 94.5 ^e	2.4
13	H ₁₄ [NaP ₅ W ₃₀ O ₁₁₀]/SiO ₂ (50%)	80	65	^a 91(90, 89, 87) ^c	92 ^d , 92 ^e	2.2
14	H ₃ [PW ₁₂ O ₄₀]/SiO ₂ (10%)	90	70	^a 78(76, 74, 71) ^c	80 ^d , 80.4 ^e	3.7
15	H ₃ [PW ₁₂ O ₄₀]/SiO ₂ (20%)	90	70	^a 79(78, 76, 74) ^c	81 ^d , 81.5 ^e	3.4
16	H ₃ [PW ₁₂ O ₄₀]/SiO ₂ (30%)	90	70	^a 82(80, 78, 75) ^c	86 ^d , 86.4 ^e	3.6
17	H ₃ [PW ₁₂ O ₄₀]/SiO ₂ (40%)	110	70	^a 88(87, 85, 82) ^c	91 ^d , 91.2 ^e	3.3
18	H ₃ [PW ₁₂ O ₄₀]/SiO ₂ (50%)	110	70	^a 90(89, 88, 86) ^c	92 ^d , 92.3 ^e	3.7
19	Hf[N(SO ₂ C ₈ F ₁₇) ₂] ₄	100	60	80 ^a	83 ^d , 89.7 ^e	3.9
20	Yb(OTf) ₃	50	24	70 ^a	71 ^d , 79.4 ^e	4
21	Bi(OTf) ₃	50	120	80 ^a	84 ^d , 91.6 ^e	4.2
22	H ₂ SO ₄	80	20	90 ^a	92 ^d , 98.5 ^e	4.4

^{a,c,d,e,f} Isolated yields. ^{a,c,d,e,f} Yields calculated by GC. ^{a,f} Yield (%) for Acylating agent/methoxybenzene = 2:1 mmol, ^b amount of catalyst: (0.25 mmol), ^c In parentheses, yields obtained in the first, second, third reuse of the catalyst. ^d Yield (%) for Acylating agent/methoxybenzene = 2:10 mmol, ^e Yield (%) for Acylating agent/methoxybenzene = 2:100 mmol *p*-MOAP = *p*-methoxyacetophenone, *o*-MOAP = *o*-methoxyacetophenone

reaction in chloroform (27%) and diethyl ether (29%) were particularly poor.

Other substrates gave different yields for Ac₂O acylation (Table 4). The most interesting feature for toluene

Table 3. The effect of the solvent on the yield for Friedel-Crafts acylation of methoxybenzene by Ac₂O catalyzed by Preyssler's catalyst

Entry	Solvent	Time (min)	Temp (°C)	^a Yield(%)
1	free	15	80	98
2	CH ₃ NO ₂	180	101	51
3	CH ₃ CN	180	82	44
4	Et ₂ O	180	35	29
5	CHCl ₃	180	60	27
6	CH ₂ Cl ₂	180	38	76
7	n-Hexane	180	67	92

^a Yields were obtained using GC analysis. ^a isolated yields.

acylation is the excellent regioselectivity for *para*-acylation. The introduction of a methoxy group afforded higher yields of the acylation products (Table 4, entries 3, 7). In general, electron-donating groups such as alkyl or alkoxy afford both satisfactory yields and high *para*-regioselectivity. As expected, acylation of methoxybenzene is faster than those of alkylbenzenes and gives the acylated product in high yield. However, the *p*-selectivity for alkoxybenzenes is lower than alkylbenzenes (Table 4, entries 1, 7, 8). For example, *o*-alkoxyacetophenones were obtained respectively when *i*-butoxy-, *n*-hexoxy-, *n*-butoxy- and 1,2-dimethoxybenzene were used (Table 4, entries 2, 3, 4, 6). In the case of anthracene, 4 equivalents of acetic anhydride were needed for complete reaction (Table 4, entry 9). Thiophene is acetylated in 92% yield with a 15 min reaction time at 60°C, (Table 4, entry 11). Rather, we focussed on halogen-free Friedel-Crafts acylation (Ta-

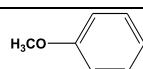
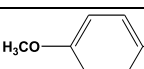
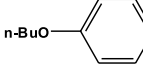
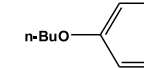
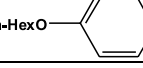
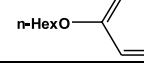
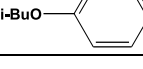
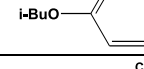
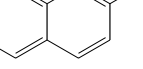
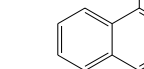
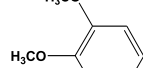
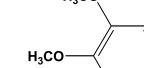
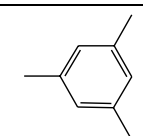
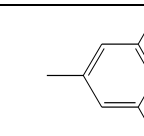
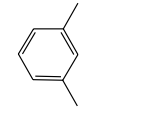
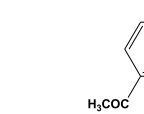
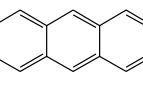
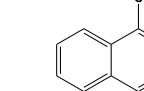
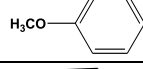
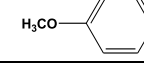
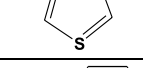
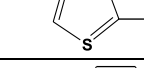
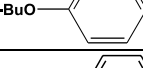
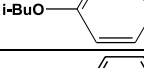
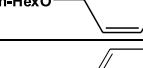
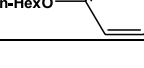
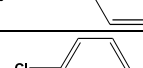
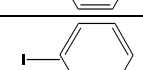
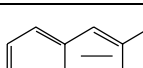
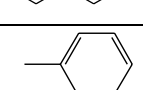
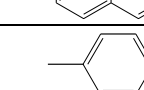
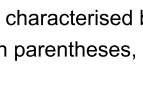
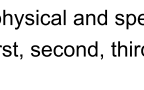
ble 4, entries 15, 16). Propionic anhydride can also be used with similar efficiency and excellent selectivity (Table 4, entries 10, 12, 13). Toluene and *m*-xylene were acylated to give methylacetophenone and dimethylacetophenone in high yields under very mild conditions (Table 4, entries 8, 18).

It is noteworthy that the catalyst may be reused without significant loss of activity.

In order to know whether the catalyst would succumb to poisoning and lose its catalytic activity during the reaction, we investigated the reusability of the catalyst. For this purpose we first carried out the reaction in the presence of the catalyst. After the completion of the reaction, the catalyst was removed and washed with diethyl ether and subjected to a second, third and fourth runs of the reaction process with the same substrates. The results of the first experiment and subsequent experiments were almost consistent in the yields (after three runs) and the catalytic activity of H₁₄[NaP₅W₃₀O₁₁₀] and the heteropolyacids (HPAs) was almost the same as that of fresh catalyst. We have thus found that Preyssler catalyst can be reused several times, without any appreciable loss of activity and after recovery the catalytic activity was decreased only 2–4%, pointing to the stability and retention of catalytic capability of this useful polyanion. The IR spectra of the resulting solids indicate that the catalyst can be recovered without structural degradation (Fig. 2). Acylation reaction was created in the presence of recycled catalysts and the results are summarized in (Table 2, entries 1–18 and Table 4, entries 1–13 and 17, 18). The recovered catalyst was reused successfully (Fig. 2).

Figure 3 compares the FT-IR spectra of the Preyssler HPA, Preyssler/F-silica, 15% Preyssler/silica, and pure silica. From Figure 3, it can be seen that the Preyssler HPA sample prepared in this work showed all the IR

Table 4. The reactions of aromatic compounds with anhydrides catalyzed by Preyssler's catalyst under solvent-free conditions at 60–80°C

Entry	Substrate	Time (min)	^a Product	^b Yield(%) <i>p</i> -MOAP	^b Yield(%) <i>o</i> -MOAP
1		15		98(97, 96, 94) ^c	<1
2		76		96(96, 95, 94) ^c	2.7
3		69		96(95, 94, 92) ^c	2.5
4		74		93(92, 90, 88) ^c	3.5
5		63		92(91, 90, 87) ^c	4.8
6		16		91(89, 87, 84) ^c	6.5
7		83		90(89, 87, 84) ^c	5.5
8		84		90(89, 88, 86) ^c	6.1
9		89		87(86, 84, 81) ^c	7.7
10		33		97(96, 95, 92) ^c	<1
11		15		92(91, 90, 87) ^c	4.5
12		106		91(89, 88, 86) ^c	6.5
13		110		94(93, 91, 89) ^c	4.3
14		180	No Reaction	0	0
15		180	No Reaction	0	0
16		180	No Reaction	0	0
17		180		89(88, 87, 87) ^c	6.8
18		180		91(90, 89, 89) ^c	3.8

^aAll products were characterised by comparison of their physical and spectral data with those of authentic samples.^bIsolated yields. ^cIn parentheses, yields obtained in the first, second, third reuse of the catalyst.

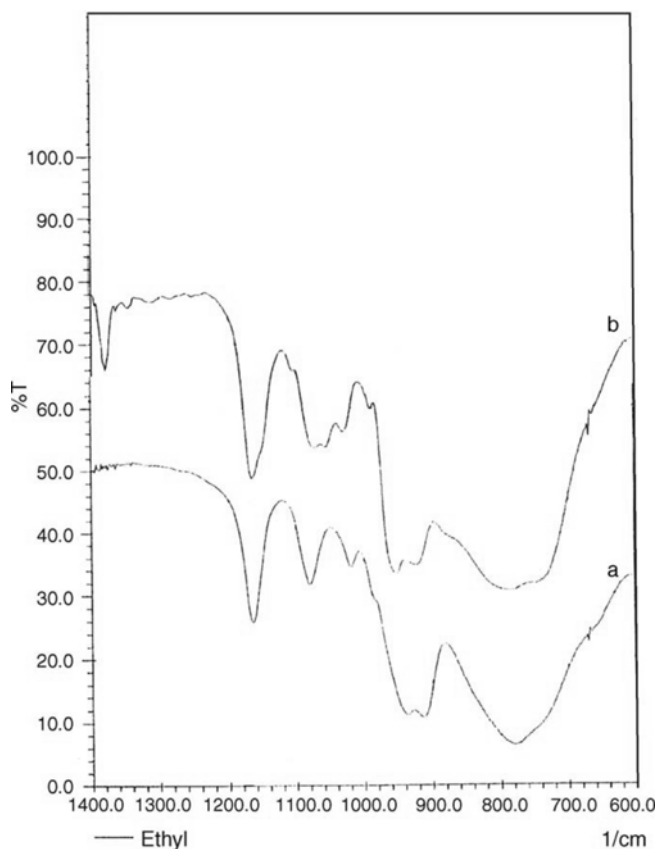


Figure 2. IR spectrum of Preyssler catalyst before (a) and after (b) the catalytic reaction

vibration peaks assigned to a Preyssler structure, and the locations of featured peaks are in well agreement with those in the previous reports^{12, 13}. In detail, the Preyssler HPA sample displayed vibrations at 1,165, 1,082 and 1,021 cm^{-1} for P-O stretching in Preyssler structure, 940 and 913 cm^{-1} for W-O-W stretching, 788 cm^{-1} for W=O stretching, and 573 cm^{-1} for P-O bending. For pure silica, a very broad Si-O-Si stretching peak occurred around 1,100 cm^{-1} ^{12, 13}. This may hinder the clear observation of the three P-O stretching peaks in this area for Preyssler/F-silica due to the strong background. However, the two W-O-W stretching peaks at 940 and 913 cm^{-1} could be clearly detected for Preyssler/F-silica, which strongly suggest that the Preyssler's anions chemically adsorbed onto the surface of F-silica through KH550 retain their Preyssler structure. A previous study showed that the reaction of Preyssler HPA with functionalized silica affected the position of the W-O-W stretching peaks^{12, 13}. However, in our case, Preyssler/F-silica in Figure. 3 only showed a widening for W-O-W stretching peaks without observing a clear shift. On the other hand, for Preyssler HPA/silica, no peaks assigned to Preyssler structure were observed. This is partially because of the strong background of pure silica, but the more important reason may be that the interaction between Preyssler's anions and hydroxyls in the surface of silica mostly caused the distortion of anions, and thus substantially weakened the IR vibrations and masked up by the silica background.

CONCLUSIONS

In conclusion, heteropolyacids (preferably $\text{H}_{14}[\text{NaP}_5\text{W}_{30}\text{O}_{110}]$), are active and environmentally

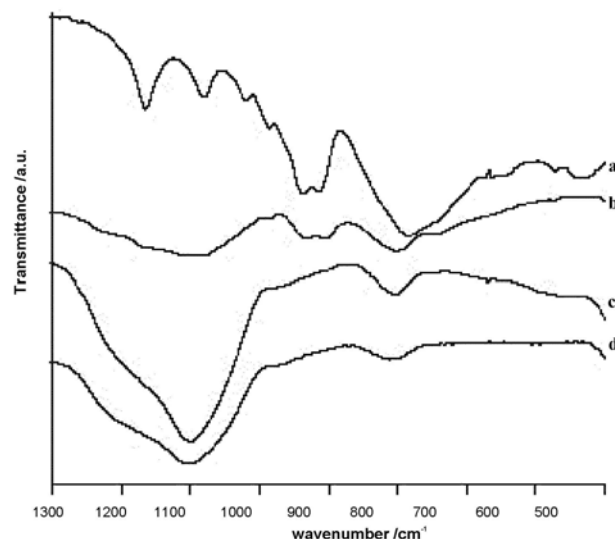


Figure 3. The FT-IR spectra of Preyssler HPA (a), Preyssler/F-silica (b), 20% Preyssler/silica (c), and pure silica (d)

friendly catalysts for the Friedel-Crafts acylation of aromatic compounds. These solid acids are superior in activity to the conventional acid catalysts such as H_2SO_4 , which is in line with the stronger acidity of HPAs. We have established Preyssler's anion as a convenient heterogeneous catalyst for the acylation of alkylbenzene and alkoxybenzene derivatives using aliphatic anhydrides as the acylating reagents. The *p*-regioselectivity for acylation of alkoxybenzenes is higher than that for acylation of alkylbenzenes. This method offers the noteworthy advantages of a heterogeneous catalyst that is easily separated, gives high yields, is inexpensive and they can be reused after a simple work-up, albeit with reduced activity.

Acknowledgements

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