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Esterification of phthalic anhydride with 1-butanol and 2-ethylhexanol catalyzed by heteropolyacids

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Abstract

Esterification of phthalic anhydride with 2-ethylhexanol and 1-butanol and ester decomposition of dioctyl phthalate (DOP) in presence of Keggin; $H_3PW_{12}O_{40}$, $H_4SiW_{12}O_{40}$, $H_4SiMo_{12}O_{40}$, Wells–Dawson; $H_6P_2W_{18}O_{62}$, $H_6P_2W_{17}MoO_{62}$ and Preyssler; $H_{14}[NaP_5W_{29}MoO_{110}]$, $H_{14}[NaP_5W_{30}O_{110}]$, type heteropolyacids have been investigated. The heteropolyacids with Preyssler and Wells–Dawson structures and their molybdenum substituted derivatives show higher activity in esterification and ester decomposition reactions than Keggin type heteropolyacids. A complete conversion of phthalic anhydride to dioctyl phthalate and dibutyl phthalate are achieved in 2 h in presence of molybdenum substituted Preyssler heteropolyacid. In the decomposition of dioctyl phthalate in the presence of Preyssler heteropolyacid, 2-ethylhexene is formed in quantitative yield.
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1. Introduction

The extensive demand for cleaner environment is forcing chemical industry to use less hazardous materials. In this regard, heteropolyacids attracted considerable amount of interest due to the less toxic behavior in addition of possessing higher acidity [1–3]. Heteropolyacids are widely used in variety of acid-catalyzed reactions such as esterification [4], etherification [5], hydration of olefin [6], de-esterification [7], dehydration of alcohol [8] and polymerization of tetrahydrofuran [9] in homogenous

and heterogeneous systems. Part of this interest also arises from their enhanced activity and selectivity [10]. Heteropolyacids in contrast to conventional acids do not cause coloration of product and a number of them have been used in the esterification of various alcohols and carboxylic acids [11–18]. The heteropolyacids are strong acids, for instance, it has been reported that their activity in dehydration reaction is about 100 times of sulfuric acid [10]. Acidity of heteropolyacids varies with the structural type of heteropolyacid. Keggin type structures show higher acidity than the other types [19], and their acid strength depends on the type of addenda and hetero atom, which can be tuned to a suitable catalyst for the acid-catalyzed reactions [20]. However, their limited hydrolytic stability is a draw back for their use in high temperature processes.

Several Keggin type heteropolyacids have been used as acid catalyst for the esterification and results show that the behavior of heteropolyacid not only depends on the acidity and the type of heteropolyacid but also strongly depends on the type of reaction system [4]. Although, the Keggin type heteropolyacids have widely been used as acid catalyst for the esterification [21], the potential applications of Wells–Dawson and Preyssler heteropolyacids in the esterification have not been fully explored. Therefore, search for finding other heteropolyacids with higher stability, specially among Dawson and Preyssler types of heteropolyacids, could be fruitful for the acid-catalyzed esterification of specific esters such as dioctyl phthalate (DOP), di-isodecyl phthalate (DIDP) and diisononyl phthalate, which are important additives in PVC formulations.

Here we report the esterification of phthalic anhydride with 2-ethylhexanol and 1-butanol at relatively low temperature in the presence of several Keggin, Dawson and Preyssler heteropolyacids in addition to ester decomposition of dioctyl phthalate and demonstrate the significance of heteropolyacids with different structure as solid catalysts in the light of previous studies [11,22].

2. Experimental

2.1. Materials

Phthalic anhydride, 2-ethylhexanol, 1-butanol, $H_4SiW_{12}O_{40}$, $Na_2MoO_4 \cdot 2H_2O$ and $Na_2WO_4 \cdot 2H_2O$ were purchased from Merck and used without further purification. The Preyssler heteropolyanion, K_{14}-$[NaP_5W_{30}O_{110}]$, was prepared from $Na_2WO_4 \cdot 2H_2O$ according to the previously reported method [23] and converted to corresponding acid by passing through Dowex-50W-X8 ion exchange column. $K_6P_2W_{18}O_{62}$ was the second crop in crystallization of $K_{14}[NaP_5W_{30}O_{110}]$ and was converted to its form acid as described above. $H_4SiMo_{12}O_{40}$ and $H_3PW_{12}O_{40}$ were prepared from $Na_2MoO_4 \cdot 2H_2O$ and $Na_2WO_4 \cdot 2H_2O$ as described by North [24] and Bailer [25], respectively. All prepared heteropolyacids were purified by crystallization and their purity was confirmed by their characteristic peaks in infrared spectrum.

For the preparation of molybdenum substituted Preyssler heteropolyanion, $K_{14}[NaP_5W_{29}MoO_{110}]$, a procedure similar to the preparation of $K_{14}[NaP_5W_{30}$-$O_{110}]$ was adapted. In a typical experiment, 56 g (0.169 mol) $Na_2WO_4 \cdot 2H_2O$ and 2 g (0.008 mol) $Na_2MoO_4 \cdot 2H_2O$ were dissolved in 70 ml water and mixed at 60 °C for 30 min. Then solution was cooled to room temperature and 45 ml concentrated phosphoric acid was added. The resulted yellow solution was refluxed for 18 h. The color turned to dark green at the end of reaction. The solution was brought to room temperature, diluted with 30 ml water and then during a vigorous stirring 20 g potassium chloride was added. The mixture was stirred for 30 min and then heated up to dryness and a greenish solid obtained. This raw product was dissolved in 70 ml warm water and upon cooling to room temperature yellow crystals formed, which were collected and recrystallized from boiling water (yield, 20%). The molybdenum substituted heteropolyanion, $H_{14}[NaP_5W_{29}MoO_{110}]$, was converted to its corresponding acid as described above for unsubstituted analogue. IR spectra: 1616s, 1165s, 1082s, 1020m, 964sh, 935s, 781s cm^{-1}. Anal. Calcd. for $H_{14}[NaP_5W_{29}MoO_{110}]$ (%): W, 72.25; Mo, 1.30; P, 2.09; Na, 0.31; H, 0.19. Found: W, 71.74; Mo, 1.32; P, 2.09; Na, 0.32; H, 0.19. The complete characterization of molybdenum substituted Preyssler heteropolyanion, $H_{14}[NaP_5W_{29}MoO_{110}]$ will be reported elsewhere. In addition to Preyssler heteropolyanion, a Wells–Dawson heteropolyanion, $K_6[P_2W_{17}MoO_{62}]$, as a byproduct was crystallized from the mother liquor overnight. IR spectra: 1607s, 1092s, 976s, 908m, 770s cm^{-1}. Anal. Calcd. for $K_6[P_2W_{17}MoO_{62}]$ (%): W, 69.30; Mo, 2.13; P, 1.37; K, 5.20. Found: W, 69.31; Mo, 2.15; P, 1.32; K, 5.16. $K_6[P_2W_{17}MoO_{62}]$ was converted to corresponding acid by passing through Dowex-50W-X8 ion exchange column.

2.2. Methods

Infrared spectra were recorded (KBr pellets) on a Shimadzu model FT-IR 4600 spectrometer. Proton NMR spectra were recorded in CDCl$_3$ on a Bruker AC-80 spectrometer. A Varian Aerograph 1400 gas chromatograph was used to analyze products. The GC–MS was performed on a Shimadzu QP 1000 EX with OV1 column. Tungsten and molybdenum were determined by XRF spectroscopy, phosphorus by atomic absorption spectroscopy, sodium and potassium by flame photometry.

2.3. Catalytic tests

All catalysts were dried overnight prior to use. Esterification and ester decomposition reactions were performed in a round bottom flask, which was equipped with Dean–Stark trap and condenser and immersed in oil bath. All catalytic tests were performed in homogenous system. In a typical reaction, 49.4 g (0.3 mol) phthalic anhydride, 61.7 g (0.6 mol) n-butanol or 78 g (0.6 mol) 2-ethylhexanol and 1.74×10^{-4} mol heteropolyacid were added to 50 ml toluene and the mixture was refluxed for 3 h. The progress of reaction was monitored by collected water in the Dean–Stark trap. After esterification, the catalyst was extracted from reaction mixture by aqueous solution of sodium carbonate and the ester was characterized by IR, NMR and GC as the sole product. Conversions were calculated from the amount of collected water. Esterification reaction also was performed without catalyst.

For the ester decomposition 117 g (0.3 mol) dioctyl phthalate was added to 50 ml toluene and mixture was refluxed for 5 h at 134 °C. The resulting water was removed by a Dean–Stark trap. TLC of the reaction mixture with ether/petroleum ether showed five spots. Four of them were easily characterized as solvent, phthalic anhydride, phthalic acid, dioctyl phthalate and the fifth spot was identified by GC–MS as 2-ethylhexene (M^{+}, 112). Phthalic anhydride and phthalic acid were isolated from reaction mixture by fractional crystallization with melting points of 130 and 210 °C, respectively. Finally, 2-ethylhexene was removed from the remaining solution by distillation. Phthalic acid was isolated only as the minor product (<0.2%). All conversions were calculated by measuring weight of products.

Stability of catalysts, $H_{14}[NaP_5W_{29}MoO_{110}]$ and $H_3[PW_{12}O_{40}]$, have also been investigated to some extent. After completion of esterification, 2–4 h, catalysts were recovered from reaction mixture in form of salts and was converted to acids and reused. There was no decrease in activity of catalysts for at least three consecutive cycles.

3. Results and discussion

Esterification of phthalic anhydride with 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 and the resulting water must be removed from the reaction mixture. Esterification yields of phthalic anhydride with 2-ethylhexanol and 1-butanol for various heteropolyacids are given in Tables 1 and 2. It is clear that esterification yield depends on several factors, and the nature of acid is the dominant parameter in esteri-

Table 1

Esterification of 1-butanol and 2-ethylhexanol catalyzed by various heteropolyacids

Catalyst	1-Butanol		2-Ethylhexanol	
	Reaction time (min)	Conversion (%)	Reaction time (min)	Conversion (%)
$H_{14}NaP_5W_{29}MoO_{110}$	210	100	120	100
$H_3PW_{12}O_{40}$	240	77	240	100
$H_4SiW_{12}O_{40}$	240	82	200	100
$H_4SiMo_{12}O_{40}$	240	49	240	54
$H_{14}NaP_5W_{30}O_{110}$	240	95	180	100
$H_6P_2W_{18}O_{62}$	240	91	180	90
$H_6P_2W_{17}MoO_{62}$	240	93	160	100
H_2SO_4	240	29	240	35
H_2SO_4[a]	240	60	240	65
PTSA[b]	240	35	240	39
HY-zeolite	240	20	240	29
Dowex-50W-80	240	20	240	29
H_2WO_4	240	20	240	29
None	240	20	240	29

[a] Five times of molar concentration of solid acids.
[b] p-Toluenesulfonic acid.

Table 2
Ester decomposition of dioctyl phthalate to phthalic acid and 2-ethylhexene with various heteropolyacid catalysts

Catalyst	Conversion (%)
$H_{14}NaP_5W_{29}MoO_{110}$	81
$H_{14}NaP_5W_{30}O_{110}$	71
$H_3PW_{12}O_{40}$	41
$H_4SiW_{12}O_{40}$	38
$H_4SiMo_{12}O_{40}$	–
$H_6P_2W_{17}MoO_{62}$	68
$H_6P_2W_{18}O_{62}$	65
H_2SO_4[a]	–
PTSA[a]	–

[a] Five times of molar concentration of heteropolyacids.

fication of both alcohols, however, the effect of alcohol also should not be ignored. Esterification yields of 2-ethylhexanol in the present work are higher than that of 1-butanol due to the higher boiling point of the former alcohol and consequently higher reaction rate. Among three heteropolyacids with Keggin structure used in present study, $H_4SiW_{12}O_{40}$ shows higher activity, however, by considering activity per unit mole of proton, a higher activity may be concluded for the $H_3PW_{12}O_{40}$. A significant decrease in esterification yield was observed with molybdenum containing Keggin heteropolyacid. The trend observed in esterification with Keggin heteropolyacids in the present study is in good agreement with the previously reported acidity order of $H_3PW_{12}O_{40} > H_4SiW_{12}O_{40} > H_4SiMo_{12}O_{40}$ [10]. Furthermore, it is well known that by changing the central atom of heteropolyacid from a high valent to a low valent element, its acidity decreases as a result of increasing the negative charge of heteropolyanion [4]. The effect of central atom in acidity strength of Keggin type heteropolyacid and consequently in esterification yields is confirmed by the reported Hammett acidity values for $H_3PW_{12}O_{40}$ and $H_4SiW_{12}O_{40}$ [26]. Generally speaking, a heteropolyacid with tungsten addenda atom shows higher acidity [10], and thermal stability and also lower reduction potential than a molybdenum analogue. It seems that with change of counter ion, addenda atom or heteroatoms in heteropolyacids one can tune them for certain application [27].

For the comparison, heteropolyacids with Dawson structures, $H_6[P_2W_{18}O_{62}]$ and $H_6[P_2W_{17}MoO_{62}]$ were also employed as acid catalysts for the ester-

ification of phthalic anhydride with 1-butanol and 2-ethylhexanol. Dawson type heteropolyacids in the present study show lower activity than $H_3PW_{12}O_{40}$, $H_4SiW_{12}O_{40}$ and higher activity than $H_4SiMo_{12}O_{40}$, per unit mole of protons, in esterification of phthalic anhydride with 1-butanol and 2-ethylhexanol. This observation is in good agreement with the previously reported esterification rate constant of propionic acid with isobutyl alcohol for $H_3PW_{12}O_{40}$, $H_4SiW_{12}O_{40}$ and $H_6[P_2W_{18}O_{62}]$ [4] and their Hammett acidity values [26]. As reported earlier, when tungsten is replaced by molybdenum the negative charge on the oxygen atoms increases which leads to decrease in acidity and esterification yields [10,28]. It is also interesting to note that by replacing one of the tungsten atoms of $H_6[P_2W_{18}O_{62}]$ with molybdenum, the esterification yield of phthalic anhydride with 2-ethylhexanol increases appreciably, however, increase in esterification yield of 1-butanol is much less drastic. The reason for this effect is not clear at this time, however, it seems by replacing tungsten with molybdenum in Dawson structure, symmetry is decreased. In this context, distortion of $H_6[P_2W_{17}MoO_{62}]$ and increase in acidity is tentatively suggested. The predominant effect may be revealed only by direct acidity measurement of the molybdenum substituted heteropolyacid.

The heteropolyacids with Preyssler structure in this work, $H_{14}[NaP_5W_{30}O_{110}]$ and $H_{14}[NaP_5W_{29}MoO_{110}]$, show higher yields in esterification due to the higher number of acidic protons. Interestingly, again by replacing one of the tungsten atoms with molybdenum in the Preyssler type heteropolyacid, rate of the reaction increased and esterification yields of 2-etheylhexanol and 1-butanol reached to 100% in 120 and 210 min, respectively. Role of molybdenum as addenda atom in the rate of reaction becomes more evident by comparing yields in esterification of 2-ethylhexanol. Apparently, heteropolyacids with Preyssler structure are more effective acid catalysts for the esterification of 2-etheylhexanol and 1-butanol. The molybdenum substituted Preyssler heteropolyacid, $H_{14}[NaP_5W_{29}MoO_{110}]$, is a blue type heteropolyacid and during esterification color of solution changes from green to blue, which indicates the reduction of Mo(VI) to Mo(V) and consequently increase in acidity.

The effect of solvent and also the amount of catalyst on the esterification of phthalic anhydride with
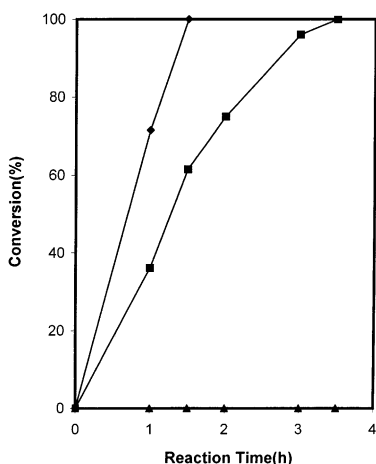
Fig. 1. Conversion of 1-butanol as a function of time in presence of $H_{14}[NaP_5W_{29}MoO_{110}]$ for various solvents; (■) toluene, (◆) xylene, (▲) dichloromethane.

1-butanol in presence of $H_{14}[NaP_5W_{29}MoO_{110}]$ are given in Figs. 1 and 2, respectively. Interestingly, conversion of 1-butanol in dichloromethane at reflux temperature, 100 °C, was below detection limit and yields in xylene were substantially higher than in toluene. Furthermore, 80% yield has been reported for the esterification of phthalic anhydride with 2-ethylhexanol in dichloroethane in presence of 3 g $H_3PW_{12}O_{40}$ at
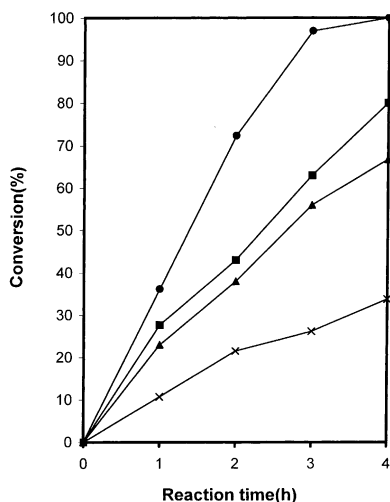

Fig. 2. Conversion of 1-butanol as a function of time for various amounts of $H_{14}[NaP_5W_{29}MoO_{110}]$; (●)1.27 g, (■) 0.7 g, (▲) 0.5 g, (×) 0.127 g.

110 °C in 2 h [22]. In the present study, the above mentioned reaction in toluene showed 57% yields with 0.5 g $H_3PW_{12}O_{40}$ in 2 h. This clearly demonstrate the influence of refluxing temperature on the yields, however, effect of other parameters such as conductivity and deprotonation rate of acid in conversion cannot be completely ruled out. Comparison of yields of several classical acids such as H_2SO_4 and PTSA in present work along with several previously reported oxide solid acids such as titanium, zirconium and zinc oxides [29], in esterification of phthalic anhydride show the unique behavior of heteropolyacids among solid acids in acid-catalyzed reactions. Furthermore, as shown in Fig. 2, the rate of esterification of phthalic anhydride with 1-butanol is a function of catalyst amount and yields reaches to 100% in presence of 1.27 g catalyst, $H_{14}[NaP_5W_{29}MoO_{110}]$, in 4 h.

Ester decomposition yields of dioctyl phthalate by various heteropolyacids are given in Table 2. The trend in ester decomposition of dioctyl phthalate by Keggin type heteropolyacids is similar to esterification reactions in this work. Similar to esterification reactions, heteropolyacids with Preyssler structure also show higher activity than Keggin and Dawson types structure. However, the role of molybdenum as addenda atom in ester decomposition yields is more pronounced. It is interesting to note that Keggin type heteropolyacid with molybdenum as addenda atom exhibits lower acidity and consequently lower activity in esterification and ester decomposition, whereas replacement of one of the tungsten by molybdenum in Preyssler and Dawson type heteropolyacids increases their acidity. It seems that a significant distortions arises by the replacement of one of the tungsten by molybdenum in the Preyssler and Dawson type heteropolyacid and causes a significant increase in their activity in acid-catalyzed reactions. In contrast to the most of heteropolyacids, which are effective acid catalysts for the ester decomposition of dioctyl phthalate; sulfuric acid and PTSA even with five times of molar concentration with respect to heteropolyacids exhibit no activity in ester decomposition. Finally, it is worth to mention that the heteropolyacids used in this work are able to dehydrate phthalic acid to phthalic anhydride, whereas sulfuric acid or PTSA are not. This is consistent with the observation of very small amount of phthalic acid in the decomposition products of dioctyl phthalate.

4. Conclusion

Heteropolyacids are effective solid acid catalysts for esterification of phthalic anhydride and ester decomposition of dioctyl phthalate. Among various heteropolyacids used for esterification and ester decomposition, the Preyssler type heteropolyacid shows higher activity than heteropolyacid with Keggin structure due to the higher number of acidic protons. Molybdenum substituted Preyssler and Wells–Dawson type heteropolyacids exhibit higher activity than unsubstituted counter part which is attributed to the reduction of Mo(VI) to Mo(V) and enhanced acidity.

Acknowledgements

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