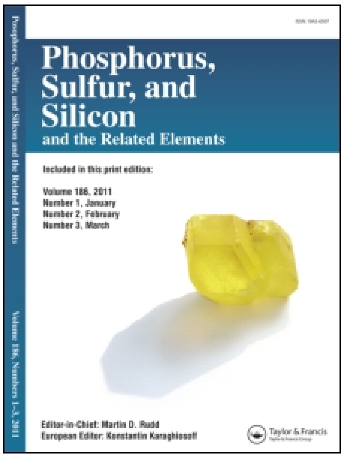

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Divanadium-substituted molybdophosphate acid, $H_5PMo_{10}V_2O_{40}$, efficiently catalyzes the synthesis of ethylhexanoate from hexanoic acid and ethanol at reflux temperature and under solventless conditions. Comparison of $H_5PMo_{10}V_2O_{40}$ with the other heteropolyacids showed that this catalyst gives the highest total yield of ethylhexanoate. The effects of the molar ratio of acid:alcohol, reaction times, and temperatures were studied.

Keywords Catalyst; esterification; ethylhexanoate; heteropolyacid; hexanoic acid; vanadium (V)-substituted heteropolymolybdates

INTRODUCTION

Esterification, with no doubt, continues to play important roles both in organic synthesis and in the chemical industry. Since acid catalysis is one of the most popular methods for esterification, numerous articles are available that relate to this purpose.[1–3] When the substrates are acid-resistant, the reaction is usually carried out in the presence of Brønsted acids such as HCl, HBr, H_2SO_4, $NaHSO_4$, $ClSO_3H$, NH_2SO_3H, H_3PO_4, HBF_4, AcOH, and camphorsulfonic acid. Most of these catalysts are corrosive and virulent, and need to be neutralized at the end of reaction with various bases.

All chemical processes, not only esterification, should be performed as "green" as possible.[4,5] For this reason, various solid acids are utilized

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for esterification reactions. Metal-containing Lewis acid catalysts,[6] Nafion-H,[7] amberlyst 15,[8] amberlyst IR120, wolfatit KSP200 (an ion-exchange resin),[9] zeolites,[10] Nb_2O_5,[11] $FeCl_3$ supported on salicylic resin,[12] $Fe(ClO_4)_3$ $(ROH)_6/SiO_2$,[13] $NaHSO_4/SiO_2$,[14] phosphorus oxides,[15] Ph_3SbO/P_4S_{10},[16] ZrO_2 and Mo-ZrO_2,[17] graphite bisulfate,[18] natural montmorillonite,[19] niobic acid,[20] sulfated oxides,[21] and heteropolyacids,[22,23] were reported in the literature for esterification reactions.

Nowadays, the research and development in the field of esterification has been directed towards the use of catalysts with strong Brønsted acidity, as they have enhanced performance, are inexpensive, less hazardous to the environment, easily prepared being recyclable and stable.[24–26] Recently, heteropolyacids have attracted much attention and being studied in many esterification reactions.[27–29]

However, because their special structural topology and versatile properties, which can be tuned at the atomic/molecular levels through modification of the structure type, the central heteroatom, and the transition metal-substituted atoms,[30–33] there is still a broad scope for research on various heteropolyacids in esterification.

The aim of the present study, in continuation of our earlier work on catalytic applications of heteropolyacids,[34,35] is to assess and use the heteropolyacid catalysts in the synthesis of ethylhexanoate. The selected catalyst was vanadium (V)-substituted heteropolymolybdate, $H_5PMo_{10}V_2O_{40}$.

We focused our study on the relationship between the yields of ester produced with molar ratio of acid:alcohol, alcohol:acid, temperatures, and reaction conditions.

RESULTS AND DISCUSSION

The esterification of hexanoic acid with ethanol is an acyl nucleophilic substitution. The reaction is relatively slow and needs activation either by high temperature or by a catalyst. This work has been performed to study the catalytic behavior of $H_5PMo_{10}V_2O_{40}$ in esterification of hexanoic acid with ethanol and was also extended to the other heteropolyacids such as $H_6PMo_9V_3O_{40}$, $H_4PMo_{11}VO_{40}$, $H_4SiW_{12}O_{40}$, $H_3PMo_{10}O_{40}$, and $H_6P_2W_{18}O_{62}$.

The results are shown in Table I. By comparison, it is evident that $H_5PMo_{10}V_2O_{40}$, is the catalyst of choice; all other catalysts were found to be less active and to have nearly identical activity. A significant interpretation for different activities of heteropolyacids is very difficult. Acidity, basicity, and pseudo liquid behavior are the principal factors

TABLE I Effect of Various Catalysts on Esterification of Hexanoic Acid in the Presence of Ethanol

Entry	Catalyst	Yield of ethylhexanoate (%)[a]
1	$H_5PMo_{10}V_2O_{40}$	93.8
2	$H_4PMo_{11}VO_{40}$	10.9
3	$H_6PMo_9V_3O_{40}$	11.8
4	$H_3PMo_{12}O_{40}$	11.8
5	$H_4\ SiW_{12}O_{40}$	11.9
6	$H_6P_2W_{18}O_{62}$	11.9

[a] Yields determined by GC/MS.

governing the acid catalysis of solid heteropolyacids. The acidic properties are mainly controlled by (i) the structure and composition of the heteropolyanion itself, (ii) the counter cations, and (iii) the dispersion on supports. The acid strength can be controlled mainly by (i), and the number of acid sites is greatly influenced by (ii) and (iii). In addition, the soft basicity of the heteropolyanion itself sometimes plays an important role for high catalytic activity in acid-catalyzed reactions. The acid strength for hydrogen forms in the solid state reflects in general the acidity in solution, and it decreases when W is replaced by Mo and when the central P atom is replaced by Si for Keggin heteropolyacids, which are stronger acids than Dawson heteropolyacids.[36] However, it was reported for heteropolyacids of Mo that its acid strength in solution is not correlated with that in solid.[37] Additionally, the acid properties of heteropolyacids are quite well documented in terms of dissociation constants and Hammett acidity function.[38,39]

As can be seen in Table I, among the studied catalysts, $H_5PMo_{10}V_2O_{40}$ gives the highest yield in this reaction. Despite the importance and versatility of reactions catalyzed by vanadium (V)-substituted heteropolymolybdates (HPA-n), there is only limited information about their acidic and redox mechanisms. HPA-n in solution is an extremely complex system, and the higher the n value, the more complex the system is. The HPA-n solutions contain a great number of polyanions, positional isomers, and monomeric metallospecies.[40,41]

One of the important factors that affects the activity of polyanions is the energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied orbital (LUMO). We believe that the energy and composition of the LUMOs have significant effects on the activity of the studied heteropolyacids. In Keggin series, for $H_5PMo_{10}V_2O_{40}$, the metal substitution may modify the energy and composition of the LUMO. In addition, the higher activity of the $H_5PMo_{10}V_2O_{40}$ can be

TABLE II Effect of Molar Ratio of Reactants on the Yield of Produced Ethylhexanoate in the Presence of $H_5PMo_{10}V_2O_{40}$

Entry	Molar ratio of acid:alcohol	Yield of ethylhexanoate (%)[a]	Molar ratio of alcohol:acid	Yield of ethylhexanoate (%)[a]
1	1:1	88.2	1:1	18.7
2	1:2	37.5	1:2	31.5
3	1:3	56.0	1:3	16.2
4	1:4	40.2	1:4	16.1
5	1:5	23.8	1:5	14.8
6	1:6	25.3	1:6	13.3
7	1:7	21.3	1:7	93.8

[a] Yields determined by GC/MS.

attributed to the concentration of protons, strong acid sites that require in esterification reactions and produced VO_2^+ in reaction course as an active species.

With the catalyst of choice for this reaction, $H_5PMo_{10}V_2O_{40}$, the reaction was carried out with various molar ratios of acid:alcohol. Different molar ratios of acid:alcohol from 1:1 to 1:7 were reacted at reflux temperature for 6 h. The results are presented in Table II. As can be seen, a nonlinear trend in yields is observed with increased molar ratios of alcohol:acid from 1:1 to 7:1. The yield of ester increased for 1:1 ratio and followed by a decrease thereafter. Although the increase in alcohol content might be expected to increase conversion, there might be dilution of hexanoic acid; hence the expected increase in conversion must be balanced by decrease in the conversion due to the increase in dilution of hexanoic acid. There might be dilution of acid by increased alcohol contents, thereby preventing hexanoic acid adsorption on the Brønsted acid sites. The reaction was also studied by using more acid content (Table I).

When the molar ratio of acid:alcohol increased from 1:1 to 7:1, the yield of ethylhexanoate increased. Since hexanoic acid probably undergoes chemoadsorption on the Brønsted acid sites, an increase in acid content increased the yield.

In order to verify the effectiveness of the catalyst, we also refluxed the reaction mixture in the absence of the catalyst for 6 h. After 6 h, the reaction mixture was analyzed by GC/MS. The yield was found to be only 4–5%.

The effect of reaction time on the yield of ethylhexanoate also was studied using $H_5PMo_{10}V_2O_{40}$ at reflux temperature with a molar ratio of 1:7 for alcohol:acid. Yields increased from 16% at 2 h to a maximum of 93.9% at 6 h. An increase in the yield was noticed with increase in the duration of the reaction time. This observation is an expected feature for this kind of reaction.

The reaction was also carried out at room temperature with a molar ratio of 1:7 for alcohol:acid for 6 h. In this case, the progress of reaction was very slow and the yield was negligible.

This result shows that the reaction needs more energy to proceed. This energy may be required to reduce intermolecular associations of alcohol and to avoid clustering of alcohol around the Brønsted acid sites by hydrogen bonding.

In summary, the results show potential use of the heteropolyacid $H_5PMo_{10}V_2O_{40}$ as a catalyst in the esterification reaction. We have shown in this study that the reaction is sensitive to the choice of catalyst and the amount of acid and alcohol. The reaction provides a simple and highly efficient catalytic method for synthesis of aliphatic esters under mild conditions.

EXPERIMENTAL

The reaction mixture was analyzed by GC/MS (GC-Mass model: 5973 network mass selective detector, GC 6890 Agilent). The products were also characterized by comparison of their spectroscopic data with those of authentic samples. Yields were determined by GC/MS.

All chemicals were purchased from Merck Company and were used without further purification.

The catalyst, $H_5PMo_{10}V_2O_{40}$, was synthesized by acidification-etherate from sodium molybdate, sodium vanadate, and sulfuric acid.[42] Other catalysts were obtained from commercial sources.

Typical Procedure

In a typical reaction, the catalytic esterification of hexanoic acid was carried out in a round bottom flask equipped with a magnetic stirrer, thermometer, and a reflux condenser. Catalyst (0.0001 mol) was added to a mixture of hexanoic acid (0.05 mol) and alcohol (0.0075 mol). The reaction mixture was stirred and refluxed for 6 h. Different reaction runs were conducted by varying the reaction parameters such as molar ratio of reactants, the catalyst type, temperature, and reaction time.

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