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Metal-Exchanged Phosphomolybdic Acid Salts-Catalyzed Esterification of Levulinic Acid

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Abstract: We examined the effectiveness of metal-exchanged phosphomolybdic acid salts in converting levulinic acid, derived from biomass, into valuable products (alkyl levulinate). We prepared salts of phosphomolybdic acid using different metals (Fe^{3+}, Al^{3+}, Zn^{2+}, Cu^{2+}, Mn^{2+}, Ni^{2+}, and Co^{2+}). The influence of metal cations on the conversion and selectivity of the reactions was assessed. We found that the salts prepared with iron and aluminum phosphomolybdate were the most effective catalysts for the esterification of levulinic acid with methanol, with the conversion and selectivity tending towards 100% after 6 h of reaction at a temperature of 323 K. The effect of catalyst loading and its recovery and reuse was evaluated; the results from the reaction using aluminum phosphomolybdate remained similar for four cycles of use. The influence of temperature on conversion and selectivity was investigated between 298 and 353 K. The reactivity of different alcohols with a carbon chain size of C1-C4 was assessed and conversions above 65% were obtained for all alcohols tested under the conditions evaluated, except for tert-butyl alcohol. These catalysts are a promising alternative to the traditional soluble and corrosive Brønsted acid catalysts. The superior performance of these catalysts was ascribed to the higher pH decline triggered by the hydrolysis of these metal cations.

Keywords: biofuel additives; metal-exchanged phosphomolybdic acid salts; levulinate esters; biomass

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1. Introduction

The search for renewable energy sources has significantly intensified due to the gradual decrease in fossil fuel reserves. Consequently, the development of processes to produce liquid fuels from renewable sources has become essential [1]. Biomass is an abundant source of compounds such as levulinic acid (LA) and its derivatives, which can reduce our dependence on fossil fuels [2,3]. LA is one of the top twelve building blocks that can be converted to chemicals or biofuels [4] and has been produced from lignocellulosic biomass through acid-catalyzed hydrolysis reactions [5]. Both the hexoses and pentoses present in cellulose and hemicellulose, respectively, can be used to obtain levulinic acid. However, the mechanism via fructose is easier, so raw materials richer in this sugar are more promising sources of levulinic acid. In addition to fructose, glucose, xylose, furfuryl alcohol, and maleic anhydride have also been studied as sources, in addition to the direct conversion of cellulose and hemicellulose themselves. Agricultural residues such as rice husk, sugarcane bagasse, corn straw, and others have already been reported as sources of this acid [6,7].

The LA obtainment process varies with the substrate chosen as the feedstock, the composition of biomass, and the concentration of hexoses present in the biomass. Since cellulose and hemicellulose are present in plant-based organic matter in large quantities, the obtainment of LA can be performed using several kinds of feedstock, including biomass residue. Wheat straw has previously been the main biomass used to produce LA, in processes where formic acid is a co-product [8].

LA synthesis processes require a biomass pretreatment step using mineral acids, leading to the depolymerization of cellulose, releasing lignin. Afterwards, glucose is dehydrated through acid catalysis with heating, transforming it into HMF, and then into LA and FA. This process is preferable compared to the hemicellulose route because furfural is quite reactive, forming more FA and other byproducts [9]. Among the products derived from levulinic acid, alkyl levulinates (ALs) have been used as flavoring agents, green solvents, and starting materials for synthesizing lactones that are synthesis intermediates of drugs and agrochemicals [10,11]. Moreover, levulinate esters are highly useful compounds that can be blended with liquid fuels to improve their physicochemical properties, such as lubricity, octane number, and flash point, minimizing the environmental impact of their combustion [12,13]. Besides their low toxicity, high-molecular-weight AL esters have a good solubility in both gasoline and diesel, thus making them bioadditives that are suitable for use in low temperatures [14,15].

Moreover, levulinic acid esters are compounds that can be blended with liquid fuels to improve their physicochemical properties, such as lubricity, octane number, and flash point, while minimizing the environmental impact of their combustion [14,15]. Besides their low toxicity, AL esters have a good solubility in gasoline and diesel, thus making them suitable bioadditives for use in low temperatures [16].

The direct production of levulinic acid esters from lignocellulosic biomass residues through alcoholysis reactions is challenging due to the variety of biomass-derived products that can also be generated [17].

Lignocellulosic biomass consists of three main components: lignin, cellulose, and hemicellulose. Acidic hydrolysis can remove lignin, leading to the production of saccharide monomers with either six or five carbon atoms, such as glucose, xylose, levoglucosan, and fructose [18]. When lignocellulosic biomass breaks down into hexose sugars like glucose or xylose, these can be converted into levoglucosan or isomerized into fructose, which subsequently yields levulinic acid (as shown in Figure 1). Conversely, when the biomass breakdown results in pentose sugars, compounds such as furfural or furfuryl alcohol can have their five-membered rings cleaved to produce levulinic acid (refer to Figure 1) [19].

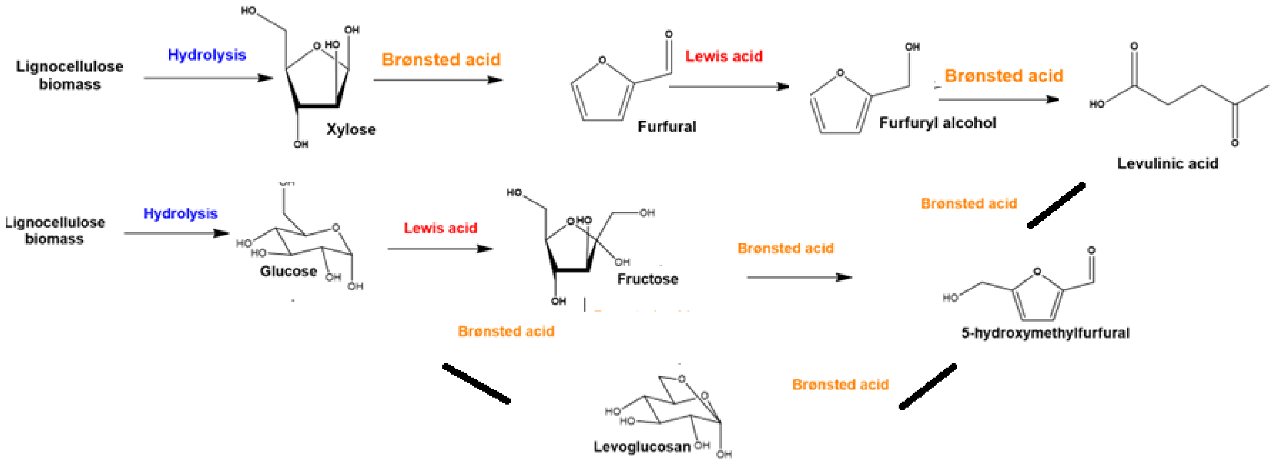


Figure 1. Levulinic acid synthesis from pentoses or hexoses.

Therefore, developing a one-pot synthesis route to produce LA from biomass remains a challenge due to the difficulty of controlling the reaction's selectivity, an aspect that sometimes does not depend on the carbohydrate [20,21]. In addition to levulinic acid, other compounds such as furfural, lactones, and carboxylic acids are also produced [20]. Although inexpensive soluble Brønsted acid catalysts like sulfuric acid have been used in the esterification of levulinic acid, they are difficult to manipulate and require neutralization steps at the end of the process, generating a large amount of effluents and residues, which need to be disposed of into the environment [22–24]. The use of solid-supported catalysts, metal oxides, sulfonic resins, and molecular sieves can meet this demand. Currently, several solid acids have been successfully evaluated in esterification reactions [24–28]. However, the laborious synthesis of solid-supported catalysts and the leaching of the active phase due to the high polarity of the reaction medium are still drawbacks of these processes.

Alternatively, Lewis acid catalysts have been effective in catalyzing levulinic acid esterification reactions and can be an attractive option compared to traditional Brønsted acids. These catalysts, whether commercially available or synthesized, have demonstrated efficiency, particularly those containing tetravalent metal cations [29–32]. Bifunctional catalysts with both Lewis and Brønsted acidity may offer an improved performance of the esterification of levulinic acid. Transition metal cations-exchanged Keggin heteropolyacid salts can combine these two types of acidity [33,34]. These compounds are metal–oxygen clusters with adjustable structural properties, capable of generating both Lewis and Brønsted acid sites [33]. On the other hand, replacing protons with metal cations with high levels of Lewis acid can keep the heteropoly salts soluble, and due to their hydrolysis, generate hydronium cations, making them bifunctional catalysts [34,35].

Fernandes et al. investigated the esterification of levulinic acid with ethanol using sulfated oxide metals (TiO_2, ZrO_2, SnO_2, and Nb_2O_5) and zeolites. The best results were obtained with Amberlyst-15, which achieved a 54% conversion at 343 K with 2.5 wt% catalyst over 5 h [28]. Rocha and Lopes tested zirconium phosphates using a microwave-assisted method. In this study, they attained a remarkable 95% conversion with a 99% selectivity for methyl levulinate, using 30 wt% of the catalyst (α-ZrP) at 273 K. Similar results were observed with γ-ZrP [29]. Costa and colleagues utilized mesoporous stannosilicates with methanol for this reaction. The material synthesized at 80 °C (SnMCM-41–80) achieved a 90% conversion with only 1 wt.% of catalyst after 3 h at 180 °C; however, the authors did not report selectivity for this reaction [36].

In this work, phosphomolybdic acid was converted to heteropoly salts with the general formula $M_{3/x}PMo_{12}O_{40}$ ((M^{x+} = Fe^{3+}, Al^{3+}, Zn^{2+}, Cu^{2+}, Mn^{2+}, Ni^{2+}, and Co^{2+}), and the salts were subsequently evaluated in esterification reactions of levulinic acid with alkyl alcohols. The effects of the main reaction variables such as time, temperature, type of alcohol, and catalyst concentration were investigated.

2. Materials and Methods

2.1. Chemicals

All the chemicals and solvents were used without previous treatment. Phosphomolybdic acid and metal chloride salts (all 99%) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Levulinic acid (97%), alcohols (i.e., methyl, ethyl, propyl, isopropyl, and butyl) with a purity between, equal to, or higher than 99.5% were also acquired from Sigma-Aldrich (St. Louis, MO, USA).

2.2. Synthesis and Characterization of $M_{3/x}PMo_{12}O_{40}$ (M^{x+} = Fe^{3+}, Al^{3+}, Zn^{2+}, Cu^{2+}, Mn^{2+}, Ni^{2+}, and Co^{2+}) Catalysts

The metal phosphomolybdate salts were synthesized through the metathesis of the protons in phosphomolybdic acid with cations of metal chloride solutions [37]. Typically, 1 g of $H_3PMo_{12}O_{40}$ was dissolved in 30 mL of water, then 30 mL of a metal chloride solution in an appropriate stoichiometry was slowly added dropwise under magnetic stirring. This system was heated at 343 K for 1 h. After this period, the temperature was increased to 373 K to evaporate the water and release HCl. The salt formed was heated in a muffle furnace at 383 K/3 h. The characterization of these catalysts is also discussed in this same work [37].

The amount and the strength of the acid sites present in the metal heteropoly salts were determined by potentiometric titration (BEL potentiometer, model W3B, with a glass electrode, Herisau, Switzerland) with an *n*-butylamine solution (ca. 0.10 $molL^{-1}$). For this, the metal heteropoly salt (50 mg) was suspended in CH_3CN (ca. 30 mL), and magnetically stirred for 3 h. Subsequently, the sample was titrated with a slow addition of portions of *n*-butylamine until the electrode potential remained stable.

2.3. Catalytic Runs

The catalytic reactions were conducted under magnetic stirring in a 50 mL glass reactor, equipped with a reflux condenser and a sampling septum. The reactor was immersed in a thermostatically controlled oil bath. A typical run was carried with a solid catalyst (1.0 mol %), and levulinic acid (4.0 mmol), both dissolved in 10 mL of methyl alcohol. The progress of the reaction was monitored through GC analysis of samples taken at regular intervals using a Shimadzu GC-2014 Plus with a flame ionization detector (FID) and a CP-WAX capillary column measuring 25 m × 0.32 mm × 0.30 µm. Dodecane (0.1 mL) was used as an internal standard. The GC peak areas for levulinic acid and its esters were plotted against their calibration curves to determine conversions and yields

2.4. Products Identification

The main reaction products were identified by GC/MS analyses (Shimadzu MS-QP 2010 ultra mass spectrometer instrument operating at 70 eV coupled Shimadzu 2010 GC) and co-injection with authentic samples previously synthesized.

3. Results Discussion

3.1. Catalytic Tests

3.1.1. Effect of Metal Phosphomolybdate Catalyst

Initially, the catalytic activity of the metal-exchanged phosphomolybdic acid salts was evaluated in esterification reactions of levulinic acid with methyl alcohol using conditions previously reported in the literature. Figure 2 displays the kinetic curves.

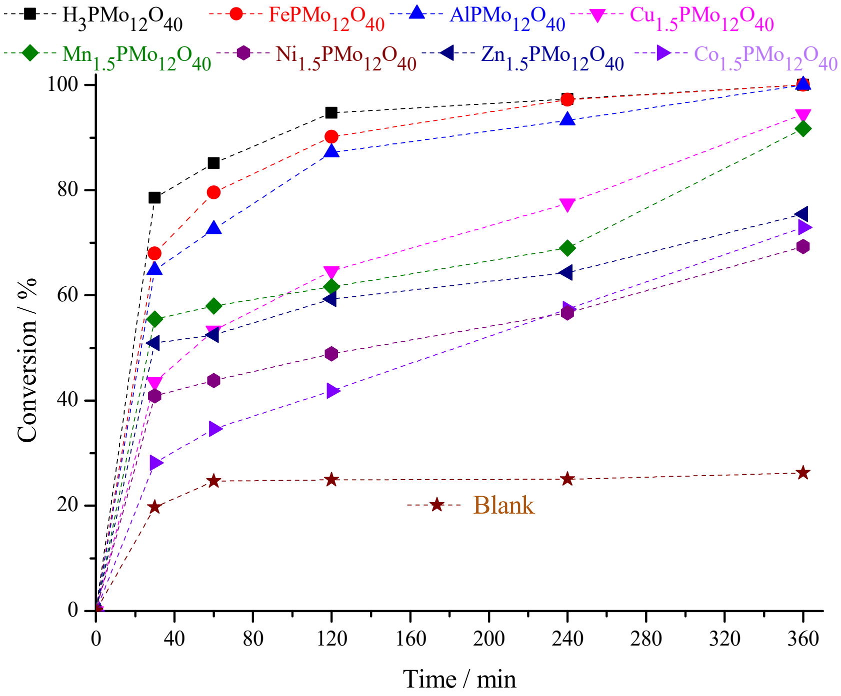


Figure 2. Effect of catalyst on the levulinic acid esterification with methyl alcohol [a]. [a] Reaction conditions: levulinic acid (4.0 mmol), methyl alcohol (9.6 mL), catalyst (1 mol %), temperature (323 K).

The nature of the metal cation also had an impact on the reaction rates. The sequence of reactivity observed was as follows: $FeMo_{12}O_{40} \cong AlMo_{12}O_{40} > Cu_{3/2}PMo_{12}O_{40} > Mn_{3/2}PMo_{12}O_{40} > Ni_{3/2}PMo_{12}O_{40} > Zn_{3/2}PMo_{12}O_{40} > Co_{3/2}PMo_{12}O_{40}$. Reactions carried out with trivalent metal cation phosphomolybdate ($AlMo_{12}O_{40}$ and $FeMo_{12}O_{40}$) catalysts showed higher initial rates and achieved greater conversions. Although these conversions were similar to those obtained using phosphomolybdic acid, using these catalysts eliminates the need for neutralization after the end of the reaction, thereby minimizing effluent and residue generation. These cations are stronger Lewis acids. In contrast, divalent cation phosphomolybdates demonstrated inferior performance, with particular note to $Mn_{3/2}PMo_{12}O_{40}$ and $Cu_{3/2}PMo_{12}O_{40}$ salts, which reached a conversion rate close to that of the trivalent salts after a 6 h reaction (see Figure 2).

The literature emphasizes that the strength of the acidity of the catalysts plays a crucial role in esterification reactions [38,39]. Evaluating the Lewis acidity strength of these catalysts involves analyzing adsorbed pyridine using FT-IR spectroscopy. Alternatively, we can estimate one property of these Lewis acids' acidity. Lewis acid metal cations can react with water molecules and release H^+ ions, decreasing the pH value. For the reaction goal of this work, these molecules can be present in the solvent (residual water), in the salts (hydration water), or still be generated in the esterification reaction (Equations (1)–(3)) [40,41].

$$M_{\frac{3}{y}}PMo_{12}O_{40} \overset{ROH}{\rightarrow} \frac{3}{y}M^{y+} + Mo_{12}{O_{40}}^{3-} \tag{1}$$

$$M^{y+} + nH_2O \rightleftharpoons [M(H_2O)]^{y+} \tag{2}$$

$$[M(H_2O)]^{y+} + H_2O \rightleftharpoons H^+ + [M(H_2O)_n(OH)]^{y-1} \tag{3}$$

Therefore, we can indirectly evaluate the strength of the Lewis acidity of metal cations by measuring the pH values of their alcoholic solutions. Table 1 shows the pH values measured.

Table 1. Measurements of "pH" values of methyl alcohol solutions containing phosphomolybdate salt catalysts [a,b].

Catalyst	pH Value [b]	Conversion [c] (%)
$H_3PMo_{12}O_{40}$	0.53	98
$AlPMo_{12}O_{40}$	0.55	98
$FePMo_{12}O_{40}$	0.54	98
$Cu_{1.5}PMo_{12}O_{40}$	0.71	95
$Mn_{1.5}PMo_{12}O_{40}$	0.68	94
$Zn_{1.5}PMo_{12}O_{40}$	1.06	72
$Co_{1.5}PMo_{12}O_{40}$	0.75	69
$Ni_{1.5}PMo_{12}O_{40}$	1.03	66

[a] Catalyst concentration: 1 mol %; methyl alcohol (10 mL); [b] glass electrode at room temperature; pH of methyl alcohol pure 6. 0; [c] conversion obtained under the conditions: levulinic acid (4.0 mmol), methyl alcohol (9.6 mL), catalyst (1 mol %), temperature (323 K), after 6 h.

Table 1 indicates that the reaction with the most acidic catalyst had the highest conversion rate. It is important to note that although these measurements were not conducted in water, and thus cannot be referred to as "pH", they released H^+ cations during the hydrolysis of the metal salt. Therefore, in this context, it is reasonable to use the term "pH". Another method for assessing the strength of acidity in metal heteropolysalts is to titrate their acid sites with n-butylamine [42]. Figure 3 presents the curves obtained from the potentiometric titrating of the solutions containing the soluble salts.

The strength of the acid sites of catalysts can be estimated from the initial electrode potential (Ei) of their solutions. According to Pizzio et al., the acidic sites of the phosphomolybdic acid and their metal salts can be classified as being very strong (Ei > 150 mv) [42]. Heteropoly salts of Fe^{3+}, Al^{3+}, and Cu^{2+} presented high Ei values, which were only lower than that of pristine heteropolyacid ($H_3Mo_{12}O_{40}$).

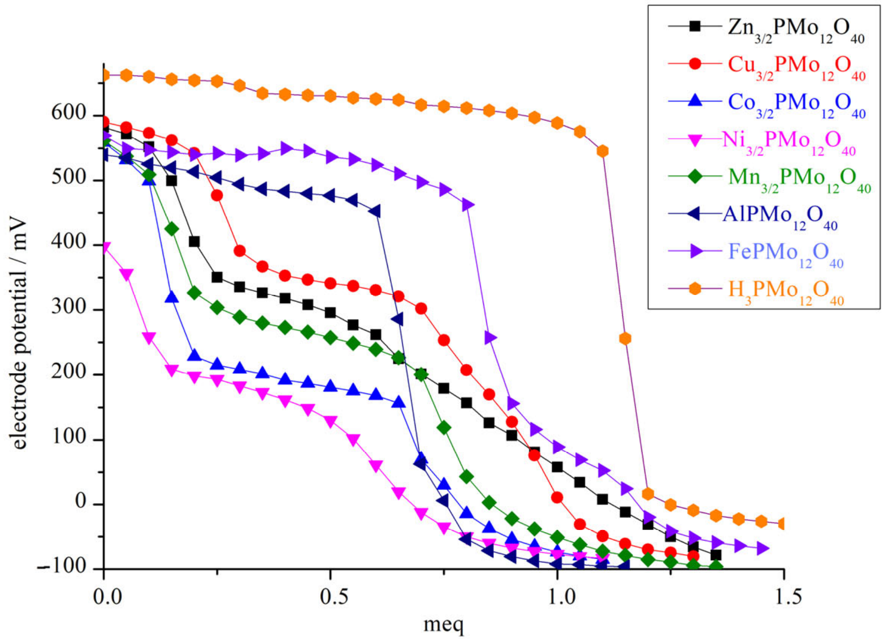


Figure 3. Curves of potentiometric titration of metal salts.

3.1.2. Mechanism Proposal of Levulinic Acid Esterification with Alkyl Alcohol Catalyzed by H^+ Cations Generated by Hydrolysis of Metal Phosphomolybdates

The measurements of pH, potentiometric titrations, and the conversion results showed that the metal with a higher amount of Lewis acid releases a higher concentration of H^+ after it has been hydrolyzed by the water in the reaction medium (hydrated water from the salt, residual water from the solvent, or even water generated in the reaction). Based on the experimental results and the literature, it is possible to propose a potential reaction pathway (see Figure 4) [43].

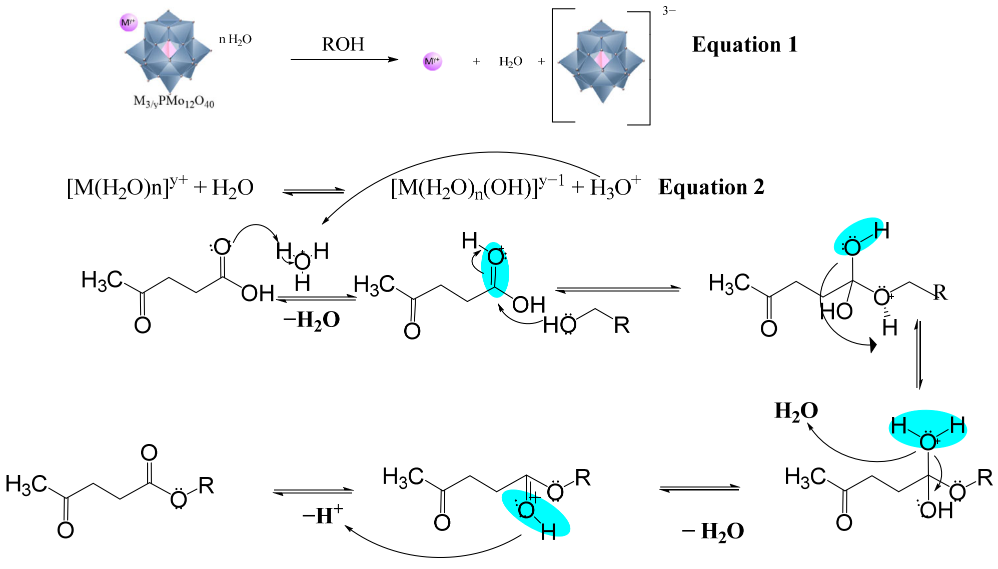
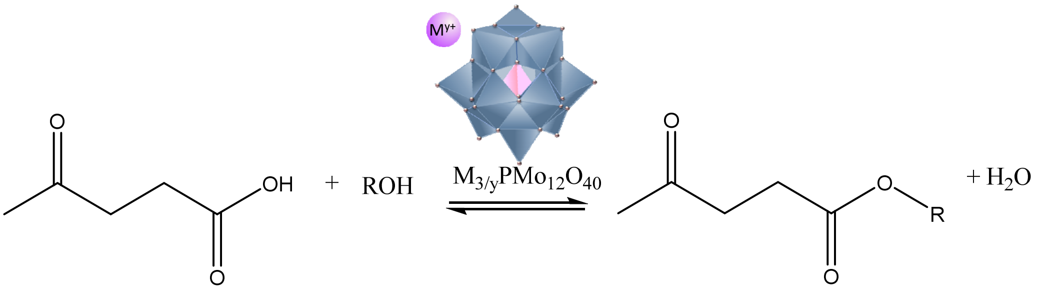


Figure 4. Reaction pathway of esterification of acid levulinic with alkyl alcohol catalyzed by H^+ cations generated in the hydrolysis of metal cation present in the phosphomolybdate salt catalyst [43].

After the metal phosphomolybdate dissolves, it releases metal cations into the solution (see Equation (1) and Figure 4). These metal cations can then react with water molecules in the reaction medium, leading to hydrolysis and the release of H^+ cations. The H^+ cations act as catalysts in this process. They react with the carboxyl group of levulinic acid, protonating its carbonyl group. This makes the carbonylic carbon more electron deficient and more susceptible to the nucleophilic attack of the hydroxyl group of alcohol. Subsequent prototropism steps lead to water loss and the formation of levulinate ester, regenerating the H^+ cations.

Typically, levulinic acid esterification produces only levulinate alkyl levulinate as a main product (Scheme 1).



Scheme 1. Heteropoly salt-catalyzed levulinic acid with alkyl alcohol.

The main product was always methyl levulinate, regardless of the catalyst (Figure 5). The reactions that achieved higher conversions also had higher selectivity. Remarkably, both aluminum and iron phosphomolybdate salts performed similarly to the pristine heteropolyacid. They are fewer corrosive catalysts, which are possibly recoverable and reusable, and do not require neutralization steps. Therefore, they were selected to study the effect of other reaction parameters.

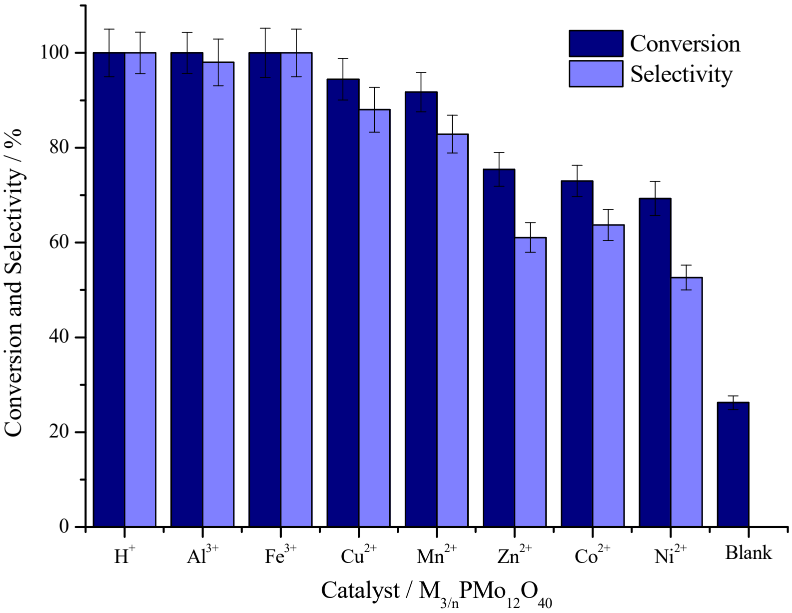


Figure 5. Conversion and methyl levulinate selectivity of phosphomolybdic heteropoly acid-catalyzed esterification of levulinic acid [a]. [a] Reaction conditions: levulinic acid (4.0 mmol), methyl alcohol (9.6 mL), catalyst (1 mol %), temperature (323 K).

3.1.3. Effect of Catalyst Load

Initially, the reactions were carried out with a variable load of catalysts. Kinetic curves are presented in Figures 6 and 7.

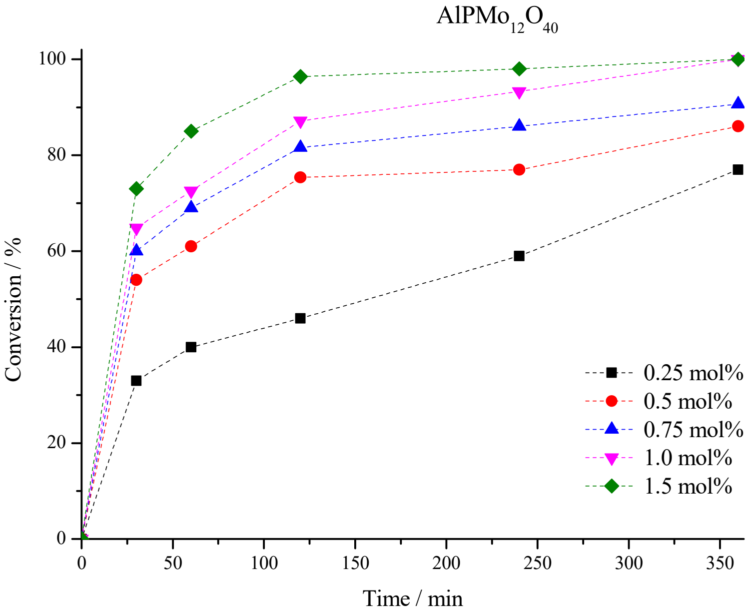


Figure 6. Impact of catalyst load on the $AlMo_{12}O_{40}$-catalyzed esterification of levulinic acid with methyl alcohol [a]. [a] Reaction conditions: levulinic acid (4.0 mmol), methyl alcohol (9.6 mL), catalyst (variable, temperature (323 K).

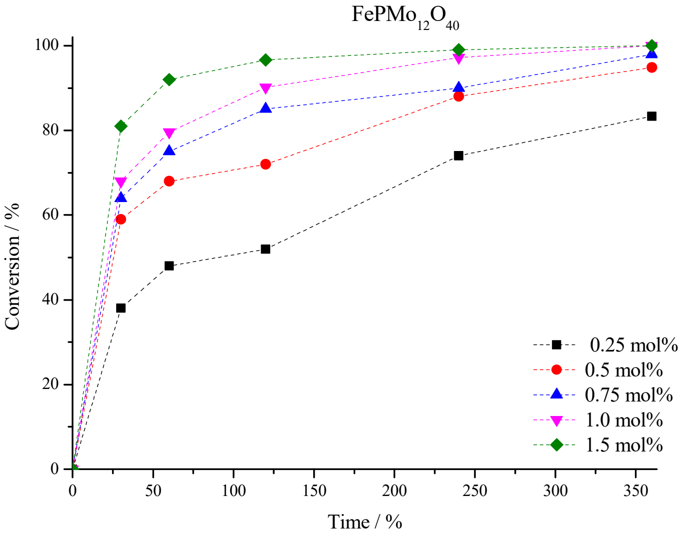


Figure 7. Effect of catalyst load on the $FeMo_{12}O_{40}$-catalyzed esterification of levulinic acid with methyl alcohol [a]. [a] Reaction conditions: levulinic acid (4.0 mmol), methyl alcohol (9.6 mL), catalyst (variable, temperature (323 K).

An increase in the load of the $AlMo_{12}O_{40}$ catalyst led to a higher initial rate and final conversion, except for the reactions with 1.0 and 1.5 mol %, which reached equal conversions. This is likely due to the higher number of active sites available to activate the carboxyl group of levulinic acid, enhancing its reaction with the hydroxyl group of alcohol. Similarly, the $FeMo_{12}O_{40}$-catalyzed reactions exhibited the same behavior (refer to Figures 6 and 7).

The reactions with $AlMo_{12}O_{40}$ catalysts or $FeMo_{12}O_{40}$ catalysts had comparable activity. However, the conversions of the reactions using the four higher loads of the $FeMo_{12}O_{40}$ catalyst were slightly better than those achieved in the $AlMo_{12}O_{40}$-catalyzed reactions (refer to Figures 6 and 7). Furthermore, the same experiment was also conducted using the $H_3Mo_{12}O_{40}$ catalyst (see Figure 8).

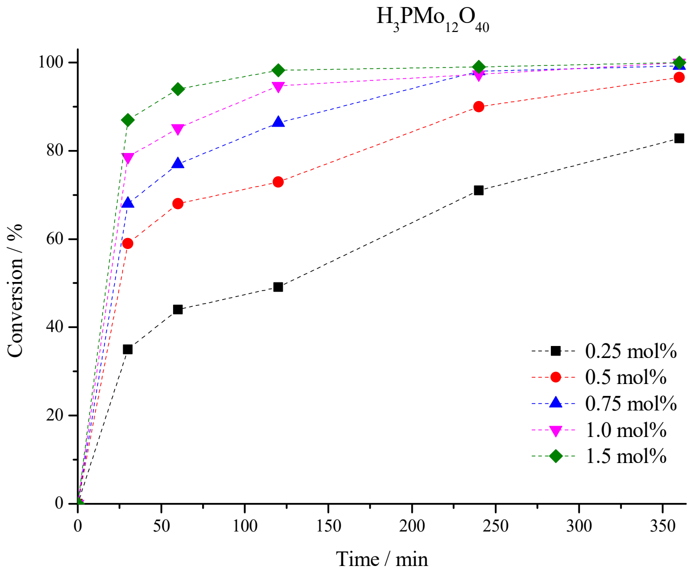


Figure 8. Effect of catalyst load on the $H_3Mo_{12}O_{40}$-catalyzed esterification of levulinic acid with methyl alcohol [a]. [a] Reaction conditions: levulinic acid (4.0 mmol), methyl alcohol (9.6 mL), catalyst (variable, temperature (323 K).

The curves obtained from the $H_3Mo_{12}O_{40}$-catalyzed reactions closely resembled those from the $FeMo_{12}O_{40}$-catalyzed reactions. This suggests that these Lewis acid metal heteropolysalts can effectively replace Brønsted acid catalysts ($H_3Mo_{12}O_{40}$). Although not mentioned here, regardless of the catalyst used, the reaction's selectivity was consistently high, around 100% for methyl levulinate.

3.1.4. Recyclability Tests

The most active catalyst, $AlMo_{12}O_{40}$, was recovered and reused successively (Table 2). Since $AlMo_{12}O_{40}$ is soluble, the aqueous phase was removed under vacuum. The net obtained was washed with ethyl ether to remove unreacted reactants and products. Afterward, it was washed with water, which extracted the catalyst. The catalyst was dried in the oven and weighed. The catalyst was successfully recovered and reused without a loss of activity.

Table 2. Recovery and reuse of $AlMo_{12}O_{40}$ catalyst.

Cycle	Conversion/%	Selectivity/%	Recovery Rate/%
1	100	100	98
2	98	98	94
3	97	97	94
4	96	97	95

3.1.5. Effect of Temperature

Besides the catalyst load, the reaction temperature is also an important variable that can impact the rate of reaction, conversion, and selectivity. Figure 9 shows the kinetic curves obtained at different temperatures in the presence of the $H_3Mo_{12}O_{40}$.

An increase in temperature leads to a higher number of effective collisions between reactant molecules, resulting in a higher initial rate of reaction as well as a greater conversion (Figure 9).

Likewise, as verified with the $AlMo_{12}O_{40}$ catalyst, the reactions performed at higher temperatures were faster and achieved higher conversions (Figure 10).

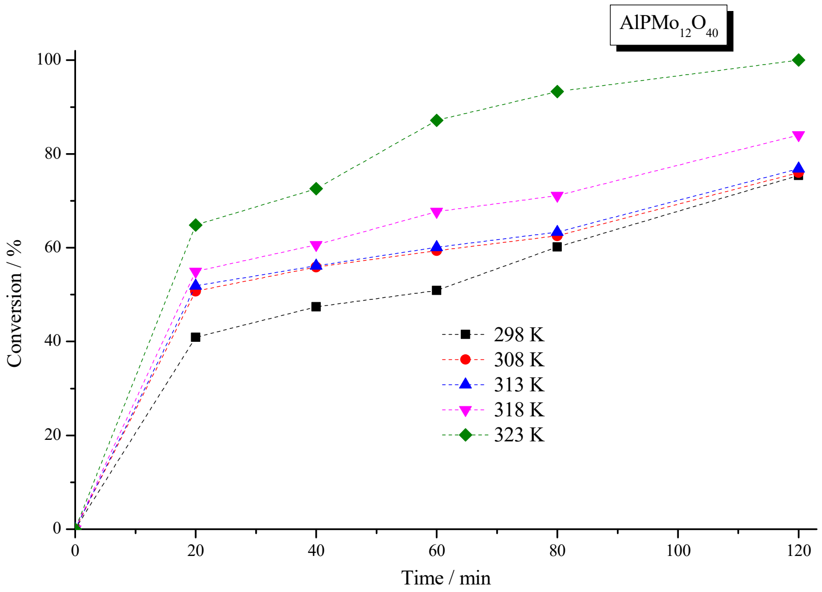


Figure 9. Effect of temperature on the kinetic curves of the $AlMo_{12}O_{40}$-catalyzed esterification of levulinic acid with methyl alcohol [a]. [a] Reaction conditions: levulinic acid (4.0 mmol), methyl alcohol (9.6 mL), catalyst (1 mol %), temperature (variable).

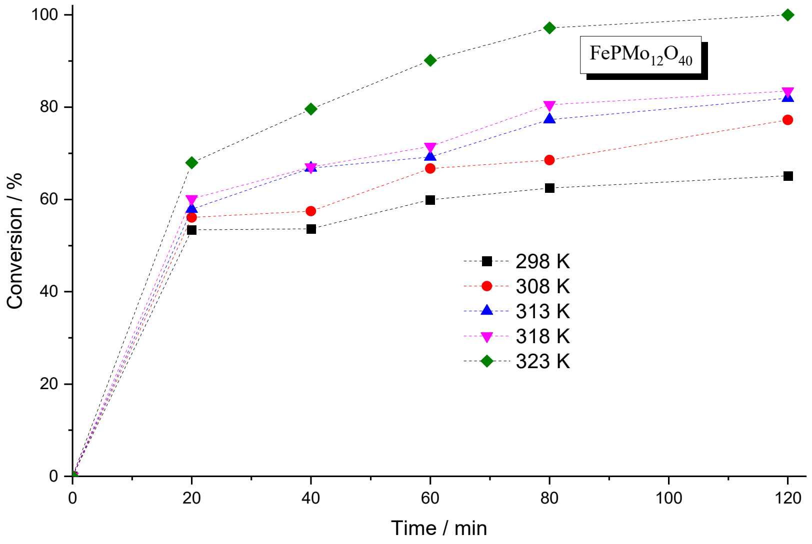


Figure 10. Impact of temperature on the kinetic curves of the $FeMo_{12}O_{40}$-catalyzed esterification of levulinic acid with methyl alcohol [a]. [a] Reaction conditions: levulinic acid (4.0 mmol), methyl alcohol (9.6 mL), catalyst (1 mol %), temperature (variable).

3.1.6. Effect of Alcohol

The reactivity of alcohols with different carbon chain lengths and hydroxyl groups was evaluated. Kinetic curves from the $FeMo_{12}O_{40}$ or $AlMo_{12}O_{40}$-catalyzed reactions of levulinic acid esterification with these alcohols were obtained. Figure 11 displays the results obtained using the $AlMo_{12}O_{40}$ catalyst.

Methyl alcohol was found to be the most reactive in the reaction. This is because the first step of the reaction involves the hydroxyl group attacking the carbonyl of the carboxyl group in levulinic acid. This higher reactivity can be attributed to the electron-donating effect of the methyl group on the hydroxyl group. This effect decreases as the distance increases. In Scheme 2, it is shown how the carbon attached to the hydroxyl group can undergo an electron-donating effect, leading to an increase in the nucleophilicity of the hydroxyl group.

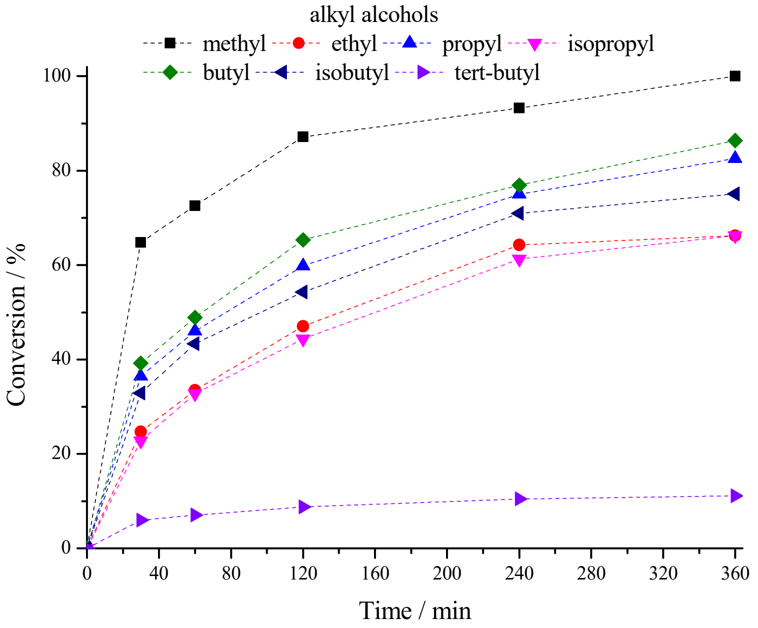
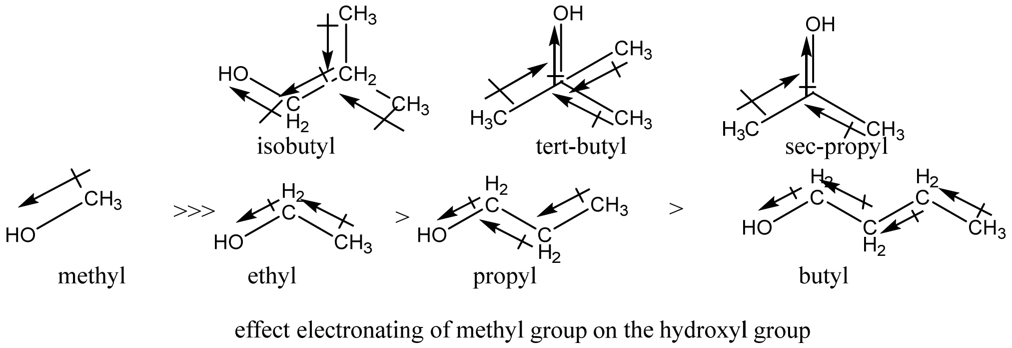


Figure 11. $AlMo_{12}O_{40}$-catalyzed esterification of levulinic acid with alkyl alcohols [a]. [a] Reaction conditions: levulinic acid (4.0 mmol), alkyl alcohol (9.6 mL), catalyst (1 mol %), temperature (323 K).



Scheme 2. Tendency of the donating effect of methyl groups.

In addition to the electronic effect, the hysteric hindrance on the hydroxyl group can also hamper its attack on the carbonylic carbon in levulinic acid. The conversions undergone by the levulinic acid in reactions with different alcohols obeyed the tendency methyl >> ethyl ≅ propyl > butyl > isobutyl > tert-butyl > isopropyl. As expected, the methyl alcohol was the most reactive. Although the hydroxyl group attached to the tertiary carbon is a more steric hindrance (tert-butyl alcohol), it was more reactive than the secondary carbon (sec-propyl alcohol), probably due to the higher donating effect undergone by this hydroxyl, due to three neighboring methyl groups [43].

Figure 12 displays the conversion achieved in the $AlMo_{12}O_{40}$- or $FeMo_{12}O_{40}$-catalyzed esterification of levulinic acid with alkyl alcohols and without a catalyst.

The hindrance caused by the hysteric effect on the hydroxyl group can hinder its attack on the carbonyl carbon in levulinic acid, in addition to its electronic effect. When levulinic acid reacts with different alcohols, the conversions follow this tendency: methyl > butyl > propyl > isobutyl > secpropyl = ethyl > tert-butyl. As expected, methyl alcohol was the most reactive. Figure 12 shows the conversions achieved in the esterification of levulinic acid with alkyl alcohols using $AlMo_{12}O_{40}$ or $FeMo_{12}O_{40}$ as catalysts, as well as without a catalyst.

Despite excess alcohol, only poor conversions were achieved in reactions with more reactive alcohols, secondary and tertiary alcohol were not esterified in the absence of a catalyst. Conversely, once more, $AlMo_{12}O_{40}$ and $FeMo_{12}O_{40}$ catalysts had a very similar performance, regardless of alcohol.

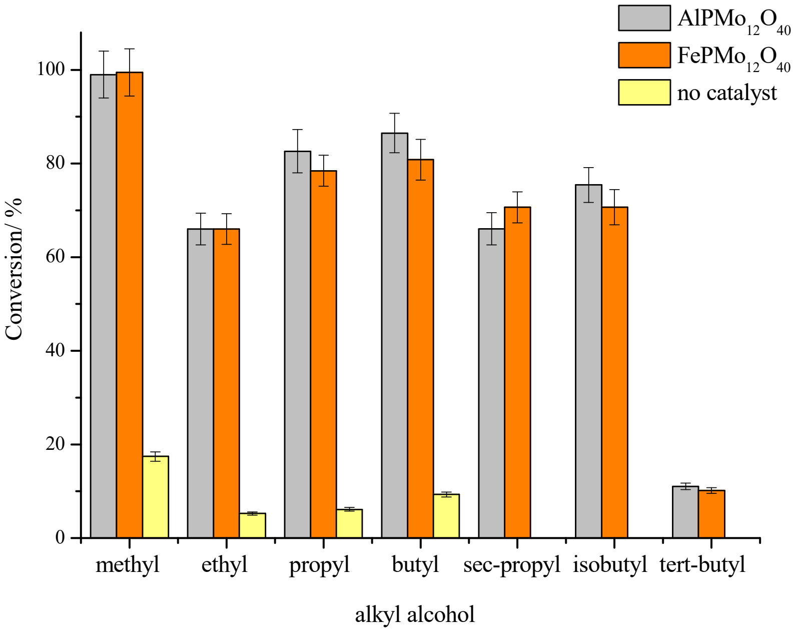


Figure 12. Conversion of $AlMo_{12}O_{40}$, or $FeMo_{12}O_{40}$-catalyzed esterification of levulinic acid with alkyl alcohols [a]. [a] Reaction conditions: levulinic acid (4.0 mmol), alkyl alcohol (9.6 mL), catalyst (1 mol %), temperature (323 K); time (6 h).

4. Conclusions

The efficiency of metal phosphomolybdate catalysts was evaluated in levulinic acid esterification with short-chain alcohols. Among the catalysts tested, $AlMo_{12}O_{40}$ and $FeMo_{12}O_{40}$ showed the highest activity, which was comparable to that of the pristine heteropolyacid ($H_3Mo_{12}O_{40}$), but with additional advantages such as a lower corrosiveness and the potential for recovery and reuse. This high efficiency was attributed to the strong Lewis acidity of Fe^{3+} and Al^{3+} cations, which release more H^+ ions upon hydrolysis, as confirmed by pH measurements. Alkyl levulinate was consistently the main product. An increase in catalyst load or temperature led to a higher conversion and ester selectivity. The alcohol reactivity was as follows: primary > secondary > tertiary alcohols, which was attributed to the steric hindrance of the hydroxyl group.

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