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# Keggin's metal phosphomolybdates: Synthesis, characterization and evaluation of catalytic activity in the esterification of levulinic acid

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Levulinic acid is obtained through acid dehydration of biomass and can be transformed into a variety of products, which makes it considered a platform molecule. Among its industrial derivatives of interest are its esters, alkyl levulinates, which can be used as biolubricants, flavoring agents, biofuel additives, and green solvents. The synthesis of levulinates is often catalyzed by homogeneous corrosive mineral acids that are difficult to recycle. Alternatively, Keggin catalysts can replace such catalysts.These materials are metal-oxygen clusters with a central heteroatom (P or Si). In addition to Brønsted's strong acidity, they are thermally stable and easily modified. In this work, salts derivatives of phosphomolybdic acid were synthesized by completely replacing the $H^+$ cation with the cations $Al^{3+}$, $Fe^{3+}$, $Co^{2+}$, $Cu^{2+}$, $Ni^{2+}$, $Zn^{2+}$, $Mn^{2+}$, which were characterized by spectroscopy analysis in the infrared region by Fourier transform coupled to attenuated total reflectance, thermogravimetric analysis, powder X-ray diffraction, nitrogen physisorption, scanning electron microscopy and energy dispersive X-ray spectroscopy. The total replacement of different protons of phosphomolybdic acid was carried out with high yield. Characterizations by infrared Raman spectroscopy showed that the synthesis preserved the primary structure of the Keggin anion and potentiometric titration showed that there was a decrease in acidity in relation to the precursor acid. The catalytic tests were carried out in a tribulated glass reactor coupled to a reflux condenser, to avoid loss of solvent. The reaction system was kept under heating in a glycerin bath and with magnetic stirring. In a typical procedure, 4.0 mmol of levulinic acid, 100 µL of toluene were used and the reaction volume was made up to 10 mL with methanol. The catalyst was added and the system was maintained at 323 K for 6h. Aliquots of 1 mL were collected at predetermined time intervals and the material was analyzed by gas chromatography with a flame ionization detector. The different synthesized catalysts were tested in the reaction and it was possible to observe that all catalysts showed conversion greater than 69%. The silicotungstic acid ($H_3PMo_{12}O_{40}$), as well as the aluminum and iron salts achieved 100% conversion and very high selectivity for ethyl levulinate (>98%).In order to understand the effect of these catalysts, the pH of the reaction medium was measured, under the same initial reaction conditions, but at room temperature. It can be noted that the catalysts that produced the greatest decrease in pH are those that also led to the greatest conversion of the substrate. Other reaction parameters were evaluated, such as the amount of catalyst, temperature and use of other alcohols as solvent. A process is being developed for the esterification of levulinic acid with methanol using phosphomolybdate salts as catalysts. The process has advantages such as ease of synthesis and storage of the catalyst, compared to other works in the literature.

## References

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