



Acidic characterization and activity of $(\text{NH}_4)_x\text{Cs}_{2.5-x}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ catalysts in the esterification reaction of oleic acid with ethanol

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ABSTRACT

Ammonium and cesium derivatives from $\text{H}_3\text{PW}_{12}\text{O}_{40}$ (H_3PW), namely $(\text{NH}_4)_x\text{Cs}_{2.5-x}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ ($x = 0.5, 1, 1.5, 2$), were synthesized and structurally characterized by FT-Raman spectroscopy, and their thermal stability was evaluated by FTIR and TGA/DTA. The acidity was characterized by the adsorption/desorption of gaseous pyridine, by FTIR and TGA/DTA as well as by the reaction of oleic acid and ethanol. The stability of the mixed salts regarding the Keggin structure was much higher than the parent acid, with the onset decomposition around 520 °C. Nonetheless, calcination up to 300 °C is recommended for the integrity of the mixed salt. The FTIR of adsorbed pyridine displayed only Brønsted acidic sites, which was confirmed by TGA measurements of the formation of $\text{Py-H}^+ \cdots \text{Py}$ adducts. The best esterification result was for $(\text{NH}_4)_2\text{Cs}_{0.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ with TOF = $1.314 \text{ mol}_{\text{EO}} \text{ mol}^{-1} \text{ proton s}^{-1}$ with a 1:6 (oleic acid:ethanol) molar ratio, at 80 °C and 10 wt% catalyst in relation to the acid.

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1. Introduction

Polyoxometalates (POMs) are a class of clusters with a unique range of physical and chemical properties [1]. These materials can be used in a variety of technological fields, but their use as catalysts continues to be their most common application. POMs with Keggin structures are the most disseminated type of catalyst and are used for a wide range of organic reactions (e.g., multi-component, oxidation, reduction, electrochemical, photochemical) [2]. Their use has been evaluated not only for bench-scale laboratory research but also for large-scale industrial processes [1–3]. Among the various POMs, 12-tungstophosphoric acid ($\text{H}_3\text{PW}_{12}\text{O}_{40}$, H_3PW), along with its salt derivatives, is the most studied material for acidic reactions because it is the strongest heteropolyacid in the series [4].

Biodiesel is the name given to long-chain alkyl esters derived from biomass feedstock [5,6]. It is a plausible substitute for petroleum diesel because it is obtained from renewable sources. It is attractive as an alternative fuel not only because of its environmental benefits (e.g., biodegradability, low emission profiles), but also due to the possibility of producing biodiesel using

second-generation resources [7]. In light of green processes, the use of heterogeneous catalysts is preferable to that of homogeneous catalysts [8]. Among several catalysts tested for biodiesel production, the POMs stand out [9], such as in the studies of Giri et al. [10] about the esterification of palmitic acid with methanol over the ammonium salt of H_3PW . Kulkarni et al. [11] achieved biodiesel production through the simultaneous esterification and transesterification of a mixture of rapeseed oil and oleic acid (90:10 wt% proportion) with ethanol, using H_3PW supported on diverse oxides. Morin et al. [12] reported the transesterification of rapeseed oil with methanol and ethanol utilizing heteropolyacids, such as H_3PW , 12-tungstosilicic acid (H_4SiW) and 12-molybdophosphoric acid (H_3PMo), as catalysts. Narasimharao et al. [13] tested a series of $\text{Cs}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$ salts ($x = 0.9–3$) and found that they were active for esterification of palmitic acid and transesterification of tributyrin. Chai et al. [14] produced biodiesel using $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ as catalyst. They have used the oil of *Eruca sativa* Gars (ESG, a kind of crucifer plant) for the transesterification reaction with methanol. A study by Sunita et al. [15] reported the production of biodiesel by the transesterification of sunflower oil with methanol, using zirconia-supported isopoly and heteropoly tungstates. Cardoso et al. [16] used H_3PW as a homogeneous catalyst to promote the esterification of different saturated and unsaturated fatty acids (myristic, palmitic, stearic, oleic and linoleic) under mild reaction

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