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Heteropolyacid salts as self-separation and recyclable catalysts for transesterification of trimethylolpropane

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ABSTRACT

A series of heteropolyacid (HPA) salts as catalysts were prepared and characterized. Transesterifications of trimethylolpropane (TMP) were carried out using these catalysts. The influence of organic cations and heteropolyanions on the reaction, optimization of reaction conditions, and catalytic reusability were investigated. The results show that the heteropolyacid (HPA) salts present a self-separation performance after reaction, which can be easily recovered and quite steadily reused as demonstrated by a eight-run recycling test. Moreover, the pyridinium with $PW_{12}O_{40}^{3-}$ as the anion ($[PyBS]_3PW_{12}O_{40}$) showed the best catalytic performance among the heteropolyacid salts for the transesterification of trimethylolpropane with various methyl esters.

1. Introduction

Biodegradable lubricants derived from vegetable oil-based stocks exhibit better lubricity, an excellent viscosity index, and lower volatility than those that are petroleum-based [1–3]. Despite these advantages, vegetable oil-based lubricants have been slow in gaining wide acceptance as lubricants because of their variable quality, higher cost compared with mineral oils, and inherent performance limitations [4]. One of the techniques used to improve the lubrication properties of the vegetable oil is to change the structure of the oil by converting it to a new type of ester called polyol esters. Transesterification of trimethylolpropane (TMP) is one of the most important reactions for the synthesis of these polyol esters [5]. These synthetic esters can be derived from combinations of various methyl esters and polyols. The vital feature of these esters is that on the alcohol portion of the molecular structure, there is no hydrogen atom on the â-carbon. This feature provides them with high oxidative and thermal stability seldom found in vegetable oil-based lubricants [6,7].

Traditionally the synthesis of polyol esters is carried out in presence of an acid or basic catalyst or an organic solvent to promote the reaction rate [4,8,9]. However, these catalysts cannot be readily recovered nor reused. Moreover, they have other disadvantages such as equipment corrosion, more byproducts, a tedious workup procedure and a difficult separation process, which may result in a series of environmental problems and reaction inefficiency. The use of lipases as biocatalysts for polyol esters production has been of great interest due to its environmental friendliness [10,11]. However, some reagents such as trimethylolpropane or polyol deactivate the lipase to some extent and the enzyme stability is poor. Because of the detrimental effects of these catalysts, great efforts have been directed towards the benign development of environmentally friendly catalysts for the synthesis of polyol esters as biodegradable lubricants.

The task specific ionic liquids (TSILs), which are environmentally friendly solvents and catalysts, have gained the attention of scholars from various fields due to their adjustable physical and chemical properties. They are non-flammable, exhibit negligible vapor pressure, as well as high catalytic activity and offer the potential for recyclability [12–14]. These results, however, are not entirely satisfactory because the present systems still suffer from high content of ionic liquids (ILs) (20–300 mol%) needed in the reaction media, relatively long reaction time, and the need to remove by-product from the IL phase in the IL recycling experiment. A family of heteropolyacid (HPA) salts as novel and special ionic liquid catalysts in esterification was first reported by Leng et al. [15]. These catalysts were used as “reaction-induced self-separation catalysts” for esterification with one of the reactants being polycarboxylic acid or polyol. The high melting points and good solubility in the polyol reactants of these heteropolyacid salts result in the switching from homogeneous to heterogeneous catalysis, which makes the recovery and the catalytic reuse of this kind of catalyst very convenient. All of these studies motivated the preparation of a series of heteropolyacid (HPA) salts (Scheme 1) for the transesterification of

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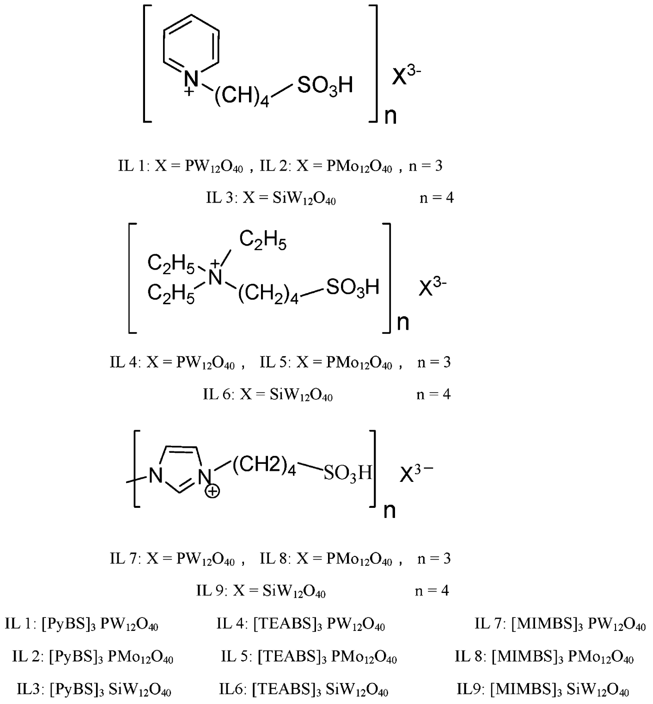


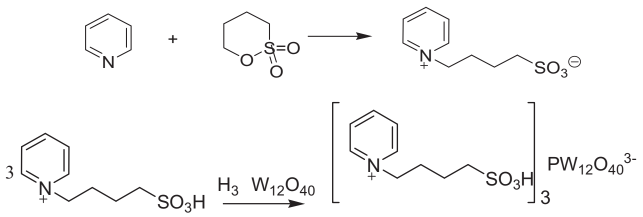
Scheme 1. Structures of heteropolyacid salts prepared in this paper.

TMP to polyol esters. These catalysts were characterized by infrared (IR) spectroscopy, nuclear magnetic resonance (NMR) and electrospray ionization mass spectrometry (ESI-MS). Various parameters including the influence of organic cations and heteropolyanions of HPA salts, the effect of reaction temperature, catalyst dosage and reaction time, and the recycling performance of the HPA salts were studied. The results showed that these catalysts exhibited high activity and good reusability in the transesterification of TMP with various methyl esters.

2. Experimental

2.1. Chemicals and instruments

Pyridine (99%), triethylamine (99%), 1-methylimidazole (99%), 1,4-butane sultone (99%), silicotungstic acid (AR), phosphotungstic acid (AR), phosphomolybdic acid (AR) and other chemicals (AR) were commercially available and were used without further purification unless otherwise stated. NMR spectra were recorded on a BRUKER AV400 spectrometer in D_2O and were calibrated with tetramethylsilane (TMS) as the internal standard. IR measurements were performed on a Nicolet.510P FT-IR absorption spectrometer using KBr windows suitable for Fourier transform infrared (FTIR) transmittance technology to form a liquid film. ESI-MS spectra were obtained on a BRUKER Corporation Esquire HCT PLUS instrument. The quantitative analysis of the product was directly carried out using a high-temperature capillary column, capillary column SGE HT5, 12 m, 0.53 mm, i.d. 0.15 μm (SGE, Melbourne, Australia). The oven temperature was set initially at 80 °C, held for 3 min, then increased at 6 °C/min to 340 °C and held for another 6 min. The injector and detector temperatures were at 300 °C and 360 °C, respectively. Nitrogen was used as the carrier gas at a flow rate of 26.7 mL/min. The split ratio was set at 1:1, and 1.0 μL of sample was injected into the GC system [16].



Scheme 2. Synthesis of heteropolyacid salts.

2.2. Preparation of HPA salt catalysts

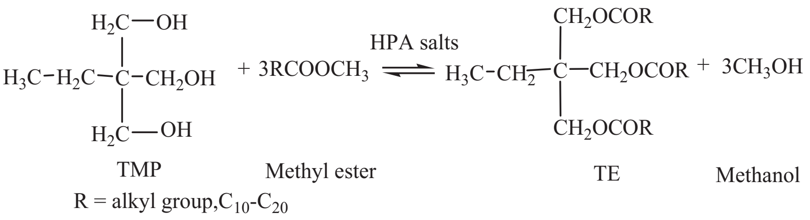
The HPA salts used in this article were synthesized in a procedure similar to the previous reported paper [15]. Scheme 1 shows the structures of HPA salts used in this study. For IL 1 ($[PyBS]_3PW_{12}O_{40}$), pyridine (0.11 mol) and 1,4-butane sultone (0.10 mol) were dissolved in toluene and stirred at 40 °C for 24 h under a nitrogen atmosphere. A white precipitate formed; it was filtered and washed with ether three times, then dried in a vacuum. The resulting white precipitate (0.006 mol) was added to the aqueous solution of $H_3PW_{12}O_{40}$ (0.002 mol), followed by the stirring of the mixture at 80 °C for 8 h. Water was removed in a vacuum to give a solid final product, other HPA salts were prepared using the same method (Scheme 2).

2.3. Determination of the Hammett acidity function of HPA salts

The indicator 4-nitroaniline was used in the experiment. The heteropolyacid salts and 4-nitroaniline were dissolved in high purity water at concentrations of 0.1 mmol/L and 2 mmol/L, respectively. The solutions were shaken vigorously and then left to stand for 6 h. Then their UV–vis spectra were recorded on an HP 8453 UV–vi spectrophotometer.

2.4. General procedure for transesterification of TMP

Transesterification of TMP with methyl oleate was first carried out as a model reaction (Scheme 3), using various heteropolyacid salts as catalysts under proposed operating conditions. The methyl oleate and catalyst were weighed into the reactor, after which the appropriate amount of TMP was added. The mixture was heated in the oil bath until the TMP melted at around 60 °C. Then the mixture was gradually heated to the operating temperature and refluxed for 1–12 h. The reaction product was sampled at certain time intervals for analyses with GC [16]. A high-temperature capillary column (SGE HT5) was used to carry out the analysis. Before



Scheme 3. Transesterification of TMP using HPA salts as catalysts.