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Transesterification reaction of triglycerides in the presence of Ag-doped $H_3PW_{12}O_{40}$

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ABSTRACT

Present work is concerned with examination of catalytic properties of 12-tungstophosphoric acid and its silver salts $Ag_xH_{3-x}PW_{12}O_{40}$ with Ag-content ranging from $x = 0.5$ up to $x = 3$ for transesterification of triglycerides with methanol to form methyl ester (biodiesel) under mild conditions (atmospheric pressure, temperature of 50–60 °C). Reaction was studied for triacetin, a model triglyceride and for vegetable oil, castor oil. Various techniques (BET, FTIR, XRD, XPS, laser diffraction, electron microscopy, SEM, and EDS) were used to characterize as-received Ag-salts and the samples separated after the catalytic tests. Because of the presence of methanol, which is the reactant, silver salts formed colloidal dispersion during the catalytic reaction. Under such conditions, all silver salts were active for transesterification of triglycerides. The conversion of triglycerides gradually decreases as the protons in heteropolyacid are replaced by Ag^+ cations. However, due to the leaching of parent $H_3PW_{12}O_{40}$ upon dissolving in methanol, the contribution of homogeneous catalysis was observed, especially in the presence of Ag-salts with low silver content such as $Ag_{0.5}H_{2.5}PW_{12}O_{40}$. Catalytic performance of Ag-salts in methanolysis of a short-chain triglyceride, triacetin, differs remarkably from that in castor oil comprising natural, long-chain triglycerides. After transesterification of castor oil, initially crystalline particles of Ag-salts partially rearrange to "gel-type" material making their further processing difficult. Although, no "gel-type" particles are formed after reaction of triacetin, the formation of "nanowires" due to partial reduction of some of Ag^+ ions is observed.

1. Introduction

Biodiesel, a nonpetroleum-based fuel consists of fatty acid methyl-esters (FAME) formed through a transesterification reaction. In this process, the triglycerides of fatty acids (C_{14}–C_{20}) from renewable sources like vegetable oils, animal fats and recycled greases from food industry are converted to methyl-esters and glycerol as a by-product in transesterification reaction with methanol (methanolysis). The reaction has traditionally been catalysed by homogeneous catalysts, such as K- or Na-alkoxides or -hydroxides, and mineral acids [1–3]. However, the application of heterogeneous catalysts is more desirable from economic, technological and environmental points of view. In particular, solid acid catalysts seem to be very useful since they are able to catalyse both the transesterification of triglycerides and esterification of free fatty acids, which becomes important when using recycled greases. Therefore, great research efforts have recently been undertaken to find efficient solid acid catalysts and the results of these studies were reviewed in general papers [1–3].

The most commonly tested vegetable oils include palm oil, soybean oil, sunflower oil, coconut oil and rapeseed oil. Moreover, castor oil derived from *Riccinus communis* plants is mentioned frequently in the literature as a potential raw material for biodiesel. The main constituent of castor oil is triglyceride of 12-hydroxy-9-octadecenoic acid (ricinoleic acid, Scheme 1). Due to the presence of OH group at C-12 carbon, castor oil exhibits unique chemical and physical properties. Castor oil is well soluble in both methanol and methyl-esters formed and the homogeneity of reaction mixture is attained during transesterification reaction [4–6].

It is well known that Keggin type heteropolyacids and their acidic salts are useful catalysts for reactions requiring strong acidity. Although they are useful solid catalysts for gas-phase reactions, they are highly soluble in polar media like water and methanol. Therefore, when studied in methanolysis of rapeseed oil, heteropolyacids ($H_3PW_{12}O_{40}$, $H_4SiW_{12}O_{40}$, and $H_3PMo_{12}O_{40}$) acted as homogeneous catalysts and their activity was higher than those of mineral acids (H_2SO_4 and H_3PO_4) [7]. However, quite recently published data demonstrated that heteropolyacids ($H_3PW_{12}O_{40}$ and $H_3PMo_{12}O_{40}$) supported on acid-treated K-10 clay were effective and stable catalysts in the transesterification of different oils with alcohols [8]. On the other hand, by combining various amounts of heteropolyacid $H_3PW_{12}O_{40}$ and large monovalent

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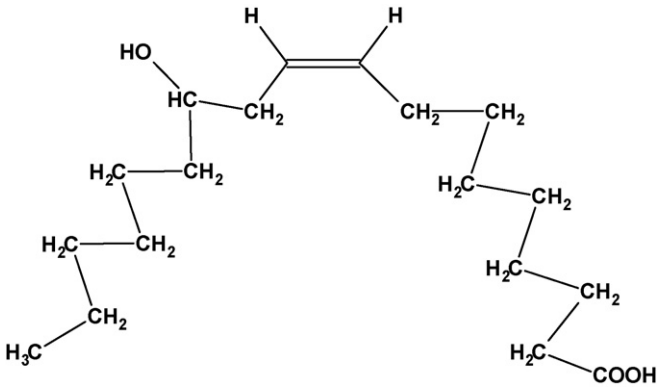
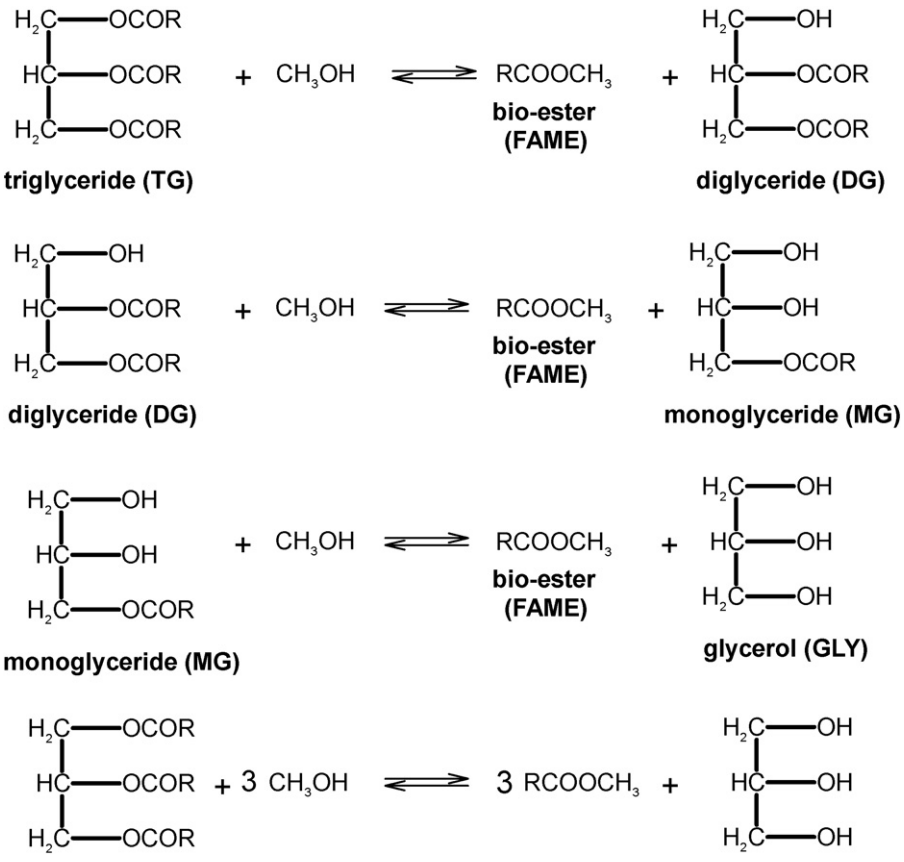
cations such as NH_4^+, K^+, Cs^+ and Ag^+ microporous solid acidic catalysts were obtained. They were highly effective in a number of catalytic reactions including isomerization, hydration, alkylation, hydrolysis, and esterification [9–13]. Catalytic efficiency of Cs- and K-salts of heteropolyacids was also evaluated for transesterification of triglycerides [13–17]. For instance, cesium salts $Cs_xH_{3-x}PW_{12}O_{40}$ with various Cs content (x = 0.9–3) were found to be effective catalysts in methanolysis of tributyrin, a model compound of natural triglycerides [13]. Their activity increased with an increase of Cs content up to x = 2.0–2.3, and then dropped rapidly. Two salts $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ and $Cs_2HPW_{12}O_{40}$ turned out to be effective acid catalysts for the transesterification of vegetable oil (*Eruca sativa Gars*) [14] and rapeseed oil [15], respectively. Cs-doped $H_4SiW_{12}O_{40}$ catalyst was found to be active in transesterification of model C_4 and C_8 triglycerides and esterification of palmitic acid [16]. In our previous work Cs- and K-salts of $H_3PW_{12}O_{40}$ were studied in methanolysis of castor oil [17]. In the reaction mixture they formed colloidal dispersion. This resulted in much higher activity of K-salts when compared to that of their Cs-analogous. Moreover, the NH_4^+, K^+ and Cs^+ salts of HPW were found to be effective catalysts in esterification of palmitic acid [16,18,19].

On the other hand, markedly less attention was directed to catalytic properties of insoluble silver salts of $H_3PW_{12}O_{40}$. Literature data show that due to the presence of acidic protons and Ag^+ cations they can act as bifunctional catalysts. This type of bifunctional activity was observed by Moffat and co-workers in a ring-expansion of methylcyclopentane and ring-contraction of cyclohexane [20]. Furthermore, such bifunctionality was noticed by Haber et al. in hydration of ethylene and dehydration of ethanol [21]. Catalytic activity of Ag-salts of $H_3PW_{12}O_{40}$ caused by the acidic centres was observed in dehydration of the 1-, 2- and tert-butyl alcohols [22]. In all these reactions gaseous reactants were used whereas Ag-salts acted as the solid catalysts (gas-phase reactions). Quite recently, Yadav et al. [23] reported that $Ag_3PW_{12}O_{40}$ was mild and selective acid catalyst in the synthesis of β-ketoesters via C–H insertion, reaction performed in liquid phase using dichloromethane as the solvent.



Scheme 1. Ricinoleic acid.

In the present work, silver salts $Ag_xH_{3-x}PW_{12}O_{40}$ with various Ag-content ranging from x = 0.5 up to x = 3 are studied. Their catalytic properties are evaluated for transesterification of triglycerides by methanol, i.e. in reaction performed in highly polar medium. Reaction is studied for triglycerides, namely castor oil and triacetin. The methanolysis of triacetin (the acetic acid triester of glycerol) which is the simplest triglyceride has already been studied as a model reaction for the transesterification of natural oils [24–29]. Triacetin exhibits the same chemical functionality of any triglyceride molecule and shares the same reactivity



Scheme 2. Tranesterification of triglyceride with methanol.