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Synthesis of Trimethylolpropane Esters of Oleic Acid Using a Multi-SO₃H-Functionalized Ionic Liquid as an Efficient Catalyst

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Abstract Biodegradable trimethylolpropane triesters of oleic acid were synthesized by esterification of trimethylolpropane and oleic acid over a multi-SO₃H-functionalized strong Brønsted acidic ionic liquid as the catalyst. The results showed that the esterification can proceed satisfactorily over the catalyst at an ambient pressure even without simultaneous removal of water. Under the optimal reaction conditions (temperature: 100 °C, reaction time: 3 h, reactant molar ratio: 3.6:1, and catalyst amount, high conversion rate of trimethylolpropane (99.0%) and selectivity of trimethylolpropane triester (92.1%) were obtained. The ionic liquid was reused six times after the removal of water and no obvious change in catalytic activity was detected. Operational simplicity, high yields along with good reusability makes the multi-SO₃H-functionalized ionic liquid a promising catalyst for the esterification of trimethylolpropane with oleic acid.

Keywords Brønsted acidic ionic liquid · Esterification · Trimethylolpropane esters · Oleic acid

Introduction

With the increasing awareness of environment protection and highly variable price of crude petroleum, lubricants

R.-J. Li · L. Chen · Z.-C. Yan (⊠) School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510640, China e-mail: zcyan@scut.edu.cn made or derived from vegetable oil have attracted more and more attention due to their excellent biodegradability, low toxicity and environmentally benign nature [1]. However, to compete with traditional petroleum-based lubricants, vegetable oil based lubricants have to overcome some inherent defects such as inadequate oxidative and thermal stability, poor corrosion protection and poor lowtemperature performance. Therefore, chemical modifications such as transesterification, epoxidation and esterification have been proposed for improving the performance. The esterification reaction between fatty acid and polyol is an industrially important tool for obtaining desired polyhydric esters. Among all those polyesters, trimethylolpropane triesters (TE) has been paid much attention in recent years due to their improved thermal and hydrolytic stability because of the absence of β -H [2]. Meanwhile, preference is being given to the use of oleic acid (OA) in the synthesis of polyhydric esters [3], since the existence of monounsaturated fatty acids is important for the balance between low-temperature and oxidation stability properties [4]. Also, the aquatic toxicity of oleochemical esters is very low or almost negligible [5]. A considerable amount of work has been done on the esterification of oleic acid with polyol [6-10]. In most of these studies, the choice of catalyst used for the esterification was problematic.

Traditionally, homogeneous inorganic acids and alkali were used as esterification catalysts. However, alkali catalysts may cause saponification and inorganic acids are responsible for the dark color of the reaction products. More importantly, they are not renewable and may result in a difficult separation process which causes environmental pollution. Heterogeneous catalysts, such as metallic or metal oxide, can also serve as an alternative choice for the preparation of polyol esters. Although these catalysts can be recycled easily, they have other shortcomings such as

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deactivation from coking, high costs and some of them still have the tendency to cause saponification [9]. Biocatalysts such as lipases have attracted much attention because they are environmentally friendly. However, long reaction time, deactivation from polyols such as trimethylolpropane (TMP) and higher amounts of lipases required compared with other catalysts limited the broad application of enzymes [7, 10].

Ionic liquids (ILs) have been shown as promising catalysts for esterification and transesterification owing to their negligible volatility, excellent thermal stability and the variety of structures available. The research and application of various -SO₃H acidic ionic liquids have received much attention because they are flexible, non-corrosive and immiscible with many organic solvents. In 2002, Cole et al. first published an article about sulfonic acid group functionalized ionic liquids with strong Brønsted acidity [11]. After that Liu [12] prepared a series of double SO₃Hfunctionalized ionic liquids as catalysts in the esterification of glycerol and acetic acid. Although the catalyst amount required is relatively small, the ionic liquids were entirely miscible with the reaction mixture, thus can't be easily separated by simple decantation. In 2009, Leng [13] reported a series of heteropoly anion-based ionic liquids containing three $-SO_3H$ functional groups in the cation. The heteropolyacid (HPA) salts have been of great interest due to its "reaction-induced, self-separation" characteristic. They can switch from homogenous to heterogeneous catalysis due to their high melting points and good solubility in the polyol reactants. This unique property makes the recovery and catalytic reuse of the catalysts very convenient. In this study the specific catalyst employed was [PyBS]₃PW₁₂O₄₀ due to its outstanding catalytic properties as opposed to other HPA salts in the polyol reaction system [14]. High conversions were obtained at ambient pressure without a water separator or azeotroping agent, whereas many other processes described in the literature are either conducted under vacuum or equipped with a water separator [10, 15, 16]. The main focus of this paper was to investigate the use of a multi-SO₃H-functionalized ionic liquid as an efficient catalyst for the synthesis of trimethylolpropane esters. To develop an optimum synthesis method, the effects of reaction time and temperature, catalyst amount, molar ratio of reactants and the recycling performance of the HPA salt must be studied.

Experimental

Chemicals and Instruments

Pyridine (99%) was obtained from J&K Chemical (Guardzhou, China), 1,4-butane sultone (99%) was obtained

from the Feng-fan reagent factory (Wuhan, China), ether (AR), OA (AR), ethyl acetate (AR) were purchased from Kermel (Guangzhou, China). Phosphotungstic acid (AR), TMP (AR) and N,O-bis (trimethylsilyl) trifluoroacetamide (BSTFA) were purchased from Aladdin (Shanghai, China). All the reagents were used without further purification unless otherwise stated. Gas chromatography analysis was performed on a GC with a flame ionization detector. A high-temperature capillary column, SGEHT5, 12 m, 0.53 mm, i.d. 0.15 µm (SGE, Melbourne, Australia) was used. 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 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 [17]. H-NMR spectra were recorded on a Varian 300 MHz spectrometer.

Preparation of the [BSPy]₃PW₁₂O₄₀ Catalyst

The HPA salts used in this article were synthesized by modification of the literature procedure [13]. Pyridine (0.11 mol) and 1,4-butane sultone (0.1 mol) were dissolved in toluene and stirred magnetically at 40 °C for 24 h until a white precipitate formed. Then, the precipitate was filtered and washed with ether three times then dried in a vacuum at 80 °C for 10 h. The resulting white precipitate (0.006 mol) was added to an 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. ¹H NMR (400 MHz, D₂O, TMS): δ 1.61 (m, 2H), 2.12 (m, 2H), 2.89 (t, 2H, J = 15.2 Hz), 4.51 (t, 2H, J = 14.8 Hz), 4.73 (s, 2H), 7.95 (t, 2H, J = 14.4 Hz), 8.41 (t, 1H, J = 1.2 Hz), 8.70 (d, 2H, J = 6.4 Hz).

Preparation of Trimethylolpropane Esters

A typical procedure for the esterification of TMP with oleic acid using HPA salts is as follows (Scheme 1). Appropriate amounts of TMP, OA, and $[PyBS]_3PW_{12}O_{40}$ were introduced into a 150-ml capacity round-bottom flask equipped with a mechanical stirrer. The flask was immersed in an oil bath maintained at the operating temperature, a condenser was connected to the reaction flask. The reaction product was sampled at specific time intervals for analyses with GC. The reaction time was calculated once the temperature reached the designated temperature. A high-temperature capillary column (SGEHT5) was used to carry out the analysis. Before injection, the sample was diluted with 1.0 mL of ethyl acetate and swirled for a few minutes to dissolve the mixture. *N,O*-bis (trimethylsilyl) trifluoroacetamide (BSTFA) (0.5 ml) was then added to the mixture



Scheme 1 Esterification of TMP and OA over $[PyBS]_3PW_{12}O_{40}$ catalyst $R = CH_3(CH_2)_7CH = CH(CH_2)_7$

and swirled. The sample was then transferred to a water bath held at 40 °C for 10 min. This procedure provided a complete separation of reaction products: TMP, oleic acid, monoesters (ME), diesters (DE), and triesters (TE) [17]. The quantitative analyses of the final products were based on the Eqs. 1 and 2, the conversion was estimated with respect to the initial and the final TMP in the mixture. The amount of TMP and TE was calculated based on external standard method. At completion, the reaction mixture was cooled to room temperature. The catalyst precipitated as a solid at the bottom layer and could be easily separated by decantation (or filtration). The produced esters with unconverted reactants were at the upper liquid layer. Three runs were conducted for each experiment, the average data were calculated.

The TMP conversion and TE selectivity were calculated as follows:

$$x = \left(1 - \frac{C_{\text{TMP,P}}}{C_{\text{TMP,S}}}\right) \times 100\% \tag{1}$$

 $C_{\text{TMP,P}}$: the amount of TMP in the product, $C_{\text{TMP,S}}$: the amount of TMP added to the reaction system.

$$y = \left(\frac{C_{\rm TE}}{C_{\rm TMP,S} - C_{\rm TMP,P}}\right) \times 100\%$$
⁽²⁾

 C_{TE} : the amount of TE in the product, $C_{\text{TMP,P}}$: the amount of TMP in the product, $C_{\text{TMP,S}}$: the amount of TMP added to the reaction system.

Reuse of the Catalyst

After reaction, the catalyst was decanted from the mixture and washed with ethyl acetate to get rid of the unreacted OA. Then the ionic liquid was subjected to a vacuum (0.01 Torr) at 80 °C to remove ethyl acetate and water.

Results and Discussion

Effect of Temperature on the Esterification

The reactions were carried out at 80, 90, 100, 110, 120, 130 and 140 $^{\circ}$ C with the aim of observing the effect of

temperature on the conversion of TMP. The temperature mentioned here was the oil bath's temperature. Experiments were conducted with a 3.7:1 molar ratio of oleic acid to TMP, 4%w/w catalyst for 3 h. The GC chromatogram of trimethylolpropane esters is shown in Fig. 1. The retent time of OA, ME, DE, and TE was 14.410, 22.934, 35.368, and 45.125 min, respectively. The results are shown in Fig. 2.

As compared with the reaction temperature in previous reports concerning the conventional homogenous and heterogeneous catalysts for esterification [9, 18], the catalyst gave a satisfactory yield of the TE at a much lower temperature. Initially, both the conversion of TMP and selectivity of TE (w%) increased with the reaction temperature and reached 99.0 and 92.8%, respectively, at 100 °C, then the yield dropped with further increases of the reaction temperature.

When the reaction temperature was in the range of 80–100 °C, increasing the reaction temperature was helpful in increasing both the reaction rate and the content of TE in the products. The explanation may be that a relatively high temperature is favorable for the increasing of reaction rate, hence leads to the increasement in the selectivity of TE. When the temperature remained under 110 °C, the selectivity of ME was higher than that of DE, indicating that, at lower reaction temperatures, the formation of ME is more predominant than that of DE. This is similar to what was reported by Liu [12] for the esterification of glycerol and acetic acid.

However, when the temperature increased above 100 °C, the yield of TE (w%) dropped accordingly, meanwhile the selectivity of ME and DE increased. This phenomenon may suggest that the reverse reaction may become more significant at higher temperatures. On the other hand, the presence of a TMP monoester with 2 free –OH moieties can act as a promoter for oligomerization leading to the formation of trimers, tetramers, etc., [19]. Carbonization and oligomerization may occur at higher temperatures (140 °C) and consequently result in some side-reaction products, which could also reduce the content of TE in the final product. This is also in agreement with the observation made during the reaction that when the temperature reached 130–140 °C, the product turned dark.

100

80

60

40

20

0

80

conversion and selectivity (w%)

Fig. 1 GC chromatogram of trimethylolpropane esters (*OA* Oleic Acid, *ME* trimethylolpropane monoesters, *DE* trimethylolpropane diesters, *TE* trimethylolpropane triesters)



Fig. 2 Influence of reaction temperature on transesterification of TMP and OA (OA: TMP, 3.7:1; catalyst 4% w/w; 3 h)

Effect of Reaction Time on the Esterification

The effect of the reaction time (1-5 h) on the product yield was investigated over the $[PyBS]_3PW_{12}O_{40}$ catalyst, as shown in Fig. 3. It can be seen that the concentration of TE reached 88.0% after reacting for 3 h, and the TMP conversion held at a high level (>95.0%). The content of TE decreased rapidly with a further increase in the reaction time to 3–5 h, while the conversion of TMP changed slightly. As has already been mentioned above, the

Fig. 3 Influence of reaction time on esterification of TMP and OA (OA:TMP, 3.7:1; catalyst 4%w/w; 100 °C)

esterification is a reversible reaction. It is natural that after a certain period of time the rate of reverse reaction gradually increases until it attained an equilibrium condition, where the rate of the reverse reaction equals the rate of the forward reaction, i.e., net $r_{\text{TE,net}} = 0$.

It also has been observed that when the reaction time is extended from 3 to 5 h, the color of the reaction system turns from light yellow to dark brown. This may suggest that polymerization, carbonation and so on may become more significant. Influence of Catalyst Amount on the Esterification

The number of alkyl sulfonic acid groups can affect the catalytic performance of the ionic liquids significantly by influencing the acidity of ionic liquids. There are three SO_3H groups in the cation, which made the acidity of the catalyst extremely high, hence the catalytic activities of heteropolyacid salts are much higher than the conventional Brønsted IL with a single $-SO_3H$ functional group when the same catalytic amount was used in the reaction [14].

The influence of the catalyst amount $(1.0 \sim 7.0\% \text{ w/w})$ on the yield of TE and conversion of TMP was examined at 100 °C, as is shown in Fig. 4. With the increase in the catalyst amount, the selectivity of TE and conversion of TMP increased accordingly at first, reaching 92.4 and 99.0 wt% respectively, when the amount of catalyst was 3.0% w/w. Therefore, the optimal catalyst amount is 3.0% w/w. Initially, the selectivity of TE and the conversion of TMP went up with the increasing amount of [PyBS]₃PW₁₂O₄₀ due to the increase on acidic sites. However, it has been observed that as the amount of catalyst increases from 1 to 7%, the color of the product turns from light yellow to dark brown. This might be a suggestion that much higher acidity may also promote side-reactions, consequently result in reduction of the selectivity of TE.

Effect of the Molar Ratio of the Reactants

The esterification reaction is an equilibrium reaction and generally requires removal of water and/or use an excess amount of the reactants for a satisfactory conversion rate [20]. In this case, an excess of OA was added to the reaction system because it is relatively cheaper compared with TMP. However, a high OA concentration may slow



Fig. 4 Influence of catalyst amount on esterification of TMP and OA (OA: TMP, 3.7:1; 3 h; 100 °C)

down the reaction rates due to various reasons. Moreover, from a practical point of view, a small amount of di- or monoesters is a much smaller problem than a large excess of unreacted free fatty acid. Therefore, it is necessary to optimize the actual excess OA concentration to be employed in a given reaction. The influence of reactants molar ratio on the selectivity of TE and conversion of TMP was investigated and the results are shown in Fig. 5.

The selectivity of TE increased rapidly with the molar ratio of reactants increasing from 3.3 to 3.6. The increase in OA in the reaction system may provide more opportunity for the collision of reactant molecules; it is also favorable for moving the equilibrium of the reversible esterification toward TE formation. However, a further increase in the reactants molar ratio caused a slight decrease in the selectivity of TE. When the molar ratio of OA to TMP is higher than 3.6, an excess of OA results in a proportional decrease in the amount of catalyst, which then leads to a decrease in acidity in the reaction system. A weak acid reaction does not promote further esterification of DE with TMP.

Reusability

Recycling of ionic liquids prevents them from ending up in the aquatic environment, at the same time, it is economically beneficial because ionic liquids still remain expensive in comparison to their alternatives. In order to investigate the reusability of [PyBS]₃PW₁₂O₄₀ as a self-separation and recyclable catalyst for the esterification of TMP, a series of recycling experiments were performed.

 $[PyBS]_{3}PW_{12}O_{40}$ catalyst has excellent solubility in water or strong polar solvents but was immiscible with non-polar components which made the catalyst insoluble in



Fig. 5 Influence of Reactants Molar Ratio on esterification of TMP and OA (catalyst 3%w/w; 3 h; 100 °C)



Fig. 6 Reusability of $[PyBS]_3PW_{12}O_{40}$ (OA: TMP, 3.6:1; 3 h; 100 °C; catalyst 3% w/w)

the OA and the TMP esters formed. An interesting phenomenon was observed when the reacted mixture cooled down to room temperature, the catalyst appeared at the bottom of the reactor as a kind of solid, while the produced ester with unconverted reactants remained as liquid at the upper layer. So the catalyst was able to be conveniently decanted out from the reaction system and recycled into the next run. The reuse results of $[PyBS]_3PW_{12}O_{40}$ are shown in Fig. 6. $[PyBS]_3PW_{12}O_{40}$ was reused six times with only a slight decrease in the selectivity of TE at the second run, after that it was rather stable during the repeated usage. The slight decrease in TE selectivity might be ascribed to the slight deactivation of IL [21]

The good reusability of $[PyBS]_3PW_{12}O_{40}$ may be due to its molecular structure. The alkane sulfonic acid group is the major constituent of the catalytic activities, and it is covalently tethered to the cation of ionic liquid, which is not readily lost.

Conclusions

The present work demonstrated the synthesis of biodegradable oleic acid trimethylolpropane ester using $[PyBS]_3PW_{12}O_{40}$ as an efficient and recyclable catalyst. Various parameters were studied; the optimal reaction temperature, the reactants molar ratio, reaction time and catalyst dosage were found to be 100 °C, 3.6:1, 3 h, and 3 wt% respectively. The ionic liquid was reused for six trials without any obvious change in catalytic activity. Even though the detailed reaction mechanism of esterification of TMP ad OA over the multi-SO₃H-functionalized ionic liquid is not clear at this stage, the preliminary experimental results show that esterification over $[PyBS]_3PW_{12}O_{40}$ catalyst is quite satisfactory. The ionic liquid made the removal of water unnecessary while achieving a high conversion rate of TMP (99.0%) and a selectivity of TE (92.4%). More importantly, the catalyst can easily be recovered by simple methods such as filtration or decantation and directly reused after removal of water under a vacuum.

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711

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