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Quaternary Ammonium Salt Functionalized Methoxypolyethylene Glycols-Supported Phosphotungstic Acid Catalyst for the Esterification of Carboxylic Acids with Alcohols

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Abstract The quaternary ammonium salt functionalized methoxypolyethylene glycols-supported phosphotungstic acid catalyst was prepared and characterized using X-ray diffraction, fourier transform infrared spectroscopy and thermogravimetric analysis. The immobilized phosphotungstic acid catalyst exhibited excellent catalytic activity and selectivity, which was shown to be an efficient heterogeneous catalyst for catalyzing the esterification of carboxylic acids with alcohols under mild conditions. The catalyst could be separated by simple separation and can be used six times without significant losing of catalytic activity and selectivity.

Keywords Quaternary ammonium salt · Methoxypolyethylene glycols · Phosphotungstic acid · Esterification

1 Introduction

Either aliphatic or aromatic esters were important compounds in industry processing, which were widely used in the field of polymer chemicals, fine chemicals and pharmaceuticals etc. [1]. Generally, the esters were manufactured through the homogeneous acid-catalyzed esterification of acids and alcohols. The acids used for esterification mainly contained heteropoly acid and other strong inorganic acid, such as sulfuric acid [2]. Although the esterification reaction was performed well in a homogeneous system and higher yields can be obtained, some problems were introduced like difficulty to separate catalyst with product, corrosion of equipment as well as side reaction etc. [3].

In order to overcome the drawbacks, the heterogeneous catalyst systems have been developed for esterification reaction [4, 5]. Among supported-acidic catalysts, the supported-heteropoly acids catalyst, with stronger acidity, showed higher catalytic activities during the reaction than the conventional acid catalysts [6, 7]. Furthermore, the heteropoly acids catalysts did not introduce undesirable side reactions, such as sulfonation and chlorination, as well as corrosion of equipment, which was considered as non-toxic, eco-friendly, and environmentally benign catalysts [8]. As a typical heteropoly acid, the supported-phosphotungstic acid (PTA) catalysts, such as PTA on clay [9, 10], MCM-41 [11], and ion-exchange resins [12] etc., had been widely studied in acid-mediated esterification reactions.

Recently, immobilization of PTA on polymer materials has attached more attentions, as catalysts, which showed good catalytic activity and reusability in esterification of acids with alcohols [13, 14]. As a catalyst carrier, the polymer should be soluble in some solvents which can be used as reaction mediums, and insoluble in other solvents. Based on the insolubility of polymer support, the catalyst can be easily separated and recycled from the reaction mixture by precipitation, centrifugalization or filtration [15].

Herein, a quaternary ammonium salt functionalized-methoxypolyethylene glycols polymer supported phosphotungstic acid (QMPEG-PTA) catalyst was prepared, which was used as a heterogeneous catalyst to catalyze esterification of different carboxylic acids with several

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alcohols and can be easily separated and recovered by precipitation and centrifugalization.

2 Experimental

2.1 Materials

All chemicals were of analytical grade, which were purchased from commercial sources and used as received, and methoxypolyethylene glycol (MPEG) was afforded with a M_W of 5,000.

2.2 Characterization

The fourier transform infrared spectra (FT-IR) of samples were performed on an AVATAR360-IR spectrometer (Nicolet, USA) using KBr pellets. X-ray diffraction (XRD) of different samples were recorded on a Rigaku D/Max-2400 (Rigaku, Japan) using Ni-filtered Cu Kα ($\lambda = 0.15406$ nm) radiation. Thermal stability of QMPEG support and QMPEG-PTA catalyst was confirmed by thermogravimetric analysis (TGA) (Perk in Elmer). Analysis of the conversion and selectivity was performed on Shimadzu GC-2010A gas chromatography (Shimadzu, Japan).

2.3 Preparation of Quaternary Ammonium Salt Functionalized MPEG Support (QMPEG)

As shown in Scheme 1, the QMPEG support was prepared in five-step procedure by modification of the method previously reported [16–18]. In a typical synthesis of QMPEG, firstly, 6.0 g MPEG was dissolved in 20 ml anhydrous CH_2Cl_2, and then 0.55 ml of mesyl chloride and 8 ml n-trioctylamine were added under stirring. After the mixture was stirred for 12 h at room temperature, the solvent was evaporated under vacuum and the crude product was purified by precipitation in diethyl ether to afford 5.85 g intermediate 1. Second, to a solution of intermediate 1 (5.7 g) in 40 ml DMF, 1.0 g Cs_2CO_3 and 0.42 g 2-(4-hydroxyphenyl) ethanol were added. After being stirred for 18 h at room temperature, the mixture was concentrated and the solvent was removed. Then the crude product was purified by precipitation in diethyl ether and 5.5 g of intermediate 2 was obtained. Third, to a solution of intermediate 2 (5.3 g) in CH_2Cl_2, 0.5 ml of PBr_3 was added at 0 °C and the solution was vigorous stirring for 5 h. After being warmed up to room temperature, the mixture was stirred for another 10 h, concentrated and the solvent was removed. Then the crude product was purified by precipitation in diethyl ether and 5.15 g of intermediate 3 was afforded. Last, to a solution of 5.0 g intermediate 3 in 20 ml toluene, 2.5 ml of $(n\text{-Bu})_3N$ was added and then the mixture was stirred at 65 °C for 72 h. After the solvent was evaporated under vacuum, the residue was purified by precipitation in diethyl ether and 4.83 g of QMPEG was obtained.

2.4 Preparation of QMPEG-Supported Phosphotungstic Acid Catalyst (QMPEG-PTA)

QMPEG-PTA catalyst was prepared in a typical procedure as follows to a solution of 4.7 g QMPEG 4(4.7 g) in 40 ml deionized water, 5.73 g of PTA was added. After the solution was stirred for 24 h at room temperature, the solvent was removed and the residue was dried under vacuum at 40 °C. The crude product was washed alternately by diethyl ether and ethanol, and then dried under vacuum [3–5].

2.5 Typical Procedure for the Esterification of Carboxylic Acids with Alcohols Employing QMPEG-PTA Catalyst

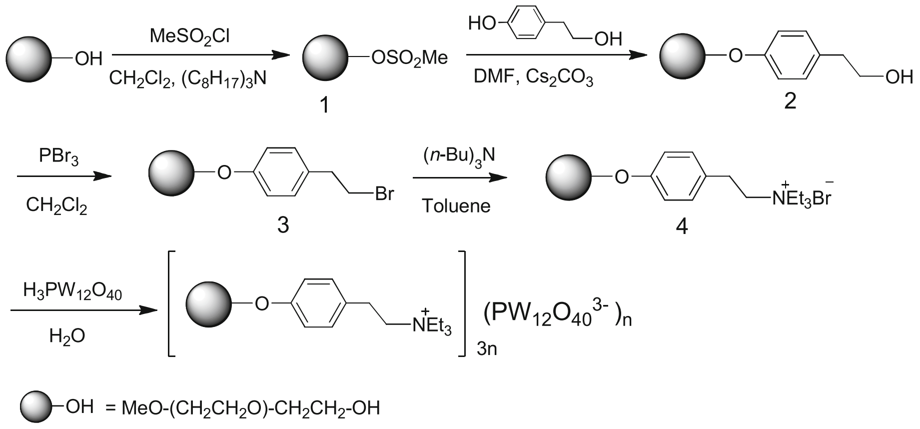
To a 10 ml round-bottomed flask with a reflux condenser, acetic acid (6 mmol), 1,4-butanediol (2 mmol), and QMPEG-PTA catalyst (116 mg, 0.009 mmol PTA) were added. The mixture was intensely stirred under air at 50 °C for 3 h. After the reaction, the mixture was poured into diethyl ether and the catalyst was precipitated as a yellow solid. This precipitation was collected, washed with diethyl ether and acetone alternately, dried under vacuum and reused in the next cycle. The combined organic phase was analyzed by the gas chromatography. Further more, the effects of the catalyst amount, reaction time and reaction temperature on the catalytic activity and selectivity over the QMPEG-PTA catalyst were investigated.

3 Results and Discussion

3.1 Characterization of QMPEG-PTA Catalyst

Figure 1 showed the FT-IR spectra of (a) QMPEG, (b) PTA and (c) QMPEG-PTA. In Fig. 1b, four characteristic bands located at 1,080, 983, 891 and 792 cm^{-1} were corresponded to the vibration of P–O_a, W=O_d, W–O_b–W and W–O_c–W for the Keggin structure of PTA, respectively [19]. For the QMPEG-PTA catalyst (Fig. 1c), the above mentioned four bands weakened distinctively, and the single band at 983 cm^{-1} was split into two bands (corresponding to 980 and 960 cm^{-1}), which may be attributed to the construction of hydrogen bonding among the terminal oxygen atoms of PTA and amino groups of organic cations and the intramolecular charge transfer between amino groups and W species [20]. All the

Scheme1 Schematic preparation of QMPEG-PTA catalyst



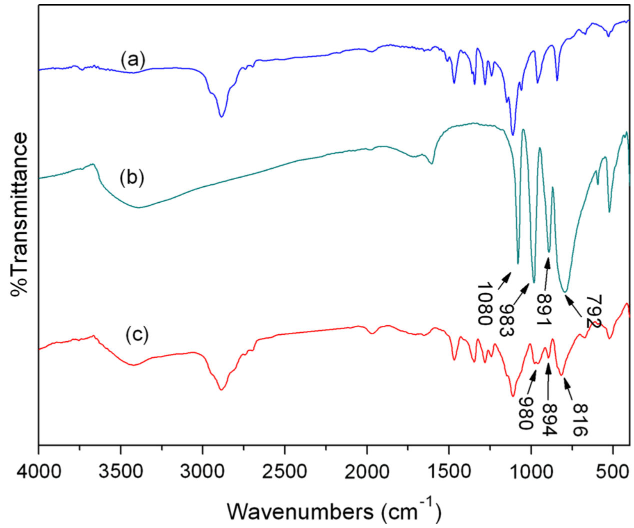


Fig. 1 FT-IR spectra of *a* QMPEG, *b* PTA and *c* QMPEG-PTA

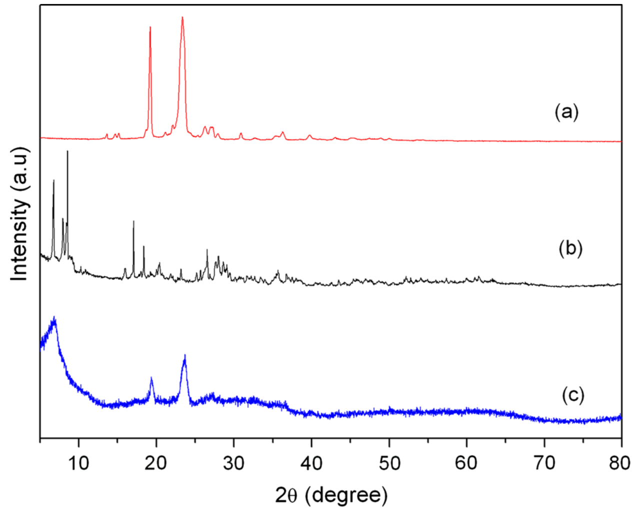


Fig. 2 XRD powder patterns of *a* QMPEG, *b* PTA and QMPEG-PTA

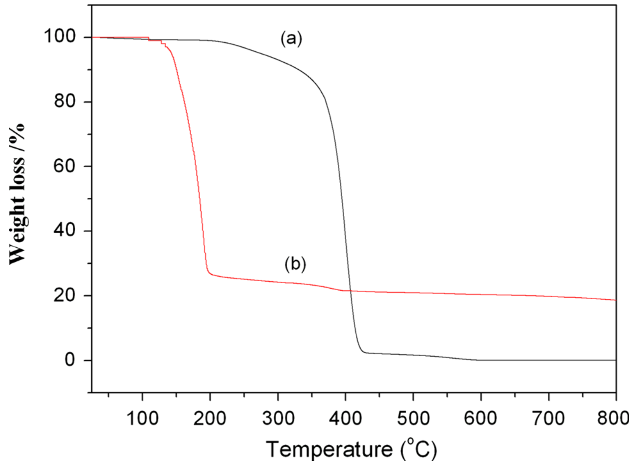


Fig. 3 TG analysis curves of *a* QMPEG and *b* QMPEG-PTA

characteristic bands in the FT-IR spectra suggested a successful preparation of QMPEG-PTA catalyst.

The XRD patterns of the (a) QMPEG, (b) PTA and QMPEG-PTA were presented in Fig. 2. In Fig. 2a, the two sharp reflections at 2θ of 19.2° and 23.4° were attributed to the polymer. The pattern of PTA displayed a set of sharp diffraction peaks, which were featured for the secondary crystal structure of the PTA (Fig. 2b) [21]. No separate crystal phase characteristic of raw PTA existed in the QMPEG-PTA catalyst (Fig. 2c), indicating a definitely noncrystal structure, which may be attributed to the rearrangement of the crystal structure of PTA when the large organic cations replaced the counter protons in the QMPEG-PTA catalyst [22].

The TG analyses of (a) QMPEG and (b) QMPEG-PTA were shown in Fig. 3. For the QMPEG, the drastically weight loss of 100 % in a temperature range 220–430 °C corresponded to the thermal decomposition of the polymer bone (Fig. 3a). The weight loss of QMPEG-PTA catalyst in the temperature range of 110–400 C was 78.5 %, which was logical to assign to the decomposition of the organic part of the QMPEG-PTA. The weight was almost

Table 1 QMPEG-PTA catalyzed esterification of carboxylic acids with alcohols

Entry	Carboxylic acid	Alcohol	Temp. (°C)	Time (h)	Conv. (%)[a]	Sele. (%)[a]
1	Acetic acid	1-Butanol	50	3	92	>99
2	Acetic acid	1,4-Butanediol	50	3	92	>99
3	Acetic acid	Benzyl alcohol	50	3	85	>99
4	Lauryl acid[b]	Methanol	30	7	82	>99
5	Stearic acid[b]	Methanol	50	7	83	>99
6	Oxalic acid	1-Butanol	50	3	91	>99
7	Cyclopropanecarboxylic acid	Ethanol	50	7	97	>99
8	Undecenoic acid	Methanol	30	7	87	>99
9	Acetic acid	1-Butanol	50	3	93[c]	>99
10	Acetic acid	1-Butanol	50	3	23[d]	>99

Reaction conditions: 6 mmol carboxylic acid, 2 mmol alcohol and (116 mg, 0.009 mmol) QMPEG-PTA catalyst

[a] The conversion and reaction selectivity were determined by GC analysis

[b] 2 ml DMF was used as solvent

[c] 0.009 mmol PTA catalyst was used

[d] After the third using of PTA catalyst

consistent in the temperature range of 400–800, and the amount of PTA catalyst supported on the QMPEG can be calculated as 21.5 %. The thermal analysis demonstrated that the PTA was successfully supported on the quaternary ammonium salt functionalized-methoxypolyethylene glycols, and the QMPEG-PTA catalyst was stable at the temperature employed in the catalytic reactions.

3.2 The QMPEG-PTA Catalyzed Esterification of Carboxylic Acids with Alcohols

The acid catalyzed esterification reaction of carboxylic acids with alcohols was an important method for synthesis of esters, ranging from aliphatic to aromatic, which were extensive applied in pharmaceuticals, foods and fine chemicals. The catalyst amount, reaction time and reaction temperature had major effect on the catalytic activity and selectivity [3]. Herein, the reaction of acetic acid with *n*-butanol was used as a model reaction for screening conditions and the results were summarized in supporting information. With the optimized reaction conditions in hand, the scope of the esterification reactions between different carboxylic acids with several alcohols was investigated employing QMPEG-PTA catalyst, and the results were summarized in Table 1.

Firstly, the esterification of aliphatic acids with different chain lengths, such as acetic acid, lauryl acid and stearic acid, were explored. The reactions of acetic acid were proceeded well and afforded conversions of 85–92 % (entries 1–3). The lauryl acid and stearic acid, with longer chain lengths, still achieved satisfactory conversions and selectivity albeit that a prolonged reaction time was needed (entries 4, 5). The oxalic acid, as a typical dibasic aliphatic acid, was esterified with two equivalents of 1-butanol at 60 °C for 3 h, and a conversion of 91 % was obtained (entry 6). Next, the alicyclic and unsaturated aliphatic acids, such as cyclopropanecarboxylic acid and undecenoic acid, were also examined and a good results obtained. The conversions of cyclopropanecarboxylic acid and undecenoic acid reached 97 % (entry 7) and 87 % (entry 8) respectively. The above results suggested that the QMPEG-PTA catalyst exhibited high activity and selectivity for the esterification of different carboxylic acids.

Moreover, the esterification reaction of acetic acid with 1-butanol was used to compare the catalytic activity of PTA with QMPEG-PTA catalysts. As shown in Table 1, the conversion of 93 % was obtained at the first using of PTA (entry 9), but 23 % was achieved after third using (entry 10). The above results suggested the poor reusability of PTA, and which was improved via the immobilization of PTA on the QMPEG support.

3.3 The Reusability of the QMPEG-PTA Catalyst

The reusability of the QMPEG-PTA catalyst was evaluated by using the esterification reaction of acetic acid with 1-butanol. After the reaction was completed, the QMPEG-PTA catalyst was precipitated by diethyl ether, washed with diethyl ether and acetone alternately, dried under vacuum and reused in the next cycle. As shown in Fig. 4, there was no obvious loss of catalytic activity for the esterification of acetic acid with 1-butanol after six consecutive runs. The conversion of 1-butanol remained 85.0 % with >99 % selectivity to *n*-butyl acetate at sixth used. The results indicate that the QMPEG-PTA catalyst was a class of robust and reusable catalyst for esterification under mild conditions.

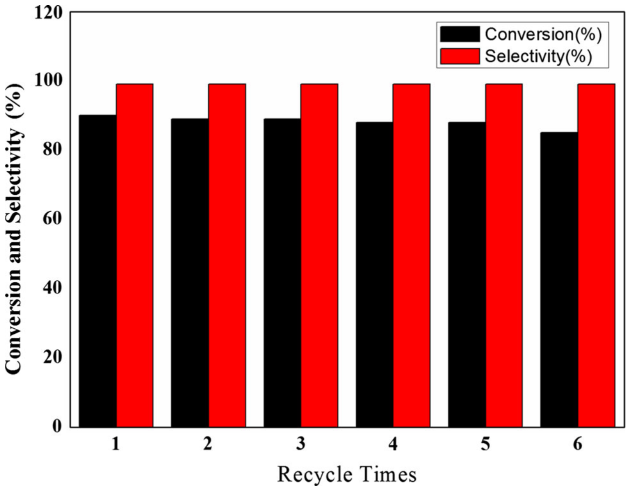


Fig. 4 Reusability of QMPEG-PTA catalyst in the esterification reaction of acetic acid with 1-butanol

4 Conclusion

A highly active and easily recoverable QMPEG-PTA catalyst was developed for the esterification of different carboxylic acids with several alcohols. The QMPEG-PTA catalyst exhibited high catalytic activity and selectivity in the esterification reaction of a wide range of carboxylic acids. The QMPEG-PTA catalyst can be easily separated and successfully used for at least six consecutive trials without obvious loss of its catalytic activity and selectivity, which suggested that the QMPEG-PTA was an efficient catalyst for the esterification reaction with excellent reusability.

5 Supporting Information

The optimizations of the reaction conditions for esterification reaction of acetic acid with 1-butanol catalyzed by QMPEG-PTA were available in the Supporting Information.

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