Esterification by solid acid catalysts—a comparison

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Abstract

The esterification of triethylene glycol (TEG) with methacrylic acid (MAA) was carried out over various solid acid catalysts and the results were compared with conventional acid catalysts. Among the catalysts studied, heteropolyacids showed higher activities than the conventional acids. These were attributed to the acidity of the catalysts. A systematic investigation was carried out for the esterification of triethylene glycol with methacrylic acid over phosphotungstic acid without any free radical inhibitor. The effects of catalyst concentration, alcohol/acid molar ratio and temperature were also studied. Parameters such as activation energy, reaction enthalpy and reaction entropy were derived for the above reaction over phosphotungstic acid in the temperature range of 353–383 K. The obtained results were also compared with silicotungstic acid.
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1. Introduction

The drive to develop green processes has led to the development of solid acid catalysts to a significant increase in research activities both in academic and industrial sections. These materials can replace the corrosive liquid acids currently used in many industries. A variety of materials have been used as solid acid catalysts such as clays, zeolites, sulfated metal oxides, heteropolyacids, etc. [1,2]. Each of these materials offers unique properties that can influence the catalytic activity. Among these solid acids, heteropoly compounds are unique in the sense, they can be tuned at atomic/molecular level to exhibit a wide variation on properties like acidity and redox behavior [3–5]. They behave like mineral acids having the protons in protected environments and exhibit Brønsted acidity, which of several orders of magnitude higher in strength than that of conventional mineral acids [6].

In the recent years, heteropoly compounds with Keggin structures have received much attention as solid acid catalysts for both homogeneous and heterogeneous reactions due to their high acid strength and high thermal stability [7–17]. Augustine et al. utilized heteropoly compounds as anchoring agents to heterogenize the homogeneous catalysts [18–20]. The protons in the secondary structure of the heteropoly acids can be easily exchanged, completely or partially, with different cations without affecting the primary Keggin structure. These materials exhibit the so called pseudoliquid phase behavior, where polar molecules like water, alcohols, amines enter into the bulk, expanding or contracting the distance between the Keggin anions in the crystal lattice, while nonpolar molecules such as hydrocarbons just adsorb on the surface with out entering the bulk [21]. This is because the protons present in the heteropolyacid form hydrogen bonds with the water present in the crystal structure and exist as guarded protons, H_3O^+ or $H_2O_5^+$ [22]. The water molecules can be replaced by incoming polar molecules and thus get protonated stiochiometrically. The isolated protons in heteropolyacids are delocalized in individual polyanions as well as neighboring polyanions at 10^3 to 10^6 times faster than the transformation of the organic molecules [23]. This delocalization is an unique property of heteropolyacids. In the case of zeolites, the acidic protons are bound in the proximity of Al–O–Si

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sites. In pseudoliquid phase of heteropoly compounds the polar molecules protonate stoichiometrically or higher than the protons, depending on the nature of the molecule (for instance 3 in the case of CH_3OH and 6 in the case of pyridine molecules) [24].

Multifunctional methacrylates are industrially important monomers for anaerobic adhesives [25], diluent monomer in dental composites [26,27], thread lockers, sealants and components for making soft contact lenses [28]. These multifunctional methacrylates are currently produced by the direct esterification of glycols with methacrylic acid using conventional acids as catalysts such as sulfuric acid and boron trifluoride etherate [29]. These processes utilize free radical inhibitors such as hydroquinone, hydroxy toluene, butylated hydroxy aniline, etc., in order to avoid the undesirable cross-linking of the vinyl groups. The process requires minimum reaction time of 24 h to obtain 80% yield and the product separation requires tedious work up procedures. To overcome these difficulties in the preparation of multifunctional methacrylates, heteropoly acids have been employed as catalysts [30].

In the present study, esterification of various diols with methacrylic acid was carried out over phosphotungstic acid. The effects of molar ratio, catalyst concentration and temperature were studied for the formation of triethylene glycol dimethacrylate. A detailed kinetic study was also carried out for the esterification of triethylene glycol with methacrylic acid over phosphotungstic acid. Various parameters such as activation energy, reaction enthalpy and reaction entropy were calculated for the formation of ester. The results obtained are compared with those obtained for silicotungstic acid.

2. Experimental

2.1. Preparation of catalysts

Phosphotungstic acid and silicotungstic acid were prepared by the known procedures [31]. The various reagents used for the preparation of catalysts were $Na_2WO_4 \cdot 2H_2O$ (SRL), $Na_2HPO_4 \cdot 2H_2O$ (Merk) and sodium silicate solution (water glass) (BDH). The prepared heteropolyacids were purified by extracting with diethyl ether and recrystallized from water. Heteropolyacids were calcined at 548 K for 6 h before use. Sulfuric acid (Fischer), *p*-toluene sulfonic acid (Thomas Baker) and amberlyst-15 (Fluka) were used as received. Ethylene glycol, diethylene glycol, triethylene glycol and polyethylene glycol 400 were vacuum distilled and trichloroethylene (TCE) (SRL) and methacrylic acid was used as received.

2.2. Characterization of catalysts

The X-ray diffraction patterns of the catalysts were recorded using Rigaku miniflex X-ray difractometer using monochromatized Cu Kα radiation (λ = 1.5406 Å) with a scan speed of 1°/min in the range 5 < 2θ < 70. Thermal analyses of the samples were recorded with thermal analyzer (Perkin-Elmer TGA 7) at a heating rate of 20 °C/min. UV–vis spectra were recorded with Perkin–Elmer Lambda 17 UV–vis spectrophotometer. Infrared spectra were recorded with Perkin-Elmer 1760 in the region 4000–400 cm^{-1}. Powder samples were ground with KBr in 1:20 ratio and pressed (5 t/cm^2) for making the pellets. ^{1}H-NMR spectra were recorded with JEOL GSX 400. The products were analyzed using gas chromatography (Nucon 5600, FID, SE 30 column).

2.3. Esterification studies

The esterification of methacrylic acid was carried out with various diols (EG, DEG, TEG and PEG) in a three-necked 100 ml flask equipped with a Dean-Stark trap, thermometer and a magnetic stirrer. The temperature was maintained with an oil bath. When the mixture in the flask reached a temperature about 10 °C lower than the desired temperature, the catalyst was added quickly. After the addition of catalyst, 1 ml of aliquot was withdrawn immediately and the reaction was arrested by adding 20 ml cold water and titrated with ∼0.1 M standard sodium hydroxide solution using phenolphthalein as indicator. For a typical reaction 82.5 mmol of TEG, 171 mmol of MAA and 55.8 mmol of trichloroethylene were employed. The reaction was carried out at 368 K for 5 h. The water formed in the reaction was removed by azeotropic distillation with the solvent TCE and the solvent was revert back to the reaction vessel. The formation of ester was monitored by IR spectroscopy as well as with gas chromatography and the physico-chemical properties of the product was compared with the ester prepared by conventional method [32]. For the equilibrium constant measurements, the reaction was carried out for 15–20 h and the acid concentration was monitored periodically. The products were further confirmed by ^{1}H and ^{13}C NMR analyses. For comparison, the same reaction was carried out on various acid catalysts such as amberlyst-15, sulfuric acid and *p*-toluene sulfonic acid.

3. Results and discussion

3.1. Esterification of methacrylic acid

The kinetics of esterification of methacrylic acid over phosphotungstic acid was carried out with various diols and the results are shown in Fig. 1. As the chain length of the diol increases from ethylene glycol to polyethylene glycol the rate of formation of ester is found to decrease [33]. This may be due to the fact that the larger molecules cannot penetrate into the bulk and can interact only with the surface of the heteropolyacid.
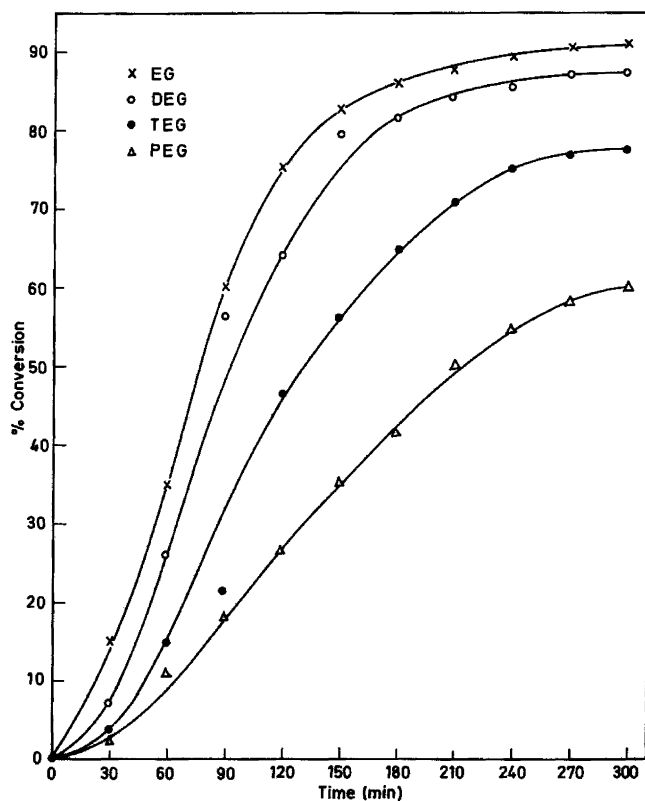
Fig. 1. Dependence of methacrylic acid conversion on various diols: TEG/MAA = 0.49; temperature = 368 K.

Fig. 2. Conversion of methacrylic acid with molar ratio of alcohol/acid: catalyst = 3 g; temperature = 368 K; TCE = 50 ml.

3.2. Effect of catalyst concentration

Effect of catalyst concentration on the percentage conversion for the reaction of triethylene glycol with methacrylic acid has been studied. It has been observed that at lower concentration of the catalyst (3.3×10^{-4} mol), polymerization is predominant. This clearly demonstrates that low acid concentration of the catalyst, heteropolyacid is enough to initiate the cross linking of the vinyl groups which leads to polymerization. This emphasizes the fact that the desired reaction can be observed with more than 1 g of catalyst. It is observed that with an increase in the catalyst concentration from 1 to 4 g, the conversion of methacrylic acid is found to increase from 40 to 90% (at 300 min). It demonstrates that the reaction is taking place in "pseudoliquid phase" manner. In general, the catalytic activity to a certain extent is proportional to the surface area of the catalyst. Even though the surface area of heteropolyacid is low (5–7 m^2/g), the high conversion in the present case can be attributed to the pseudoliquid behavior [34]. The rate constant value increases with an increase in the concentration of catalyst.

3.3. Effect of molar ratio

The effect of molar ratio (TEG/MAA) was studied for the esterification of triethylene glycol with methacrylic acid over phosphotungstic acid and the results obtained are given
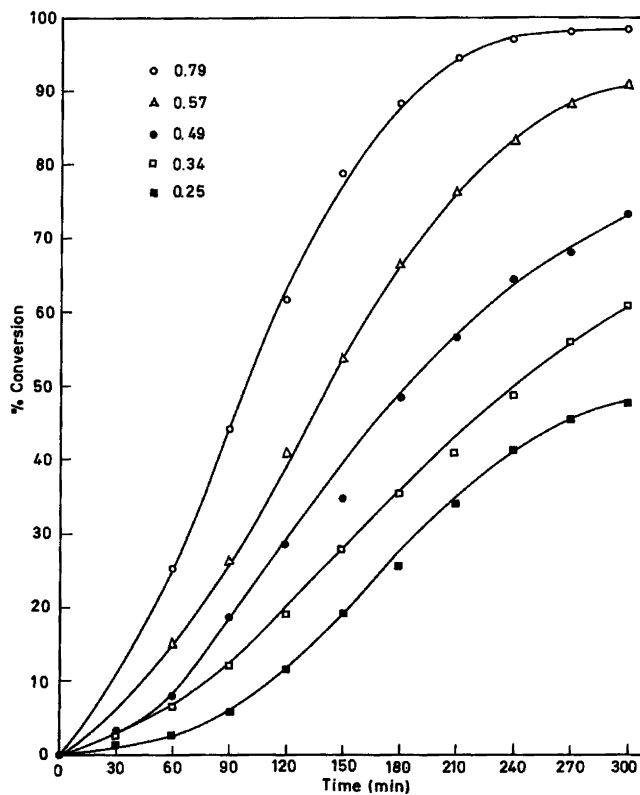
in Fig. 2. The results show that the formation of the monoester is directly proportional to the molar ratio.

3.4. Effect of temperature

The effect of temperature was studied for the formation of triethylene glycol dimethacrylate over phosphotungstic acid, keeping all other parameters constant. As the temperature is increased from 358 to 383 K, the conversion of methacrylic acid has also increased from 30 to 93% (at 300 min).

3.5. Recycling of the catalyst

Recycling of the catalyst is an important aspect of any industrial process. For this purpose, the reaction was stopped after 5 h and the resulting reaction medium was transferred and dried. The resulting solid was then reused as catalyst for a new reaction under the same conditions. After three cycles, the conversion at 5 h had slightly decreased from 83 to 73% indicating that these heteropoly acids can be easily recycled (Table 1).

3.6. Kinetic studies

Typical changes in conversion of methacrylic acid with reaction time for the formation of ester over different catalysts are represented in Fig. 3. Among the catalysts

Table 1
Comparison of catalytic activity and product selectivity over various acid catalysts

Catalyst	Initial rate (mmol g^{-1} min^{-1})	H_0[a]	Conversion of methacrylic acid (%)	Selectivity (%)	
				Diester	Monoester
$H_3PW_{12}O_{40}$	510	−3.6	83	64	36.4
$H_4SiW_{12}O_{40}$	320	−3.4	62.2	76	24
Amberlyst-15[b]	291	–	64.7	41	59
PTSA[b]	187	−2.6	21.5	18.6	81
H_2SO_4[b]	71	−2.6	41	55	45

Reaction conditions—TEG: 82.5 mmol; MAA: 171 mmol; TCE: 55.8 mmol; temperature: 368 K; reaction duration: 5 h; catalyst: 3 g.

[a] Hammet acidity values taken from literature [35].
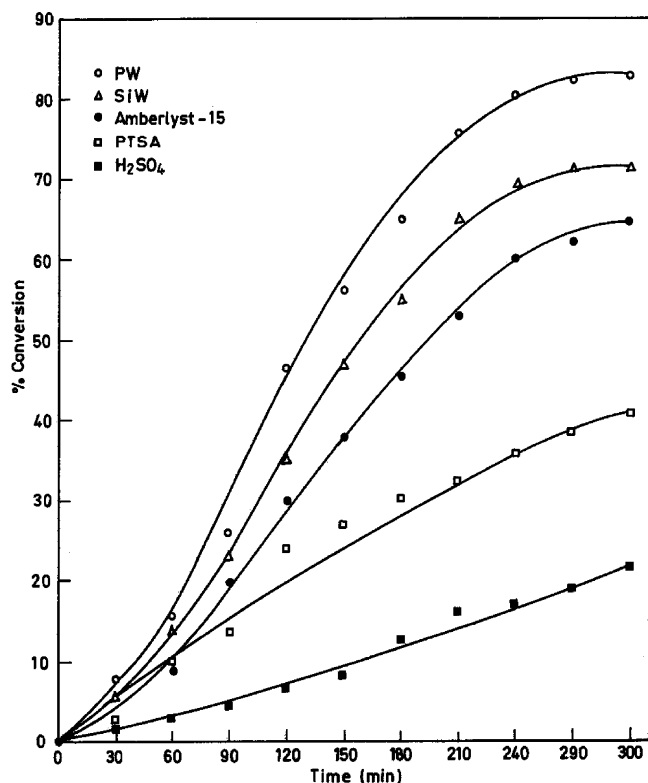
[b] About 200 mg of hydroquinone was added.

Fig. 3. Time courses of esterification of triethylene glycol with methacrylic acid over acid catalysts: catalyst (PW, SiW, PTSA, H$_2$SO$_4$) = 1 × 10^{-3} mol; amberlyst-15 = 2.5 g; TEG/MAA = 0.49; TCE = 50 ml.

studied, heteropolyacids showed higher conversion compared to amberlyst-15, *p*-toluene sulfonic acid and sulfuric acid. Among the heteropolyacids, phosphotungstic acid showed higher activity than silicotungstic acid, which can be attributed to the higher acid strength of phosphotungstic acid [35]. It is reported that the acid strength of the catalysts and hence the catalytic activity follows the order $H_3PW_{12}O_{40}$ > $H_4SiW_{12}O_{40}$ > amberlyst-15 > PTSA > H_2SO_4. The catalytic activity followed the same order (PW > SiW > amberlyst-15 > PTSA > H_2SO_4) in the present study also. The rate law for the esterification reaction was deduced by determining the order with respect to each reactant and is found to obey Eq. (1).

$$\frac{-d[MAA]}{dt} = k[TEG][MAA][HPW] \tag{1}$$

The parameters, energy of activation (E_a) and the frequency factor (A), for the esterification of triethylene glycol with methacrylic acid over phosphotungstic acid and silicotungstic acid (Table 2) were determined from the plot of ln k against T^{-1}.

3.7. Equilibrium constant

The equilibrium constant for the esterification of triethylene glycol with methacrylic acid over phosphotungstic acid as well as silicotungstic acid was determined at different temperatures. The increase in the value of the equilibrium constant with an increase in temperature indicates that the reaction is endothermic in nature. Reaction enthalpy (ΔH°) and reaction entropy (ΔS°) (Table 2) were obtained from Eq. (3) by plotting ln K against T^{-1}. The positive reaction enthalpy suggests that the esterification reaction is endothermic.

$$\underset{(a-x)}{TEG} + \underset{(b-2x)}{2MAA} \rightleftarrows \underset{(x)}{TEGDMA} + \underset{(2x)}{2H_2O}$$
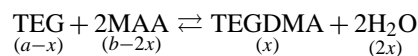
$$K = \frac{[x][2x]^2}{[a-x][b-2x]^2} \tag{2}$$

$$\ln K = \frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \tag{3}$$

Table 2
Kinetic and thermodynamic parameters for the esterification of triethylene glycol with methacrylic acid over heteropolyacids

Catalyst	Activation energy (E_a) (kJ mol^{-1})	Pre-exponential factor (A) (l mol^{-1} min^{-1})	Reaction enthalpy (ΔH°) (kJ mol^{-1})	Reaction entropy (ΔS°) (J K^{-1} mol^{-1})
$H_3PW_{12}O_{40}$	124.7	3.19 × 10^{15}	135	383
$H_4SiW_{12}O_{40}$	138.4	1.72 × 10^{17}	128	360

Reaction conditions—catalyst: 3 g; reaction temperature: 353–383 K; reaction duration: 15–20 h.

4. Conclusions

Esterification of triethylene glycol (TEG) with methacrylic acid (MAA) was carried out over various acid catalysts and the results clearly demonstrate that phosphotungstic acid is a better catalytic system when compared to conventional acid catalysts. The procedure adopted in the present study eliminates the use of free radical inhibitor thus minimizing the alkali washing steps involved in the conventional processes. The kinetic parameters reveal that phosphotungstic acid has got higher initial rate and low activation energy compared to silicotungstic acid. The thermodynamic parameters, ΔH° and ΔS° were evaluated and it has been found that phosphotungstic acid is better catalyst than silicotungstic acid for the above esterification reaction.

References

[1] R.A. Sheldon, R.S. Downing, Appl. Catal. A: Gen. 189 (1999) 163.
[2] A. Mitsutani, Catal. Today 73 (2002) 57.
[3] L.P. Kazanskii, E.A. Torchenkova, V.I. Spitsyn, Russ. Chem. Rev. 43 (1974) 1137.
[4] I.V. Kozhevnikov, K.I. Matveev, Russ. Chem. Rev. 51 (1982) 1075.
[5] Y. Ono, Perspective in Catalysis, Blackwell Scientific Publications, London, 1992.
[6] M. Misono, T. Okuhara, Chemtech (1993) 23.
[7] P. Dupont, F. Lefebvre, J. Mol. Catal. A: Chem. 114 (1996) 299.
[8] S. Sato, K. Sagara, H. Furuta, F. Nozaki, J. Mol. Catal. A: Gen. 114 (1996) 209.
[9] C. De Castro, J. Primo, A. Corma, J. Mol. Catal. A: Gen. 134 (1998) 215.
[10] M.J. Verhoef, P.J. Kooyman, J.A. Peters, H. van Bekkum, Micropor. Mesopor. Mater. 27 (1999) 365.
[11] T. Okuhara, M. Kimura, T. Kawai, Z. Xu, T. Nakato, Catal. Today 45 (1998) 73.
[12] K. Johnson, B. Viswanathan, T.K. Varadarajan, Ind. J. Chem. 36B (1997) 246.
[13] I.V. Kozhevnikov, Catal. Rev. Sci. Eng. 37 (1995) 311.
[14] T. Okuhara, N. Mizuno, M. Misono, Adv. Catal. 41 (1996) 113.
[15] I.V. Kozhevnikov, Chem. Rev. 98 (1998) 171.
[16] N. Mizuno, M. Misono, Chem. Rev. 98 (1998) 199.
[17] T. Okuhara, Chem. Rev. 102 (2002) 3641.
[18] R.L. Augustine, S. Tanielyan, S. Anderson, H. Yang, Chem. Commun. (1999) 1259.
[19] S. Tanielyan, R.L. Augustine, World Patent Appl.WO98/28074 (1998).
[20] S. Tanielyan, R.L. Augustine, US 6,025,295 (2000).
[21] M. Misono, N. Mizuno, K. Katamura, A. Kasai, Y. Kohishi, K. Sakata, T. Okuhara, Y. Yoneda, Bull. Chem. Soc. Jpn. 55 (1982) 400.
[22] I.V. Kozhevnikov, Russ. Chem. Rev. 56 (1987) 811.
[23] S. Uchida, K. Inumaru, M. Misono, J. Phys. Chem. B 104 (2000) 8108.
[24] K. Young Lee, T. Arai, S. Nakata, S. Asaoka, T. Okuhara, M. Misono, J. Am. Chem. Soc. 114 (1992) 2836.
[25] B. George, Y.G.F. Touyeras, J. Vebrel, Int. J. Adhes. Adhes. 20 (2000) 245.
[26] Z. Yang, W. Jia, US 5,969,000 (1999).
[27] K. Naito, T. Fuse, I. Tanuma, Y. Fukuura, H. Ishikawa, US 4,591,618 (1986).
[28] N. Moszner, U. Salz, Prog. Polym. Sci. 26 (2001) 535.
[29] J. Meixner, J. Pedain, P. Hohlein, D. Margotte, US 4,748,269 (1988).
[30] S. Shanmugam, B. Viswanathan, T.K. Varadarajan, Bull. Catal. Soc. India 1 (2002) 116.
[31] J.C. Bailor, Inorg. Synth. 1 (1939) 132.
[32] S. Shanmugam, B. Viswanathan, T.K. Varadarajan, Bull. Catal. Soc. India 1 (2002) 1.
[33] T. Salmi, E. Paatero, J. Lehtonen, P. Nyholm, T. Horju, K. Immonen, H. Harrrio, Chem. Eng. Sci. 56 (2001) 1293.
[34] K. Takahashi, T. Okuhara, M. Misono, Chem. Lett. (1985) 841.
[35] R.S. Drago, J.A. Dias, T.O. Maier, J. Am. Chem. Soc. 119 (1997) 7702.