

# Sulfonic acid functionalized poly (ethylene glycol dimethacrylate-1-vinyl-1,2,4-triazole) as an efficient catalyst for the synthesis of methyl propionate

Beyhan Erdem\*, Ali Kara

Department of Chemistry, Faculty of Science and Arts, Uludag University, 16059 Bursa, Turkey

## ARTICLE INFO

### Article history:

Received 26 May 2010

Received in revised form 30 November 2010

Accepted 5 December 2010

Available online 10 December 2010

### Keywords:

Esterification

Methyl propionate

Heterogeneous catalyst

Poly (EGDMA-VTAZ)

## ABSTRACT

Sulfonic acid functionalized poly (ethylene glycol dimethacrylate-1-vinyl-1,2,4-triazole), poly (EGDMA-VTAZ-SO<sub>3</sub>H) (average diameter 1.0–1.5 mm), was found to be efficient solid acid catalyst for the esterification of methanol and propionic acid under heterogeneous reaction conditions. The pristine polymer, poly (EGDMA-VTAZ), was produced by suspension polymerization and then proton-conducting polymer was obtained by blending of poly (EGDMA-VTAZ) with different percentage of H<sub>2</sub>SO<sub>4</sub> solutions. The protonation of aromatic heterocyclic rings was proved with Fourier-transform infrared spectroscopy (FT-IR). Thermo gravimetric (TG) analysis showed that the catalyst is thermally stable up to 573 K. The surface morphology of the catalyst was characterized by scanning electron microscopy (SEM). Poly (EGDMA-VTAZ-SO<sub>3</sub>H) beads can be regenerated and reused, so this provides a potential application. It has a rate constant which exceeds that of Amberlyst-15 by a factor of about four at 333 K. As for the reaction equilibrium constant ( $K_e$ ), which is independent of temperature ranging from 318 to 343 K, was determined to be 3.16. The apparent activation energy was found to be 41.6 kJ mol<sup>-1</sup> for poly (EGDMA-VTAZ-SO<sub>3</sub>H).

© 2010 Elsevier Ltd. All rights reserved.

## 1. Introduction

Esterification of carboxylic acid with alcohols belongs to classical chemical reactions, the kinetics and equilibria of which have been investigated throughout the history of physical chemistry; the pioneering efforts date back to the time of Bertholet and de Saint Gilles [1]. The esterification reaction is a liquid-phase process, where the limiting conversion of the reactants is determined by equilibrium. Typically esterification reactions are very slow; it requires several days to attain the equilibrium in the absence of catalyst [2]. To accelerate the reaction rate, catalysts are always employed in a liquid-phase esterification. Despite the strong catalytic effect, the use of homogeneous catalyst, such as sulphuric acid and p-toluene sulfonic acid suffers from several drawbacks, such as the existence of side reactions, corrosion of the equipment and the need to deal with acidic wastes [3–6]. Under this situation the use of solid acid catalyst has received great attention because of having distinct advantages, such as the higher purity of the products and easily removing of catalyst from the reaction mixture [7,8]. However, some critical factors such as the activity and the stability of the catalyst, the availability and cost of the catalyst and the short development time for a production process are probably most decisive [9].

There exist quite a few publications in literature having polystyrene-based ion exchange fibre as acid catalyst and they have been

used for some years in esterification reactions [10–15]. Typical resin catalysts are sulfonic acids fixed to a polymer carrier, such as polystyrene crosslinked with divinylbenzene (DVB). Several catalysts of this kind are commercially available, e. g. the Amberlyst family. In the use of polyvinyl benzene-based catalysts, the process typically becomes diffusion limited, and the polymer is swelled and deactivated in aggressive reaction media [1]. In recent time, the development of environmentally benign catalyst for the production of fine chemicals has been an area of growing interest. In this context, solid acid catalysts play prominent role in organic synthesis under heterogeneous reaction conditions.

In the present manuscript, we have demonstrated that sulfonic acid functionalized poly (EGDMA-VTAZ) can be efficiently used as heterogeneous catalyst in the synthesis of methyl propionate in short reaction time and its catalytic performance was compared with that of a classical polyvinylbenzene-supported catalyst, Amberlyst-15. Esterification of propionic acid with methanol was selected to the model system. In this model reaction, the effects of catalyst loading, temperature and initial mole ratio of alcohol to acid were investigated over poly (EGDMA-VTAZ-SO<sub>3</sub>H).

## 2. Experimental procedure

### 2.1. Catalyst preparation

The poly (EGDMA-VTAZ) beads were produced by suspension polymerization technique in an aqueous medium as described in

\* Corresponding author. Tel.: +90 2242941738; fax: +90 2242941899.

E-mail address: [gbeyhan@uludag.edu.tr](mailto:gbeyhan@uludag.edu.tr) (B. Erdem).

### Nomenclature

$A, B, E, W$	propionic acid, n-amyl alcohol, amyl propionate and water, respectively	$T$	temperature (K)
$k_1$	forward reaction rate constant	$R$	gas constant ( $\text{kJ mol}^{-1} \text{K}^{-1}$ )
$C_{A,0}$	initial concentration of propionic acid ( $\text{mol L}^{-1}$ )	$t$	time (min)
$K_e$	equilibrium constant of the reaction	$X_{Ae}$	equilibrium conversion of propionic acid
$X_A$	conversion of propionic acid	$C_A$	concentration of propionic acid ( $\text{mol L}^{-1}$ )
$A$	Arrhenius preexponential factor ( $\text{L}^2 \text{mol}^{-1} \text{min}^{-1}$ )	$C_B$	concentration of methanol ( $\text{mol L}^{-1}$ )
$E_A$	apparent activation energy ( $\text{kJ mol}^{-1}$ )	$C_E$	concentration of methyl propionate ( $\text{mol L}^{-1}$ )
		$C_W$	concentration of water ( $\text{mol L}^{-1}$ )

our previous articles [16,17]. EGDMA and VTAZ were polymerized in suspension with AIBN and PVAL as the initiator and the stabilizer, respectively. Toluene was included in the polymerization recipe as the diluent (a pore former). A typical preparation procedure with little differences is as follows. A continuous medium was prepared by the dissolution of PVAL (200 mg) in purified water (100 mL). For the preparation of dispersion phase, EGDMA (4 mL; 20 mmol) and toluene (10 mL) were stirred for 15 min at room temperature. Then, VTAZ (3 mL; 35 mmol) and AIBN (100 mg) were dissolved in the homogeneous organic phase. We dispersed the organic phase in the aqueous medium by stirring the mixture magnetically (700 rpm) in a sealed cylindrical Pyrex polymerization reactor. The reactor content was heated to the polymerization temperature (i.e. 323 K) within 2 h, and the polymerization was conducted for 12 h with 800 rpm stirring rate at 343 K. The final beads were washed extensively with ethanol and water to remove any unreacted monomer or diluent and then stored in distilled water at 277 K. The poly (EGDMA–VTAZ–SO<sub>3</sub>H) beads were prepared by mixing of different percentages of H<sub>2</sub>SO<sub>4</sub> solution (10%, 15%, 20% and 30%, respectively) with poly (EGDMA–VTAZ) polymer at 298 K in a sealed cylindrical Pyrex reactor for 2 h. The solid was filtered and vacuum dried at 343 K overnight and stored in the glove box for characterizations.

### 2.2. Catalyst characterization

FT-IR measurements were performed on a Thermo Nicolet 6700 series FT-IR spectrometer in normal transmission mode with a KBr detector over the range 4000–400 cm<sup>-1</sup> at a resolution 8 cm<sup>-1</sup> averaged over 32 scans.

In order to test whether sulphur enters to the polymeric structure, poly (EGDMA–VTAZ) (Sample I), and poly (EGDMA–VTAZ–SO<sub>3</sub>H) having different percentages of H<sub>2</sub>SO<sub>4</sub> (Samples II–V) beads were subjected to elemental analysis with LECO CHNS-932 model elemental analyzer.

Thermal stabilities of the poly (EGDMA–VTAZ) (Sample I) and its sulfonic acid functionalized forms (Samples II–V) were examined by TG analyses with SII-EXSTAR TG/DTA 6200. The samples (~5–10 mg) were heated from room temperature to 800 °C under dried-air atmosphere at a scanning rate of 10 °C/min.

The surface morphology of poly (EGDMA–VTAZ–SO<sub>3</sub>H) catalyst was investigated by scanning electron microscopy (SEM, Carl Zeiss Evo 40). All observations were made at Uludag University Science and Art Faculty Microscopy Laboratory. Selected representative materials were sputter-coated with gold–palladium for two minutes in a BAL-TEC SCD 005. The micrographs were obtained by using a voltage of 20 kV.

The acid exchange capacities of the poly (EGDMA–VTAZ–SO<sub>3</sub>H) (Samples II–V) were measured by means of titration, using sodium chloride as exchange agent. In a typical experiment, 0.05 g of solid was added to 10 g of aqueous solution of sodium chloride (2 M). The resulting suspension was allowed to equilibrate and thereafter

titrated potentiometrically by drop-wise addition of 0.01 M NaOH (aq) [18,19].

### 2.3. Catalytic tests

The esterification of propionic acid with methanol was carried out in an isothermal glass reactor equipped with a heating jacket. A reflux condenser was placed on top of the reactor in order to prevent the escape of the volatile compounds. The stirring speed was 700 rpm and temperature was controlled within  $\pm 0.1$  °C by circulating water from a thermostat into a cylindrical water-jacketed of the reactor. The reactions were realized in the solution of dioxane of 99.8% purity (Merck). In a typical run, catalyst (about 1 g), methanol and dioxane of known amount were charged into the reactor and preheated to the reaction temperature and the esterification was commenced by injecting preheated propionic acid into the mixture. This was considered as the zero time for a run. The total liquid volume was 100 cm<sup>3</sup>. Samples were withdrawn and the amount of unreacted acid was analyzed by titration with 0.1 M sodium hydroxide. Stoichiometric ratio of propionic acid to methanol was changed from (2:1) to (1:2) in the experiments performed at 333 K. To calculate the apparent activation energy the reaction temperature was changed from 318 K to 343 K.

## 3. Results and discussion

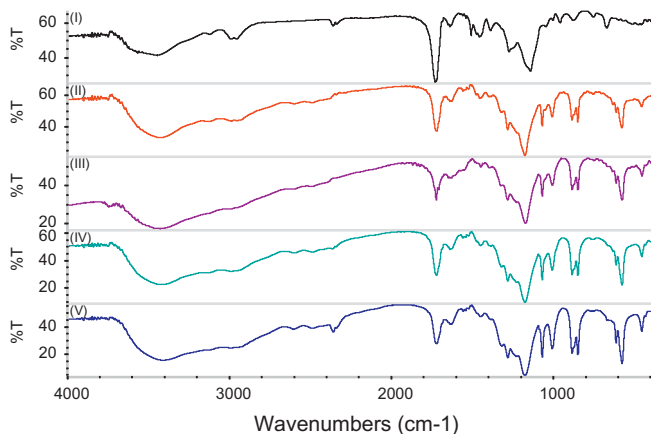
### 3.1. FT-IR studies

The FT-IR spectra of poly (EGDMA–VTAZ) (Sample I) and poly (EGDMA–VTAZ–%SO<sub>3</sub>H) with various degrees of sulfonation (10%, 15%, 20% and 30%) (Samples II–V) are shown in Fig. 1. Compared to poly (EGDMA–VTAZ), the distinguished features of poly (EGDMA–VTAZ–SO<sub>3</sub>H) were the presence of new absorption bands at 1070 cm<sup>-1</sup> and 1009 cm<sup>-1</sup> which are attributed to SO<sub>3</sub>H groups [20]. This indicates that the SO<sub>3</sub>H groups were successfully incorporated into the matrix by adding H<sub>2</sub>SO<sub>4</sub> in the synthesis system. The intensities of these peaks also increase in parallel with the increase in the percentage of H<sub>2</sub>SO<sub>4</sub> in the blends [21].

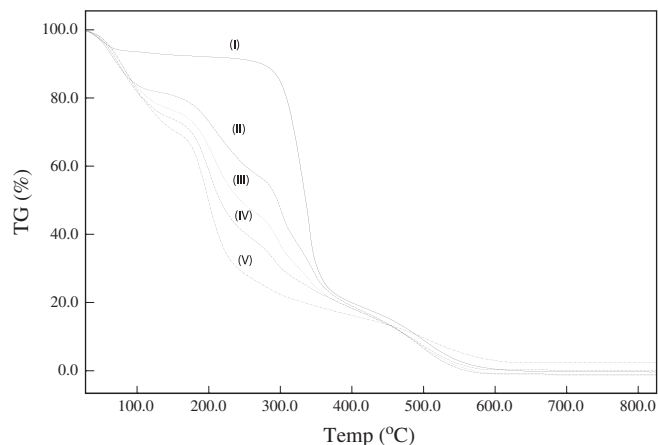
On the other hand, the bands due to C=O stretching at 1722 cm<sup>-1</sup>, C–O vibrations at 1177 cm<sup>-1</sup> for EGDMA, C–N, C=N vibrations in the 1448–1638 cm<sup>-1</sup> and N–N stretching at 1270 cm<sup>-1</sup> for triazole ring were observed for all samples independent of sulfonation. Additionally, a broadening of the band between 3500 and 2000 cm<sup>-1</sup> can be related to hydrogen bonding network formation [22].

### 3.2. Elemental analysis

Data from elemental analyses of pristine polymer and its sulfonic acid modified forms (Samples I–V) are shown in Table 1. This is clear evidence indicating that SO<sub>3</sub>H groups are located in the polymer, thus being accessible and useful for adsorption and



**Fig. 1.** FT-IR spectra of poly(EGDMA-VTAZ) (Sample I) and poly(EGDMA-VTAZ-SO<sub>3</sub>H) respectively for 10%, 15%, 20% and 30% (Samples II–V).



**Fig. 2.** TG thermograms of poly(EGDMA-VTAZ) (Sample I) and its sulfonic acid modified forms (Samples II–V) recorded at a heating rate of 10 °C/min under air-dried atmosphere.

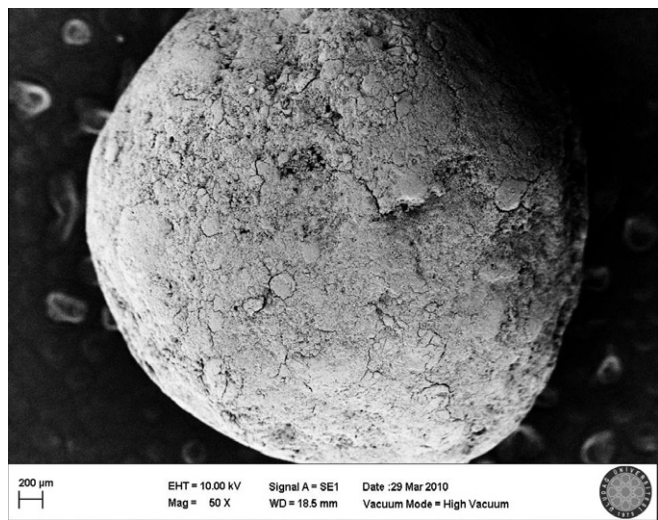
catalytic reaction processes. It is important to note that every synthesised sample shows close agreement between ion-exchange capacities (measured by titration) and sulphur loading (determined by elemental and TG analyses).

### 3.3. Thermal analysis

Fig. 2 shows the thermo gravimetric analyses of poly(EGDMA-VTAZ) and poly(EGDMA-VTAZ-SO<sub>3</sub>H) (Samples I–V). The pristine polymer has a considerable thermal stability under inert conditions. For this polymer, the exponential weight decay until 100 °C can be attributed to absorbed humidity. Above 300 °C a remarkable weight loss derives from the thermal decomposition of the side groups and polymer main chain. The poly(EGDMA-VTAZ-SO<sub>3</sub>H) (Samples II–V) illustrate that there is weight decay up to 170 °C because of absorbed humidity similar to pristine polymer. If all sulphur elements in the catalyst are assumed as –SO<sub>3</sub>H groups, weight change from 170 °C to 300 °C can be attributed to self-condensation of –SO<sub>3</sub>H. Above this temperature further condensation of acid as well as the degradation of the host polymer occurs.

### 3.4. SEM Micrographs

Surface morphology of the poly(EGDMA-VTAZ-SO<sub>3</sub>H) was investigated by scanning electron microscopy (Fig. 3). The SEM micrographs reveal that the mean particle diameter for poly(EGDMA-VTAZ-SO<sub>3</sub>H) is about 1.0–1.5 mm. As clearly seen Fig. 3, the beads have a spherical form and very rough surface due to the pores which formed during the polymerization procedure. The roughness of the surface should be considered as a factor providing an increase in the surface area. In addition, these pores reduce



**Fig. 3.** SEM micrograph of the surface of the poly(EGDMA-VTAZ-SO<sub>3</sub>H).

mass transfer resistance and facilitate the diffusion because of high internal surface area [23].

### 3.5. Recycle of catalyst

Regeneration is one of the most important strengths of supports, with this capability of supports being considered to have a great influence on their extended applications in improving the proceconomics. For this reason, the regeneration property of poly(EGDMA-VTAZ-SO<sub>3</sub>H) beads is worthy of study.

**Table 1**

Physicochemical and acidic-related properties for acid modified poly(EGDMA-VTAZ) catalyst.

Samples	Type	Elemental analysis results				Acid capacities	
		C%	H%	N%	S%	Titration <sup>a</sup>	S Content <sup>b</sup>
I	Poly(EGDMA-VTAZ)	51.85	6.35	8.73	0.00	–	–
II	Poly(EGDMA-VTAZ-10%SO <sub>3</sub> H)	30.72	6.06	5.24	9.59	3.05	3.00
III	Poly(EGDMA-VTAZ-15%SO <sub>3</sub> H)	26.40	6.07	4.41	11.45	3.85	3.78
IV	Poly(EGDMA-VTAZ-20%SO <sub>3</sub> H)	22.21	6.07	3.80	12.82	4.39	4.46
V	Poly(EGDMA-VTAZ-30%SO <sub>3</sub> H)	16.27	5.87	2.72	14.23	5.45	5.49

<sup>a</sup> Acid capacities defined as mmol of H<sup>+</sup> per gram of sample.

<sup>b</sup> Sulfur content calculated from TG and elemental analyses.

At this stage we envisioned that the only manner in which the poly (EGDMA–VTAZ–SO<sub>3</sub>H) could be restored to its original activity would be to oxidise it back to its beginning form. For this purpose, following isolation of the polymer catalyst from the reaction mixture via filtration, it was washed with deionised water and waited in the potentially containing 30% H<sub>2</sub>SO<sub>4</sub> solution for 2 h and then evaporated to dryness at 343 K overnight. New esterification reaction components were added to any residues present and the reaction run as before. After five consecutive reactions the esterification conversions (2 h and 4 h) could still be maintained 22.5% and 42.5% levels in the fifth cycle (Table 2). By using this mode five successive runs of the test reaction were performed manually without significant losses in activity. poly (EGDMA–VTAZ–SO<sub>3</sub>H) beads can be regenerated and reused, so this provides a potential application.

### 3.6. Comparison of catalysts

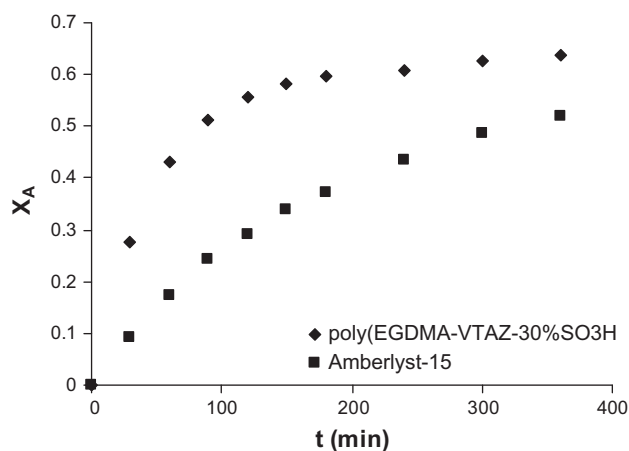
A comparison of the catalyst behaviour of the fibrous polymer-supported sulfonic acid catalyst, Amberlyst-15; and poly (EGDMA–VTAZ–30%SO<sub>3</sub>H) is shown in Fig. 4. Experiments were carried out under identical conditions except for the type of catalyst. poly (EGDMA–VTAZ–30%SO<sub>3</sub>H) (1.0–1.5 mm) showed the higher acid activity than Amberlyst-15 (560 μm). The values of the rate constants are  $14.1 \times 10^{-3}$  and  $3.5 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ min}^{-1}$  for the poly (EGDMA–VTAZ–SO<sub>3</sub>H) and Amberlyst-15 respectively. The equilibrium conversion of propionic acid was the same in both experiments as expected. Analogous results have been obtained by Rodriguez and Setinek [24]. The equilibrium swelling values in 1,4-dioxane (reaction solution) were determined both for the traditional catalyst Amberlyst-15 and poly (EGDMA–VTAZ–SO<sub>3</sub>H) and it was obtained very close results, 44.2% and 44.7% for poly (EGDMA–VTAZ–SO<sub>3</sub>H) and Amberlyst-15 respectively. The driving force for swelling of a polymer network bearing fixed charges on the skeleton or on the side groups comes from the free energy of polymer–solvent mixing and from the translational entropy of mobile ions, whose distribution among inside the gel and outer bath is described by the Donnan equilibrium theory [25].

### 3.7. Effect of catalyst loading

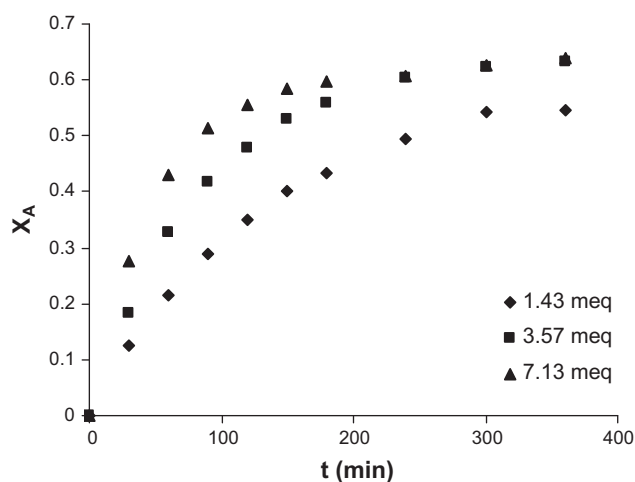
The effect of catalyst loading on the conversion of propionic acid is represented in Fig. 5. Catalyst loading was varied from 1.43 meq to 7.13 meq at a temperature of 333 K, feed mole ratio of 1:1, and stirrer speed of 700 rpm. In the absence of mass transfer resistance, the rate of reaction is directly proportional to the catalyst loading based on the entire liquid phase volume. It was also stated that the reaction rate is linearly depended on resin concentration [26]. It was seen that the conversion of propionic acid increased with an increase in the catalyst loading. Thus, the time required to reach the reaction equilibrium was reduced owing to the increase in the total number of acid sites available. But the catalyst loading does not have any effect on the equilibrium conversion.

**Table 2**  
The conversions for poly (EGDMA–VTAZ–SO<sub>3</sub>H) in cycle usage test.

Round	2 h Conversion (%)	4 h Conversion (%)
1	22.5	41.9
2	22.9	43.2
3	22.4	42.5
4	22.6	42.7
5	22.8	43.0



**Fig. 4.** Comparison of poly (EGDMA–VTAZ–SO<sub>3</sub>H) and the traditional solid acid catalyst, Amberlyst-15 with respect to propionic acid conversions versus time (feed mole ratio: 1:1; temperature: 333 K; stirrer speed: 700 rpm, catalyst loading: 10 g L<sup>-1</sup>).



**Fig. 5.** Effect of catalyst loading on conversion of propionic acid at 333 K (feed mole ratio: 1:1; catalyst: poly (EGDMA–VTAZ–SO<sub>3</sub>H); stirrer speed: 700 rpm).

### 3.8. Kinetic model

A pseudo-homogeneous model can be effectively applied to correlate the kinetic data of the liquid solid catalytic reaction. The esterification reactions are known to be reversible reactions of second-order [14,27,28]. The general rate expression can then be written as

$$-r_A = -\frac{dC_A}{dt} = k_1 \left( C_A \cdot C_B - \frac{C_E \cdot C_W}{K} \right) \quad (1)$$

where subscripts A, B, E and W refer to acid, alcohol, ester and water respectively,  $k_1$  is forward reaction rate constant,  $K$  is the equilibrium constant of the reaction.

Eq. (1) can be integrated to give the following equation while keeping the acid:alcohol molar ratio at (1:1), the catalyst weight at 10 g dry resin L<sup>-1</sup>.

$$\ln \frac{X_{Ae} - (2X_{Ae} - 1)X_A}{X_{Ae} - X_A} = 2k_1 \left( \frac{1}{X_{Ae}} - 1 \right) C_{A0} t \quad (2)$$

where  $X_A$ , fractional conversion of reactant A;  $X_{Ae}$ , fraction of the equilibrium conversion of reactant A which was found to be independent of temperature ranging from 318 to 343 K is, about 0.64.

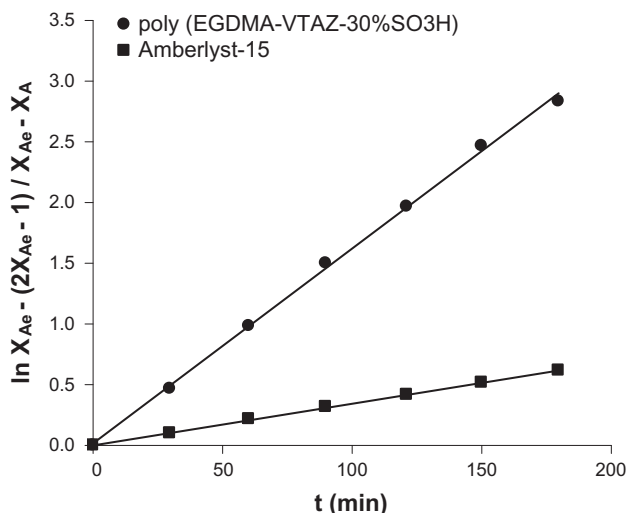


Fig. 6. Suitability of pseudo-homogeneous model for the esterification of methanol with propionic acid over poly (EGDMA-VTAZ-SO<sub>3</sub>H) and Amberlyst-15 catalysts.

Plotting of left-hand side of (Eq. (2)) versus time, a straight line with the slope of  $2k_1 \left( \frac{1}{X_{Ae}} - 1 \right) C_{A0}$  is obtained for the bimolecular type second-order reactions [29]. These lines were presented in Fig. 6 in the presence of Amberlyst-15 and poly (EGDMA-VTAZ-30%SO<sub>3</sub>H).

### 3.9. The effect of reaction temperature and reactant ratio

The temperature dependency of the rate constant is expressed by the Arrhenius law:

$$k_1 = A \exp\left(-\frac{E_A}{RT}\right) \quad (3)$$

where  $E_A$ , activation energy;  $A$ , frequency factor. From Eq. (3), a plot of  $\ln k_1$  versus  $1/T$ , at constant acid and alcohol concentrations, gives a straight line with the slope of  $(-E_A/R)$  as shown in Fig. 7. As revealed by the figure, the esterification rate increases with increasing temperature. A value of the activation energy of  $E_A = 41.6 \text{ kJ mol}^{-1}$  was obtained.

The results from the experiments with different initial molar ratios of methanol and propionic acid (1:2, 1:1 and 2:1) at 333 K over poly (EGDMA-VTAZ-30%SO<sub>3</sub>H) are compared in Fig. 8. The higher the excess of the alcohol, the higher is the final conversion

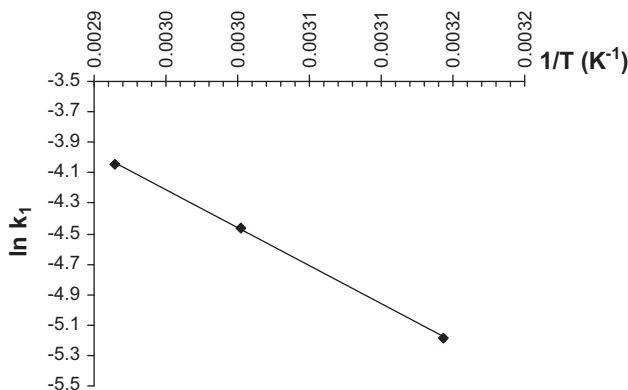


Fig. 7. Arrhenius plot of esterification of propionic acid with methanol over poly (EGDMA-VTAZ-SO<sub>3</sub>H) catalyst (feed mole ratio: 1:1; stirrer speed: 700 rpm; catalyst loading: 10 g L<sup>-1</sup>).

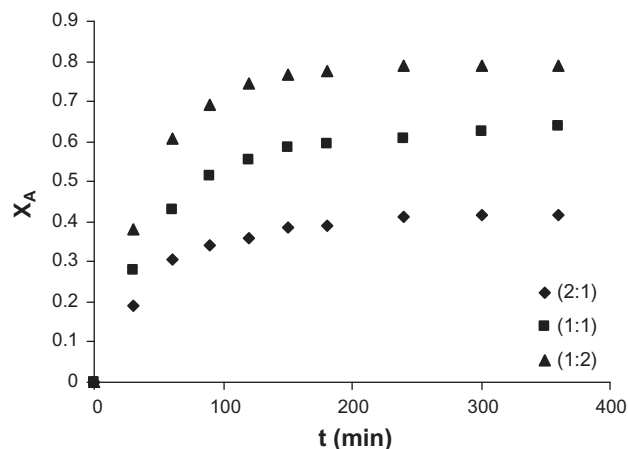


Fig. 8. Effect of different initial molar ratio of methanol to propionic acid on the acid conversions ( $T = 333 \text{ K}$ , catalyst: poly (EGDMA-VTAZ-SO<sub>3</sub>H); stirrer speed: 700 rpm).

of the acid. The kind of experiment is valuable in the evaluation of the competing kinetic models.

## 4. Conclusion

In this work, the catalytic performance of a new polymer catalyst, sulfonic acid functionalized form of poly (EGDMA-VTAZ), was evaluated for the esterification of propionic acid with methanol. Kinetic parameters confirm that poly (EGDMA-VTAZ-SO<sub>3</sub>H) is an efficient catalyst; it has a rate constant which exceeds that of Amberlyst-15 by a factor of about four in the reaction of esterification of propionic acid with methanol. As for the reaction equilibrium constant ( $K_e$ ), which is independent of temperature ranging from 318 to 348 K, was determined to be 3.16. The cycle usage test indicated that the polymer catalyst poly (EGDMA-VTAZ-SO<sub>3</sub>H) was relative stable.

The conversion of propionic acid increased with an increase in the amount of catalyst. But the equilibrium conversion was not affected. Therefore, the time required to reach the reaction equilibrium was shortened due to the increase in the total number of acid sites available. The apparent activation energy was found to be 41.6 kJ mol<sup>-1</sup> for poly (EGDMA-VTAZ-SO<sub>3</sub>H).

## References

- [1] P. Maki-Arvela, T. Salmi, M. Sundell, K. Ekman, R. Peltonen, J. Lehtonen, Appl. Catal. A: Gen. 184 (1999) 25–32.
- [2] J. Lilja, D.Yu. Murzin, T. Salmi, J. Aumo, P. Maki-Arvela, M. Sundell, J. Mol. Catal. A 182–183 (2002) 556.
- [3] W.T. Liu, C.S. Tan, Ind. Eng. Chem. Res. 40 (2001) 3281.
- [4] B. Erdem, M. Cebe, Z. Phys. Chem. 220 (2006) 735.
- [5] H.T.R. Teo, B. Saha, J. Catal. 228 (2004) 174.
- [6] J. Lilja, J. Warna, T. Salmi, L.J. Pettersson, J. Ahlkvist, H. Grenman, M. Rönholm, D. Yu. Murzin, Chem. Eng. J. 115 (2005) 4.
- [7] T.A. Peters, N.E. Benes, A. Holmen, J.T.F. Keurentjes, Appl. Catal. A: Gen. 297 (2006) 182.
- [8] M.R. Altokka, A. Çitak, Appl. Catal. A: Gen. 239 (2003) 141.
- [9] A.H.M. Vries, F.J. Parlevliet, L.S. Vondervoort, J.H.M. Mommers, H.J.W. Henderickx, M.A.M. Walet, J.G. Vries, Adv. Synth. Catal. 344 (2002) 996–1002.
- [10] T. Yoshioka, M. Shimamura, Bull. Chem. Soc. Jpn. 57 (1994) 334–337.
- [11] G.D. Yadav, H.B. Kulkarni, React. Funct. Polym. 44 (2000) 153–165.
- [12] Y. Liu, E. Lotero, J.G. Goodwin Jr., J. Catal. 242 (2006) 278–286.
- [13] A. İzci, E. Uyar, E. İzci, Chem. Eng. Comm. 196 (2009) 56–67.
- [14] A. İzci, F. Bodur, React. Funct. Polym. 67 (2007) 1458.
- [15] B. Erdem, A. İzci, Z. Phys. Chem. 224 (2010) 781.
- [16] L. Uzun, A. Kara, N. Tüzmen, A. Karabakan, N. Beşirli, A. Denizli, J. Appl. Polym. Sci. 102 (2006) 4277.
- [17] A. Kara, J. Appl. Polym. Sci. 114 (2009) 949.
- [18] B. Sow, S. Hamoudi, M.H.Z. Niaki, S. Kaliaguine, Microporous Mesoporous Mater. 79 (2005) 131.

- [19] D. Margolese, J.A. Melero, S.C. Christiansen, B.F. Chmelka, G.D. Stucky, *Chem. Mater.* 12 (2000) 2451.
- [20] B. Zhang, J. Ren, X. Liu, Y. Guo, Y. Guo, G. Lu, Y. Wang, *Catal. Commun.* 11 (2010) 629–632.
- [21] A. Aslan, S.Ü. Çelik, Ü. Şen, R. Haser, A. Bozkurt, *Electrochim. Acta* 54 (2009) 2958.
- [22] A. Bozkurt, *Turkey J. Chem.* 29 (2005) 117.
- [23] A. Kara, L. Uzun, N. Beşirli, A. Denizli, *J. Hazard. Mater.* 106B (2004) 95.
- [24] O. Rodríguez, K. Setinek, *J. Catal.* 39 (1975) 449–455.
- [25] M.J. Molina, M.R. Gomez-Anton, I.F. Pierola, *J. Phys. Chem. B.* 111 (2007) 12066.
- [26] B. Erdem, M. Cebe, *Korean J. Chem. Eng.* 23 (2006) 899.
- [27] S.I. Kırbaşlar, H.Z. Terzioğlu, U. Dramur, *Chin. J. Chem. Eng.* 1 (2001) 90–96.
- [28] Z.P. Xu, K.T. Chuang, *Can. J. Chem. Eng.* 74 (1996) 493–500.
- [29] O. Levenspiel, *Chemical Reaction Engineering*, second ed., John Wiley & Sons, Inc., Canada, 1972, p. 63.