

ZSM-5 위에 지지된 Heteropolyacid 하에서 Methacrylic acid와 Ethylene glycol의 에스테르화 반응

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Esterification of Methacrylic acid with Ethylene glycol over Heteropolyacid supported on ZSM-5

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요약. methacrylic acid과 ethylene glycol과의 에스테르화 반응을 ZSM-5에 지지된 heteropolyacids [HPA: $H_4SiW_{12}O_{40}$ (STA)와 $H_3PW_{12}O_{40}$ (PTA)] 하에서 수행하였다. 비교를 위하여, 지지하지 않은 HPA, H_2SO_4 , BF_3 와 PTSA 하에서 같은 반응을 수행하였다. 연구한 촉매 중에서, HPA는 H_2SO_4 , BF_3 와 PTSA와 비교하여 더 좋은 활성을 보여주었다. 촉매 활성을 HPA 지지 ZSM-5 촉매와 비교하였는데, 그 결과 ZSM-5위에 지지된 30 wt% PTA는 bulk PTA와 거의 같은 활성을 나타내었다. 이 반응은 methacrylic acid에 관하여 1차 속도 법칙을 따랐으며, 반응 생성물은 1H -NMR과 FT-IR을 이용하여 확인하였다.

주제어: 에스테르화, 고체 산 촉매, Methacrylate, Heteropolyacid, 제올라이트

ABSTRACT. Esterification of methacrylic acid with ethylene glycol was carried out over Heteropolyacids [HPA: $H_4SiW_{12}O_{40}$ (STA) and $H_3PW_{12}O_{40}$ (PTA)] supported on ZSM-5. For comparison, the same reaction was carried out over unsupported HPA, H_2SO_4 , BF_3 and PTSA. Among the catalysts studied, HPA showed better activity compared to H_2SO_4 , BF_3 and PTSA. Catalytic activity was compared with HPA supported ZSM-5 catalysts. Typical results indicated that 30 wt% PTA supported on ZSM-5 showed nearly the same activity as that of bulk PTA. It was found that the reaction follows first order kinetics with respect to methacrylic acid. The reaction products were identified by 1H -NMR and FT-IR.

Keywords: Esterification, Solid acid catalysts, Methacrylate, Heteropolyacid, Zeolites

INTRODUCTION

Acid catalyzed reactions are important in the chemical industry not only for the synthesis of commodity chemicals, but also for the syntheses of specialty chemicals used in pharmaceuticals, agrochemicals, and fragrances. Esterification represents one of the most important reactions in chemical industry and the esters produced have applications in a variety of applications such as plasticizers, flavors, fragrances, pesticides, and surface active agents. Some esters are converted into their derivatives and used as chemical intermediates and monomers for resins and high molecular weight polymers. Catalytic esterification has conventionally been carried out in liquid phase. Esterification reactions are equilibrium processes and must be displaced towards the desired ester by using excess of one of the reactants or by continuous removal of water by

azeotropic distillation. Homogeneous catalysts such as H_2SO_4 , HF, H_3PO_4 , HCl, and $ClSO_3H$ catalyzed reactions may lead to unwanted side products posing environmental and corrosion problems. Also, separation of the catalyst from the reaction mixture is difficult. In addition, these processes require minimum reaction time of 24 h to obtain 80% yield and it requires free radical inhibitor to prevent polymerization. Hence, it is an immediate challenge to find a suitable 'green' chemical technology for synthesis of esters. Heterogeneous catalysts offer several advantages over their homogenous counterparts like ease of product separation and catalyst reuse. However, to maintain economic viability, a suitable heterogeneous system must not only minimize the production of waste, but should also exhibit activities and selectivity comparable with the existing homogenous route.^{1,2}

Among the solid acid catalyst, Keggin heteropolyacid

(HPA) offers unique advantages over other solid acid catalysts in terms of thermal stability, hydrolytic stability and acidity.³⁻⁶ However HPAs are highly soluble in polar solvents thereby exhibiting “pseudo liquid” behavior. In addition, the major disadvantage of HPA as catalyst is moderate thermal stability, low surface area (1-10 m²/g) in addition to separation problem from the reaction mixture. HPA can be made heterogenous by supporting them onto suitable supports. Various support like hydrous zirconia,^{7,8} silica,^{9,10} titania, clay,^{11,12} neutral alumina,^{13,14} activated carbon,¹⁵ MCM-41¹⁶ and acidic ion exchange resins¹⁷ have been used for supporting HPA.

Multifunctional Methacrylates are industrially important monomers for anaerobic adhesives,¹⁸ diluents in dental composites,^{19,20} thread lockers, sealants and components for making soft contact lenses.²¹ This methacrylate is currently produced by the esterification of glycols with methacrylic acid using industrial catalyst like either sulphuric acid or borontrifluoride etherate.²² During the present study, esterification of methacrylic acid (MAA) with ethylene glycol (EG) was carried out over various catalysts including HPA were studied and results were compared with various catalysts. HPA supported on micro porous ZSM-5 catalyst was prepared and studied for this reaction. A detailed kinetic study was carried out in order to understand the nature of the reaction.

EXPERIMENTAL

Materials

The HPA (silicotungstic acid (STA) and phosphotungstic acid (PTA)) were obtained from Sigma Aldrich and ZSM-5 was purchased from S□D Cheme and has a surface area of 320 m²/g.

Synthesis of the catalyst (HPA supported onto ZSM-5)

The supported catalysts were prepared by impregnation method. A series of catalyst containing 10-50 wt% HPA were synthesized by suspending the required amount of ZSM-5 in an aqueous solution of HPA with stirring for 30 h and dried at 373 K for 10 h. Then the substance were calcined at 773 K in a muffle furnace.

Characterization

The PTA supported ZSM-5 samples are characterized by x-ray powder diffraction (schimadzu, XD-DI diffractometer, Japan) with Cu K α radiation ($\lambda=0.154056$ nm) and data collected over the 2θ range of 20-60°, using a step size of 0.05° and step time of 2s with ramp speed of 1°/1

min. The reaction products were identified by ¹H-NMR and FT-IR.

Experimental setup

The esterification of MAA was carried out with ethylene glycol in 100 ml three neck RB flask. The temperature was maintained in oil bath. The required amount of the reaction mixture was taken in flask and required amount of inhibitor is added to the mixture while stirring. A blank titration was carried out for reaction mixture without catalyst. When flask reached temperature of about 10 K lower than the desired temperature, the catalyst was added quickly. After the addition of catalyst, 1 ml of aliquot was withdrawn immediately into a conical flask and the reaction was arrested by adding ice and titrated using 0.5 M sodium hydroxide solution using phenolphthalein as indicator. In order to understand the pseudo liquid behavior of HPAs, the reaction mixture was filtered under hot conditions and the reaction was monitored further. The water formed as the product was removed by azeotropic distillation with the solvent TCE. The % conversion with respect to acid can be calculated by

$$\% \text{ conversion} = (\text{moles of MAA reacted} / \text{moles of MAA fed}) \times 100$$

RESULTS AND DISCUSSION

Characterization of catalyst

The XRD patterns of the PTA supported ZSM-5 were shown in Fig. 1, which showed intense peak around 22° (2θ) due to presence of ZSM-5 and the peaks at 25°, 35°,

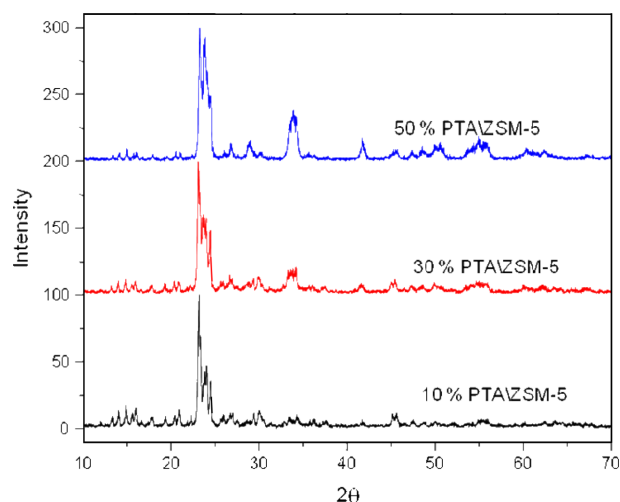


Fig. 1. XRD patterns of: (a) 10 wt% PTA/ZSM-5 (b) 30 wt% PTA/ZSM-5 (c) 50 wt% PTA/ZSM-5.

37.5° due to the presence of PTA. 10 wt% PTA/ZSM-5 shows very high intensity peak for ZSM-5 at 23°, whereas, 30 wt% PTA/ZSM-5 shows relevant peak for PTA and ZSM-5. The XRD patterns revealed that at low loadings of PW (below 20 wt%) no distinct diffraction peaks due to HPA crystallites are observed. But when the loading exceeded above 20 wt% broad diffraction peaks appeared at $2\theta = 26.6^\circ$ and 30.9° which were attributed to PW12 crystalline, revealing that most of the PW12 molecules aggregated on the surface of the support. 50 wt% PTA/ZSM-5 also shows relevant peaks for ZSM-5 and PTA.

Comparison of catalytic performance

HPA were compared with various conventional acid catalysts during esterification reaction at 353 K and results are presented in Fig. 2. As seen from the Fig. 2 with each catalyst the conversion increased with time. The conventional catalysts like H_2SO_4 , BF_3 and PTSA showed a maximum of 53% conversion, whereas HPA catalysts showed still higher conversion. Among the catalysts studied, PTSA shows lower activity and STA shows higher activity. After 300 min on stream, STA shows nearly 65% conversion compared to 53% with H_2SO_4 . Both STA and PTA shows higher activity compared to mineral acids. Interestingly, for HPAs with the hot filtrate of the reaction mixture, nearly 30% conversion was observed, which confirms the pseudo liquid behavior of HPAs. A similar behavior was observed earlier.³ The reaction product was separated by column chromatography and identify with $^1\text{H-NMR}$ and FT-IR.

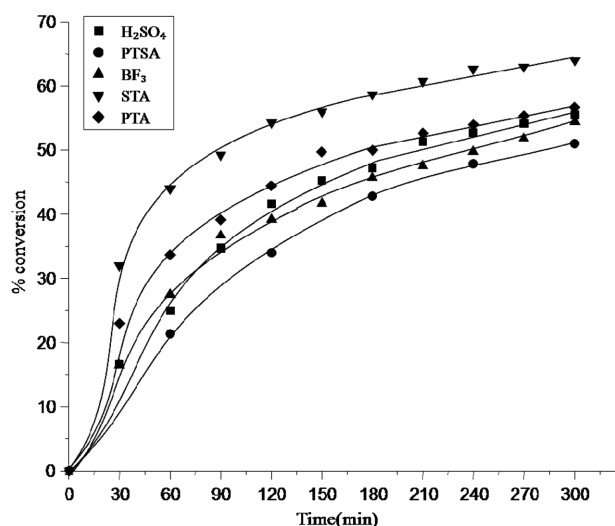


Fig. 2. Esterification of ethylene glycol with methacrylic acid over selected acidic catalysts [(MAA: EG)=1:1, catalyst=1 mmol, Hydroquinone (HQ)=100 mg, Temp=353 K].

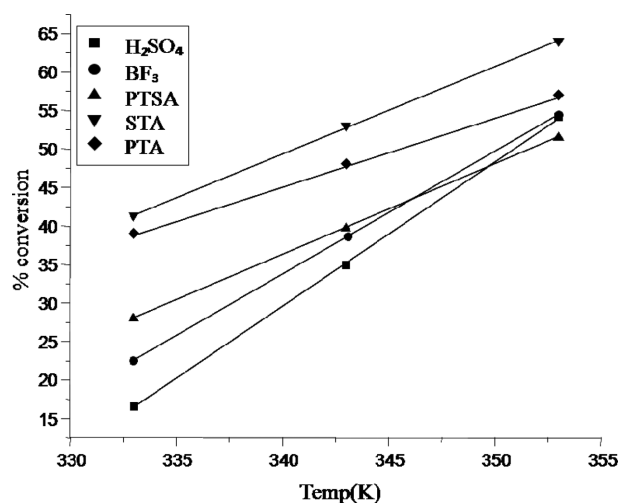


Fig. 3. Esterification of ethylene glycol with methacrylic acid over selected acidic catalysts as a function of temperature [(MAA: EG)=1:1, catalyst=1 mmol, HQ=100 mg, Time=5 h].

Fig. 3 represents the activity of various catalysts as a function of temperature varied between 333-353 K. Among the catalysts studied, HPA showed higher acid conversion compared conventional acids like PTSA and H_2SO_4 . Among the HPAs, STA showed higher activity than PTA. For esterification of methacrylic acid with ethylene glycol, catalytic activity follows the order $\text{H}_4\text{SiW}_{12}\text{O}_{40} > \text{H}_3\text{PW}_{12}\text{O}_{40} > \text{HSO} > \text{PTSA}$. As seen from the Fig. 3 temperature has a strong influence on the activity for all the catalysts studied. With H_2SO_4 , conversion increased from 15% at 333 K to 53% at 353K. With each other catalyst studied, a similar observation was made. However, STA shows high conversion of 43% at 333K, which increased to 65% at 353K. This strong influence temperature may be due to decrease in the activation energy and also due to pseudo liquid behavior. In order to understand the influence of temperature, activation energy was calculated and presented in Fig. 4. As seen from the Fig. 4, among the catalysts studied, BF_3 and PTSA showed low and higher activation energy of 110 and 60 kJ/mol, respectively, whereas, for PTA, E_a was 71 kJ/mol. The activation energy of various catalysts followed the order of $\text{PTSA} < \text{PTA} < \text{H}_2\text{SO}_4 < \text{STA} < \text{BF}_3$. The order of the esterification reaction was determined by isolation technique, which confirms that the reaction follows first order for acid as shown in Fig. 5.

Previous results demonstrate that the activity of HPA is comparable with conventional mineral acids catalysts. However, the applicability of HPA is limited mainly due to their pseudo liquid behaviour, as they are highly soluble in polar solvents. Hence, recovery of the catalyst would be

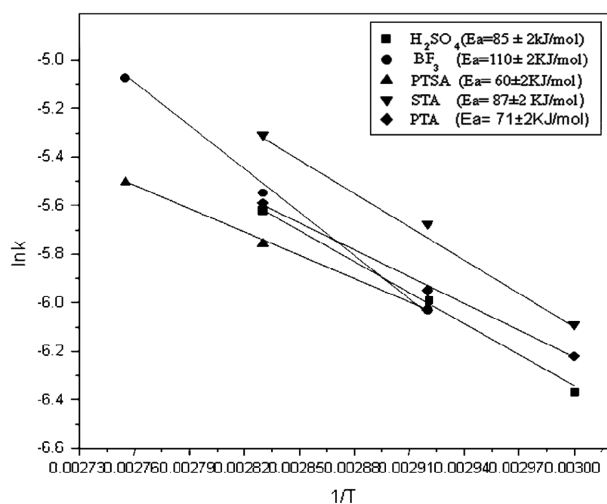


Fig. 4. Arrhenius plot for the esterification of methacrylic acid with ethylene glycol over H_2SO_4 , BF_3 , PTSA, STA, PTA catalyst (Amount=1 mmol) HQ=100 mg.

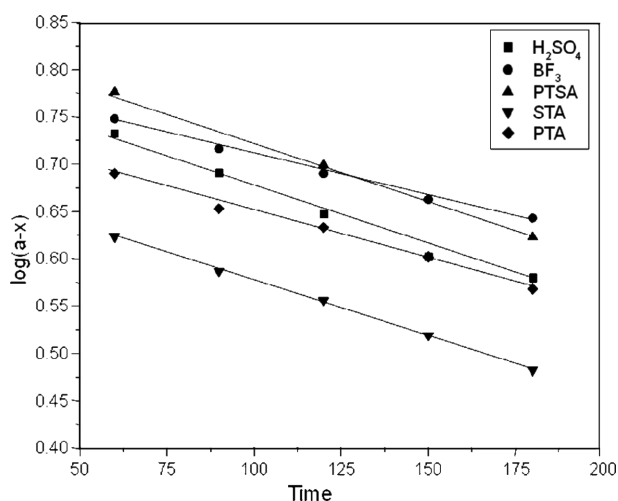


Fig. 5. First order plot for the esterification of methacrylic acid with ethylene glycol over H_2SO_4 , BF_3 , PTSA, STA, PTA catalyst (Amount=1 mmol) HQ=100 mg.

difficult. It is possible to overcome these limitations by converting the catalytic system heterogeneous by supporting HPA on a high surface area support. During the present study a microporous ZSM-5 was chosen as the support for HPA.

Esterification reaction has been carried out over PTA supported ZSM-5 at 373 K and results are presented in Fig. 6. It is worth mentioning that activity of unmodified ZSM-5 is negligible compared to HPA supported ZSM-5, which may be attributed to lack sufficient number of acidic sites. However, as seen from the Fig. 6, 30 wt% PTA loaded ZSM-5 shows higher activity, whereas both increasing

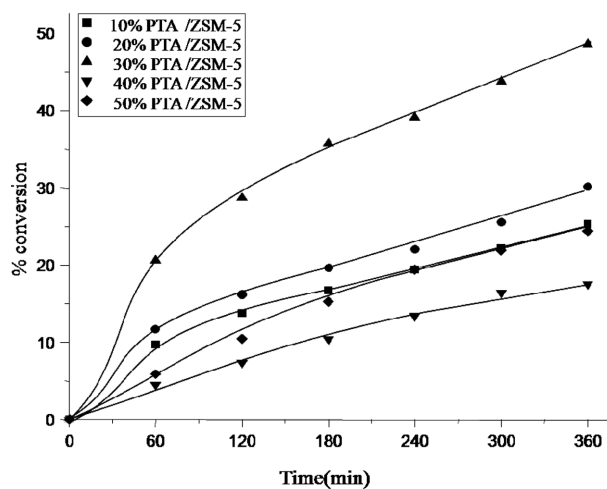


Fig. 6. Esterification of ethylene glycol with methacrylic acid over PTA modified ZSM-5 [MAA:EG=1:1, catalyst=1 mmol, HQ=100 mg, Temp=383 K].

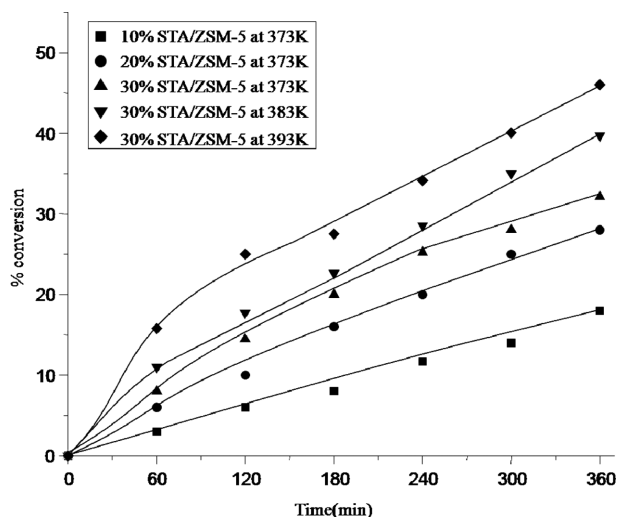


Fig. 7. Esterification of ethylene glycol with methacrylic acid over STA modified ZSM-5 [MAA:EG=1:1, catalyst=1 mmol, HQ=100 mg, Temp=373-383K].

and decreasing PTA loading results in decrease in the conversion. This may be due the formation of bulk HPA at higher loadings as observed in XRD, whereas at loadings less than 30% required amount of acidic sites may not be available for the reactants. In order to confirm this observation, varying amounts of STA was loaded on ZSM-5 and tested for esterification reaction and results were presented in Fig. 7. As seen from the Fig. 7 the results followed a similar trend to PTA supported system, where conversion increased upto 30 wt% loading of STA. Interesting observation is that when the reaction was monitored with hot filtrate conversion was not significant, which confirms the heterogeneous behavior of the HPA/ZSM-5 system.

CONCLUSIONS

Esterification of methacrylic acid with ethylene glycol was carried out over HPA catalysts and the activity was compared with conventional acids like H₂SO₄, BF₃, and PTSA. Among the catalysts studied, HPA showed better activity compared to H₂SO₄, BF₃ and PTSA. In order to overcome the practical limitations of HPA like recovery of the catalyst, HPA were supported on ZSM-5 to make the system truly heterogeneous. Typical results indicate that 30 wt% PTA supported on ZSM-5 showed nearly the same activity as that of bulk PTA and with further increase in the PTA loading decreases the activity. The reaction was found to be first order with respect acid. The reaction product methacrylate was confirmed by ¹H-NMR and FT-IR.

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