Esterification of Acrylic Acid with Butanol to Butyl Acrylate over Sulfonated Polystyrene

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Highlights

- Esterification of acrylic acid catalyzed by sulfonated polystyrene (SEP) was studied.
- SEP was synthesized using waste expanded polystyrene.
- High activity was observed due to the stronger Bronsted acid sites of SEP.
- SEP is recyclable by simple filtration

Summary

The sulfonated polystyrene (SEP) was synthesized from the waste expanded polystyrene It exhibited high catalytic activity in the esterification of acrylic acid with butanol because of the strong Bronsted acid sites. The maximum butyl acrylate yield was 70% at the reaction temperature of 80^{o}C with the butanol in excess. The catalyst loading adopted is within the practical range of the industries. The SEP can be recycled by simple filtration and it is a potential catalyst for esterification of acrylic acid.

Keywords

Sulfonated polystyrene, heterogeneous catalyst, esterification, acrylic acid

Introduction

Butyl acrylate is the important building blocks in the production of paint, adhesive, textile and leather industries.[1,2] This acid-catalysed chemically reversible reaction requires removal of water and/or use excess amount of reactant.[3] Homogeneous catalyst is commonly used in the conventional method to accelerate the reaction. In spite of their strong activity, these homogeneous catalysts, imposed several drawbacks such as corrosion problems, difficult to be separated from reaction mixture and necessity to be neutralized after the reaction.[4] Heterogeneous catalyst has been developed to overcome the aforementioned shortcomings and to suppress the side reactions.[5]

To date, most of the heterogeneous catalysts used for the esterification of acrylic acid with alcohol were deactivated by water.[6]The unique sulfonated expanded polystyrene (SEP) was reported as the potential catalyst for the esterification reaction due to its' strong Bronsted acid sites and water super-adsorbent properties.[7] Expanded polystyrene (EPS) is lightweight rigid plastic foam produced by steam moulding. It is consumed in large quantity as packaging or insulating materials and disposed as waste. Considering the environmental and economic perspectives, EPS can be chemically recycled as the catalyst for the esterification reaction.

Methodology

Catalyst preparation

The SEP was prepared by reacted 1 gram EPS with 20ml sulphuric acid for 2 hours at 105^{o}C. The brown slurry was transferred into 100ml of water and filtered. The slurry was washed with 0.1mol/L *NaOH* , acid hydrochloric solution (1:50) and de-ionized water in excess. The slurry that obtained was dried at 70^{o}C. The ion exchange capacity of the SEP was determine by titration.[7,8]

Catalyst testing

The esterification was carried out in three necked flask equipped with condenser, temperature controller and temperature probe. The butanol (BuOH) was charged into the flask. After the requied temperature reached, acrylic acid (AA) and catalyst was charged and the reaction time was started. The total sample taken was less than 10% of total volume (30ml) of reaction mixture. The product was analyzed using FID gas chromatography. The catalyst was separated from the reaction mixture by filtration and washed with BuOH and dried at 70^{o}C before it was reused for further run.

Results and Discussion

The screening has been done for a few types of catalysts by comparing their catalytic activities. The experimental studies were carried with the appropriate stirring rates (as stated in figure 1) to eliminate the mass transfer limitation. In figure 1, the polymer catalysts has shown higher butyl acrylate (BA) yield as compared to the oxide, phosphate and carbon base catalysts. The SEP has given the highest yield due to its' stronger sulfonic acid sites and hydrophobicity than the commercial catalyst (Amberlyst-15).

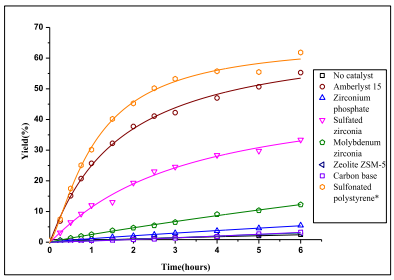

Figure 1: Esterification of butanol with acrylic acid Reaction conditions: 80°C, molar ratio of 1:1, 40wt% catalyst loading, 600rpm; * Reaction conditions: 80°C, molar ratio of 1:1, 10wt% catalyst loading, 400rpm

The reactions were carried out in the excess BuOH and AA.

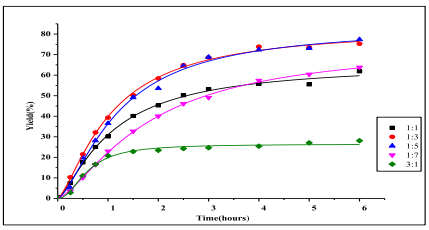

Figure 2: Effect of reactants molar ratio on the BA yield. At temperature of 80°C, catalyst loading of 10% and 400rpm

Figure 2 shows that the yield is increased as molar ratio of AA to BuOH, $M_{AA:BuOH}$ increases from 1:1 to 1:5. The excess BuOH has promoted the forward reaction.[9] Nevertheless, BuOH would start accumulateing on the catalyst surface which offset the increased acid conversion or even deactivated the catalyst.[9] The yield is decreased in the excess of AA due to the limiting amount of oxonium ion form through the protonation of AA. The optimum MAA:BuOH is 1:3.The catalyst loading was varied from 0-15wt% (weight of catalyst/weight of AA) and its' effect on the BA yield is shown in figure 3.

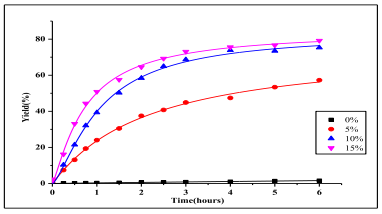

Figure 3: Effect of catalyst loading on BA yield. At temperature of 80°C, molar ratio of 1:3, stirring rate of 400rpm and reaction time of 6hours.

The increasing of catalyst loading has lead to an increase in the BA yield because the higher reaction rate attributed to the higher total number of active catalytic sites.[10]The best catalyst loading is 10wt% since the increment in BA yield is not significant when the catalyst loading is increased to 15wt%. Moreover, the catalyst loading is not practical to use more than 10wt% for heterogeneously catalysed reaction.[11]

The reusability studies were carried out to examine the SEP activity and the stability. Figure 4 has proven that the SEP can be recovered by simple filtration. The BA yield decreases for about 10% when the catalyst is reused for 2nd time. Nevertheless, the yield reduction is not significant when the catalyst is used in the 3rd consecutive run. The deactivation and regeneration of SEP are currently being studies. Subsequently, the deactivation mechanism could be identified to justify the yield decrease in consecutive runs.

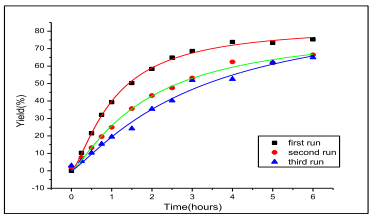

Figure 4: BA yields obtained for the reusability study. At temperature 80oC, molar ratio of 1:3, stirring rate of 400rpm, catalyst loading of 10% and reaction time of 6 hours.

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