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Ionic Liquid for Esterification: A Review

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ABSTRACT

Esterification reaction is one of the major reactions in the industries. These reactions are usually carried out conventionally by homogeneous catalysis and heterogeneous catalysis. These conventional methods have certain limitation. The phenomenon of green chemistry suggests a 'green catalyst' called ionic liquid that can be used as catalyst for this reaction. This is a very brief review about choosing ionic liquid as an alternative for the conventionally used catalysts for esterification.

Keywords--- Esterification, Homogenous Catalyst, Heterogeneous Catalyst, Ionic Liquids.

1. INTRODUCTION

In this present world, the amount of waste produced is increasing day by day. Chemical industries are producing a huge bulk of wastes. Thus in the present scenario, the principles of green chemistry have been introduced to eliminate or at least to reduce the use of hazardous materials in chemical processes to minimise the human and environmental impact without stifling scientific progress. One of the key areas of green chemistry is the replacement of hazardous solvent with environmentally benign ones. Recently, the progress in the field of ionic liquids (ILs) is gaining significance due to their unique properties. Ionic Liquids are salt-type compounds, which are liquids at room temperature and possessing low vapour pressure. Due to the lack of evaporation, they are considered as 'green solvents'. These compounds are known as environment friendly solvents or catalysts and much attention has currently been focused o the organic reactions with ILs as catalysts or solvents.

Esterification reactions are industrially important reactions and are studied widely. The reaction in which the two reactants i.e., an alcohol and an acid, reacts together to give an ester as the product is known as esterification. Esters are basically derived from an acid (organic or inorganic) from which at least one hydroxyl group is replaced by an alkoxy group [-OH group replaced by –O- group]. The commonly used acid is carboxylic acids.

The esterification reaction is endothermic, slow, and reversible in nature with high activation energy barrier in the absence of catalyst. The equilibrium constant of this reaction has very low value of about 4-7. So addition of catalyst, using excess alcohol and also removing the water produced by some physical means can be used to increase the amount of ester produced and thereby the equilibrium constant can be increased.

The catalysts used for the esterification reaction are homogeneous catalysts and heterogeneous catalysts. Homogeneous catalysts include sulphuric acid, hydrogen iodide etc. Heterogeneous catalysts include mainly ion exchange resins. But there are many disadvantages associated with these catalysts which are discussed in the review. Thus a new catalyst has been found out to carry out the esterification reaction that is the ionic liquid. This catalyst gives good conversion and purity of products. An ionic liquid (IL) is a salt in the liquid state. In some contexts, the term has been restricted to salts whose melting point is below some arbitrary temperature, such as 100 °C (212 °F). In general, ionic liquid is a liquid wholly composed of ions. Ionic liquid is called as the 'green catalyst'. There are many reasons for this. The first and foremost one is that ionic liquid possess negligible vapor pressure and hence they do not evaporate to the environment. The functionalised ionic liquids are one with functional group such as –SO3H, -OH, -NH, -SH etc. covalently attached to cations or anions or both. The ionic liquids with a built-in –SO3H group are acidic in nature and are called Bronsted Acid Ionic Liquid (BAIL). It can function as both catalyst and solvent. The first non-chloroaluminate room temperature acidic ionic liquid, i.e. SO3H functionalised ionic liquid, was prepared by Forbes et al.

2. ESTERIFICATION USING HOMOGENEOUS CATALYSIS

Homogeneous catalysis is catalytic reactions in which the catalysts are in the same phase as that of the reactants. Gas phase, liquid phase and even solid phase homogeneous catalytic reaction are there. This homogeneous catalysis can be acid catalysis or base catalysis i.e. the reactions are either catalysed by an acid or a base. In the acid catalysis the proton transfer takes place and this type of catalysis is mainly used for organic chemical reactions. And among the reactions in which the acid catalysis is taking place, esterification is one of the prominent reactions. There are many possible chemical compounds that can act as a source for the protons to be transferred in an acid catalysis system. Acids specifically used for acid catalysis include inorganic acids like sulphuric acid, hydrogen iodide, hydrochloric acid, phosphoric acid etc and organic acids like acetic acid, toluene sulfonic acid, polystyrene sulfonate, zeolites, heteropolyacids, and graphene oxide.

The catalysis is done in the esterification by creating a leaving group by converting the OH group in the acid to H2O+ by adding up with the proton and later this is eliminated as water. The remaining part of the acid and alcohol combines to give ester.

Maha et al.[12]studied the esterification of acetic acid with ethanol using the inorganic acid sulphuric acid as the catalyst with isothermal batch experiments in the temperature range 50-600C and also at different molar ratio of ethanol to acetic acid. They found that a maximum conversion of 80% was obtained at 600C for molar ratio of EtOH/Ac. The effects of activity coefficient on the reaction kinetics were also calculated using UNIFAC program. Atalay[2]investigated the esterification reaction between the reactants ethyl alcohol and acetic acid in the presence of sulphuric acid as catalyst, over a wide range of temperature and catalyst concentrations. The forward and backward reaction orders were obtained as 1 and 2 respectively. The relation between the reaction temperatures for each catalyst concentration on the reaction rate constant was developed. Models to represent these relations were also developed.

Berrioset al.[15]also found that the order of forward and backward reactions as 1 and 2 respectively by studying the esterification of Free Fatty Acids (FFA) in sunflower oil with methanol in the presence of sulphuric acid as catalyst at concentrations 5 to 10 wt% relative to fatty acids and reactants molar ratios 10:1 to 80:1.

Konakaet al.[1]studied the effect of different reactant mole ratios on the reaction kinetics of the reaction between formic acid and ethanol in the presence of sulphuric acid as catalyst. The second order reaction is confirmed but the change in order of reaction as a result of change in the mole ratio was also explained. Three different ranges of mole ratios i.e. 35, 5 to 12 and 1 to 5 were used to conduct the studies. Out of these 3, 1 to 5 ranges was found to be most practical for commercial production.

Hung su [20]reported that among the different catalysts used i.e. HCl, H2SO4 and HNO3 for the esterification of enzyme-hydrolysed FFA and methanol, only HCl could be considerably recovered and reused unlike the higher yield by all the catalysts. With HCl he investigated under varying catalyst loading, reaction temperature and reactant mole ratio. Model was also developed. He also found that the yield was high within five times of reuse.

Ronnbacket al.[5]studied the esterification of acetic acid with methanol in the presence of HI as the catalyst with the isothermal batch experiments at 30-600C, also the catalyst concentrations was varied from 0.05 to 10 wt%. Along with the main reaction, a side reaction between hydrogen iodide and methanol also took place to produce methyl iodide. Both forward and backward reactions were found to follow second order. Rate equations based on concentration and also based on activity coefficient were calculated. UNIFAC model was used to calculate the activity coefficients. Regression analysis was used to estimate the kinetic and equilibrium parameters in the rate equation. From the above literatures it is clear that homogeneous catalysts are efficient and gives high yield in the esterification reaction.

3. ESTERIFICATION USING HETEROGENEOUS CATALYSTS

Heterogeneous catalysis is the catalysis form in which the phase of the reactants and the catalysts are not the same. The great majority of practical heterogeneous catalysts are solids and the great majority of reactants are gases and liquids. Heterogeneous catalysis has much importance in many areas of chemical and energy industries. Amberlyst-15, Amberlyst-36, sulphated zirconia, Filtrol-24, activated acidic alumina, Nafion/Silica nano composite, heteropolyacids, etc are some of the examples of heterogeneous catalysts.

Yang Zhang et al.[7]reported about the kinetics of esterification of lactic acid with ethanol in the presence of 5 different cation- exchange resins. Langmuir-Hinshelwood mechanism was used to study about the rate equation. UNIFAC model was used to calculate the activity coefficients.

Tsai et al.[14]determined about the kinetic behaviour of esterification of acetic acid with methanol using Amberlyst-36 as the catalyst. The experiment was conducted in a packed bed reactor and at different conditions like the varying temperatures i.e. from 313.15 to 328.15 K and varying reactant mole ratios in the feed stream from 1 to 5. To get the kinetic parameters for the rate equation, the Ideal-Quasi-Homogeneous (IQH), the Non-Ideal-Quasi-Homogeneous (NIQH), the Eley-Rideal (ER), and the Langmuir-Hinshelwood-Hougen-Watson

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(LHHW) models were used and out of these the ER and the LHHW gave comparable results results with experimental data.

Kirbaslaret al.[6] performed the esterification of acetic acid with ethanol in the presence of the acidic ion exchange resin (Amberlyst 15). The reaction carried out in a batch reactor with temperature in the range 323 to 353 K at various starting compositions.

Pal Tooret al. [12] also used Amberlyst 15 as the catalyst to study the esterification reaction of acetic acid with n-butanol and iso-butanol. This reaction was also carried out in batch reactor in the temperature range 351.15 to 366.15 K. Effects of various other parameters such as catalyst loading, initial reactant molar ratios were also studied.

Yadavet al. [3] studied about the esterification reaction between acetic acid and two alcohol i.e. phenethylalcohol and cyclohexanol in the presence of various solid acidic catalysts such as Filtrol-24, Amberlyst-15, sulphated zirconia, heteropolyacids both silica and carbon supported. The activities and kinetics of the reaction and reusability of the catalyst were studied and among these catalysts used Amberlyst-15 followed by heteropolyacid has got good activity. When the catalysts were reused, a small decrease in activity was observed. The various other factors influencing the reaction were also discussed. The order of reaction was fit to second order kinetics.

Calvar et al. [8] investigated about the esterification reaction between acetic acid and ethanol catalysed by both acetic acid (homogeneous) and Amberlyst-15 (heterogeneous). The reactions were carried out in the temperature range of 30 to 800C and various initial reactant molar ratios. They used the model developed by Popkenet al. for their study. A comparison of homogeneous and heterogeneous catalysis was done and it was obtained as to get 84% conversion at 700C in homogeneous catalysis it took 13 days whereas heterogeneous catalysis took only 7 hours to get 81% coversion at 700C and initial reactant molar ratio 1.6.

Hasanoglu et al. [9] also did similar studies on the esterification of acetic acid and ethanol using sulphuric acid and Amberlyst-15 as catalysts in a temperature range of 50-700C and initial alcohol to acid mole ratio as 1 to 1.5. They found that as temperature and mole ratio is increasing, the conversions also increased. Also found the conversion is more for homogeneous catalysts as compared to heterogeneous catalysts at the same reaction conditions.

Yijunet al.[7]also studied the esterification reaction comparing the homogeneous and heterogeneous catalysis. They studied the reaction between acetic acid and methanol in the presence of catalysts H2SO4 and Nafion/Silica nano composite catalyst SAC-13. Reaction was carried out at 600C. The activity site of SAC-13 was comparable with that of H2SO4. The kinetic model developed using Eley-Rideal mechanism.

Guravet al.[10]studied the production of ethyl acetate from acetic acid and ethanol using heteropolyacid on montmorillonite K10. The heteropolyacid used is dodecatungestophosphoric acid (DTPA). The reaction condition was optimised by studying the different conditions influencing the reaction.

Lerkkasemsanet al. [17] reported the esterification of palmitic acid and methanol over sulphated zirconia (SO¬4/ZrO2) and activated acidic alumina (AcAl2O3) in a batch reactor. They also used the Eley-Rideal mechanism to develop the model. Thus the heterogeneous reaction gives the product easily and the product separation is easy.

4. ADVANTAGES AND DISADVANTAGES OF HOMOGENEOUS AND HETEROGENOUS CATALYSIS

Homogeneous catalysis has advantages like more efficiency and good conversion. It has also many disadvantages like final neutralization of homogeneous acid catalysts, occurrence of side reactions, corrosion problems, disposal of acid containing wastes and difficult separation of catalyst from mixture.

The advantages of heterogeneous catalysis include easy recovery, easy disposal of waste liquor, negligible corrosion problems, good product purity. The disadvantages include high expense, easy deactivation of catalyst, product adsorption on the catalyst surface, instability during reaction, to remove the adsorbed products a large amount of volatile organic solvents [15]. Both have merits and demerits. But demerits are more. So an alternative is found by using ionic liquid as catalyst for the esterification reaction.

5. ESTERIFICATION USING IONIC LIQUID AS CATALYST

Guiet al.[19] studied about the esterification reaction of ethanol with acetic acid in the presence of three new halogen free Bronsted acidic Ionic liquids; 1-(4-sulfonic acid)butyl-3-methylimidazolium hydrogensulfate, 1-(4-sulfonic acid)butyl pyridinium hydrogen sulphate and N-(4-sulfonic acid)butyl triethyl ammonium hydrogen sulphate. The results were highly convincing, the conversion and selectivity obtained was comparable with that obtained when sulphuric acid is used as the catalyst. They also found that the length of the alkyl chain do not affect the selectivity and conversion obtained, by conducting the experiment with deconoic acid, benzoic acid, etc. Also the ionic liquid could be reused after removal of water.

Huan Li et al. [16] discussed about one particular ionic liquid which forms the family of polyoxometalate-based ionic liquids (POM-IL). They synthesized, characterised and used this as catalyst for the esterification process between various alcohols and acetic. They found that the ionic liquid catalyst gives higher activity and yield.

Zhao et al. [22] performed experiments on the esterification of aliphatic acids with alcohols using series of Bronsted acidic ionic liquids as catalysts. The ionic liquid used included SO3H functionalised ionic liquids and non-functionalised ionic liquids. Out of these the functionalised ionic liquids showed high activity and good reusability even at low catalyst loadings. To determine the acidity of ionic liquids, Hammett method was used. The results showed that activity also increases with the acidity.

Ganeshpureet al. [23] studied about the reaction between acetic acid and 1-octanol using ionic liquids derived from alkylamines as catalysts. Almost 14 different ionic liquids were used. Som of these ionic liquids include [EtNH3][HSO4], [EtNH3][H2PO4], [Et3NH][HSO4], etc. This study results explained that the yield/conversion decreases with the increase in size of the cation and increase with increase in acidity of anion in the ionic liquid.
Wu et al. [20] investigated about the catalytic performance of acidic ionic liquid in the reaction between benzyl alcohol and butyric acid. The experiment was done by using four SO3¬H functionalised Bronsted acidic ionic liquids. Among these [HSO3-Pmim]HSO4 was used to do other studies that included the effect of various conditions like reaction time, initial reactant molar ratios, the amount of water carrying agent and the amount of ionic liquid. Box-Behnken experimental analysis showed that the amount of water carrying agent and the amount of ionic liquid are the main factor that affects the yield of Benzyl butyrate. And the optimal yield was 99.4%. Reusability was also checked. The catalyst could be reused five times with negligible reduction in activity.

Zhou et al. [21] studied about the higher activity of SO3H functionalised ionic liquids as compared to non-functionalised ionic liquids. When the SO3H functionalised ionic liquids were used as dual-solvent catalysts, the conversion was more than 90%. The reusability of the catalyst was also checked and found to be reused 7 times after vacuum drying.

Yong Liu et al. [24] showed that the equilibrium constant was increased to 27-34 when ionic liquid was used as the catalyst. High conversions have been obtained when ionic liquid is used as the catalyst as the water formed in the reaction is effectively solvated by the ionic liquid. When the ionic liquid used are in bulk quantities, the ionic liquid and water forms the lower phase and esters the upper phase. Thus, the product is conveniently separated from the catalyst. Use of ionic liquid also obviates need of volatile organic solvents generally used for azeotropic removal of water formed in the esterification. So other solvents need not be used.

6. CONCLUSION

The esterification reaction is an industrially important reaction. As the equilibrium constant of the reaction is very low, catalyst is used to carry out the reaction. The conventionally used catalysts are both heterogeneous and homogeneous catalysts. Both of them have advantages and disadvantages. But disadvantages are more as compared to advantages. Thus a ‘green catalyst’, ionic liquid is gaining much importance. From the above review, we can conclude that ionic liquid is an environment friendly alternative to the conventional catalysts.

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