CHEMICAL ENGINEERING TRANSACTIONS Volume 24, 2011
Editor Sauro Pierucci
 ISBN 978-88-95608-15-0 ISSN 1974-9791
DOI: 10.3303/CET1124018

Transesterification of Ethylacetate over $Na_2Si_2O_5$ Solid Catalyst

Zahira Yaakob[a], Silija Padikkaparambil[a], Narayanan Binitha[*b], Ramakrishnan Resmi[b], Viswanathan Suraja[a]

[a]Department of Chemical and Process Engineering, Faculty of Engineering, National University of Malaysia, 43600 UKM Bangi, Selangor, Malaysia

[b]Department of Chemistry, Sree Neelakanta Govt. Sanskrit College, Pattambi, Palakkad - 679306, India,
binithann@yahoo.co.in

In this era of green chemistry, solid base catalysts are well established in the field of biofuel research as the promising catalysts for transesterification reaction to produce biodiesel. Present study monitors the use of $Na_2Si_2O_5$ catalyst, which is proved to be effective in biodiesel production, for the transesterification of low molecular weight esters like ethylacetate. The catalyst is prepared using sol gel method. Reaction is done with a number of alcohols and the reaction parameters are optimized to get better yield. Solid catalyst, $Na_2Si_2O_5$, provides an opportunity for carrying out reactions under mild conditions leading to better quality products suitable in fragrance and flavor industry.

1. Introduction

Organic esters are used in a variety of industries such as perfumery, flavor, pharmaceuticals etc. Esters are one of the most important natural fragrances. The traditional extraction from plant materials and direct biosynthesis by fermentation is not economical as well as results in low yield of desired esters and, therefore, better processing methods need to be developed. Most of the protic acid catalysts are highly corrosive and are not ecofriendly. Several better alternatives can be found in current reports. Recently, (Heravi et al. 2009) found out a method for the selective acetylation of alcohols in the presence of amines and phenols using $KHSO_4$ catalyst. (Zhang et al. 2005) carried out the esterification of acetic acid with ethanol in the presence of ionic liquid 1-butyl-3-methylimidazolium hydrogen sulphate ([bmim][HSO_4]) and scCO_2. (Oliveira et al. 2009) studied the synthesis of decyl acetate, by the transesterification of vinyl acetate with decanol, using supercritical CO_2 as solvent and immobilized *Candida antarctica* lipase B as catalyst (NovozymR 435). Lipases (triacylglycerol hydrolases enzymes) are capable of catalyzing hydrolysis reactions of esters as well as their synthesis and transesterification (Radzi et al. 2005). But biocatalysts can catalyze reactions only in organic solvents (Yang et al. 2003, Romero et al. 2005), supercritical fluids (SCFs) (Reetz et al. 2002, Nagesha et al. 2004, Lozano et al. 2003), or in ionic liquids (ILs) (Kim et al. 2001, Kaar et al. 2003). Use of homogeneous base catalysts involves the series of environmental problems related to the use of high consumption of

Please cite this article as: Yaakob Z., Padikkaparambil S., Binitha N., Resmi R. and Suraja V., 2011, Transesterification of ethylacetate over na2si2o5 solid catalyst, Chemical Engineering Transactions, 24, 103-108
DOI: 10.3303/CET1124018

energy. Also neutralization and separation of the catalyst from the reaction mixture is a tedious process. Since Green chemistry is becoming increasingly relevant in this heavily polluted world, we have to think about an eco-friendly catalytic technique. There is an increasing focus on transesterification using heterogeneous catalyst under mild conditions among researchers in this field.

From the standpoint of environmentally benign organic synthesis, development of novel heterogeneous catalysts is challenging and important. In an ideal system, they can be recovered from the reaction mixture by simple filtration and re-used infinitely, without any contamination of products by catalyst. Even though numerous methods of transesterification have been reported in the literature with improved procedures, there is still a constant need to discover and apply new protocols, which require mild conditions.

The aim of our work is to obtain a number of esters by transesterification of ethylacetate following a simple synthetic procedure. We have reported $Na_2Si_2O_5$ as an outstanding catalyst for transesterification of Jatropha oil (Emil et al. 2009). In the present work, the above catalyst is used as for transesterification of Ethylacetate. The catalyst was prepared by using sol-gel method. Esters are produced under mild conditions. The reaction parameters are also optimized to get better yields.

2. Experimental

2.1 Catalyst preparation

The catalyst is prepared adopting the reported procedure from our lab (Emil et al. 2009). The details of preparation are as follows. NaOH (Merck) is added to a mixture of 40 ml ethanol (Merck) and 40 ml distilled water in order to get a 50:50 ratio of Na: Si. To this 20g pluronic P123 (Sigma Aldrich) is also added and mixed thoroughly for 1 h. 20 g Tetraethylorthosilicate (Aldrich) is introduced to the above mixture drop wise and is again mixed for 1 h. The transparent sol obtained is then dried at 80˚C for 48 h. Calcination is done at 600˚C for 6 h. It is also found that the catalyst has a $Na_2Si_2O_5$ structure with more of δ-$Na_2Si_2O_5$. Small amounts of α, β and γ forms of $Na_2Si_2O_5$ are also found to be present.

2.2 Catalytic activity

The typical reaction procedure for the transesterification of ethylacetate using methanol is as follows. 0.02 mol ethylacetate is refluxed with the catalyst and methanol for 30min. After the reaction, the mixture is cooled by ice water, separated from the solid catalyst by filtration and analysed using Agilent HEWLETT PACKARD 5890 Gas chromatograph equipped with Equity-1 capillary column and Flame ionization detector. The reaction parameters such as catalyst loading, reactant molar ratio and time are varied to optimize the conditions. Then the same optimum condition is also selected for the trasesterification using other alcohols. The temperature selected for all the reactions is 65˚C.

3. Results and Discussion

Transesterification reaction of ethylacetate and methanol at 65°C was conducted to study the catalytic activity of $Na_2Si_2O_5$ towards lower esters. Influence of variation of the reaction parameters such as catalyst weight, alcohol volume and reaction time on the conversion of ethylacetate is investigated in detail. The reaction is also done using other alcohols such as butanol and isopropanol.

3.1 Effect of catalyst concentration on catalytic activity of methylation of ethylacetate

Amount of catalyst is crucial in the determination of catalytic activity over heterogeneous systems. Figure 1 shows the effect of catalyst concentration on the catalytic activity for methylation of ethyl acetate. It can be seen that the catalytic activity increases as the catalyst concentration is increased, and reaches a maximum at 0.3 g catalyst. However, the activity is found to remain almost constant beyond 0.3 g catalyst. This behavior of the catalyst can be attributed to the reason that adsorption of substrates on the catalyst could reach a balance when 0.3 g catalyst was used, so that more quantity of catalyst did not affect the reaction anymore.

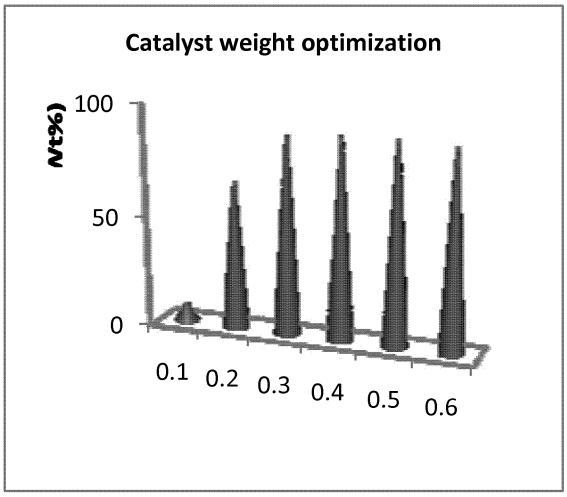

Figure 1: Effect of catalyst weight on the methylation of 0.02 mol ethylacetate with 10 ml methanol for 30 min

3.2 Effect of Volume of Methanol

In order to assess the influence of the initial concentration of substrates on the catalytic activity, the quantity of ethyl acetate was kept constant as 0.02 mol and that of methanol was varied from 5 to 20 ml. The temperature and time were kept constant in this set of experiments. It was found that with an increase in amount of methanol from 5 to 10 ml, the rate of reaction was found to increase and beyond that, there was no perceptible increase in the rate was observed. From the results shown in Figure 2, it is clear that the optimum volume of methanol can be fixed as 10 ml.

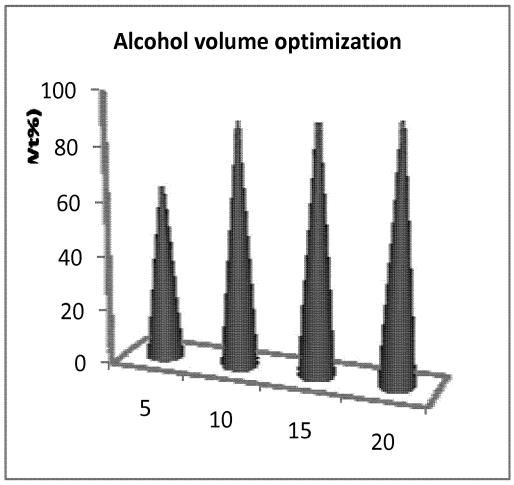

Figure 2: Effect of volume of methanol on the methylation of 0.02 mol ethylacetate with 0.3g catalyst for 30 min

3.3 Catalytic Activity under Optimum Conditions

The reaction is also done using other alcohols in the selected optimum conditions. The alcohols used for transesterification includes n-propanol, isopropanol, n-butanol and t-butanol. The results obtained are summarized in Table 1. The catalyst show good activity for transesterifiation even at a lower temperature of 65˚C. Among the different alcohols tried, methanol yielded the best % conversion of ethylacetate which may be due to the reason that the reaction temperature selected was the reflux temperature of methanol. The transesterification of ethyl acetate with methanol over magnesium oxide as solid base catalyst was investigated (Tanguy et.al, 2005) and it is found that the system shows a conversion of about 70% under optimum conditions. Thus present catalyst system is found to be a good heterogeneous catalyst for methylation of ethylacetate.

Table 1: Conversion of Ethyl acetate with various alcohols under optimum conditions

Alcohol	Ethylacetate Conversion (Wt %)
Methanol	90.24
n-Butanol	74.45
t-butanol	61.65
Propanol	26.61
Isopropanol	51.26

4. Conclusions

The heterogeneous catalyst $Na_2Si_2O_5$ is successfully used for the transesterification of ethylacetate. The activity of the catalyst for transesterification of ethylacetate is tested with a number of alcohols. The activity of the catalyst is tuned by changing the reaction conditions. Among the different alcohols selected, methanol showed best conversion. The present procedure provides a new possibility of synthesizing mono-transesterification products in sufficiently moderate yields.

Acknowledgement

The authors acknowledge UKM, the grant number UKM-GUP-BTT- 07-30-191 for the financial support.

References

Emil A., Binitha N.N., Zahira Y., Kamarudin S.K. and Salimon J., 2009, Preparation of Na doped SiO_2 solid catalysts by the sol-gel method for the production of biodiesel from jatropha oil, Green Chemistry 1, 1862-1866.

Heravi M.M., Bakhtiari K. and Saeedi M., 2009, Selective transesterification of alcohols in the presesnce of amines and phenols catalyzed by $KHSO_4$, Iranian Journal of Organic Chemisthry 2, 84-86.

Kaar J.L., Jesionowski A.M., Berberich J.A, Moulton R. and Russell A.J., 2003, Impact of ionic liquid physical properties on lipase activity and stability, Journal of the American Chemical Society 125, 4125-4131.

Kim K.W., Song B., Choi M.Y. and Kim M.J., 2001, Biocatalysis in ionic liquids: Markedly enhanced enantioselectivity of lipase, Organic Letters 3, 1507-1509.

Lozano P., Diego T., Carri´e D., Vaultier M. and Iborra J.L., 2003, Enzymatic ester synthesis in ionic liquids, Journal of Molecular Catalysis B: Enzymatic 21, 9-13.

Nagesha G.K., Manohar B. and Sankar K.U., 2004, Enzymatic esterification of free fatty acids of hydrolyzed soy deodorizer distillate in supercritical carbon dioxide, Journal of Supercritical Fluids 32, 137-145.

Oliveira V.M., Rebocho S.F., Ribeiro A.S., Macedo E.A. and Loureiro J.M., 2009, Kinetic modelling of decyl acetate synthesis by immobilized lipase-catalysed transesterification of vinyl acetate with decanol in supercritical carbon dioxide, Jouranal of Supercritical Fluids 50, 138-145.

Radzi S.M., Basri M., Salleh A.B., Ariff A., Mohammad R., Rahman M.B.A. and Rahman RNZRA., 2005, High performance enzymatic synthesis of oleyl oleate using immobilized lipase from Candida antartica, Electronic Journal of Biotechnology 8, 1-13.

Reetz M.T., Wiesenhofer W., Francio G. and Leitner W., 2002, Biocatalysis in IL: batch wise and continous flow processes using supercritical carbon dioxide as the mobile phase, Chemical Communications 9, 992-993.

Romero M.D., Calvo L., Alba C., Habulin M., Primosie M. and Knez Z., 2005, Enzymatic synthesis of isoamyl acetate with immobilized Candida antarctica lipase in supercritical carbon dioxide, Journal of Supercritical Fluids 33, 77-84.

Tanguy F.D., Marie F.R. and Guy B.M., 2006, Kinetics of heterogeneously MgO catalyzed transesterification, Applied Catalysis B: Environmental 61, 35-45.

Yang Y.C., Vali S.R. and Ju Y.H., 2003, A process for synthesizing high purity monoglyceride, Journal of the Chinese Institute of Chemical Engineers 34, 617-623.

Zhang Z., Wu W., Han B., Jiang T., Wang B. and Liu Z., 2005, Phase separation of the reaction system induced by CO_2 and conversion enhancement for the esterication of acetic acid with ethanol in ionic liquid, Journal of Physical Chemistry B 109, 16176-16179.