Asian Journal of Chemistry; Vol. 26, No. 22 (2014), 7776-7778

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2014.17797

A Novel ZnF_2-Catalyzed Esterification of Oleic Acid

PINGPING NIU, WEIHAO ZHAO, GUOFANG JIANG* and CANCHENG GUO

College of Chemistry and Chemical Engineering, Hunan University, Changsha 410082, P.R. China

*Corresponding author: E-mail: gfjiang@hnu.edu.cn

Received: 11 April 2014; *Accepted*: 22 June 2014; *Published online*: 6 November 2014; AJC-16233

Esterification reactions of oleic acid with alcohols have been performed by using zinc fluoride as catalyst. High conversion and good yields were obtained. In this study, the influence of various reaction parameters such as reaction time, catalyst loading and mole ratio of starting materials were investigated. With a mole ratio of oleic acid to glycerol of 3.4, 15 wt % zinc fluoride added and the reaction were completed smoothly at 170 °C for 8 h with good yield of 81.9 % and the esterification rate reached 97.5 %. The ester was easily separated from the reaction mixture and the zinc fluoride used could be recycled and reused at least five times without obvious loss of catalytic efficiency.

Keywords: Zinc fluoride, Catalyst, Esterification, Reusable.

INTRODUCTION

Esters are an important class of organic compounds widely used in both organic synthesis and in our daily life, such as plasticizes, perfumes, flavor chemicals and cosmetic[1]. The most direct and convenient way for the preparation of esters is esterification of carboxylic acid with alcohols[2]. These esterification reactions are usually carried out by using homogeneous acid[3] such as sulfuric acid, *p*-toluene sulphonic acid, orthophosphoric acid or hydrogen chloride as catalyst[4-8]. However, it is well known that these traditional acids suffer from the problems of corrosiveness, environmental hazards, difficulty in catalyst separating and recycling and high susceptibility to water. Moreover, these homogeneous acids need to be neutralized with large volumes of base after completion of the reaction which is not environmentally friendly.

To overcome these shortcomings, many different catalysts such as zeolites[9,10,15], ion-exchanged resin[11-13], heteropoly acids[14-16], molecular sieves[17-19] and others have been developed for esterification reactions. For example, Ferreira *et al.*[15] studied the esterification of glycerol with acetic acid with dodecamolybdophosphoric acid encaged in the USY zeolite as catalysts. The results showed that the catalytic activity increased with the amount of heteropolyacid immobilized in the USY. However, a decrease was observed at high amount of the dodecamolybdophosphoric acid encaged in the USY zeolite. Jiang *et al.*[20] employed sulfonated cation exchange resin as catalysts for oleic acid esterification. The results show the oleic acid conversion rate reached approximately 93 % at 82 °C for 8 h. Balaraju *et al.*[16] studied the acetylation of glycerol with niobic acid supported tungstophosphoric acid as catalyst, It was observed that the glycerol conversion and selectivities depend on the acidity of the catalysts, which in turn is related to the content of tungstophosphoric acid on niobic acid. To the best of our knowledge, there is no report about the zinc fluoride used as catalyst for the esterification reactions.

In this paper, zinc fluoride was identified as a highly efficient catalyst for the synthesis of oleate. High conversion rate and good yields were obtained. The influence of various reaction parameters such as reaction time, catalyst loading and mole ratio of starting materials were investigated. As zinc fluoride and ester remain in different phases after the reaction making the recycling of catalyst very facile. The stability and reuse performance were tested. For comparison, the performance of *p*-toluene sulphonic acid was also examined.

EXPERIMENTAL

For the reaction, the acid was oleic acid and the alcohols were glycerol, pentaerythritol, diethylene glycol, triethylene glycol or trimethylolpropane. All the chemical reagents were used as received. The infrared (IR) spectra were recorded on FTIR650 spectrometer using KBr plates in a frequency range 4000-500 cm^{-1}. ^1H NMR spectra were recorded on BRUKER-400 instrument with tetramethylsilane (TMS) as reference. The conversion of oleic acid into ester was calculated by measuring the acid number of the product and the yield of ester was based on silica gel chromatogram.The acid number (the mass of KOH in milligrams that is required to neutralize one gram of chemical substance) was determined by titration using phenolphthalein as the indicator.

$$\text{Conversion } (\%) = [(a_1 - a_2) \times 100]/a_1$$

Note: "a_1" is the acid number of oleic acid and "a_2" is the acid number of the crude reaction mixture.

Typical esterification procedure: Oleic acid (0.045 mol), glycerol (0.015 mol) and zinc fluoride (2.114 g) were added to a round bottom flask with toluene (15 mL). The flask was fitted with reflux condenser and at the top of the condenser a nitrogen balloon was fitted to maintain the inert atmosphere. The reaction mixture was vigorously stirred at 170 °C for 8 h in oil bath. After the completion of the reaction, the reaction mixture was filtrated. The filtrate was concentrated under reduced pressure to get a crude product and the catalyst zinc fluoride can be reused after decompress filtration.

RESULTS AND DISCUSSION

Esterification of oleic acid with glycerol: In our studies, the esterification of oleic acid with glycerol was chosen as the model reaction to optimize the reaction parameters such as reaction time, mole ratio of starting materials and catalyst loading. The results are outlined in Table-1.

TABLE-1
ESTERIFICATION OF OLEIC ACID WITH GLYCEROL IN DIFFERENT CONDITION

Entry	Time (h)	Mole ratio	Catalyst usage	Conversion (%)	Yield (%)
1	4	3	15	96.9	70.1
2	8	3	15	97.5	77.9
3	10	3	15	97.3	77.0
4	8	3	5	95.0	64.2
5	8	3	20	97.5	76.5
6	8	3.2	15	97.3	77.9
7	8	3.4	15	97.1	81.9
8	8	4	15	96.0	75.5
9	8	3	10	95.6	67.6
10	8	3	0	60.9	12.2

Reaction condition: temperature =170 °C; the catalyst usage = the total quantity of acid and alcohol %. Mole ratio =oleic acid to alcohol. Yield is based on isolated yield

It is reasonable that better results are obtained when the reaction time is prolonged appropriately. The effect of mole ratio on the esterification was studied. The results indicate that the yield was enhanced while increasing the oleic acid because the excess of one of the reactants makes the equilibrium of the esterification shifting toward the reaction products. However, the results showed a decrease when the mole ratio rising to 4:1 may due to the decrease in the concentration of the catalyst. The reaction were conducted with different catalyst loading which range from 5-20 % (total quantity of acid and alcohol) with 3:1 (oleic acid: glycerol) mole ratio for 8 h. The yield of target product glycerol trioleate increased with the increase in amount of the catalyst. 97.5 % conversion of oleic was achieved when 15 wt % catalyst was used. Further increase of the catalysts even offers a slight decrease in yield. Evidently 15 wt % catalyst is enough to catalyze the esterification of oleic acid with glycerol efficiently. Additionally, blank experiment under the same condition manifested that the application of zinc fluoride could effectively promote the reaction.

Esterification of alcohols catalyzed by zinc fluoride: To evaluate the scope of zinc fluoride as catalyst for esterification, other alcohols were used for the reaction with oleic acid. The optimal results were presented in Table-2. Solid alcohols such as pentaerythritol and trimethylolpropane showed a slight decrease in yield compared with other liquid alcohols. Contact experiments were also carried out without ZnF_2, affording the corresponding products in very low yields albeit the conversions were moderate in some cases indicating the high efficiency of ZnF_2 in these reactions.

TABLE 2
RESULTS OF ESTERIFICATION FOR OLEIC ACID AND DIFFERENT ALCOHOL WITH ZnF_2 AS CATALYST

Entry	Alcohol	Mole ratio	Conversion (%)		Yield (%)	
			Blank	ZnF_2	Blank	ZnF_2
1	Glycerol	3.4	60.9 (3/1)	97.1	12.2	81.9
2	Pentaerythritol	5.0	34.3 (4/1)	96.6	1.2	71.4
3	Diethylene glycol	2.6	71.6 (2/1)	90.1	7.9	76.0
4	Triethylene glycol	2.5	72.8 (2/1)	89.7	5.9	72.8
5	Trimethylolpropane	3.6	56.1 (3/1)	92.1	2.6	69.5

Reaction condition: Catalyst usage = 15wt % of total quantity of acid and alcohol. Temperature =170 °C, 8 h

Esterification catalyzed by zinc fluoride and *p*-toluene sulphonic acid: For comparison, some esterification reactions of oleic acid with alcohols were carried out under otherwise identical conditions with zinc fluoride and *p*-toluene sulphonic acid as catalyst, respectively (Table-3). It has been sowed that the catalytic performance of zinc fluoride could be better than that of the *p*-toluene sulphonic acid under otherwise same conditions. Moreover, with *p*-toluene sulphonic acid as catalyst, more byproducts were found in the reaction and the product also gives a darker color.

TABLE-3
ESTERIFICATION CATALYZED BY *p*-TOLUENE SULPHONIC ACID AND ZINC FLUORIDE

Entry	Alcohol	Mole ratio	Conversion (p) %	Conversion (F) %	Yield (p) %	Yield (F) %
1	Glycerol	3/1	94.2	95.6	28.0	67.6
2	Pentaerythritol	4/1	95.4	94.2	41.9	50.5
3	Diethylene glycol	2/1	95.3	93.5	18.7	62.9
4	Triethylene glycol	2/1	94.6	94.7	24.6	62.9
5	Trimethylopropane	3/1	93.8	92.8	39.7	53.9

The catalyst usage = 10 wt % of total quantity of acid and alcohol. Reaction time 8 h, mole ratio: oleic acid to alcohol, reaction temperature = 170 °C. Conversion (p) % = catalyzed by *p*-toluene sulphonic, conversion (F) % = catalyzed by zinc fluoride

Recycling of zinc fluoride: As a novel catalyst, the regeneration is an important parameter in application. To investigate the possibility of recyclability and reusability of the zinc fluoride, a series of recycle experiments were conducted. Table-4 shows that zinc fluoride recycled can be reused at least five times in the esterification of oleic acid with glycerol without noticeable loss of activity, which indicates that as the catalyst for esterification, zinc fluoride has excellent reusability and stability.

TABLE-4
CATALYST RECYCLING OF GLYCEROL ESTERIFICATION

Cycle	Conversion (%)	Yield (%)
1	97.4	75.5
2	96.6	74.8
3	97.3	76.8
4	96.0	72.8
5	96.5	74.2

Mole ratio of acid to alcohol = 3:1, the catalyst usage = 15 wt % of total quantity of acid and alcohol. Reaction time 8 h, reaction temperature 170 °C

Conclusions

Esterification of oleic acid with alcohols using easily available zinc fluoride as catalyst showed good results. From the studies, the features of zinc fluoride as catalyst for esterification can be concluded as follows:

• It showed excellent catalytic activity with high conversion and good yield.

• In this reaction, the catalyst and ester remain in different phases after the reaction making the ester can be separated from the catalyst easily.

• Zinc fluoride used could be recycled easily and reused without obvious loss of the catalytic activity.

ACKNOWLEDGEMENTS

This work was financially supported by the NSF of China (J1210040).

REFERENCES

1. P.W. Greene and P.G.M. Wuts, Protective Groups in Organic Chemistry, Wiley, New York, Chap. 5 (1999).
2. O.J. Esterification, WILEY-VCH Verlag GmbH &Co KGaA, Weinheim (2003).
3. S.R. Sandler and W. Karo, In: Organic Functional Group Preparations, Organic Chemistry, Academic Press, New York, Vol. 12, Chap. 10 (1968).
4. P. Mäki-Arvela, T. Salmi, M. Sundell, K. Ekman, R. Peltonen and J. Lehtonen, *Appl. Catal. A*, **184**, 25 (1999).
5. J.S. Wilkes, *J. Mol. Catal. Chem*., **214**, 11 (2004).
6. Esso Research and Engineering Co, German Patent, 007,757 (1957).
7. K. Nagasawa, K. Ohhashi, A. Yamashita and K. Ito, *Chem. Lett*., 209 (1994).
8. M.A. Schwegler, H. Van Bekkum and N.A. De Munck, *Appl. Catal*., **74**, 191 (1999).
9. L.N. Silva, V.L.C. Goncalves and C.J.A. Mota, *Catal. Commun*., **11**, 1036 (2010).
10. V.L.C. Goncalves, B.P. Pinto, J.C. Silva and C.J.A. Mota, *Catal. Today*, **133-135**, 673 (2008).
11. G. Sartori and R. Maggi, *Chem. Rev*., **106**, 1077 (2006).
12. A. Heidekum, M.A. Harmer and W.F. Hoelderich, *J. Catal*., **181**, 217 (1999).
13. M. Gruffaz and O. Micaelli, USP 4275228 (1981).
14. P. Ferreira, I.M. Fonseca, A.M. Ramos, J. Vital and J.E. Castanheiro, *Appl. Catal. B*, **91**, 416 (2009).
15. P. Ferreira, I.M. Fonseca, A.M. Ramos, J. Vital and J.E. *Castanheiro*, *Catal. Commun*., **10**, 481 (2009).
16. M. Balaraju, P. Nikhitha, K. Jagadeeswaraiah, K. Srilatha, P.S. Sai Prasad and N. Lingaiah, *Fuel Process. Technol*., **91**, 249 (2010).
17. B.R. Jermy and A. Pandurangan, *J. Mol. Catal. Chem*., **237**, 146 (2005).
18. H.Q. Yang, H.Y. Song, H. Zhang, P. Chen and Z.X. Zhao, *J. Mol. Catal. Chem*., **381**, 54 (2014).
19. R.A. Sheldon and R.S. Downing, *Appl. Catal. A Gen*., **189**, 163 (1999).
20. Y.W. Jiang, J.Lu, K.A. Sun, L.L. Ma and J.C. Ding, *Energy Convers. Manage*., **76**, 980 (2013).