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$Fe_2(SO_4)_3 \cdot 4H_2O$/concentrated H_2SO_4: an efficient catalyst for esterification

Yong-min Liang[a,b], Qi-hai Xu[a], Xiao-li Wu[a] and Yong-xiang Ma[a]*

[a]*State Key Laboratory of Applied Organic Chemistry, Lanzhou University,Lanzhou 730000, P. R. China*

[b]*Laboratory of Solid Lubrication, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, P. R. China.*

The mixed catalyst system, $Fe_2(SO_4)_3 \cdot 4H_2O$ / concentrated H_2SO_4 has been applied to catalyse effectively the esterification of α,β-unsaturated acids, aliphatic acids and heterocyclic aromatic acids with ethanol and methanol.

Keywords: esterification, $Fe_2(SO_4)_3 \bullet 4H_2O/H_2SO_4$catalyst, carboxylic acid

Esterification is an important reaction in organic synthesis and industrial chemistry. Many investigators have worked to optimise the yields of ester formation. Various compounds, such as sulfuric acid, tosyl chloride,[1] trifluoroacetic anhydride,[2] polyphosphate ester,[3] dicyclohexylcarbodiimide,[4] and graphite bisulfate[5] have been used as catalysts in esterification. In recent years, esterification using aqueous ferric sulfate as catalyst has been reported.[6] For all of these compounds, a large quantity of catalyst is generally needed for completion of the esterification reaction. Furthermore, there are other disadvantages in using those catalysts, such as long reaction times, low yields, expensive reagents and tedious work-up procedures.

In the present work, we report the esterification of α,β-unsaturated acids, aliphatic acids and heterocyclic aromatic acids with ethanol and methanol using a mixed catalyst, $Fe_2(SO_4)_3 \cdot 4H_2O$ / concentrated H_2SO_4. This catalytic process has an efficient catalytic ability and gives excellent esterification yields in short reaction times.

$$R^1COOH + R^2OH \xrightarrow[\text{refluxing}]{\text{Cat.}} R^1COOR^2 + H_2O$$

The esterification results using this mixture as catalyst are shown in Table 1. This process was carried out as follows and gave a series of esters *via* the reaction of organic acids with methanol or ethanol.

In Table 2, we list the esterification results of 4 acids with methanol or ethanol using the mixed catalyst, $Fe_2(SO_4)_3 \cdot 4H_2O$ / concentrated H_2SO_4(molar ratio=2:1), which are compared with the corresponding processes using $Fe_2(SO_4)_3 \cdot 4H_2O$ or concentrated H_2SO_4 as esterification catalysts alone under otherwise identical conditions.

It can be seen from Table 2 that the mixed catalyst system is a more efficient esterification catalyst than H_2SO_4 or $Fe_2(SO_4)_3 \cdot 4H_2O$ alone. In particular the esterification yields were improved greatly for inert and hindered acids, such as 2-thiophenic acid and 1-naphthylacetic acid. The yields of methyl 2-thiophenate are 19, 71 and 95% using H_2SO_4, $Fe_2(SO_4)_3 \cdot 4H_2O$ and $Fe_2(SO_4)_3 \cdot 4H_2O/H_2SO_4$ as catalyst, respectively. All esterification products were characterised by GC retention times agreed with those of standard samples, boiling point and NMR spectra. The data were found to be in agreement with the literature values.

Table 1 The esterification of various acids with methanol and ethanol

Entry	R^1	R^2	Reaction time/h	Yield/%	B.p./°C/mmHg	
					Found	Lit.[7]
1	$CH_2{=}CH–$	Et	3	98	95(634)	100
2	$CH_2{=}CH–$	Me	3	99	76(634)	80.3
3	1-Naphthyl	Et	1.5	97	209(633)	220.5(741)
4	$PhCH_2–$	Et	3.5	98	213(633)	226
5	1-Naphthylmethylene	Et	3.5	86	231(32)	220-225(20)
6	Cyclohexylpropanylene	Me	5	97	132(34)	124(24)
7	$ClCH_2–$	Me	1	94	124(633)	129.8
8	Cl_3C-	Me	3	98	146(634)	153.8
9	$HOCH(CH_3)–$	Me	3	97	75(35)	58(19)
10	2-Furfurl	Et	1	89	122(633)	195;128(95)
11	2-Furfurl	Me	1	87	172(633)	181
12	2-Thienyl	Et	1	86	105(33)	96(18)

Table 2 Esterification using different catalysts under reflex.

Acid	Alchohol	Ester	React. time/h	Catalyst	Yield/%	B.p./°C(mmHg)	
						Found	Lit.[7]
Propanoic acid	Ethanol	Ethyl propanoate	2	A	92	94/634	99.1
				B	94		
				C	96		
Phenylacetic acid	Methanol	Methyl phenylacetate	3.5	A	91	204(634)	215
				B	58		
				C	96		
1-Naphthylacetic acid	Methanol	Methyl 1-naphthyl- acetate	1.5	A	82	167(35)	162-165(11)
				B	95		
				C	98		
2-Thiophenic acid	Methanol	Methyl 2-thiophenate	1	A	19	55(35)	40(0.5)
				B	71		
				C	95		

A: $Fe_2(SO_4)_3 \cdot 4H_2O$ (2% of the acid weight), B: 1μl concentrated H_2SO_4, C: the mixture of A and B.

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* Correspondence. E-mail: mayx@lzu,edu.cn

It is shown from the data in Table 1 that this mixed catalyst is suitable for esterification of various types of acid and gives the esters in high yield compared with those methods previously in the literature. For example, Vogel carried out the esterification of chloroacetic acid with absolute methanol in the presence of concentrated H_2SO_4, refluxing for 7 hours, to obtain merely 36% yield of ester.[8] Downie *et al.* reported the esterification of trichloroacetic acid through diethyl trichloromethylphosphonate kept for a day at 120 °C, but only obtained a 77% yield of the ester.[9] Esterification of furoic acid with ethanol in presence of thionyl chloride had also been reported,[10] but the operation is complicated and the thionyl chloride is toxic and acrid.

Experimental

All reagents, such as organic acids, alcohols, $Fe_2(SO_4)_3{\cdot}4H_2O$ and sulfuric acid are analytical grade from a commercial source and used directly. The mixed catalyst is prepared by direct mixing according to a molar ratio of $Fe_2(SO_4)_3{\cdot}4H_2O$: concentrated H_2SO_4 = 1:1. The GC was performed on a Shimadzu GC-9AM spectrometer equipped with flame ionisation detection (FID). The separations were performed using a 50m×0.2 mm I.D. HP-5 column with a 0.33µm film thickness of 5% diphenyl 95% dimethyl polysiloxane as stationary phase and pure argon as carrier gas (a flow of 40ml/min). Other operating conditions were changed with the substrates.[11] ^1H NMR spectra were determined in $CDCl_3$ on a FC-80A spectrometer with TMS as internal standard.

General procedure for the esterification and determination
1mmol organic acid (72-162 mg), 5ml methanol or anhydrous ethanol, 0.3% mmol of $Fe_2(SO_4)_3{\cdot}4H_2O$/ H_2SO_4 (1.7 mg) were mixed and placed in a flask with a condenser, and heated in an oil bath at reflux. After the required time as shown in the table, the free alcohol was removed by distillation, the reaction mixture was cooled to room temperature, 10ml water was added and the mixture was extracted with diethyl ether (3×10ml). The extract was washed with sodium carbonate solution (1%) and then with water until the ester was neutral to litmus. The ether layer was dried over sodium sulfate overnight and filtered. The filtrate was evaporated under reduced pressure to leave the ester.

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