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A STUDY ON SYNTHESIS OF ESTERS BY SUPERACID RESIN CATALYSTS

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Abstract: Superacid resin as catalyst, instead of the strong acid cation exchange resin and sulfuric acid was used to synthesis n - butyl lactate. Some factors affection reaction, such as time, moles ratio of reactants and catalyst amount were studied. Result made known that time was shorten very much. Under our optimum conditions the ester yield was over 99.5%. In the other hand, superacid resin as catalyst was used to synthesis other esters, had result of raise ester yield and shorten the time of esterification.

Most of the lower carboxylic esters are aromatic and used as raw material for making perfume, solvent and organic synthetics. There are methods of synthesizing carboxylic acid ester and the most popular one is direct esterification of alcohol and carboxylic acid under the catalysis of concentrated sulfuric acid. However, when concentrated sulfuric acid is used as catalyst, problems like side reactions, dark colour of product, low ester yield serious corrosion to equipment and discharge of environmentally polluting waste acids, etc. will unavoidably accompany. Hence the searching for substitutes for esterification catalysts becomes the hot point of direct esterification development. In recent years, the use of strong acidic

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cation exchange resin of sulfonated crosslinked polystyrent type as esterification catalyst to replace sulfuric acid has been tried¹, but the catalysis is not good enough due to long esterification time and low ester yield.

The development of solid superacids adds to the catalyst family a high performance one, a super acid is of 10^4 times stronger in acidity than 100%concentrated sulfuric acid. With its super strong acidity and great high activity, it activates so many reactions which were previously not easy to be made, so it is of important significance in resources exploitation, energy saving, etc^{2-4} . Among solid superacid, the one reported in this paper is super acid resin $DOO1 - A1C1_3$ with sulfonated crosslinded polygstyrene type strong acidic macroporous cation exchange resin as polymer - support, and with which as catalyst, a series of carboxylic esters were successfully synthesized. The method of this superacid resins synthesis and its use on alkyl isomerication and cracking, had once been reported⁵. But thereafter no attention was given by people due to its limited use . Nevertheless, we have made research again into the synthetic process of this catalyst to improve its catalyzing activity and make it usable in esterification catalysis by use of solvent rather than gaseous phase method. Experimental results indicate that catalysis effect of the superacid resin is far better than that of macroporous strong acidic cation exchange resin, thus it is possible to notably shorten the time of esterification and raise ester yield while at the same time the corrosion to equipment and polluton to environment abate. DOO1 - A1C1₃ resin has synthesis.

I. Experiment

1. Preparation of DOO1-A1C1₃ superacid resin catalyst

DOO1 is the Chinese code for sulfonated crosslinked polystyrene type macroporous strong acidic cation exchange resin. The resin used in this experiment is the product of Sian Electric Resin Factory, China. Before preparation, the DOO1 resin was transformed into H type by use of inorganic acid, washed with deionized water and finally dried in vacuum for 24 horus to make it ready for use.

SYNTHESIS OF ESTERS

20 g of fully dried DOO1 resin, 5 g of freshly sublimed anhydrous AlCl₃, 30 ml of anhydrous ethyl alcohol and 5 ml of carbon sulfide of class A. R. were put into a triport flask, mixed well, and the mixture was heated to a state under which it circulated and was maintained in such circulation for 5 hours. Afterwards the mixture cooled down, the resin was filtered out and washed with deionized water in a mode of vigorous stirring to remove the surplus AlCl₃ through hydrolysis. After this the resin was again washed consecutively with deionized water, acetone, ether, isopropyl alcohol and ether. The resin was drided at 60° C in a vacuum dryer and then put in a P₂O₅ dryer for storage.

Aluminium content in the resin was determined at 3. 80% and it was found that ΛICl_3 was complexed to the resin with a complexed quantity of 70% of theoretic value.

2. Operation of esterification reaction

Alcohol, carboxylic acid and catalyst were put at a preset ratio in a triport flask. The mixture of the two was heated to boiling circulation while at the same time a separator was used to remove water therefrom. From time to time samples were taken to check the ester yield by means of gas chromatography for plotting time — yield curve and determining the end of reaction. After reaction, the catalyst was recollected through filtration for use next time, and the ester was separated from the filtered liquid by a separating funnel. Then, the crude ester so obtained was neutralized with 5%Na₂CO₃ to a pH value of 7, and washed two to three times with lukewarm saturated salt water and twice times with saturated CaCl₂ solution. Finally, it was dried with anhydrous MgSO₄, and then subjected to fractional distillation. The distillation cuts were collected according on the boiling points of the esters for test and ascertaining by IR optical spectra and 'HNMR spectra.

I. Results and discussion

 Experimental results of esterification conditions for lactic acid and n -- butanol

1) Optimzation experiment result of lactic acid butanol ratio and quantity of catalyst

No.	acid/butanol (moL/moL)	catalyst(g)	tempture(°C)	time(h)	yield(%)
1	0.108/0.350	1. 45	116118	2.5	96
2	0. 108/0. 400	1. 45	116118	2.5	98
3	0. 108/0. 493	1. 45	116118	2.5	99. 5
1	0. 108/0. 600	1. 15	116118	2.5	98
5	0. 108/0. 650	1. 45	116118	2. 5	97
6	0. 108/0. 193	1.00	116118	2.5	81
7	0. 108/0. 493	1. 25	116118	2.5	92
8	0. 108/0. 493	1.65	116118	2.5	99
9	0. 108/0. 493	1.85	116118	2. 5	99

Table I the result of optimization experiment

As shown in Table 1. the ratio and catalyst quantity for experiment No. 3 is the best material ratio.

2)Influence of time duration of esterification reaction on ester yield 1. 45g of DOO1 – A1Cl₃ catalyst and DOO1 catalyst respectively were put in two triport flasks. Materials were added at the ratio as listed in No. 3. i. e. 0. 108 mol of lactic acid and 0. 493 mol of n – butanol. Esterification was performed as described above. Time – ester yield curves obtained for different catalysts are listed in Fig. 1. As shown in Fig. 1, catalysis effect of DOO1 – A1Cl₃ was far better than that of DOO1. For the former, 2. 5 hours was needed to attain an ester yield of 99. 5% while for the contrast one, only an ester yield of 61% was attained in the same hours.

3) The product i. e butyl lactate was ascertained and testifide by IR spectrograph and HNMR spectrograph.

2. Synthesis of other esters

Different alcohol and carboxylic acid were used for esterification also at the ratio listed on No. 3 and with the same operation procedures. For these



Fig. 1. the time-yield curves of esterification

x DOO1-AICI, o DOO1

experiments, 20 ml of benzene was used as water carrying agent. Experimental results including measured IR spectra and ¹HNMR spectra of the products are listed in Table 2.

products	time (h)	yield (%)	ъ.р. (°С.)	LR(KBr)[v(cm 1]	'HNMR(CC14)[δ(ppm)]
lsoamyi acetate	1 . 5	95	142. 5	$1735(s, -CO -)$ $1235(s, C - O)$ $2930(m, -CH_3)$ $1380(m, -CH_2 -)$ $1035[m, (CH_3)_2CH -]$	0. 92(d,6H) 1. 50(m,3H) 2. 03(s,3H) 4. 03(1,2H)
Butyl propionate	2	99. 5	145	1720(s CO -) 1196(s, C - O) $725, 720(w, - CH_2 -)$ $2940(m, - CH_3)$	0.93(1.6H) 1.58(q.1H) 2.21(1.2H) 3.98(1.2H)

Table 2. the synthesis results of esterification

(continued)

Table 2. Continued

Propyl bulyrate Isoamyl bulyrate	3. 7	91 93	142	$1705(s, -CO -)$ $1180(s, C-O)$ $2950(m, -CH_3)$ $700, 710(w, -CH_2 -)$ $1725(s, -CO -)$ $1185(s, C-O)$ $2930(s, -CH_3)$ $1080[m, (CH_3)_{3}C -]$ $725, 720(w, -CH_2 -)$	0.95(1,3H) $1.22(d,3H)$ $1.70(m,3H)$ $2.18(d,2H)$ $4.92(m,1H)$ $0.93(d,3H)$ $0.96(1,3H)$ $1.10-2.00(m,5H)$ $2.21(1,2H)$ $4.05(1,2H)$
Isobutyi propionete	4. 8	90	137	$1710(s, -CO -)$ $1175(s, C - O)$ $1075(m, -CH (CH_3)_2$ $700 - 725(w, -CH_2 -)$ $2925(m, -CH_3)$	0.93(d,3H) 1.10(t,3H) 1.86(m,1H) 2.25(q,2H) 3.78(d,2H)
Butyl butyrate	1. 5	97	165	$1705(s, -CO -)$ $1185(s, C - O)$ $2920(s, -CH_3)$ $715, 720(w, -CH_2 -)$	0.92(1,6H 1.10-1.90(m,6H) 2.19(1,2H) 3.99(1,2H)
Isoamyl Propionate	4. 5	91	160	1730(s, -CO -) 1180(m, C - O) $2900(m, -CH_3)$ $1075[m, -CH(CH_3)_2]$ $800(w, -CH_2 -)$	0.93(d,3H) 1.10(1,3H) 1.53(m,3H) 2.23(p,2H) 4.03(1,2H)
Amy] butyrate	1. 0	91	186	$2950(s, -CH_3)$ $1710(s, -CO -)$ $1175(s, C - O)$ $600 - 710(v, -CH_2 -)$	0.95(1,6H) 1.67(m,8H) 2.19(1,2H) 4.02(1,2H)
lsopropy) butyrate	3. 8	90	130	2930(s, - CH ₃) 1700(s, - CO-) 1180(m, C - O) 1090[m, - CH(CH ₃) ₂] 700-720(w, - CH ₂ -)	0.95(1,3H) 1.22(d,3H) 1.70(m,2H) 2.18(1,2H) 4.82(m,1H)
Propy) propionate	3. 5	92	121	$2950(s, -CH_3)$ $1710(s, -CO -)$ $1180(s, -CO)$ $600 - 700(m, -CH_2 -)$	0.93(1,3H) 1.11(1,3H) 1.60(m,2H) 2.25(q,2H) 3.97(1,2H)

SYNTHESIS OF ESTERS

I. Conclusions

1. The use of $DOO1 - A1C1_3$ superacid resin as catalyst for esterification is a creative approach. As indicated by experiments, much better catalyzing effect was obtained by the novel esterifiction catalyst than by DOO1 strongacidic cation exchange resin, This shows an attractive prospect both in theoretical research and practical application.

2. Eleven different esters were synthesized with high yield in the experiments. This indicates that $DOOI - A1C1_3$ superacid resin catalyst is some what universally suitable for synthesis of carboxylic ester.

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