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A Novel Method for the Synthesis of Carboxylic Esters Catalyzed by Expandable Graphite

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Abstract: Esterification reaction of carboxylic acid and alcohol has been carried out in excellent yield with expandable graphite as a catalyst.

Keywords: Expandable graphite, esterification.

The conventional method of the synthesis of carboxylic ester was essentially carried out with catalysis of sulphuric acid. However, this method has not been entirely satisfactory, associating with the formation of higher undesired by-products, the problem of corrosion, long reaction time and so on. In the recent years, researchers have tried to use other catalysts, such as heteropoly acid, sodium bisulfate, polymer supported Lewis acid, ammonium ferric sulfate and solid super acid as the catalysts for esterification of the carboxylic acid [1-5]. While each of the above methods still has shortcomings, such as long reaction time and the catalysts are not recoverable.

Expansive graphite is a widely used sealing material in industry and it has been used as efficient catalyst for a variety of organic reactions [6-10]. Herein we wish to report an efficient procedure for the synthesis of carboxylic ester catalyzed by expandable graphite.

$$\mathrm{RCOOH + R'OH} \xrightarrow[71 \sim 97\ \%]{\text{Expandable graphite}} \mathrm{RCOOR'}$$

As shown in **Table 1**, a series of carboxylic ester were synthesized with catalysis of expandable graphite. Both primary and secondary alcohols gave good to excellent yield of the corresponding carboxylic ester. Tertiary alcohols, however, afford dehydration products instead of the expected ester under these conditions. In some case, toluene was added as azeotropic solvent.

In conclusion, we have developed an efficient method for the preparation of carboxylic ester with high yields, short reaction time, minimal environment impact, using inexpensive and recoverable catalyst -expandable graphite. The recovered catalyst could be reused without any treatment.

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Table 1 Synthesis of carboxylic ester in the presence of expandable graphite

Acid	mol	Alcohol	mol	Reaction Time (h)	Yield (%)[b]
HCOOH	0.1	$PhCH_2OH$	0.15[a]	3	90.4
HCOOH	0.1	cycrohexanol	0.15[a]	1.5	93.0
CH_3COOH	0.12	$CH_3(CH_2)_2CH_2OH$	0.1	1	97.0
CH_3COOH	0.12	$CH_3CH_2CH(OH)CH3$	0.1	1.5	84.1
CH_3COOH	0.12	$CH_3(CH_2)_3CH_2OH$	0.1	0.8	96.0
CH_3COOH	0.12	$CH_3CH(CH_3)CH_2CH_2OH$	0.1	0.6	95.5
CH_3CH_2COOH	0.1	$CH_3(CH_2)_3CH_2OH$	0.12[a]	0.5	97.0
CH_3CH_2COOH	0.1	$PhCH_2OH$	0.12[a]	2	86.1
CH_3CH_2COOH	0.1	cycrohexanol	0.12[a]	2	88.4
PhCOOH	0.05	$PhCH_2OH$	0.15[a]	2	71.3
PhCOOH	0.05	$CH_3(CH_2)_2CH_2OH$	0.15	2	94.3
PhCOOH	0.05	$CH_3CH(CH_3)CH_2CH_2OH$	0.15	2	96.2
$CH_3CH(OH)COOH$	0.05	$CH_3(CH_2)_2CH_2OH$	0.15	1.5	86.4
$CH_3CH(OH)COOH$	0.05	$CH_3(CH_2)_3CH_2OH$	0.15	1.5	81.2

a. 8 mL toluene was added , b. Yield of isolated

Experimental

The products were characterized by ^1H NMR spectra and comparison of their boiling points with authentic samples.

Preparation of expandable graphite

A mixture of concentrated sulfuric acid (98 %,40 g) , natural flake graphite (10 g) and potassium permanganate (0.5 g) was stirred at room temperature for 40 min. The expansive graphite was filtered, washed with water until pH = 6 ~ 7, and dried at 60 ~ 80°C for 1 h.

General procedure of the preparation of carboxylic ester

A mixture of alcohol, carboxylic acid and expansive graphite (4 % of the total weight of corresponding carboxylic acid and alcohol) was stirred in a round-bottomed flask with at refluxing temperature for the length of time as indicated in **Table 1**. In some cases toluene was added as azeotropic solvent.

After completion of the reaction, the mixture was cooled to room temperature and the expansive graphite was filtered off and washed with Et_2O (2×5 mL), and then the filtrate was washed with 5 % $NaHCO_3$, saturated brine, saturated solution $CaCl_2$, successively and dried over Na_2SO_4, the residue was purified by distillation. In some cases, the filtrate could be distillated directly without any washing procedure.

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