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An overview on synthetic methods of tributyl citrate

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ABSTRACT

Synthetic methods of tributyl citrate using different catalysts such as phosphotungstic acid, modified silica gel supported phosphotungstic acid, carbon-based solid acid, solid superacid SO_4^{2-}/ZnO-TiO_2, strong acidic resin, cerium-doped mesoporous MCM - 41, acid ionic liquid and dealuminated USY have been reviewed. The above mentioned catalysts improved the yield of tributyl citrate. These methods have the advantage of simple process and low investment costs.

KEYWORDS

Overview;
Synthetic methods;
Tributyl citrate;
Catalysts.

INTRODUCTION

Tributyl citrate is one of nontoxic and biodegradable plasticizers. It also is widely used in polyethylene, polyvinyl chloride, polypropylene, celluosic resin, etc. There are a lot of advantages listed as follows: good intermiscibility with resin, high plasticizing efficiency, no poison and low volatility, etc. Concentrated sulphuric acid is one of the main catalysts, but apart from several advantages, such as more secondary reaction taking place, low yield and purity of tributyl citrate, it has a lot of disadvantages also. Lot of waste water is discharged during the process causing severe environmental pollution problem and at the same time equipments are corroded[1].

In the present paper, different catalysts such as as phosphotungstic acid, modified silica gel supported phosphotungstic acid, carbon-based solid acid, solid superacid SO_4^{2-}/ZnO-TiO_2, strong acidic resin, cerium-doped mesoporous MCM - 41, acid ionic liquid and dealuminated USY have been discussed.

DISCUSSION

Phosphotungstic acid as a catalyst

Li Hongchao[2] studied on the synthesis of tributyl citrate by using phosphotungstic acid as a catalyst on catalytic citric acid and n-butyl. The optimum reaction conditions were: phosphotungstic acid (3 % of butanol acid total mass), the molar ratio of citric acid to butanol (1.0 : 4.0), the reaction time (3.5 hr), and the reaction temperature (150 °C) respectively. The maximum yield of tributyl citrate was 97.96 %.

Modified silica gel supported phosphotungstic acid as a catalyst

Nie Lijuan[3] used modified silica gel supported phosphotungstic acid as a catalyst to synthesise tributyl citrate. The optimum reaction conditions were: modified silica supported phosphotungstic acid catalyst (2.5 g), phosphotungstic acid loading amount (43.5 %), the reaction time (4 hr), the ratio of citric acid to n-butanol (4.0 : 1.0), and the reaction temperature (140 °C) respec-

tively. The maximum yield of tributyl citrate was 92.1 %.

Carbon-based solid acid as a catalyst

Hu Renguo[4] studied how to use carbon-based solid acid as a catalyst to synthesis tributyl citrate. The optimum reaction conditions were: carbon-based solid acid (3.0 g per 1.0 mol of citric acid), the molar ratio of citric acid to butanol (1.0 : 4.5), and the reaction time (4 hr) respectively. The maximum yield of tributyl citrate was 99.1 %.

Solid superacid SO_4^{2-}/ZnO-TiO_2 as a catalyst

Feng Xilan[5] described how to use citric acid and n-butanol as feedstocks and solid superacid SO_4^{2-}/ZnO-TiO_2 as a catalyst to synthesise tributyl citrate (TBC). The effects of reaction conditions on the yield of tributyl citrate were studied. The optimum reaction conditions were: solid superacid SO_4^{2-}/ZnO-TiO_2 (1 % of citric acid total mass), the molar ratio of citric acid to n-butanol (1.0 : 4.0), the reaction temperature (130 °C - 140 °C), and the reaction time (2.5 hr) separately. The maximum yield of tributyl citrate was 98.9 %.

Strong acidic resin as a catalyst

Yang Hao[6] explained how to prepare tributyl citrate with acid and n-butanol catalyzed by high acid resin. The optimum reaction conditions were: strong acidic resin (11 % of citric acid total mass), the molar ratio of citric acid to butanol (1.0 : 5.5), the reaction time (4 hr), and the reaction temperature (130 °C) separately. The maximum yield of tributyl citrate was 91.08 %. As well, the catalyst was reused after the simple treatment.

Cerium-doped mesoporous MCM - 41 as a catalyst

He Xifeng[7] described a synthesis of tributyl citrate by using cerium-doped mesoporous MCM - 41 as a catalyst. The optimum reaction conditions were: cerium-doped mesoporous MCM - 41 (5 % of citric acid total mass), the molar ratio of citric acid to butanol (1.0 : 5.0), the reaction time (7 hr), and the reaction temperature (140 °C) respectively. The maximum yield of tributyl citrate was 91.2 %.

Acid ionic liquid as a catalyst

Yang Lan[1] used four kinds of acid ionic liquids as a catalyst to synthesis tributyl citrate(TBC). The optimum reaction conditions were: acid ionic liquids (15 % of butanol acid total mass), the molar ratio of citric acid to butanol (1.0 : 5.0), and the reaction time (3 hr) separately. The maximum yield of tributyl citrate was 97.4 %. After the reaction, the separated ionic liquid was reused 10 times without any treatment. The yield of tributyl citrate was still 96 %.

Dealuminated USY as a catalyst

Li Donyan[8] described how to use dealuminumed ultrastable Y-type zeolite (USY) as a catalyst treated with water vapour and ammonium nitrate aqueous solution, and immobilized 12-tungstophosphoric acid (PW) to synthesis tributyl citrate. The optimum reaction conditions were: the reaction temperature (110 °C), and balanced time (90 min) respectively. The maximum yield and selectivity of tributyl citrate were 97.3 % and 98.8 %, respectively. The catalyst was reused 4 times. The yield of tributyl citrate was maintained at 80 % or more. In addition, the product selectivity was more than 98 %.

CONCLUSION

Based on the above discussion and review, carbon-based solid acid is one of the best catalysts for the highest yield of tributyl citrate (99.1 %). On the other hand, strong acidic resin is one of the worst of the catalysts since the maximum yield of tributyl citrate was only 91.08 %.

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