

Recyclable Heterogeneous Catalyst NMFP•TFA for Green Synthesis of n-Butyl Acetate

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Abstract

n-Butyl acetate is widely used in industries due to its favorable physicochemical properties which is conventionally synthesized via Fischer esterification catalyzed by strong Brønsted acids like sulfuric acid to activate a carboxyl group via protonation. However, the fact that corrosion, separate difficulty, environment pollution are problems that need the replacement of more sustainable substitute. Currently, heterogeneous catalysts such as ionic liquid and supported catalysts have been widely researched in this area to address these drawbacks. Herein, we have studied the effectiveness of a novel solid-liquid heterogeneous catalyst N-methylfulleropyrrolidinium triflate (NMFP•TFA) which can effectively catalyze esterification and separate itself easily for reuse. Under the experimental condition of catalyst loading of 1.4 mol%, NMFP•TFA could effectively catalyze esterification and achieve isolated yields of 82.7%-85.8% after three recycling, and no significant decline of its catalytic activity was observed. NMFP•TFA overcomes the current shortcomings caused by strong Brønsted acids, shows excellent reusability and catalyst stability, and has obvious potential for green and industrially scale-up ester synthesis production.

Keywords

n-Butyl acetate; esterification; heterogeneous catalyst; N-methylfulleropyrrolidinium triflate (NMFP•TFA); reusability

1. Introduction

Esters, which are common organic products, have wide range use to various sectors of industry. Their pleasant flavor is mainly used in the flavor and fragrance industries, and the volatility and solubility are also widely used in the production of inks, coatings, cosmetics and pharmaceuticals, etc. Moreover, esters are also intermediate of making fuels from plants, polymers, and lots of medicines. One ester of particular industrial importance is n-butyl acetate ($\text{CH}_3\text{COOC}_4\text{H}_9$), a clear, colorless liquid ester characterized by its sweet, fruity odor and excellent solvent properties. Traditionally, Fischer esterification is used to synthesize n-butyl acetate via the reaction of acetic acid and 1-butanol, catalyzed by a strong Brønsted acid to activate a carboxyl group via protonation. Because the reaction is reversible and incomplete under standard conditions, strategies such as adding an excess of alcohol or continuous removal of water through azeotropic-distillation are often employed to shift the position of equilibrium to favor the formation of ester [1-3]. However, strong mineral acids like sulfuric acid and phosphate acid pose several severe issues despite its low cost and effectiveness. They are highly corrosive, homogeneous and difficult to separate and reuse. Thus, exploring other catalysts to replace strong mineral acid is necessary in order to improve sustainability in the synthesis of esters.

To replace traditional mineral acid catalysts, a variety of alternative catalysts have been studied to overcome the drawbacks associated with sulfuric acid. Supported metal oxide catalysts, such as WO_3 -based systems, have demonstrated high catalytic activity due to enhanced surface acidity and thermal stability, however, complex preparation procedures and gradual activity loss during reuse limit their long-term stability [4]. Brønsted acidic ionic liquids have been studied as noncorrosive alternatives and can promote esterification efficiently, but high cost, high viscosity, and difficult catalyst–product separation restrict their industrial applicability [5]. Consequently, those catalysts do not fully satisfy the requirements for a recyclable, stable, and sustainable esterification system.

Herein, to address these issues, we explored a new solid-liquid heterogeneous catalyst NMFP•TFA, N-methylfulleropyrrolidinium triflate [6-8]. This new acid-base salt catalyst aims to provide effective proton catalysis simultaneously minimizing the corrosion and environmental impact associated with traditional acids. Additionally, being a solid-liquid heterogeneous catalyst, NMFP•TFA can be more easily separated from the reaction mixture be readily recovered and reused, demonstrating potential advantages in sustainability and efficiency. In this study, the catalytic performance and reusability of NMFP•TFA in the esterification of acetic acid and 1-butanol were investigated.

2. Experimental

2.1 Chemicals

All chemical reagents were obtained from commercial resources and used in experiments without purification. N-Methylpyrrolidine-functionalized fullerene (NMFP) and trifluoromethanesulfonic acid were purchased from J&K Scientific. 1-butanol, acetic acid, sulfuric acid, hexane and toluene were purchased from Sinopharm Chemical Reagent Co. Ltd.

2.2 Catalyst preparation

The reaction for preparation of catalyst NMFP•TFA is shown in Figure 1. To a 50 ml CHCl_3 solution of 77 mg N-methylfulleropyrrolidine (0.1 mmol) in single-neck round-bottom flask added with a drop of trifluoromethanesulfonic acid (0.11 mmol) while stirring for 0.5 hr. Then remove solvent under vacuum to yield brown powder NMFP•TFA.

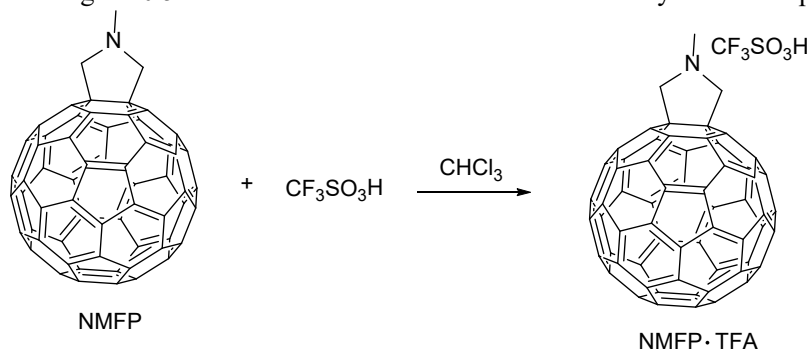


Figure 1. Preparation of catalyst NMFP•TFA.

2.3 Typical Esterification Procedure

In a 250 mL single-neck round-bottom flask equipped with Dean-Stark trap and reflux condenser, a mixture of 8.0 mL (0.1399 mol) of acetic acid, 12.8 mL (0.1399 mol) of 1-butanol, 6.0 mL of cyclohexane, and 0.5 mL of sulfuric acid heated by oil bath (130°C) and keep reflux for 6 hrs until no further increase in volume of water collected in the Dean-Stark trap is observed. Then the reaction mixture is cooled to room temperature and washed with saturated sodium chloride solution, followed by drying over anhydrous sodium sulfate. The pure product 15.9 g was obtained by distillation of the crude product. An Abbe refractometer was used to measure the refractive index of the product to assess purity at 26°C . The refractive index of n-butyl acetate is determined to be 1.3910 at 26°C (literature value n_{D}^{20} 1.3941).

2.4 NMFP•TFA-Catalyzed-Esterification

The same procedure as above mentioned was performed using the heterogeneous catalyst, NMFP•TFA, to replace

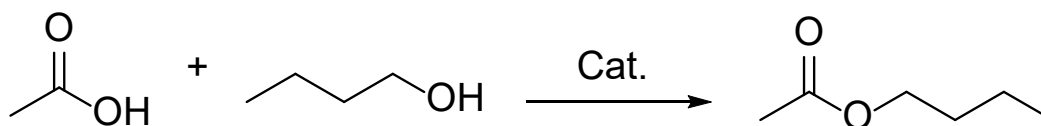
sulfuric acid. The reaction mixture consisted of 8.0 mL (0.1399 mol) of acetic acid, 12.8 mL (0.1399 mol) of 1-butanol, 6.0 mL of cyclohexane, and 0.2 mmol of NMFP•TFA catalyst that corresponds to a catalyst-to-acid molar ratio of 1.4%. The reaction was conducted under identical conditions, and product purification was performed via same distillation process right after esterification when the liquid product separated from the solid catalyst. Pure n-butyl acetate 13.4 g was obtained and its refractive index is observed to be 1.3875 at 26°C, confirming its identity as a pure product.

2.5 Catalyst Reusability

In the first run, after pouring out the crude liquid product, the solid catalyst left at the bottom of the flask can be easily recovered and was directly reused in three consecutive reaction cycles with identical reaction conditions. For each cycle, fresh acetic acid, 1-butanol, and cyclohexane were added into the same flask, and the reaction will perform again. The refractive index of the product tested for each recycle were 1.3875, 1.3895, and 1.3905, respectively, showing consistent purity as n-butyl acetate.

3. Results and Discussion

Table 1. Comparison of catalytic performance of sulfuric acid and NMFP•TFA in the synthesis of n-butyl acetate



Entry	Catalyst	Catalyst loading	Recycling cycle	Yield (%)
1	H ₂ SO ₄	0.5 mL	–	98.4
2	NMFP•TFA	1.4 mol%	Fresh	82.7
3	NMFP•TFA	1.4 mol%	1st	82.7
4	NMFP•TFA	1.4 mol%	2nd	85.2
5	NMFP•TFA	1.4 mol%	3rd	85.8

Table 1 shows the yield comparison of n-butyl acetate produced by the esterification of acetic acid and 1-butanol using sulfuric acid and the heterogeneous NMFP•TFA as catalyst. The isolated yields of N-butyl acetate obtained using sulfuric acid, fresh NMFP•TFA catalyst, and recycled NMFP•TFA catalyst are compared under identical conditions. For the conventional reaction catalyzed by sulfuric acid, entry 1, 12.5g n-butyl acetate was obtained after purification by distillation, resulting an isolated yield of 98.4%. For the reactions catalyzed by the new NMFP•TFA catalyst, 13.4g of n-butyl acetate was obtained, corresponding to an isolated yield of 82.7%.

The reusability of the NMFP•TFA catalyst was evaluated over three consecutive reaction cycles under identical reaction conditions. After the first run, 13.4g of n-butyl acetate was produced with the first recycled catalyst, maintaining an isolated yield of 82.7%. The second and third cycle runs gave isolated yields of 85.2% and 85.8%, respectively. No drop in catalytic efficiency was found during the recycling experiments and thus the catalyst stability of NMFP•TFA in multiple reaction cycles has been proven.

The NMFP•TFA catalyst had good consistency of catalytic performance throughout three consecutive reaction cycles, achieving isolated yields of 82.7-85.8% with a catalyst loading of only 1.4 mol %. These yields are comparable to those obtained using conventional homogeneous acid catalysts under similar esterification conditions, while offering the advantage of facile recovery and reusability. These catalytic performances highlight the potential of NMFP•TFA as a solid-liquid heterogeneous catalyst for sustainable esterification.

High yields are obtained in multiple cycles, indicating that the catalyst has a good stability and is resistant to deactivation, which is also a means of decreasing the consumption of the catalyst and the overall production cost in large-scale production. Although only three recycling cycles were examined in this study, the stable trend of the yield suggests that further optimization and extended use can improve process efficiency, and NMFP•TFA also demonstrates the characteristics of low cost and friendly use in the field of industrial ester synthesis.

4. Conclusion

In this study, the heterogeneous catalyst NMFP•TFA was successfully applied in the esterification synthesis of n-butyl acetate and it has the catalytic activity similar to sulfuric acid, which maintains an isolated yield of 82.7-85.8% at a low concentration of 1.4 mol%. The stable catalytic activity without activity loss in three consecutive recycling cycles also demonstrates good sustained catalytic performance and stability and durability. And most importantly, the convenience and reusability of the catalyst point to NMFP•TFA in solid-liquid heterogeneous state as a superior choice to traditional liquid-phase acid catalysts. Therefore, NMFP•TFA is proposed as a practical and sustainable replacement for esterification reactions, particularly in cases where reusability of the catalyst and reduction of environmental impact are important. Further optimization of catalysts structure, property, and recycling may enhance its performance and broaden its application potential.

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