Direct Esterification of Succinic Acid with Phenol using Zeolite Beta Catalyst

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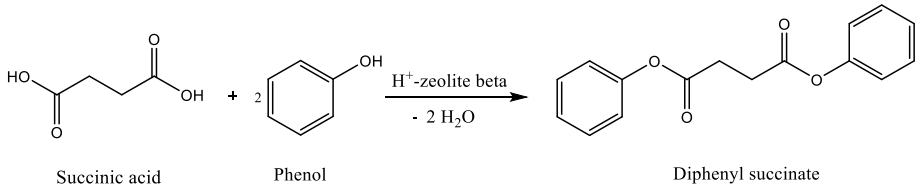
Abstract: Direct esterification of succinic acid with unreactive phenol in the presence of zeolite catalysts was investigated. Among various types of catalysts, H^+-zeolite β (SiO_2/Al_2O_3=150) was found to be the most effective solid acid catalyst which can accelerate the reaction toward diphenyl succinate with a good yield (~70%). The present method not only offers essential features of the heterogeneous system but also brings simplicity in operation, which make it more economical and environment-friendly.

Keywords: Esterification, succinic acid, phenol

1. Introduction

Diphenyl dicarboxylates are important intermediates which are typically used as a starting material in the preparation of para-quinone methides which exist in a variety of pharmaceuticals, medicinal and biological processes.[1] Furthermore, it can be employed as a reactive dienophile for effecting Diels-Alder reaction with quinodimethanes[2], and a useful plasticizer for the synthesis of polyvinyl chloride, copolymers various cellulose esters and synthetic rubbers.[3] In particular, diphenyl succinate had been reported as an effectively bifunctional electrophile in the production of Spiro-lactones which may be useful for medical indications.[4,5]

Direct esterification with phenol had been a challenge for many years, especially for the reaction with dicarboxylic acids using heterogeneous catalysts.[6] Recently, metal-exchanged montmorillonites were reported to be potential solid catalysts for the esterification of dicarboxylic acids with various alcohols and phenol, however, only low and moderate yields of diphenyl dicarboxylates were obtained.[7,8] Here, for the first time, a good yield of diphenyl succinate (~70%) was successfully achieved from the esterification of succinic acid with phenol using H^+-zeolite β as a potential solid acid catalyst. (**Scheme 1**)



Scheme 1. Synthesis of diphenyl succinate from succinic acid and phenol over H^+-zeolite β

2. Experimental

Typical reaction procedure: The esterification of succinic acid with phenol was carried out in a 20-mL round-bottom flask fitted with a reflux condenser. First, the flask was charged with succinic acid (1 mmol), phenol (3 mmol), catalyst (0.1 g), and solvent (5 mL). Subsequently, the reaction mixture was heated at 130 °C and 400 rpm for 6 h before being cooled to the ambient temperature.

Isolation procedure: After reaction, the catalyst was filtered off by a Büchner funnel and the combined filtrates were transferred into a separatory funnel. Sodium hydroxide (5%) was then added to wash unreacted succinic acid and the water phase was removed. Next, the organic phase was washed with water and saturated brine before being removed by rotary evaporator. After that, the obtained product was further dried in vacuum for one night to obtain the final product.

Analysis methods: To confirm the product, proton nuclear magnetic resonance (^{1}H-NMR) was employed (Bruker Avance III, 400 MHz). Acetonitrile-d_3 was used to dissolve the product, while maleic (purity = 99%) was added as the internal standard. For the convenience, the synthesized products with high purity (99%) were collected to draw a calibration curve with an internal standard (dodecane) for gas

chromatography (GC, Shimadzu GC-2014, Agilent DB-1). The yield of the product was then calculated based on the mole of succinic acid.

3. Results and discussion

A wide diversity of solid acid catalysts was investigated for the synthesis of diphenyl succinate. The results are shown in **Table 1**.

Preliminary experiments with various montmorillonite (mont) catalysts were carried out. In this series of experiments, Al^{3+}-mont gave the highest yield of the product, 10% (entry 2). Similar results were seen in case of Zr^{4+}-mont and sulfated zirconia (entries 3 and 4). Next, 4 types of zeolites were examined for the reaction. Interestingly, H^+-zeolite β which possesses SiO_2/Al_2O_3 (SA) ratio of 150 (HB150), could accelerate the reaction to yield approximately 70% of the target product (entry 5), while other zeolites gave very low yield (entry 7) or failed to produce the product (entries 6 and 8).

Several kinds of Amberlyst catalysts were also investigated, of which Amberlyst 45 and 46 brought the highest yield of the product, 42% and 44%, respectively (entries 11 and 12). While the similar results, around 30% yields were obtained in the case of Amberlyst 15 and 35 (entries 9 and 10).

Table 1. Esterification of phenol with succinic acid over solid acid catalysts

Entry	Catalyst	GC yield/%
1	Cu^{2+}-mont	4
2	Al^{3+}-mont	10
3	Zr^{4+}-mont	7
4	Sulfated ZrO_2	7
5	H^+-Zeolite β	67
6	H^+-Zeolite Y	0
7	H^+-ZSM-5	< 2
8	H^+-Mordenite	0
9	Amberlyst 15	29
10	Amberlyst 35	30
11	Amberlyst 45	44
12	Amberlyst 46	42
13	None	0

Reaction conditions: succinic acid (1 mmol), phenol (3 mmol), dehydrated toluene (5 mL), catalyst (0.1 g), reaction time (6 h), temperature (130 °C). Montmorillonites were activated at 110 °C, while zeolites were calcinated at 500 °C for 5 h before use. Other catalysts were used without any pre-treatment.

The potential catalytic activity of zeolite β was further studied to achieve the highest yield of diphenyl succinate. We examined catalysis of a class of zeolite β with different SA ratios (25, 42.2, 104, 440, 1700). However, the results for those zeolites were lower than that of HB150 since the yield of the desired products were just in the range of 30-50%, except for zeolite β (SA=1700) with only 3%. Additionally, no clear relationship between the yield of the product and SA ratio was observed.

4. Conclusions

In conclusion, H^+-zeolite β (SiO_2/Al_2O_3=150) was found to be an efficient solid acid catalyst for the esterification from succinic acid with phenol in toluene solvent. The remarkable features of this heterogeneous system not only make it a potential candidate for laboratory but also capable of commercial applications.

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