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Factors influencing the formation of 2-hydroxy-6-naphthoic acid from carboxylation of naphthol

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ABSTRACT

The synthesis of 2-hydroxy-6-naphthoic acid (2,6-HNA) from carboxylation of alkali-naphthoxide was studied with varying alkali cation types and reaction conditions such as reactant concentration, reaction time, temperature, and pressure. The product selectivity was strongly affected by the types of alkali cation, reaction time, and temperature, while the product yield was governed by reaction pressure. The maximum HNA yield, 28.6%, was achieved with 2,6-HNA selectivity of 81.6% at 6 atm of CO_2, 543 K, and 6 h of reaction. The addition of K_2CO_3 led to further increase in the productivity of 2,6-HNA via suppression of the decarboxylation of HNA.

1. Introduction

The reduction of CO_2 has been an environmental concern for the past decade due to its greenhouse effect. Considering its abundance from various combustion processes, finding a practical method for chemical fixation of CO_2 would not only be environmentally helpful, but would also provide a cheaper source of carbon. The Kolbe–Schmitt reaction offers a direct CO_2 fixation on hydroxy-aromatic compounds, producing aromatic hydroxy-carboxylic acids, such as salicylic acid, p-hydroxy-benzoic acid, 2-hydroxy-3-naphthoic acid (2,3-HNA), and 2-hydroxy-6-naphthoic acid (2,6-HNA) [1–14]. 2,6-HNA is a very important intermediate for polyesters and polymeric liquid crystals. The synthesis of 2,6-HNA by Kolbe–Schmitt reaction consists of three steps: (1) the production of alkali-2-naphthoxide, (2) the carboxylation with CO_2, and (3) the purification with acid. Alkali-2-naphthoxides are generally prepared from a mixture of alkali-hydroxides and 2-naphthol. Yamaguchi et al. have found that the introduction of K-2-naphthoxide resulted in better selectivity of 2,6-HNA (63.6%) than the case with Na-naphthaxide (2.8%) [8–14]. They have also examined the effects of reaction conditions of temperature and reaction time on the product distribution of HNA's, in which the product selectivity of HNA's was dependent on the thermodynamic stability; the formation of 2-hydroxy-1-naphthoic acid (2,1-HNA) was favored at 473 K then the thermal rearrangement led to 2,3-HNA at temperatures of 473–513 K and 2,6-HNA at high temperatures over 513 K [15–18].

In spite of the importance of the 2,6-HNA, there have been few studies reported to elucidate the effects of the reaction parameters determining the product yield and selectivity. This study was focused on the investigation of the effects of various reaction conditions of alkali cation type, reactant concentration, reaction time, temperature and pressure to better understand the key factors influencing the product selectivity and yield of 2,6-HNA in the carboxylation of K-2-naphthoxide. Particular efforts were made to examine the thermal stability of HNA isomers and verify the role of K_2CO_3 base catalyst in the formation of 2,6-HNA.

2. Experimental

2.1. Synthesis procedure of HNA

The general procedure to synthesize the HNA is as follows: in preparing alkali-naphthoxide, 6.8 mmol 2-naphthol (Sigma–Aldrich, 98%), 6.8 mmol alkali hydroxide (NaOH, KOH, RbOH), and 5 ml water were mixed and stirred at room temperature for 1 h. The mixture was combined with hexadecane (Tokyo Chemical Industry, 98%) of 20 ml in 100 ml autoclave. The autoclave was heated to 513 K under a slow purge of N_2 for 40 min and heated to 543 K, charged with CO_2 by 4 atm, and then maintained for 6 h. In addition, the reaction conditions of temperature, pressure, time of run were varied. The product was analyzed by high performance

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liquid chromatography (HPLC pump: Lab alliance series 1500; UV/VIS detector (254 nm): Hitachi L-7400; column: Inertsil ODS-2, 4.6ØΦ × 250 mm; solvent: a mixture of acetonitrile and water (50:50, v/v), which was slightly acidified by the addition of 1% acetic acid). For all the quantification the instrument error was confirmed by the measurement of standard reference before and after each sample, which gave an error range below 1.0%. HNA yield and selectivity are defined as follows:

$$\text{HNA yield} = \frac{\text{Total moles of HNA isomers}}{\text{Total moles of reactant}} \times 100$$

$$\text{Selectivity} = \frac{\text{Moles of each HNA}}{\text{Total moles of HNA isomers}} \times 100$$

2.2. Thermal stability tests

K-exchanged HNA's of K-2,1-HNA, K-2,3-HNA, K-2,6-HNA were prepared by mixing 3.4 mmol HNA and 6.8 mmol KOH in 5 ml water at room temperature for 1 h. The mixture was introduced into the autoclave with 20 ml of hexadecane, and the rest of test procedure and quantification method was the same as done for the synthesis of HNA. The HNA recovery yield is defined as follows:

$$\text{HNA recovery yield} = \frac{\text{Moles of HNA unconverted}}{\text{Moles of HNA reacted}} \times 100$$

3. Results and discussion

3.1. Effects of alkali-naphthoxide type and concentration

Table 1 summarizes the product distribution of the carboxylation of various alkali 2-naphthoxides. In case of Na-2-naphthoxide, CO_2 substitution on C_1 and C_3-position was dominant as the selectivity of 2,1-HNA and 2,3-HNA was 63.4% and 36.6%, respectively, while the formation of 2,6-HNA was almost negligible. In contrast, use of K-2-naphthoxide led to a substantial increase in the formation of 2,6-HNA with the selectivity of 81.3%. It was noteworthy that Rb cation gave rise to even higher selectivity to 2,6-HNA of 88.8% than other alkali-2-naphthoxides. These results indicate that the product selectivity of HNA is strongly influenced by the types of alkali cation on naphthoxide. The trend of 2,6-HNA selectivity is well correlated with the size of alkali cations, i.e. Rb > K > Na. Similar results were reported for the case of Na-2-naphthoxide carboxylation with the ortho-selectivity being dominant [16]. In addition, the larger cation of Cs preferred para-selectivity to ortho-selectivity in the carboxylation of alkali-phenoxide [11,17,18]. In the similar manner, the larger cation on naphthoxide resulted in the higher selectivity to 2,6-HNA. These results thus suggest that the increase in the selectivity to 2,6-HNA is ascribed to the longer distance between alkali cation and oxygen atom of alkali-naphthoxides.

Table 1
Product distribution of alkali-2-naphthoxide carboxylation.

Reactant (concentration)	HNA yield (%)	HNA selectivity (%)		
		2,1-HNA	2,3-HNA	2,6-HNA
Na-naphthoxide, 10 mol%	32.4	63.4	36.6	0
Rb-naphthoxide, 10 mol%	25.3	0.9	10.3	88.8
K-naphthoxide, 5 mol%	7.3	0	20.4	79.6
K-naphthoxide, 10 mol%	26.9	2.3	16.4	81.3
K-naphthoxide, 20 mol%	27.3	21.2	12.1	66.8

Table 1 also summarizes the product distribution obtained from different reactant concentrations of 5, 10, and 20 mol% of K-2-naphthoxide. The increase of the K-2-naphthoxide concentration from 5% to 10% led to the increase of the total yield of HNA about 4 times from 7.3% to 27.0% but with the selectivity of 2,6-HNA remaining constant, while, higher concentration of 20% led to only a slight change in HNA yield at 27.3% but with a drop of 2,6-HNA selectivity from 81.3 to 66.8%. These results suggest that the product yield and selectivity of 2,6-HNA is strongly affected by the reactant concentration. In a low reactant concentration below 5 mol%, K-2-naphthoxide might be difficult to react with CO_2 due to a dilution effect, resulting in the low conversion of K-2-naphthoxide and low yield of HNA. Instead, a high reactant concentration above 20 mol% could lower the product selectivity toward 2,6-HNA. From a practical point of view, the use of K-2-naphthoxide might be more cost-effective than the case with heavier alkali-naphthoxide. Thus, K-2-naphthoxide was adopted as a major reactant to examine the effect of various reaction conditions on the product selectivity and yield for 2,6-HNA.

3.2. Effects of reaction time

The effect of reaction time was examined to elucidate the reaction progress. The K-2-nphthoxide carboxylation was performed at 543 K under a CO_2 pressure of 4 atm, and monitored for 8 h at 1 or 2 h intervals. Fig. 1 shows the product yield and selectivity as a function of the reaction time. In a short reaction time of 1 h, it was found that 2,3-HNA and 2,1-HNA were formed over 50% of selectivity. With the progress of reaction, the portion of 2,3-HNA and 2,1-HNA was diminished, while the 2,6-HNA selectivity came to grow and reached to 80% at 6 h, resulting in a gradual increase of the product yield of 2,6-HNA, 22%. Over 6 h of run, the yield of 2,6-HNA began to decrease. These results can be explained by the thermal stability of HNA isomers. It was observed that the 2,6-HNA remains most stable among the HNA isomers at 543 K as given below in Table 2. It can be demonstrated that all the HNA isomers are generated within 1 h, then 2,1-HNA and 2,3-HNA tend to undergo thermally decarboxylation to give naphthol or rearrangement to render 2,6-HNA, at last, followed by the decarboxylation of 2,6-HNA.

3.3. Effects of reaction pressure and temperature

A series of K-2-nphthoxide carboxylation tests as a function of CO_2 pressures ranging from 2 to 8 atm were conducted, while the

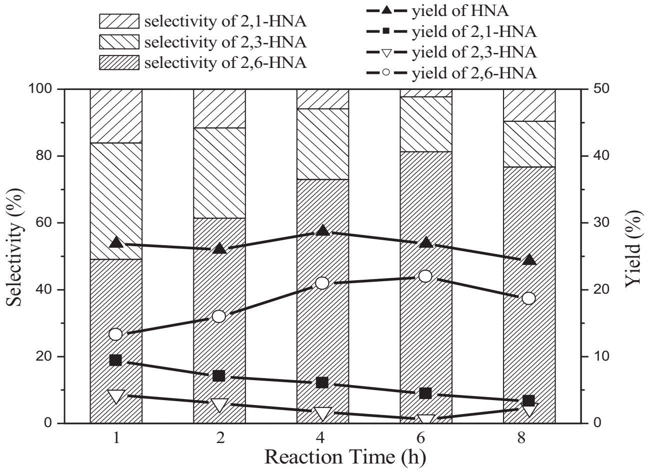

Fig. 1. Carboxylation of K-2-naphthoxide vs. reaction time at 543 K and 4 atm of CO_2.