Effect of reaction conditions on naphthalene sulfonation

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Abstract:
Various factors affecting electrophilic aromatic sulfonation of naphthalene with sulfuric acid were investigated. Reaction temperature, time, composition and type of solvents were varied in the reaction. It was confirmed that reaction temperature over 150ºC, and use of a naphthenic solvent played an important role in the increase of the product yield to 2-naphthalene sulfonic acid. Furthermore, a new reactor type which was introduced to suppress sublimation of naphthalene led to a drastic impact to increase the product yield close to 98%.
Keywords: Naphthalene, sulfonation, sulfuric acid, naphthalene sulfonic acid

1. Introduction

Aromatic sulfonation is a very important chemical transformation of organic compounds.[1,2] Naphthalene sulfonic acid, for example, is widely employed as a crucial intermediate for pharmaceuticals, detergents, surfactants, dyes, and pesticides. The most commonly used sulfonating agents are sulfur trioxide (SO_3), oleum, sulfuric acid and chlorosulfuric acid.[1,2] In the sulfonation of naphthalene, two isomers of α or β-sulfonic acid are formed, while the isolation of the indivisual compound is usually very difficult.[3] Nonetheless, a loss of product yield commonly occurs due to the sublimation property of naphthalene. The present study is thus to investigate the effect of reaction condition on the product distribution to increase product yield and selectivity to β-naphthalene sulfonic acid. In particular, more emphasis was made to employ a new reactor design to suppress sublimation of naphthalene.

2. Experimental

The sulfonation was conducted using a concentrated H_2SO_4(95%) combined with naphthalene at various temperature conditions of 100-200℃for 0.5 h. To examine the effects of composition and type of reaction solvents naphthalene was dissolved in various solvents such as decalin, decane, or tridecane. During the synthesis N_2 was flowed at 5cm^3min^{-1} through the Schlenk line to avoid air-exposure. After the reaction was completed, the temperature was lowered to room temperature. The product was then recovered for quantification using an HPLC analysis.

3. Results and discussion

Figure 1 compares the product yield to product yield of β-naphthalene sulfonic acid from naphthalene sulfonation at 170ºC for 0.5h. In the conventional synthesis condition the product yield was very low at below 50%, because of loss of naphthalene during the reaction via sublimation. In order to restrict the sublimation of naphthalene various solvents as dispersant of naphthalene were used. It was observed that the use of decalin as a solvent led to a considerable improvement in the product yield close to 93%. A new reactor designed for suppressing the sublimation of naphthalene gave rise to further improvement of the product yield close to 98%. Overall, it was demonstrated that the restriction of sublimation of naphthalene at the reaction temperature is of great importance to achieve the high product yield.

References

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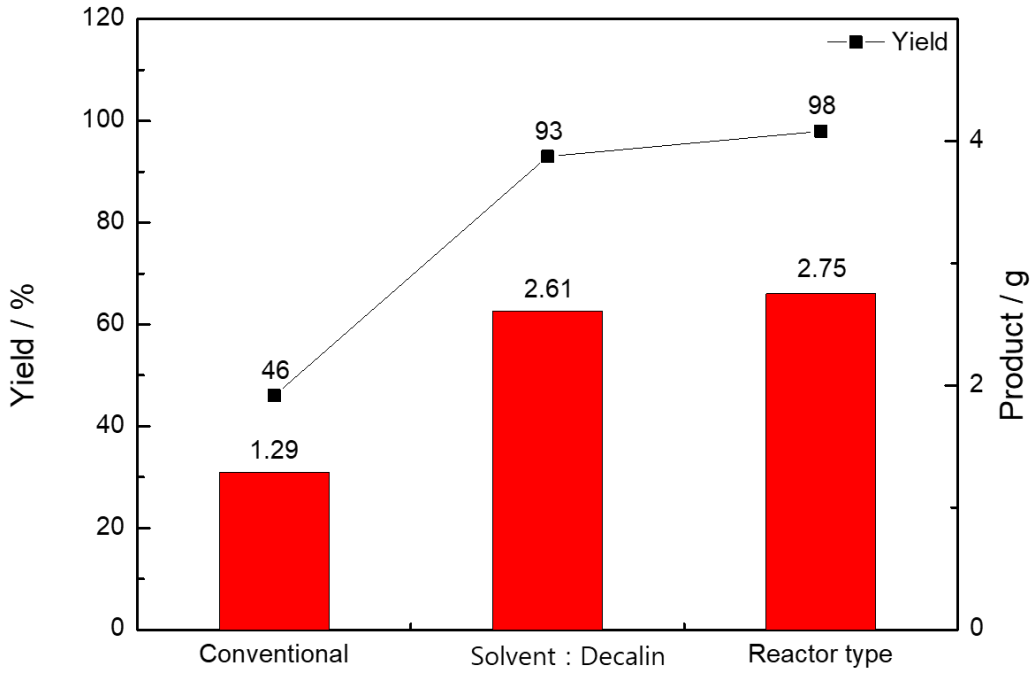

Fig.1. Product yield of β-naphthalene sulfonic acid