

Poly (4-vinylpyridine) catalyzed isomerization of maleic acid to fumaric acid



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ABSTRACT

Fumaric acid is an important industrial intermediate compound that is mostly produced by isomerization of maleic acid under the catalysis of thiourea. In this study, a solid catalyst, poly (4-vinylpyridine) resin, was firstly used instead of thiourea for the catalytic isomerization of maleic acid because of its ease of separation and reusability. A high isomerization conversion rate of 86% was obtained for 100 mL of 200 mg/L maleic acid solution with resin dosage of 0.1 g under 353 K. This high isomerization conversion was due to the high nucleophilicity of PVP molecules. The optimum pH of 1.5 was determined by the degree of ionization of maleic acid. In the kinetics study, the conversion of maleic acid exhibited a second-order kinetic equation with apparent activation energy of 226.06 kJ/mol. Furthermore, the regenerated resin demonstrated no loss of catalytic activity. The excellent catalytic performance and high recyclability suggest that PVP resin has promising application in the isomerization of maleic acid to fumaric acid.

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1. Introduction

Fumaric acid is an important industrial intermediate compound for food processing, pharmaceutical manufacturing, feed processing, paint production and resin synthesis [1–6]. Till to-date, fumaric acid is mainly derived from the isomerization of maleic acid in the presence of catalysts [7–13]. Numerous catalysts are used for the isomerization reaction, which include HCl, HBr, H₂SO₄, HClO₄, KCNS, NH₄CNS, NaBr, Br₂ and NH₄Br; the processes are conducted under high temperature and/or in the presence of oxidizing agents [14–17]. Maleate isomerase from thermophilic bacteria is involved in the enzyme activity in isomerization reaction, but its poor thermal stability hinders its application [10,18]. To the best of our knowledge, thiourea is still most widely used in the isomerization of maleic acid for the industrial production of fumaric acid due to its low cost [7,8,11,16]. This reaction occurs between 323 K and the boiling point of the solution. The produced fumaric acid has low purity and requires further purification [19,20]. Moreover, all these catalysts are homogeneous and difficult to be separated and reused, leading to water pollution and product purity reduction.

In contrast to homogeneous catalysts, heterogeneous catalysts can be easily separated and recycled [21–25]. Many heterogeneous

catalysts have been developed based on solid supports, such as silica, clays, zeolites, carbon, as well as mesoporous and polymeric ligands [26,27]. Although catalytically active species can be immobilized onto the solid supports through adsorption, electrostatic interaction or entrapment, stability is still a considerable disadvantage for its application [28,29]. Many resins with nitrogen groups such as Amberlyst-15, Amberlyst-35, Amberlite IRA-900, Amberlite IRC-72, Amberlite IRC-93 resins are widely used in catalytic reactions [30–33]. However, these resins with nitrogen groups are easily decomposed at high temperatures. Since cross-linked poly (4-vinylpyridine) has a higher thermal stability [34], it has been used as a green and efficient catalyst for the synthesis of chromene derivatives [35]. Some studies have reported that pyridine, 4,4-bipyridine can catalyze isomerization of maleic acid in the presence of polar solvents [19,36,37]. Therefore, PVP resin with pyridine group may have the potential to catalyze isomerization of maleic acid. When compared with the traditional thiourea catalyzed isomerization, PVP resin can be easily separated and recycled, which makes the reaction more suitable for industrial applications. Furthermore, resin usually offers better selectivity toward the desired product and better reusability than homogeneous catalysts [38]. Therefore, using PVP resin as catalyst will lead to a new development in the industrial production of fumaric acid. However, limited information on this work is available.

In this study, PVP resin was first used to catalyze isomerization of maleic acid to fumaric acid. The conditions of the reaction,

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such as solution pH, initial reactant concentration, temperature, and salt concentration, were all investigated. The catalytic reusability of the resin was also evaluated through several continuous batch experiments.

2. Experimental

2.1. Materials

All chemicals used in this study were guaranteed grade unless otherwise specified. The cross-linked PVP resin, which was 25% cross-linked with divinylbenzene, was purchased from Sigma-Aldrich U.S. Its particle size distribution ranged mainly from 30 to 60 mesh, and its water content was 60%. Prior to use, the resin was rinsed with methanol in a glass column at 323 K and dried under vacuum at 333 K for 8 h. Maleic acid, HCl, NaCl, Na₂SO₄, and other chemicals were supplied in analytical grade by Nanjing Chemical Reagent Company (Jiangsu Province, China). All reagents were used without further purification. Aqueous solutions were prepared using distilled deionized water.

2.2. Reaction systems

Catalyzed isomerization of maleic acid to fumaric acid was carried out at atmospheric pressure using PVP resin as catalyst. The 250 mL flask was shaken at 150 rpm in a water-bathing constant temperature vibrator (THZ-82, Shanghai Jiangxing Instrument Co., Ltd., Shanghai, China). In a typical experiment, 100 mL of 200 mg/L maleic acid solution and 0.1 g PVP resin were loaded to the reactor at 333 K. Samples for HPLC analysis were taken at selected reaction times. The reaction system lasted for 160 h, and was used to study the effect of pH. The pH value was adjusted by con. HCl (12 M) and NaOH (1 M) solution. The initial maleic acid concentration was varied in order to obtain data for its effect on the reaction. The effect of reaction temperature (323, 333, 343, and 353 K) and co-existing salts were also investigated. Finally, the used catalyst was separated through filtration, and regenerated by 0.1 M NaOH solution after six consecutive uses.

The conversion of the reaction was calculated according to the following equations:

$$\text{maleic acid conversion}(\%) = \frac{C_{m0} - C_{mt}}{C_{m0}} \times 100 \quad (1)$$

$$\text{fumaric acid yield}(\%) = \frac{C_{ft}}{C_{m0}} \times 100 \quad (2)$$

where C_{m0} is the initial concentration of maleic acid and C_{mt} and C_{ft} (mg/L) are the concentrations of maleic acid and fumaric acid at time t in the corresponding solutions, respectively.

All experiments were duplicated and the average standard deviation of the duplicated experiments was less than $\pm 10.0\%$ for the individual composition of the reaction system. The average standard deviation for conversion was lower than 6%.

2.3. Sample analysis

All samples were analyzed through high-performance liquid chromatography (HPLC, Agilent 1200, Germany) with a DAD detector and a reverse-phase Krornasil-C18 column (150 mm \times 4.6 mm \times 5 μ m). The mobile phase consisted of 3% methanol and 97% phosphoric acid aqueous solution (pH=2.53) with flow rate of 1 mL/min and sample size of 20 μ L. The DAD detection wavelength was 210 nm and the column temperature was set at 303 K. All samples were filtered through 0.45 μ m membrane filters before detection.

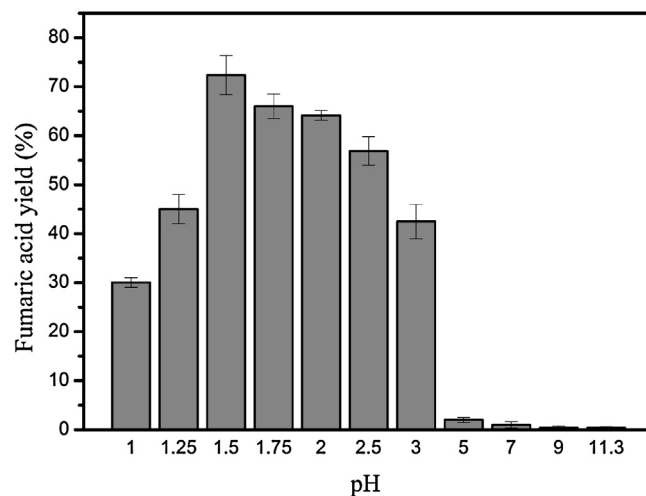


Fig. 1. Effect of pH on catalytic activity for isomerization reaction catalyzed by PVP resin.

3. Results and discussion

3.1. Effect of pH

To investigate the effect of pH on the reaction system, the experiments were carried out at pH 1 to 11.3 (Fig. 1). At pH 1.5, fumaric acid (%) reached the highest conversion (72%), indicating that 1.5 was the optimum pH for the overall reaction. Fumaric acid yield (%) decreased when pH was less than 1.5 and more than 1.5. Fumaric acid yield (%) decreased to 2% at pH 5 and 30% at pH 1. When pH was higher than 7.0, almost no fumaric acid formed. The phenomenon was related to the ionization equilibrium constant of maleic acid. Given that pK_a 1 and pK_a 2 of maleic acid were 1.92 and 6.23, respectively [39], pH decrease from 7.0 to 1.92 was propitious to the ionization of maleic acid. When pH was lower than 1.92, the ionization equilibrium was enhanced, forming more maleate and contributing to the increase in fumaric acid yield (%). When pH decreased further from 1.5, increased formation of maleate resulted in electron pair repulsion, causing decrease of fumaric acid yield (%). The fumaric acid could not form when the pH was under alkaline solution, similar to Hayon and Simic's report. They suggested that maleate anions were formed by an electron transfer process at acidic pH, which was not observed at higher pH [40]. These findings indicated that fumaric acid yield (%) was closely related to pH, and was probably decided by the reaction mechanism (Scheme 1).

According to the study of Karaman and Chatterjee et al. [36,37], the possible mechanism of isomerization of maleic acid to fumaric acid catalyzed by PVP resin involved mainly four steps: (1) a proton transferred from the maleic acid into the nitrogen of PVP resin to form ion pair S1; in this process, PVP will first break the intermolecular hydrogen bonding of maleic acid. (2) PVP cation approached the C=C double bond of the maleic acid moiety to yield S2; (3) rotation about the central C–C single bond of S2 followed by proton abstraction by PVP molecule to yield unstable S3; and (4) proton transferred from the PVP moiety and formed into the carboxylate moiety of the fumarate, leading to the formation of fumaric acid. In step 1, different pH directly affected the ionization degree of maleic acid, resulting in different formation numbers of ion pair S1. In the overall reaction, PVP molecules exhibited an intensely nucleophilic attack on the C2 of maleate. The C2–C3 double bond was converted to C2–C3 single bond, which allowed free rotation.

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