



# 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, H<sub>2</sub>SO<sub>4</sub>, HClO<sub>4</sub>, KCNS, NH<sub>4</sub>CNS, NaBr, Br<sub>2</sub> and NH<sub>4</sub>Br; 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, Na<sub>2</sub>SO<sub>4</sub>, 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  $\mu$ 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  $\mu$ L. The DAD detection wavelength was 210 nm and the column temperature was set at 303 K. All samples were filtered through 0.45  $\mu$ m membrane filters before detection.

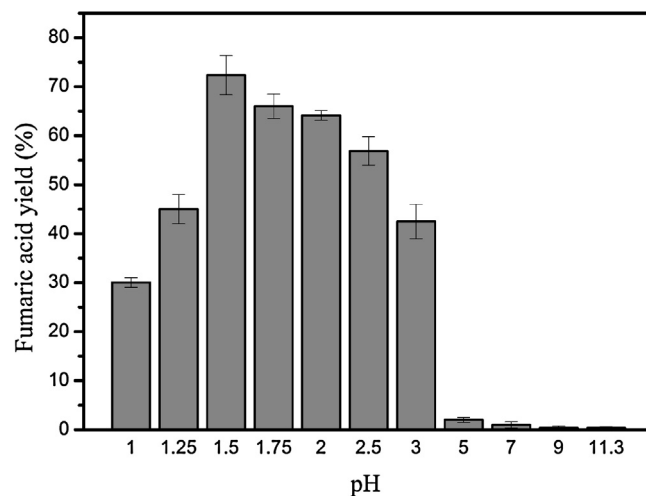


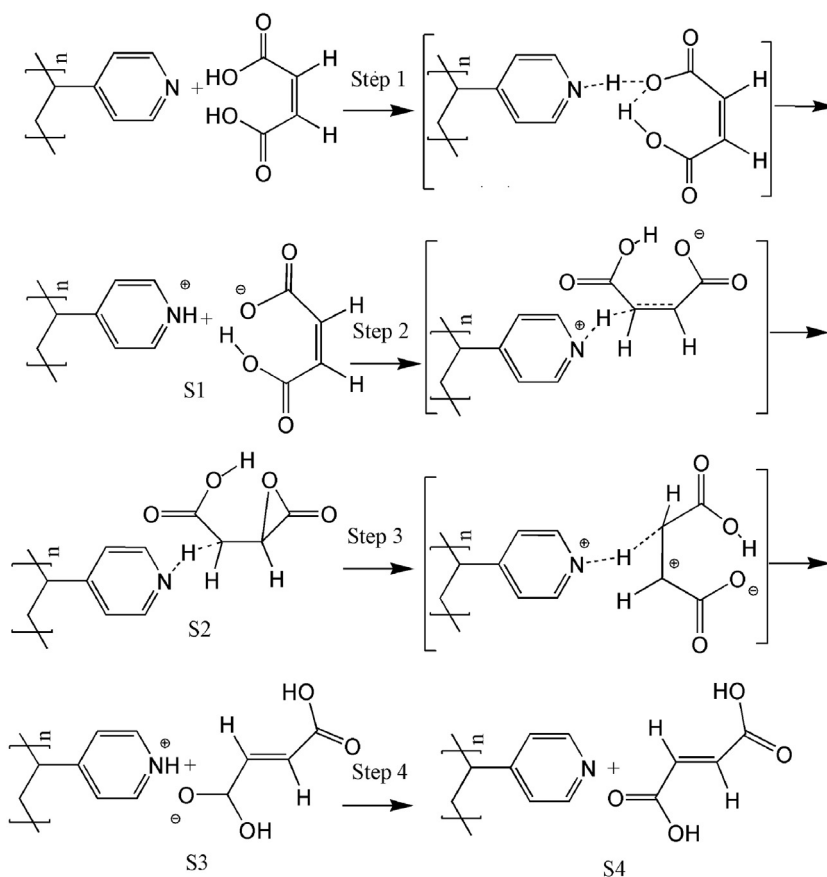
Fig. 1. Effect of pH on catalytic activity for isomerization reaction catalyzed by PVP resin.

## 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  $pK_{a1}$  and  $pK_{a2}$  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.



**Scheme 1.** The mechanism for catalyzed isomerization of maleic acid to fumaric acid by PVP resin.

### 3.2. Effect of the initial reactant concentration

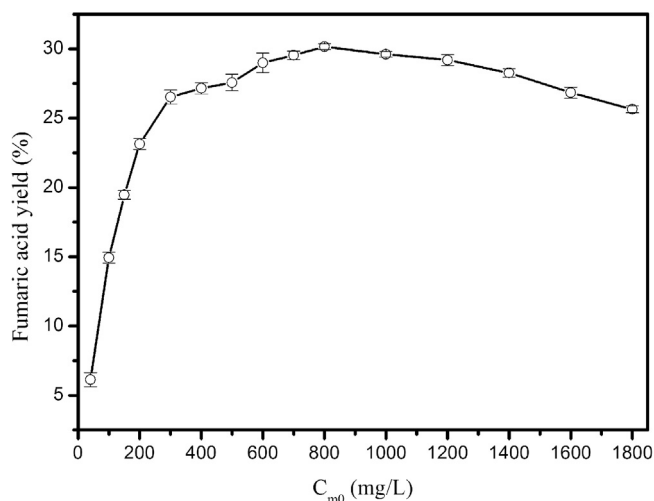
To study the optimum reaction condition, knowing the influence of reactant concentration on the overall reaction is necessary to obtain optimum fumaric acid yield (%). The effect of initial reactant concentration was studied at conditions of resin dosage of 0.1 g, reaction temperature of 333 K, and reaction time of 26 h. In Fig. 2, the initial maleic acid concentration was arranged in 40 mg/L to 1800 mg/L. Fumaric acid yield (%) increased with an increase in the concentration of initial maleic acid in the range of 40 mg/L

to 800 mg/L. Fumaric acid yield (%) displayed a slightly declining tendency when initial maleic acid concentration increased from 800 mg/L to 1800 mg/L, indicating that the active sites of the resin were saturated. The resin could not catalyze much more maleic acid molecules because the initial maleic acid concentration was more than 800 mg/L. Meanwhile, the maleic acid molecules blocked the pores of the resin and covered some active sites, inhibiting the chemical reaction on the active sites.

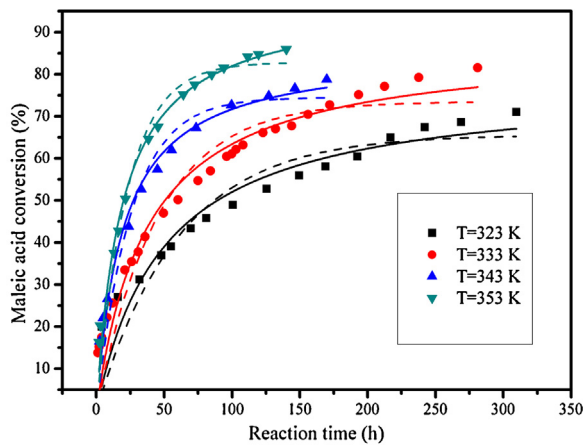
### 3.3. Kinetics

Reaction temperature is usually closely related to catalytic efficiency [33]. In this study, 1% maleic acid isomerization to fumaric acid catalyzed by PVP resin was observed when the catalytic reaction occurred under room temperature. However, when the reaction reached suitable temperature, the maleic acid conversion (%) increased significantly. Fig. 3 shows the maleic acid conversion (%) of maleic acid isomerization to fumaric acid catalyzed by PVP resin as a function of temperature under the following conditions: reaction temperature of 323, 333, 343, and 353 K, as well as catalyst dosage of 0.1 g, 100 mL, and 200 mg/L maleic acid solution. Maleic acid conversion (%) increased with an increase in temperature. Almost 86% conversion was obtained at 353 K, which showed high catalytic activity.

For heterogeneous reaction catalyzed by the resin, six basic steps were involved in the sequence of mass transfer under a liquid–solid catalytic system: (1) diffusion of reactants to the external surface of the resin; (2) adsorption of reactants onto the surface of the resin and catalytic reaction on the surface active sites; (3) diffusion of reactants from the external surface to the internal pore surface of the resin; (4) adsorption of the reactants onto the internal pore



**Fig. 2.** Effect of the initial reactant concentration on catalytic activity for isomerization reaction catalyzed by PVP resin.



**Fig. 3.** Maleic acid conversion (%) versus reaction time at four different temperatures for catalyzed isomerization by PVP resin. The dashed lines and solid lines represent the result of the first-order kinetic model and second-order kinetic model, respectively.

surface and catalytic reaction; (5) desorption of the products and diffusion from internal pore surface to the external surface; and (6) desorption and diffusion from the external surface to the external liquid [41].

In this study, the conversions of maleic acid isomerization to fumaric acid catalyzed by PVP resin were 55%, 60%, and 61% at shaking speeds of 100, 150 and 200 rpm, respectively. Thus, it was concluded that external diffusion was probably a control step when the shaking speed was under 150 rpm. The internal diffusion resistance under the liquid–solid system with small beads can be neglected [42–44]. The PVP resin was composed of microspheres with small particles of 30 to 60 mesh, so the internal diffusion resistance was probably absent. To gain insight into the internal diffusion resistance and rate-controlling steps of the isomerization reaction, the kinetic experimental results were fitted by Weber–Morris's intra-particle diffusion equation [45,46]. The rate of intra-particle diffusion was a function of  $t^{0.5}$  and can be defined as follows:

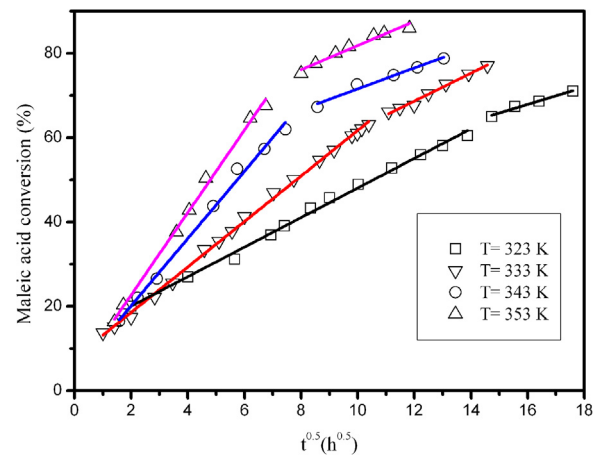
$$\text{maleic acid conversion (\%)} = k_d t^{0.5} + I \quad (3)$$

where, diffusion constant  $k_d$  can be obtained by plotting maleic acid conversion (%) against time ( $t^{0.5}$ ). The intercept value  $I$  represents the resistance to mass transfer in the intra-particle diffusion. In the equation, if the plot is linear and passes through the origin, pore diffusion controls the rate of mass transfer. Otherwise, chemical reaction or film-diffusion will control the rate of mass transfer [47–49].

As shown in Fig. 4 and Table 1, the plots for intra-particle diffusion model for isomerization of maleic acid to fumaric acid at four different temperatures were straight lines at initial and subsequent stages, but do not pass through the origin. This finding indicates that the chemical reaction or film-diffusion mechanism was the rate-controlling step in the whole reaction process. This reaction was a multi-step heterogeneous catalytic reaction, so chemical reaction

**Table 1**  
Fitting constants for catalyzed isomerization reaction by PVP resin using Weber–Morris model equation.

PVP resin (K)	Initial stage			Subsequent stage		
	$k_d$	$I$	$R^2$	$k_d$	$I$	$R^2$
323	3.51	13.03	0.995	2.04	35.26	0.977
333	5.40	7.77	0.998	3.32	28.82	0.986
343	7.98	4.18	0.993	2.47	46.88	0.965
353	9.78	3.12	0.996	2.87	53.17	0.958



**Fig. 4.** Intra-particle diffusion plot for catalyzed isomerization reaction by PVP resin at four different temperatures.

and film-diffusion possibly coexisted. At the initial stage, the value of  $I$  decreased with the increase in temperature, approaching the origin. It indicated that chemical reaction had an important role in controlling the overall rate in this stage. At the subsequent stage, the value of  $I$  almost increased with the increase in temperature, indicating that film-diffusion was mainly the rate-controlling step in the subsequent stage because of less active sites of resin and less accessibility, which enlarged the resistance of mass transfer after the reaction lasting for a period.

Obviously, the overall reaction was influenced by chemical reaction and external mass diffusion. Although many studies have suggested that kinetics under the absence of mass transfer limitation was reliable [50], kinetics still had certain significance in the presence of mass transfer limitation. The experiments were fitted using simplified first-order model (Eq. (4)) and second-order model (Eq. (5)). The residual sum of squares (RSS) could be defined as Eq. (6) to evaluate the two kinetic equations.

$$q_t = q_e (1 - \exp(-k_1 t)) \quad (4)$$

$$q_t = \frac{k_2 t q_e^2}{1 + k_2 t q_e} \quad (5)$$

$$\text{RSS} = \sum_{i=1}^n (q_{e,\text{fit}} - q_{e,\text{exp}})^2 \quad (6)$$

where  $q_e$  and  $q_t$  are the maleic acid conversion (%) at equilibrium and at  $t$  point, respectively (h).  $k_1$  (g/mmol/h) and  $k_2$  (g/mmol/h) are the constants in the first-order and second-order equations, respectively, which are both related to the conversion rate.  $q_{e,\text{fit}}$  and  $q_{e,\text{exp}}$  are the maleic acid equilibrium conversion (%) for model fitting and test measurement, respectively. Experimental results were compared with the first-order and second-order model in Fig. 3. The kinetic parameters were obtained and listed in Table 2. In all cases, second-order kinetic model fitted better than the first one with higher correlative coefficients ( $R^2$ ) and smaller values of RSS.

Meanwhile, the apparent activation energy and pre-exponential factor of the overall reaction were determined by the Arrhenius equation (Eq. (7)) as follows:

$$K_r = A \exp\left(\frac{-E_a}{RT}\right) \quad (7)$$

where  $T$  is the absolute temperature (K);  $R$  is the universal gas constant (J/molK); and  $K_r$ ,  $A$ , and  $E_a$  stand for the reaction rate [ $\mu\text{mol}/(\text{g s})$ ], rate constant ( $\text{s}^{-1}$ ), pre-exponential factor ( $\text{s}^{-1}$ ), and apparent activation energy (kJ/mol), respectively. The  $K_r$  values could be calculated by reaction rates and reactant conversion.



**Table 2**  
Parameters of first-order and second-order models for catalyzed isomerization reaction by PVP resin.

Model temperature (K)	First-order				Second-order			
	$q_{e,fit}$	$k_1 \times 10^{-2}$	$R^2$	RSS	$q_{e,fit}$	$k_2 \times 10^{-4}$	$R^2$	RSS
323	65.617	1.653	0.839	39.281	77.830	2.586	0.898	24.925
333	73.542	2.186	0.913	38.813	87.742	3.048	0.952	21.679
343	74.491	3.890	0.945	27.368	85.675	5.993	0.981	9.504
353	82.852	4.374	0.965	20.817	97.614	5.371	0.984	9.604

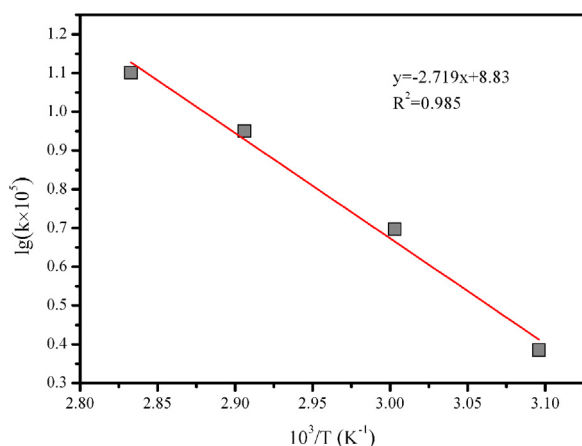
Fig. 5 shows the Arrhenius plot with  $R^2 = 0.985$  for the catalyzed isomerization of maleic acid to fumaric acid using PVP resin. According to the slope of the Arrhenius plot, we calculated that  $A$  was  $6.76 \times 10^8 \text{ s}^{-1}$ , and  $E_a$  was 226.06 kJ/mol. The apparent activation energy is the minimum energy required to overcome the potential barrier to start the reaction. The activation energy ( $E_a = 226.06 \text{ kJ/mol}$ ) reflects the substantial influence of temperature on the reaction rate.

### 3.4. Effect of salt

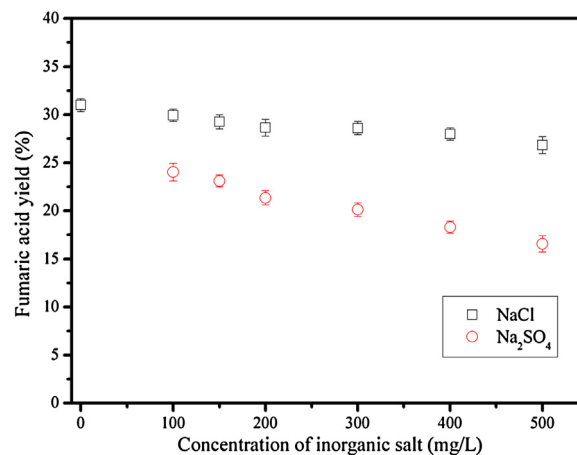
The solution of industrially produced maleic acid has many kinds of salts, the main components of which are  $\text{Na}_2\text{SO}_4$  and  $\text{NaCl}$  [20]. The co-existing inorganic salts may affect the catalytic performance. Thus, it was important to evaluate the influence of inorganic salts on the reaction catalyzed by PVP resin. The results of this evaluation are shown in Fig. 6. The fumaric acid (%) decreased as the concentration of inorganic salt increased from 100 mg/L to 500 mg/L because of the competing effect between the anions and PVP resin. This competing effect has also been reported in other studies [51]. PVP cation partially interacted with chloride anion and sulfate anion, partially resulting in the PVP cation not being able to approach the  $\text{C}=\text{C}$  double bond of the maleic acid moiety to yield S2 (Scheme 1). Therefore, chloride anion and sulfate anion affected the form of fumaric acid, resulting in the decline of fumaric acid (%). Compared with chloride anion, sulfate anion could bond with much more PVP cations because of its higher affinity [52], resulting in lower fumaric acid (%) in  $\text{Na}_2\text{SO}_4$  solution than in  $\text{NaCl}$  solution.

### 3.5. Regeneration and recyclability

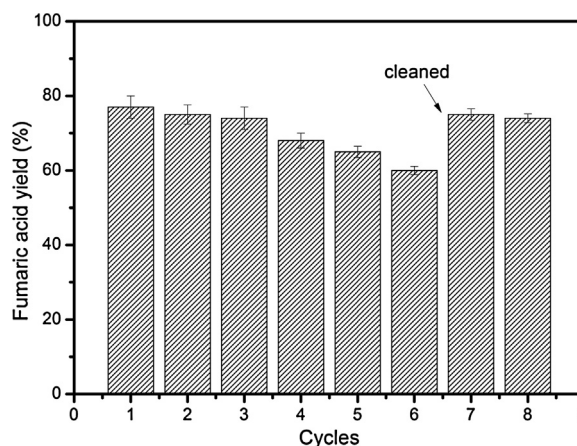
The regeneration and recyclability of PVP resin were investigated by repeating the catalytic reaction eight times (Fig. 7). In the first three cycles, catalytic performance was steady, and the fumaric acid yield was close to 78%. However, the fumaric acid



**Fig. 5.** Arrhenius plot of catalyzed isomerization reaction using PVP resin at four different temperatures.



**Fig. 6.** Effect of salt on the catalyzed isomerization reaction using PVP resin (reaction temperature of 333 K, catalyst dosage of 0.1 g, and 100 mL of 200 mg/L maleic acid solution, and reaction time of 48 h).



**Fig. 7.** Effect of regeneration cycles on the performance of catalyzed isomerization reaction using PVP resin (reaction temperature of 333 K, and catalyst dosage of 0.1 g, and 100 mL of 200 mg/L maleic acid solution).

yield decreased to 60% after six consecutive cycles, which was similar to the study [53]. This result was ascribed to the adsorption of maleic acid and fumaric acid by resin that covered partial active sites of the resin. Consequently,  $\text{NaOH}$  solution (0.1 M) was used as regenerant to remove them at the 7th cycle. After regeneration, the fumaric acid yield was recovered from 60% to 75%, which showed highly reusable performance without any loss in the catalytic activity. Therefore, PVP resin is a promising catalyst with high reusability for application on isomerization of maleic acid to fumaric acid.

## 4. Conclusions

PVP resin was used for the first time to catalyze isomerization of maleic acid to fumaric acid and it showed excellent catalytic performance. Reaction temperature and pH had an important role in

the yield of fumaric acid. Almost 86% conversion was obtained at 353 K and the optimized pH was 1.5. Fumaric acid yield (%) evidently decreased when pH was less than 1.5 and more than 1.5, which were determined by the degree of ionization of maleic acid. The overall reaction rate showed a second-order kinetic equation to the conversion of maleic acid compared with the first-order kinetic equation in the kinetic study. The apparent activation energy calculated for the overall reaction was 226.06 kJ/mol. The presence of inorganic salt could reduce the yield of fumaric acid, affecting the catalytic performance of PVP resin. Furthermore, the regenerate resin showed strong catalytic ability without any loss in the catalytic activity. PVP resin has a promising application in isomerization of maleic acid to fumaric acid.

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