

Reaction process and kinetics of the selective hydrogenation of resorcinol into 1,3-cyclohexanedione



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ABSTRACT

The reaction process and kinetics of the selective hydrogenation of resorcinol to 1,3-cyclohexanedione on Pd/C were studied. The optimized reaction conditions were as follows: mole ratio of sodium hydroxide to resorcinol, 1.1–1.2; catalyst loading, 15% (w/w); hydrogen pressure, 2 MPa; reaction temperature, 353 K; and stirring speed, >800 rpm. A kinetic model was then established based on a report that two hydrogenation pathways simultaneously control hydrogenation: one is the simultaneous addition of two hydrogen atoms while a van der Waals complex forms between the aromatic π -bond and the catalyst surface; the other is the sequential addition of a single hydrogen atom while a π/σ complex forms between a single double-bond and the catalyst surface. Subsequently, the model parameters and activation parameters were estimated. Results showed that the reaction was mainly controlled by the sequential pathway and that the addition of the first hydrogen atom was the rate-determining step. The activation energies for the sequential addition of two hydrogen atoms were 19.9 and 35.0 kJ/mol, whereas the activation energy for the simultaneous addition of two hydrogen atoms was 54.1 kJ/mol. The adsorption heats for resorcinol and 1,3-cyclohexanedione on the catalyst surface were 63.4 and 25.7 kJ/mol, respectively.

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1. Introduction

1,3-Cyclohexanedione (CHD), an important chemical intermediate, is widely used to synthesize pharmaceuticals, pesticides, cosmetics, and polymer additives [1–4]. It is generally manufactured by two ways based on the availability of raw materials. First is the aldol-condensation method, in which a γ -acylcarboxylic or α,β -unsaturated carboxylic acid ester with a ketone is used as starting material and reacted with a strongly basic condensing agent through intramolecular or intermolecular condensation to yield CHD [5–7]. Second is the hydrogenation method, in which resorcinol (RES) is used as a starting material and reduced to CHD by hydrogen or a hydrogen donor such as formate salt and isopropanol (also called the catalytic transfer hydrogenation process) with noble metal or nickel as a catalyst [8,9].

The selective hydrogenation of RES with hydrogen gas under pressure and alkaline conditions is the most effective industrial production method because of its simple reaction steps, high selectivity to CHD, and easy separation of the product [9–15]. An

alkaline atmosphere is essential to achieve a high selectivity to CHD. Under this condition, RES forms its sodium salt and only a 1:1 molar ratio of hydrogen is added to RES molecule. CHD is finally obtained by neutralizing the hydrogenation product with a strong acid [10,13–15]. A deep hydrogenation process occurs without alkali participation, and the final products are 1,3-cyclohexanediol or *m*-hydroxyl cyclohexanone [16]. The exact form of RES sodium salt during alkaline hydrogenation, *i.e.*, whether one or two hydroxyls of RES are neutralized by the alkali, is unknown. Few works have been conducted on the selective hydrogenation mechanism, and even the hydrogenation pathways involved are somewhat conflictly reported. For example, Thompson [14,15] proposed a monosodium salt pathway, whereas other studies [11,12] have reported the involvement of a bisodium salt pathway.

Most conventional metal catalysts for hydrogenation such as nickel, platinum, rhodium, and palladium are effective for the hydrogenation of RES to CHD [12,16]. Among them, Pd/C is the most favorable heterogeneous catalyst because it has higher reactivity and longer deactivation life than Raney Ni and is relatively inexpensive compared with other noble metals [17,18]. However, studies on the optimization of RES hydrogenation and its reaction kinetics, which is crucial to industrial design and manufacturing, are limited. In the present research, we systemically

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optimized the reaction process of the selective hydrogenation of RES to CHD using Pd/C as a catalyst, including the molar ratio of NaOH to RES, catalyst amount, reaction pressure, temperature, and stirring speed. An adsorption-reaction mathematical model based on the kinetics of the reaction was then proposed to estimate the relevant kinetics parameters. The results were analyzed for a better understanding of the reaction.

2. Experimental

The hydrogenation of RES was performed at 0.5–4 MPa and 338 K to 393 K in a 100 ml stainless steel reactor, which was immersed in an insulated, constant-temperature oil bath and stirred with a magnetic stirrer to maintain a constant temperature within ± 0.5 K. For each entry, a predetermined amount of Pd/C [Baoji City Ruike Pharmaceutical & Chemical Co., Ltd., China; water content, 53 wt%; Pd loading, 3 wt% (dry weight); specific surface area, ca. 1500 m²/g], RES (AR, Rugao Jinling Reagent Factory, China), sodium hydroxide, and distilled water were introduced into the reactor, which was purged with 1 MPa of N₂ to remove air and filled with constant 2 MPa H₂ by a connected H₂ cylinder with a back-pressure valve. The reactor was then immersed in the preheated oil bath. Approximately 0.1 ml of the reaction solution was withdrawn at appropriate time intervals, neutralized with an adequate amount of concentrated hydrochloric acid, freeze dried, and extracted with 1 ml of acetonitrile for quantitative analysis using a gas chromatography equipped with a FID detector [19].

3. Results

To optimize the hydrogenation process of RES, several reaction parameters were considered, including alkali amount, catalyst loading, reaction pressure, temperature, and stirring speed for the removal of external diffusion.

3.1. Alkali amount

NaOH was used for the alkalization of RES during hydrogenation, and NaOH/RES molar ratios ranging from 0.9 to 1.5 was investigated (Fig. 1). Results showed that RES conversion is almost 100% and remains stable while the molar ratio of NaOH/RES is below 1.2. Further increased NaOH amount reduces the hydrogenation of RES. The same trend is found for the CHD yield. A maximum yield of ca. 90% is obtained when the NaOH/RES molar ratio is 1.2.

The exact hydrogenation mechanism of RES in the presence of an alkali is still unclear. Our experimental results and other laboratories' work [9,10,13–15] show that the NaOH/RES molar ratio of 0.9–1.2 provides a favorable alkali amount, indicating that RES is alkalized to its monosodium salt form apart from its bisodium salt form before hydrogenation. Therefore, a reaction pathway for the alkali-assisted hydrogenation of RES is proposed as shown in Scheme 1: RES is first alkalized to its monosodium salt,

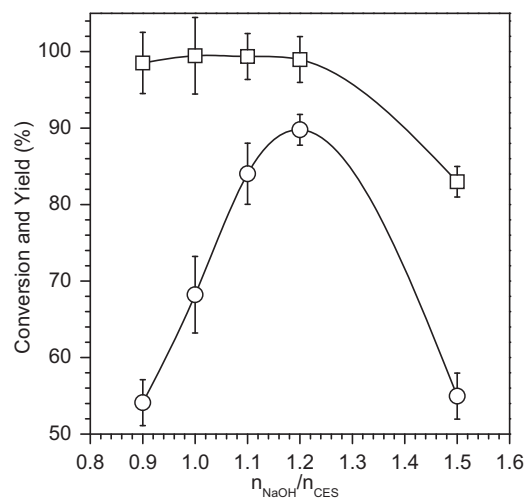


Fig. 1. Effect of NaOH amount on the selective hydrogenation of resorcinol (\square conversion of RES; \circ yield of CHD). Reaction conditions: $T = 353$ K, $P = 2.0$ MPa, ω (Pd/C) = 25%, $c_{\text{RES}} = 0.830$ mol/l, $t = 240$ min.

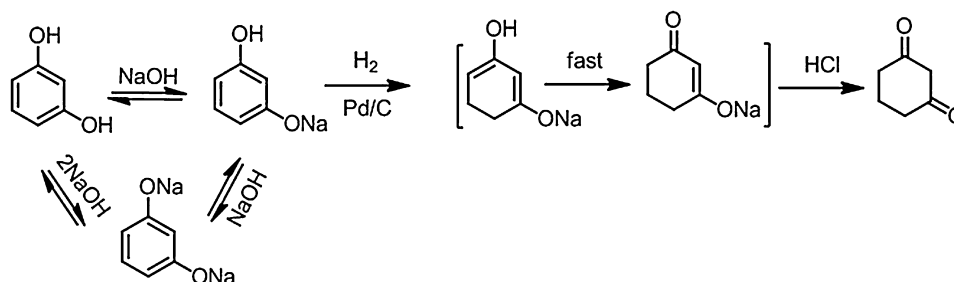
thereby forming a phenolic oxygen negative ion. The density of the electron cloud in the benzene ring thus increases, and electrophilic hydrogenation easily occurs. When one hydrogen molecule is added to a benzene ring, two C=C bonds remain. One forms a ketone by enol isomerization with the adjacent hydroxyl. The other forms a stable low-energy p - π conjugate structure with the negative oxygen ion, which blocks its further hydrogenation to a higher-energy alcohol anion. After being neutralized with hydrochloric acid, the newly-formed hydroxyl and its adjacent C=C bond produce another ketone by enol isomerization. Hence, selective hydrogenation to CHD can be achieved.

3.2. Catalyst loading

Pd/C catalyst loadings of 5%, 10%, 15%, 25%, and 35% (mass ratio of wet Pd/C to RES) were investigated (Fig. 2). When Pd/C loading is less than 15%, it is not enough for the selective hydrogenation and leads to low conversion of RES. A higher Pd/C loading only slightly affects the conversion and yield; besides, it will increase the cost of industrial production. Therefore, the optimized Pd/C loading is 15%, which corresponds to 0.21 wt% of Pd to RES.

3.3. Initial concentration of RES

The initial concentration of RES may considerably affect the reaction rate and selectivity. As shown in Fig. 3, the initial hydrogen-uptake rate peaks when the initial concentration of RES is 1.42 mol/l. With increased initial concentration of RES to 1.86 mol/l, the initial hydrogenation rate is the lowest. The effect of the initial concentration of RES on CHD selectivity only slightly changes compared with that on the reaction rate. The maximum



Scheme 1. Possible existence forms of resorcinol sodium salts during the hydrogenation process in an alkali solution.

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