

Article

# Liquid-Phase Hydrogenation of Maleic Acid over Pd/Al<sub>2</sub>O<sub>3</sub> Catalysts Prepared via Deposition–Precipitation Method

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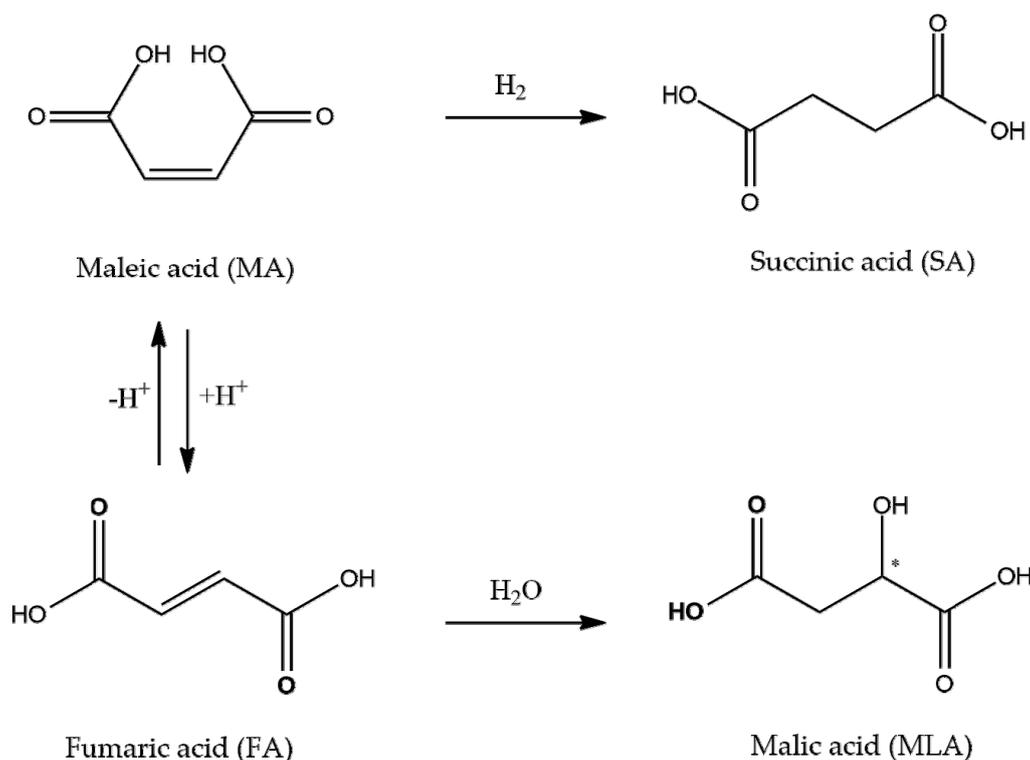
**Abstract:** Succinic acid (SA) is a valuable raw material obtained by hydrogenation of maleic acid (MA). The product selectivity of this reaction is highly dependent on the reaction conditions. This study therefore investigated the effect of the reaction temperature, hydrogen pressure, and reaction time on the liquid-phase hydrogenation of MA by a Pd/Al<sub>2</sub>O<sub>3</sub> catalyst. Complete conversion of MA and 100% selectivity for SA were achieved at a temperature of 90 °C, H<sub>2</sub> pressure of 5 bar, and reaction time of 90 min. Fumaric acid (FA) was formed as an intermediate material by hydrogenation of MA under nonoptimal conditions. The impact of the percentage of Pd dispersion and phase of the Al<sub>2</sub>O<sub>3</sub> support ( $\gamma$ ,  $\theta + \alpha$ , and  $\alpha$ ) was also examined. The Pd/Al<sub>2</sub>O<sub>3</sub> catalyst with 29.8% dispersion of Pd and  $\gamma$  phase of Al<sub>2</sub>O<sub>3</sub> exhibited the best catalytic performance. Thus, catalytic activity depends not only on the amount of Pd dispersion but also on the physicochemical properties of Al<sub>2</sub>O<sub>3</sub>.

**Keywords:** hydrogenation; succinic acid; supported catalyst; Pd catalyst

## 1. Introduction

The growth of the petrochemical industry has brought about environmental problems such as industrial waste, pollution, and global warming. Therefore, many researchers have been investigating sustainable and renewable resources. In this regard, succinic acid (SA) has attracted attention as an eco-friendly raw material for the production of biodegradable plastics and biosolvents. SA is widely used as an intermediate material in the production of high value products such as  $\gamma$ -butyrolactone, 1,4-butanediol, and tetrahydrofuran [1,2]. It is usually obtained by hydrogenation of maleic anhydride (MAN), although the product of this reaction varies depending on the reaction conditions. Several researches have investigated various catalysts for this reaction, such as Ru/C, Ni/HY-Al<sub>2</sub>O<sub>3</sub>, Pd/C, Pd/SiO<sub>2</sub>, Ni/TiO<sub>2</sub> and Pd/Al<sub>2</sub>O<sub>3</sub> [3–9]. The reaction pathways of hydrogenation of maleic acid (MA) are shown in Figure 1. Kim et al. reported a yield of 99.97% SA using Pd/C as the catalyst and conducting the reaction under 1.0 MPa of H<sub>2</sub> at 90 °C for 150 min [3]. Torres et al. reported achieving 100% selectivity for succinic anhydride through the reaction catalyzed by a mesoporous Ni/TiO<sub>2</sub> catalyst at low temperature [8]. Yuan et al. reported achieving MA conversion of 98% and succinic anhydride selectivity of 99% using Pd/Al<sub>2</sub>O<sub>3</sub> catalyst under 1.0 MPa of H<sub>2</sub> pressure and 1,4-dioxane as solvent [5]. Among the various catalysts, the Pd/Al<sub>2</sub>O<sub>3</sub> catalyst has an advantage for the chemical industry due to the high thermal stability and high dispersion of Pd [10,11]. However, few studies have been performed on the optimization of reaction conditions for the hydrogenation of maleic acid (MA)

to SA over a Pd/Al<sub>2</sub>O<sub>3</sub> catalyst. In our previous study, we reported that the particle size distribution of Pd is influenced by the physicochemical properties of Al<sub>2</sub>O<sub>3</sub> (specific surface area and surface functional groups) and catalyst preparation conditions (pH, solution temperature, and reduction agent) [12,13]. Herein, we investigated the effect of reaction temperature (*T*), H<sub>2</sub> pressure (*P*<sub>H<sub>2</sub></sub>), and reaction time (*t*) on the liquid-phase hydrogenation of MA over a Pd/Al<sub>2</sub>O<sub>3</sub> catalyst. The catalytic activities of Pd/Al<sub>2</sub>O<sub>3</sub> with varying percentage of Pd dispersion and Al<sub>2</sub>O<sub>3</sub> phase ( $\gamma$ ,  $\theta + \alpha$ , and  $\alpha$ ) were also compared. Finally, the reusability of the Pd/Al<sub>2</sub>O<sub>3</sub> catalyst was assessed.



**Figure 1.** Reaction pathways in hydrogenation of maleic acid in water.

## 2. Experiment

### 2.1. Catalyst Preparation

The catalyst support, Al<sub>2</sub>O<sub>3</sub> ( $\geq 99\%$ , Alfa Aesar,  $\gamma$  phase, average particle size: 20 nm), was dried at 105 °C for 4 h and calcined at various temperatures (900, 1100, and 1150 °C) for 4 h. The Pd/Al<sub>2</sub>O<sub>3</sub> catalysts, containing 5 wt % Pd, were prepared by the deposition–precipitation method. The detailed procedure has been described in our previous research [12]. Briefly, Al<sub>2</sub>O<sub>3</sub> was dispersed in the Pd precursor solution at 60 °C, and the pH was adjusted using 0.25 M NaOH solution. Reduction of the catalyst was carried out in the liquid phase using formalin solution (10 wt %, Sigma Aldrich, St. Louis, MO, USA). The prepared Pd/Al<sub>2</sub>O<sub>3</sub> catalysts are denoted as Pd/Al<sub>2</sub>O<sub>3</sub> (X)<sub>p</sub>HY, where X is the heat treatment temperature of the Al<sub>2</sub>O<sub>3</sub> support, and Y is the pH. The physicochemical properties of the catalysts are summarized in Table 1.

**Table 1.** Summary of physicochemical properties of Pd/Al<sub>2</sub>O<sub>3</sub> catalysts [12,13].

Catalysts	Pd/Al <sub>2</sub> O <sub>3</sub> (105)_pH 7.5	Pd/Al <sub>2</sub> O <sub>3</sub> (900)_pH 7.5	Pd/Al <sub>2</sub> O <sub>3</sub> (900)_pH 11.5	Pd/Al <sub>2</sub> O <sub>3</sub> (1100)_pH 7.5	Pd/Al <sub>2</sub> O <sub>3</sub> (1150)_pH 7.5
Al <sub>2</sub> O <sub>3</sub> phase <sup>1</sup>	γ	γ	γ	θ + α	α
Al <sub>2</sub> O <sub>3</sub> surface area <sup>2</sup>	195	146	146	54	6
Al <sub>2</sub> O <sub>3</sub> Pore volume <sup>2</sup>	0.82	0.62	0.62	0.28	0.007
Al <sub>2</sub> O <sub>3</sub> Acidity (mmol/g) <sup>3</sup>	0.47	0.37	0.37	0.22	0.07
Pd dispersion (%) <sup>4</sup>	20.6	29.8	13.1	11.0	2.9

<sup>1</sup> X-ray diffraction, <sup>2</sup> Brunauer–Emmett–Teller analysis of N<sub>2</sub> adsorption–desorption, <sup>3</sup> NH<sub>3</sub> temperature programmed desorption, <sup>4</sup> CO chemisorption.

## 2.2. Hydrogenation of Maleic Acid

Liquid-phase hydrogenation of maleic acid was conducted in a 100 mL stainless steel autoclave. MA (0.29 mol), 46 g distilled water, and 0.1 g Pd/Al<sub>2</sub>O<sub>3</sub> were placed in the autoclave. The reactor was purged with nitrogen three times to remove air, and hydrogen was then used to purge out nitrogen. The sealed autoclave was pressurized to the desired pressure and heated to the desired temperature, and the reaction mixture was stirred at 700 rpm. The catalytic reaction was carried out for 15–90 min. The reaction products were analyzed by high-performance liquid chromatography (HPLC, Shimadzu Co. Model Prominence) equipped with a refractive index detector and Agilent Hi-Plex H (7.7 mm × 300 mm × 8 μm). The mobile phase was 5 mM H<sub>2</sub>SO<sub>4</sub> with a flow rate of 6 mL min<sup>-1</sup>. The MA, SA, fumaric acid (FA), and malic acid (MLA) standards (Sigma Aldrich) were analytical grade and used without purification. The reaction was conducted at varying temperature, hydrogen pressure, and reaction time. Conversion and selectivity were calculated as follows:

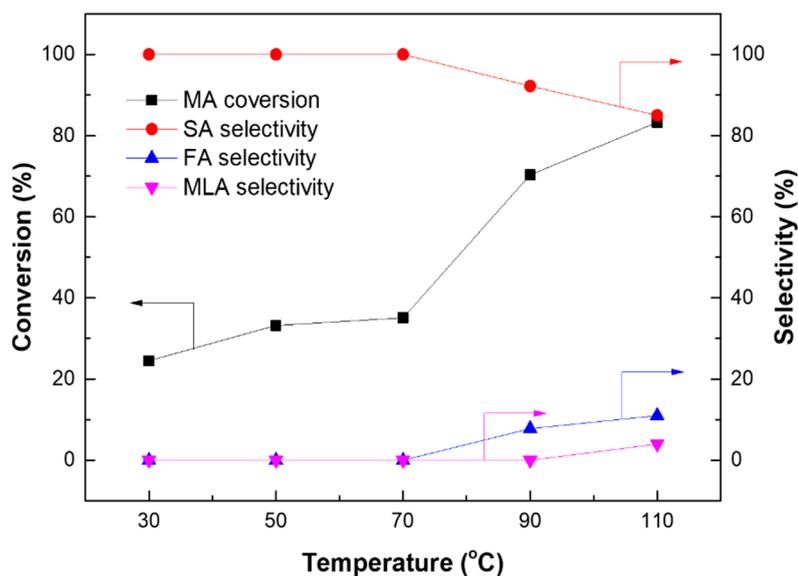
$$\text{Conversion (\%)} = \frac{\text{Initial mole of MA} - \text{final mole of MA}}{\text{Initial mole of MA}} \times 100 \quad (1)$$

$$\text{Selectivity (\%)} = \frac{\text{mole of desired product}}{\text{Initial mole of MA} - \text{final mole of MA}} \times 100 \quad (2)$$

## 3. Results and Discussion

### 3.1. Effect of Reaction Temperature

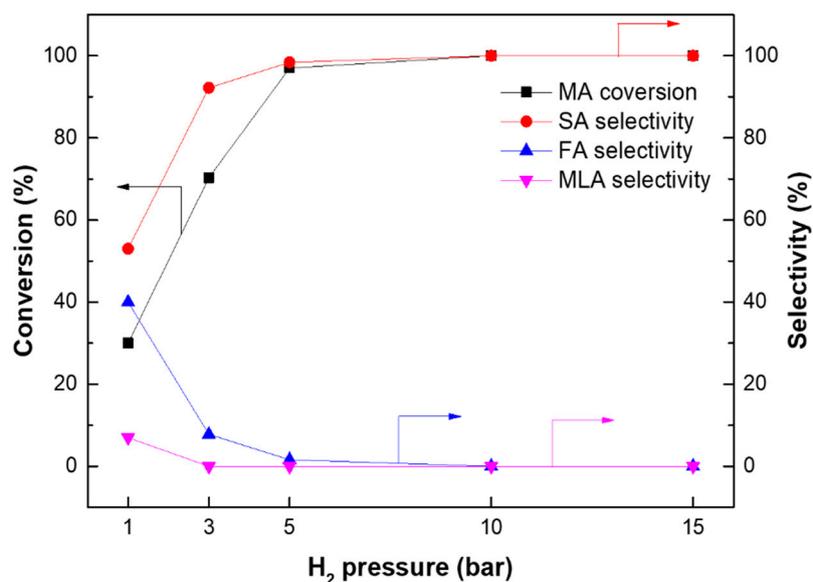
The effect of reaction temperature on MA hydrogenation over the Pd/Al<sub>2</sub>O<sub>3</sub> (900)\_pH7.5 catalyst was investigated within the range of 30–110 °C (Figure 2). As the reaction temperature increased, the conversion of MA increased, while the selectivity for SA decreased from 100% to 85%. At temperatures above 90 °C, the selectivity for FA and MLA slightly increased. It has been reported that, at high temperature, MA is unstable and can isomerize to the more stable FA [14]. On the other hand, the isomer FA undergoes hydration to form MLA at high temperature. Thus, 90 °C is the optimal temperature for high conversion of MA and selectivity for SA.



**Figure 2.** Effect of reaction temperature on maleic acid (MA) hydrogenation over Pd/Al<sub>2</sub>O<sub>3</sub> (900)<sub>pH7.5</sub> at  $P_{H_2} = 3$  bar and  $t = 60$  min.

### 3.2. Effect of H<sub>2</sub> Pressure

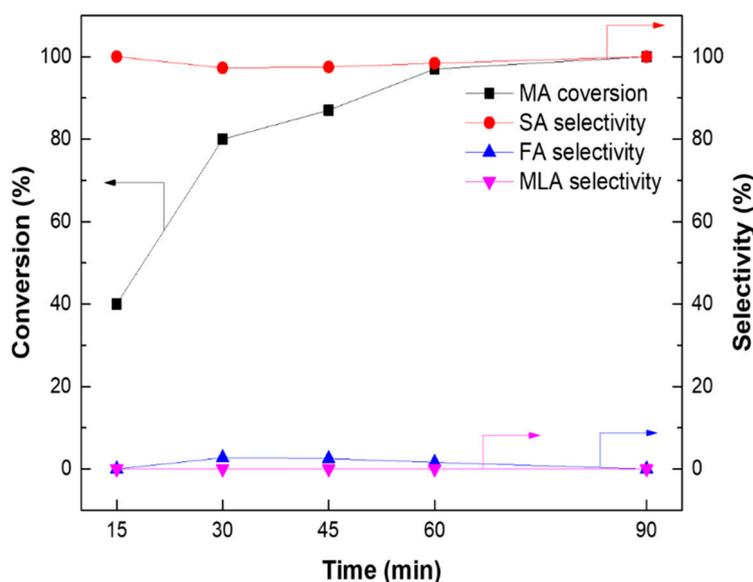
The effect of H<sub>2</sub> pressure on MA hydrogenation over the Pd/Al<sub>2</sub>O<sub>3</sub> (900)<sub>pH7.5</sub> catalyst was investigated within the range of 1–15 bar (Figure 3). MA conversion and SA selectivity increased from 30% to 100% and 53% to 100%, respectively, as the H<sub>2</sub> pressure increased from 1 to 15 bar. Within the range of 1–5 bar, the selectivity for FA gradually decreased from 40% to 1.6%. As demonstrated above, FA can be produced by isomerization of MA at high temperature. However, FA is predominantly produced at low H<sub>2</sub> pressure, indicating that FA is an intermediate in the conversion of MA to SA. Kim et al. reported that the formation of FA is determined by the relative reaction rates of hydrogenation and protonation [3]. Protonation occurs faster than hydrogenation at H<sub>2</sub> pressures lower than 5 bar but slower at higher pressures.



**Figure 3.** Effect of H<sub>2</sub> pressure on MA hydrogenation over Pd/Al<sub>2</sub>O<sub>3</sub> (900)<sub>pH7.5</sub> at  $T = 90$  °C and  $t = 60$  min.

### 3.3. Effect of Reaction Time

The effect of reaction time on MA hydrogenation over the Pd/Al<sub>2</sub>O<sub>3</sub> (900)\_pH7.5 catalyst was investigated within the range of 15–90 min at a fixed reaction temperature of 90 °C and H<sub>2</sub> pressure of 5 bar (Figure 4). The conversion of MA dramatically increased up to 80% upon increasing the reaction time from 15 to 30 min. It subsequently changed more gradually as the reaction time was prolonged from 30 to 90 min. The selectivity for FA initially increased between 15 and 30 min and then decreased as the reaction time increased from 30 to 90 min. Thus, 100% MA conversion and SA selectivity were achieved at a temperature of 90 °C, H<sub>2</sub> pressure of 5 bar, and reaction time of 90 min.

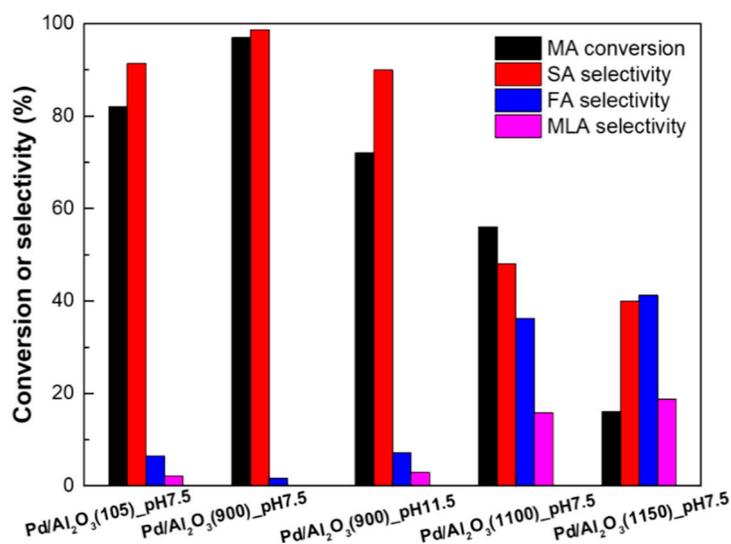


**Figure 4.** Effect of reaction time on MA hydrogenation over Pd/Al<sub>2</sub>O<sub>3</sub> (900)\_pH7.5 at  $T = 90$  °C and  $P_{H_2} = 5$  bar.

### 3.4. Effect of Al<sub>2</sub>O<sub>3</sub> Support Properties and Pd Dispersion

The effect of the properties of the Al<sub>2</sub>O<sub>3</sub> support and dispersion of Pd on the catalytic activity for liquid-phase hydrogenation of MA were investigated under the following conditions:  $T = 90$  °C,  $P_{H_2} = 5$  bar,  $t = 60$  min, and stirring rate = 700 rpm. The physicochemical properties of the different Pd/Al<sub>2</sub>O<sub>3</sub> catalysts are summarized in Table 1. The order of decreasing catalytic activity was Pd/Al<sub>2</sub>O<sub>3</sub> (900)\_pH7.5 > Pd/Al<sub>2</sub>O<sub>3</sub> (105)\_pH7.5 > Pd/Al<sub>2</sub>O<sub>3</sub> (900)\_pH11.5 > Pd/Al<sub>2</sub>O<sub>3</sub> (1100)\_pH7.5 > Pd/Al<sub>2</sub>O<sub>3</sub> (1150)\_pH7.5 (Figure 5). The conversion of MA and selectivity for SA increased with increasing dispersion (i.e., decreasing particle size) of Pd, indicating that Pd was the more active species in the hydrogenation of MA. The dispersion of Pd in the Pd/Al<sub>2</sub>O<sub>3</sub> (900)\_pH11.5 and Pd/Al<sub>2</sub>O<sub>3</sub> (1100)\_pH7.5 catalysts was similar at 13.1% and 11.0%, respectively. However, the catalysts exhibited significantly different MA conversion and SA selectivity owing to the difference in the properties of the Al<sub>2</sub>O<sub>3</sub> support. It has been reported that the isomerization of MA to FA can occur without a catalyst and is strongly affected by the concentration of maleic acid, the reaction temperature, and the pH of the solution [15]. Al<sub>2</sub>O<sub>3</sub> in the Pd/Al<sub>2</sub>O<sub>3</sub> (900)\_pH11.5 catalyst was in the  $\gamma$  phase, which has a large specific surface area and strong acid sites, whereas in the Pd/Al<sub>2</sub>O<sub>3</sub> (1100)\_pH7.5 catalyst, it was in the  $\theta + \alpha$  phase, which has a small specific surface area and weak acid sites. The physicochemical properties of the Al<sub>2</sub>O<sub>3</sub> support affect the adsorption strength of the reactant and Pd nanoparticles on the active sites. Al<sub>2</sub>O<sub>3</sub> in the  $\gamma$  phase can provide a large number of active sites for the hydrogenation reaction and allows increased retention time on the catalyst surface, resulting in high conversion of MA and high selectivity for SA. In contrast, the low Pd dispersion, small specific surface area, and weak acid sites in Pd/Al<sub>2</sub>O<sub>3</sub> catalysts with Al<sub>2</sub>O<sub>3</sub> in the  $\theta + \alpha$  or  $\alpha$  phase can cause reduced retention time

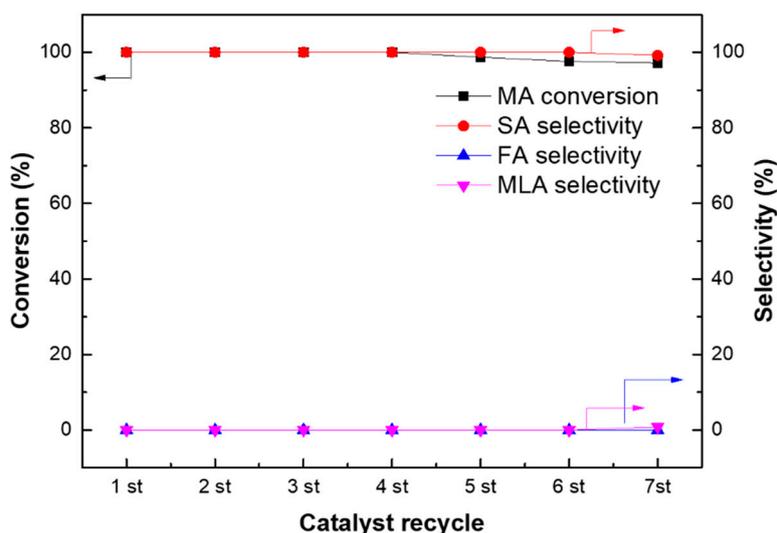
on the catalyst surface, resulting in low efficiency for the hydrogenation reaction. These results suggest that a decrease in the retention time of MA and H<sub>2</sub> on the catalyst surface leads to a lower reaction rate.



**Figure 5.** Effect of Al<sub>2</sub>O<sub>3</sub> phase and Pd dispersion on MA hydrogenation at  $T = 90\text{ }^{\circ}\text{C}$ ,  $P_{\text{H}_2} = 5\text{ bar}$ , and  $t = 60\text{ min}$ .

### 3.5. Reusability of Pd/Al<sub>2</sub>O<sub>3</sub> (900)\_pH 7.5 Catalyst in Hydrogenation of MA

Reusability and stability are important factors in the chemical industry. The reusability of the Pd/Al<sub>2</sub>O<sub>3</sub> (900)\_pH7.5 catalyst was therefore investigated. Liquid-phase hydrogenation of MA was carried out under optimized reaction conditions. After each reaction, the catalyst was separated from the reactant and washed with deionized water. The conversion of MA and selectivity for SA did not decrease significantly for seven cycles, indicating that the Pd/Al<sub>2</sub>O<sub>3</sub> (900)\_pH7.5 catalyst was stable during the liquid-phase hydrogenation of MA (Figure 6).



**Figure 6.** Reusability of Pd/Al<sub>2</sub>O<sub>3</sub> (900)\_pH7.5 catalyst in MA hydrogenation at  $T = 90\text{ }^{\circ}\text{C}$ ,  $P_{\text{H}_2} = 5\text{ bar}$ , and  $t = 90\text{ min}$ .

## 4. Conclusions

Liquid-phase hydrogenation of MA to SA with different Pd/Al<sub>2</sub>O<sub>3</sub> catalysts was investigated, focusing mainly on the effect of two factors on catalytic activity and selectivity: reaction conditions

and physicochemical properties of the catalyst. The effect of the reaction conditions was investigated by varying the reaction temperature,  $H_2$  pressure, and reaction time. Depending on the reaction conditions, FA was formed as an intermediate or final product through isomerization of MA. Under the optimal reaction conditions of  $T = 90\text{ }^\circ\text{C}$ ,  $P_{H_2} = 5\text{ bar}$ ,  $t = 90\text{ min}$ , 100% MA conversion and 100% SA selectivity were achieved using the Pd/ $Al_2O_3$  (900)\_pH7.5 catalyst. The effect of the  $Al_2O_3$  phase and Pd dispersion were also investigated. Catalytic activity and selectivity were found to increase with Pd dispersion. The characteristics of the  $Al_2O_3$  phase strongly affected the adsorption strength of the reactant and Pd nanoparticles on the active sites and, consequently, the catalytic activity.

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