Cumene hydroperoxide hydrogenation over Pd/C catalysts

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ARTICLE INFO

ABSTRACT

Pd/C catalysts were prepared by wet impregnation using K_2PdCl_4 as precursor and their performance in hydrogenation of cumene hydroperoxide (CHP) was investigated. The catalytic activity was examined on the formaldehyde-reduced and on the hydrogen-reduced Pd/C catalysts. Results from XRD, TEM and CO chemisorption showed that reduction methods have a significant impact on the palladium particles size of resulting catalysts. Formaldehyde-reduced Pd/C catalyst has larger palladium particles than hydrogen-reduced Pd/C catalyst. Consequently, higher activity but lower selectivity to α-cumyl alcohol (CA) was obtained on formaldehyde-reduced Pd/C catalyst. Moreover, hydrogenation of CHP over hydrogen-reduced Pd/C catalyst can give similar CA selectivity to Na_2SO_3 reduction process, an industrial process for CA production. High rate of CHP conversion and CA selectivity can be obtained at an elevated temperature and H_2 pressure. Kinetics studies revealed that CHP hydrogenation is zero-order for CHP concentration and the activation energy was calculated to be 13.6 kJ/mol.

1. Introduction

Cumene hydroperoxide (CHP), a kind of typical organic peroxide, posses a potential hazard owing to its relatively weak oxygen–oxygen linkage. It may result in fire or explosion when it contacts with heat, acids, bases, metal, contaminants, etc. [1]. Besides the major application in producing phenol and acetone [2–4], CHP is also a source material for producing dicumyl peroxide (DCP). In the process of DCP production, CHP is catalyzed by dilute about 45 wt% NaOH [1] or reduced by sodium sulfite (Na_2SO_3) solution [5] to yield α-cumyl alcohol (CA). Both of them have the problem of pollution. As a more economical and environmental technology, catalytic hydrogenation of CHP to CA with the aid of a catalyst is promising.

In the field of fine chemical, especially in the hydrogenation process, carbon supported palladium catalysts (Pd/C) are the most widely used hydrogenation catalysts both in research laboratories of academia and the chemical industry [6]. Although many organic groups, such as C—X, C=C, C—O, C=O, can be hydrogenated over Pd/C catalysts, few studies on hydrogenation of hydroperoxides were reported. For example, Il'ina et al. [7] reported that pinanol can be prepared with high selectivity by the hydrogenation of pinane hydroperoxide on a Pd/C catalyst under mild conditions.

In this paper, hydrogenation of CHP was performed in a fix-bed reactor, using Pd/C catalyst with low Pd loading. The purpose of this study was to address: (i) comparing the performance of hydrogen reduction with Na_2SO_3 reduction; (ii) establishing the reduction method for Pd/C catalyst; (iii) establishing the reaction order and activation energy of CHP hydrogenation. Moreover, the catalysts were characterized by BET, CO chemisorption, XRD and TEM to correlate the physicochemical properties to the catalytic performance.

2. Experimental

2.1. Chemicals

CHP was obtained from Shanghai Gaoqiao Company, SINOPEC. The composition of the feedstock and product reduced by Na_2SO_3 is reported in Table 1. The other reagents, such as $PdCl_2$, KCl, $Na_2S_2SO_3$, KI, glacial acetic acid and formaldehyde were analytical grade and were supplied by Sinopharm Chemical Reagent Co., Ltd. Activated carbon was purchased from Shanghai Activated Carbon Co., Ltd. and treated by 35 wt% HNO_3 at 60 °C before utilization. Water used in the reaction was deionized. The purities of hydrogen used in the experiments were more than 99.99%.

2.2. Catalyst preparation

Pd/C catalysts used in the experiments were prepared by wet impregnation using K_2PdCl_4 (prepared from $PdCl_2$ and KCl) as precursor. Following impregnation, the sample was divided into two parts; one was directly reduced by formaldehyde at 80 °C with vigorous stirring. After reduction, the sample was washed by deionized water for several times and then dried in an oven at 120 °C for 2 h,

Table 1
Composition of CHP feedstock and product distribution of CHP reduced by Na_2SO_3.

Entry	Composition (mol%)				
	CHP	Cumene	CA	AP	α-MS
Feedstock	44.1	55.3	0	0.6	0
[a]Product	0	52.2	46.6	0.8	0.4

[a] Data from CA unit in Shanghai Gaoqiao Company Refinery Plant.

and the resulting catalyst was referred as Pd/C(FR). The other part was dried in an oven at 120 °C for 2 h and reduced in flowing hydrogen at 300 °C for 3 h; the resulting catalyst was referred as Pd/C(HR). The final Pd loadings of the Pd/C catalysts are determined using ICP-AES to be approximate 0.5 wt%.

2.3. Catalyst characterization

The specific surface area of the different catalysts was determined by nitrogen adsorption at −77 °C, according to the BET method using Micrometrics ASAP2010 apparatus.

Palladium dispersion was measured by CO chemisorption on a Micrometrics AutoChem II 2920 apparatus at room temperature, using a thermal conductivity detector (TCD) to monitor CO consumption and assuming a CO:Pd = 1:1 stoichiometric ratio. Prior to chemisorption, the catalyst was reduced in flowing hydrogen at 300 °C for 2 h and then treated in flowing helium for 1 h.

X-ray powder diffraction (XRD) patterns of all catalysts were recorded on a Rigaku D/Max 2550VB/PC X-ray diffractometer using Ni filtered Cu Kα radiation (λ = 0.15406 nm) with a scan range of 10–80° at 40 kV and 100 mA. Diffraction peaks of crystalline phases were compared with those of standard compounds reported in the JCPDS Data File.

TEM images of reduced catalysts were obtained on a JOEL JEM 2010 apparatus. Prior to observation, the catalysts were abraded to fine powder and then collected on holey carbon films supported on Cu grids by placing a few droplets of a suspension of the ground samples in alcohol on the grids, followed by drying at ambient conditions. The size distribution of all catalysts was determined by observing several areas of the grid. Several hundred particles visible on the micrographs were counted and the average value of

palladium particle size was calculated by the following equation:

$$\bar{d} = \frac{\sum n_i d_i}{\sum n_i} \tag{1}$$

where n_i is the number of particles of diameter d_i.

2.4. Catalytic activity test

Liquid phase hydrogenation of CHP was preformed in a vertical fixed-bed, continuous down-flow stainless micro-reactor (i.d. 8 mm, length 400 mm, Fig. 1) with a jacket. In a typical run, 0.5 g catalyst was diluted with 10 ml quartz sand (treated by strong hydrochloric acid and calcined in air at 700 °C for 3 h) and packed at the centre of the reactor. Moreover, one plug of quartz wool was used at the bottom of the reactor to avoid the leaching of catalyst. The reaction system was flushed with hydrogen gas and the system pressure was controlled by a back-pressure regulator. The temperature was maintained through a circulating constant temperature bath. After the desired reaction pressure and temperature were attained, CHP in cumene solution was pumped into the reactor at a flow rate of 0.15 ml/min while hydrogen gas was at a flow rate of 90 ml/min.

2.5. Product analysis

The conversion of CHP was measured by iodimetry and the hydrogenation products were analyzed using a gas chromatography (HP-6890) with a flame ionization detector (FID) and a 30.0 m × 32 mm × 0.3 μm capillary column (HP-1). The injection temperature and detect temperature were both at 200 °C with a temperature programmed from 100 to 200 °C at a ramp temperature rate of 10 °C/min.

CHP conversion and CA selectivity were calculated using the following equations:

$$CHP\,conversion\,[\%] = \frac{Initial\,CHP\,[wt.\%] - Final\,CHP\,[wt.\%]}{Initial\,CHP\,[wt.\%]} \times 100\% \tag{2}$$

$$CA\,selectivity\,[mol\%] = \frac{CA\,[mol\%]}{Initial\,CHP\,[mol\%] - Final\,CHP\,[mol\%]} \times 100\% \tag{3}$$
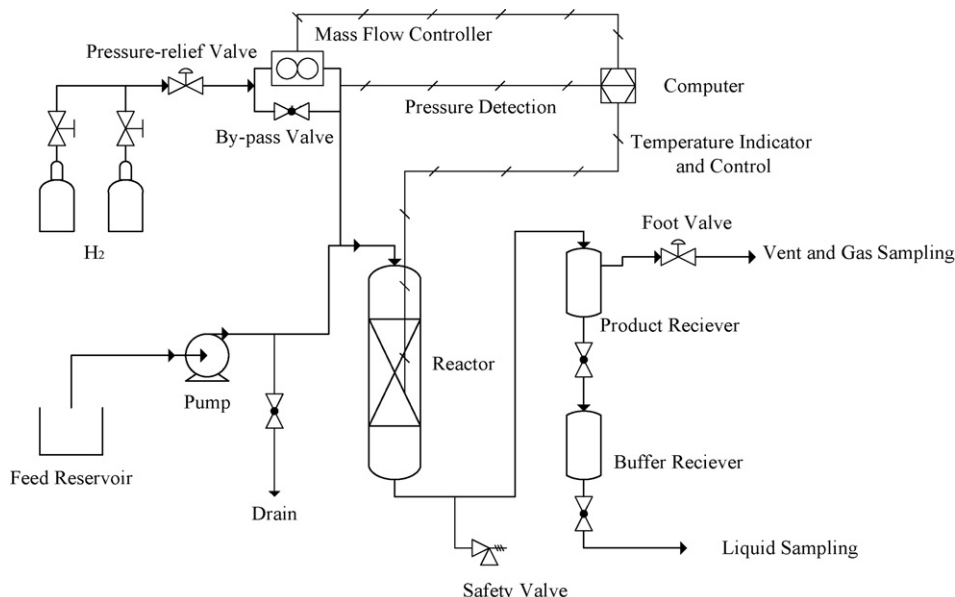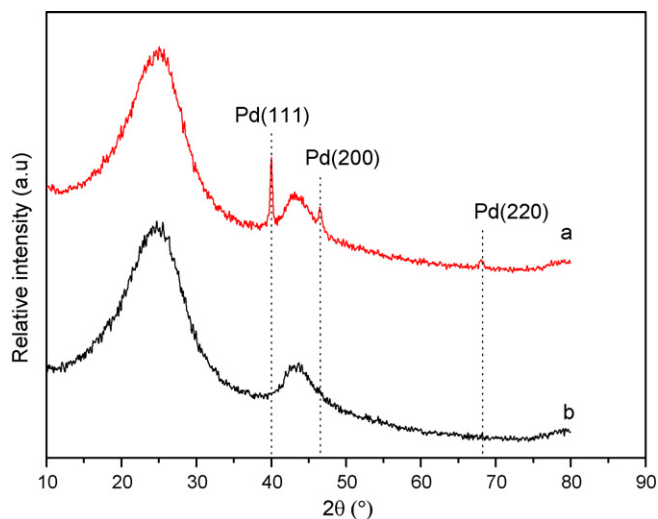

Fig. 1. Catalytic test apparatus.

Table 2
Physicochemical properties of Pd/C catalysts.

Catalyst	BET surface area (m^2/g)	Pd dispersion	Pd particle size (nm)		
			[a]d_{chem}	d_{XRD}	d_{TEM}
Pd/C(FR)	1032	0.39	2.9	2.8	2.5
Pd/C(HR)	1012	0.61	1.8	[b]n.d.	1.6

[a] Based on $d = 1.12/D$ (nm), where D = Pd dispersion [9].
[b] Not detected.

Fig. 2. XRD patterns of the supported palladium catalysts (a) Pd/C(FR); (b) Pd/C(HR).

3. Results and discussion

3.1. Characteristics and catalytic performance for CHP hydrogenation

The characteristics of the catalysts based on BET, CO chemisorption, XRD and TEM results are reported in Table 2. No obvious difference in BET surface area between the various catalysts can be observed. It suggests that the reduction methods have no impact on the BET surface area of the catalysts. The presence of Pd phase after reduction was confirmed by XRD results (Fig. 2). Three diffraction peaks for Pd were detectable at $2\theta = 40.02°$, $46.54°$, $68.04°$ for the catalyst reduced by formaldehyde, corresponding to Pd(1 1 1), Pd(2 0 0) and Pd(2 2 0), respectively. The average Pd crystallite sizes were calculated using the Scherrer's equation [8] based on Pd(1 1 1). The catalyst reduced by hydrogen did not exhibit distinct Pd diffrac-

tion peak. This suggests that the crystallite size of Pd reduced by hydrogen was below the lower limit for XRD detectability. TEM measurement was used to highlight the morphology and particle size of palladium. The representative TEM images of various Pd/C catalysts are shown in Fig. 3. The Pd particle was nearly spherical and according to Eq. (1), the average particle size was calculated to be about 2.5 nm and 1.6 nm for Pd/C(FR) and Pd/C(HR) catalysts, respectively, which are in agreement with the crystallite size inferred from CO chemisorption and XRD results.

Hydrogenation of CHP over Pd/C catalysts has been carried out at 65 °C and H_2 pressure of 1.1 MPa and the results are reported in Table 3. As can be seen in Table 3, Pd/C(FR) catalyst showed a little higher hydrogenation activity as compared to Pd/C(HR) catalyst. Four products were observed in GC analysis, identified as cumene, CA, AP (acetophenone) and α-MS (α-methyl styrene) using GC–MS. The amount of AP and α-MS was trace and can be ignored. The CA content in the products varies in the order: Pd/C(HR) > Pd/C(FR), suggesting the highest selectivity to CA can be obtained by hydrogenation of CHP over Pd/C(HR) catalyst.

When compared with the feedstock composition and the product distribution of CHP reduced by Na_2SO_3 (Table 1), a decrease in cumene content can be easily observed in the case of Pd/C(HR) catalyst. It can be attributed to the reaction between CHP with cumene to form CA [10]. However, decrease in cumene content can also be observed in the product distribution of CHP reduced by Na_2SO_3. Thus, the reaction between CHP with cumene to form CA can undergo without the aid of a catalyst as long as the reaction temperature has reached. In addition, similar product distribution was observed, whatever CHP was reduced by Na_2SO_3 or hydrogenated over Pd/C(HR) catalyst.

As for catalyst Pd/C(FR), the low selectivity to CA can be explained by two possible reasons. First, CHP can not react with cumene over Pd/C(FR) catalyst. Second, CHP reacted with cumene to form CA and the formed CA was further hydrogenated to cumene. Since the above-mentioned reaction has taken place in the case Pd/C(HR) catalyst and Na_2SO_3 reduction, the second one seems more reasonable.

The high activity of Pd/C(FR) catalyst can be attributed to the larger Pd particle size. Although no data on the relationship between catalytic activity and metal particle size was reported in CHP hydrogenation. Higher activity on larger particles has been found in benzene hydrogenation over Rh/Al_2O_3 and Pt/Al_2O_3 catalysts [11–13]. Benedetti et al. [14] have also reported that the hydrogenation of 2, 4-DNT over Pd/SiO_2 is favored by an increase of the metal particle size. They attributed the higher activity to the formation of a Pd-β-H phase which would act as a hydrogen reservoir and the amount of hydrogen dissolved in the Pd crystallites
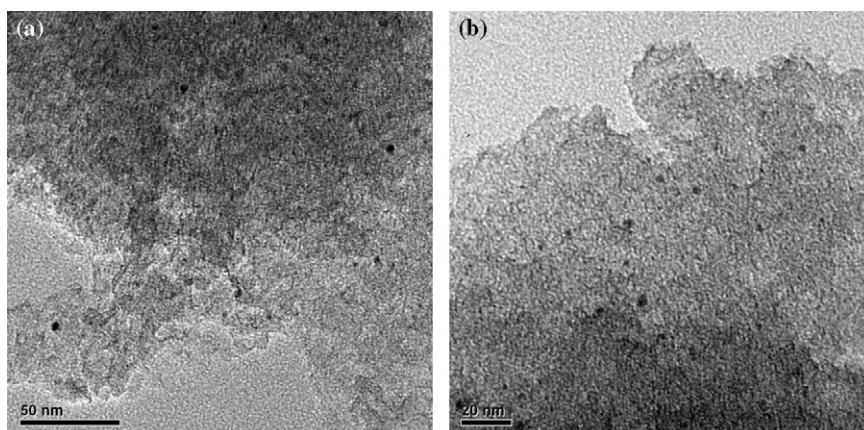
Fig. 3. TEM micrographs of reduced catalysts (a) Pd/C(FR); (b) Pd/C(HR).

Table 3
Comparative performance of CHP hydrogenation over Pd/C catalysts.

Catalyst	r_i (mol g^{-1} Pd s^{-1}) × 10^3	[a]Product distribution (mol%)				[b]TOF (s^{-1})
		Cumene	CA	AP	α-MS	
Pd/C(FR)	2.72	55.4	43.8	0.6	0.2	0.74
Pd/C(HR)	2.67	51.6	47.2	0.6	0.6	0.46

[a]At 100% conversion of CHP.
[b]Number of CHP molecules converted per surface Pd atom per second.
CA = α-cumyl alcohol; AP = acetophenone; α-MS = α-methyl styrene.
Reaction conditions: Temperature = 65 °C; H$_2$ pressure = 1.1 MPa; H$_2$ flow rate = 90 ml/min; Flow rate of CHP solution = 0.15 ml/min; Catalyst weight = 0.5 g.

Table 4
Effect of temperature on CHP hydrogenation over Pd/C(HR) catalyst.

Temperature (°C)	Conversion (%)	Product distribution (mol%)			
		Cumene	CA	AP	α-MS
35	51.1	51.9	46.8	0.6	0.7
45	65.3	51.9	46.9	0.6	0.6
55	79.2	51.8	47.1	0.5	0.6
65	90.8	51.6	47.2	0.6	0.5
75	97.7	51.8	47.0	0.6	0.6

Reaction conditions: Catalyst weight = 0.5 g; H$_2$ flow rate = 90 ml/min; H$_2$ pressure = 1.1 MPa; CHP solution flow rate = 0.15 ml/min.

increases with increasing Pd particle size has been evidenced by TPR. Poor selectivity to CA in catalyst Pd/C(FR) can also account for its larger Pd particle size. The higher hydrogenation activity on larger Pd particle can facilitate the formed CA to be further hydrogenated to cumene. Thus, Pd/C(HR) was chosen as the catalyst for further investigation on CHP hydrogenation due to its higher CA yield.

3.2. Effect of temperature

Table 4 reports the effect of temperature on the rate of CHP conversion and the products distribution. As expected, the rate of CHP conversion was found to increase with the temperature, while the products distribution did not vary with the temperature. As a consequence, a higher conversion of CHP can be obtained at an elevated temperature without reduction of selectivity to CA.

3.3. Effect of H$_2$ pressure

The influence of H$_2$ pressure on the catalytic performance of Pd/C(HR) catalyst for CHP hydrogenation was studied at 65 °C and the results are presented in Table 5. At low H$_2$ pressure, the overall reaction rate is strongly reduced and the product selectivity to CA is at a low level. A noticeable increase of the selectivity to CA and decrease of the selectivity to α-MS is observed when the H$_2$ pressure is increased. As known, dehydration of alcohols to alkenes can undergo in the presence of acidic catalyst. At low H$_2$ pressure, activated hydrogen atom is much less and the support may act as an acidic catalyst for the dehydration of CA to α-MS. As the H$_2$ pressure is increased, activated hydrogen atom is also increased, which

Table 5
Effect of H$_2$ pressure on CHP hydrogenation over Pd/C(HR) catalyst.

Pressure (MPa)	Conversion (%)	Product distribution (mol%)			
		Cumene	CA	AP	α-MS
0.3	42.5	49.1	41.6	0.6	8.7
0.6	55.3	49.8	44.3	0.5	5.4
1.0	86.4	51.1	47.2	0.6	1.1
1.5	91.6	51.4	47.3	0.6	0.7

Reaction conditions: Catalyst weight = 0.5 g; H$_2$ flow rate = 90 ml/min; Temperature = 65 °C; CHP solution flow rate = 0.15 ml/min.
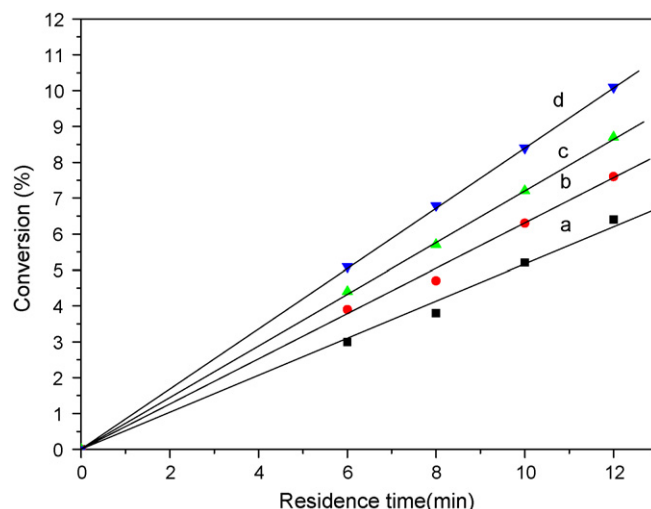
Fig. 4. A plot of CHP conversion as a function of residence time: (a) T = 30 °C; (b) T = 40 °C; (c) T = 50 °C; (d) T = 60 °C. Reaction conditions: Catalyst weight = 0.1 g; H$_2$ flow rate = 300 ml/min; H$_2$ pressure = 1.1 MPa; CHP solution flow rate = 1, 1.2, 1.5, 2 ml/min.

can both accelerate the hydrogenation of CHP and α-MS, leading an enhancement of CA and cumene content in products. Thus, an elevated H$_2$ pressure is also good for CHP hydrogenation to CA.

3.4. CHP hydrogenation kinetics

On the basis of above investigation on temperature and H$_2$ pressure effects on CHP hydrogenation, kinetics experimental was carried out at a various temperature from 30 to 60 °C and a constant H$_2$ pressure of 1.1 MPa. Prior to the investigation on kinetics, the absence of internal and external diffusion under the operating conditions used was checked. The particle size of the catalysts was always small enough (less than 0.1 mm) to ensure negligible internal diffusion. The CHP conversion was found to be dependent on the amount of catalyst used (0.1–0.2 g) when W (catalyst weight)/F (flow rate of CHP solution) is less than 0.1 g ml^{-1} min^{-1}; the two was related by a linear relationship with a correlation coefficient of 0.994. This suggests that CHP hydrogenation rate was kinetically controlled over the catalyst weight range investigated [15].

The CHP hydrogenation rate law for CHP decay concentration can be written as the following equation:

$$(-r) = -\frac{dC_{CHP}}{dt} = C_{CHP0}\frac{dx}{dt} = kC_{CHP}^m \tag{4}$$

where r, C_{CHP}, C_{CHP0}, x, t, k, and m denote the reaction rate, CHP concentration, initial CHP concentration, CHP conversion, residence time, reaction rate constant and reaction order, respectively. A plot of CHP conversion as a function of residence time is shown in Fig. 4. A linear relationship between CHP conversion and residence time can be obtained. This suggests that CHP hydrogenation over Pd/C catalyst is a zero-order reaction, which is in agreement with the

Table 6
Kinetics parameters for CHP hydrogenation over Pd/C(HR) catalyst.

Temperature (K)	k (min^{-1})
303.15	0.5151
313.15	0.6256
323.15	0.7221
333.15	0.8436

Reaction conditions: Catalyst weight = 0.1 g; H$_2$ flow rate = 300 ml/min; H$_2$ pressure = 1.1 MPa; CHP solution flow rate = 1, 1.2, 1.5, 2 ml/min.
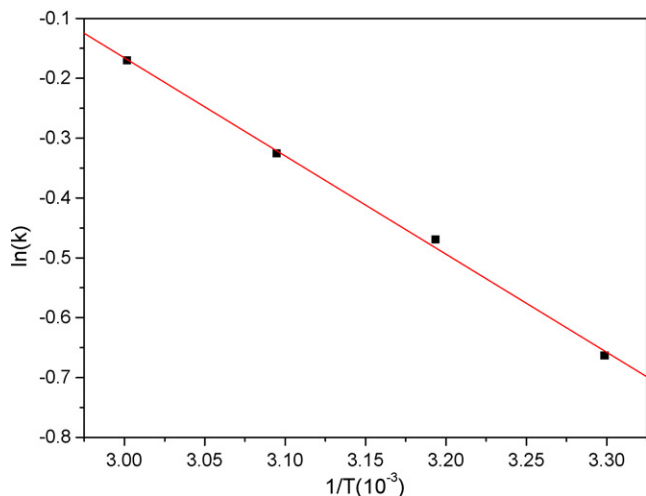

Fig. 5. Arrhenius plot of the hydrogenation of CHP over Pd/C(HR) catalyst.

previous data [16]. Based on the results, the reaction rate constants under various temperatures are reported in Table 6.

According to Arrhenius formula, the rate constant (k) can be related to absolute temperature (T) as following equation:

$$k = A \exp \left(\frac{-E_a}{RT} \right) \qquad (5)$$

where A, E_a, R and T denote frequency factor, activation energy, gas constant and absolute temperature. A logarithm transformation for Eq. (5), then it can be expressed as following form:

$$\ln(k) = \ln(A) - \left(\frac{E_a}{R} \right) \left(\frac{1}{T} \right) \qquad (6)$$

A linear relationship can be obtained by plotting $\ln(k)$ as a function of $1/T$ and the regression analysis gave an R^2 value of 0.998 (Fig. 5). The activation energy can be obtained from the slope and calculated to be 13.6 kJ/mol, which is a little lower than that of CHP hydrogenation over Raney Ni [16].

4. Conclusions

In this study, the catalytic performance of the Pd/C catalysts on liquid phase hydrogenation of CHP in a fixed bed reactor was inves-

tigated. It was found that reduction methods have no impact on the BET surface area of the catalysts but have a significant impact on the palladium particle size and catalytic performance. Hydrogen-reduced Pd/C catalyst showed a little lower activity but higher CA selectivity. A higher conversion of CHP can be obtained at an elevated temperature without reduction of selectivity to CA. High rate of CHP conversion and CA selectivity was favored under high H$_2$ pressure. It can be attributed to the formation of Pd-β-H phase. The reaction order of liquid-phase hydrogenation of CHP was determined to be zero. The results can be used to study the reaction mechanism in future.

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