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Supporting Online Material for

Selective Phenol Hydrogenation to Cyclohexanone Over a Dual Supported Pd–Lewis Acid Catalyst

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1. Experimental

1.1 *Chemicals* Phenol, cyclohexanone, cyclohexanol, PdCl₂, AlCl₃, ZnCl₂, SnCl₂·2H₂O, InCl₃, HCl (36% aqueous solution), dichloromethane (CH₂Cl₂), N, N-dimethylformamide (DMF), trichloromethane (CHCl₃), 1-butylchloride, tetrahydrofuran, cyclohexane, and n-hexane were analytical grade and purchased from Beijing Chemical Reagent Company. n-Decane (A. R. grade) was provided by ACROS Organics. The phenol was recrystallized in n-hexane three times. The CO₂ (99.99%), H₂ (99.99%), Ar (99.99%), and N₂ (99.95%) were provided by Beijing Analytical Instrument Company.

1.2 *Catalysts* The Pd/C catalyst used was produced by Baoji Rock Pharmachem Co., Ltd., China (5 wt% Pd, Product No. D_5L_3). The Pd/Al₂O₃ catalyst was produced by Xi'an Kaili Chemical Engineering Company, China (5 wt% Pd, Product No. KL11205). The Pd/NaY zeolite catalyst (2.5 wt% Pd) was prepared by wet impregnation technique in this work. The NaY zeolite (Si: Al=5.3: 1) was provided by Research Institute of Petroleum Processing, Sinopec, China. The NaY zeolite is an aluminosilicate with framework structure (*S1*). It can be used as catalysts directly or the supports of active components. To synthesize the catalyst, 1.0 g of NaY zeolite was dispersed in 5.0 mL of H₂PdCl₄ (Pd, 0.025 g, 0.235 mmol) aqueous solution. The mixture was stirred for 12 h. Then water was removed using a rotary evaporator at 50°C under vacuum. The obtained solid was dried at 120°C for 2 h and calcined at 400°C for 2 h. The catalyst was reduced at 300°C for 2 h with H₂ and cooled to 100°C in H₂ flow (20 mL/min). Then the catalyst was cooled to room temperature in nitrogen flow (30 mL/min).

The catalysts were characterized by nitrogen adsorption-desorption method, scanning electron microscopy (SEM), transmission electron microscopy (TEM), and high-resolution TEM (HRTEM) techniques. The nitrogen adsorption-desorption isotherms were measured at 77 K on ASAP 2020 Accelerated Surface Area and

Porosimetry Analyzer. The sample was degassed at 250°C for 12 h under vacuum before the measurement. The SEM examination was conducted on a Hitachi-s4300 electron microscope operated at 15 kV. The samples were spray-coated with a thin layer of platinum before observation. The TEM and HRTEM observation was carried out on JEM 2011 at an accelerating voltage of 200 kV. The samples were dispersed in ethanol and dropped on a carbon film supported on copper grid for TEM analysis.

1.3 *FTIR* study of the interaction between Lewis acids and cyclohexanone The procedures were similar to those reported previously (*S2*, *S3*). In a typical experiment, 30 mmol of Lewis acid and 10 mmol of cyclohexanone were added into 4 mL of dichloromethane in a glass tube. The mixture was treated by ultrasound for 15 min, and then stirred for 1 h. Then some sample was loaded between two ZnS windows (*S2*) and FTIR spectra were recorded on Bruker Tensor 27 spectrometer. Each sample was recorded with 32 scans at an effective resolution of 2 cm⁻¹.

1.4 *Hydrogenation of phenol or cyclohexanone* For the reaction in liquid solvents, the hydrogenation was carried out in a Teflon-lined stainless-steel reactor of 6 mL in capacity with a magnetic stirrer, which was similar to that used previously (*S4*). The inner diameter of the reactor was 16 mm. The reactor was connected to a hydrogen cylinder of the reaction pressure, so that hydrogen of fixed pressure could be supplied continuously. The pressure was determined by a pressure transducer (FOXBORO/ICT, Model 93), which could be accurate to ± 0.025 MPa. In a typical experiment, 1.0 mmol of phenol (or cyclohexanone), catalyst (0.05 mmol of Pd), Lewis acid (0.1 mmol) and 1 mL of solvent were loaded into the reactor. The reactor was sealed and purged with hydrogen to remove the air at ice water temperature. Then the reactor was placed in an air bath, which was controlled by a PID temperature fluctuation of the air bath was $\pm 0.1^{\circ}$ C. Hydrogen was introduced into the reactor after desired temperature was reached and the stirrer was started. After reaction the reactor was placed in ice water and the gas was released and collected in a gas bag that was

purged with H_2 five times. The gaseous samples were analyzed using a GC (Agilent 4890D) equipped with a TCD detector and a packed column (Carbon molecular sieve TDX-01, 1 m in length and 3 mm in diameter) using Argon as the carry gas. A known amount of internal standard n-decane was then added to the reactor if used. The reaction mixture was transferred into a glass tube and the catalyst-Lewis acid was separated by centrifugation. The catalyst-Lewis acid was then rinsed with dichloromethane (3×1 mL) and all the samples were combined for analysis. The quantitative analysis of the reaction mixture was conducted using a GC (Agilent 6820) equipped with a flame ionization detector (FID) and a PEG-20M capillary column (0.25 mm in diameter, 30 m in length). Identification of the products and reactant was done using a GC-MS (SHIMADZU-QP2010) as well as by comparing the retention times to respective standards in GC traces. The conversion and selectivity were calculated from the GC data. Our experiments showed that the apparent reaction rate was independent of the stirring speed as the speed was larger than 300 rpm. Then we controlled the speed at 400 rpm in the experiments.

For the reaction conducted in compressed CO₂, a high pressure view reactor of 50 mL (*S5*) was used to conduct the reaction and observe the phase behavior. The procedures were similar to those for the reaction in dichloromethane. The main difference was that dichloromethane was not used in the reaction. After charging H₂, CO₂ was compressed into the reactor. The amounts of Pd and Lewis acid were also 5 mol% and 10 mol% relative to phenol, respectively. The reactor was immersed in a constant temperature water bath, which was controlled by a Haake-D3 temperature controller, and the temperature was measured by an accurate mercury thermometer with the accuracy of better than $\pm 0.05^{\circ}$ C.

1.5 *Recycling of the catalyst system* The reusability of Pd/C-ZnCl₂ was tested for phenol hydrogenation in dichloromethane. After the reaction, the reaction mixture was centrifuged and the solid Pd/C-ZnCl₂ was recovered, followed by rinsing with dichloromethane and centrifugation (2×3 mL). The Pd/C-ZnCl₂ was reused directly for the next run after drying. The reusability of Pd/C-AlCl₃ was tested for the phenol

hydrogenation in compressed CO₂. After the reaction, the CO₂ and H₂ in the reactor were released passing through a cold trap containing N, N-dimethylformamide as the absorbent after the reaction. Then the products and the reactant remained in the reactor were extracted in-situ with CO₂ at 35° C and 9.0 MPa and collected in the cold trap. Control experiment using known amounts of phenol, cyclohexanone and cyclohexanol showed that all of the phenol and products could be extracted and collected in the cold trap by 100 g of CO₂, while the catalyst and Lewis acid remained in the reactor because they are not soluble in supercritical CO₂. The composition of the collected samples was determined by GC and identified by GC-MS. The Pd/C-AlCl₃ left in the reactor was reused directly for the next run.

1.6 *Carbon balance of the reaction system* All the GC traces of the gaseous samples were similar. As an example, Figure S1 presents the GC trace of one of the gaseous samples. GC trace of a blank gaseous sample (the reactor contained only 2 MPa of hydrogen and 1 mL of dichloromethane) is also given in the figure. The two GC traces are the same in that only hydrogen and trace amount of dichloromethane that was entrained by hydrogen because it is volatile, were detected in the gaseous sample. This indicates that no gaseous product was produced in the reaction. We also determined the carbon balance of the reaction using liquid samples under some typical conditions with n-decane as the internal standard. Figure S2 gives the GC traces with the internal standard. The number of moles of component *i* was calculated by equation E1.

$$n_i = n_s \times \frac{A_i f_i}{A_s f_s} \tag{E1}$$

Where n_i is the moles of component *i*, f_i is the response factor of component *i*, n_s is the moles of n-decane added, A_i is the peak area of component *i*, A_s is the peak area of n-decane, and f_s denotes the response factor of the internal standard that is equal to unity. The carbon balance of the reaction system was calculated from the ratio of the number of moles of carbon in the reactant and products after the reaction to that in the phenol added. The values of the carbon balance obtained at different conditions are

listed in Table S1. Cyclohexanone and cyclohexanol were the only reaction products observed at all the experimental conditions, and the carbon balance values calculated from phenol, cyclohexanone and cyclohexanol were around 100%, as shown in Table S1. This confirms that cyclohexanone and cyclohexanol were the only products, which is the same as that reported by other authors (*S6-S8*). In addition, this also supports the conclusion that no gaseous product was produced in the reaction as discussed above. Besides, the carbon balance of the blank experiments, in which known amounts of phenol, cyclohexanone, cyclohexanol, and hydrogen were added to the reactor without adding catalyst, was also around 100% (Table S1, entries 1-3). This confirms the reliability of the experiments.



Figure S1. a) GC trace of the gaseous sample at 100° C and 2.0 MPa of H₂ with a reaction time of 0.5 h (Other reaction conditions: phenol, 1.0 mmol; Pd (5 wt% in Pd/C), 5 mol% relative to phenol; AlCl₃, 10 mol% relative to phenol; solvent, 1 mL of dichloromethane); b) GC trace of the blank gaseous sample (the reactor contained only 2 MPa of H₂ and 1 mL of dichloromethane).

Entry	Reaction conditions	In (mmol)	Out (mmol)			Total out	Carbon
-		phenol	phenol	-C=O	-OH	(mmol)	balance
1^{a}	30°C/1.0 MPa/1 h	1.000	1.000			1.000	100.0%
2^{a}	30°C/1.0 MPa/1 h	b	0.392	0.401	0.205	0.998	99.8%
3 ^a	30°C/1.0 MPa/1 h	с	0.528	0.246	0.231	1.005	100.5%
4	30°C/1.0 MPa/12 h	1.000	nd.	1.003	nd.	1.003	100.3%
5	50°C/1.0 MPa/7 h	1.000	nd.	0.997	nd.	0.997	99.7%
6	80°C/1.0 MPa/1.8 h	1.000	0.139	0.863	0.004	1.006	100.6%
7	100°C/1.0 MPa/0.5 h	1.000	nd.	0.987	0.010	0.997	99.7%
8	100°C/2.0 MPa/0.05 h	1.000	0.645	0.340	0.009	0.994	99.4%
9	100°C/3.0 MPa/0.07 h	1.000	0.199	0.778	0.027	1.004	100.4%
10	100°C/2.0 MPa/0.5 h	1.000	nd.	0.956	0.038	0.994	99.4%
11	100°C/3.0 MPa/0.3 h	1.000	nd.	0.941	0.056	0.997	99.7%

Table S1. Results of phenol hydrogenation and carbon balance

Reaction conditions: phenol, 1.0 mmol; Pd (5 wt% in Pd/C), 5 mol% relative to phenol; $AlCl_3$, 10 mol% relative to phenol; solvent, 1 mL of dichloromethane. nd. denotes not detectable.

a, Without the catalyst and AlCl₃;

b, The amounts of phenol, cyclohexanone, and cyclohexanol initially added were respectively 0.393 mmol, 0.402 mmol, and 0.205 mmol;

c, The amounts of phenol, cyclohexanone, and cyclohexanol initially added was respectively 0.523 mmol, 0.245 mmol, and 0.232 mmol.



























Table S1 Entry 10





Figure S2. GC traces for the experiments in Table S1.

1.7 *Calculation of the conversion and selectivity* The composition of the reaction mixture was determined by equation E2.

$$X_i = \frac{A_i f_i}{\sum_i A_i f_i} \times 100\%$$
(E2)

Where X_i is the mole fraction of component *i*, f_i is the response factor of component *i*, and A_i is the peak area of component *i*. The conversion of phenol is defined as the ratio of number of moles of phenol consumed in the reaction to the total moles of phenol initially added (Eq. E3). The selectivity to cyclohexanone is defined as the ratio of number of moles of cyclohexanone produced to the total number of moles of all products (Eq. E4).

$$Conversion of phenol = \frac{Moles of phenol consumed}{Moles of phenol initially added}$$
(E3)
Selectivity to cyclohexanone = $\frac{Moles of cyclohexanone}{Moles of all products}$ (E4)

As discussed above, cyclohexanone and cyclohexanol were the only reaction products observed. Therefore, we calculated the conversion and selectivity using the GC traces without the internal standard in order to avoid the error originated from the internal standard. Figure S3a shows a representative GC trace without internal standard. Other GC traces for the data in Tables 1 and 2 are presented in the Appendix (see the last section). At 30°C and 1.0 MPa of hydrogen pressure and a reaction time of 12 h, the phenol was not completely converted and both cyclohexanone and cyclohexanol were produced over Pd/C in the absence of Lewis acid. Therefore, there are four peaks in the GC trace, *i.e.* solvent (dichloromethane), cyclohexanone, cyclohexanol, and phenol (Figure S3a). On the basis of equations E2-E4, the conversion and selectivity data were easily obtained and is given in Table 1 (entry 1).

Our control experiment showed that the phenol and cyclohexanol in the solution of phenol, cyclohexanone, and cyclohexanol in dichloromethane with a molar ratio of phenol: cyclohexanone: cyclohexanol=0.1: 100: 0.1 could be easily detected by the GC at the operation condition of this work, as shown in Figure S3b. Figure S3c shows the GC trace of the reaction mixture at 50°C and 1.0 MPa of hydrogen pressure with a reaction time of 7 h in the presence of Pd/C-AlCl₃, which indicates that the phenol and cyclohexanol are not detectable, *i.e.*, the amounts of cyclohexanol and phenol are less than the detection limit of the GC (the datum processing system of the GC cannot recognize the peaks and does not give the retention times on the GC trace). While the control experiment (Figure S3b) shows that the cyclohexanol or phenol can be easily detected when the concentration in the reaction mixture is 0.1% (the retention times of cyclohexanol and phenol peaks are shown on the GC trace automatically). This confirms that both the conversion and selectivity are >99.9%. For other data in the tables, a conversion of >99.9% denotes that the phenol is not detectable.



Figure S3. (a) GC trace for the solution of the reaction mixture of (Table 1, entry 1) in dichloromethane.



Figure S3. (b) Magnified GC trace for the solution of phenol, cyclohexanone, and cyclohexanol in dichloromethane with a molar ratio of phenol: cyclohexanone: cyclohexanol=0.1: 100: 0.1 at the same concentration of the reaction experiments, the big peak for the dichloromethane at 3.8 min is not included in order to magnify the peaks for phenol, cyclohexanone, and cyclohexanol; the inset is the magnified part of the GC trace containing the peaks of cyclohexanone and cyclohexanol; the shape of the magnified peak of phenol is similar to that of cyclohexanol (not shown here).



Figure S3. (c) Magnified GC trace for the solution of the reaction mixture of (Table 1, entry 5) in dichloromethane, which indicates that phenol and cyclohexanol are not detectable, the big peak for the dichloromethane at 3.8 min is not included in order to magnify the peaks for phenol, cyclohexanone, and cyclohexanol; the inset is the magnified part of the GC trace covering the retention times of cyclohexanone and cyclohexanol, which shows that the cyclohexanol is not detectable; similarly, the phenol is not detectable (not shown here).

2. Results and discussion

2.1 *Characterization of the Pd/C catalyst* Figure S4a shows the N₂ adsorption-desorption isotherm. The catalyst had a BET surface area of 1202 m²·g⁻¹, and a pore volume of 0.82 cm³·g⁻¹. The pore size distribution of the Pd/C catalyst is presented in Figure S4b, which was calculated using Original Density Functional Theory. The figure shows several peaks in the range of 0.5 to 8 nm, indicating that the pore size of the activated carbon support was not uniform. The observed particle size of the catalyst was mainly in the range of 10-50 µm (Figure S4c). The Pd nanoparticles of 3-8 nm were highly dispersed on the support (Figure S4d). The HRTEM image shows (Figure S4e) the crystalline nature of the Pd nanoparticles (S9).



Figure S4. (a) Nitrogen adsorption-desorption isotherm, (b) The pore size distribution, (c) SEM image, (d) TEM image, and (e) HRTEM image of the Pd/C catalyst.

2.2 Characterization of the Pd/Al₂O₃ catalyst The N₂ adsorption-desorption isotherm is given in Figure S5a. The BET surface area and pore volume of the catalyst obtained were 100.4 m²·g⁻¹ and 0.26 cm³·g⁻¹, respectively. Figure S5b gives the pore size distribution calculated using Original Density Functional Theory, which shows a main peak at about 8 nm. The observed particle size of the catalyst was in the range of 60-150 μ m (Figure S5c). The size of the Pd particles was in the range of 4-8 nm (Figure S5d), and the particles were highly dispersed. The HRTEM image also shows the crystalline nature of the Pd nanoparticles (Figure S5e).



Figure S5. (a) Nitrogen adsorption-desorption isotherm, (b) The pore size distribution, (c) SEM image, (d) TEM image, and (e) HRTEM image of the Pd/Al₂O₃ catalyst.

2.3 Characterization of the Pd/NaY zeolite catalyst The BET surface area and pore volume of the catalyst obtained from N_2 adsorption-desorption isotherm (Figure S6a) were 451 m²·g⁻¹ and 0.23 cm³·g⁻¹, respectively. The steep adsorption at a relative

pressure P/P₀ < 0.02 was clearly observed, suggesting a large amount of micropores. The pore size distribution of the Pd/NaY catalyst, which was obtained using Horvath-Kawazoe method, is illustrated in Figure S6b. The pore size distribution curve shows that the size of pores was less than 0.8 nm. The SEM image shows that particle size of the catalyst was mainly in the range of 1-3 μ m (Figure S6c). The size of the Pd particles was in the range of 5-8 nm (Figure S6d) and the Pd particles were well dispersed on the support. The HRTEM image also shows that Pd nanoparticles were crystalline (Figure S6e).



Figure S6. (a) Nitrogen adsorption-desorption isotherm, (b) The pore size distribution, (c) SEM image, (d) TEM image, and (e) HRTEM image of the Pd/NaY catalyst.

2.4 *Effect of solvent on the reaction* Different solvents were tested for the hydrogenation of phenol at 30° C and 1.0 MPa of hydrogen pressure with a reaction time of 4.0 h over Pd/C-AlCl₃. The results are listed in Table S2. It is clear that dichloromethane is one of the best solvents on the basis of the conversion and selectivity, and the optimization was carried out using dichloromethane in this work.

Table S2 Hydrogenation of phenol in different solvents. The conversion and selectivity were determined by GC method. Identification of the products and reactant was done using GC-MS as well as by comparing the retention times to respective standards in GC traces. Reaction conditions: phenol, 1.0 mmol; Pd (5 wt% in Pd/C), 5 mol% relative to phenol; AlCl₃, 10 mol% relative to phenol; temperature, 30°C; pressure of H₂, 1.0 MPa; reaction time, 4.0 h; solvent, 1 mL.

Solvents	Conversion	Selectivity (%)			
Solvents	(%)	Cyclohexanone	Cyclohexanol		
CH_2Cl_2	51.8	>99.9	<0.1		
CHCl ₃	43.3	>99.9	<0.1		
1-Butylchloride	48.3	98.9	1.1		
Cyclohexane	36.6	96.2	3.8		
Tetrahydrofuran	0	0	0		

2.5 *FTIR* study of the interaction between Lewis acids and cyclohexanone The interaction between the Lewis acids and cyclohexanone were studied in this work. Figure S7 shows the FTIR spectra of cyclohexanone in dichloromethane with and without AlCl₃. The absorption band at 1714 cm⁻¹ is typical for C=O stretching vibration. The absorption band shifts to 1624 cm⁻¹ in the presence of AlCl₃, which results from the acid-base interaction (*S3*).



Figure S7. The carbonyl stretching bands of cyclohexanone in dichloromethane determined at room temperature: (a) without AlCl₃ and (b) with AlCl₃.

The shifts of wave number caused by AlCl₃, InCl₃, ZnCl₂, and SnCl₂ are 90, 59, 57, and 23 cm⁻¹, respectively, indicating that all the Lewis acids used in this work have acid-base interaction with cyclohexanone in the reaction system. In addition, the shift in wave number increases with the increasing acidity of the Lewis acids (*S3*). Therefore, the acidity of the Lewis acids follow the order AlCl₃>InCl₃>ZnCl₂>SnCl₂. Cook (*S3*) determined the acidity of AlCl₃, InCl₃, and ZnCl₂. The order of this work agrees with that reported by Cook (*S3*).

2.6 *Reproducibility of the reaction* The kinetic curves of the reaction at 50°C and 1.0 MPa of H₂ were determined four times separately, and the results are shown in Figure S8. At all the reaction times, the selectivity to cyclohexanone was better than 99.9% in all the repeated experiments up to complete conversion of phenol. The maximum deviation of the conversion was $\pm 2\%$, which was very satisfactory.



Figure S8. Four kinetic curves of the reaction at 50°C and 1.0 MPa of hydrogen determined separately. Open symbols, selectivity; Solid symbols, conversion. Reaction conditions: phenol, 1.0 mmol; Pd (5 wt% in Pd/C), 5 mol% relative to phenol; AlCl₃, 10 mol% relative to phenol; solvent, 1 mL of dichloromethane.

2.7 *Preliminary kinetics* The kinetic curves of phenol hydrogenation at some typical conditions are presented in Figure S9. As expected, the conversion increases with the reaction time and temperature up to complete conversion. The $\ln(C_0/C)$ *vs*. reaction time (t) curves in the figures up to complete conversion are also given. C_0 and C are the concentrations of phenol before the reaction and at a reaction time of t, respectively. The straight line indicates that the reaction follows standard pseudo-first-order kinetics for phenol at the experimental conditions, which is the same as those reported by many other authors (*S6, S10, S11*).



(a) Pd/C, 30°C and 1.0 MPa of hydrogen; solvent, 1 mL of dichloromethane.



(b) Pd/C, 50°C and 1.0 MPa of hydrogen; solvent, 1 mL of dichloromethane.



(c) Pd/C, 80°C and 1.0 MPa of hydrogen; solvent, 1 mL of dichloromethane.



(d) Pd/C, 100°C and 1.0 MPa of hydrogen; solvent, 1 mL of dichloromethane.



(e) Pd/C, 80° C and 2.0 MPa of hydrogen; solvent, 1 mL of dichloromethane.



(f) Pd/C, 80°C and 3.0 MPa of hydrogen; solvent, 1 mL of dichloromethane.



(g) Pd/C, 100°C and 2.0 MPa of hydrogen; solvent, 1 mL of dichloromethane.



(h) Pd/C, 100°C and 3.0 MPa of hydrogen; solvent, 1 mL of dichloromethane.



(i) Pd/C, 30°C and 1.0 MPa of hydrogen; solvent, 6.0 MPa of CO₂.



(j) Pd/C, 30° C and 1.0 MPa of hydrogen; solvent, 6.5 MPa of CO₂.



(k) Pd/C, 30°C and 1.0 MPa of hydrogen; solvent, 7.0 MPa of CO₂.



(1) Pd/Al₂O₃, 50°C and 1.0 MPa of hydrogen; solvent, 1 mL of dichloromethane.



(m) Pd/NaY, 50°C and 1.0 MPa of hydrogen; solvent, 1 mL of dichloromethane.

Figure S9. The kinetic curves of phenol hydrogenation under some typical conditions. Reaction conditions: phenol, 1.0 mmol; Pd (5 wt% in Pd/C and Al_2O_3 ; 2.5 wt% in Pd/NaY), 5 mol% relative to phenol; AlCl₃, 10 mol% relative to phenol.

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Appendix The GC traces of the samples for the data listed in Tables 1 and 2 are presented in Figure S10.

Table1 Entry 1



Table1 Entry 2







Table 1 Entry 4



Table 1 Entry 5



Table 1 Entry 6



Table 1 Entry 7







Table 1 Entry 9



Table 1 Entry 10







Table 1 Entry 12



Table 1 Entry 13







Table 1 Entry 15















Table 1 Entry 16‡







Table 1 Entry 18



Table 1 Entry 19









































































Table 2 Entry 13









Figure S10. The GC traces of the samples for the data listed in Tables 1 and 2.