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quantum dots, and barriers. We believe that this approach should apply to solid catalyst materials other than AlAu alloys, and indeed to wire materials other than Si and Ge, provided that the catalyst and wire material satisfy requirements for eutectic temperature, orientation, and stability. We speculate that a solid catalyst could be similarly advantageous in forming abrupt doping profiles, such as are required for high-subthreshold slope devices such as tunnel and avalanche field-effect transistors. More generally, Si and Ge device fabrication that requires sophisticated control of composition and structure can be addressed using this approach.

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Materials and Methods

Figs. S1 to S3

References

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

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Cyclohexanone is an industrially important intermediate in the synthesis of materials such as nylon, but preparing it efficiently through direct hydrogenation of phenol is hindered by over-reduction to cyclohexanol. Here we report that a previously unappreciated combination of two common commercial catalysts—nanoparticulate palladium (supported on carbon, alumina, or NaY zeolite) and a Lewis acid such as AlCl₃—synergistically promotes this reaction. Conversion exceeding 99.9% was achieved with >99.9% selectivity within 7 hours at 1.0-megapascal hydrogen pressure and 50°C. The reaction was accelerated at higher temperature or in a compressed CO₂ solvent medium. Preliminary kinetic and spectroscopic studies suggest that the Lewis acid sequentially enhances the hydrogenation of phenol to cyclohexanone and then inhibits further hydrogenation of the ketone.

Cyclohexanone is a key raw material in the synthesis of many useful chemical intermediates, such as caprolactam for nylon 6 and adipic acid for nylon 66 (1, 2). The industrial production of cyclohexanone typically involves either the oxidation of cyclohexane (3, 4) or the hydrogenation of phenol. The former route requires high temperature and generates byproducts such as cyclohexanol and organic acids that complicate purification, and the yield of cyclohexanone is usually low. The phenol hydrogenation route is undertaken through either two-step or one-step processes. In the two-step procedure, phenol is first hydrogenated to cyclohexanol, which in turn is dehydrogenated to cyclohexanone at high temperature. The one-step selective hydrogenation of phenol to cyclohexanone is advantageous from an efficiency standpoint, and

the reaction can be conducted in either the gas phase or liquid phase. The gas-phase phenol hydrogenation is usually performed in the temperature range of 150° to 300°C over supported Pd catalysts (5–9), and different supports have been used, including alumina, that may act as Lewis acids (9). The gas-phase process can be carried out easily in continuous reactors for higher throughput. Liquid-phase phenol hydrogenation offers cost and energy savings, because the reaction can be performed at relatively low temperatures (10–15). Many researchers have contributed to this area, and multiple catalysts have been screened, such as Rh/C (10), Rh/C nanofiber (11), Pd/hydrophilic C (12), Ru/poly(*N*-vinyl-2-pyrrolidone) (PVP) (13), Pd/Mg and Pd/Fe (14), mesoporous Ce-doped Pd (15), and Pd/C (16). However, the attainment of high selectivity (>95%) at elevated conversion (>80%) with a satisfactory rate is a great challenge (8, 17), because the cyclohexanone product can be further hydrogenated to cyclohexanol under the reaction conditions (7, 15).

We report here that Pd/C, Pd/Al₂O₃, and Pd/NaY zeolite (18) (NaY zeolite is hereafter denoted NaY) catalysts and solid Lewis acids show excellent synergy in the hydrogenation of phenol to cyclohexanone, together substantially enhancing both activity and selectivity. The reaction can be carried out effectively at temperatures as low as 30°C, and >99.9% conversion of phenol is observed with >99.9% selectivity to cyclohexanone. Separation of the product from the catalyst–Lewis acid system is simple, and the catalyst system can be reused directly. This route has great potential for industrial application.

Our experiments (18) showed that dichloromethane is the best reaction solvent among several tested (table S2). Table 1 presents the results of phenol hydrogenation under different conditions over Pd/C, Pd/Al₂O₃, and Pd/NaY catalysts with and without AlCl₃. The conversion of phenol was very low, and considerable byproduct was produced when only the Pd/C catalyst was used (Table 1, entry 1), and the reaction did not occur at all when only Lewis acid (AlCl₃) was used (Table 1, entry 2). When Pd/C and AlCl₃ were used at the same time, the reaction proceeded with a selectivity of >99.9% up to complete conversion at 1.0 MPa of H₂ and a temperature at or below 50°C (Table 1, entries 3 to 5). At higher temperature, the reaction reached completion in 1 hour and the selectivity remained >99% (Table 1, entries 9 and 10). With other conditions fixed, an increase in hydrogen pressure (Table 1, entries 6 to 12) shortened the time to completion but slightly reduced the selectivity to cyclohexanone. Other Lewis acids were also effective in promoting the reaction [Table 1, entries 13 to 18; see also fig. S7 and supporting online material (SOM) text]. The activity and selectivity of the reaction using Pd/Al₂O₃ and Pd/NaY (18) were also enhanced effectively by AlCl₃ (Table 1, entries 19 to 26). The prospects for recycling Pd/C–ZnCl₂ were tested (18), and the results indicated that the catalyst system could

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be reused after simple separation without a decrease in conversion and selectivity (Table 1, entries 16*, 16†, and 16‡). Preliminary kinetics measurements indicated that the reaction exhibits

a standard pseudo-first-order rate dependence on phenol concentration (fig. S9 and SOM text).

We also explored the use of CO₂ as a reaction solvent for its characteristic advantages of waste

minimization, ease of product separation, and pressure tunability (19–21). The Pd/C–Lewis acid systems were very efficient catalysts for the reaction in compressed CO₂ at suitable pressures (Table 2, entries 3 to 12). The reaction in CO₂ also follows standard pseudo-first-order kinetics with respect to phenol (fig. S9). The pressure of CO₂ had a significant effect on the apparent reaction rate. At optimized pressures, both the conversion and selectivity were >99.9% (Table 2, entries 3 to 12), and the apparent reaction rate was faster than that in dichloromethane (Table 1, entry 3, versus Table 2, entries 3 to 6; Table 1, entry 13, versus Table 2, entries 7 to 9; Table 1, entry 15, versus Table 2, entries 10 to 12), which may result mainly from the larger diffusion coefficient of the reactants in CO₂ and the higher miscibility of gaseous H₂ with CO₂ than with liquid solvents (22). In addition, CO₂ is a weak Lewis acid, which may also enhance the reaction. To further explore the effect of CO₂ pressure on the reaction rate, we observed the phase behavior of the reaction system directly by using a high-pressure view reactor (21). A vapor phase (a mixture of H₂ and CO₂) and a solid phase (a mixture of catalyst, Lewis acid, and phenol) were evident at total pressures of 5.0 MPa (Table 2, entry 1) and 6.5 MPa (Table 2, entry 2). The phenol, Pd, and Lewis acid could not come in contact efficiently, and therefore the reaction proceeded slowly. At higher pressures, a liquid phase formed in addition to the vapor phase, due to the liquefaction of CO₂. The catalyst and Lewis acid were dispersed and the reactants dissolved under stirring, allowing the reaction to proceed effectively. Above 7 MPa, however, the apparent reaction rate decreased with increasing pressure (Table 2, entries 3 to 6), which may have resulted from dilution as the volume of the liquid phase increased. Separation of CO₂, product, and catalyst proved quite facile, because the product could be extracted in situ by CO₂, whereas the solid catalyst and Lewis acid remained in the reactor (18). At 30°C and a total H₂/CO₂ pressure of 8.0 MPa, the Pd/C–AlCl₃ system could be recycled three times with no loss in conversion or selectivity (Table 2, entries 5 and 13 to 15).

Prior research on the hydrogenation of phenol has indicated that this reaction proceeds mainly in a sequential manner (Fig. 1A) (15, 23, 24). The benzene ring of phenol is first partially hydrogenated to an enol in step 1, which is unstable and isomerizes rapidly to form cyclohexanone (23); cyclohexanone can then be further hydrogenated to form cyclohexanol. Cyclohexanone and cyclohexanol were the only reaction products observed in the present study, and under all reaction conditions, selectivity approached 100% at sufficiently low conversion (fig. S9). We conclude from the results in Tables 1 and 2 that under the likely operation of this two-step mechanism, the supported Pd catalyst–Lewis acid systems are very active for the first step but are not active for the second step under the experimental conditions. This is further discussed below.

Table 1. Hydrogenation of phenol under different conditions. Conversions and selectivities were determined by gas chromatography (GC). Reactants and products were identified by GC mass spectrometry (MS) as well as by comparing retention times to respective standards in GC traces. At >99.9% conversion, the minimum time required for reaction completion is given. Cyclohexanone and cyclohexanol were the only reaction products observed. Reaction conditions were as follows: phenol, 1.0 mmol; Pd [5 weight percent (wt %) in Pd/C or Pd/Al₂O₃; 2.5 wt % in Pd/NaY], 5 mol % relative to phenol; Lewis acid, 10 mol % relative to phenol; solvent, 1 ml of dichloromethane. *p*, pressure; *T*, temperature. Dashes indicate that no catalyst or Lewis acid was added. C=O indicates cyclohexanone, and OH denotes cyclohexanol.

Entry	Catalysts	Lewis acids	<i>P</i> _{H₂} (MPa)	<i>T</i> (°C)	Time (hours)	Conversion (%)	Selectivity (%)	
							C=O	OH
1	Pd/C	–	1	30	12	12.6	93.8	6.2
2	–	AlCl ₃	1	30	12	0	0	0
3	Pd/C	AlCl ₃	1	30	12	>99.9	>99.9	<0.1
4	Pd/C	AlCl ₃	1	40	11	>99.9	>99.9	<0.1
5	Pd/C	AlCl ₃	1	50	7	>99.9	>99.9	<0.1
6	Pd/C	AlCl ₃	1	80	3	>99.9	99.3	0.7
7	Pd/C	AlCl ₃	2	80	2.5	>99.9	96.8	3.2
8	Pd/C	AlCl ₃	3	80	2	>99.9	95.1	4.9
9	Pd/C	AlCl ₃	0.5	100	1	>99.9	99.2	0.8
10	Pd/C	AlCl ₃	1	100	0.5	>99.9	99.0	1.0
11	Pd/C	AlCl ₃	2	100	0.3	>99.9	97.3	2.7
12	Pd/C	AlCl ₃	3	100	0.2	>99.9	96.2	3.8
13	Pd/C	InCl ₃	1	30	16	>99.9	>99.9	<0.1
14	Pd/C	InCl ₃	1	100	4	>99.9	99.3	0.7
15	Pd/C	ZnCl ₂	1	30	20	>99.9	>99.9	<0.1
16	Pd/C	ZnCl ₂	1	100	6	>99.9	98.7	1.3
16*	Pd/C	ZnCl ₂	1	100	6	>99.9	98.3	1.7
16†	Pd/C	ZnCl ₂	1	100	6	>99.9	98.7	1.3
16‡	Pd/C	ZnCl ₂	1	100	6	>99.9	98.6	1.4
17	Pd/C	SnCl ₂	1	30	22	>99.9	>99.9	<0.1
18	Pd/C	SnCl ₂	1	100	8	>99.9	98.9	1.1
19	Pd/Al ₂ O ₃	–	1	30	12	15.5	89.5	10.5
20	Pd/Al ₂ O ₃	AlCl ₃	1	30	8	>99.9	>99.9	<0.1
21	Pd/Al ₂ O ₃	AlCl ₃	1	50	3	>99.9	99.3	0.7
22	Pd/Al ₂ O ₃	AlCl ₃	1	80	2	>99.9	99.0	1.0
23	Pd/NaY	–	1	30	12	10.6	82.3	17.7
24	Pd/NaY	AlCl ₃	1	30	9	>99.9	>99.9	<0.1
25	Pd/NaY	AlCl ₃	1	50	4	>99.9	>99.9	<0.1
26	Pd/NaY	AlCl ₃	1	80	3	>99.9	99.3	0.7

*Second run to test the reusability of Pd/C–ZnCl₂ under the conditions of entry 16. †Third run to test the reusability of Pd/C–ZnCl₂ under the conditions of entry 16. ‡Fourth run to test the reusability of Pd/C–ZnCl₂ under the conditions of entry 16.

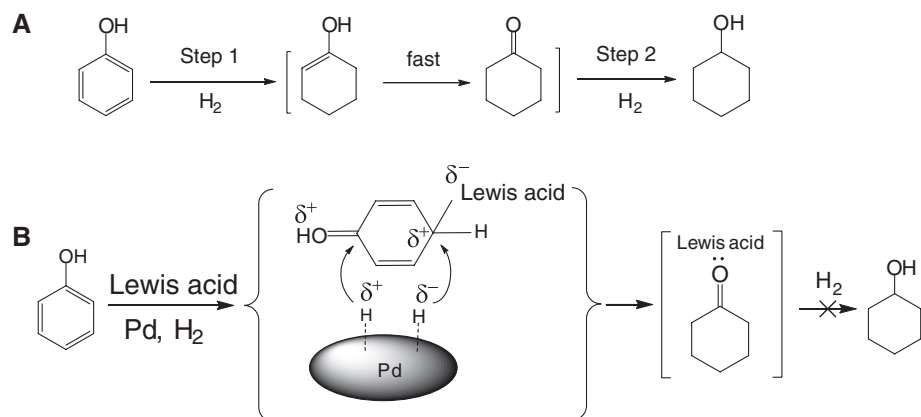


Fig 1. (A) General reaction pathway for hydrogenation of phenol. (B) Possible mechanism of dual activation in phenol hydrogenation and stabilization of cyclohexanone by Lewis acid.

It is known that Pd nanoparticles themselves are not active for the hydrogenation of benzene at low temperature (25), and they have very low activity for phenol hydrogenation (Table 1, entries 1, 19, 23). It has also been reported that Lewis acids can activate aromatic rings (26–28). Electrophilic aromatic substitution reactions have been extensively studied using experimental and theoretical techniques. Koltunov *et al.* (26) studied the reaction of 5-amino-1-naphthol with benzene in the presence of AlCl₃. Tarakeshwar *et al.* (28) studied the role of Lewis acids theoretically by performing high-level ab initio calculations on two model systems: C₆H₆-BCl₃ and C₆H₆-AlCl₃. Their results clearly indicated that one of the carbons in benzene tends to become highly nucleophilic, thereby facilitating attack of the benzene ring by an incipient electrophile. Furthermore, it is well known that Pd can activate H₂ (29). Based on the experimental data presented here and the literature results, we can conclude that in the hydrogenation of phenol, these two types of activation work cooperatively, resulting in high activity for producing cyclohex-

anone. This synergy also enhances the selectivity, because the reaction in the first step becomes relatively faster than that in the second step.

Inhibition of cyclohexanone hydrogenation (Fig. 1A, step 2) is another crucial factor underlying the high selectivity that we observed. We conducted the hydrogenation of cyclohexanone under some typical conditions using Pd/C and Pd/C-AlCl₃ as the catalysts (Table 3). The conversion of cyclohexanone catalyzed by Pd/C-AlCl₃ is much lower than that catalyzed by Pd/C. This result indicates that the Lewis acid suppresses the second step in Fig. 1A effectively. To account for this phenomenon, we studied the interaction between cyclohexanone and AlCl₃ in dichloromethane by Fourier transform infrared spectroscopy (fig. S7 and SOM text). The absorption band of the C=O stretching vibration shifts from 1714 cm⁻¹ in the absence of AlCl₃ to 1624 cm⁻¹ in the presence of AlCl₃. This shift is consistent with coordination of the Lewis basic C=O group to the Lewis acid (30). We believe that this Lewis acid–base interaction inhibits further hydrogenation of cyclohexanone.

Table 2. Hydrogenation of phenol in CO₂ under different pressures. Parameters were determined as in Table 1, and no additional products were observed. Reaction conditions were as follows: temperature, 30°C; p_{H_2} , 1.0 MPa; phenol, 2.0 mmol; Pd (5 wt % in Pd/C), 5 mol % relative to phenol; Lewis acid, 10 mol % relative to phenol.

Entry	Lewis acids	$P_{H_2} + P_{CO_2}$ (MPa)	Time (hours)	Conversion (%)	Selectivity (%)	
					Cyclohexanone	Cyclohexanol
1	AlCl ₃	5.0	17.0	49.7	98.9	1.1
2	AlCl ₃	6.5	13.0	63.9	98.2	1.8
3	AlCl ₃	7.0	1.7	>99.9	>99.9	<0.1
4	AlCl ₃	7.5	3.0	>99.9	>99.9	<0.1
5	AlCl ₃	8.0	4.0	>99.9	>99.9	<0.1
6	AlCl ₃	8.5	5.5	>99.9	>99.9	<0.1
7	InCl ₂	7.0	8.0	>99.9	>99.9	<0.1
8	InCl ₂	7.5	9.5	>99.9	>99.9	<0.1
9	InCl ₂	8.0	10.0	>99.9	>99.9	<0.1
10	ZnCl ₂	7.0	7.0	>99.9	>99.9	<0.1
11	ZnCl ₂	7.5	7.3	>99.9	>99.9	<0.1
12	ZnCl ₂	8.0	8.0	>99.9	>99.9	<0.1
13*	AlCl ₃	8.0	4.0	>99.9	>99.9	<0.1
14†	AlCl ₃	8.0	4.0	>99.9	>99.9	<0.1
15‡	AlCl ₃	8.0	4.0	>99.9	>99.9	<0.1

*Second run to test the reusability of Pd/C-AlCl₃ under the conditions of entry 5. †Third run to test the reusability of Pd/C-AlCl₃ under the conditions of entry 5. ‡Fourth run to test the reusability of Pd/C-AlCl₃ under the conditions of entry 5.

Table 3. Hydrogenation of cyclohexanone under different conditions. Conversions and yields were determined by GC. Reaction conditions were as follows: cyclohexanone, 1.0 mmol; p_{H_2} , 1.0 MPa; Pd (5 wt % in Pd/C), 5 mol % relative to cyclohexanone; AlCl₃ (if used), 10 mol % relative to cyclohexanone; solvent, 1 ml of dichloromethane.

Entry	Catalysts	T (°C)	Time (hours)	Conversion (%)	Yield of cyclohexanol (%)
1	Pd/C	30	12	0.7	0.7
2	Pd/C-AlCl ₃	30	12	<0.1	<0.1
3	Pd/C	50	7	12.9	12.9
4	Pd/C-AlCl ₃	50	7	0.4	0.4
5	Pd/C	100	0.5	37.3	37.3
6	Pd/C-AlCl ₃	100	0.5	1.8	1.8
7	Pd/C	100	4	53.7	53.7
8	Pd/C-AlCl ₃	100	4	2.8	2.8

On the basis of the above discussion, the high activity and selectivity of the dual catalyst systems can be explained reasonably, as shown in Fig. 1B. The Pd, Lewis acid, and reactants contact each other when stirred. Lewis acid coordination makes the benzene ring of phenol more active, while Pd activates H₂, and cyclohexanone is formed quickly. At the same time, acid-base interaction between the Lewis acid and cyclohexanone inhibits further hydrogenation to cyclohexanol.

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SOM Text

Figs. S1 to S10

Tables S1 and S2

References

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