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Selective hydrogenation of phenol and the related derivatives

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Selective hydrogenation of phenol and the related derivatives to cyclohexanone and analogues remains a challenging task. In the present minireview, we highlight the research advancement in this field. The front part introduces the significance, pathway and mechanism of the reaction. The main part summarizes the reaction over different kinds of mediums (vapor phase, organic solvent, supercritical carbon dioxide, ionic liquid and water) and catalyst systems (Non-supported catalyst, supported catalyst with metal oxide, polymer, carbon material, mesoporous silica, metal-organic framework and graphitic carbon nitride *etc.* as the support). Then the influence factors such as acid-base property of the support, promoter, metal precursor, structure sensitivity and deactivation are discussed in details. The final section summarizes the kinetics studies.

1. Introduction

Cyclohexanone is of great commercial significance as one of the key raw material in the synthesis of caprolactam and adipic acid which are the main ingredients for the productions of nylon 6 and nylon 66, respectively.[1-4] Currently, the industrial production of cyclohexanone production can be classified into three routes including the Asahi process,[5, 6] the oxidation of cyclohexane[7, 8] and the hydrogenation of phenol[9-12] (Fig. 1). Asahi process contains partial hydrogenation of benzene to cyclohexene, hydration of cyclohexene to cyclohexanol and dehydrogenation of cyclohexanol. The second route requires high operating pressure and temperature, and produces undesirable secondary products. Therefore, it lowers the overall yield of cyclohexanone and complicates the recovery and separation stage. Regarding the third route, cyclohexanone can be obtained from phenol in a "two-step" or a "one-step" process. In the conventional two-step process, phenol is firstly hydrogenated to cyclohexanol, and cyclohexanol is subsequently dehydrogenated to yield cyclohexanone.[13-16] Therefore, the one-step process, selective hydrogenation of phenol to cyclohexanone, has a great amount of advantages. It simplifies reaction steps, improves efficiency of hydrogen utilization, reduces waste disposal,[3, 17-19] and avoids the difficult separation of phenol–cyclohexanol and phenol-cyclohexanone azeotropes.[20, 21]

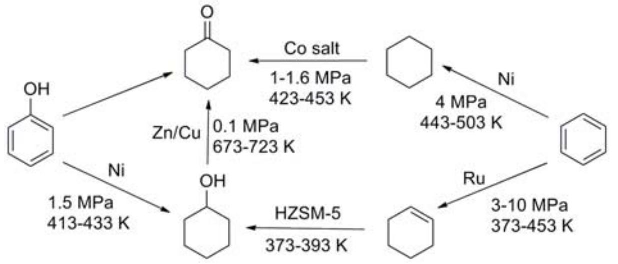


Fig 1. Industrial production of cyclohexanone.

2. Reaction Pathway

The standard free energy changes of the reactions are negative for each hydrogenation step, thus cyclohexanone (ΔG = -145 kJ/mol) and cyclohexanol (ΔG = -211 kJ/mol) are thermodynamically favorable products.[22, 23]

Based on the literatures to date, three classes of reaction pathways have been proposed. Some published reports claimed that phenol hydrogenation follows a consecutive pathway. The benzene ring of phenol is partially hydrogenated to 1-hydroxycyclohexene, and the thermodynamically unstable enol isomerizes rapidly to yield cyclohexanone.[24-27] However, cyclohexanone is readily further hydrogenated to cyclohexanol under the investigated conditions.[18, 22, 28-35] Another proposed reaction pathway involves cyclohexanol formation not only *via* cyclohexanone but also from 1-hydroxycyclohexene or directly from phenol.[36-45] In addition, some research groups revealed that cyclohexanone and cyclohexanol are formed independently rather than at the expense of each other (Fig. 2).[46-48] In summary, it is a challenging task to attain high selectivity (>95%) for cyclohexanone production at elevated phenol conversion (>80%) with a satisfactory rate.[30, 49]

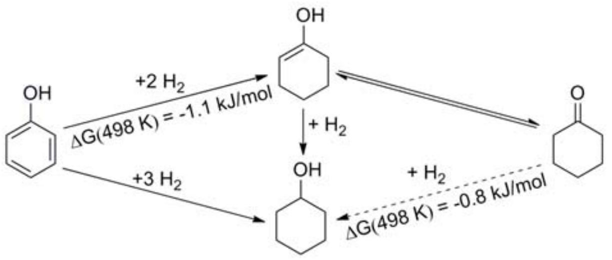


Fig 2. Reaction pathway (showing thermodynamically favourable steps) in the hydrogenation of phenol.

3. Reaction Mechanism

It has been established that hydrogenation of phenol occurs between the activated hydrogen and chemisorbed phenol. The hydrogen is supplied to the aromatic ring by a spill-over mechanism.[28, 50] In addition, when strongly adsorbed on the support *via* the oxygen atom of the hydroxyl group in the form of phenolate (confirmed by FT-IR),[51, 52] phenol can adopt two different modes. Phenol, absorbed on the acid sites in coplanar form,[52] favors the formation of cyclohexanol owing to stronger interaction between the aromatic ring and the support (Fig. 3a). On the contrary, phenol can be chemisorbed on the base sites in nonplanar form, which usually facilitates the production of cyclohexanone (Fig. 3b).[28] In generally, high phenol adsorption capacity (confirmed by TPD *et al.*)[30, 53, 54 55] on the support promotes high catalytic activity and selectivity to cyclohexanone. Whereas, weak interaction between cyclohexanone and support (confirmed by TPD)[56] favors cyclohexanone desorption and prevent its over hydrogenation.

By comparison, in the case of palladium catalyst supported on the calcined hydrotalcite (CHT), Chen *et al.* proposed that both phenol and hydrogen molecules are chemisorbed on the metal sites of the Pd/CHT. The benzene ring of phenol might adopt coplanar (Fig. 3c) or nonplanar (Fig. 3d) form, which is determined by the number and strength of the acid and base sites in the vicinity of metal sites. For instance, phenol, absorbed on the support with more and stronger base sites in the form of coplanar, prefers to yield cyclohexanone.[50]

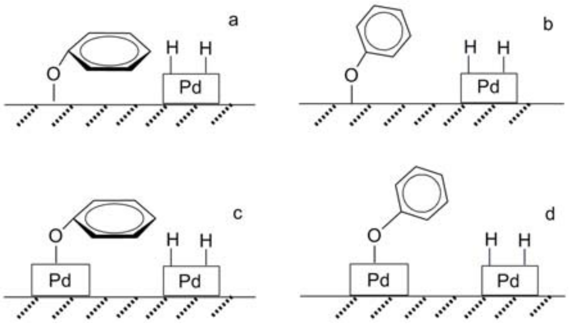


Fig 3. (a) Coplanar mode (Two-site model), (b) Nonplanar mode (Two-site model), (c) Coplanar mode (One-site model), (d) Nonplanar mode (One-site model). Adapted with permission from Ref. 28 and Ref. 50. Copyright © 1994, Elsevier, Copyright © 1999, Elsevier.

4. Vapor Phase Hydrogenation of Phenol

4.1. Monometallic catalyst

It is widely recognized that Pd-based catalyst exhibits best performance for the reaction among supported noble metal catalysts. Haruhiko *et al.* investigated the catalytic performances of Group VIII metals. They pointed out that palladium shows no hydrogenolysis activity and the lowest hydrogenation activity for phenol and cyclohexanone, respectively. The major product is cyclohexanone while benzene and cyclohexane are not detected.[57] Table 1 summarizes the developed catalytic systems for vapor hydrogenation of phenol.

In general, the vapor phase hydrogenation is carried out over Pd/MgO and Pd/Al_2O_3. However, magnesia supported catalyst is unsuitable for large scale commercial application, owing to the poor mechanical strength of the magnesia. In the case of alumina supported catalyst, it generally suffers from deactivation by coke deposition, owing to the strong acid sites on the alumina.[51] Narayanan and team members made systematic studies of CHT and uncalcined hydrotalcite (UHT) supported palladium catalysts. They drew the conclusion that calcination temperature, preparation method, interlayer anions and aluminium content affect the metal dispersion and the catalytic activity.[58-62] For instance, HT, synthesized with the high supersaturation method or with interlayer CO_3^{2-} anion, shows better performance than that synthesized with low supersaturation or with other interlayer anion (SO_4^{2-}, HCO_3^{2-}, Cl^-), respectively.[58, 59]

Polymer-supported transition metal catalysts have received growing attention as well. For instance, Sulman *et al.* deposited palladium onto hyper-cross-linked polystyrene (HPS) which is with relative inertness and high durability. It is found that the selectivity to cyclohexanone is unaffected by temperature within specific phenol conversion range.[40, 63] Baumgarten *et al.* resorted to polymer with nitrogen function such as poly{acrylamide-co-[3-(acryloylamino)propyltrimethylammonium chloride]}. The electron donation from nitrogen center of the support to the active metal sites changes the adsorption property of metal. It is proposed that weakly absorbed phenol and strongly absorbed hydrogen results in 100% selectivity for cyclohexanone.[64]

The metal-support interaction[65] has been extensively studied in decades. Talukdar *et al.* investigated the performances of palladium and platinum catalysts supported on basic zeolite LTL and non-acidic alumina. It is shown that palladium catalyst favors the cyclohexanone formation while platinum catalyst prefers to formation of cyclohexanol. However, the latter shows higher overall conversion rate than the former. The author attributed the result part to strong metal support interactions (SMSI), since the charge transfer capacity of Pt is larger than that of Pd.[66] Claus *et al.* proposed that electron-enriched palladium particle, resulted from metal–support interaction, cause better activation of hydrogen.[67] Keane *et al.* proposed that SMSI decreases in following order: Pd/Ta_2O_5 > Pd/graphite ≈ Pd/SiO_2 > Pd/“herringbone” graphitic carbon nanofibers (GCN) > Pd/“ribbon” GCN ≈ Pd/activated carbon (AC). The high catalytic activity of Pd/Ta_2O_5 can be attributed to the strong SMSI. Besides, Pd/Ta_2O_5 adopts a crystallographic orientation, which favors the cyclohexanone formation.[36, 68]

4.2. Bimetallic catalyst

Owing to the high catalytic activity, long lifetime, and the effective suppression of side reaction, great industrial and scientific interest has been focused on the bimetallic catalyst.

Rao and team members found that Pt-Cr/C and Pt-V/C show high selectivity to cyclohexanone, owing to the dilution effect of the platinum sites to some extent.[69] The differences in catalytic activity and selectivity to cyclohexanone between Pt-Cr/C and Pt-V/C can be ascribed to the degree of metal-metal interaction between platinum and the alloying element.[19, 70] Keane and group members reported that Pd-Yb/SiO_2, derived from cyanide bridged lanthanide palladium complex $\{(DMF)_{10}Yb_2[Pd(CN)_4]_3\}_\infty$, exhibits higher phenol conversion and overall yield of cyclohexanone than Pd/SiO_2.[34] The promotion effect of Yb is ascribed to the electron donation from strongly electropositive Yb that activates reactant.[71] Later on, their group proposed that Pd-Yb synergistic effect results from the hydrogen transfer from Yb hydride.[72]

Table 1 Catalytic systems for vapor hydrogenation of phenol

Catalyst	*T* [K]	H_2/phenol mole ratio	Parameter	Reactor	Phenol Conversion [%]	Cyclohexanone Selectivity [%]	TOF	Ref.
1% Pd/Al_2O_3	503	5.4	0.0135 mol h^{-1} [a]	Fixed bed reactor	77.0	98.0	0.13 [f]	48
1% Pd/MgO	503	5.4	0.0135 mol h^{-1} [a]	Fixed bed reactor	90.0	82.0	0.13 [f]	48
1% Pd/TiO_2	473	4.5	2.5 mL h^{-1} [a]	Fixed bed reactor	79.6	99.0	n/a	75
Pd membrane	473	n/a	0.5 cm^3 min^{-1} [b]	Catalytic palladium membrane reactor	90.0	>75.0	n/a	73
Pd-1% Na/Al_2O_3	503	5.4	7.5×10^{-6} mol s^{-1} g^{-1} [c]	Fixed bed reactor	88.0	>95.0	n/a	76
1% Pd/HT	453	4.0	0.037 mol h^{-1} g^{-1} [c]	Fixed bed reactor	98.0	92.0	n/a	60
3% Pd/CeO_2-MS	453	6.0	23 mol h^{-1} kg^{-1} [c]	Fixed bed reactor	93.7	47.0	≈ 0.03 [f]	77
3% Pd/ZrO_2-MS	453	6.0	23 mol h^{-1} kg^{-1} [c]	Fixed bed reactor	62.9	93.0	n/a	77
Pd/Ta_2O_5	423	n/a	128 g mol^{-1} h [d]	Fixed bed reactor	54.0	87.0	n/a	36
Pd/AC	423	n/a	385 g mol^{-1} h [d]	Fixed bed reactor	55.0	90.0	n/a	36
Pd-K/silica-gel	448	4.0	200 g mol^{-1} h [d]	Fixed bed reactor	100	85	n/a	78
5% Pd-Yb/SiO_2	423	n/a	128 g mol^{-1} h [d]	Fixed bed reactor	69.1	68.0	n/a	72
5% Pt-0.5% Cr/C	473	4.7	26.7 μmol g^{-1} [e]	Fixed bed reactor	55.0	100	n/a	69
5% Pt-4% V/C	473	4.7	9.8 μmol g^{-1} [e]	Fixed bed reactor	50.0	96	n/a	70
Pd/HPS	393	n/a	n/a	Steel tube	>99.0	>95	n/a	40

Flow rate of Phenol for [a], Flow rate of hydrogen for [b], Weight hourly space velocity (WHSV) for [c], Ratio of catalyst weight to phenol molar flow rate (W/F_{phenol}) for [d], Hydrogen uptake for [e], and TOF (s^{-1}) for [f]. n/a indicates not available.

By contrast, Itoh *et al.* explored catalytic palladium membrane reactor (CPMR) and pointed out that pure palladium membrane promotes catalytic activity and cyclohexanone selectivity to a greater extent compared with $Pd_{93}Ni_7$, $Pd_{93}Ru_7$ and $Pd_{77}Ag_{23}$. In addition, the whole permeated hydrogen can participate in the reaction, while just a part of the premixed hydrogen reacts with the substrate. Therefore, the use of permeated hydrogen leads to higher yield of cyclohexanone than that of premixed hydrogen.[73] Similarly, Gryaznov *et al.* reported that the penetrated hydrogen results to higher yield of cyclohexanone over Pd-Ru alloy. [74]

5. Liquid Phase Hydrogenation of Phenol

Though catalyst filtration and circulation are not necessary[40], the vapor phase hydrogenation suffers from deficiencies such as high reaction temperature (150 °C - 300 °C) and catalyst deactivation caused by the generation of carbonaceous deposits (coking). Thus, liquid phase hydrogenation has attracted a great amount of research activities, owing to the relatively mild reaction conditions, reasonable cost and energy savings.[49, 79, 80] In general, the liquid phase hydrogenation is performed in organic solvents, supercritical carbon dioxide (*sc*CO_2), ionic liquid and water. Table 2 summarizes the developed catalytic systems for liquid phase hydrogenation of phenol.

It is generally agreed that chemically controlled regime in liquid phase reaction should be in the absence of mass transfer limitation. The absence of mass transfer limitations typically has been probed by varying the catalyst particle size and/or the stirring speed.[43, 54, 81] In particular, Gonzalez-Velasco *et al.*[21] and Gutierrezortiz *et al.*[82] had done systematic works to address the issue of mass transfer.

5.1. Organic Solvent

Decades ago, Benkeser *et al.* found that lithium dissolved in low molecular weight amines partially hydrogenates aromatic hydrocarbon to monoolefin. For example, lithium dissolved in ethylamine provides 96% yield of cyclohexanone which is tautomerised from enol.[27]

Many investigations have been focused on the solvent effect. Higashijima *et al.* pointed out that basic Pd/C and acid-treated Pd/C exhibit higher conversion rate of phenol and better yield of cyclohexanone in nonpolar cyclohexane than in *tert*-pentyl alcohol. It is proposed that solvation of alcohol around phenoxide ion on the basic Pd/C weaken the adsorption of phenoxide ion.[43] Likewise, Chen *et al.* concluded that nonpolar solvent enhance the catalytic activity of silica-supported polytitazane-platinum bimetallic complex (Ti-N-Pt-Mn). However, the authors ascribed it to higher initial hydrogen uptakes in nonpolar solvent.[83]

The polymer-metal complex has been investigated deeply by Chen, Tang and team members. By studying silica-supported polytitazane-platinum monometallic complex (Ti-N-Pt) and the corresponding bimetallic complexes such as Ti-N-Pt-Mn, the authors concluded that the electron-deficient metal such as Mn (II), Fe (III) and Sn (II), functioning as Lewis adsorption site for cyclohexanone, effectively suppress the further hydrogenation of cyclohexanone. In the case of Ti-N-Pt, the maximum yield of cyclohexanone (62.2%) can be obtained when the mole ratio of N/Pt is 28.[84] As for Ti-N-Pt-Mn, the maximum yield to cyclohexanone (49.2%) can be attained with the mole ratio of Mn/Pt to be 4.[83, 85] Besides, silica-supported chitosan-palladium complex (SiO_2-CS-Pd) was synthesized. It is found that SiO_2-CS-Pd is inertial to the further hydrogenation of cyclohexanone and the highest yield of cyclohexanone is obtained with the N/Pd mole ratio of 8.[86, 87]

Many studies have been devoted to developing effective phase-transfer catalysts. Blum *et al.* synthesized the solvated ion pair from aqueous rhodium trichloride and methyltrioctylammonium chloride (aliquat-336) in dichloroethane, and performed the reaction under phase transfer condition. The cyclohexanone formation is ascribed to tautomerization of cyclohexenol.[26] Januszkiewicz *et al.* performed the reaction over phase-transfer catalyst of tetrabutylammonium hydrogen sulfate (THS) and dimer of chloro(1,5-hexadiene)rhodium in benzene and buffer solution, and reached a 73% yield to cyclohexanone.[88]

Table 2 Catalytic systems for liquid phase hydrogenation of phenol

Catalyst	Solvent	*T* [K]	P_{H2} [MPa]	Time [h]	Reactor	Phenol Conversion [%]	Cyclohexanone Selectivity [%]	Parameter	Ref.
RhCl{N,N,N-p-$(CF_3)_2$}	2-Propanol	333	0.1	5	Flask	>99.9	>99.9	30 [d]	24
Ce-doped Pd(H)	EtOH	353	1	1.5	Autoclave	100	83	195.7 [e]	49
5.8% Pd-Ce-B/HT	EtOH	393	1	4	Autoclave	82	80.3	259.8 [e]	89
SiO_2-CS-Pd	Cyclohexane	343	0.1	48	Flask	94.6	100	n/a	86
Ru/Al_2O_3	Cyclohexane	433	5	2	Autoclave	88	83	n/a	90
Pd/C	Cyclohexane	393	5	0.67	Autoclave	79.6	98	n/a	43
$[(C_8H_{17})_3NCH_3]^+[RhCl_4]^-$	CH_2Cl_2	303	0.1	5	n/a	56	67	n/a	26
5% Pd/MHSS	CH_2Cl_2	303	1	12	Autoclave	75	95	n/a	91
PdAu/MHSS	CH_2Cl_2	323	1	0.75	Autoclave	97.5	96.6	n/a	92
Pd-SH-MCM-41	CH_2Cl_2	353	1	1	Autoclave	>99	98.1	n/a	93
Pd/C-$AlCl_3$	CH_2Cl_2	323	1	7	Teflon-lined reactor	>99.9	>99.9	n/a	29
Pd/Al_2O_3-$AlCl_3$	CH_2Cl_2	303	1	8	Teflon-lined reactor	>99.9	>99.9	n/a	29
Pd/NaY-$AlCl_3$	CH_2Cl_2	303	1	9	Teflon-lined reactor	>99.9	>99.9	n/a	29
Pd/C-$Sc(OTf)_3$	CH_2Cl_2	298	0.1	2	Schlenk flask	>99.9	>99.9	n/a	94
Pt@TNT	CH_2Cl_2	323	0.5	n/a	Autoclave	96	n/a	3200 [f]	95
Rh/C	*sc*CO_2	353	3	0.17	Batch reactor	35	68	n/a	45
Rh/PFA	*sc*CO_2	323	1	0.33	High pressure cell	100	60	n/a	96
5% Rh/CNF	*sc*CO_2	323	4	0.5	Autoclave	100	43.3	n/a	97
Pd/Al-MCM-41	*sc*CO_2	323	4	4	Batch reactor	98.4	97.8	n/a	47
Pd/B-MCM-41	*sc*CO_2	323	4	4	Batch reactor	98.5	100	n/a	98
Pd/C-$InCl_3$	*sc*CO_2	303	1	8	High pressure view reactor	>99.9	>99.9	n/a	29
Pd/C-$ZnCl_2$	*sc*CO_2	303	1	7	High pressure view reactor	>99.9	>99.9	n/a	29
Rh-PAA	$N_{8881}Cl$	353	4	3	Autoclave	100	100	n/a	99
Pd/hydrophilic-C	H_2O	373	1.0	20	Autoclave	99	95	n/a	100
1.5% Pd/Al_2O_3-CWE	H_2O	373	0.5	0.83	Batch reactor	100	98.0	0.15 [g]	39
Pd/HA	H_2O	373	0.5	0.83	Batch reactor	100	97.0	0.04 [g]	39
0.5% PdNPs@CNC	H_2O	298	0.4	24	Multiple reactor	90	100	n/a	101
Pd/mpg-C_3N_4	H_2O	353	0.1	3	Flask	100	>99	33 [h]	54
5% Pd-MIL-101	H_2O	298	0.1	11	Autoclave	>99.9	>99.9	n/a	102
Pd/MIL-101	H_2O	323	0.5	2	Batch reactor	85	98.8	52 [h]	53
Pd/Al-MIL-53-NH_2	H_2O	363	0.5	2	Batch reactor	98.8	95.1	44 [h]	103
Pd/Fu-TiO_2-C	H_2O	373	0.5	n/a	Batch reactor	99.0	97.0	71 [i]	104
Pd/TiO_2-AC_{ZnCl2}	H_2O	373	0.5	n/a	Batch reactor	99.0	96.0	91.1 [h]	104
Pd-PVP	H_2O	363	0.1	16	Round bottle	99.7	99.5	n/a	105
Pd/ABO-X	H_2O	353	0.5	4	Batch reactor	99	99	n/a	106
Pd/Copolymer-HPW	H_2O	353	0.1	7	Flask	>99	>99	n/a	32
Pd–PANI/CNT	H_2O	353	0.1	9	Schlenk flask	>99	>99	n/a	31
Pd–PANI/CNF	H_2O	353	0.1	9	Schlenk flask	>99	>99	n/a	31
Pd–PANI/CB	H_2O	353	0.1	9	Schlenk flask	>99	>99	n/a	31
$Pd^{2.5}@FDU^3–N^H$	H_2O	373	0.1	2	Fixed bed reactor	99	99	n/a	107
Pd/La_1-Al_2O_3	MeOH	490	[a]	n/a	Fixed bed reactor	44.4	96.3	≈13 [h]	108
Ba-Pd/Al_2O_3	MeOH	473	[a]	n/a	Fixed bed reactor	96.8	82.9	n/a	109
Pd/Al_2O_3	EtOH	490	[b]	n/a	Tubular reactor	40.4	92.4	n/a	41
Pd/C	H_2O	353	[c]	0.25	Tube	100	98.0	n/a	42
$RuCl_2(PPh_3)_3$	H_2O	343	[c]	3	Flask	100	95.1	n/a	110
Pd-PANI/CNF	H_2O	353	[c]	5	Pressure Tube	>99	>99	n/a	111

Hydrogen is obtained from APR of methanol for [a], APR of ethanol for [b], and $HCOONa/H_2O$ for [c]. TOF (mol_{H2} mol_{Rh}^{-1} h^{-1}) for [d], Specific activity ($mmol_{H2}$ g_{Pd}^{-1} h^{-1}) for [e], Quartz TOF (g_{phenol} g_{Pt}^{-1} h^{-1}) for [f], TOF (s^{-1}) for [g], TOF (h^{-1}) for [h], and TOF (μmol_{phenol} g^{-1} s^{-1}) for [i]. n/a indicates not available.

Hollow sphere has attracted a great amount of interests recently due to the properties such as high surface area. For example, with Bu_4PBr as the vesicle template, a novel mesoporous Ce-doped Pd nanosphere with hollow chamber [Ce-doped Pd(H)] was synthesized. The highly dispersed metal atoms in hollow structure lead to activity improvement. The phenol, adsorbed on both the outer and interior shell of the hollow chamber, adopts nonplanar fashion, which results to high selectivity to cyclohexanone.[49] Likewise, Liao and coworkers developed the mesoporous hollow silica sphere (MHSS) through tetraethyl orthosilicate (TEOS) emulsion droplet with the assistance of 1-dodecanamine (DDA). TEOS acts as the silicate precursor, whereas DDA serves as not only neutral surfactant for mesoporous template but also catalyst for silica precursor hydrolysis and condensation. The hollow structure of MHSS and high BET surface area lead to significant increase in the activity of Pd/MHSS.[91] Besides, their group continued to research on mesoporous silica materials. They deposited palladium on mercapto group (–SH) grafted mesoporous silica (MCM-41 and SBA-15). The –SH group functions as anchoring point for the palladium attachment on the support, which results in high distribution of metallic sites and excellent catalytic performance.[93]

The combination of metal nanoparticles (NPs) and solid Lewis acids has triggered considerable interests. Han *et al.* reported that the combination of supported palladium catalysts (Pd/C, Pd/Al_2O_3, Pd/NaY zeolite) and solid Lewis acids yields cyclohexanone as dominant product with a complete phenol conversion. Pd activates hydrogen molecule while Lewis acid activates benzene ring of phenol, which favors the formation of cyclohexanone. Meanwhile, acid-base interaction between the cyclohexanone and Lewis acid suppresses over reduction of cyclohexanone (Fig. 4).[29] Nevertheless, it is important to highlight that the Lewis acids such as $AlCl_3$ are highly moisture sensitive. Thus, moisture-free solvent, anhydrous catalyst and dry atmosphere are essential for the investigated catalytic system.[112] In addition, due to the solubility of $AlCl_3$ in the organic solvent in the reaction system, the catalyst suffers from limitation in recycling ability.[91] Recently, emphasis has been laid on Lewis acids which are stable to water. Lee *et al.* resorted to lanthanide triflates such as $Sc(OTf)_3$, $Sm(OTf)_3$, and $Eu(OTf)_3$. The Pd-C/$Sc(OTf)_3$ hydrogenates phenol to cyclohexanone in mild reaction condition and short time with >99.9% conversion of phenol and >99.9% selectivity of cyclohexanone. The high cyclohexanone selectivity can be attributed to the activation of the ring of phenol with lanthanide triflates.[94]

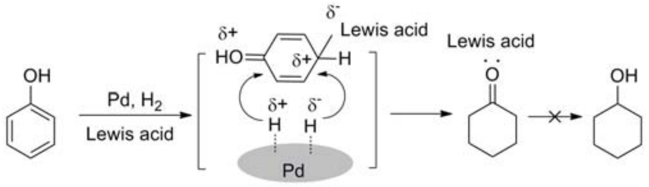


Fig 4. Proposed mechanism for the hydrogenation of phenol to cyclohexanone over a dual supported Pd-Lewis acid catalyst

It is widely acknowledged that metal NPs tend to agglomerate, thus stabilizers such as poly-N-vinyl-2-pyrrolidone (PVP) or ligand containing pyridine are of great necessity. Galletti and group members developed an *in situ* solvothermal synthesis of Ru/Al_2O_3. Al_2O_3, ethanol solution of $RuCl_3$ and stabilizer PVP are introduced before the reduction step, which leads to small diameter and narrow dimensional distribution of Ru NPs.[90] They further developed an *in situ* microwave-assisted synthesis of Ru/Al_2O_3, which shortens the reaction time and leads to excellent catalytic performance.[80] Buil *et al.* synthesized Rh NPs from Chloro[2,6-bis{1-(phenyl)iminoethyl}pyridine] rhodium(I) complexes [RhCl(N,N,N)] in the presence of Brønsted base. 100% yield of cyclohexanone is attained over RhCl{N,N,N-p-$(CF_3)_2$}, including a *p*-CF_3 substituent at the phenyl groups of the ligand. However, it is noteworthy that RhCl{N,N,N-p-$(CF_3)_2$} complex is air sensitive.[24]

It should be stressed that pretreatment can post great impact on the structure and property of material. Watanabe *et al.* observed that acid treatment induces graphitized activated carbon. The electron donation from graphitized activated carbon to Pd NPs contributes to easier desorption of phenoxy species and enhances cyclohexanone selectivity.[113] Li *et al.* entrapped Pt NPs into titanate nanotubes (TNT) by using hydrophobic modification. The Pt NPs are mainly dispersed in the inner pores and on the external surface of the TNT for Pt@TNT (2-3 nm) and Pt/TNT (3-5 nm), respectively. It is found that the confinement effect enhances the catalytic activity by intensifying the Pt–TiO_2 interaction (electronic effect) and decreasing the particle size (morphological effect) (Fig. 5).[95]

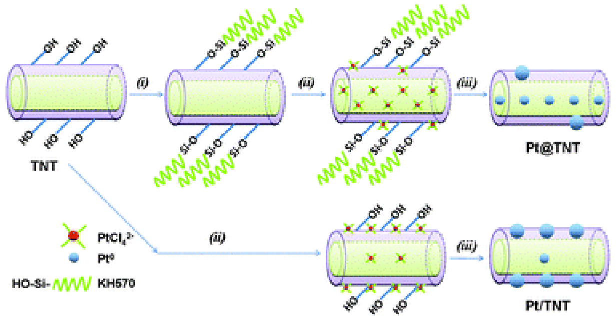


Fig 5. Route to synthesize Pt@TiO_2. (i) Hydrophobic modification; (ii) Wet impregnation; (iii) Thermal reduction. Reproduced from Ref. 95.

5.2. Supercritical carbon dioxide

From the environmental point of view, it would be much better to eliminate the use of hazardous and toxic organic solvent. In addition, considering the low solubility of H_2 in most organic solvents[114] and the high solubility of phenol in *sc*CO_2,[115] phenol hydrogenation working in *sc*CO_2 have advantages of minimizing waste generation, increasing solubility of hydrogen gases,[47, 97, 98] avoiding mass-transfer limitation and separating catalyst from product easily.[114, 116-119]

A great deal of researches is focused on Rh-based catalysts supported on carbon material. Rode and colleagues pointed out that Rh/C shows higher activity than Ru/C, Pd/C and Pt/C at relevantly low temperature in *sc*CO_2.[37, 45] The observation is, however, inconsistent with that attained in the gas/liquid phase phenol hydrogenation in which the Pd-based catalyst is considered to be the most effective. The authors attributed it to the different hydrogen solubility, adsorption property of phenol and electronic surrounding of the metal particles in *sc*CO_2. In addition, it is proposed that CO_2 strongly adsorbed on Pd surface leads to inaccessible Pd surface and slower activity of Pd. Similarly, Arai and coworkers performed the reaction over carbon nanofibers (CNT) supported Rh NPs and found that the presence of CO_2 suppresses over reduction of cyclohexanone. It is proposed that the cyclohexanone may be adsorbed too strongly on the surface of support/Rh NPs, or instead the target product is too difficult to be adsorbed.[97] The over reduction of cyclohexanone is suppressed over Rh/C and Rh/Al_2O_3 as well. Besides, it is found that the formation and adsorption of CO inhibit the phenol hydrogenation rate.[38 120]

Ohde and coworkers have focused on the issue of aggregation. It is found that polymer such as high density polyethylene (HDPE) granules and fluoropolymer (PFA) tube prohibit agglomeration of metal NPs and facilitate the interactions between phenol and metal particle in swelled plastic structures. Similarly, they observed that Rh NPs show better performance than Pd NPs.[96] In addition, their group synthesized the Rh NPs in a water-in-CO_2 microemulsion for the first time and achieved excellent phenol conversion rate (>92%) and high cyclohexanone selectivity (ratio of cyclohexanone to cyclohexane ≈ 15:1). Nevertheless, the Rh NPs only maintain catalytic activity in a short time due to the subsequent aggregation.[118]

By contrast, the reaction has also been performed over Pd-based catalyst. Chatterjee *et al.* carried out the reaction over

Pd/Al-MCM-41 and Pd/B-MCM-41.[47, 98] It is proposed that the interaction between polar phenol and quadropolar *sc*CO_2 is weaker than that of substrate-catalyst, thus less space is available for the concentrated phenol absorbed on the catalyst active site, which results in the nonplanar form. The high selectivity to cyclohexanone in *sc*CO_2 is also confirmed by transition state calculations using density functional theory (DFT).[47] Han *et al.* reported that the reaction can be accelerated over the supported palladium catalyst-solid Lewis acids system in *sc*CO_2, owing to the large diffusion coefficient and weak Lewis acidity of CO_2.[29]

5.3. Ionic liquid

Ionic liquid (ILs), green alternatives to the toxic and volatile organics, contain advantages such as negligible vapour pressure and high thermal stability.[121, 122] In addition, ILs function as stabilizers for the synthesis of metal NPs.[123] However, there is a dearth of literature on selective hydrogenation of phenol in ILs.

Maksimov *et al.* carried out the reaction over Rh NPs stabilized by polyacrylic acid (PAA) in ionic liquids. Tetraalkylammonium ionic liquids reduce the particle size and prevent the aggregation of metal NPs. 100% yield of cyclohexanone is obtained with methyl(trioctyl)ammonium chloride [$CH_3(C_8H_{17})_3NCl$].[99]

5.4. Aqueous Media

Generally, hydrogenation of phenol in *sc*CO_2 needs high H_2 and CO_2 pressure.[37, 47, 97] In contrast, water has high capacity to dissolve H_2[124] and it is easily available, environmentally innocuous and relatively cheap solvent in nature. Moreover, phenol is completely water soluble at temperature higher than 66°C while cyclohexanone and cyclohexanol are slightly soluble in water.[79, 125] Thus, aqueous hydrogenation facilitates the separation of products from the aqueous phase.

It is well known that the hydrophobicity/hydrophilicity of support play a vital role in affecting the adsorption–desorption equilibrium of the adsorbed species (phenol and cyclohexanone). Titirici *et al.* synthesized Pd/hydrophilic-C through one-pot hydrothermal carbonization. The author suggested that the hydrophilic support inhibits cyclohexanone from over reduction by pushing the hydrophobic cyclohexanone away from the hydrophilic reactive pocket around Pd NPs.[100] Corma and group members reported that Pd NPs supported on hydroxyapatite (HA) or hydrophilic alumina with high surface area (Al_2O_3-CWE)[126] reach excellent catalytic performance.[39] The use of hybrid TiO_2-C or binary TiO_2-AC with high polarity and hydrophilicity increases catalytic activity and cyclohexanone selectivity, owing to the suppression of the further reduction of cyclohexanone.[104] By DFT calculation, Li *et al.* concluded that the hydrophilic activated carbon- and carbon nanotube (pretreated by HNO_3)-supported catalysts exhibit high selectivity to cyclohexanone by favoring desorption of cyclohexanone. However, the hydrophilic catalysts preferentially adsorb water and inhibit others, which results to low conversion of phenol hydrogenation.[127] Snelders *et al.* observed that PVP-stabilized Rh NPs yield approximately same amounts of cyclohexanone and cyclohexanol. However, the addition of phosphine ligand with hydrophobic group repels the relatively hydrophilic phenol and cyclohexanone, thus inhibits the hydrogenation of phenol to some degree.[128] Guan *et al.* observed that Pd/Al-MIL-53-H and Pd/Al-MIL-53-OCH_3 with higher hydrophilicity have easier accessibility to water, lower parent activation energy and higher reactivity by contrast to the counterparts with substituted group of NH_2, Cl and NO_2.[103]

Polymeric semiconductor mesoporous graphitic carbon nitride (mpg-C_3N_4), with excellent thermal and chemical stability, is explored as catalyst support recently.[129] Wang and coworkers synthesized Pd@mpg-C_3N_4 by means of deposition–precipitation (DP) route. Phenol conversion of 99% is attained with cyclohexanone selectivity >99% within 2 h at 65 °C. The mpg-C_3N_4 effectively anchors phenol by forming strong O-H···N or O-H···π interactions.[130] The nitrogen atoms in mpg-C_3N_4 favor the tight coordination and stabilization of metal particles. Besides, as basic host, mpg-C_3N_4 favors nonplanar adsorption of phenol, since the π···π interaction between the aromatic ring of phenol with mpg-C_3N_4 is relatively weaker. With the electrons donated from mpg-C_3N_4 to Pd NPs, the transfer of electron density in the semiconductor-metal heterojunction[131] enhances the hydrogenation rate. The benzene ring of phenol is hydrogenated to the enol which rapidly isomerizes to cyclohexanone. The cyclohexanone was replaced by the strongly binding phenol eventually (Fig. 6).[30] Recently, their group developed a more effective ultrasonic-dispersion method. 100% phenol conversion is attained with 100% cyclohexanone selectivity for 6 h at 65°C. It is proposed that the strong absorption capacity of mpg-C_3N_4 with phenol rather than cyclohexanone leads to high cyclohexanone selectivity and prevents cyclohexanone from over reduction. Besides, the DFT calculation proved that water can lower the transition state free energy and accelerate the reaction, which testify the superior catalytic activity in aqueous phase than in organic solvents. In addition, they revealed that hydrogen is activated by metal and explained the reaction mechanism clearly by isotopic tracing.[54] However, the environmentally unfriendly hydrogen fluoride (HF) or ammonium bifluoride (NH_4HF_2) are used for the preparation of the mpg-C_3N_4.

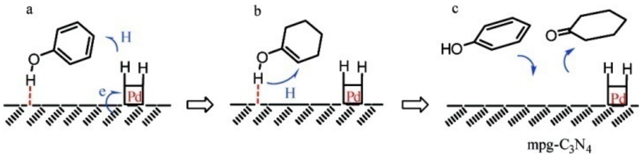


Fig 6. Possible Mechanism of Phenol over Pd@mpg-C_3N_4. Reproduced with permission from Ref. 30. Copyright (2011) American Chemical Society.

Due to the robust structure and large surface area by contrast with other micro- and mesoporous materials, metal-organic framework (MOF) has attracted growing attention in recent years. Liu *et al.* develop a water-tolerant bifunctional catalytic system which is composed of Pd NPs supported on acidic chromium terephthalate MIL-101 $\{Cr_3F(H_2O)_2O[(O_2C)\text{-}C_6H_4\text{-}(CO_2)]_3\}$.[132] Phenol conversion >99.9% is attained with >99.9% selectivity to cyclohexanone. It is proposed that Pd metal sites activate hydrogen and Lewis acid activates the phenol,[102] which is in good accordance with the mechanism proposed by Han *et al.*.[29] Guan and coworkers reported that the catalytic performance of Pd/MIL-101 is superior to that of Pd/MIL-53, which is attributed to the smaller palladium particle size, mesoporous structure and strong hydrophilicity of MIL-101.[53] Their team further deposited Pd NPs on mono-group (H, OCH_3, NH_2, Cl, and NO_2) substituted Al-MIL-53. By contrast to the catalysts with electron-withdrawing groups (Cl and NO_2), the counterparts with electrondonating groups (H, OCH_3, NH_2) exhibit higher hydrogen dissociation abilities, lower apparent activation energy and higher reactivity.[103] Their group also investigated the performance of aluminoborate (ABO-X, $9Al_2O_3.2B_2O_3$ and PKU-1) supported palladium catalyst and observed that Pd/ABO-X exhibits superior performance, owing to the high BO_4/BO_3 ratio of ABO-X.[106] In addition, they investigated the solvent effect and observed that phenol conversion drops remarkably in ethanol. They ascribed it to the competitive adsorption of solvents and reactants (phenol/H_2) on the same active site, which is in line with that observed by Velu *et al*.[77]

Currently, there is considerable interest in the role of polymer as support or stabilizer. Cirtiu *et al.* deposited Pd NPs on biopolymer colloidal cellulose nanocrystallites (CNCs). The high catalytic performance can be ascribed to CNC's excellent thermal, chemical and colloidal stabilities.[101] Liu *et al.* synthesized the water-soluble Pd NPs stabilized by PVP and observed that Pd-PVP exhibits high catalytic activity, which is ascribed part to the uniformly accessible Pd sites.[105]

Recently, our group has also made some effort in this field. We performed the selective hydrogenation of phenol by catalytic system consisted with heteropoly acid and "water soluble'' Pd NPs. Phenol conversion exceeding 99% is attained with >99% cyclohexanone selectivity. The polar and hydrophilic cages, formed by an ionic liquid-like copolymer, were suggested to enrich phenol and repel the comparatively hydrophobic cyclohexanone.[32] In addition, our team developed palladium catalyst supported on polyaniline-functionalized carbon nanotube (Pd–PANI/CNT). Phenol conversion exceeding 99% is attained with a cyclohexanone selectivity of >99%. It is proposed that the cyclohexanone selectivity and phenol conversion rate are related to the nitrogen-containing nature and the conductive property of PANI/CNT, respectively. The PANI/CNT results in not only stable and uniform Pd dispersion but also nonplanar adsorption of phenol. Phenol is chemisorbed over basic nitrogen sites and H_2 is activated by Pd NPs. The benzene ring of phenol is hydrogenated to enol that isomerizes rapidly to cyclohexanone. Eventually the weakly bound cyclohexanone is replaced by the strongly bound phenol (Fig. 7).[31]

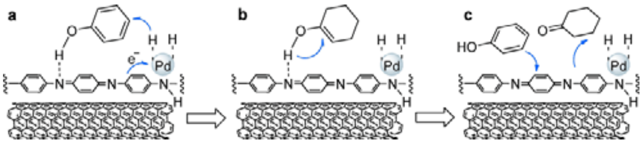


Fig 7. Proposed mechanism of the selective hydrogenation of phenol over Pd–PANI/CNT. Reproduced with permission from Ref. 31. Copyright © 2013 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

5.5. *In situ* hydrogenation

The classical liquid phase hydrogenation commonly uses H_2 as the reducing agent. It has potential danger and obvious limitations such as the necessity of special facilities for H_2 generation, storage and transportation.[133] Therefore, increasing attentions have been devoted to *in situ* catalytic hydrogenation.

Li and coworkers coupled the endothermic aqueous-phase reforming (APR) or dehydrogenation of alcohols for hydrogen production and the exothermic liquid phase hydrogenation of phenol.[133] Their team pointed out that the hydrogenation of phenol with hydrogen from the APR of methanol or ethanol reaches higher cyclohexanone selectivity than that with H_2. It is concluded that limited amount of adsorbed hydrogen, surrounding the ortho-position of phenol, lowers hydrogenation degree of phenol and prevents cyclohexanone from over reduction.[41]

As is known, HCOONa as alternatives of molecular hydrogen have attracted increasing attention in the catalytic transfer hydrogenations. Li *et al.* reported that the homogeneous catalyst tris(tirphenylphosphine)ruthenium(II) chloride $RuCl_2(PPh_3)_3$ showed excellent catalytic performance in the hydrogenation of phenol to cyclohexanone with HCOONa as hydrogen source.[110] Recently, our team carried out the phenol hydrogenation over polymer [polyaniline, polypyrrole, poly(4-vinylpyridine) and poly(1-vinylimidazole)]-functionalized carbon-nanofiber-supported palladium with HCOONa as hydrogen source. Phenol conversion exceeding 99% is achieved with a cyclohexanone selectivity of >99%. It is suggested that hydrogen-transfer mechanism is involved.[111]

By contrast, Zhao *et al.* carried out the reaction over Pd/C catalyst in the presence of HCOONa with the assistance of microwave. It is proposed that the reaction goes through hydrogen production and hydrogenation pathway, which is not in line with the mechanism mentioned above[111]. Besides, the low hydrogen concentration from HCOONa/H_2O may inhibit 1-hydroxycyclohexene from conversion into cyclohexanol.[42]

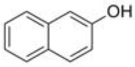
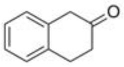
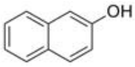
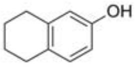
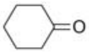
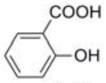
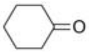
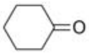
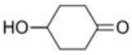
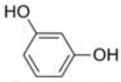
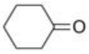
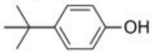
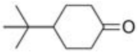
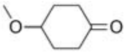
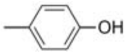
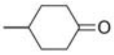
6. Selective Hydrogenation of Phenol Derivatives

According to the studies, some catalysts are applicable to extend to hydrogenation of other hydroxyl aromatic compounds. Table 3 summarizes the catalytic systems for hydrogenation of hydroxyl aromatic derivatives.

In general, methylphenol. methoxyphenol and 4-tert-butylphenol yield the corresponding ketone.[42, 92, 94, 100] As for dihydroxybenzene, the major product is hydroxyl cyclohexanone commonly.[92, 100, 102] However, resorcinol yields cyclohexanone over Pd/mpg-C_3N_4 due to reductive dehydration.[30] Likewise, hydroquinone and resorcinol yield cyclohexanone over Pd/Copolymer-HPW.[32] As for salicylic acid and 4-chlorophenol, cyclohexanone is the major product due to reductive dechlorination and decarboxylation, respectively.[31, 32, 111] In the case of naphthol, Pd/hydrophilic-C[100] and Pd-MIL-101[102] are selective for the hydrogenation of the non hydroxylated ring, due to the different resonance stabilization energy of the transition states.

In particular, 4-position substituted cyclohexanone such as 4-(4-propylcyclohexyl)-cyclohexanone is important chemical intermediate for the manufacture of liquid crystal compounds. Vogel *et al.* found that palladium-on-charcoal, modified with sodium carbonate, hydrogenates 4-(4-propylcyclohexyl)-phenol to the corresponding cyclohexanone derivative effectively in non-polar solvent.[134] It is suggested that the substrate and target product do not compete for catalytically active sites, which is inconsistent with the results obtained by Gut *et al.*[135] and Nishimura *et al.*[43, 136] Li *et al.* pointed out that hydrogen reduction method leads to better Pd dispersion and higher catalytic activity compared with formaldehyde reduction method. Besides, K and Sn dopants enhance 4-(4-proplycyclohexyl)-phenol conversion rate and selectivity to 4-(4-proplycyclohexyl)-cyclohexanone.[137]

Table 3 Catalytic systems for hydrogenation of hydroxyl aromatic derivatives.

Substrate	Catalyst	Solvent	T [K]	P_{H2} [MPa]	Time [h]	Reactor	Conversion (%)	Selectivity (%)	Ref.
	PdAu/MHSS	CH_2Cl_2	323	1	1	Autoclave	>99	 >99	92
	Pd/hydrophilic-C	H_2O	373	1	20	Autoclave	80	 70	100
	Pd-PANI/CNT	H_2O	373	0.1	18	Schlenk flask	>99	 98	31
	Pd/Copolymer-HPW	H_2O	373	0.2	18	Flask	>99	 98	32
	Pd/Copolymer-HPW	H_2O	353	0.2	6	Flask	>99	 98	32
	5% Pd-MIL-101	H_2O	298	0.1	7	Autoclave	>99.9	 93.8	102
	Pd/mpg-C_3N_4	H_2O	353	0.1	6	Flask	>99	 99	30
	Pd-PANI/CNF	H_2O	393	[a]	24	Pressure Tube	72	 96	111
	Pd-PANI/CNF	H_2O	353	[a]	18	Pressure Tube	>99	 85	111
	Pd/C	H_2O	353	[a]	0.25	Tube	95.4	 92.8	42

Hydrogen is obtained from $HCOONa/H_2O$ for [a].

Wang *et al.* observed that Pd/C catalyst, treated with 2% sodium nitrate and 5% disodium EDTA, can effectively hydrogenate 4-(4-propylcyclohexyl)-phenol to its corresponding cyclohexanone analogue (99.77% conversion and 64.11% selectivity).[138] C□erveny *et al.* proposed that the hindrance of the hydroxyl group and the amount of alkyl-substituent enhance the yield of alkyl- substituted cyclohexanone.[139]

7. Influence Factor

7.1. Acid-base Property of the Support

As mentioned in section 3, the majority of published reports claimed that phenol, adopting nonplanar mode over the basic support, favors cyclohexanone formation.

Tanabe *et al.* suggested that phenol is adsorbed on basic MgO and acidic silica-alumina with the ring nonplanar and coplanar to the surface, respectively.[140] By comparing the catalytic performances of Pd/Al_2O_3, Pd/CeO_2 and Pd/La_2O_3, Scirč *et al.* suggested that the higher basicity of catalytic system, the higher selectivity to cyclohexanone and catalytic activity.[56] Velu *et al.* suggested that the basic sites are stronger than the acid sites in Pd/ZrO_2-MS, and phenol adsorbed on the basic sites in nonplanar fashion, which leads to high selectivity to cyclohexanone. Whereas, in the case of Pd/CeO_2-MS, phenol adsorbed on the Lewis acidic sites in coplanar fashion, which results in low cyclohexanone selectivity.[77] Sikhwivhilu *et al.* investigated the structure and morphology of TiO_2 (tubular, sheet-like and amorphous). It is envisaged that phenol adopts nonplanar form on the base sites of tubular support, which results in higher cyclohexanone selectivity.[75] Chen *et al.* and Narayanan *et al.* ascribed the excellent performance of Mg/Al hydrotalcite supported Pd catalysts to the strong base sites of hydrotalcite.[50, 62]

Moreover, it must be underlined that acid-base property of the support can be greatly adjusted by the promoters.[28, 109, 141, 142] Neri *et al.* proved that the Pd/MgO possesses higher selectivity to cyclohexanone than Pd/Al_2O_3. However, the selectivity to cyclohexanone over Pd/Al_2O_3 can be increased by the addition of alkali or alkaline earth metals (Ca, K, Cs).[28] In particular, many studies have been devoted to the influence of one specific modifier. Scirč *et al.* proposed that Ca additive on alumina increases the number and strength of basic sites and decreases the number of acid sites, thus resulting to increased selectivity to cyclohexanone.[142] The similar result was obtained over Ba additive[109] and Sr modifier.[141]

It should be noted that suitable amounts of acid sites are of great necessity for the isomerization of 1-hydroxycyclohexene to cyclohexanone. Vishwanathan *et al.* observed that the selectivity to cyclohexanone decreases with excessive amount of Ca dopant over alumina.[143] Li and coworkers achieved high catalytic activity and cyclohexanone selectivity over Ce-doped Pd(H), amorphous Pd-Ce-B and Pd-Ce-B/HT. The presence of Ce_2O_3 favors phenol adsorption in the nonplanar mode and the high concentration of Ce_2O_3 neutralizes the acidic sites and impedes the isomerization of enol.[49, 89, 144] Similarly, their group concluded that excessive amount of La_2O_3 over amorphous Pd–La–B retards the acid catalyzed isomerization.[145] It is known that proper amount of La increases the amount of weak acid sites while excess amount of La decreased the amount of strong and weak acid sites.[146] Therefore, Li *et al.* observed that suitable content of La in Pd/La_x-Al_2O_3 enhances acidity and accelerates the isomerization of enol.[108]

Nevertheless, a minority of exceptional observations have also been reported. For example, Vishwanathan *et al.* found that Pd/Al_2O_3 exhibits complete selectivity to cyclohexanone while

Pd/MgO yields a fraction of cyclohexanol. It is proposed that over MgO a part of strongly bound phenol in the form of phenolate and then enolate, undergoes complete hydrogenation before desorption.[48] Chatterjee *et al.* revealed that phenol prefers the nonplanar form on Pd/Al-MCM-41 with strong surface acidity. However, it should be stressed that the nonplanar form is decided by the difference between the interaction of substrate-solvent and that of substrate-catalyst.[47]

7.2. Promoter

Up to date, the role of promoter has attracted great interests in modifying acid-base property of the support (discussed in section 7.1), affecting electronic surroundings of metal sites,[43, 49, 108,135108, 144] increasing metal dispersion,[141] changing adsorption–desorption equilibrium of adsorbed species (phenol or cyclohexanone),[28, 76, 143-145] and enhancing resistance to deactivation (will be discussed in section 7.5).

First of all, a considerable number of literatures focused on the promotion effect of alkali and alkaline earth metal. Neri *et al.* reported that introduce of Ca, K and Cs into Pd/Al_2O_3 improves the catalytic activity since the presence of alkali metal enhances cyclohexanone desorption.[28] Scirč *et al.* proposed that promoter (Ca, K, Cs) enriches the electron density of palladium and causes a better activation of hydrogen.[51, 56, 142] Vishwanathan and group member pointed out that alkali metal results in higher hydrogenation activity while alkaline earth metal leads to better thermal stability.[147] It is proposed that the positively charged promoting ions interact with the oxygen atom of phenolate. Thus, the desorption rate of cyclohexanone and catalytic activity of phenol hydrogenation are improved.[76, 143] However, the selectivity to cyclohexanone over Pd/Al_2O_3 is basically uninfluenced by alkali or alkaline earth modifier. Instead, catalytic activity depends on the electron density of the metal site and is enhanced with increasing charge transfer capacity of Group I and II promoter.[76, 148] Pillai *et al.* investigated the promoting effect of Sr on Pd/zeolite-β, Pd/Al_2O_3, Pd/SiO_2, Pd/HT and Pd/MgO. The Sr additive enhances surface area, dispersion and net charge density of Pd, which results in improved catalytic activity.[141]

In addition, the influences of elements of lanthanide series on the reaction have been extensively studied. Li and group members proposed that Ce dopant partially donates electrons to Pd, which prevents cyclohexanone from further hydrogenation.[89, 144] Similarly, their group found the electron donation from La_2O_3 to Pd prohibits the over reduction of cyclohexanone *via* facilitating desorption of cyclohexanone from the catalyst surface. Besides, that presence of the La_2O_3 improves surface area and stabilizes the amorphous alloy structure of Pd–La–B.[145] By comparison, Li *et al.* observed that the presence of proper content of La (the atomic ratio of La/Pd = 0.05-1) effectively improves the Pd dispersion, which results in excellent catalytic activity of $Pd/La_xAl_2O_3$ for the APR of methanol.[108]

At last, the role of other transition metal or nonmetal has also been investigated. Yang *et al.* prepared gold-promoted Pd catalyst with mesoporous hollow silica spheres (MHSS) as support. PdAu/MHSS shows higher catalytic activity than Pd/MHSS, owing to high dispersion of active component and the Pd-Au alloy formation.[92] Chatterjee *et al.* found that the incorporation of B enhanced the electron density of metal, which resulted in strong interaction between metal and hydrogen.[98] Likewise, N-doping plays pivotal roles in tuning properties of support, activating substrate and stabilizing metal NPs.[30] Therefore, Li *et al.* incorporated nitrogen to FDU-type[149] ordered mesoporous carbons (OMC). The N-hybrid immobilizes Pd NPs by electron donation, and increases the catalytic activity and cyclohexanone selectivity by interaction with phenol.[107]

7.3. Metal precursor

According to the literature, a great number of investigations have addressed the influence of metal precursor on deactivation (will be discussed in section 7.5) and structural properties of catalysts.

Generally, chloride precursor yields larger metal particle attributed to crystallite growth involving volatile metal chloride.[150] In addition, the residual chlorine reduce the charge density of metal site, thus less electron transfer from metal site to the π^* antibonding orbital of the aromatic ring of phenol, which results in decreased activity of aromatic ring.[48] The residual chlorine also reduces the activity of surface-activated hydrogen.[18] Amine precursor suffers from auto-reduction and the facile surface mobility results in lower metal dispersion.[151, 152] As for acetate precursor, the large counter anion effectively set metal ion apart, leading to smaller crystallite and ultimately large metal dispersion.[18, 48]

For instance, Vishwanathan and co-workers observed that Pd/MgO and Pd/Al_2O_3 prepared from $Pd(OOCCH_3)_2$ show better metal dispersion and phenol hydrogenation activity than those prepared from $PdCl_2$ or $Pd(NH_3)_4Cl_2$ precursors.[18, 48, 147] Scirè *et al.* also suggested that Pd/Al_2O_3, Pd/CeO_2 and Pd/La_2O_3 synthesized from $Pd(OOCCH_3)_2$ present higher selectivity to cyclohexanone than those synthesized from the $PdCl_2$.[56] Similarly, Sailu *et al.* found that Pd/silica-gel prepared from $Pd(NO_3)_2$ shows better catalytic performance than that prepared from $PdCl_2$ or $Pd(NH_3)_4Cl_2$.[78]

On the contrary, Narayanan *et al.* pointed out that Pd/HT prepared with chloride precursor is more active than the one prepared by acetate or amine precursor.[59] Since $PdCl_2$ and K_2PdCl_4 can provide $PdCl_4^{2-}$ anions to replace interlayer CO_3^{2-}, which increases metal dispersion and enhances catalytic activity finally.[58, 153]

7.4. Structure Sensitivity

So far, there is a lack of systematic investigation on the structure-activity relationship. The activities of the catalyst can generally be expressed by the turnover frequency (TOF) or turnover number (TON).

On one hand, it is indicated that chemoselective reduction of phenol on some kinds of catalyst is structure sensitive. There is a dependence of specific catalytic activity on particle size. For example, Rao *et al.* found an increase in TOF with the increasing second metal loading over Pt-alloy catalyst. The authors ascribed it to both crystallite size effect and the promotion effect of alloy ensembles.[19] Chen *et al.* proved a decrease of TOF with the increasing Pd loading over Pd/MgAl-CHT.[50] Velu *et al.* observed that TOF increases with the decreasing Pd loading and crystallite size over Pd/CeO_2-MS[77]. Li found that the TOF increases remarkable with the increase of the atomic ratio of La/Pd from 0.05 to 5 over Pd/Lax–Al_2O_3.[108]

On the other hand, some authors proposed that the reaction over some kind of catalysts is structure insensitive. The specific catalytic activity has no relationship with the particle size. For instance, Vishwanathan and group members observed the constancy of TOF with changing metal particle size.[48] Besides, they proved that palladium content beyond 3 wt% has no significant effect on the TON of phenol hydrogenation over Pd/C[46] and Pd/Al_2O_3.[143] In addition, their group observed an invariant TOF with the Pd crystallite size in the range of 3-7 nm over Pd/MgO,[18] which is in agreement with the result observed by Galvagno *et al.*[154] Scirč *et al.* pointed out that hydrogenation of phenol over Pd/Ta_2O_3, Pd/CeO_2 and Pd/Al_2O_3 is not affected by the Pd particles size (at least within the range from 5 to 15 nm).[56] Since the particle size shows no significant impact on the cyclohexanone selectivity, Chatterjee *et al.* classified the reaction over Pd/Al-MCM-41 as structure-insensitive.[47] Since there is no significant effect of crystallite size on the TON, Narayanan *et al.* classified the reaction over Pd/HT as structure-insensitive.[59]

7.5. Deactivation

Up till now, many researchers have made great efforts on the investigation of catalyst deactivation which is mainly caused coke deposition. Generally, the coke deposition depends on the presence of strong acid sites on the surface.

For instance, Pd/Al_2O_3 suffers from deactivation owing to the strong acid sites on alumina,[48, 51, 154] while Pd/Al_2O_3 promoted with alkali or alkaline earth metal shows better resistance towards deactivation.[28, 76, 143, 147] Likewise, Pd/HT with alumina phase and high alumina content suffered from deactivation.[61] By comparison, Pd/CeO_2 and Pd/Ta_2O_5, showing weak Lewis acid sites, resists to the coke formation.[56] Basic MgO-based catalyst also shows better resistance to deactivation.[48] Similarly, Pd/C has a better resistance towards coke formation, owing to the absence of strong acid-sites on the support surface.[46]

It should be noted that acidic sites can form during catalyst preparation, pretreatment, and even during the reaction. Therefore, coke deposition may be promoted by the presence of residual chlorine. Vishwanathan and co-workers observed that Pd/MgO synthesized from $Pd(OOCCH_3)_2$ exhibits stable catalytic activity than that from $PdCl_2$ and $Pd(NH_3)_4Cl_2$.[18] It is proposed that $MgCl_2$, produced during catalyst preparation/pretreatment, act as a Lewis acid site to induce coke formation. Likewise, Gonzalez-velasco *et al.* pointed out acidic character of the $PdCl_2$ almost invalidate the promotion effect of CaO in Pd/CaO-Al_2O_3.[20]

8. Kinetics

For decades, a great amount of studies have been devoted to the kinetics of hydrogenation of phenol and derivatives. However, it should be mentioned that limited papers[82, 135, 155, 156] are available concerning reaction mechanism and kinetic models (Langmuir-Hinshelwood-Hougen-Watson model or Langmuir-Hinshelwood model *et al.*). By contrast, many studies have adopted a more or less simplified power-law model. For instance, phenol hydrogenation to cyclohexanone is usually treated with pseudo-first-order approximation (Pd/Ta_2O_5,[36] Pd@mpg-C_3N_4,[54] Pd-Yb/SiO_2,[34, 71] supported Pd catalyst–Lewis Acid,[29] Pd/HPS[40]).

So as to ensure reliable reaction kinetics, it have been established that mass transfer should be absent.[40, 43, 48, 54, 82, 135] Table 4 summarize apparent activation energy for selective hydrogenation of phenol to cyclohexanone.

In addition, taking the differences between catalysts, supports and experimental conditions into consideration, it is almost impossible to take a direct comparison. However, considering the various kinetic equations, there are different opinions on the exact rate-determining step. Firstly, investigation over Pd/molecular sieve[157] proposes the following mechanism: fast interaction of phenol from gas phase with an adsorbed hydrogen atom, slow attachment of another surface hydrogen atom, fast attachment of extra surface hydrogen atom and rearrangement of cyclohexanol into cyclohexanone. Besides, the studies over Pd/CaO-Al_2O_3[155] and Pd/Al_2O_3[28] indicate that desorption of cyclohexanone from one active site is the rate controlling step. Moreover, reports over Pd/MgO,[154, 158] and Pt/SiO_2[156] suggested the rate controlling step is the surface reaction between strongly chemisorbed phenol and one molecule of adsorbed hydrogen. In addition, the observation over Pd/TiO_2[159] shows that the rate determining step is the surface reaction between the strong adsorbed phenol and two adsorbed hydrogen atoms. At last, the investigation over Pd/CHT[50] shows that the rate-controlling step is the surface reaction between adsorbed phenol, one adsorbed hydrogen molecule and one hydrogen which is not adsorbed.

Table 4 Apparent activation energy for selective hydrogenation of phenol to cyclohexanone over different catalytic systems.

Catalyst	T (K)	E_a (kJ mol^{-1})	Ref.
Pd/MgO [a]	473-563	63	18, 154, 158
Pd/HPS [a]	393-474	49	40
Pd/TiO_2 [a]	458-503	46	159
Pd-Ca/Al_2O_3 [a]	493-563	37.2	155
Pd/Al_2O_3 [a]	473-533	30	143
Pd/Al_2O_3 [b]	433-473	56.8	21
Pd/Al-MIL-53-OCH_3 [b]	293-323	68	103
Pd/Al-MIL-53 [b]	293-323	59	103
Pd@mpg-C_3N_4 [b]	303-353	35.9	54

Vapor phase hydrogenation of phenol for [a], Liquid phase hydrogenation of phenol for [b].

9. Conclusions and outlook

Selective hydrogenation of phenol and the related derivatives have attracted great interests in industrial as well as scientific communities. To sum up, some points in the following ought to be addressed in the near future: (1) Thorough understanding of the mechanisms and kinetics by means of isotopic tracing and density functional theory *etc.*; (2) Strategic design and exploration of environment friendly, highly active and stable catalyst systems; (3) In-depth investigation on the relationship between acid-base property of the support and the reaction mechanism; (4) Deep analysis of the reaction medium effect on the substrate conversion rate and target product selectivity; (5) Thorough investigation of the influential factors of deactivation (metal precursor and leaching *etc.*).

In particular, the reaction performed in aqueous media is more advantageous compared with that performed in vapour phase, organic solvent, *sc*CO_2 and ILs. This research area will be extended dramatically in the near future.

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‡ Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

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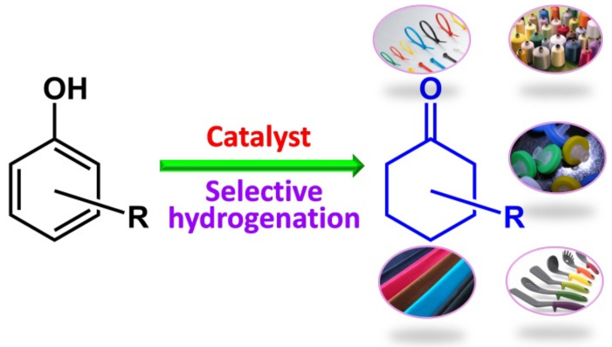
Biography and Photograph

Jiawei Zhong was born in Guangdong, China. He received his Bachelor of Science in Applied Chemistry in 2011. In September 2012, he began to take the master degree's courses in University of Science and Technology of China. In September 2013, he joined the CAS Key Laboratory of Renewable Energy in Guangzhou Institute of Energy Conversion. He is pursuing a Master of Science in Engineering from the University of Chinese Academy of Sciences. The focus of his current research is catalytic conversion of renewable biomass into fuels and chemicals.

Jinzhu Chen received the PhD degree (2005) in organic chemistry from Dalian Institute of Chemical Physics, Chinese Academy of Sciences. He was a postdoctoral associate at University of Arizona (2005–2007), University of Illinois at Urbana-Champaign (2007–2008), and Brookhaven National Laboratory (2008–2010). He joined the faculty of Guangzhou Institute of Energy Conversion, Chinese Academy of Sciences in 2010 as a full professor. His research focuses on the development of heterogeneous and homogeneous catalysts for use in sustainable chemical processes and the utilization of renewable resource, specifically the production of fuels and chemicals from biomass and carbon dioxide.

Limin Chen received the PhD degree (2007) in physical chemistry from State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences. She was a postdoctoral scholar at Pennsylvania State University-University Park (2007–2009). She joined the College of Environment and Energy, South China University of Technology in 2010, as an assistant professor. Her research focuses on the development of heterogeneous catalysts for use in the utilization/degredation of organic pollutants and energy conversion, specifically hydrogen production from steam reforming of hydrocarbons/alcohols, carbon dioxide conversion to fuels and chemicals and FCC decant oil hydrodesulfurization.

TOC



Selective hydrogenation of phenol and the related derivatives to corresponding cycloketones requires rationally designed catalysts, which has attracted significant attentions.