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Highly Selective Hydrogenation of Phenol and Derivatives over a Pd@Carbon Nitride Catalyst in Aqueous Media

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Supporting Information

ABSTRACT: Cyclohexanone is an important intermediate in the manufacture of polyamides in chemical industry, but direct selective hydrogenation of phenol to cyclohexanone under mild conditions is a challenge. We report here a catalyst made of Pd nanoparticles supported on a mesoporous graphitic carbon nitride, Pd@mpg-C_3N_4, which was shown to be highly active and promoted the selective formation of cyclohexanone under atmospheric pressure of hydrogen in aqueous media without additives. Conversion of 99% and a selectivity higher than 99% were achieved within 2 h at 65 °C. The reaction can be accelerated at higher temperature, but even at room temperature, 99% conversion and 96% selectivity could still be obtained. The generality of the Pd@mpg-C_3N_4 catalyst for this reaction was demonstrated by selective hydrogenation of other hydroxylated aromatic compounds with similar performance.

Cyclohexanone is of high industrial importance because of its use as an intermediate in the production of caprolactame and adipic acid, which are used to manufacture nylon 6 and nylon 66, respectively.[1] Cyclohexanone production on a commercial scale typically involves either the oxidation of cyclohexane[2−4] or the hydrogenation of phenol.[5] The former route requires high temperatures and high pressures and generates undesirable byproducts that lower the product yield and complicate the recovery/separation steps.[3,4] In the latter route, phenol can be hydrogenated to cyclohexanone in a "one-step" or a "two-step" process.[6] The two-step process involves hydrogenation of phenol to cyclohexanol followed by dehydrogenation to cyclohexanone.[7] The one-step, selective direct hydrogenation of phenol to cyclohexanone is certainly preferable, as it avoids the endothermic dehydrogenation step. However, cyclohexanone is an active intermediate and is easily hydrogenated to cyclohexanol and other byproducts. The distribution of products from phenol hydrogenation is highly dependent on the type of catalyst and the properties of the support,[8] and the development of an effective catalyst for this process has attracted broad research activity.[9−11] The hydrogenation of phenol is generally carried out in the vapor phase with supported palladium catalysts such as Pd@Al_2O_3 and Pd@MgO.[12−15] The incorporation of promoters such as alkali and alkaline-earth metals has been shown to enhance the selectivity, while changes in the reaction temperature have had a considerable impact on the ultimate product composition.[13] Al_2O_3-supported Pd catalysts, however, have a low resistance to deactivation by coke deposition, and the use of MgO as a catalyst support is not suitable for industrial applications because of its poor mechanical performance. Carbons, including activated carbon, carbon nanofibers, and hydrophilic carbon, etc., are also good supports because of their high surface area.[16−18] Pd@C catalysts can catalyze the hydrogenation reaction in the liquid phase, but even if the required reaction temperature in a batch process is lower than for gas-phase reactions, the selectivity of phenol hydrogenation toward cyclohexanone remains poor, which imposes further separation steps and strongly limits the usefulness of these catalysts. Other catalysts systems, such as Pt@C, Ru@C, and Rh@C, are not for general use and entail important practical drawbacks regarding low conversion, low selectivity, and harsh reaction conditions. For instance, when Ru@C was used as the catalyst in the hydrogenation of phenol, only 30% conversion and 5% selectivity toward cyclohexanone were achieved, evne under a hydrogen pressure of 10 MPa.[18] Because of that, attaining high selectivity (>95%) at elevated conversions (>80%) remains a challenging catalytic problem. Most recently, Han and co-workers achieved both excellent conversion and selectivity in the hydrogenation of phenol by using a dual-supported Pd Lewis acid catalyst.[19] However, the fact that these hosts contain Lewis acids such as $AlCl_3$ imposes severe limitations on their use in hydrogenation applications in general and adds another chemical sensitivity restricting substrates, purities, and reaction conditions. Therefore, alternative heterogeneous catalysts for selective hydrogenation of phenol under ambient conditions are desirable.

Previous investigations have in fact shown that the support plays a key role in the hydrogenation of phenol. Modern views suggest that the reaction occurs mainly between phenol chemisorbed on the support and hydrogen activated on the metal (normally Pd) sites. Generally, phenol adsorbed in nonplanar fashion over basic sites gives rise to cyclohexanone while that adsorbed on acidic sites in coplanar fashion leads to the formation of cyclohexanol and cyclohexane.[13,20] We have recently shown that an abundant and easily accessible polymeric semiconductor, polymeric mesoporous graphitic carbon nitride (mpg-C_3N_4), exhibits extreme chemical and thermal stability,

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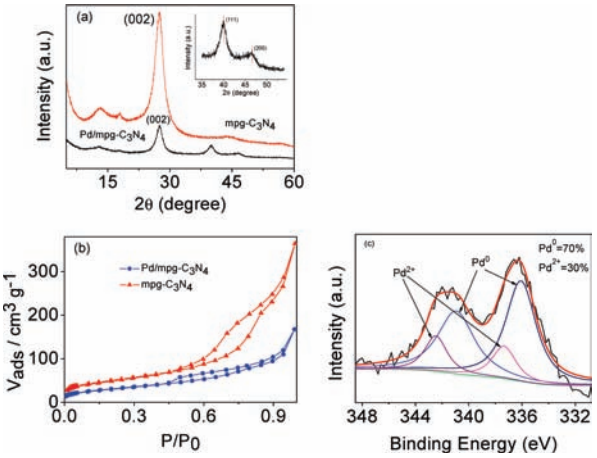
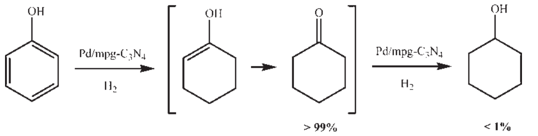


Figure 1. (a) XRD patterns of the parent mpg-C_3N_4 and Pd@mpg-C_3N_4. (b) N_2 adsorption/desorption isotherms. (c) XPS spectra of Pd@mpg-C_3N_4.

Scheme 1. Phenol Hydrogenation over Pd@mpg-C_3N_4



can be chemically shaped to a variety of nanostructures, and can be directly used in heterogeneous catalysis.[2,21−24] The most active system in mpg-C_3N_4 is in fact presumably an incompletely condensed, N-bridged "poly(tri-*s*-triazine)" polymer. The nitrogen functionalities on the surface might act as strong Lewis base sites, while the π-bonded planar layered configurations are expected to anchor phenol via special $O{-}H\cdots N$ or $O{-}H\cdots\pi$ interactions. In this work, we focused on supported Pd as the catalytic agent and considered the use of this nitrogen-rich mesoporous material as a basic host to construct binary Pd@mpg-C_3N_4 catalytic metal−semiconductor heterojunctions for the hydrogenation of phenol (Scheme 1).

Mesoporous carbon nitride was prepared by thermally induced self-condensation of cyanamide using Ludox HS40 as a hard template, which resulted in a yellow powder with graphitic packing structure [as revealed by X-ray diffraction (XRD); Figure 1a] and a Brunauer−Emmett−Teller (BET) surface area of 179 $m^2\,g^{-1}$ (as determined from the desorption branch of the nitrogen adsorption/desorption isotherm; Table S1 in the Supporting Information). A deposition−precipitation (DP) route was then employed to deposit Pd on mpg-C_3N_4. In Figure 1b, nitrogen adsorption isotherms of the parent and modified carbon nitride materials are presented. The isotherm of the parent mpg-C_3N_4 shows a small hysteresis (typical of the existence of randomly connected spherical pores) but only weak microporosity. After the modification, the isotherm shape was preserved, indicating that the Pd nanoparticles do not block or alter the pore system.

The formation of Pd nanoparticles was proven by powder XRD (Figure 1 a) and high-resolution transmission electron microscopy (HRTEM) (Figure 2). The XRD patterns show the characteristic peak of (002) packing of graphitic carbon nitride. The diffraction peaks at 40.0 and 46.6° in the XRD patterns can be assigned to the (111) and (200) planes of Pd metal particles, respectively.[25] The average size of the crystallites was calculated to be ~7 nm from the major diffraction peak (111) using Scherrer's formula. The morphologies of Pd@mpg-C_3N_4 composite materials were also investigated by HRTEM (Figure 2b). The HRTEM images revealed well-dispersed Pd particles with a mean size of 3.3 nm (Figure 2d), which is a little bit smaller than that the value predicted by XRD. The Pd X-ray photoelectron spectroscopy (XPS) of the catalyst presents a doublet corresponding to Pd $3d_{5/2}$ and Pd $3d_{3/2}$. The Pd $3d_{5/2}$ peak at 335.9 eV is attributed to Pd^0 (metallic palladium), while the Pd $3d_{5/2}$ peak at 337.3 eV is related to Pd^{2+} (palladium oxide).[26] According to XPS data, Pd^0 was formed as the major phase on the surface of the catalyst (~70%). A previous report showed that the introduction of amine groups in the carbon carrier resulted in increased proportions of Pd^0 that were resistant to reoxidation during air contact.[26] In our case, mpg-C_3N_4 has a high nitrogen content of 60 wt %. These π-bonded planar C−N−C-layers along with their incompletely condensed amino groups in the carrier are suitable for stabilizing highly dispersed Pd^0 particles and prevent their oxidation.

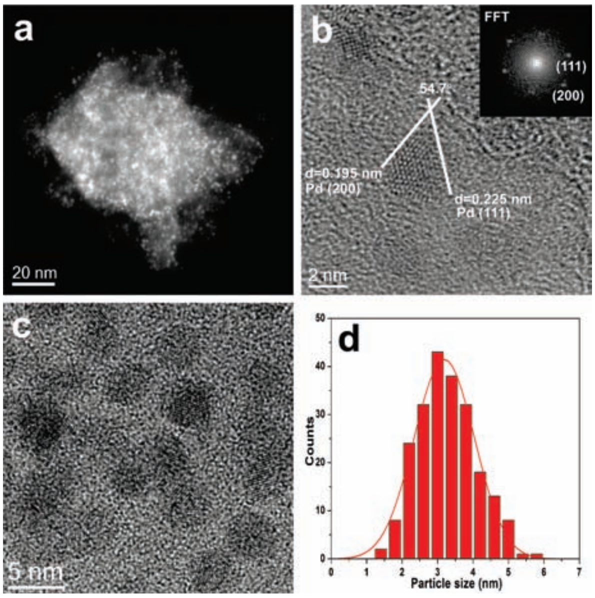


Figure 2. (a) STEM, (b) HRTEM, and (c) TEM images and (d) particle size distribution of Pd@mpg-C_3N_4. The inset in (b) is the local fast Fourier transform.

The activity of Pd@mpg-C_3N_4 for the hydrogenation of phenol was then investigated. For our purpose, we first investigated the effect of various solvents for the reaction. The corresponding conversions and selectivities are listed in Table S2. With Pd@mpg-C_3N_4 under the primary conditions, we could readily achieve selectivities toward cyclohexanone in the range 57−92%, with a conversion of phenol of 30−100% in 6 h at 100 °C and 3 MPa hydrogen pressure (Table S2). Among the solvents tested, water and CH_2Cl_2 exhibited the highest activity. Ethanol also gave high activity but with a low selectivity toward cyclohexanone. It seems that the catalyst is very active even in water under atmospheric pressure of hydrogen (Table S2); accordingly, we afterward limited the subsequent catalytic study to an aqueous phenol feed at atmospheric hydrogen pressure and temperatures less than 100 °C.

Under similar operating conditions, the catalytic performance of Pd@mpg-C_3N_4 was found to be far better than that of any

Table 1. Hydrogenation of Phenol with Pd@mpg-C_3N_4 Catalyst in Water under Various Conditions[a]

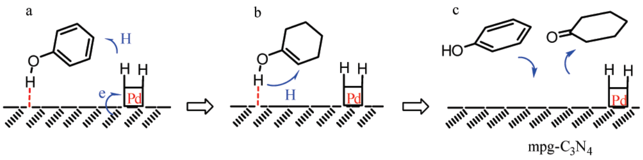
					selectivity (%)	
entry	P_{H_2} (MPa)	T (°C)	time (h)	conv. (%)	C=O	C−OH
1[b,c]	1	30	12	13	94	6
2[c]	0.1	30	12	45	>99	<1
3	0.1	30	12	46	>99	<1
4	0.1	100	1	>99	>99	<1
5	0.1	65	1.2	91	>99	<1
6	0.1	65	2	>99	>99	<1
7	0.1	45	3	57	>99	<1
8	0.1	45	6	74	>99	<1
9	0.1	45	9	86	99	1
10	0.1	45	12	99	98.5	1.5
11[d]	0.1	45	12	81	>99	<1
12	0.1	25	24	62	>99	<1
13	1	25	24	66	98	2
14[c]	0.1	25	24	60	>99	<1
15[e]	0.1	25	24	56	>99	<1
16	0.1	25	48	81	97	3
17	0.1	25	72	>99	96	4

[a] Reaction conditions: phenol (0.5 mmol), Pd (5 mol % relative to phenol), water solvent (2 mL), unless otherwise noted. [b] Data taken from ref 19; Pd@C was used as the catalyst. [c] Using 2 mL of CH_2Cl_2 as the solvent. [d] V_{H_2}/V_{N_2} = 7:3. [e] Using 6 mL of water as the solvent.

commercial Pd@C catalyst. It is evident that the Pd@C catalyst (without a Lewis acid as cocatalyst) generally produces a mixture of cyclohexanone and cyclohexanol with low phenol conversion (13%; Table 1, entry 1), even using CH_2Cl_2 as the solvent at a hydrogen pressure of 1 MPa.[19] In contrast to that, Pd@mpg-C_3N_4 produced cyclohexanone as the major product with very high selectivity (>99%) and good conversion (45%) under 0.1 MPa hydrogen pressure (Table 1, entry 2). Even in the case of water as the solvent, selective hydrogenation could be achieved (Table 1, entry 3). The use of water as a solvent complies with the rules of green chemistry.

Variation of the reaction temperature had a considerable effect on the reaction conversion, as illustrated in Table 1. Conversion of 99% was achieved with a selectivity exceeding 99% within 2 h at an ambient hydrogen pressure and 65 °C. The reaction was accelerated at higher temperature; for example, full conversion in 1 h was obtained at 100 °C with a high selectivity of 99%. Even at room temperature, 99% conversion and 96% selectivity could be reached after a longer reaction time of 72 h. The partial loss of the reaction selectivity may be caused by the hydrogenation of cyclohexanone to cyclohexanol after a long reaction time, which could also be observed when the hydrogen pressure was increased during the reaction process (Table 1, entries 13 and 14). The Pd@mpg-C_3N_4 could be easily recovered several times by simple washing using acetonitrile. However, a slightly decrease in the conversion was observed, which may be caused by leaching of the Pd nanoparticles (Figure S1). Moreover, control experiments indicated that a high purity of hydrogen is not necessary. The reaction could be conducted even under a gas mixture of hydrogen and nitrogen (V_{H_2}/V_{N_2} = 7:3), which is a prerequisite for low-price practical applications (Table 1, entry 11).

Scheme 2. Possible Reaction Mechanism of Phenol over Pd@mpg-C_3N_4

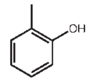
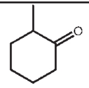
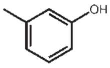
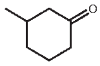
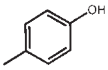
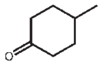
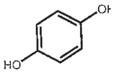
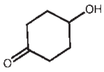
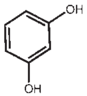
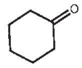
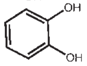
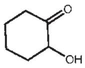
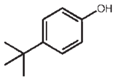
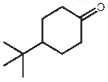


Cyclohexanone and cyclohexanol were the only reaction products observed over the entire range of conditions studied. Furthermore, cyclohexanol was detected at all only beyond a distinct reaction time, which suggests that the hydrogenation of phenol is going stepwise with cyclohexanone as the "intermediate" (Scheme 1). Depending on the nature of the catalyst's active site, phenol can interact with the surface through the hydroxy group to form strong O−H···N or O−H···π interactions. Recently, Jhung and co-workers reported the efficient use of the NH and NH_2 groups on the surface of carbon nitride for the effective adsorption of phenol.[27] Although an interaction of the aromatic ring of phenol with the π electron of the carbon nitride could not be excluded, we expected that such a $\pi \cdots \pi$ interaction is weaker and that the phenol therefore adsorbs in nonplanar fashion over basic sites. The transfer of electron density in the heterojunction from the semiconductor g-C_3N_4 enriches the electron density of the metallic Pd and accelerates the hydrogenation reaction, as compared to Pd@C. Scheme 2 illustrates the step sequence of the hydrogenation of phenol. In the initial stage, phenol can be easily absorbed on the surface of the catalyst, and H_2 is activated by the electronically supported Pd (Scheme 2 a). The benzene ring of phenol is then partially hydrogenated to the enol (Scheme 2 b), which can isomerize rapidly to give cyclohexanone. There is only a weaker H-bridge donor, and the cyclohexanone leaves the surface of the catalyst quickly, being replaced by a more strongly binding new phenol molecule (Scheme 2 c) and avoiding further hydrogenation to cyclohexanol.

To illustrate the general applicability of Pd@mpg-C_3N_4, the method was extended to ring hydrogenation of other hydroxylated aromatic compounds. Table 2 shows the results of these hydrogenations. As can be seen, 99% conversion was achieved in all cases, and the selectivitvies toward substituted cyclohexanones were excellent (>96%). As expected, methylphenol derivatives gave methylcyclohexanones with both excellent conversions and selectivities (Table 2, entries 1−3). Hydrogenation of hydroquinone (Table 2, entry 4) and pyrocatechol (Table 2, entry 6) yielded the synthetically very valuable hydroxylcyclohexanones, again with high conversions and selectivities. Interestingly, in the case of resorcinol, the obtained product was not hydroxylcyclohexanone but the reductive dehydration product cyclohexanone (Table 2, entry 5). Furthermore, this Pd@mpg-C_3N_4 catalyst is predicted to be active in the hydrogenation of other phenol derivatives, such as naphthols, methoxyphenols, aminophenols, etc. Work focused on more detailed hydrogenation studies of Pd@mpg-C_3N_4 material is ongoing.

In conclusion, palladium nanoparticles have been heterogeneously supported on mesoporous carbon nitrides with their special base properties and electronic behavior. The novel Pd catalyst exhibits a high activity for the direct hydrogenation of phenol to cyclohexanone. The hydrogenation proceeds efficiently, with highest selectivity found under atmospheric pressure of hydrogen at room temperature using water as a clean solvent. The high catalytic performance has been attributed to the special

Table 2. Hydrogenation of Hydroxyl Aromatic Derivatives with Pd@mpg-C_3N_4 Catalyst in Water[a]

entry	substrate	temperature (°C)	time (h)	conv. (%)	product	sel. (%)
1		100	6	>99		>99
2		100	6	>99		>99
3		100	6	>99		>99
4		80	6	>99		96
5		60	6	>99		99
6		80	6	>99		99
7		100	8	>99		99

[a] Reaction conditions: Pd@mpg-C_3N_4 (25 mg), substrate (0.5 mmol), H_2 (1 bar pressure).

structure of the catalytic semiconductor−metal heterojunction, which leads not only to a very stable and uniform dispersion of Pd but also to additional electronic activation of the metal nanoparticles and a "nonplanar" adsorption of phenol, which finally gives rise to the fast and selective hydrogenation to cyclohexanone.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Experimental details and more characterization results. This material is available free of charge via the Internet at http://pubs.acs.org.

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