

Selective partial hydrogenation of hydroxy aromatic derivatives with palladium nanoparticles supported on hydrophilic carbon†

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Selective hydrogenation of phenol to cyclohexanol in the aqueous phase was achieved using a new catalytic system based on palladium particles supported on hydrophilic carbon prepared by one-pot hydrothermal carbonisation.

Cyclohexanone is one of the main intermediates in the preparation of caprolactam and adipic acid which are for instance used in the manufacturing of nylon-6, nylon-6,6 and polyamide resins.¹ Cyclohexanone is usually prepared from phenol in one or two steps (Fig. 1). The one-step reaction is becoming the preferred industrial process, because it is more advantageous with regard to energy efficiency and processing than the two-step reaction proceeding *via* cyclohexanol.² The hydrogenation of phenol to cyclohexanone is run in the gas phase, and supported palladium catalysts have been reported as the best catalysts for this reaction.^{3–10} Only a few studies report such selective hydrogenation of phenol in the liquid phase, at the best in water.^{11,12} Even if the required reaction temperature in a batch process is lower than for gas phase reactions, the selectivity of the phenol hydrogenation reaction remains poor, which imposes further separation steps. Such a separation is rather difficult due to the formation of phenol–cyclohexanol and phenol–cyclohexanone azeotropes.¹¹

Here, we report a simple and environmentally friendly route for the synthesis of a novel metal–carbon nanocomposite catalyst, which is highly selective for the hydrogenation of phenol to cyclohexanone. The catalyst is made by a one-pot and mild hydrothermal carbonisation using furfural and palladium acetylacetonate.

Hydrothermal carbonisation of water soluble carbohydrates is a well known process to produce monodisperse carbon spheres featuring a hydrophilic surface.^{13–15} A simplified reaction mechanism for the formation of the carbon spheres involves the dehydration of the carbohydrate in the first step and subsequent polymerisation and carbonisation of the so-formed organic compounds in the second step. Furfural and

hydroxymethylfurfural are the main products of the first, dehydration, step. We have already shown that, using furfural as a carbon precursor, we could produce monodisperse hydrothermal carbon particles, which were identical in terms of chemical composition and structural properties to those produced from glucose.¹³

In the present approach, furfural was used as the carbon source and reducing agent and Pd(acac)₂ as the metal source. Thus, a 10 wt% aqueous solution of furfural was mixed with 1 mmol Pd(acac)₂ in an autoclave with a Teflon inlet. This mixture was then hydrothermally treated at 190 °C for 14 h. As can be seen from scanning electron micrographs (Fig. 2a), well-defined, spherical carbon particles† of about 200–400 nm were obtained.

As a result of the mild hydrothermal treatment, the carbon framework keeps oxygen rich functional groups at its surface, which increase both the hydrophilicity and colloidal stability of the carbon spheres. This was confirmed by the FT-IR measurements (Fig. 3). The carbon nanocomposite produced after hydrothermal carbonisation, denoted by Pd@hydrophilic-C, features absorption bands at 3000, 1700 and 1590 cm⁻¹, typical for –OH bending, C=O and C=C vibration, respectively. In contrast, almost no such functional polar groups could be detected on commercial palladium supported on activated charcoal (used as a reference catalyst).

Recently, we reported on the synthesis of metal oxide hollow spheres using hydrothermal carbonisation in the presence of water soluble metal precursors. During the carbonisation, metal oxide nanoparticles were formed *in situ* and were bound and positioned in the hydrophilic shell of the carbon particles.¹⁶ In contrast, when noble metal salts are used, they are effectively reduced by furfural or *in situ* formed aldehydes yielding metal(0) nanoparticles (analogously to the Tollens reaction) in the early states of particle formation. This was evidenced by X-ray diffraction† showing the typical fcc pattern of Pd(0) and transmission electron microscopy showing

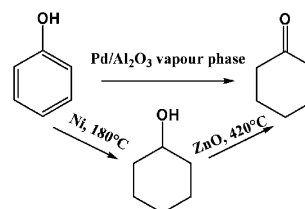


Fig. 1 Synthesis of cyclohexanone.

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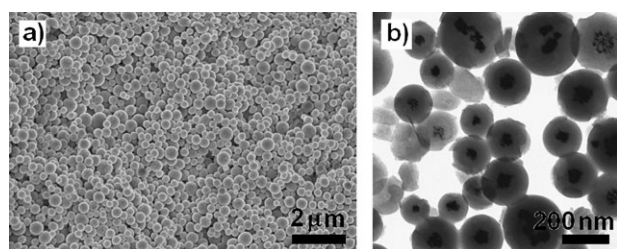


Fig. 2 (a) SEM image and (b) TEM image of Pd@hydrophilic-C.

Pd nanoparticles sitting in the centre of the carbon spheres (Fig. 2b). This is probably due to the fact that the Pd nanoparticles are relatively hydrophobic and thus enter the oily droplets rather early upon condensation, while the metal oxide nanoparticles are rather close to the particle surface. According to the thermogravimetric analysis,[†] the Pd content of the carbon spheres is around 20 mass%.[‡]

Upon hydrothermal carbonisation, a microporous material is formed (exhibiting about $15 \text{ m}^2 \text{ g}^{-1}$ of specific surface area), therefore reagents can penetrate inside the catalytically active core. For this penetration and surface enrichment, the surface properties of the carbon support however play a decisive role.

The catalytic activity of our powders was tested in the hydrogenation of phenol in water. Reference catalysts used in this work, charcoal- and alumina-supported palladium, were purchased from Fluka and used as received. Hydrogenation reactions were carried out in 100 mL Teflon-lined stainless steel autoclaves (Berghof BR 100). The weighed amounts of catalyst and phenol in water were placed in the autoclave, which was flushed twice with hydrogen and pressurised with 10 bars of hydrogen. The reactor was then heated up to 100°C . The quantitative analysis of the reaction mixture after filtration was conducted by GC-MS and GC-FID.

Table 1 displays the catalytic activity of differently supported Pd for the hydrogenation of phenol. A complete conversion of the phenol into cyclohexanol was observed using commercial charcoal- and alumina-supported palladium. Even with shorter reaction times (down to 1 h) partial hydrogenation products could not be detected. Moreover, no differences in the reactivity were observed between charcoal and alumina. Both supports loaded with a similar amount of Pd led directly to cyclohexanol.

In contrast, in the case of palladium supported on hydrophilic hydrothermal carbon, the hydrogenation is selective. After 20 h of reaction, we obtained 95% of cyclohexanone with a conversion rate close to 99%. As expected, the selectivity decreased with increasing reaction time. For example, after

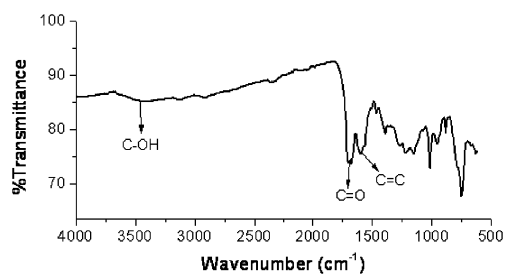


Fig. 3 FT-IR spectra of carbon samples: Pd@hydrophilic-C.

Table 1 Catalytic activity of differently supported Pd for the hydrogenation of phenol^a

Catalyst	Time/h	Conversion (%)	Selectivity (%)	
			Cyclohexanol	Cyclohexanone
Pd@hydrophilic-C	10	60	—	>99
Pd@hydrophilic-C	20	>99	5	95
Pd@hydrophilic-C	72	>99	50	50
Pd@hydrophilic-C ^b	20	45	30	70
10% Pd@C	20	100	100	0
10% Pd@C	1	100	100	0
10% Pd@Al ₂ O ₃	20	100	100	0

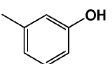
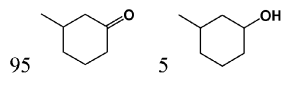
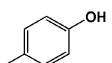
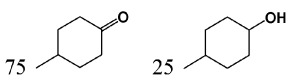
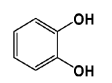
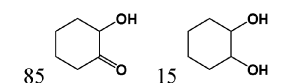
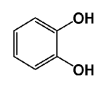
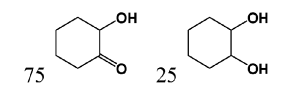
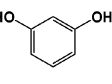
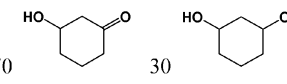
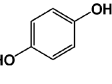
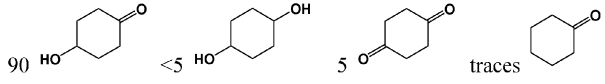
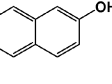
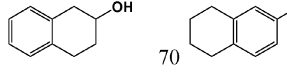
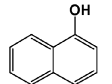
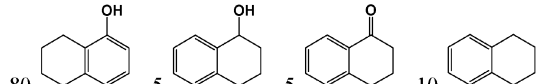
^a In a typical reaction, 50 mg of catalyst were added to 100 mg of phenol and the mixture was heated to 100°C under 1 MPa of hydrogen pressure. ^b Reference test in cyclohexane.

3 days of reaction at 100°C , only 50% of cyclohexanone was obtained, while another 50% had further reacted to cyclohexanol. This indicates that the observed selectivity towards the formation of cyclohexanone relies on kinetic control, *i.e.* cyclohexanone reacts much more slowly on our catalyst system than phenol. A reference test in cyclohexane as a nonpolar solvent provided evidence that under otherwise similar conditions our catalyst was both less active and less selective.

The lower hydrogenation speed of the ketone compared with the aromatic ring is not likely to rely on the intrinsic properties of the palladium nanoparticles as no such effect is observed with the commercial catalysts. Actually, the active particles are placed in a confined microenvironment with special chemical functionalities. The reactive pocket around our nanoparticles is very hydrophilic and decorated with $-\text{OH}$, $\text{C}=\text{O}$ and $-\text{COOH}$ species. A possible mechanism accounting for the observed reactivity could then rely on the fact that phenol, being a strongly H-bridge interacting system, is enriched in the pores, while cyclohexanone, being more hydrophobic, is displaced from the reactive pocket and thus cannot easily further react. Such mechanisms, involving specific interactions between the substrate and the reactive pocket, are known to control the reactivity of enzymes and are a major goal for biomimetic catalysis.^{17–19} This could explain why our hydrophilic support provided a more selective catalyst than the commercial hydrophobic charcoal-supported system. At this point it has, however, to be mentioned that our catalyst is less active than the commercial one, possibly because the palladium particles are less accessible in our microporous system.

In order to explore the scope of application of our catalyst we investigated the hydrogenation of various hydroxy aromatic compounds under similar conditions. Table 2 shows the results of these hydrogenations. As can be seen, hydrogenation products are always obtained in moderate to high yields, and the selectivity towards partial hydrogenation products is good. Indeed, as could be expected, methylphenol derivatives gave methylcyclohexanones with high yields. Interestingly, dihydroxybenzene derivatives yielded hydroxyl cyclohexanones, again in high yields. In the case of naphthol, the obtained products are mainly not ketones but tetrahydronaphthols, with a relatively good selectivity for the hydrogenation of the non hydroxylated ring.

Table 2 Hydrogenation of hydroxy aromatic derivatives with hydrophilic carbon-supported palladium^a

Substrate	t/h	Conversion	Products
	20	85%	
	20	>95%	
	20	25%	
	72	70%	
	20	80%	
	20	55%	
	20	80%	
	20	60%	

^a In a typical reaction, 50 mg of Pd@hydrophilic-C were added to 100 mg of substrate and the mixture was heated to 100 °C under 10 bars of hydrogen pressure.

In conclusion, we found an easy, one-pot method, *i.e.* hydrothermal carbonisation in the presence of water soluble noble metal precursors, to synthesise palladium based, hydrophilic, selective catalysts for the batch partial hydrogenation of hydroxy aromatic derivatives. Interestingly, the scope of application of this catalyst was shown to be extremely broad, which makes it a promising system for applications in speciality chemistry. We are currently investigating the activity of this material in attractive C–C and C–N bond forming reactions, such as the functionalisation of allylic derivatives.²⁰ We also believe that the performance of our catalysts can be further improved by combining hydrothermal carbonisation with templating methods¹³ or also recently published functionalisation strategies for hydrothermal carbon.²¹

Notes and references

† Elemental analysis of the obtained powders indicated an average C and H content of 65 and 5.2 mass%, respectively.

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