Phenol is its own selectivity promoter in low-temperature liquid-phase hydrogenation

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ABSTRACT

Phenol hydrogenation is widely studied for selective production of the chemical intermediate cyclohexanone. A plethora of studies in the literature have reported catalysts aiming to achieve high selectivity compared to Pd/C. However, we demonstrate that selective and high-yielding reactions are inherent features of liquid-phase phenol hydrogenation using conventional Pd/C catalysts. We also show there is a very strong dependance of selectivity upon conversion, with high selectivity being maintained until near complete consumption of the phenol, after which subsequent reaction to the unwanted, fully hydrogenated cyclohexanol occurs rapidly. Furthermore, through competitive reactions with other aromatic molecules it is demonstrated that the phenol molecule effectively self-poisons the onwards reaction of weakly bound cyclohexanone, likely by virtue of its relative adsorption strength, and this is the source of the intrinsic selectivity. The implications of this to the reaction mechanism, and in turn to the rational design of catalysts, especially for obtaining chemicals from phenolic bio-oils, are discussed.

1. Introduction

Cyclohexanone is a commercially significant chemical building block, being the precursor to both caprolactam and adipic acid. These are used in turn for producing nylon 6 and nylon 6,6, respectively. The two major routes for cyclohexanone production are either cyclohexane oxidation or reduction of phenol. The former oxidative route suffers from the fact that temperature (125–165 °C) and elevated oxygen pressures (8–15 bar) combine with limited cyclohexane conversion (typically 3–10 % required to limit the formation of by-products from over oxidation), which renders the process far from ideal [1,2]. Phenol reduction, however, is challenging: the sequential steps (a) phenol to cyclohexanone and (b) cyclohexanone to cyclohexanol are both thermodynamically downhill. A selective catalyst must promote only the first stage. This is sufficiently challenging that industrial practice has often been to fully reduce to cyclohexanol and then reoxidise [3,4], which is clearly again inefficient, both energetically and due to the additional plant stage required. It is reported that > 90 % of cyclohexanone production is (2014 figure) *via* the oxidation route avoiding the

hydrogenation altogether [5]. However, as pointed out by Keane *et al.*, phenol is potentially an available feed-stream as an undesirable environmental toxin from other processes (petrochemicals and polymer manufacture), usually in aqueous form [6,7]. Additionally, the cost/availability of phenols may be anticipated to become more favourable relative to fossil derived cyclohexane with a future prevalence of bio-refining – bio-oils typically contain 30 % of lignin derived phenolic components [8]. These factors, and the consequent appeal of selective hydrogenation to cyclohexanone, have unsurprisingly led to a plethora of work rapidly appearing on this topic [9]. Selective phenol hydrogenation in general has recently been thoroughly reviewed elsewhere, so only important details for understanding the liquid phase hydrogenation are given here [10].

Research on selective phenol hydrogenation has generally focussed on Pd catalysts (which for the most part are more selective than other metals). The reaction has typically been carried out in the vapour phase. Catalysts containing acidic sites such as Pd/Al_2O_3 are found to behave fundamentally differently to Pd supported on basic supports such as MgO [9,11] and calcined Mg/Al hydrotalcites [12]. This is widely

attributed to a so called two-site model in which palladium sites dissociate hydrogen and support sites, either on the support or at the metal-support interface, adsorb phenol. On acidic supports the phenol can absorb either in a planar geometry (promoting rapid full hydrogenation) or a non-planar geometry (leading to partial hydrogenation) [3, 11]. On the acidic supports it is found that alkali metals may be used to improve the selectivity to non-planar hydrogenation, presumably by titration of the acidic sites. Work on Pd/C catalysts agrees with this two-site model by showing that the turnover rate is not correlated with the number of Pd metal sites found by CO chemisorption. Since selectivity is not a function of conversion, but does change with different catalysts the authors argue this is further evidence for each catalyst containing specific selective and unselective sites, although it should be noted that the range of conversions studied are all below 90 % [13]. More generally, a trend of dropping selectivity with higher phenol conversion is seen in the literature [9]. Even Pd with no support (in the form of a membrane) is only able to reach around 75 % selectivity at 90 % conversion [14]. The effect of temperature on selectivity is not well understood, most probably due to the large changes in conversion (which decreases markedly above about 160 °C in most cases and is attributed to low surface coverages of the reactant) [3]. Overall, selectivity in vapour phase hydrogenation appears to depend strongly on the catalyst support (non-acidic supports being more selective at all conversions), and on the extent of conversion, selectivity at high conversion being hard to attain [15].

Liquid phase phenol hydrogenation (in aqueous or organic solvent) has been highlighted as an attractive alternative – lower temperatures potentially affording energy/cost savings, and avoiding coking of the catalyst, which generally occurs less at solid/liquid interfaces and lower temperatures [16]. Elegant thermodynamic work shows that adsorption of phenol on metal surfaces in solution tends to result in a more consistent coverage as a function of temperature [17] and while the interaction between phenol and the surface is similar changes to the solvent weaken the overall heat of adsorption preventing poisoning by reactants/products [18]. Additionally, if the origin of the phenol is from biomass or other waste streams, it may already be in aqueous form and liquid phase reaction would negate costly separation / solvent removal.

Several examples of high conversion, high selectivity catalysts have appeared – notably in each case using specially prepared / unconventional catalyst materials. The addition of AlCl$_3$ Lewis acid in dichloromethane to promote a supported Pd catalyst has been reported to work by both activating the phenol to hydrogenation, but then complexing with the cyclohexanone product such that further hydrogenation is inhibited [19]. A heteropoly acid additive to a Pd/C catalyst, again in dichloromethane has been observed to perform similarly, but with much lower selectivity in water or cyclohexane [20]. The use of a mesoporous graphitic carbon nitride support in the liquid phase also exhibits high selectivity at high conversion [21]. In this case the catalyst is thought to favour non-planar absorption, as is the case in vapour phase hydrogenations, and may additionally electronically activate the Pd. More recent work also claims the origin may lie in dramatically different adsorption selectivities for phenol over cyclohexanone [22]. Ionic liquid-like polymers as stabilisers for water soluble Pd nanoparticles have also been shown to be highly selective at high conversion [16]. Electrospun fibre supported Pd catalysts are reported with high selectivity at high conversions [23]. Membrane engineering has been used to bring about marginally higher selectivities and conversions that are intrinsically present over a Pd/Al$_2$O$_3$ catalyst [24]. Soluble Pd nanoparticles have also been used to catalyse the reaction to high conversion and selectivity [25], although with all nanoparticle synthetic agents still present this makes the results hard to interpret. Finally supercritical CO$_2$ has been used as a solvent with a Pd based catalyst – again high selectivity at high conversion is attributed to promoting the non-planar adsorption of phenol on the catalyst [4]. In each case however, the unusual materials or use of undesirable solvents (DCM, scCO$_2$) or additives such as AlCl$_3$ make the application of such catalysts on a large scale less attractive than a conventional supported Pd catalyst. While the changes in these liquid phase systems are often attributed to the unusual or advanced catalyst materials, these examples seldom carefully detail the effect of conversion on the reaction selectivity. [2]

Interestingly there is some evidence for more conventional catalysts being able to exhibit high conversions and selectivity in this reaction in the liquid phase. Cheng et al. used a Pd nanoparticle containing catalyst, prepared by conventional impregnation, but including a sonication step to improve dispersion [26]. With both silica and alumina as supports they were able to obtain > 97 % selectivity at 99 % conversion. They also commented that "if the phenol is not converted completely, the formation of cyclohexanol is almost not observed," but gave no further details. We speculate that the origin of this observation is the tendency for the cyclohexanone to leave or be displaced from the surface and phenol to adsorb. It should be noted here that the SiO$_2$ and Al$_2$O$_3$ used here selectively contrast with the vapour phase, where they are found to contain unfavourable acidic sites that are unselective. Historically, Pd/charcoal catalysts have also been known industrially to be able to achieve high selectivity and high conversion, with a patent on the importance of removing impurities giving an example of a 94 % yield of cyclohexanone product in batch mode using neat liquid phenol [27,28].

In the present work we show that simple, commercially obtained Pd/C catalysts are highly selective in the liquid phase hydrogenation of phenol up to high conversions, albeit at lower temperatures than liquid phase conditions apparently previously practiced industrially. We also demonstrate this is the result of phenol self-promoting selectivity in the reaction with a dramatic decrease in selectivity observed as soon as near complete phenol consumption is attained. By addition of aromatic additives that can competitively adsorb during reaction we also show phenol's adsorption strength controls access of phenol versus cyclohexanone to the hydrogenating catalyst's surface. It is therefore a privilege to contribute this work to a special issue in honour of Prof. S. D. Jackson, who is renowned for pioneering work on Pd selective hydrogenation of a different kind [29], and has recently devoted effort in the area of aromatic hydrogenation and hydrodeoxygenation, unlocking significant understanding through competitive adsorption studies during these hydrogenation reactions over Rh [30], as discussed later.

2. Experimental section

2.1. Materials

Pd/C (5 wt% loading (dry basis), matrix activated carbon, wet support, Degussa type E101 NO/W, product code 330116), Phenol (≥ 99 %), dodecane (reagent plus ≥ 99 %), hexane (HPLC grade, ≥ 97.0 % (GC)), cyclohexanone (≥ 99 %), cyclohexanol (≥ 99 %) and 1-methyl naphthalene (≥ 95 %) were all purchased from Sigma Aldrich and used as received, except for Pd/C treated as below. Other solvents were all of analytical reagent grade or greater and obtained from Fischer Scientific UK. Gases (industrial grade) were all obtained from BOC and purified as required in house using moisture and hydrocarbon traps for gas chromatography. Ultra-pure water was obtained from a Purite Neptune purification system (18.2 MΩ).

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[2] One notable, very detailed study has been conducted by Lercher and co-workers with Pd/C in aqueous conditions, but although liquid phase it was carried out at 200 °C under pressure – this temperature is higher than many of the reactions conducted in the vapour phase and so is possibly more comparable to these than other liquid phase studies [31]. In situ infrared in this case shows both some cyclohexanol as well as cyclohexanone forming from the start of the reaction, much as was observed in vapour phase plugged flow reactor experiments.

2.2. Catalyst pre-treatment

Pd/C Catalyst was reduced by loading into a quartz glass tube plugged with quartz wool, heating to 200 °C at a ramp rate of 10 °C min^{-1} and holding for 3 h before cooling to room temperature, all under a flow of H$_2$/N$_2$ (20 %/80 %) in a horizontal tube furnace. The catalyst was stored with minimal exposure to air in a sealed dry container until ready to use.

2.3. Hydrogenation reactions

All high-pressure hydrogenation reactions were performed in a Baskerville multi-cell autoclave reactor. The reactor was heated using a generic lab stirrer-hotplate placed underneath the reactor. Heating was controlled *via* a K-type thermocouple that was placed into one of the wells of the Baskerville reactor that contained the same solvent and solvent volume as the reaction mixtures being tested at the time. The thermocouple was connected to an omega engineering CN 7500 PID temperature controller that was auto-tuned prior to reactions and controlled the hotplate heater. Stirring was achieved by using magnetic stirrer plate which could be stirred independently from the heating power supply and cross shaped magnetic fleas that maximise stirring efficiency in the reactors.

In a typical phenol hydrogenation, a reaction solution was prepared by dissolving phenol (13 mmol, 1.223 g) and an internal standard, dodecane (4.4 mmol, 1 mL) to 50 mL total volume in the reaction solvent (usually n-hexane). 5 mL of reaction solution (containing 1.3 mmol phenol and 0.44 mmol dodecane) and 111 mg of reduced Pd/C catalyst (0.05 mmol by Pd) were added to each well of the reactor, along with any required toluene or 1-methylnapthalene. The reactor was purged thrice with hydrogen to remove air before heating to 40 °C. Once at temperature the mixture was stirred under hydrogen by pressurizing to 20 bar H$_2$ and sealing the reactor vessel (the pressure was seen to drop by no more than 3–4 bar as a result of hydrogen consumption across the course of any reaction). The reaction was ended by depressurising and allowing the mixture to cool to room temperature and the catalyst to settle to the base of the reactor. An aliquot of the reaction mixture was removed carefully to avoid solid catalyst, or where necessary filtered through a Pasteur pipette filter comprising filter paper and glass wool, before being diluted with DCM (1:1) for analysis by GC or GCMS. In the case of reactions with water this procedure was varied to extract the organic component by mixing the aliquot of reaction mixture 1:1 with ethyl acetate, adding NaCl until the aqueous layer was saturated, shaking thoroughly and then removing a sample from the organic layer for analysis by GC or GCMS.

In the case of cyclohexanone, the same procedure was followed, except that the reaction solution was prepared by dilution of cyclohexanone (6.6 mmol, 0.6478 g) and dodecane (2.2 mmol, 0.5 mL) to 25 mL with hexane such that 5 mL of the reaction solution contained 1.3 mmol cyclohexanone and 0.44 mmol dodecane.

Atmospheric pressure reactions were carried out in standard laboratory glassware. Phenol or cyclohexanone (13 mmol) and dodecane (1 mL, 4.4 mmol) were diluted to 50 mL in hexane to prepare the reaction solution, and as for the high pressure reactions 111 mg of Pd/C, and 5 mL of the reaction solution containing 1.3 mmol of hydrogenation substrate and 0.44 mmol of dodecane were added to the reaction vessel. Toluene (1.3 mmol) was then also added if required. The reaction mixture was then stirred at room temperature while bubbling a flow of 5 mL min^{-1} H$_2$ through the solution. These reactions were sampled hourly, 100 μl aliquots were taken and diluted with hexane (HPLC grade, 100 μl) before analysis by GC.

2.4. GC/GCMS characterisation of products

GC was performed on a HP 5890 GC equipped with a Restek, Stabilwax column (30 m, 0.25 mm OD, 0.1 μm ID) and flame ionisation detector. GC-MS was carried out on a Shimadzu QP2010-Ultra equipped with a Rxi-5Sil MS (10 m, 0.15 mm OD, 0.15 μm ID) column, EI was carried at 70 eV and the working mass range is 35 – 650 a.m.u.

The amount of material present in the GC sample was calculated using relative response factors with respect to the internal standard, dodecane, used in the reactions. The RRF were found empirically for phenol (0.78), cyclohexanone (0.74) and cyclohexanol (0.73) (based on duplicate samples the errors in these values are negligible). Conversion was calculated as the moles of all products divided by the moles of phenol and all products observed in the GC trace. Mass balances based on comparison the initial weight / moles of phenol were (with the exception of reactions involving water discussed in the text) > 90 % and within the error of the reaction measurements / handling losses expected. Selectivity was calculated as the moles of cyclohexanone divided by the moles of all products observed in the GC trace.

Reactions and GC analysis were repeated for two values of conversion (79 % and 97 %) and indicated that the overall experiment was highly reproducible in terms of selectivity (< 1 % change in selectivity at a given conversion). Similarly, errors in conversion in Fig. 3 were estimated by repetition of one entire hydrogenation run.

The identity of an initially unexpected GC peak at long reaction times was found by GCMS to be dicyclohexyl ether (see Supplementary Material). For reaction in ethanol the unknown peak by GC was found by GCMS to be cyclohexyl ethyl ether by GCMS (see Supplementary Material).

2.5. TEM

The supported reduced catalyst structure was confirmed using electron microscopy to appear similar to other Pd/C catalysts by casting one droplet of sonicated ethanolic catalyst dispersion onto a holey carbon coated copper grid (Agar Scientific) and allowing to evaporate to dryness. TEM imaging was performed in bright and dark field modes using a JEOL 2100 F FEG TEM with a Schottky field emission source. The accelerating voltage was 200 kV. The images supplied are typical of images obtained from imaging 6 different areas of the grid.

2.6. CO Chemisorption surface area measurement

Chemisorption surface areas were determined using a Hiden Catlab in pulse chemisorption mode with a 5 μl sample loop, and detecting CO *via* the $m/z = 28$ a.m.u. signal in a mass spectrometer. The Pd/C sample was reduced in the instrument at 180 °C for 2 h prior to measurement. Adsorption measurements were conducted at 35 °C, with 90 s intervals between pulses. Measurement errors were estimated by conducting two consecutive experiments, CO being desorbed at 400 °C for 1 h between measurements (it should be noted that it is possible this led to slight sintering of the sample, but only a small decrease in dispersion was seen). The CO:Pd surface atom ratio is taken to be 1:1, the surface density 1.27×10^{19} atoms m^{-2} and the shape of the particles assumed to be spherical in order to calculate metal surface areas.

3. Results

In order to better understand the plethora of reports of liquid phase phenol hydrogenation catalysts that are highly selective, and the interplay between conversion and selectivity in this reaction, we have explicitly investigated the reaction selectivity using a very typical, commercially available Pd/C catalyst. This was used after a simple reduction procedure in hydrogen gas, but otherwise as obtained from the manufacturer (Fig. 1 shows typical electron micrographs of the as used / reduced catalyst). Carbon monoxide chemisorption shows the reduced catalyst has a surface area of 2.1±0.3 m^{2}g^{-1} (9.4±1.4 % metal dispersion).

Fig. 2 shows the selectivity obtained at different conversions for liquid phase hydrogenation of phenol in hexane at 40 °C with 20 bar H$_2$
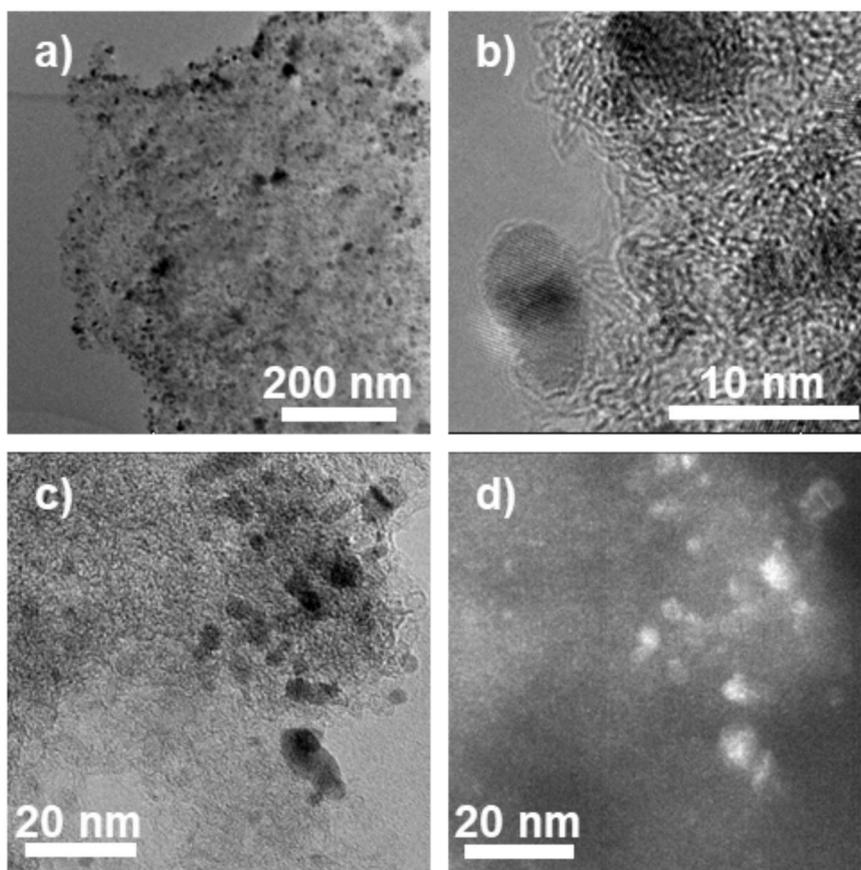
Fig. 1. Typical transmission electron micrographs of the reduced Pd/C catalyst employed in this work obtained from Sigma Aldrich and reduced at 200 °C in flowing H_2 for 3 h. (a) Low magnification image showing region of catalyst, (b) HR-TEM of several individual Pd particles, (c) + (d), bright and dark field images, respectively, of the same region of the sample to show location of Pd component.
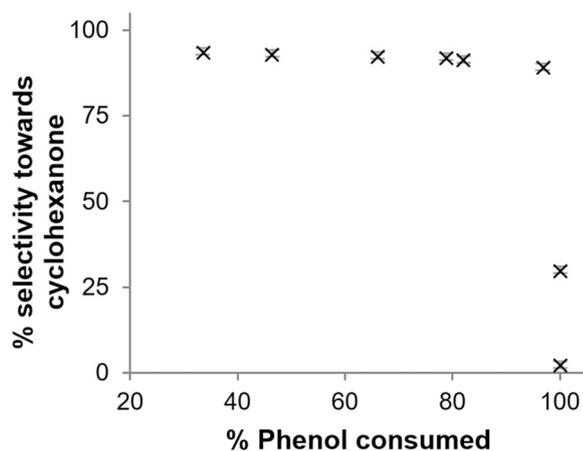

Fig. 2. Graph showing the selectivity to cyclohexanone as a function of phenol hydrogenation as monitored by gas chromatograph. Reaction conditions: 1.3 mmol phenol, 0.44 mmol dodecane (internal standard), 111 mg reduced 5 wt% Pd/C (4 mol% catalyst/substrate), 40 °C, 20 bar H_2, 5 mL hexane, time = 0.5 – 3.5 h (or run to extreme upper limit of conversion for 15 hours for final data point). Error bars for selectivity < 1 % obtained from repeat runs with the same conversion.

pressure. This very clearly shows that the selectivity to the desired cyclohexanone product remains high (∼ 90 %) throughout the reaction and until almost complete conversion (>96 %) is attained. This is a striking result when contrasted with a plethora of reports described in the introduction in which hard to synthesize or otherwise costly or environmentally harmful agents are employed to achieve only slight, potentially within error, improvements in selectivity against this baseline.

The above reaction was conducted in hexane as this simplified quantitative analysis (removing the need for extraction steps prior to analysis by gas chromatography), produced no hydrogenation products of its own on reaction with H_2/phenol and was found to adequately solubilise phenol (under reaction conditions near the phenol's melting point). However, a number of solvents used in the literature for phenol hydrogenation were also investigated (Table 1). As indicated by Lercher and coworkers, phenol hydrogenation using alcohol solvents (methanol, ethanol) has been reported but leads to reactions *via* an acetal (*e.g.* methoxycylohexanol in methanol) to form an ether hydrogenated product [31]. In our case, use of methanol or ethanol lead to a complete absence of desired product (Table 1, entries 6–7), which may also be attributed to cyclohexyl methyl or ethyl ether. For the ethanol to cyclohexyl ether case this was confirmed by GC-MS of the products (as shown in the Supplementary Material). Water has also been widely used and postulated to be beneficial, both being a "green solvent" [32], but also potentially being beneficial to the reaction selectivity. DFT calculations have been used to suggest this selectivity enhancement results from acceleration of proton transfer to form cyclohexanone [33]. A study of a homemade Pd/Carbon Nitride catalyst reported improved stability in water versus organic solvents, *e.g.* cyclohexane, however the metal salt impregnated material was only thermally stabilised below reaction temperature prior to use (leaving it more susceptible to sintering) [34]. Equally other reports exist in which no advantage or even an adverse influence on selectivity is seen as a result of using water [35]. In our case a similar general trend as observed in *n*-hexane is observed with water as solvent (Table 1). However, some caution must be given to

Table 1

showing the selectivity (as proportion of products detected) and conversion obtained for phenol hydrogenation in a number of solvents and at various reaction times. Other conditions: 1.3 mmol phenol, 0.44 mmol dodecane (internal standard), 111 mg reduced 5 wt% Pd/C (4 mol% catalyst/substrate), 40 °C, 20 bar H_2, 50 mL solvent.

Entry	Solvent	Reaction Time / h	Phenol Consumption / %	Selectivity to Cyclohexanone / %
1	n-hexane	0.5	34	94
2	n-hexane	2	82	91
3	n-hexane	3.5	97	89
4	n-hexane	6	100	16[β]
5	1,4-dioxane	17	40	87
6	methanol	17	100	0[‡]
7	ethanol	24	100	0[‡]
8	water	6	66	93[†]
9	water	17	97	96[†]
10	water	22	100	5[†]

[‡]The overwhelmingly dominant reaction products were cyclohexyl methyl or ethyl ether for methanol and ethanol respectively. [β] At long reaction times, dicyclohexyl ether was also observed, as is consistent with the literature (J. Liu, H. Li and H. Li, *Chinese Journal of Catalysis*, 2007, **28**, 312–316). At all shorter times the only other product was full hydrogenation to cyclohexanol. [†]Selectivities values (cyclohexanone concentration/product concentration × 100 %) in water are less reliable due to low mass balance, but show a similar qualitative general trend to those in *n*-hexane – see text.

the results we could obtain in water. Unlike in hexane (or 1,4-dioxane, which was also tested as an alternative organic solvent), in our hands we were unable to avoid some loss of the hydrocarbon reactant or products when working in water solvent and exposure to the catalyst, probably through strong interactions of the reactant or products with the Pd/C that must necessarily be separated before analysis.[3] This manifested itself as an incomplete, ~ 65 % mass balance, rather than the > 90 % (and within experimental error) balance reliably obtained in the organic solvents used.

Since the reaction is only selective until the phenol concentration drops on reaching near complete consumption, it could be postulated that this is simply a result of stronger adsorption on the catalyst active site by the phenol, preventing adsorption and further hydrogenation of the more weakly binding cyclohexanone. To test this hypothesis, we have investigated competitive reactions with other aromatic molecules and both phenol and the cyclohexanone partially hydrogenated species. Toluene is a similar size to phenol, containing one benzene ring and therefore is an ideal candidate to investigate the inhibition of cyclohexanone hydrogenation to cyclohexanol. Initial reactions under the same conditions (40 °C, 20 bar H_2, 4 mol% Pd/C) showed that in 0.5 h cyclohexanone to cyclohexanol conversion was 94 %, although this dropped to 8 % conversion if 0.5 eq. of toluene (relative to cyclohexanone) was added to the reaction. This can be seen more clearly / reliably if the reaction rate is decreased by working at atmospheric hydrogen pressure and room temperature in Fig. 3(a), which shows the relative rate of cyclohexanone hydrogenation in the presence or absence of 1 mol. eq. of toluene. Clearly in the presence of toluene the reaction is strongly inhibited. For comparison, the same reaction with phenol also

[3] Control experiments showed the organic extraction of reactant and product compounds from water into ethyl acetate/NaCl was very effective in solution. However, in control experiments in the presence of the Pd/C catalyst we were unable to obtain full recovery of the hydrocarbons. This low mass balance is possibly due to substrate/product adsorption to the catalyst surface in water/ the tendency of the Pd/C catalyst to form wet clumps during extraction attempts. Numbers quoted for reactions in water therefore assume that all products are equally likely to stick to the catalyst surface. This also highlights a possible concern for the reliability of other reported selectivity values obtained in water where mass balance data is not given.
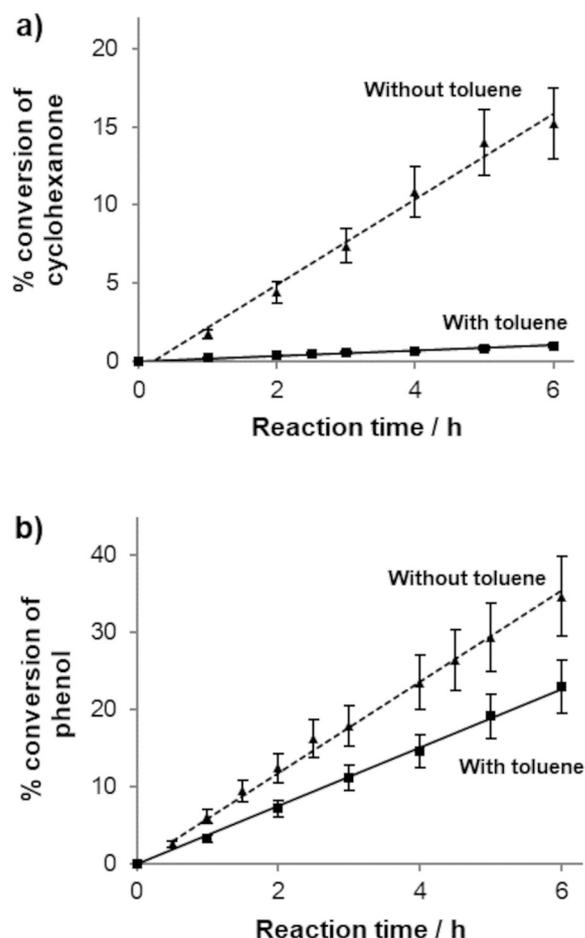
Fig. 3. Graph showing the rates of consumption in the presence or absence of 1 mol eq. of toluene (with respect to hydrogenation substrate) of (a) cyclohexanone and (b) phenol as monitored by gas chromatograph. Reaction conditions: 25 °C; atmospheric H_2 bubbled at 5 mL min⁻¹, 1.3 mmol phenol or cyclohexanone, 0 or 1.3 mmol toluene as indicated, 0.44 mmol dodecane (internal standard), 111 mg reduced 5 wt% Pd/C (4 mol% catalyst/substrate), 50 mL hexane. Errors in conversion are found to be ~ 15 % of conversion value based on repeat hydrogenation experiments.

shows a slight decrease in rate, but much less significantly than for the intermediate cyclohexanone product.

Further insight can be gained by using an aromatic molecule that is anticipated to absorb more strongly than phenol (as opposed to toluene that should absorb with broadly similar strength). Accordingly, we investigated phenol hydrogenation in the presence of 1-methylnaphthalene. If any methylnaphthalene is present in the reaction mixture, no phenol hydrogenation was seen to occur. Reactions initiated with even a

Table 2

showing the inhibition effect of addition of various molar equivalents of 1-methylnapthalene (1-MN) to the hydrogenation of phenol. Reaction conditions: 1.3 mmol phenol, 0.44 mmol dodecane (internal standard), 111 mg reduced 5 wt% Pd/C (4 mol% catalyst/substrate), 40 °C, 20 bar H_2, 50 mL solvent, 1-methylnapthalene as specified in table.

Entry	Molar Eq. 1-MN: phenol	Reaction Time / h	Phenol Consumption / %	Selectivity to Cyclohexanone / %
1	0	4	75	91
2	0.05	4	26	91
3	0.10	4	0	N/A
4	0.50	6	0	N/A
5	1.00	6	0	N/A

small proportion of methylnaphthalene relative to phenol completely inhibit the reaction as seen in Table 2. The 0.05 mol eq. case (Entry 2) is seen to undergo a small extent of conversion, but this is because all the methylnaphthalene is hydrogenated to 1-methyltetralin or 5-methyltetralin (both containing one saturated and one unsaturated ring) – which then, like toluene, can be expected to not completely inhibit the reaction. This was confirmed by GC-MS of the reaction products for Entry 2 in Table 2 (see Supplementary Material). It is instructive to note that these quantities of methylnaphthalene are still more than sufficient to completely cover the surface a number of times (based on the CO chemisorption derived metal dispersion, the 0.05 mol eq. case corresponds to an initial presence of around thirteen 1-methylnaphthalene molecules for every surface Pd atom).

4. Discussion

The above results show firstly that a standard Pd/C catalyst is able to carry out selective reactions in the liquid phase with selectivity dropping from 95 % to 90 % over almost the entire range of conversions when the reaction is run in a batch mode. This contrasts with gas phase reactions, where retaining selectivity at high conversion is known to be challenging. We postulate that this is because the phenol (or other aromatics) must displace the cyclohexanone or prevent it from remaining on the surface for a long enough time for unselective further hydrogenation to occur (seen in the reaction network shown in Fig. 4 as steps A and C, where the sites for step C remain occupied by phenol until it has all been consumed). The importance of kinetic removal of adsorbed phenol has also been reported to be important in understanding the role of low CO_2 partial pressures in removing the cyclohexanone from the metal surface, also promoting selective phenol hydrogenation [36].

Our findings also suggest that step B does not occur under these conditions directly, but only stepwise hydrogenation (*i.e.* under these liquid phase conditions there are not selective and unselective sites as sometimes postulated when discussing catalyst design). The stepwise hydrogenation rather than any direct pathway (C in Fig. 4) is consistent with theoretical studies reported elsewhere [37]. It should be noted that these findings do not explicitly address whether or not a two-site model is occurring on Pd/C in the liquid phase, just that the location of phenol adsorption is that same as the site for cyclohexanone adsorption. However, the high selectivity to cyclohexanone does suggest selectivity to Pd/C is not strongly controlled by geometry over Pd/C as proposed for gas phase reaction over other supports in the two-site model [3,11].

Overall, these findings suggest that reactor design and fine-tuning conditions, rather than just alterations to the catalyst, may afford high conversion/selectivity with standard catalyst materials.

Elsewhere, similar effects have been seen in the interplay of solvent, substrate and hydrogen donor in hydrogen transfer reactions [38]. Interestingly with Rh catalysts in alcohol solvent, presence of phenol was reported not to inhibit the rate of cyclohexanone hydrogenation, but anisole (where the -OH of phenol is replaced with -OCH$_3$) did show a similar effect to that seen here with anisole inhibiting the cyclohexanone to cyclohexanol reaction until all the anisole was consumed [30]. This points to a fine balance of the conditions needed to take advantage of a self-promotion effect. Electrochemical and XAS studies have tried to elucidate a thermodynamic difference for different adsorbates on Pt surfaces based on the Pt-H interaction, but while the importance of strong adsorption of aromatic versus non-aromatic molecules was identified (*e.g.* phenol vs cyclohexanol) it was challenging to disentangle from the depletion of hydrogen from the surface and consequent reduced coverage for the case of rapidly hydrogenated cyclohexanone [18]. Interesting work is now appearing to show that this interplay with the support polarity is important with different carbon supports being implicated in selectivity changes [39], and elegant work on mesoporous organosilicas with different surface polarities showing different phenol adsorption effects in different solvents [40]. In light of our present findings, further understanding of this type of control is likely invaluable for controlling this reaction. In aerobic oxidation reactions of alcohols (*e.g.* benzyl alcohol to benzaldehyde), self-promotion of selectivity to aldehydes rather than carboxylic acids is well-known, with the α-C-H relative to the hydrogen in the alcohol quenching further oxidation by intercepting radical intermediates [41]. While the end effect is conceptually similar, the mechanistic origin is now shown to be rather different in this oxidation system, although preferential bonding of benzyl alcohol over benzaldehyde had previously been postulated as a possible mechanistic origin [42]. Finally, liquid phase hydrogenation of alkynes selectivity over alkenes using Lindlar's catalyst, Pd poisoned by Pb and typically a nitrogen containing aromatic such as quinoline, bears some similarities. However, this catalyst system is complex with possibly different alkyne and alkene sites where adsorption occurs independently, but those responsible for alkene hydrogenation clearly being blocked by the presence of the aromatic quinoline (much as toluene and naphthalene do in the present study) [43].
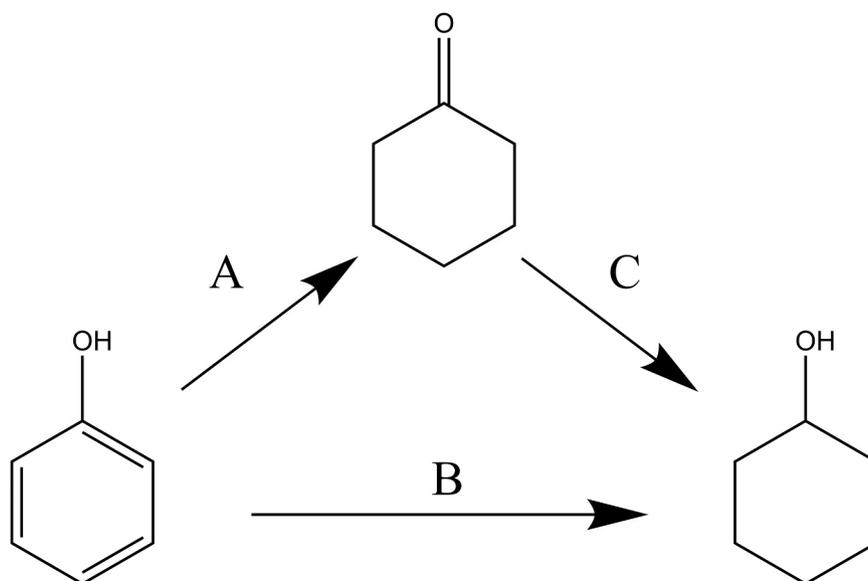

Fig. 4. Reaction network showing indirect (A + C) vs direct (B) hydrogenation steps that can occur during phenol hydrogenation.

5. Conclusions

Liquid phase hydrogenation of phenol at 40 °C in hexane and at 20 bar H_2 occurs selectively to cyclohexanone on a typical, widely available Pd/C type catalyst. However, at very high conversions where all the phenol is used up, the selectivity suddenly drops markedly. This suggests the reaction pathway is dominated by a two-step reaction from phenol first to cyclohexanone and then to cyclohexanol, which can be successfully disrupted after the first stage. At lower temperature and in the liquid phase (in contrast to the gas phase reaction where the surface is likely less crowded), the more strongly absorbing phenol is able to inhibit the second step of the reaction by preventing access by cyclohexanone to the catalytic sites. This site competition was demonstrated by competitive reactions of phenol and cyclohexanone with aromatic molecules that absorb similarly to, or more strongly than, phenol and also inhibit the hydrogenation reactions. This is fundamentally different from the vapour phase reaction where most kinetic data shows that hydrogenation of cyclohexanone occurs in proportion to its concentration. Qualitatively, similar selectivity as a function of conversion data was seen in water, which is important for processing biomass derived streams which are often aqueous. Overall, these findings imply lower-temperature liquid-phase hydrogenation of phenol can afford high selectivity and conversion and offers the possibility of designing catalytic processes or catalytic reactors that take advantage of this mechanistic self-promotion behaviour.

CRediT authorship contribution statement

Simon K. Beaumont: Writing – review & editing, Writing – original draft, Supervision, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Conceptualization. **Keith Whiston:** Writing – review & editing, Writing – original draft, Conceptualization. **Andrea Zachariou:** Writing – review & editing, Methodology, Investigation, Formal analysis, Conceptualization. **Li Li:** Writing – review & editing, Writing – original draft, Methodology, Investigation, Formal analysis, Conceptualization. **Alexandra Poncet:** Writing – review & editing, Writing – original draft, Methodology, Investigation, Formal analysis, Conceptualization. **Jonathan Bell:** Writing – review & editing, Writing – original draft, Methodology, Investigation, Formal analysis, Conceptualization.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

Data will be made available on request.

Acknowledgments

AI Disclosure Statement

During the preparation of this work the authors used ChatGPT 3.5 and DALL·E 3 in order to improve phrasing and clarity of certain sentences and generate parts of the graphical abstract. After using this tool/service, the authors reviewed and edited the content as needed and take full responsibility for the content of the publication.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.cattod.2024.114875.

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