The application of supported palladium catalysts for the hydrogenation of aromatic nitriles

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Abstract

The use of a Pd/C catalyst in the liquid phase hydrogenation of various nitriles (benzonitrile, benzyl cyanide, 3-phenyl propionitrile and cinnamonitrile) has been studied in order to assess the effectiveness of this type of catalyst for this class of reaction. On modifying the nitrile substituent and upon introducing conjugation, varying degrees of conversion are observed. For benzyl cyanide and 3-phenylpropionitrile, incomplete mass balance profiles are linked to spill-over to the carbon support. In the case of benzonitrile hydrogenation, a hydrogenolytic step leads to a loss of selectivity to the primary amine to yield toluene with, ultimately, complete selectivity. Co-hydrogenation measurements on mixtures of benzonitrile and benzylamine indicate the presence of site-selective chemistry. Co-hydrogenation studies on mixtures of benzonitrile and benzyl cyanide highlight the competitive nature of the reaction system and, indirectly, establish a contribution from adsorbed imine species.

Keywords

1. Introduction

The hydrogenation of nitriles to amines is a valuable reaction of significance to many areas of the chemical industry, for example pharmaceuticals and agrichemicals [1-3]. Mechanistic detail of the hydrogenation of nitriles stems from early work reported by Sabatier *et al.*, who proposed the hydrogenation to a primary amine occurred via an aldimine intermediate [4]. Historically, it has proven rather difficult to identify intermediate species in the hydrogenation of nitriles, which is attributed to their inherently high reactivity [5,6]. The presence of imines and enamines as intermediates has since been repeatedly established [7,8] and this mechanism is now almost universally accepted [7,9].

In 1923, Von Braun *et al.* further developed the understanding of the mechanism, by proposing a route by which secondary or tertiary amines can be formed as a result of a reaction between aldimine intermediates and amine products [10]. Scheme 1 shows some of the possible side reactions that can occur when the primary amine is the target product [11]. The addition of primary amine to intermediate aldimine, followed by subsequent hydrogenolysis leads to the formation of secondary amines. However, an equally valid pathway could be the elimination of ammonia to give a Schiff base, which is then hydrogenated to the final secondary amine [9,12]. The exact mechanisms followed are still under debate, but it has been shown that these further steps can take place on the surface of the catalyst/support system [13,14].

Hydrogenation of the nitrile group is assumed as being a relatively facile transformation [15], but selectivity is of great importance in such reactions, due to the often high-purity requirements of products and multiple possibilities of side reactions [10,16]. Skeletal metal catalysts based on Ni or Co have been used to control selectivity to primary amines [5,17] but considerable care is required in handling such pyrophoric catalysts on scale-up and, moreover, reactions often need to be carried out at relatively high pressure and temperatures [18,19]. Volf *et al.* showed that amongst transition metal catalysts, Rh displayed the highest selectivity to the primary amine. For Pd or Pt supported metal catalysts the reaction can be carried out under milder conditions, enabling hydrogenation of the nitrile group to be carried out without disruption to other functionalities [5], however, selectivity towards the primary amine is not as high. Many factors can influence the selectivity of the reaction in the liquid phase. Catalyst choice is the most important but the temperature, pressure, solvent, mixing conditions and even the type of reactor used can vary the outcome of the reaction. Secondary and tertiary amines are the most widely reported side products due to the highly reactive

imine intermediate participating in a series of condensation reactions [19-21]. The selectivity of such reactions can also be affected by the occurrence of a hydrogenolysis reaction.

Hydrogenolysis of the primary amine is often an unwanted side reaction that has been reported previously [15] but, historically, has not featured prominently in the heterogeneous catalysis literature. It is often low-yielding and, typically, only occurs under harsh reaction reactions. However, recent work from Bakker and co-workers has highlighted the importance of this reaction pathway in their study of hydrogenation of benzonitrile over a 5% γ-Al$_2$O$_3$ supported Pd catalyst, where toluene was observed as a by-product [22]. Here, the formation of a β-PdH phase at the catalyst surface, populated at hydrogen pressures in excess of 10 bar hydrogen pressure were thought to be responsible for preventing the hydrogenolysis reaction, that is mirrored by an increase in the formation of the coupling product dibenzylamine [22]. The formation of β-palladium hydrides has previously been shown to affect the selectivity of other hydrogenation reactions, such as in the hydrogenation of ethyne, were a transition from the alpha to the beta hydride phase decreases ethane selectivity [23]. Further, inelastic neutron scattering (INS) measurements on various Pd supported catalysts has shown the presence of a beta hydride phase to have a noticeable effect on nitrobenzene hydrogenation activity [24]. Recently, INS has also detected the presence of a β-PdH phase during conditions that support selective propyne hydrogenation over a supported Pd catalyst [25].

Maschmeyer and co-workers have examined the hydrogenation and hydrogenolysis of benzonitrile over a carbon-supported Pd catalyst under mild conditions (80°C, 1 bar H$_2$) [26]. They report benzylamine to be strongly bound to the catalyst surface and to be capable of reversibly poisoning the hydrogenolysis function. Thus, high yields of the hydrogenolysis product (toluene) are prevented at low catalyst loadings [26]. This work follows on from earlier work from these authors, where they studied the hydrogenolysis of various nitriles, imines and amines over Pd/C [27].

Continuing the investigations of hydrogenation of aromatic nitriles, Segobia and co-workers have looked at the chemoselective hydrogenation of cinnamonitrile over a range of supported metal catalysts [28]. That work, concentrating on the selective formation of the primary amine (cinnamylamine) establishes how the reaction profile may be influenced by the metal catalyst used and also its dispersion. This work concentrates on the effectiveness of a generic carbon-supported Pd catalyst for the hydrogenation of a variety of aromatic nitrile compounds [benzonitrile

(C_6H_5CN)), benzyl cyanide ($C_6H_5CH_2CN$), 3-phenyl propionitrile ($C_6H_5CH_2CH_2CN$) and cinnamonitrile ($C_6H_5CH=CHCN$)] that have application in the fine chemical and agri-chemical industries. In this way, the work builds upon the earlier studies of Maschmeyer and co-workers [27] but concentrates on how the catalyst may be facilitating the chemical transformations observed. Reaction trends are considered with respect to issues such as the influence of aliphatic chain length and electronic factors. Significant retention of product by the support material is observed in several cases. Co-hydrogenation studies of benzonitrile and benzylamine are used to gain insight in to the operational phases of the catalyst particles and, importantly, reveal a role for site-selective chemistry. Co-hydrogenation studies on mixtures of benzonitrile and benzyl cyanide highlight the competitive nature of the reaction system and, indirectly, establish a contribution from adsorbed imine species. A reaction scheme is proposed to account for these observations.

2.   Experimental

2.1   Materials

A commercial grade 5% Pd/C catalyst (Sigma-Aldrich, code number: 205680) was used throughout and was intended to represent a generic fine chemicals hydrogenation catalyst. The percentage metal loading was determined by atomic absorption spectroscopy (Perkin Elmer 1100 Atomic Absorption Spectrometer at 247.6 nm) and found to be $3.60 \pm 0.02\%$. The CO adsorption isotherm was determined by mass spectrometry (Hiden CATLAB), Figure 1. A maximum CO capacity of 9.24×10^{-5} moles $CO/g_{catalyst}$ was obtained. Assuming a $CO:Pd_{(s)}$ ratio of 1:2 [29], this equates to 1.11×10^{20} Pd(s) atoms$/g_{(cat)}$, which corresponds to a Pd dispersion of 39 % and a mean particle size of 2.8 nm [29]. TEM analysis (JEOL 1200EX) reveals a narrow particle size distribution centred around 2.5 nm in diameter, in good agreement with the chemisorption measurements. Figure 2 shows the CO temperature-programmed desorption profile for the Pd/C catalyst with three features centred around 475, 640 and 850 K. The lower CO bands are assigned to CO chemisorption on Pd crystallites, with the higher temperature CO band attributed to (partial) decomposition of carboxy species present on the carbon support material [30].

Benzonitrile (Sigma-Aldrich, 99.9% purity), phenylacetonitrile (Sigma-Aldrich, 98% purity), 3-phenylpropionitrile (Sigma-Aldrich, 99% purity) and cinnamonitrile (Sigma-Aldrich, 97% purity), were used as received. Propan-2-ol (Riedel-de Haën, 99.5% purity) was selected as the solvent in all cases.

2.2   Hydrogenation reactions

The hydrogenation reactions were carried out in a 500 mL stirred autoclave (Buchi Glas Uster). An automated gas flow controller (BPC 1202) allowed the delivery of inert (N_2, BOC, 99.999 % purity) and active (H_2, BOC, $\geq$ 99.995% purity) gases to be delivered directly to the reactor via a gas reservoir. Reactions were heated by silicon oil passed around the reactor via a heating circulator (Julabo F25). The hydrogen uptake provided a direct indication of reaction rate and hydrogen consumption.

The reactor was charged with the catalyst (0.5 g), then the solvent (300 mL, methanol) and the reactor was purged with inert gas (N_2). The catalyst/solvent mixture was heated and stirred at 300 rpm for 1 hour under a constant flow of hydrogen in order to reduce the catalyst. Meanwhile, the nitrile substrate (17-23 mmol) was dissolved in 50 mL of solvent and degassed under a constant flow of helium. Upon addition of the nitrile, stirring was stopped, the reactor sealed and the hydrogen pressure raised. Once reaction pressure (4 bar g) was obtained, the reaction mixture was stirred at 800 rpm and samples taken periodically via an outlet valve throughout the course of the reaction. An agitation rate of 800 rpm corresponded to a mid-point of the plateau region of a plot of hydrogenation rate versus agitation rate, where increased agitation speeds yield no improvement in hydrogenation rate. In this way, the reaction system was determined to be free from diffusion limitations and to be under kinetic control. All reactions were performed at least in duplicate, with the profiles presented here being representative of the replicate measurements.

2.3   Analysis

Liquid samples were collected periodically and filtered (Minisart 0.2 µm single use sterile filter) to remove any catalyst residue and analysed off-line. GLC analysis was carried out on a Perkin-Elmer 8500 Series Gas Chromatograph fitted with a Varian Chrompack CP-Sil 8 CB column (30 m x 0.20 mm ID, 0.33 µm film). A_o (initial concentration of starting material) values were calculated based on the amount of pre-weighed starting material added to the reactor prior to commencement of reaction. Errors in GC output and hydrogen consumption were determined by repeat analysis of a known stock of standards and repeat reactions respectively and both were found to be below 5%.

3. Results and Discussion

3.1. *Single reagent hydrogenation studies.*

3.1.1 The hydrogenation of benzonitrile (C_6H_5CN).

Figure 3 shows the concentration *vs.* time plot for the liquid phase hydrogenation of benzonitrile over 5% Pd/C at 338K. Benzonitrile was consumed quickly, with full consumption observed at *ca.* 60 min., corresponding to a turnover number of 218. Figure 3 shows the reaction to be complete at around 75 min, with the reaction ultimately returning a complete mass balance. An initial mass imbalance is observed that is in excess of the number of Pd sites, as determined by the CO adsorption isotherm (missing mass : Pd(s) at 10 mins = 88 : 1), therefore it is assumed that this quantity of reagent is retained by the carbon support [31]. The mass balance is recovered following the completion of reaction indicating desorption of organic material from the catalyst. The reaction profile is consistent with a consecutive reaction [32], whereby significant amounts of benzylamine are formed (31% selectivity at 50% conversion), before being consumed by a further reaction to form the undesired toluene (100% selectivity at 100% conversion of benzonitrile). Repeat results at lower temperature and atmospheric pressure also showed significant amounts of toluene formation, by the route suggested in Scheme 2. No secondary or tertiary amines were formed, in contrast to the generally accepted product distribution of hydrogenation of nitriles over Pd [19-21]. Thus, the hydrogenolysis product is achieved in high yields under mild reaction conditions using low catalyst loadings. Indeed, the complete mass balance evident in Fig. 3 shows that the hydrogenation of benzonitrile is not complicated by a contribution from coupling reactions. Given the modest hydrogen overpressure used here (4 bar), it is assumed that the palladium is buffering hydrogen as chemisorbed hydrogen and sub-surface hydrogen [33]. A role for β-hydride formation within this reaction system, as proposed by Bakker and co-workers [22], is also possible.

Bakker *et al.* looked at this reaction over a Pd/Al$_2$O$_3$ catalyst and reported that toluene can be formed by direct hydrogenolysis of benzonitrile or indirectly from re-adsorbed benzylamine [22]. As the reaction profile presented in Figure 3 adopts the form of a classic A → B → C consecutive process, it is thought that toluene is exclusively formed here as indicated in Scheme 2 by the hydrogenolysis of benzylamine that has formed via the reduction of the benzonitrile starting material. Further, it is noted that the extent of toluene formed in the present investigation (100% selectivity on completion of reaction) significantly exceeds that reported by Bakker *et al*, who also experience significant quantities of dibenzylamine production; something not observed here. In contrast to Bakker but in closer agreement to this work, Maschmeyer's and co-workers' report high

toluene yields (over 99% selectivity to toluene for benzonitrile hydrogenation over Pd/C at *ca*. 1 bar H_2 [27]), indicating the hydrogenolysis process to be facile in their reactions. Differences in the product distributions between different groups are thought to reflect differences in catalyst specifications and possibly Pd crystallite morphology or the type of support that is used.

3.1.2 *The hydrogenation of benzyl cyanide ($C_6H_5CH_2CN$).*

It was anticipated that benzyl cyanide would be readily hydrogenated to its corresponding primary amine in much the same way as benzonitrile. However, whilst conversion of benzyl cyanide occurred, as was determined by the reaction profile in Figure 4, no products were observed in the liquid phase. The hydrogen uptake curve shows that a stoichiometric amount of hydrogen was consumed by the reaction, *i.e.* sufficient to facilitate complete conversion of benzyl cyanide to phenethylamine ($C_6H_5CH_2CH_2NH_2$). From comparisons with the initial mass imbalance for benzonitrile hydrogenation (Section 3.1.1), it is believed that phenethylamine was retained (via strong adsorption of the amine) by the carbon support, since it too is in large excess compared with the available Pd surface sites (phenethylamine $_{(missing)}$: Pd(s) at 200 mins = 365 : 1). Interestingly, the assumed (total) retention of phenethylamine by the catalyst has not caused catalytic activity to be shut down; this is consistent with the vast majority of the product residing on the high surface area carbon support. It is noted that no ethyl benzene was detected, indicating no hydrogenolysis channel to be accessible in this instance.

Previous work has highlighted the relevance of the nitrile unit being in conjugation with the aromatic ring [34]. Although conjugation is absent with benzyl cyanide, the substrate has obtained 100 % conversion (albeit with the absence of any detectable products), so it appears that the nitrile group can be reduced with this catalyst despite no conjugation within the π network (overlap of p orbitals associated with the nitrile functional group and the aromatic ring). To further test this hypothesis, an extended aliphatic 'spacer' unit was examined, Section 3.1.3.

3.1.3 *The hydrogenation of 3-phenylpropionitrile ($C_6H_5CH_2CH_2CN$).*

The reaction profile for the hydrogenation of 3-phenylpropionitrile is seen in Fig. 5 where, in stark contrast to Figure 3 but consistent with Figure 4, no products are observed in the liquid phase. Interestingly, the reaction does not produce a complete mass balance, suggesting some degree of substrate/product retention by the catalyst. The quantity of 'missing' material (moles$_{(missing)}$: Pd$_{(s)}$ at 200 mins = 76 : 1) again indicating retention of hydrocarbon by the carbon support. With little

perceived conversion of nitrile and minimal hydrogen uptake (*ca.* 0.005 moles consumed; full conversion to primary amine equates to a hydrogen uptake of *ca.* 0.0335 moles, *i.e.* ≈ 15% conversion), it is suggested that a small quantity of 3-phenylpropionitrile has been hydrogenated to 3-phenylpropylamine ($C_6H_5CH_2CH_2CH_2NH_2$), where the amine functionality strongly binds to the surface and, thereafter, effectively blocks further catalytic activity. Further, the mass imbalance evident at short reaction times is thought to indicate an initial activity, which is then somehow quenched. Arai *et al.* have shown that catalyst deactivation in the initial stages of reaction could be attributed to strongly adsorbed amines blocking active sites [35]. Since the substrate concentration is in large excess compared to the surface Pd sites, only a fraction of the mass imbalance would be required to poison such sites. The precise reason why catalytic activity may be retained during production of phenethylamine and yet the assumed formation of 3-phenylpropylamine formation effectively poisons the catalyst is unknown at this time. However, one possible reason could be that, when formed, phenethylamine binds to the carbon support, whereas the 3-phenylpropylamine formed irreversibly binds to the metal.

3.1.4   The hydrogenation of cinnamonitrile ($C_6H_5CH=CHCN$).

The above section demonstrates problems in hydrogenating 3-phenylpropionitrile. As previous reports have noted, conjugation of the nitrile group can assist reduction of that unit [36], so it was deemed useful to consider the case of cinnamonitrile within this systematic investigation. Could the presence of the double bond and conjugation between the nitrile group and the aromatic ring be used to induce hydrogenation of the nitrile group and lead to detectable products in the liquid phase? If so, this could therefore be a route to formation of 3-phenylpropylamine. The reaction profile is shown in Figure 6 and shows hydrogenation of the double bond to yield 3-phenylpropionitrile to be rapid and comprehensive. However, interestingly, no further reduction takes place thereafter, with the nitrile functional unit remaining intact and the system returning a complete mass balance. Thermodynamically, in systems without ammonia, the C=C bond has been shown to preferentially adsorb and be selectively reduced in preference to the C≡N group [37]. This is entirely consistent with Figure 6, where only reduction of the olefinic unit is seen; no 3-phenylpropylamine is detectable over the full reaction coordinate

3.2   Co-adsorption studies

3.2.1   The co-adsorption of benzonitrile (C_6H_5CN) and benzylamine ($C_6H_5CH_2NH_2$).

To explore the consecutive nature of benzonitrile hydrogenation, equimolar amounts of both benzonitrile and benzylamine were studied. These experiments were undertaken in order to determine how the hydrogenation step (benzonitrile $\rightarrow$ benzylamine) might influence the hydrogenolysis step (benzylamine $\rightarrow$ toluene). The resulting reaction profile is presented in Figure 7 and quite definitively shows benzonitrile hydrogenation to be independent of benzylamine hydrogenolysis. The former conforms to a single exponential decay curve (consistent with a first order process) with a rate coefficient comparable to reactions without addition of benzylamine (Section 3.1.1). On the other hand, toluene formation commences from the onset of reaction at a rate that is independent of time/concentration up to a saturation value that represents full conversion. This zero order profile indicates that the hydrogenolysis reaction is occurring independently of the hydrogenation process. This situation is indicative of *site-selective chemistry* and can be explained within the confines of a 3-site model as depicted in Figure 8. Firstly, all processes require a steady supply of hydrogen, so Site I is attributed to Pd sites which support dissociative adsorption of dissolved dihydrogen. Site II is responsible for the hydrogenation step, whilst the hydrogenolysis reaction takes place at Site III. This arrangement would permit hydrogenation and hydrogenolysis to occur simultaneously, as is seen in Figure 7. We acknowledge that this is in contrast to what Bakker *et al.* have previously reported [22], where their co-adsorption studies saw a drop in hydrogenation and hydrogenolysis activities, which is attributed to competitive adsorption on the same active sites of the catalyst.

Scheme 3 attempts to demonstrate how the molecules participating in the benzonitrile hydrogenation process are partitioned between the catalyst surface and the liquid phase. k_1 and k_2 are rate coefficients associated with the hydrogenation and hydrogenolysis steps respectively. K_1, K_2, K_3 and K_4 represent adsorption coefficients, with K_2 strongly favouring the adsorbed state whilst K_4 favours the presence of toluene in the liquid phase. Scheme 3 can also be used to describe outcomes seen for nitriles other than benzonitrile. For benzyl cyanide and 3-phenylprionitrile, no amine is seen in the liquid phase in either case. Concentrating on benzyl cyanide first, which exhibits full conversion with associated hydrogen uptake within 200 minutes (Figure 4), it is assumed that the absence of phenethylamine indicates that this material is bound to the catalyst surface. However, as the quantity of amine vastly exceeds the surface Pd density (365:1), then this capacity can only be accommodated by the carbon support material. Assuming that hydrogenation only occurs on the metal, one needs to invoke a spillover process where the amine is actually bound

to the carbon. In this situation K_3 disfavours partitioning from the metal to the liquid phase and the rate of spillover is a relatively facile process under the conditions examined here.

The situation is different with 3-phenylprionitrile as, in contrast to benzyl cyanide, only a finite degree of conversion (10 - 15 %) is seen (Figure 5). Thus, with reference to Scheme 3, it is thought that K_3 strongly favours retention of amine at the metal surface which effectively poisons the catalyst and prevents any further hydrogenation activity. The fact that the degree of retained molecules exceeds the surface Pd density (76:1) indicates that spillover is occurring in this instance as well.

In order to define the more global nature of this reaction system, Scheme 3 needs to include a description for material spilling over on to the carbon support. Figure 8 schematically links the concepts of the 3 site model with the interchange of molecules between the liquid phase, Pd crystallites and the carbon support. Figure 8 is defined within the confines of the benzonitrile reaction profile (fFigure 3) but is intended to be generic, in that it provides an overview of the elementary process associated with the hydrogenation of aromatic nitriles over a Pd/C catalyst.

The initial mass imbalance observed in the hydrogenation of benzonitrile (Figure 3) is also consistent with the proposed schemes, if one acknowledges that mass transport of reactants and products can be mediated through the carbon support. Retention of reactants/products on the support, where no further reaction is thought to occur, would thus render that molecule undetectable in the liquid phase. Thus, in the case of benzonitrile hydrogenation at least, this pathway is thought to be the origin of the low mass balance in the initial stages of that reaction. Thereafter, reverse spillover occurs [31].

3.2.2   The co-adsorption of benzonitrile (C_6H_5CN) and benzyl cyanide ($C_6H_5CH_2CN$).
In an attempt to further understand the connection between different amines and hydrogenation lability, the hydrogenation of equimolar amounts of benzonitrile and benzyl cyanide were investigated. Figure 9 shows the resulting reaction profile. In line with their individual profiles (Figures 3 and 4 respectively), both reagents are fully converted, although at a slower rate than seen previously. This is thought to reflect competition for hydrogenation sites (Site II). Hydrogen consumption corresponds to a smooth growth curve and stops once no reagents remain. Concentrating first on benzonitrile, a similar profile to Figure 3 is discernible, with benzylamine displaying an intermediate profile and toluene identified as the final product. However, the profile

connected with benzyl cyanide conversion is different to that seen in Figure 4 because significant quantities of phenethylamine are now seen in Figure 9. Previously (Section 3.1.2), the absence of this product was attributed to retention by the carbon support. Its presence in the liquid phase in Figure 9 suggests there to be a degree of competition for adsorption sites on the carbon under co-adsorption conditions. Moreover, the fact it is observable in this case gives some credibility to the assumption that phenethylamine is actually produced but does not partition in to the liquid phase when only benzyl cyanide and dihydrogen are added as reagents (Figure 4).

A further point worth noting in Figure 9 is an incomplete mass balance. This mass loss (not explicitly shown in Figure 9) is accounted for by formation of the secondary amine N-benzyl-2-phenethylamine ($C_6H_5CH_2CH_2$-NH-$CH_2C_6H_5$) via the cross-coupling of intermediate benzylimine ($C_6H_5CH=NH$) with phenethylamine, or possibly of phenethyimine ($C_6H_5CH_2CH=NH$) with benzylamine. No products were observed corresponding to the symmetrical secondary amines that one would expect from the coupling of (i) phenethyimine with phenethylamine or (ii) benzylimine with benzylamine. The remaining mass imbalance (small) can be accounted for by residual phenethylamine on the carbon support.

Clearly, the co-adsorption of benzonitrile and benzyl cyanide (Figure 9) leads to a series of competing interactions which perturb the reaction profiles seen in the single hydrogenation reactions (Figures 3 and 4). Not least, this includes competition for adsorption sites on the carbon support by the benzyl cyanide derived amine (phenethylamine), as well as the formation of a secondary amine (N-benzyl-2-phenethylamine). Further, since neither benzylimine nor phenethyimine are observed in the liquid phase, it is believed that the coupling reactions that lead to formation of the secondary amine must be catalyst mediated.

4.0   Conclusions

The liquid phase hydrogenation of benzonitrile, benzyl cyanide, 3-phenylpropionitrile and cinnamonitrile over a 5 wt % Pd/C catalyst was investigated in methanol at 4 bar g and 333 K. The following observations can be made.

- Benzonitrile hydrogenation appears as a consecutive process. First benzonitrile is hydrogenated to form benzylamine. This product then undergoes a hydrogenolysis reaction to form toluene.

- Co-hydrogenation studies on a mixture of benzonitrile and benzylamine show the hydrogenation and hydrogenolysis reactions to be occurring simultaneously and independently. This behaviour in interpreted in terms of a 3 site model: dissociative hydrogen adsorption takes place at Site I; hydrogenation takes place at Site II; Site III is associated with the hydrogenolysis reaction.

- Benzyl cyanide and 3-phenylpropionitrile hydrogenation result in no product formation in the liquid phase. In the case of 3-phenylpropionitrile loss of activity is attributed to amine product poisoning Pd sites. For benzyl cyanide, converted product is believed to partition on to the carbon support.

- 3-phenylpropionitrile is the only product in the hydrogenation of cinnamonitrile. The carbon-carbon double bond is selectively reduced with respect to the carbon-nitrogen triple bond. The conjugation between the nitrile group and the aromatic ring does not assist nitrile reduction in this case.

- Hydrogenation of a mixture of benzonitrile and benzyl cyanide indicates the competitive nature of the reaction system. The presence of phenethylamine (source = benzyl cyanide hydrogenation) in to the liquid phase is also induced. This coincides with the formation of the secondary amine N-benzyl-2-phenethylamine which, due to the absence of imines in the reaction mixture, is thought to form at the catalyst (Pd) surface.

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Reaction Schemes
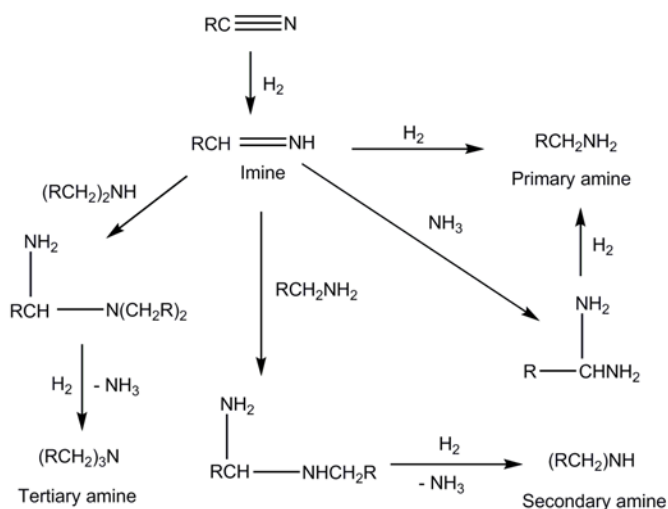
Scheme 1. Proposed reaction pathway to primary, secondary and tertiary amines via the reaction of intermediate imine species [11].
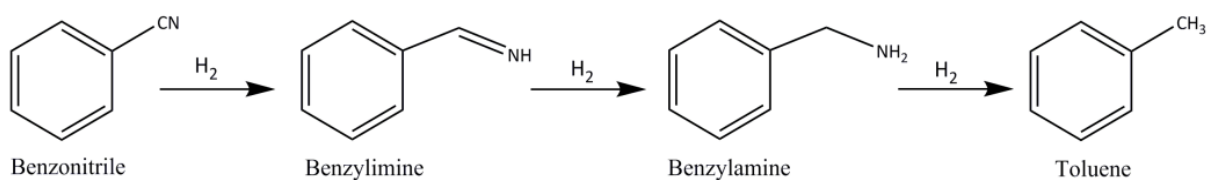
Scheme 2. Proposed reaction scheme for the hydrogenation of benzonitrile to benzylamine and subsequent hydrogenolysis to toluene over Pd/C.
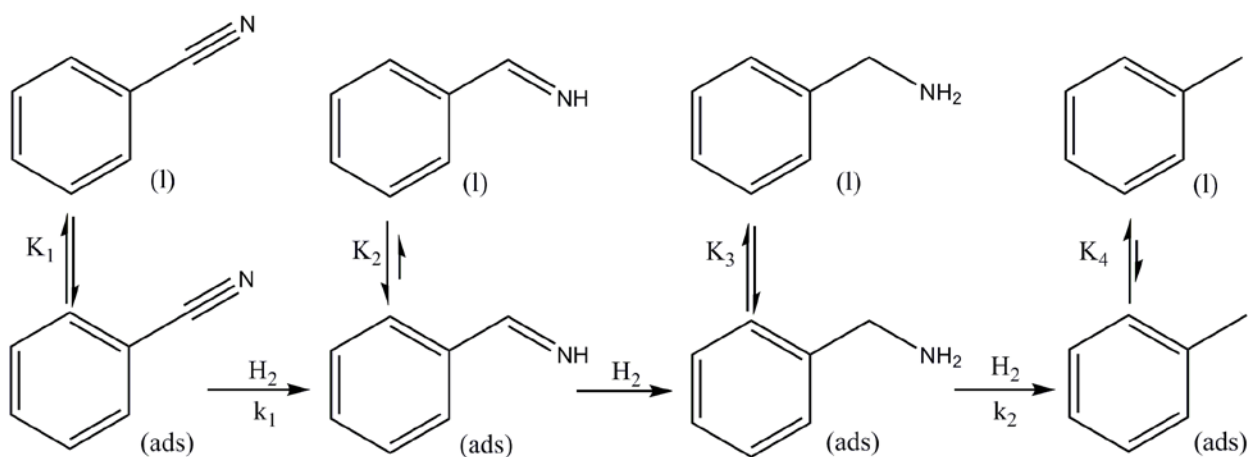
Scheme 3. Partitioning of adsorbed and liquid phase species in the hydrogenation of benzonitrile over Pd/C.

Figures
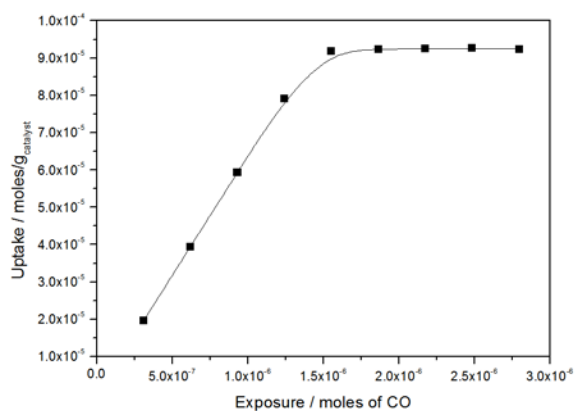
Figure 1. CO adsorption isotherm for 5% Pd/C at 313 K.
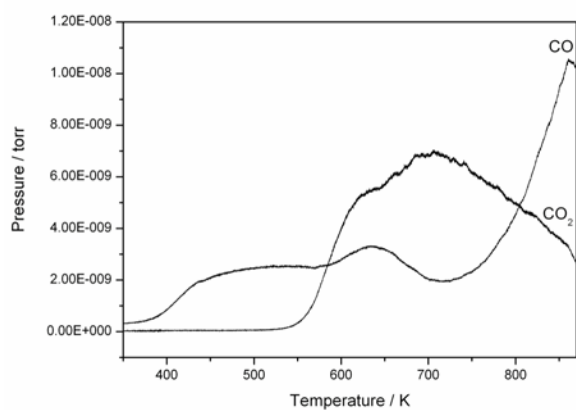
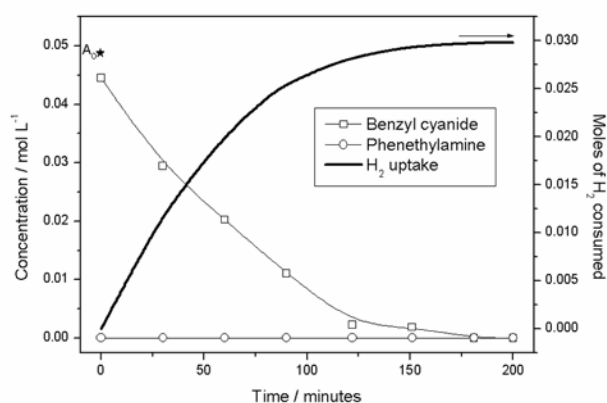**Figure 2.** CO temperature-programmed desorption profile for a saturation dose of CO on 5% Pd/C.
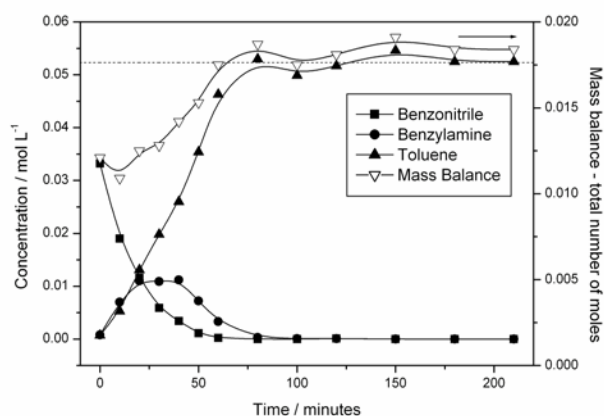
Figure 3. Reaction profile and mass balance for the hydrogenation of benzonitrile over 0.5 g 5% Pd/C, at 333 K, 4.0 bar g, *ca.* 0.018 moles of benzonitrile. The dashed line represents the incident concentration of benzonitrile.

Figure 4. Reaction profile and hydrogen uptake for the hydrogenation of benzyl cyanide over 0.5g 5% Pd/C, at 333 K, 4.0 bar g, *ca.* 0.017 moles of benzyl cyanide. A_0 represents the incident concentration of benzylcyanide.
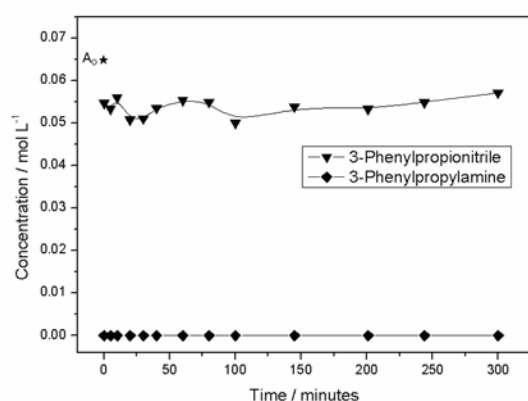
Figure 5. Reaction profile for the hydrogenation of 3-phenylpropionitrile over 0.5 g 5% Pd/C at 333 K, 4.0 bar g, *ca.* 0.023 moles of 3-phenylpropionitrile. A_0 represents the incident concentration of 3-phenylpropionitrile.
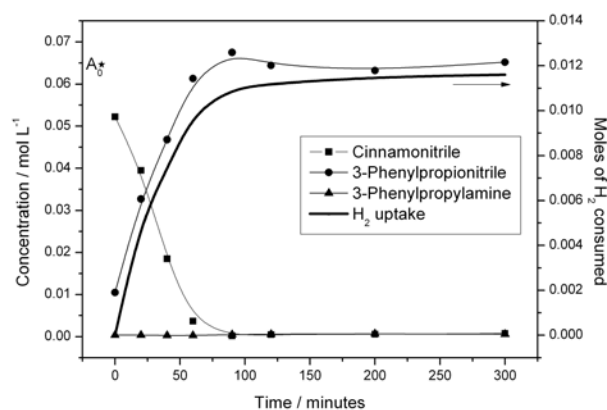

Figure 6. Reaction profile for the hydrogenation of cinnamonitrile over 0.5 g 5% Pd/C at 333 K, 4.0 bar g, *ca.* 0.020 moles of cinnamonitrile. A_0 represents the incident concentration of cinnamonitrile.
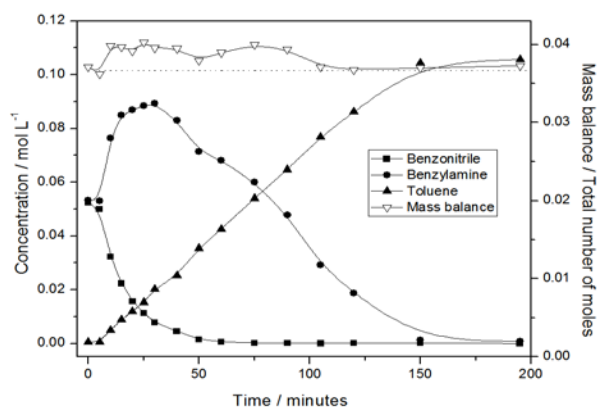
Figure 7. Reaction profile for the co-hydrogenation of benzonitrile and benzylamine over 5% Pd/C at 338 K, 4.0 bar g *ca.* 0.021 moles of nitrile and amine. The dashed line represents the incident combined concentration of benzonitrile and benzylamine.
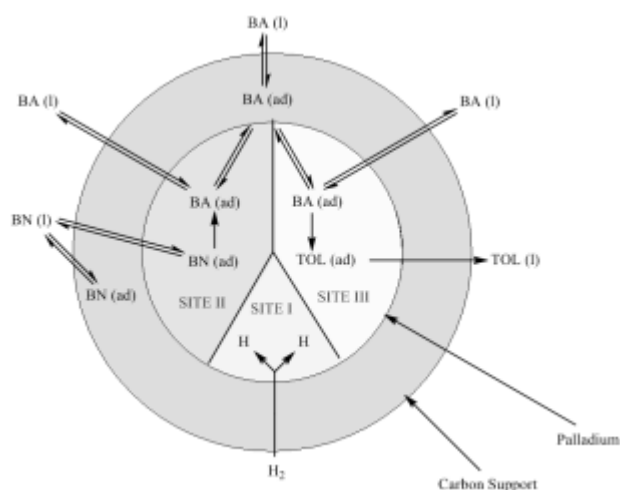

Figure 8. Schematic representation of how the Pd/C affects turnover in the benzonitrile (BN) hydrogenation reaction. Hydrogen dissociation occurs at Site I, hydrogenation occurs at Site II [benzonitrile $\rightarrow$ benzylamine (BA)] and hydrogenolysis takes place at Site III [benzylamine $\rightarrow$ toluene (Tol)].
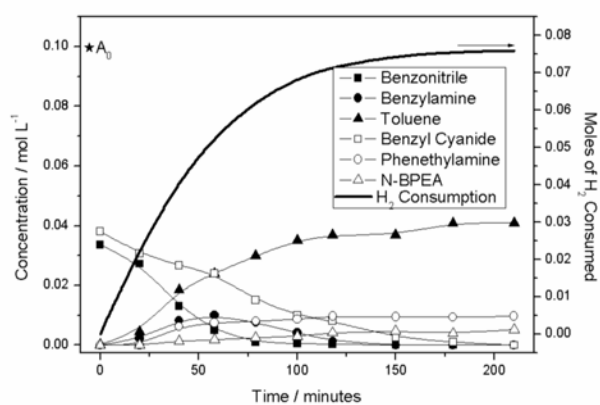
Figure 9. The co-hydrogenation of benzonitrile and benzyl cyanide over 0.5 g 5% Pd/C, 333 K, 4.0 bar g, ca. 0.017 moles of benzonitrile and benzyl cyanide. A_0 represents the incident combined concentration of benzonitrile and benzyl cyanide. N-BPEA = N-benzyl-2-phenethylamine.