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The application of a supported palladium catalyst 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 aromatic 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.

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 and Senderens 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, 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 and Pasek 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 was not as high. Many factors can influence the selectivity of the reaction in the liquid phase. Catalyst choice is

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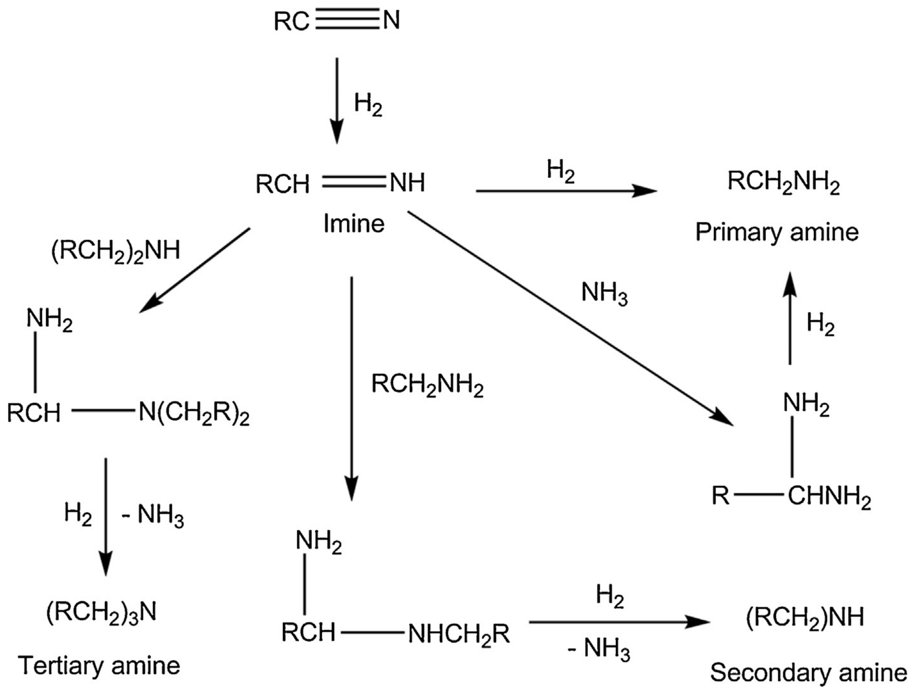


Scheme 1. Proposed reaction pathway to primary, secondary and tertiary amines via the reaction of intermediate imine species [11].

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]. Nevertheless, Hegedűs and Máthes' studies on the liquid phase hydrogenation of benzonitrile over a Pd/C catalyst report complete benzonitrile conversion and very high benzylamine selectivity [15], clearly demonstrating the usefulness of supported Pd catalysts for high value hydrogenation reactions of aromatic nitriles.

Hydrogenolysis of the primary amine is a recognised side reaction [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 [15]. 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_2O_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. Thus, 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. In particular, this work explores the interplay between nitrile hydrogenation and associated hydrogenolysis reactions over a supported Pd catalyst. Given the significance of amine chemistry within the fine chemicals sector [1–3], it is important to improve our awareness of how heterogeneous catalysis can be applied to access primary amines via the selective hydrogenation of aromatic nitriles.

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.

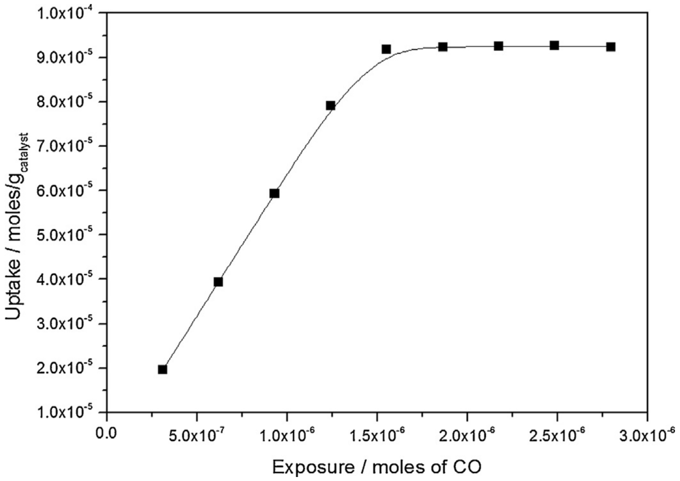


Fig. 1. CO adsorption isotherm for 5% Pd/C at 313 K.

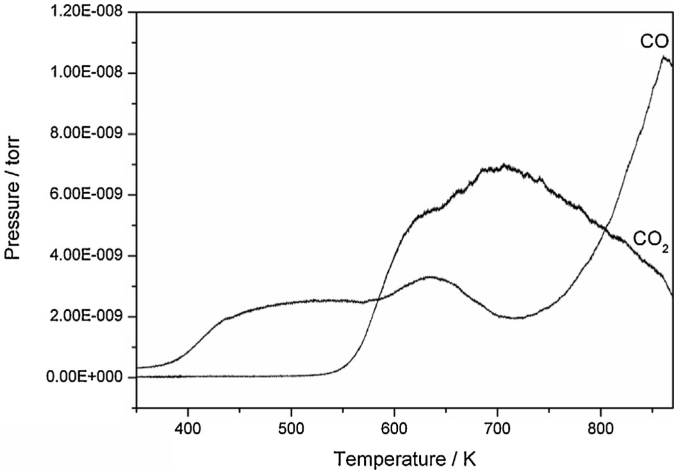


Fig. 2. CO temperature-programmed desorption profile for a saturation dose of CO on 5% Pd/C.

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 (PerkinElmer 1100 Atomic Absorption Spectrometer at 247.6 nm) and found to be 3.60 ± 0.02%. The CO adsorption isotherm was determined by mass spectrometry (Hiden CATLAB), (Fig. 1). A maximum CO capacity of 9.24×10^{-5} mol 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. Fig. 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, ≥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 h 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 *vs.* 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 PerkinElmer 8500 Series Gas Chromatograph fitted with a Varian Chrompack CP-Sil 8CB column (30 m × 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)

Fig. 3 shows the concentration *vs.* time plot for the liquid phase hydrogenation of benzonitrile over 5% Pd/C at 338 K. Benzonitrile was consumed quickly, with full consumption observed at *ca.* 60 min., corresponding to a turnover number of 218. Fig. 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 benzonitrile molecules: Pd$_{(s)}$ at 10 min = 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 to benzylamine at 50% benzonitrile con-

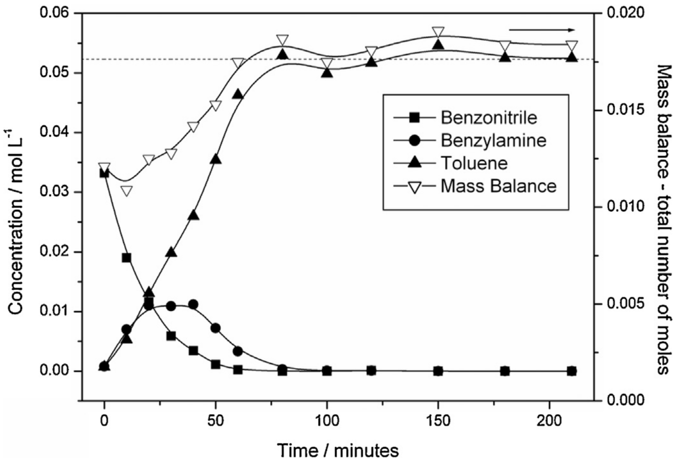


Fig. 3. Reaction profile and mass balance for the hydrogenation of benzonitrile over 0.5 g 5% Pd/C, at 333 K, 4.0 bar g, *ca.* 0.018 mol of benzonitrile. The dashed line represents the incident concentration of benzonitrile.

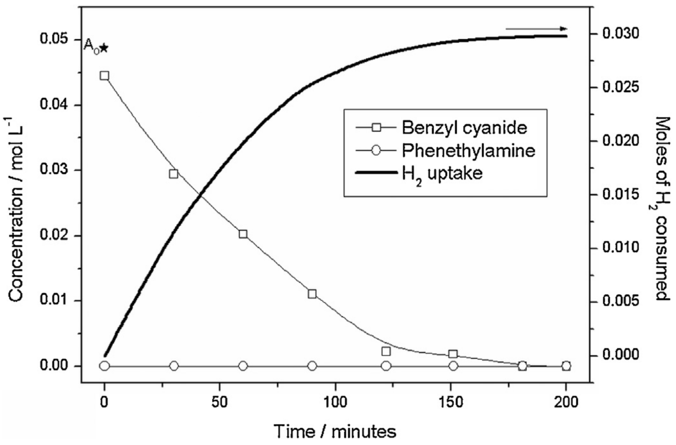


Fig. 4. Reaction profile and hydrogen uptake for the hydrogenation of benzyl cyanide over 0.5 g 5% Pd/C, at 333 K, 4.0 bar g, *ca.* 0.017 mol of benzyl cyanide. A_0 represents the incident concentration of benzylcyanide.

version), before being consumed by a further reaction to form the undesired toluene (100% toluene selectivity at 100% conversion of benzonitrile). Repeat results at lower temperature and atmospheric pressure also showed significant amounts of toluene formation, by the route indicated 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 g), 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_2O_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 Fig. 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 even the type of support that is used.

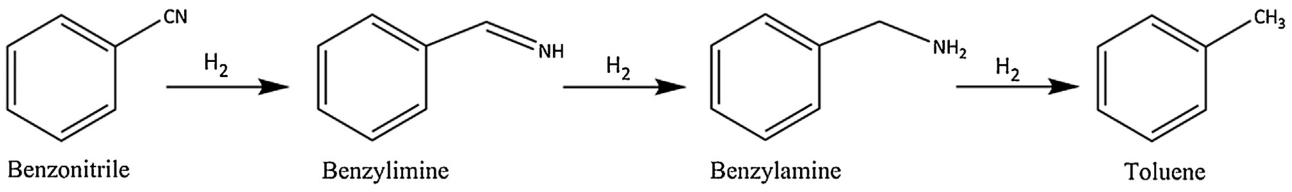
3.1.2. The hydrogenation of benzyl cyanide ($C_6H_5CH_2CN$)

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 Fig. 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 again the number of substrate molecules is in large excess compared with the available Pd surface sites (phenethylamine $_{\text{(missing)}}$: $Pd_{(s)}$ at 200 min = 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. Moreover, 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 in the liquid phase), 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 examine this hypothesis further, 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 Fig. 3 but consistent with Fig. 4, no products are observed in the liquid phase. Interestingly, the reaction does not produce a complete



Scheme 2. Proposed reaction scheme for the hydrogenation of benzonitrile to benzylamine and subsequent hydrogenolysis to toluene over Pd/C.

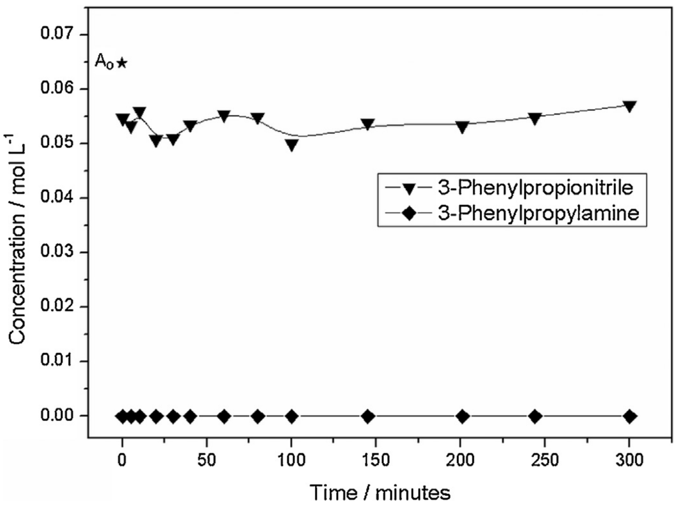


Fig. 5. Reaction profile for the hydrogenation of 3-phenylpropionitrile over 0.5 g 5% Pd/C at 333 K, 4.0 bar g, *ca.* 0.023 mol of 3-phenylpropionitrile. A_0 represents the incident concentration of 3-phenylpropionitrile.

mass balance, suggesting some degree of substrate/product retention by the catalyst. The quantity of 'missing' material (molecules of phenylpropionitrile $_{\text{(missing)}}$: $Pd_{(s)}$ at 200 min = 76: 1), again indicating retention of hydrocarbon by the carbon support. With little perceived conversion of nitrile and minimal hydrogen uptake (*ca.* 0.005 mol H_2 consumed; full conversion to primary amine equates to a hydrogen uptake of *ca.* 0.0335 mol H_2, *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 quenched. Arai et al. have shown that catalyst deactivation in the initial stages of reaction may 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. In their work on nitrile reduction for a variety of unsaturated nitrile compounds over a range of Co and Ni based catalysts in the liquid phase, Kukula and Koprivova demonstrated a role for conjugation in affecting the reducability of the nitrile group [36]. Therefore, is it possible that the presence of a double bond in the ring side chain that permits conjugation between the nitrile group and the aromatic ring could be used to induce hydrogenation of the nitrile group and lead to detectable products in the liquid phase? If so, this could be a route to formation of 3-phenylpropylamine. The reaction profile for cinnamonitrile hydrogenation over Pd/C is shown in Fig. 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 Fig. 6, where only reduction of the olefinic unit is seen; no 3-phenylpropylamine is detectable over the full reaction coordinate and the induced conjugation has been ineffectual for enhancing the reducability of the nitrile group.

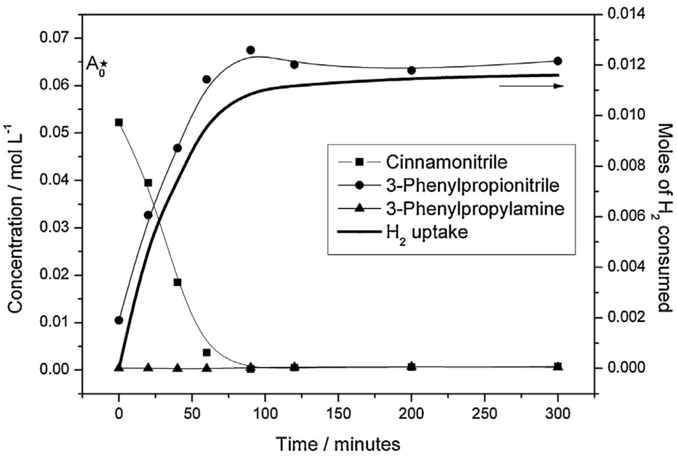


Fig. 6. Reaction profile for the hydrogenation of cinnamonitrile over 0.5 g 5% Pd/C at 333 K, 4.0 bar g, *ca.* 0.020 mol of cinnamonitrile. A_0 represents the incident concentration of cinnamonitrile.

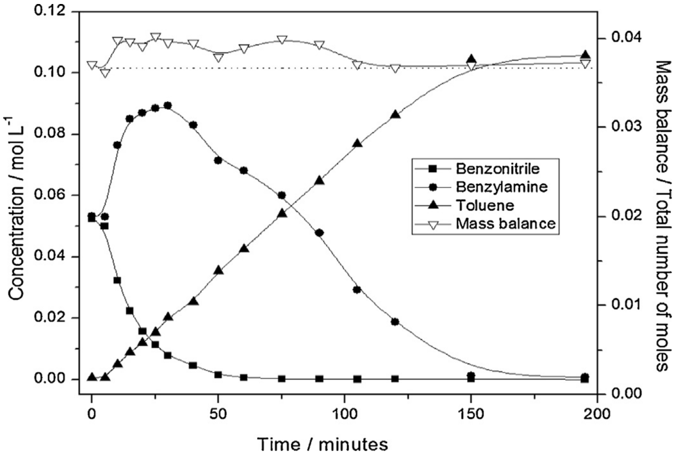


Fig. 7. Reaction profile for the co-hydrogenation of benzonitrile and benzylamine over 5% Pd/C at 338 K, 4.0 bar g *ca.* 0.021 mol of nitrile and amine. The dashed line represents the incident combined concentration of benzonitrile and benzylamine.

3.2. *Co-adsorption studies*

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

In order to explore further 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 → benzylamine) might influence the hydrogenolysis step (benzylamine → toluene) [Scheme 2]. The resulting reaction profile is presented in Fig. 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

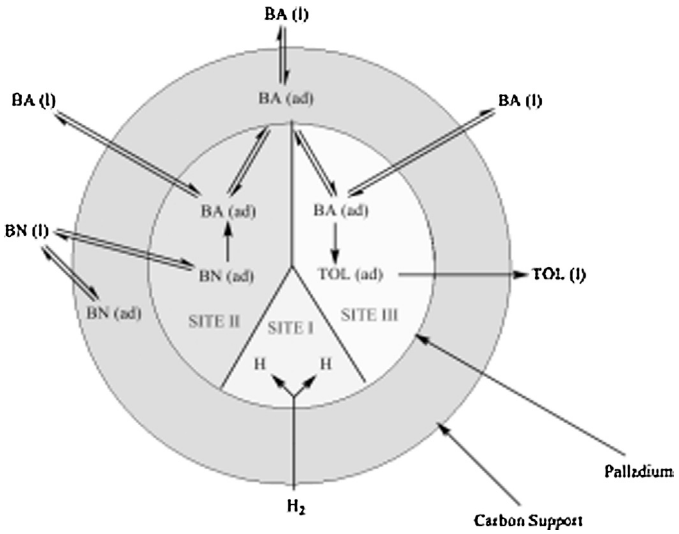


Fig. 8. Schematic representation of how the Pd/C affects turnover in the benzonitrile (BN) hydrogenation reaction. Hydrogen dissociation occurs at Site I, hydrogenation occurs at Site II [benzonitrile → benzylamine (BA)] and hydrogenolysis takes place at Site III [benzylamine → toluene (Tol)].

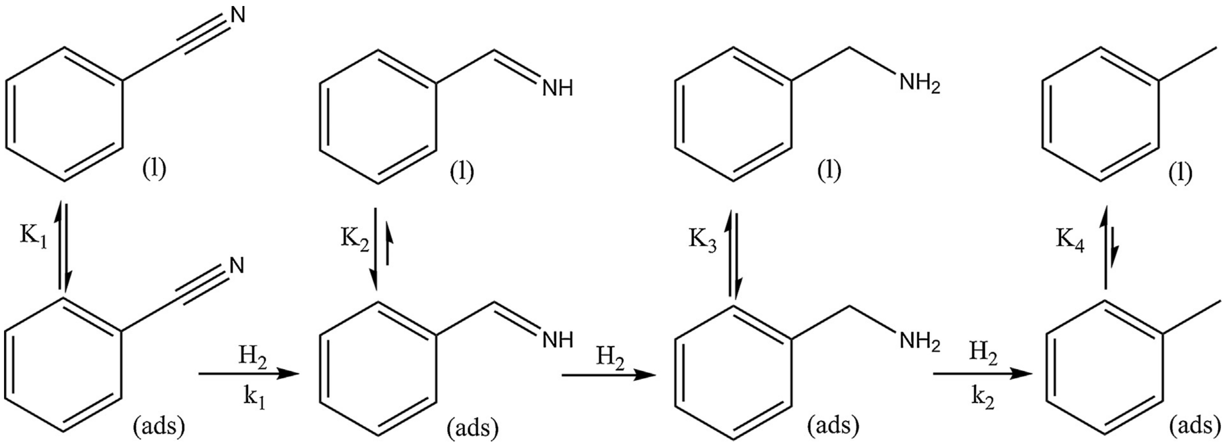
a saturation value that represents full conversion. This zero order profile indicates that the hydrogenolysis reaction is occurring independently of the hydrogenation process. This situation is indicative of site-selective chemistry and can be explained within the confines of a 3-site model as depicted in Fig. 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 Fig. 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.

It is recognised that Sites I and II, as defined above, could actually be a single site. Namely, hydrogen dissociative adsorption and hydrogenation could occur at the same site, *e.g.* low index planes of the Pd crystallites. Comparisons between the contrasting profiles presented in Fig. 4 (benzyl cyanide hydrogenation, Section 3.1.2) and 5 (3-phenylpropionitrile hydrogenation, Section 3.1.3) are unhelpful in this matter. In the former case, complete hydrogen uptake is achieved with concomitant conversion of benzyl cyanide, and in the latter case hydrogen uptake and 3-phenylpropionitrile hydrogenation are rapidly halted to comparable degrees. Whereas this coincidence of hydrogen uptake and hydrogenation activity is consistent with a two site model (dissociative hydrogen adsorption/hydrogenation and hydrogenolysis), it can also be explained by the three site hypothesis: (i) in the case of benzyl cyanide hydrogenation, sites I and II are active; (ii) for 3-phenylpropionitrile hydrogenation although sites I and II are initially active, sufficient 3-phenylpropylamine is produced that irreversibly binds to either Site I or Site II, or both Sites I and II, to shut down all hydrogenation activity. Clearly, further work is required, including a Langmuir–Hinshelwood kinetic analysis, to refine the multi-site model, however such an analysis is deemed to be beyond the scope of the present communication. Nevertheless, it is noted that a three-site model is entirely consistent with the reaction profile presented in Fig. 7.

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 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 min. (Fig. 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.

The situation is different with 3-phenylprionitrile as, in contrast to benzyl cyanide, only a finite degree of conversion (10–15%) is seen (Fig. 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 substrate molecules exceeds the surface Pd density (76:1) indicates that spillover is occurring in this instance as well.



Scheme 3. Partitioning of adsorbed and liquid phase species in the hydrogenation of benzonitrile over Pd/C.

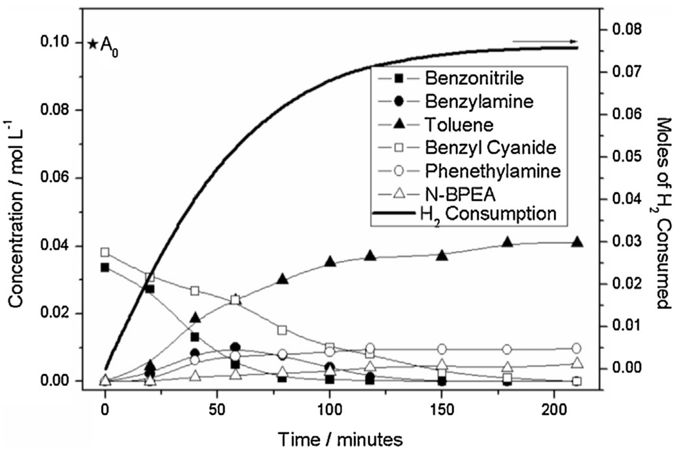


Fig. 9. The co-hydrogenation of benzonitrile and benzyl cyanide over 0.5 g 5% Pd/C, 333 K, 4.0 bar g, *ca.* 0.017 mol of benzonitrile and benzyl cyanide. A_0 represents the incident combined concentration of benzonitrile and benzyl cyanide. N-BPEA = *N*-benzyl-2-phenethylamine.

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. Fig. 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. Fig. 8 is defined within the confines of the benzonitrile reaction profile (Fig. 3) but is intended to be generic, in that it provides an overview of the elementary process associated with the liquid phase hydrogenation of aromatic nitriles over a Pd/C catalyst.

The initial mass imbalance observed in the hydrogenation of benzonitrile (Fig. 3) is also consistent with the proposed scheme (Fig. 8), 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 ($C_6H_5CH_2CN$)

To further understand the connection between different amines and hydrogenation lability, the hydrogenation of equimolar amounts of benzonitrile and benzyl cyanide were investigated. Fig. 9 shows the resulting reaction profile. In line with their individual profiles (Figs. 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 Fig. 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 Fig. 4 because significant quantities of phenethylamine are now seen in Fig. 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 Fig. 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 (Fig. 4).

A further point worth noting in Fig. 9 is the 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. A small mass imbalance is evident in Fig. 9 (not shown) that may be accounted for by residual phenethylamine on the carbon support.

Clearly, the co-adsorption of benzonitrile and benzyl cyanide (Fig. 9) leads to a series of competing interactions which perturb the reaction profiles seen in the single hydrogenation reactions (Figs. 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.

3.3. 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 induced. This coincides with the formation of the secondary amine *N*-benzyl-2-phenethylamine which, due to the absence of imines in the liquid phase, is thought to form at the catalyst (Pd) surface.

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