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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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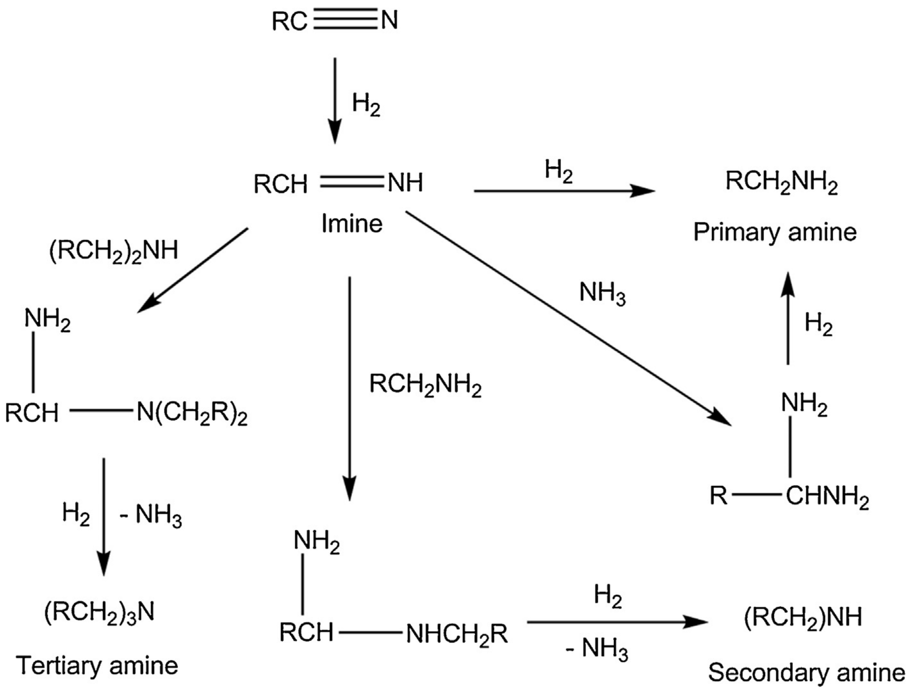

Scheme 1. Proposed reaction pathway to primary, secondary and tertiary amines via the reaction of intermediate imine species [11].

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.