



The application of palladium catalysts for the hydrogenation of aromatic nitriles in the liquid phase

Liam McMillan¹, Justin Baker¹, David T. Lundie², Colin Brennan³, Alan Hall³ and David Lennon¹

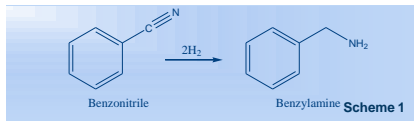
1. Department of Chemistry, Joseph Black Building, University of Glasgow, Glasgow G12 8QQ, U.K.

2. Hiden Analytical Ltd., 420 Europa Boulevard, Warrington, WA5 7UN, U.K.

3. Process Studies Group, Syngenta, PO Box A38, Leeds Road, Huddersfield, HD2 1FF, U.K.

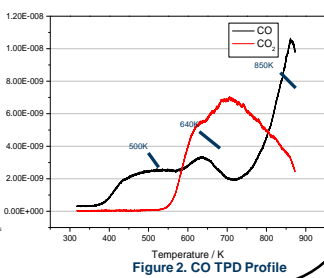
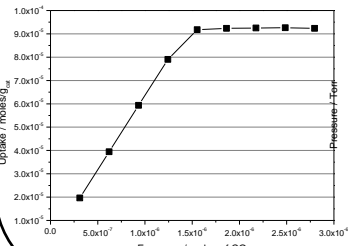
1.0 Introduction

- The hydrogenation of aromatic nitrile compounds is a reaction of considerable significance within the agricultural and pharmaceutical industries [1]. Raney-type nickel catalysts are often used but in *fine chemical* applications they may compromise selectivity to the desired amine by additionally facilitating the reduction of other functional groups [2].
- Against this background, and following previous research [3], the effectiveness of a supported palladium catalyst for this role was investigated.
- The present work highlights some of the issues relevant to the hydrogenation of benzonitrile – a conventional liquid phase hydrogenation reaction – to develop an understanding of the chemistry involved.



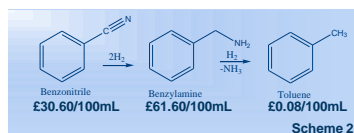
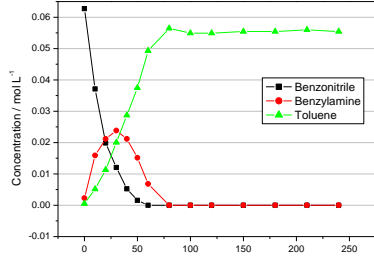
2.0 Experimental and Catalyst characterisation

- A 5% Pd/C catalyst was used in the hydrogenation of benzonitrile in a Buchi autoclave at 4.0 bar and 338 K with a stirring speed of 800 rpm.
- The CO adsorption isotherm for the Pd/C catalyst was determined by mass spectrometry (Hiden CATLAB), Figure 1. The maximum CO capacity corresponds to a Pd dispersion of 54% and a mean particle size of 2.0 nm. TEM analysis reveals a narrow particle size distribution.
- The CO temperature programmed desorption (TPD) profile is presented in Figure 2 and shows 3 features centred around 500, 640 and 850K. The corresponding CO₂ signal rises abruptly at ca. 550K and exhibits a maximum at peak ca. 710K. The CO band at 500K is assigned to CO chemisorption on Pd crystallites. The higher temperature CO bands are attributed to (partial) decomposition of carboxy species present on the carbon support material [4].



3.0 Hydrogenation of benzonitrile

- This reaction profile was unexpected. The catalyst readily hydrogenated the benzonitrile to the desired primary amine, however, disappointingly, this was then further hydrogenated to produce low value toluene.
- This latter step is an example of a hydrogenolytic reaction that, although well documented in conventional synthetic organic chemistry literature [5], is rarely reported in the heterogeneous catalysis literature [3].



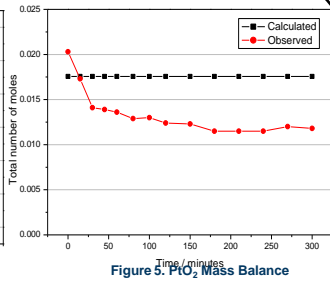
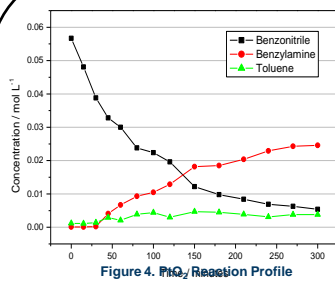
- Clearly, there is no economic drive to produce toluene via such a valuable intermediate as the desired primary amine product. How does one control selectivity to the amine and therefore limit its conversion to toluene?

4.0 Minimising conversion to toluene – Choice of catalyst

- Two possible ways of limiting conversion to toluene include:
 - The choice of catalyst and,
 - Employing favourable chemistry *i.e.* the use of additives.

- Literature indicates that Adam's catalyst (PtO₂) has useful application in this type of hydrogenation reaction [6]. The reaction profile (Figure 4) shows a much slower reaction rate than with Pd/C, but interestingly the profile reveals a decrease in hydrogenolysis as is observed by the low levels of toluene. Indeed at high conversion, benzylamine selectivity improved from 0% over Pd/C to 86% over PtO₂.

4.0 Continued



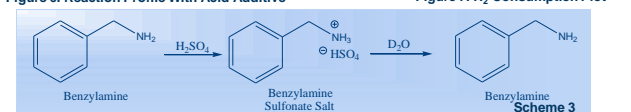
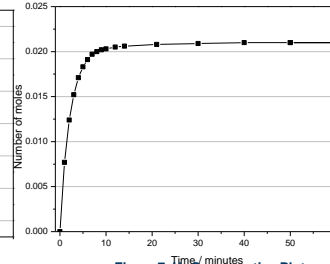
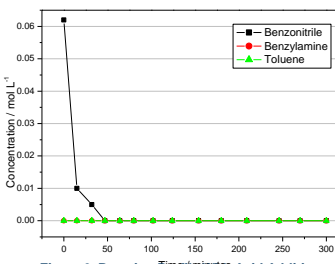
Catalyst	Selectivity to Benzylamine (%) at 50% Conversion	Initial Reaction Rate (μ mol/L/s)
5% Pd/C	38	27.16
PtO ₂	71	9.97

Table 1

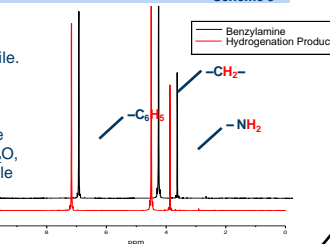
- When the selectivity to benzylamine at 50% conversion is considered, PtO₂ offers considerable improvement in selectivity (Table 1) over 5% Pd/C, despite its lower activity.
- However, a complete mass balance was unobtainable with this system (Figure 5). This is thought to arise from carbon laydown in the initial stages of the reduction process. This could quite reasonably occur via oligomerisation of the amine product.

4.1 Minimising conversion to toluene – Acid Additive

- Previous studies have shown H₂SO₄ to be a useful additive in controlling the selectivity to primary amine in nitrile hydrogenation reactions [7]. The acid functions by forming a salt with primary amine product, thus preventing formation of 2°/3° amines or by-products – in this case, toluene. Hydrogenation reactions were carried out using 5% Pd/C with equimolar amounts of benzonitrile and acid.



- H₂ consumption plot (Figure 7) confirms no further reaction after conversion of benzonitrile and no toluene is observed in the reaction profile. The rate of hydrogenation was comparable to reactions when an acid additive is not used (26.12 μ mol/L/s). A white solid product was identified as the desired benzylamine-sulfonate salt in a yield of 82% and, after dissolving in D₂O, NMR analysis identified benzylamine as the sole product (Figure 8).



5.0 Conclusions

- Hydrogenation of an aromatic amine over a Pd/C catalyst results in an unfavourable hydrogenolytic step.
- This reaction can be avoided using Adam's catalyst, however, that reaction system returns an incomplete mass balance.
- The primary amine product is obtainable in high yield (82%) by running the Pd/C catalyst under acidic conditions, and then affecting an aqueous work-up.

6.0 References

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