

# Selective Production of Benzylamine via Gas Phase Hydrogenation of Benzonitrile over Supported Pd Catalysts

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Abstract The continuous gas phase hydrogenation of benzonitrile has been studied over Pd/C and Pd/Al<sub>2</sub>O<sub>3</sub> (mean Pd size = 2.5–3.0 nm from STEM). Toluene was the predominant product over Pd/C whereas benzylamine was preferred over Pd/Al<sub>2</sub>O<sub>3</sub>. This is linked to differences in Pd electronic character (from XPS) that impact on nitrile adsorption. Greater surface acidity and hydrogen availability (based on chemisorption/TPD) for Pd/C resulted in higher conversion rates. Operation at lower contact time for multiple Pd/Al<sub>2</sub>O<sub>3</sub> beds in series promoted exclusive formation of benzylamine at an appreciably higher rate than reported in the literature.

## **Graphical Abstract**



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<sup>1</sup> Chemical Engineering, School of Engineering and Physical Sciences, Heriot-Watt University, Edinburgh EH14 4AS, Scotland, UK **Keywords** Selective hydrogenation  $\cdot$  Benzonitrile  $\cdot$ Benzylamine  $\cdot$  Pd/C  $\cdot$  Pd/Al<sub>2</sub>O<sub>3</sub>  $\cdot$  Catalyst beds in series

# **1** Introduction

Benzylamine is a versatile chemical used in the production of Vitamin H (Biotin), as an intermediate for photographic chemicals, in the manufacture of cationic paints and as an active ingredient in the synthesis of nylon fibres [1]. The hydrogenation of benzonitrile as the principal route to benzylamine [2, 3] is challenging due to undesired condensation with the benzylideneimine intermediate to give dibenzylamine (with NH<sub>3</sub> elimination) and amine hydrogenolysis to toluene [4-6]; see Fig. 1. Benzonitrile hydrogenation has been established at elevated H<sub>2</sub> pressure (6–100 bar) [4, 6–11] over supported metal (Ni [6, 12], Pt [10], Rh [10] and Pd [4, 7, 9–11] ) catalysts. Palladium has delivered the highest combined activity and selectivity [10] where biphasic separation (for reactions in  $CO_2 + H_2O$ ) under supercritical conditions (70 bar) served to elevate benzylamine selectivity (up to 98 %) by preventing condensation [7]. The energy demands associated with supercritical CO<sub>2</sub> lowers process efficiency. Conventional batch liquid phase operation is a less energy intensive alternative. Benzylamine has been generated as principal product over supported Pd [9] where the factors proposed to inhibit dibenzylamine formation and increase benzylamine yield include support [4], solvent [12] and incorporation of (acid) additives to the reaction medium [6]. The requirement for separation and purification unit operations to extract the target product represents a decided drawback in terms of sustainable/clean synthesis.

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Fig. 1 Reaction pathways associated with the hydrogenation of benzonitrile (BN) to target (framed) benzylamine (BA, *solid arrows*), condensation to dibenzylamine (DBA, *dotted arrows*) and hydrogenolysis to toluene (TOL, *dashed arrow*)

pharmaceutical corporations identified the move from batch to continuous processing as #1 priority to achieve sustainable chemical production and related research was given the highest strategic importance [13]. Low activity has been a common feature of the reported work on gasphase continuous benzonitrile hydrogenation, which has been limited to the use of Cu-MgO [14] and Ni/Al<sub>2</sub>O<sub>3</sub> [15]. Palladium has exhibited higher activity in liquid phase operation but low benzylamine yield [10, 11]. Gas phase continuous operation facilitates control over contact time by varying the volume and number of catalyst beds, which can influence product selectivity [16, 17]. The use of multiple catalyst beds in catalytic processes has been considered to a limited extent [18-20] and we could not find any reported application in catalytic hydrogenation. In this work we examine for the first time the possible role of support (C and Al<sub>2</sub>O<sub>3</sub>) on the catalytic action of Pd in the gas phase continuous hydrogenation of benzonitrile to benzylamine and evaluate the use of multiple beds in series as a means to fine-tune contact time and promote selective amine production.

#### 2 Experimental

### 2.1 Materials and Catalyst Activation

Commercial (1 % w/w) Pd/C and (1.2 % w/w) Pd/Al<sub>2</sub>O<sub>3</sub> catalysts were obtained from Sigma-Aldrich. Prior to use, the samples were sieved to 75  $\mu$ m mean diameter and activated in 60 cm<sup>3</sup> min<sup>-1</sup> H<sub>2</sub> at 2 K min<sup>-1</sup> to 573 K, which was maintained for 1 h to ensure complete reduction to zero valent Pd [21]. Samples for off-line characterisation were passivated in 1 % v/v O<sub>2</sub>/He at ambient temperature.

The Pd content was measured by inductively coupled plasmaoptical emission spectrometry (ICP-OES, Vista-PRO, Varian Inc.) from the diluted extract in HF. Hydrogen and NH<sub>3</sub> chemisorption, temperature programmed desorption (TPD) and specific surface area (SSA) measurements were conducted on the commercial CHEM-BET 3000 (Quantachrome) unit equipped with a thermal conductivity detector (TCD) and TPR Win<sup>TM</sup> software for data acquisition/manipulation. Samples were loaded into a U-shaped Ouartz cell (3.76 mm i.d.) and heated in 17 cm<sup>3</sup> min<sup>-1</sup> (Brooks mass flow controlled) 5 % v/v  $H_2/N_2$  at 2 K min<sup>-1</sup> to 573 K where the effluent gas passed through a liquid N<sub>2</sub> trap. The reduced samples were maintained at the final temperature in a flow of H<sub>2</sub>/N<sub>2</sub> until the signal returned to baseline, swept with 65 cm<sup>3</sup> min<sup>-1</sup> N<sub>2</sub>/He for 1.5 h, cooled to ambient temperature and subjected to H<sub>2</sub> (BOC, 99.99 %) or NH<sub>3</sub> (BOC, 99.98 %) pulse (50–1000 µl) titration. Samples were thoroughly flushed in N<sub>2</sub>/He (65 cm<sup>3</sup> min<sup>-1</sup>) to remove weakly bound H<sub>2</sub> or NH<sub>3</sub> and subjected to TPD (at 10-50 K min<sup>-1</sup>) to 950-1200 K. The resultant profile was corrected using the TPD recorded in parallel directly following TPR to explicitly determine H<sub>2</sub> or NH<sub>3</sub> release. SSA was recorded with a 30 % v/v N<sub>2</sub>/He flow using N<sub>2</sub> (99.9 %) as internal standard. Three cycles of N2 adsorption-desorption in the flow mode were employed to determine SSA using the standard single point BET method. SSA and H<sub>2</sub>/NH<sub>3</sub> uptake/ desorption were reproducible to  $\pm 5$  % and values quoted represent the mean. X-ray photoelectron spectroscopy (XPS) analyses were conducted on an Axis Ultra instrument (Kratos Analytical) under ultra-high vacuum conditions ( $<10^{-8}$  Torr) using a monochromatic Al Ka X-ray source (1486.6 eV). The source power was maintained at 150 W and the emitted photoelectrons were sampled from a  $750 \times 350 \ \mu\text{m}^2$  area at a take-off angle =  $90^{\circ}$ . The analyser pass energy was 80 eV for survey spectra (0-1000 eV) and 40 eV for high resolution spectra (Pd  $3d_{5/2}$  and  $3d_{3/2}$ ). The adventitious carbon 1s peak was calibrated at 284.5 eV and used as an internal standard to compensate for charging effects. Palladium particle morphology (shape and size) was determined by scanning transmission electron microscopy (STEM, JEOL 2200FS field emission unit) employing Gatan DigitalMicrograph 1.82 for data acquisition/manipulation. Samples for analysis were crushed and deposited (dry) on a holey carbon/Cu grid (300 Mesh). Up to 800 individual Pd particles were counted for each catalyst and the surface area-weighted mean Pd diameter ( $d_{\text{STEM}}$ ) calculated from

$$d_{\text{STEM}} = \frac{\sum_{i}^{n_i} n_i d_i^3}{\sum_{i}^{n_i} n_i d_i^2} \tag{1}$$

where  $n_i$  is the number of particles of diameter  $d_i$ .

#### 2.3 Catalytic Procedure

Reactions of benzonitrile/benzylamine (Sigma-Aldrich, >99 %) were conducted in situ, immediately following catalyst activation, under atmospheric pressure at 353 K in a fixed bed vertical glass reactor (i.d. = 15 mm). The reactant was delivered as a 2-propanol (Sigma-Aldrich, >99.5 %) solution at a fixed calibrated flow rate (Model 100 kd scientific microprocessor-control infusion pump) to the reactor via a glass/Teflon air-tight syringe and Teflon line in a co-current flow of H<sub>2</sub> (BOC, >99.98 %). The 2propanol serves as a carrier and did not undergo any reaction. A layer of borosilicate glass beads served as preheating zone where the organic reactant was vaporised and reached reaction temperature before contacting the catalyst. Isothermal conditions  $(\pm 1 \text{ K})$  were maintained by diluting the catalyst bed with ground glass (75 µm) which was mixed thoroughly with catalyst before insertion in the reactor. The reaction temperature was continuously monitored using a thermocouple inserted in a thermowell within the catalyst bed. Catalyst performance in a multiple bed arrangement was investigated where each catalyst bed was separated by glass wool (10 mm); catalyst activation followed the procedure described above. The inlet molar reactant flow rate was in the range 0.18–0.36 mmol  $h^{-1}$ where H<sub>2</sub> content was up to 900 times in excess of the stoichiometric requirement for benzylamine production. Gas flow rate was monitored using a Humonics (Model 520) digital flowmeter. The molar palladium to inlet reactant ratio (*n/F*) spanned the range  $1.3 \times 10^{-3}$ - $3.6 \times 10^{-2}$  h. In blank tests passage of benzonitrile or benzylamine in a stream of H<sub>2</sub> through the empty reactor did not result in any detectable conversion. The reactor effluent was frozen in liquid N2 for subsequent analysis using a Perkin-Elmer Auto System XL chromatograph equipped with a programmed split/splitless injector and flame ionisation detector, employing a DB-1 capillary column (i.d. = 0.33 mm, length = 50 m, film thickness = 0.20  $\mu$ m). Benzonitrile conversion (X) is given by

$$X(\%) = \frac{[\text{Benzonitrile}]\text{in} - [\text{Benzonitrile}]\text{out}}{[\text{Benzonitrile}]\text{in}} \times 100 \qquad (2)$$

with selectivity (S) to product "i"

$$Si \quad (\%) = \frac{[\text{Product}]i, \text{out}}{[\text{Benzonitrile}]\text{in} - [\text{Benzonitrile}]\text{out}} \times 100$$
(3)

where subscripts "in" and "out" represent the reactor inlet and outlet effluent streams. Repeated reactions with different samples of catalyst delivered raw data reproducibility and a mass balance better than  $\pm 5$  %.

### **3** Results and Discussion

## 3.1 Pd/C: Characterisation and Catalyst Test Results

The physicochemical properties of Pd/C are summarised in Table 1. Total surface area (SSA) is consistent with the literature [22]. Palladium particle size was determined by H<sub>2</sub> chemisorption assuming dissociative adsorption (H<sub>2</sub>/Pd adsorption stoichiometry = 1/2 [23]) and validated by STEM analysis. The representative STEM image given in Fig. 2a reveals pseudo-spherical Pd nano-particles with a narrow size distribution (<5 nm, Fig. 2b) and mean of 2.5 nm that is in good agreement with that (2.2 nm) obtained from H<sub>2</sub> titration. Hydrogen temperature programmed desorption (TPD) generated the profile in Fig. 2c where a two stage H<sub>2</sub> release is evident with temperature maxima  $(T_{\text{max}})$  at 789 and 1148 K. Desorption at  $T \ge 770$  K can be attributed to loss of spillover hydrogen generated during thermal activation [24], i.e. migration of atomic hydrogen to the support following dissociation at Pd sites. Reported surface acidity measurements of supported metal systems have relied on NH<sub>3</sub> desorption [25-27]. In this study,  $NH_3$  chemisorption matched that released in TPD (Table 1) with an associated  $T_{\text{max}} = 490 \text{ K}$  (Fig. 2d) within the range (444–573 K) reported for activated carbon supported Pd [28]. In order to gain insight into the electronic character of the Pd phase, XPS analysis over the Pd 3d binding energy (BE) region was conducted and the profile is given in Fig. 2e. The Pd  $3d_{5/2}$  signal (at 335.9 eV) is 0.7 eV higher than that characteristic of metallic Pd (335.2 eV) [29], suggesting electron transfer to the carbon support with the generation of  $Pd^{\delta+}$  as proposed elsewhere for nano-scale (4–12 nm) Pd on carbon [21, 30].

Conversion (X) and product selectivity  $(S_i)$  as a function of contact time (n/F) are presented in Fig. 2f where an increase in benzonitrile conversion was recorded at higher n/F. Toluene was generated as the principal product  $(S_i > 80 \%)$  with secondary benzylamine formation at lower n/F (<8 × 10<sup>-3</sup> h). At extended contact time, toluene was the sole product via amine hydrogenolysis (dashed arrow in Fig. 1). Under the same reaction conditions, use of benzylamine as feed generated toluene. There was no detectable dibenzylamine, a result that deviates from liquid phase reaction systems where significant by-product formation (*S* < 14 %) was observed over Pd/C [6, 8]. Condensation of the imine intermediate with benzylamine can be circumvented due to the shorter contact time in continuous gas phase operation. Nitrile reduction to primary amine proceeds via a nucleophilic mechanism where hydrogen (as a weak

**Table 1** Palladium loading, specific surface area (SSA), Pd particle size (from  $H_2$  chemisorption and STEM analysis),  $H_2$  and  $NH_3$  chemisorption and release during TPD. Benzonitrile hydrogenation

rate (*R*) and selectivity ( $S_i$ ) to benzylamine (BA) and toluene (TOL) at X = 20 % over Pd/C and Pd/Al<sub>2</sub>O<sub>3</sub>

Catalyst	Pd (% w/w)	$SSA (m^2 g^{-1})$	Pd size (nm)	$H_2 \;(mmol \; g_{Pd}^{-1})$	$NH_3 \ (mmol \ g^{-1})$	$R \pmod{\mathbf{h}^{-1} \operatorname{mol}_{\operatorname{Pd}}^{-1}}$	$S_{i, X = 20 \%}$ Product (%)
Pd/C	1.0	870	2.2 <sup>a</sup> /2.5 <sup>b</sup>	2.5 <sup>c</sup> /80 <sup>d</sup>	0.94°/0.92 <sup>d</sup>	230 (527) <sup>e</sup>	BA (10) TOL (90)
Pd/Al <sub>2</sub> O <sub>3</sub>	1.2	145	2.4 <sup>a</sup> /3.0 <sup>b</sup>	2.1 <sup>c</sup> /10 <sup>d</sup>	0.52°/0.51 <sup>d</sup>	99 (272) <sup>e</sup>	BA (96) TOL (4)

 $^{a}$  from H<sub>2</sub> chemisorption

<sup>b</sup> from STEM

 $^{c}\ H_{2}/NH_{3}$  uptake from titration at ambient temperature

<sup>d</sup> H<sub>2</sub>/NH<sub>3</sub> release from TPD

<sup>e</sup> TOF (h<sup>-1</sup>) based on Pd dispersion from STEM analysis

**Fig. 2** a Representative STEM image with **b** associated Pd particle size distribution, **c**  $H_2$ and **d** NH<sub>3</sub> TPD profiles, **e** XPS spectrum over the Pd 3*d* region and **f** variation of conversion (*X*, *open triangle*) and selectivity (*S<sub>i</sub>*) to benzylamine (*filled square*) and toluene (*filled circle*) with contact time (*n/F*) for reaction over Pd/C





Fig. 3 Surface benzonitrile orientation for reaction over a Pd/C and b Pd/Al\_2O\_3

nucleophile) attacks activated  $-C \equiv N$  to generate the reactive imine (-CH=NH) that undergoes further hydrogenation (to  $-CH_2-NH_2$ ). A number of adsorption modes (i.e. parallel, perpendicular and side-on) [4] on Pd surfaces has been proposed for nitrile hydrogenation. Nitrile interaction should be favoured via the lone pair electron on nitrogen with electron deficient Pd<sup> $\delta$ +</sup> in a perpendicular orientation (Fig. 3a), where the adsorbed nitrile undergoes attack by surface dissociated hydrogen with cleavage of C–N to generate toluene. A perpendicular adsorption of the basic nitrile group on support acid sites [31–34] is also possible with hydrogenolytic bond scission by spillover hydrogen.



**Fig. 4** a Representative STEM image with **b** associated Pd particle size distribution, **c** H<sub>2</sub> and **d** NH<sub>3</sub> TPD profiles, **e** XPS spectrum over the Pd 3*d* region and **f** dependence of conversion (*X*, open triangle) and selectivity ( $S_i$ ) to benzylamine (filled square) and toluene (filled circle) on contact time (n/F) for reaction over Pd/Al<sub>2</sub>O<sub>3</sub>

## 3.2 Pd/Al<sub>2</sub>O<sub>3</sub>: Characterisation and Catalyst Test Results

The SSA of Pd/Al<sub>2</sub>O<sub>3</sub> was appreciably lower than Pd/C (Table 1) and is comparable with values  $(94-185 \text{ m}^2 \text{ g}^{-1})$ reported in literature for commercial y-Al<sub>2</sub>O<sub>3</sub> supported Pd [35, 36]. The Pd phase on Al<sub>2</sub>O<sub>3</sub> took the form of discrete pseudo-spherical particles (Fig. 4a) with a similar size distribution (Fig. 4b) and mean (3.0 nm) to Pd/C that was again in good agreement with H<sub>2</sub> chemisorption (Table 1). Hydrogen TPD from Pd/Al<sub>2</sub>O<sub>3</sub> resulted in a broad signal (Fig. 4c) over the 610–950 K range. Total H<sub>2</sub> desorbed exceeded uptake during pulse titration but was significantly lower than that measured for Pd/C (Table 1). Spillover is influenced by the concentration of initiating and acceptor sites, degree of contact between participating phases and metal-support interaction(s) [37]. Greater H<sub>2</sub> desorption from Pd/C can be linked to the higher available surface area relative to Pd/Al<sub>2</sub>O<sub>3</sub> which can accommodate more spillover. Ammonia desorption from Pd/Al<sub>2</sub>O<sub>3</sub> (Fig. 4d) exhibited a lower  $T_{\text{max}}$  (470 K) relative to Pd/C, suggesting weaker interaction of NH<sub>3</sub> with surface acid sites. Total NH<sub>3</sub> release from Pd/Al<sub>2</sub>O<sub>3</sub> coincided with chemisorption and is close to that  $(0.54 \text{ mmol g}^{-1})$  reported for Pd/Al<sub>2</sub>O<sub>3</sub> by Nam et al. [27]. Ammonia adsorption/desorption measurements confirm a greater level of surface acidity for Pd/ C relative to Pd/Al<sub>2</sub>O<sub>3</sub>. The XPS profile for Pd/Al<sub>2</sub>O<sub>3</sub>, given in Fig. 4e, is characterised by a Pd  $3d_{5/2}$  BE that is 0.3 eV lower than the metallic Pd [29], suggesting partial electron transfer from support to metal phase. This is in accordance with reported electron-rich  $Pd^{\delta-}$  (2–10 nm) on Al<sub>2</sub>O<sub>3</sub> [21].

In contrast to Pd/C, Pd/Al<sub>2</sub>O<sub>3</sub> exhibited full selectivity to the target benzylamine at low contact time (n/  $F < 3 \times 10^{-3}$ ) as shown in Fig. 4f. This result is significant in terms of clean synthesis of benzylamine when compared with existing literature where dibenzylamine production (up to 16 % selectivity) has been reported over Pd/Al<sub>2</sub>O<sub>3</sub> in liquid phase reaction [4, 7, 9]. From a consideration of Pd electronic character, a partial negative charge ( $Pd^{\delta-}$ ) should favour interaction with the polarised carbon  $(C^{\delta+})$  of the  $-C \equiv N$  group through a side-on adsorption due to repulsion of  $Pd^{\delta-}$  with the nitrogen lone pair (Fig. 3b). Hydrogenation of unsaturated  $-C \equiv N$  to saturated amine -CH2-NH2 reduces carbon polarity, weakening adsorption with the result that the primary amine product desorbs without further reaction. In common with Pd/C, toluene selectivity was increased at higher n/F, indicative of a sequential pathway, i.e. benzonitrile  $\rightarrow$  benzylamine  $\rightarrow$  toluene. Reaction of benzylamine as feed  $(n/F = 3 \times 10^{-3} \text{ h})$  over Pd/Al<sub>2</sub>O<sub>3</sub> generated toluene as product but at a much lower rate (3 mol h<sup>-1</sup> - mol<sub>Pd</sub><sup>-1</sup>) than Pd/C (70 mol h<sup>-1</sup> mol<sub>Pd</sub><sup>-1</sup>). Taking a common fractional nitrile conversion (X = 20 %, see Table 1), Pd/ Al<sub>2</sub>O<sub>3</sub> delivered an appreciably higher selectivity to benzylamine but at a lower rate compared with Pd/C. This deviation in selectivity can be attributed to differences in Pd electronic character (from XPS) that impact on the mode of adsorption of benzonitrile. The higher nitrile consumption rate over Pd/C can be linked to greater availability of surface reactive hydrogen (from H<sub>2</sub> chemisorption/TPD) and possible enhanced nitrile activation at support acid sites (with higher acidity based on NH<sub>3</sub> chemisorption/TPD).

# 3.3 Use of Catalyst Beds in Series: Enhanced Benzylamine Production Over Pd/Al<sub>2</sub>O<sub>3</sub>

The results presented in Fig. 4f established full selectivity to benzylamine over Pd/Al<sub>2</sub>O<sub>3</sub> at low contact time, where X < 15 %. This falls short in terms of the productivity required for practical applications where reaction exclusivity must be targeted at high conversion. An increase in n/F served to increase conversion (Fig. 4f) but this was accompanied by undesired toluene formation. Hydrogenolysis to toluene was suppressed over Pd/Al<sub>2</sub>O<sub>3</sub> at low contact time and a configuration based on discrete catalyst beds in series, each operated at low n/F, should serve to increase overall nitrile conversion while retaining hydrogenation selectivity. Unreacted nitrile is converted to target product in subsequent catalyst beds and given the low rate of benzylamine hydrogenolysis over Pd/Al<sub>2</sub>O<sub>3</sub> the amine can be carried through without further reaction. Reaction rates and product selectivities obtained in the multi-bed catalyst arrangement (see Fig. 5) are recorded in Table 2. The same total mass of catalyst was divided equally into N (= 1-4) beds with the same inlet benzonitrile and H<sub>2</sub> flow rate. Selectivity is assessed at two representative nitrile conversions (X = 45 and 60 %). An increase in overall reaction rate and benzylamine selectivity (to 100 %) was observed with increasing bed number up to the quadruple bed arrangement. Our results demonstrate the beneficial effect of multi-beds of the same catalyst in series to enhance selective amine formation. We have achieved a rate (99 mol  $h^{-1}$   $mol_{Pd}^{-1}$ ) with full selectivity to benzylamine that is significantly higher than that reported (ca. 0.01 mol  $h^{-1}$  mol<sub>Cu</sub> calculated from data provided) for reaction over Cu-MgO (at 513 K) with the highest reported selectivity to benzylamine (99 %) in gas phase continuous reaction [14].

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Fig. 5 Schematic diagram for the catalytic system based on single and multiple Pd/Al<sub>2</sub>O<sub>3</sub> catalyst beds in series with reactant and product distribution. *Note*: "m" represents the total mass of catalyst; *BN* benzonitrile reactant, *BA* benzylamine, *TOL* toluene

Single-bed	Double-bed	Triple-bed	Quadruple-bed	N-bed
BN m BN+ BA+ TOL	BN m/2 BN+ BA+ TOL m/2 BN+ BA+ TOL	BN m/3 BN+ BA+ TOL m/3 BN+ BA+ TOL m/3 BN+ BA+ TOL M/3	BN m/4 BN+ BA m/4 BN+ BA m/4 BN+ BA m/4 DN+ BA m/4 BN+ BA	BN m/N BN+ BA m/N BN+ BA m/N BN+ BA m/N BN+ BA m/N BA

**Table 2** Selectivity ( $S_i$ ) to benzylamine (BA) and toluene (TOL) at X = 45 and 60 % and benzonitrile hydrogenation rate (R) using multiple Pd/Al<sub>2</sub>O<sub>3</sub> catalyst beds in series

Catalyst beds	$S_{i, X = 45 \%}$ (%)		$S_{i, X} = 60$	% (%)	$R \pmod{\mathbf{h}^{-1} \operatorname{mol}_{\operatorname{Pd}}^{-1}}$
	BA	TOL	BA	TOL	
Single-bed	78	22	62	38	48
Double-bed	93	7	90	10	75
Triple-bed	97	3	96	4	84
Quadruple-bed	100	0	100	0	99

# 4 Conclusions

Gas phase continuous hydrogenation of benzonitrile over Pd/C (mean Pd size = 2.5 nm) generated toluene as principal product with higher nitrile consumption rates than Pd/  $Al_2O_3$  (mean Pd size = 3.0 nm). This is ascribed to greater available surface reactive hydrogen and a contribution of surface acidity to nitrile activation. Electron transfer to the carbon support with the formation of  $Pd^{\delta+}$  (from XPS analysis) favours a perpendicular adsorption of benzonitrile through the nitrogen lone pair with hydrogen attack to generate consecutively, imine, amine and toluene. The occurrence of  $Pd^{\delta-}$  on Al<sub>2</sub>O<sub>3</sub> results in a side-on activation of benzonitrile and desorption of benzylamine as exclusive product at  $n/F < 3 \times 10^{-3}$  h; hydrogenolysis to toluene was observed at higher n/F. Utilisation of multiple Pd/ Al<sub>2</sub>O<sub>3</sub> beds in series serves to retain full selectivity to benzylamine, delivering a far higher production rate than previously reported. We have established the viability of operating catalyst beds in series under isothermal conditions as an effective means of delivering high and exclusive amine throughput.

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