The Reductive Amination of Benzaldehyde Over Pd/C Catalysts: Mechanism and Effect of Carbon Modifications on the Selectivity

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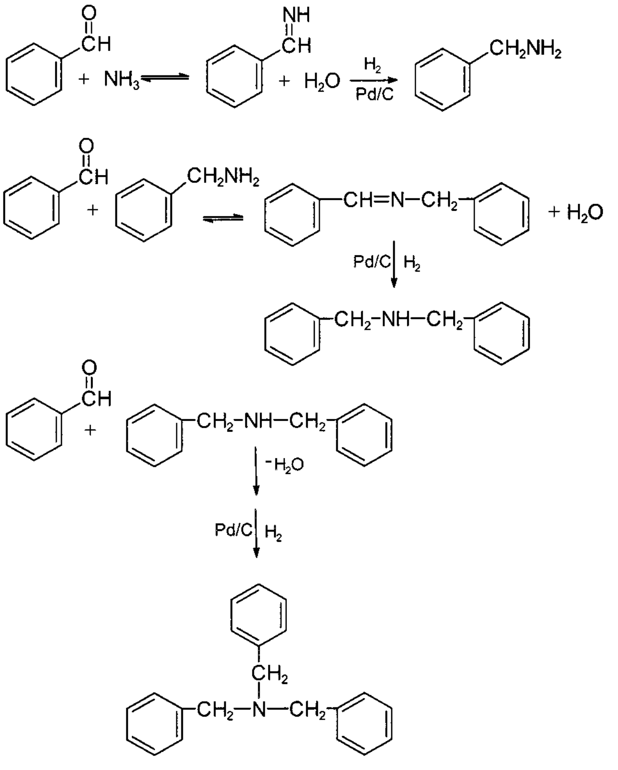
The effects of the acidity of the carbon surface on the reactivity and selectivity of carbon supported noble metal catalysts in the reductive amination of benzaldehyde with ammonia was studied. The equilibria involved in the homogeneous solution were studied with ^{1}H NMR. At the start of the reductive amination, dibenzylimine is rapidly formed, which is subsequently hydrogenated to give dibenzylamine. Benzylamine is formed by disproportionation of dibenzylimine to benzylamine and benzylimine. An increase in the number of acidic sites on the carbon support results in higher reaction rates. This may be ascribed to an acid catalysis in the establishment of relevant homogeneous equilibria and/or reduction of the concentration of the inhibiting *gem*-diamine intermediate at the catalyst surface. A fully selective synthesis of dibenzylamine is achieved by hydrogenation of the intermediate dibenzylimine.

Introduction

Dibenzylamine is an industrially interesting compound that is used in rubber and tire compounding, as corrosion inhibitor, and as an intermediate in the pharmaceutical industry. It is produced by a reductive amination of benzaldehyde with ammonia, via benzylamine (Scheme 1). The benzylamine that is formed, however, can react with benzaldehyde in a similar reaction to dibenzylamine, which in turn can react with benzaldehyde yielding tribenzylamine. It is obvious, therefore, that the selectivity of this process is a major problem. In addition, waste products such as benzyl alcohol and toluene can be formed. Several review papers concerning the reductive amination of carbonyl compounds have been published.[1−4]



Scheme 1. Overall steps in the reductive amination of benzaldehyde

The most frequently used catalytic system for this reaction is Pd/C. The advantages of activated carbon as a support are its cheapness, its stability in both strongly acidic and strongly alkaline environments, and, due to its high porosity, its large surface area. Another advantage, especially in the case of noble metal catalysts, is the easy recovery of the precious metal by burning off the carbon. However, since carbon originates from natural products, like peat or wood, every batch of activated carbon can have different properties, which may be reflected in the performance of the catalyst.

In this study, the various equilibria and hydrogenation reactions involved in the reductive amination of benzaldehyde are investigated. To investigate the effect of the carbon properties on the reductive amination, we modified a batch of carbon by oxidative and reductive treatments, to obtain supports with different amounts of oxygen surface groups. This changes both the acidity and hydrophilicity of the support.[5]

Results and Discussion

Catalyst Characterization

Palladium was supported on activated carbon, pretreated with $(NH_4)_2S_2O_8$. The effect of different oxidation treatments on the acidity of this carbon has been described previously.[5] Upon treatment of carbon with $(NH_4)_2S_2O_8$, mainly carboxylic acid sites are formed, which can be concluded from neutralization experiments and IR spectra. The

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Table 1. Relative intensity of 1700 cm^{-1} band ($I_{1700/1580}$ cm^{-1}) and average Pd particle size (d_{Pd}) of the Pd/C catalysts ion exchanged with Na^+ and reduced at different temperatures (T_{red}) in 10% H_2/N_2

T_{red} [°C]	cation	$I_{1700/1580}$ cm^{-1}	d_{Pd} [nm]
150	Na^+	0.15	3.0
	H^+	0.30	3.0
300	H^+	0.23	3.2
400	H^+	0.18	4.9

neutralization experiments with NaOH revealed 1.4 meq/g acidic sites to be present on the oxidized carbon. Another measure of acidity is the intensity, in the IR spectra, of the 1700 cm^{-1} band (carboxylic acid groups[6,7]) relative to that of the 1580 cm^{-1} band (C-skeleton).[5,8] Upon oxidation, this ratio increased from 0.0 to 0.45.

After oxidation, the carbon was impregnated with an aqueous solution of $Pd(NH_4)Cl_2$ and reduced (10% H_2/N_2) at different temperatures during 2 h. As Table 1 indicates, reduction at temperatures ranging from 150 to 400 °C resulted in a decrease of the amount of carboxylic acid groups present on the carbon. As shown previously[5], the hydrophilicity decreases with the loss of oxygen surface sites, and increases upon sodium exchange. The Pd particle size distribution of the catalysts is displayed in Figure 1. After reduction at 150 °C, most particles measure 3 nm; when applying 400 °C the average particle size increases to about 5 nm.

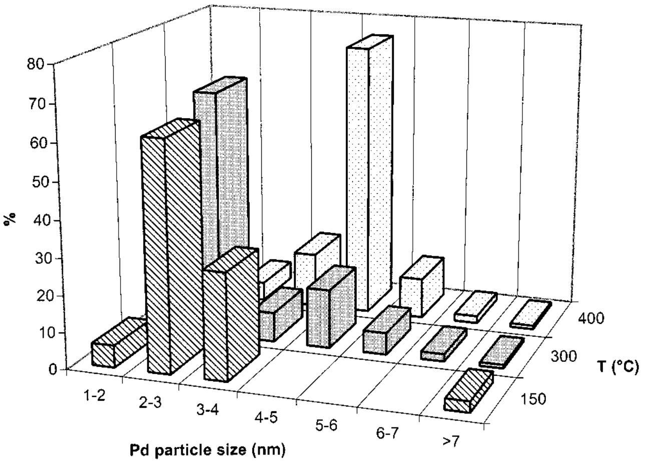
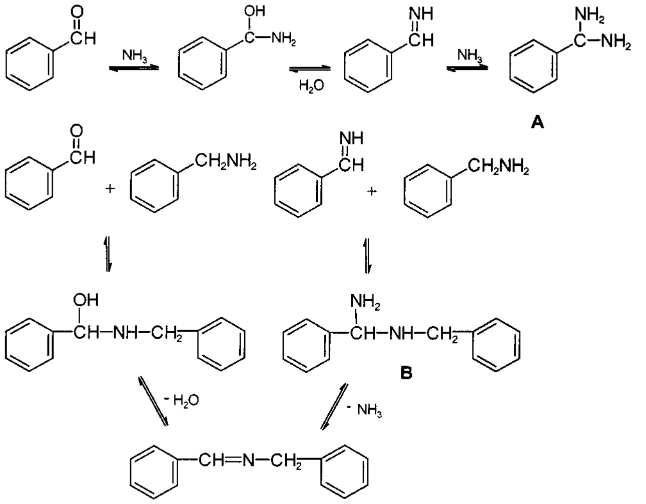


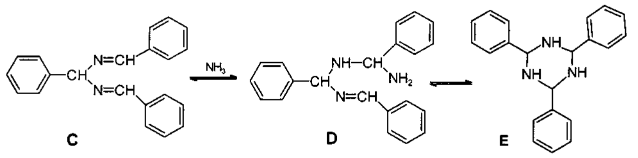
Figure 1. Pd particle size distribution of Pd/SX1GNS versus catalyst reduction temperature

Hydrobenzamide Formation

The homogeneous steps in the reductive amination, the equilibria leading to the imines, are shown in Scheme 2. In the reaction between benzaldehyde and ammonia, the benzylimine formed is highly reactive and readily forms hydrobenzamide (compound C, Scheme 3). The formation of this compound was already reported in 1837 by Laurent.[9] Two mechanisms have been proposed for its formation: (i) trimerization of benzylimine with loss of ammonia,[10] and (ii) condensation of benzaldehyde with either two benzylimine or α-amino benzyl alcohol molecules, followed by dehydration to give hydrobenzamide.[11]



Scheme 2. Equilibria leading to benzylimine and dibenzylimine



Scheme 3. Hydrobenzamide (C) in equilibrium with NH_3, leading to compound D, and possibly E

The formation of hydrobenzamide was studied before by Dobler[12] and Ogata et al.[11] The latter authors monitored the reaction with UV spectroscopy. In the present study we used ^1H NMR to follow this reaction, in an attempt to better identify the products and intermediates formed. A typical ^1H NMR spectrum is shown in Figure 2. We monitored the disappearance of benzaldehyde and the formation of hydrobenzamide. Hydrobenzamide was present in two of the three possible isomers (*ZZ*), (*EE*), and (*ZE*). It crystallizes from more concentrated mixtures of benzaldehyde and ammonia in methanol as white crystals with a sharp melting point of 101 °C, which suggests that these crystals consist of just one isomer.

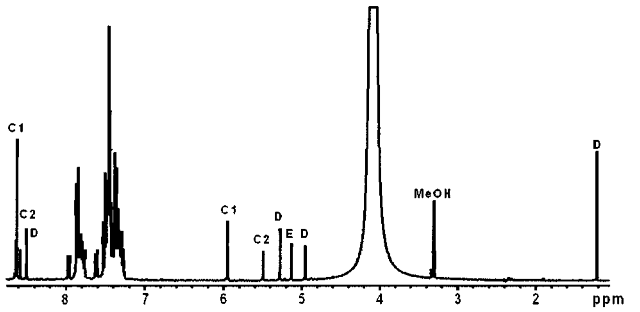


Figure 2. ^1H NMR spectrum of a mixture of benzaldehyde and NH_3 in $[D_4]MeOH$. C1 and C2 indicate resonances of the different isomers of hydrobenzamide (C, Scheme 3); D and E mark the resonances of compound D and E (Scheme 3), respectively

At molar ratios NH_3/benzaldehyde greater than 1, and upon addition of NH_3 to hydrobenzamide, additional peaks at δ = 8.4, 5.3, 4.9, and 1.2 appear in the ^1H NMR spectrum, which indicate the formation of compound D (Scheme 3). A peak at δ = 5.1 appeared at the same time,

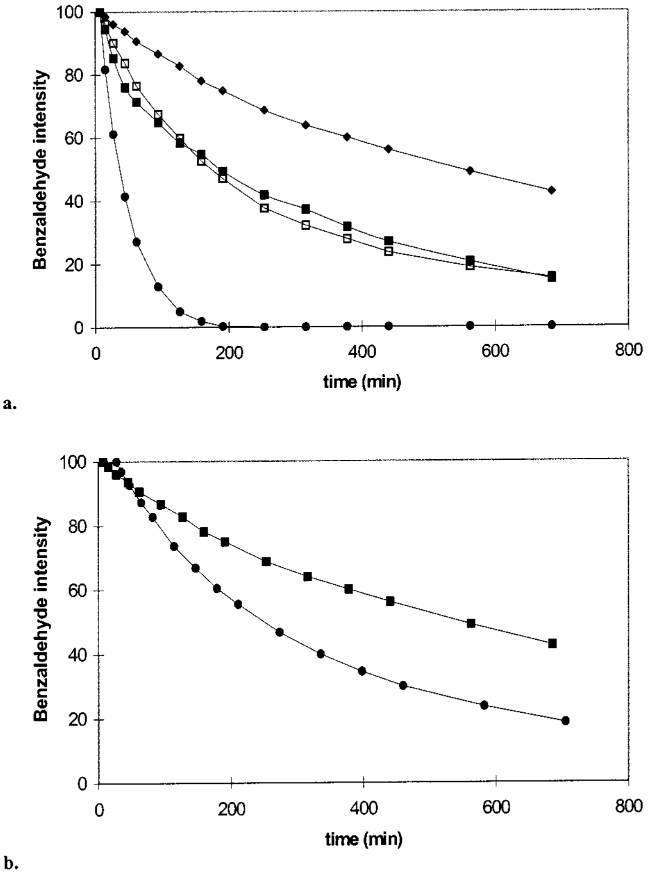


Figure 3. Relative intensity of benzaldehyde peak (δ = 9.9) vs. time during the reaction with ammonia to hydrobenzamide in [D_4]MeOH at (a) 25 °C and different benzaldehyde/NH_3/D_2O ratios: (◆) 1:1:0; (■) 1:2:0; (□) 1:2:1.6; (•) 1:10:0; and (b) benzaldehyde/NH_3 = 1:1 and different temperatures: (■) 25 °C and (•) 40 °C

possibly due to the formation of the benzylimine cyclotrimer (compound E, Scheme 3).

The formation of hydrobenzamide was followed, over time, with ^1H NMR. In Figure 3a the relative intensity of the aldehyde peak (δ = 9.9) is shown, during reactions with different ratios of benzaldehyde to ammonia. The only intermediate observed is possibly α-amino benzyl alcohol, as suggested by a small peak at δ = 5.5 (< 15% of the initial benzaldehyde intensity). The system was checked for the formation of benzaldehyde dimethyl acetal by using CH_3OD as solvent. No peaks corresponding to the acetal-CH_3 shifts were observed.

As expected from earlier reports,[11,12] the reaction of benzaldehyde with NH_3 shows second order kinetics (Table 2). The second order rate constants k_2, displayed in Table 2, were determined by fitting the data with the following equation:

$v = k_2[NH_3][PhCHO]$
with $[NH_3] = [NH_3]_{t=0} - {}^2/_3([PhCHO]_{t=0} - [PhCHO])$

Addition of water had no effect on the reaction rate (see Figure 3a). Acid, in the form of NH_4NO_3, accelerates the hydrobenzamide formation considerably (Table 2), which suggests that the acid catalyzed dehydration[13] of the aminocarbinol is the rate-determining step. Due to the equilibrium, the concentration of α-amino benzyl alcohol depends on the starting concentrations of NH_3 and benzaldehyde, which explains the observed second order kinetics.

Table 2. Second order rate constants for conversion of benzaldehyde at different ammonia to benzaldehyde ratios (MeOH solution)

$[NH_3]$ (M)	[benzaldehyde] (M)	additive	T [°C]	k_2 [10^{-4} L mol^{-1}s^{-1}]
0.33	0.33	–	25	0.8
0.39	0.37	0.31 M NH_4NO_3	25	16.3
0.33	0.33	–	40	2.7
0.67	0.33	–	25	0.9
0.67	0.33	0.53 M D_2O	25	1.0
3.33	0.33	–	25	1.2

Figure 3b shows the effect of temperature on this reaction. Higher temperatures result in a faster reaction. This explains the slightly higher rate constants observed by Ogata et al.,[11] that were measured at 30 °C. The equilibria, however, shift back to benzaldehyde and ammonia[12] at higher temperatures. This was clearly observed at 90 °C by the formation of benzaldehyde starting from a solution containing hydrobenzamide and NH_3.

Dibenzylimine Formation

Upon reaction of benzaldehyde with benzylamine, formation of dibenzylimine is observed. The formation of this relatively stable imine (See Scheme 2) is faster than the reaction between benzaldehyde and ammonia at the same temperature (25 °C, Figure 4); a complete conversion is reached within 1.5 h. In contrast to the formation of hydrobenzamide, a strong effect of the D_2O concentration is observed. Apparently, D_2O shifts the equilibrium to benzaldehyde and benzylamine. From the ^1H NMR intensities, equilibrium constants K_1, K_2, and K were calculated to be 1.5, 27, and 40, respectively. K, K_1, and K_2 are defined as:

$K_1 = [PhCH(OD)(NH_2)]/[PhCHO][PhCH_2NH_2]$
$K_2 = [C_{14}H_{13}N][D_2O]/[PhCH(OD)(NH_2)]$
$K = K_1 \cdot K_2 = [C_{14}H_{13}N][D_2O]/[PhCHO][PhCH_2NH_2]$

Only a small amount of aminocarbinol (δ = 5.5) was observed. Its intensity decreased at the same rate as that for

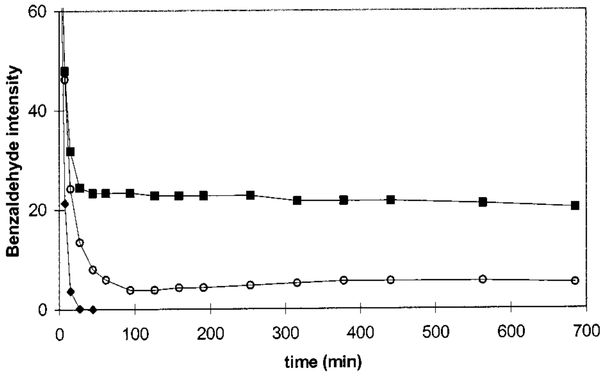


Figure 4. Relative intensity of the benzaldehyde peak (δ = 9.9) vs. time during the reaction with benzylamine to dibenzylimine in [D_4]MeOH (25 °C) at different benzaldehyde/benzylamine/D_2O ratios: (o) 1.1:1:0; (◆) 1:2.1:0; (■) 1:1.1:2.6

benzaldehyde. The molar ratio benzaldehyde/aminocarbinol remained at the constant value of 12.

The reaction of benzylamine with benzylimine (see Scheme 2) could not be studied because benzylimine cannot be isolated. Starting from dibenzylimine and ammonia, no reaction occurred. Even at 90 °C, dibenzylimine is stable.

Reductive Amination

The reductive amination was started after 1 h of equilibration at 90 °C under nitrogen, by applying the H_2 pressure. Under the conditions applied, neither tribenzylamine nor by-products like benzyl alcohol and benzaldehyde dimethyl acetal were observed. Only a minor amount of toluene ($< 1\%$) was formed. The NMR experiments showed that hydrobenzamide is not stable under these conditions, so initially mainly benzaldehyde and ammonia are present.

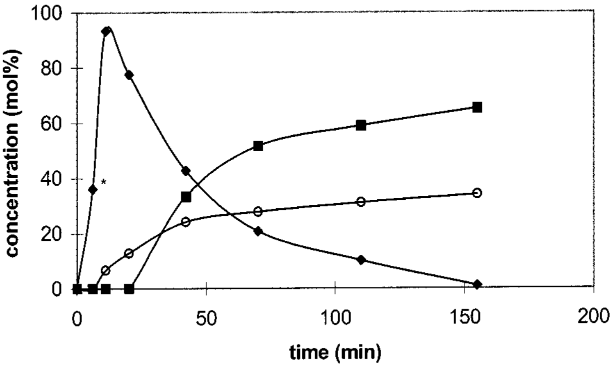


Figure 5. Concentrations of benzylamine (■), dibenzylamine (o), and dibenzylimine (◆) during the reductive amination of benzaldehyde; 80 mL of 2 M NH_3/MeOH, 17 mg Pd/SX1GNS150, 1 g of benzaldehyde, 90 °C and 40 bar H_2. *At this point, the mass balance was < 100%, most probably due to the formation of hydrobenzamide when the sample was cooled down. This compound was not analyzed, but could be precipitated on the catalyst

Figure 5 shows the concentrations of benzylamine, dibenzylimine, and dibenzylamine as a function of time. This figure displays a rapid formation of dibenzylimine. It is only after the complete conversion into dibenzylimine that benzylamine and dibenzylamine are observed. Additionally, Figure 6 shows that the ammonia concentration has a strong effect on the selectivity to the two products. Higher NH_3 concentrations increase the benzylamine production.

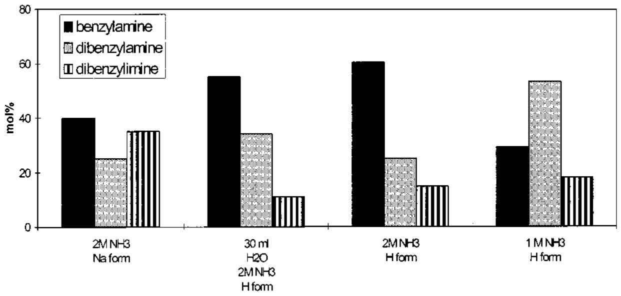


Figure 6. Composition of the reaction mixture after 2 h in the reductive amination of benzaldehyde with ammonia over 5% Pd/SX1GNS150. Effect of the cationic form of the catalyst, of addition of water and of NH_3 concentration; 80 mL solution, 17 mg of Pd/SX1GNS150, 1 g of benzaldehyde, 90 °C and 40 bar H_2

Two possible mechanisms may explain the results obtained: either benzylamine is formed by hydrogenation of benzylimine (or compound A), formed from dibenzylimine via the *gem*-diamine intermediate (compound B, Scheme 2), or it is formed by direct hydrogenolysis of compound B. In both cases, the ammonia concentration will affect the selectivity. The absence of benzylamine in the reaction mixture during the first 20 min (Figure 5) is due to its consumption by reaction with benzaldehyde or benzylimine with the formation of dibenzylimine. The stability of dibenzylimine under these reaction conditions was shown by the NMR experiments.

From Figure 6 we can also conclude that water does not significantly affect the reaction rate and selectivity. Sodium exchange, however, decreased the activity of the catalyst, as is shown by the larger amount of unconverted dibenzylimine. It may be noted that the H-form of the catalyst will mainly occur as carbon$-COO^-NH_4^+$.

Hydrogenation of Dibenzylimine

Since dibenzylamine and benzylamine are formed starting from dibenzylimine, the hydrogenation of this compound in the absence of NH_3 was studied separately. Reaction conditions similar to those used in the reductive amination were applied: 40 bar H_2, 90 °C, 0.9 g dibenzylimine, and 0.017 g catalyst. In this reaction, dibenzylamine was formed with 100% selectivity.

Both the linear relationship between the initial reaction rate and the initial dibenzylimine concentration and the straight line obtained when $\ln(c_{\text{dibenzylimine}})$ was plotted against time, suggest first order kinetics in dibenzylimine. The rate constant was not affected by the impeller speed, but increased linearly with the amount of catalyst. External transport limitation can therefore be ruled out.

The catalyst reduction temperature does not affect the hydrogenation rate (Table 3). However, the sodium exchanged catalyst showed a higher activity. The hydrogenation of dibenzylimine in these experiments is significantly faster than during the reductive amination on the same catalysts. This indicates inhibition effects during the latter process.

Addition of benzylamine does not retard the hydrogenation of dibenzylimine (see Table 3). Apparently, dibenzylimine adsorbs much more strongly on the Pd surface. Upon addition of NH_3, benzylamine is formed (Figure 7). During the reductive amination, a similar effect of ammonia on the selectivity was observed (see Figure 6). This confirms our

Table 3. Initial rate of dibenzylimine hydrogenation with different catalysts and in the presence of benzylamine; 0.9 g of dibenzylimine, 17 mg of catalyst, 80 mL of MeOH, 90 °C, 40 bar H_2

catalyst	additive	r_0 [mol $L^{-1}h^{-1}$]
Pd/SX1GNS150	–	0.46
	1.5 g benzylamine	0.46
Pd/SX1GNS300	–	0.47
Pd/SX1GNS400	–	0.43
NaPd/SX1GNS150	–	0.74

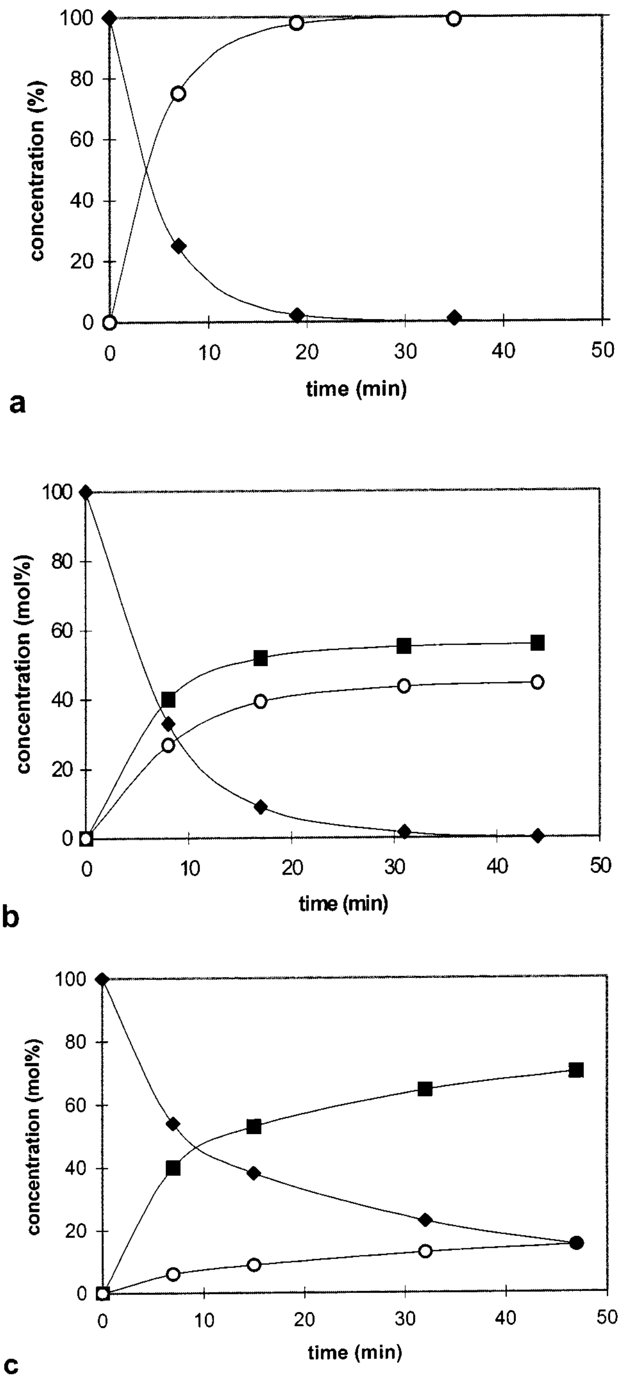


Figure 7. Hydrogenation of dibenzylimine in the presence of (a) 0 M NH_3, (b) 1 M NH_3, and (c) 4 M NH_3; Benzylamine (■), dibenzylamine (o), and dibenzylimine (◆); 80 mL of NH_3/MeOH, 17 mg of Pd/SX1GNS150, 0.9 g of dibenzylimine, 90 °C and 40 bar H_2

suggestion that dibenzylimine forms benzylamine in the presence of ammonia during the reductive amination.

With increasing NH_3 concentration, the overall dibenzylimine conversion slows down, whereas the initial rate remains the same, indicating that inhibition effects play a role.

From these observations, we must conclude that the hydrogenation of dibenzylimine to dibenzylamine competes with the formation of benzylamine, either via hydrogenolysis of compound B, or hydrogenation of benzylimine (see Scheme 2). Because benzylimine is hydrogenated very rapidly, and benzylamine does not inhibit the reaction, we suggest that the adsorption of compounds A and/or B (Scheme 2) on the catalytic surface is stronger than the adsorption of dibenzylimine, which would explain the inhibition effects observed during hydrogenation of dibenzylimine in the presence of NH_3.

Catalyst Acidity and Selectivity

Figure 8 shows the concentrations of dibenzylimine, benzylamine, and dibenzylamine obtained with the different Pd/C catalysts after 2 h of reductive amination. Comparison of Figure 5 and 8 suggests that the difference in product distributions have to be ascribed to a difference in activity, rather than to a difference in selectivity.

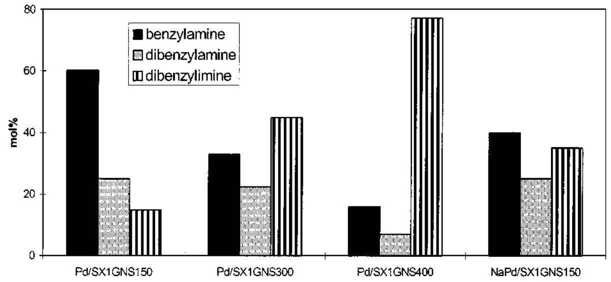


Figure 8. Composition of the reaction mixture after 2 h in the reductive amination of benzaldehyde with ammonia over 5% Pd/C catalysts, reduced at different temperatures; 80 mL of 2 M NH_3/MeOH, 17 mg of catalyst, 1 g of benzaldehyde, 90 °C and 40 bar H_2

First, it must be noted that the available Pd surface decreases with increasing reduction temperature. However, the activity of the differently reduced catalysts in the hydrogenation of dibenzylimine was approximately the same (Table 3).

The number of acidic groups on the carbon surface decreases with increasing reduction temperature during the catalyst preparation. This effect of the acidic surface sites is shown by comparing the H- and Na-form, and is remarkable, considering the small amount of H^+ (eq NH_4^+) present in the system. H^+ is only present on the catalytic surface, leading to locally high H^+ concentrations and a large effect on the catalytic performance in the reductive amination.

As shown by NMR (see above), the establishment of the homogeneous equilibria is acid catalyzed. Probably, this also plays an important role in the reductive amination. Furthermore, the local concentrations of A and B near the acidic sites at the carbon surface may be relatively low and, consequently, the inhibiting effect of these species might decrease upon increasing the amount of acidic sites at the catalyst surface.

The performance of the Na^+ exchanged catalyst, which is the most hydrophilic, but least acidic one, is in between the two most acidic catalysts. The hydrogenating activity of NaPd/SX1GNS150 is higher than the activity of Pd/SX1GNS150 (Table 3), but any inhibition will be more severe, due to the lower acidity. The importance of the local acidity on the catalyst is clear from the fact that addition of 50 mg SX1GNS to a reaction with 17 mg NaSX1GNS150 did not influence the activity or selectivity.

Conclusions

In the reductive amination of benzaldehyde on Pd/C catalysts, the two main products both result from dibenzylimine. Benzylamine is formed by hydrogenation of benzylimine, which is formed by transimination of dibenzylimine with ammonia. The *gem*-diamine intermediate adsorbs strongly on the catalyst, inhibiting the hydrogenation of dibenzylimine. Acidic supports catalyze the establishment of the equilibria involved, and possibly reduce the concentration of the inhibiting intermediate, which results in higher hydrogenation rates.

Experimental Section

Materials: Benzaldehyde was obtained from Fluka Chemie AG (Buchs, Switzerland). Benzylamine, dibenzylamine, and $Pd(NH_3)_4Cl_2 \cdot H_2O$ were purchased from Aldrich Chemical Comp., Inc. (Milwaukee, USA). D_2O and deuterated methanol (CD_3OD), were obtained from the Cambridge Isotope Laboratories (Andover, USA) and CH_3OD and $(NH_4)S_2O_8$ from Merck KGaA (Darmstadt, Germany). The steam activated, peat based activated carbon SX1G was a gift from Norit NV (Amersfoort, The Netherlands).

^{1}H- and ^{13}C NMR Experiments: To study the equilibria, ^{1}H NMR experiments were performed on a Varian Unity-Inova 300 spectrometer. [D$_4$]Methanol was used as solvent. Kinetic experiments were performed by following the ^{1}H resonance of benzaldehyde at δ = 9.9 as a function of time. ^{1}H NMR spectra were recorded at regular time intervals, during 12 h.

Carbon Preparation and Characterization: SX1G (10 g) was added to 175 mL of a saturated solution of $(NH_4)_2S_2O_8$ in 1 M aqueous H_2SO_4. After 22 h of stirring at room temperature, the carbon was filtered off, washed until the filtrate was free of sulfate (as tested with $BaCl_2$), and dried as described above. The carbon treated in this way is denoted as SX1GNS.

The amount of acid sites on the carbon surface was determined by selective neutralization with NaOH, according to the method of Boehm.[14] To 100 mg of carbon, 10 mL of 0.05 M NaOH was added. After shaking the suspension for four days, the carbon was centrifuged, washed, and filtered over a 0.45 μm filter (Chromofil) and then titrated with 0.05 M HCl.

An indication of the amount of carboxylic acid sites was obtained by infrared spectroscopy. Infrared spectra were recorded with a Perkin−Elmer spectrum 1000 FT-IR spectrometer. KBr pellets were used, containing 2 mg of carbon in 250 mg of KBr. The spectra were obtained by co-adding 20 spectra with a resolution of 4 cm^{-1}. The original spectra were corrected for a curved baseline.

Catalyst Preparation and Characterization: 5 wt.-% Pd/C catalysts were prepared by incipient wetness impregnation of 0.95 g SX1GNS with 127 mg of $Pd(NH_3)_4Cl_2$ in 2 mL of water. After drying at 120 °C, the catalyst was reduced in a 10% H_2/N_2 flow (2 h) at different temperatures, and passivated at room temperature with a slowly increasing O_2 concentration. A Pd catalyst based on SX1GNS and reduced at 150 °C is denoted as Pd/SX1GNS150. A sodium exchanged catalyst was prepared from Pd/SX1GNS150 by exchange of the carboxylic acid protons with 0.05 M NaOH. This catalyst is coded NaPd/SX1GNS150.

The metal loadings and impurities in and on the support were measured using X-ray fluorescence spectroscopy, XRF (Philips PW1480). The particle diameter and the dispersion of Pd were studied with transmission electron spectroscopy (TEM) using a Philips CM 30 T electron microscope, combined with Energy Dispersive analysis of X-rays (EDX).

Reductive Amination: Methanol was saturated with NH_3. Of the resulting 7 M solution 23 mL was introduced into a Parr 4842 autoclave, made of Hastelloy C276. Methanol (57 mL), the Pd/C catalyst (0.017 g), and benzaldehyde (1 g) were added. The reaction mixture was heated to the desired temperature under a N_2 atmosphere and, after 1 h, the H_2 pressure was applied. Unless otherwise stated, these experiments were performed at 90 °C and 40 bar H_2.

The hydrogenation of dibenzylimine was performed in the same autoclave and under similar conditions. Dibenzylimine (0.9 g) was prepared by mixing of equimolar amounts of benzylamine and benzaldehyde. Full conversion into dibenzylimine was obtained. Samples taken during the reaction were analyzed with a Varian Star 3400 gas chromatograph (CP Sil-5 CB column), applying a temperature gradient from 50 to 300 °C.

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