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Reductive Debenzylation of Hexabenzylhexaazaisowurtzitane using Multi-walled Carbon Nanotube-supported Palladium Catalysts: an Optimization Approach

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Abstract: This study focuses on the optimization of parameters affecting the reductive debenzylation of hexabenzylhexaazaisowurtzitane using multi-walled carbon nanotube-supported palladium catalysts. Initially the influence of functionalized carbon nanotubes, including OH and COOH groups, were compared with basic multi-walled carbon nanotubes, and their impact on the reaction yield was evaluated. Among these catalyst supports, hydroxylated multi-walled carbon nanotubes showed superior efficiency for producing tetraacetyldibenzylhexaazaisowurtzitane from hexabenzylhexaazaisowurtzitane. The effect of catalyst preparation factors on the reaction yield were screened by using a 2^{5-2} fractional factorial design. Parameters, including percent palladium, adsorption time, pH and adsorption temperature, were optimized by applying a central composite design. The optimum values of these factors were: 12.97% Pd, adsorption time 1.81 h, pH 9.61 and adsorption temperature 42.78 °C. A value of 76% was obtained for the reaction yield under optimum conditions.

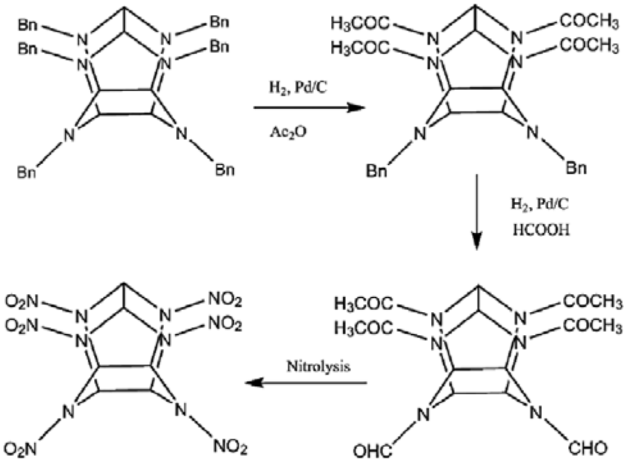
Keywords: HBIW, palladium catalyst, MWCNTs, CCD

1 Introduction

Nitramines, $R_1R_2N–NO_2$, are an important class of energetic materials. This group includes the two most widely applied energetic materials, 1,3,5,7-tetranitro-

1,3,5,7-tetraazacyclooctane (HMX) and 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX), as well as emerging materials such as 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (CL-20). However, in the recent decades, much attention has been given to investigating the properties of CL-20 and searching for efficient methods for the synthesis of this polycyclic nitramine [1, 2]. It is superior to HMX with respect to density, enthalpy of formation and oxygen balance [3, 4]. In addition, the high detonation velocity and pressure of CL-20 make it a suitable candidate for replacing HMX [5]. In view of its superior performance, CL-20 can be regarded as a high energy material. Propellants or explosives containing CL-20 are expected to have increased performance in terms of specific impulse, burning rate, ballistics, and detonation velocity [6].

All known methods of producing CL-20 are based on the same starting material, hexabenzylhexaazaisowurtzitane (HBIW), which is first reductively acetylated to form tetraacetyldibenzylhexaazaisowurtzitane (TADB) [7, 8]. Direct nitration of HBIW to CL-20 by nitrolysis fails due to the competing nitration of the phenyl rings [9] and thereby necessitates debenzylation by catalytic hydrogenation prior to nitration. The synthesis steps for CL-20 are presented in Scheme 1.



Scheme 1. Scheme for the conversion of HBIW to HNIW.

The first step, conversion of HBIW to TADB, is the major challenge of the CL-20 synthesis. Most of the investigations for TADB production from HBIW were carried out using palladium (5-20%) on activated carbon catalysts [10, 11]. Some attempts were made to optimize the requirement of the Pd catalyst as an economic measure [12-14].

To maximize the active surface of the metal and to obtain better efficiency of the catalyst, palladium is usually supported on porous materials in the form of extremely small particles [15]. The catalyst support plays an important role on both catalytic activity and stability [16]. The specific characteristics of the carbon materials used include: (i) easy recovery of the precious metal, by burning up the support, associated with a low environmental impact, (ii) resistance to acidic or basic media, (iii) the possibility to control the porosity and surface chemistry, up to a certain limit, have made them excellent supports for heterogeneous catalysts. Carbon nanotubes (CNTs) – a new allotrope of carbon – have attracted enormous attention owing to their unique electronic and mechanical properties [17-19]. Catalysts supported by CNTs, due to their nanostructure, are less likely to be deactivated by by-products released during the reaction. According to theoretical predictions, the geometry of the ring structure imparts either a metallic or semi-metallic nature to the carbon nanotubes [20]. This naturally has an effect on the properties of metals loaded onto the support [21]. In the majority of cases, carbon nanomaterials need to be pre-treated in order to introduce functional groups (*e.g.* oxygen-containing surface groups) to the surface, guaranteeing optimal interactions between the relatively inert support and the catalyst precursor [22]. The catalytic activity of Pd supported on carbon nanotubes strongly depends on its physicochemical properties, such as size and dispersion of the loaded Pd, as well as on the porosity and morphology of the support [23]. Hence, controlling the factors which affect these properties have been studied in order to construct suitable catalysts [24, 25]. Banett *et al.* investigated the effects of the operating variables on the catalytic activity of Pd catalysts for the hydrogenation of pent-2-yne [26]. Iwasa and co-workers studied the effects of variables in additive preparation on the selective oxidation of CO with different modified Pd catalysts [27]. Gurrath *et al.* explored the influence of the reduction temperature, origin of support and pretreatment of the carbon surface in order to investigate the possible effects of preparation variables on the catalytic activity of activated-carbon palladium catalysts [28].

Traditionally, the planning of experiments for optimizing the effective factors has been carried out by studying one factor (variable) at a time. The primary assumption of this technique is that factors do not influence each other. However, as is already well known, this statement is not correct in most cases. In order to overcome these problems, the multivariate statistical approach, known as design of experiment (DoE), has been applied to different types of chemical problems. The experimental design is the most suitable method for identifying the effects of individual and interaction factors, simultaneously detecting the optimum setting of every factor and reducing the expended time and cost [29]. Over the past decades, some researchers have applied the experimental design methodology for controlling different factors affecting heterogeneous catalytic reactions. Cukic *et al*. applied D-optimal design, as the well-known DoE approach, for evaluation of the influence of preparation variables on the performance of a Pd/Al_2O_3 catalyst for the hydrogenation of buta-1,3-diene [30]. A fractional factorial design, as another DoE approach, was applied to investigate the influence of 7 preparation factors on the hydrogenolysis of aryl halides by palladium/carbon catalysts [31]. Blondet *et al*. employed Pd supported on chitosan hollow fiber for the hydrogenation of nitrotoluene [32]. The DoE technique was carried out to test the impact of several parameters on the performance of the catalyst.

The aim of the present study was to employ multi-walled carbon nanotubes (MWCNTs) as a support for a Pd catalyst for the reductive debenzylation of hexabenzylhexaazaisowurtzitane, the most difficult step in CL-20 synthesis. In this regard, experimental design approaches have been applied to optimize the catalyst preparation factors such as percent Pd, pH, adsorption time, precipitation temperature and adsorption temperature, and their effect on the yield in the conversion of HBIW to TADB.

2 Material and Methods

2.1 Reagents

HBIW as a precursor material for CL-20 was synthesized as proposed in Ref. [7] and primarily washed with ethanol and then recrystallized from ethyl acetate. Purified HBIW was characterized by its melting point and TLC. Merck grades of DMF, acetic anhydride and phenyl bromide were used as a solvent, acetylating agent and co-catalyst respectively. $PdCl_2$ was purchased from a local source. Multi-walled carbon nanotubes and sodium carbonate, which were used as the catalyst support and basic agent respectively, were both Merck grade. Deionized water was used throughout the study. The synthesized TADB samples were characterized by melting point (Electro thermal 9100 apparatus), thin layer chromatography (TLC) and IR spectroscopy (Shimadzu FT-IR-8400 spectrophotometer). ^{1}H NMR, and ^{13}C NMR Spectroscopy were recorded on a Bruker FT-500 MHz and FT-200 MHz instruments respectively (Brucker Biosciences, USA). Elemental CHN analysis were carried out by Perkin-Elmer 2400 Elemental analyzer.

2.2 Catalyst preparation

Palladium catalysts were prepared by the adsorption-precipitation method using $PdCl_2$ as the precursor with a nominal palladium loading of 5 to 15 wt.%.

A solution was prepared by dissolving $PdCl_2$ (0.074 g to prepare 12.97% Pd catalyst) in concentrated HCl (37%, 5 mL), and this solution was then diluted with deionized water to 100 mL, in order to generate H_2PdCl_4. Thereafter, MWCNTs (0.3 g) was added to this solution with magnetic stirring for 1 to 5 h to adsorb the Pd onto the MWCNTs support. It should be mentioned that the solution vessel was held in a water bath to maintain the adsorption temperature between the DoE-specified temperatures of 25 and 80 °C. Subsequently, at the precipitation step, sodium carbonate solution (Na_2CO_3 20%) was added dropwise to the solution until the solution pH was between 8 and 11, according to the planned experiments. The solution was held at 40 °C overnight. The catalyst was then filtered off on a sintered-glass funnel and rinsed several times with water. Finally, the catalyst was oven dried at 110 °C for 2 h.

2.3 Reductive debenzylation of HBIW

The catalytic debenzylation of HBIW was carried out in a homemade stainless steel reactor (working capacity 2 L) equipped with a mechanical stirrer, temperature probe, heating jacket and an inlet for gaseous hydrogen. A schematic representation of the experimental setup is shown in Figure 1.

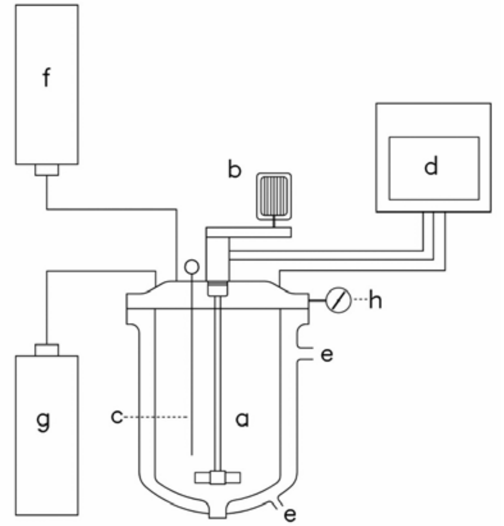


Figure 1. Schematic representation of the experimental set up. a: impeller; b: motor; c: thermocouple; d: temperature and agitation speed control panel; e: oil circulation; f: hydrogen cyclinder; g: nitrogen cylinder; h: pressure gauge.

Each experiment was carried out by mixing HBIW (10 g) in dimethylformamide (DMF, 100 mL) with freshly synthesised palladium catalyst (0.5 g). As pointed out by Koskin *et al.* [33], bromobenzene (0.45 mL), a source of hydrogen bromide, was added to the reaction mixture as a co-catalyst. The hydrogenolysis of the C-N bond can be accelerated by the presence of HBr. Acetic anhydride (Ac_2O, 15 mL), the acetylating agent, was then added to the mixture. During the reaction the hydrogen pressure and reaction temperature were kept at values of 4 bar and 40 °C, respectively. The hydrogenation was performed over a 4 h period. At the end of an experiment, the catalyst and the product (TADB) were filtered off (sinter porosity 4) and rinsed with acetone. The mixture of TADB and MWCNT was dried in an oven and the TADB was then extracted with hot acetic acid (MWCNT was filtered off). The TADB was precipitated as a white solid after adding methanol (acetic acid : methanol 2:5 (solvent/antisolvent method)) at 0 °C. The precipitate was washed with acetone. All of the products reported in Tables 2 and 5 were purified by column chromatography eluting with EtOAc/n-hexane (1:1). Melting point (318-321 °C). IR (cm^{-1}): 3426, 3028, 2931, 2866, 1685, 1663, 1448, 1403, 1308, 1117, 1076, 987, 695. ^1H NMR (DMSO-d_6) δ ppm 1.75-2.15 (m, 12H, Me), 3.9-4.17 (d, 4H, CH_2), 5.29-5.55 (m (br), 4H, $CH_{3,5,9,11}$), 6.21-6.71 (m, 2H, $CH_{1,7}$), 7.3-79 (m (br). ph, 10H). ^{13}C NMR (DMSO-d_6 , CH_3COOH was added as a co-solvent) δ ppm 22.7 (CH_3), 58.19 (CH_2), 72.77(CH, $C_{3,5,9,11}$)73.41 (CH, $C_{1,7}$). 130.02-132.2(ph, $C_{2\text{-}6}$), 139.94 (ph, C_1), 172.6 (CO). Elemental Analysis calculated for TADB (%): C, 65.10; H, 6.24; N, 16.27; O, 12.39, found (%): C, 64.83, H, 6.21, N, 16.31.

3 Calculation

One of the most used multivariate tools is the two-level factorial design (full or fractional) [34-36]. It is used to check the preliminary significance of the variables in the system under study, to screen them out from the non-significant variables. In this approach, the main effects of the variables and their interactions are estimated. This is one of the great advantages of multivariate optimization compared to univariate optimization. Another advantage is that the number of experiments is considerably reduced, particularly in cases with many factors.

In some cases, the experimental domain of a real chemistry problem, may contain maxima, minima or saddle points. Therefore, it is necessary to add some extra terms in order to have an adequate description. In order to estimate these terms the experimental design has to ensure that all factors are carried out at a minimum of three levels [37]. Response surface methodology, which was introduced by Box and Wilson, is a sequence of experiments that can be used for obtaining the optimal response. Central composite design (CCD) is the most common class of response surface methodology, and is used for fitting second order models [38]. The optimum values of the factors can be determined with a high degree of reliability using CCD [34-36]. Central composite designs are a natural extension of two-level, full or fractional factorial designs [39]. They consist of N experiments distributed as following [40]:

(1) Factorial points; each factor at these points has a coded value of +1 and −1. They can be used for the estimation of the main and two-factor interactions. Actually, this part is a two-level full or fractional factorial design with 2^{k-m} data points, where k stands for the number of factors and m is an integer defining the fraction of the corresponding full factorial design.

(2) Star (axial) points; each point in this part is obtained when one factor has a coordinate of $+\alpha$ or $-\alpha$, while all other factors have their center values. The number of experiments for this part is equal to $2k$.

(3) Center points; at these point, all factors have their center values. These experiments are used for the estimation of the pure experimental error, and also for the quadratic terms of the model.

The experimenter has to use an appropriate value for α, and also the number of center points based on characteristics that they desire for the design. When $a = \sqrt{k}$ the points are spread on a (hyper) spherical surface. Rotatability and orthogonality are two desirable characteristics of a design. Rotatability implies that confidence in the predictions depends only on the distance from the center point. However, it does not depend on the number of the center points. It can be obtained by Equation 1.

$$a = \sqrt{k} \qquad N_f\text{: number of factorial points} \tag{1}$$

Orthogonality implies that all terms of the model are independent of each other. The conditions of orthogonality can be obtained by Equation 2.

$$a = \sqrt{\frac{\sqrt{N' N_f} - N_f}{2}} \qquad N\text{: total number of experiments} \tag{2}$$

As can be seen, the orthogonality depends on the number of replications of the center points.

Design-Expert 7 software (State Ease Inc., Minneapolis, MN. USA) was used to produce the experimental design and to perform all statistical analyses. A fractional factorial design was employed to screen the behaviour of each variable involved in the preparation of the catalyst. Five factors, namely, Pd percent (A), adsorption time (B), pH (C), precipitation temperature (D), and adsorption temperature (E), were evaluated using a fractional factorial design. Subsequently, a CCD response surface design was employed to locate the optimum conditions of the selected variables. A central composite design was chosen due to its pervasive use and versatility [41].

4 Results and Discussion

4.1 Selection of multi-walled carbon nanotubes as support

As an initial stage of the investigation, three types of MWCNTs were tested on the basis of the yield of the reaction. These nanotubes were used as the support for the preparation of the Pd catalysts according to the method described above. Basic multi-walled carbon nanotubes (MWCNTs), hydroxylated multi-walled carbon nanotubes (MWCNTs−OH), and carboxylated multi-walled carbon nanotubes (MWCNTs−COOH) were studied in order to investigate the influence of functional groups on the efficiency of the catalyst. Of these catalysts, MWCNTs−OH showed the highest efficiency, and was therefore selected as the support for the Pd catalyst. As can be seen from Figure 2, the highest yield of TADB was produced using MWCNTs−OH.

Figure 2. Effect of various MWCNTs on the reaction efficiency.

Each reaction was replicated three times. As the surface of the basic MWCNTs is mostly covered with inert C−H bonds, the corresponding interaction between the supported metal and the MWCNT surface is very weak [42]. Therefore, as indicated by the results, the non-functionalized MWCNT shows the lowest efficiency. The presence of oxygen containing functional groups, like carboxyl and hydroxyl, anchors the interaction between the support and the Pd particles. The higher catalytic activity of MWCNTs−OH, in comparison with MWCNTs−COOH and MWCNTs, could be due in part to the smaller particle size and the more finely dispersed Pd particles on the surface of the support.

4.2 Screening of the effective variables using a fractional factorial design

Fractional factorial designs are arguably the most widely used designs in experimental investigations and are used mainly for identifying the important factors. Such designs are good alternatives to a full factorial design, especially in the initial stages of a project, and are considered as a carefully prescribed and representative subset of a full factorial design. In fractional factorial designs, the number of experiments is reduced by a number m according to a 2^{k-m} design.

Based on preliminary studies, five factors including palladium percent (A), adsorption times (B), pH (C), precipitation temperature (D), and adsorption temperature (E), were considered. A full factorial design would have included $2^5 = 32$ experiments. To reduce the number of experiments, a quarter-fractional factorial design was chosen. Table 1 shows the main factors, notation and their levels.

Table 1. Experimental range and levels of the variables in the factorial design

Variables	Levels	
	–1	1
A : Palladium, [%]	5	15
B: Adsorption time, [h]	1	5
C: pH	8	11
D: Precipitation temperature, [°C]	25	80
E: Adsorption temperature, [°C]	25	80

The design was performed in eight experiments. The design matrix, together with the corresponding responses, the reaction yields, is listed in Table 2.

Table 2. Design matrix and the responses for the fractional factorial design

Run order	A	B	C	D	E	Reaction yield*
1	–1	–1	1	1	–1	47
2	1	–1	1	–1	1	50
3	1	1	1	1	1	54
4	1	1	–1	1	–1	64
5	–1	1	–1	–1	1	55
6	1	–1	–1	–1	–1	62
7	–1	–1	–1	1	1	37
8	–1	1	1	–1	–1	25

*Calculated after column chromatography using EtOAc/n-hexane (1:1).

The ratio between the maximum and minimum values of the responses is a crude estimate of the testing requirement for data transformation. A threshold value of 3 is usually chosen for this purpose. In accord with this estimate, and also the Box-Cox plot recommendation, there was no need to transform the responses. So, the raw data were used for the evaluation of the factors. The significance of the effects was checked by analysis of the variances (ANOVA) and a normal probability plot. In a normal probability plot, the negligible effects fall on a straight line, whereas the significant effects would be located off the line. The normal plot and the ANOVA table for the fractional factorial design are shown in Figure 3 and Table 3, respectively.

Table 3. Analysis of Variance table for the fractional factorial design

Source	S.S [a]	d.f [b]	M.S [c]	F-Value	p-value	
Model	1166.0	4	291.5	64.8	0.003	Sig.[d]
A	544.5	1	544.5	121.0	0.002	
C	220.5	1	220.5	49.0	0.006	
BC	180.5	1	180.5	40.1	0.008	
BE	220.5	1	220.5	49.0	0.006	
Residual	13.5	3	4.5			
Cor total	1179.5	7				

[a] sum of squares, [b] degrees of freedom, [c] mean square, [d] significant

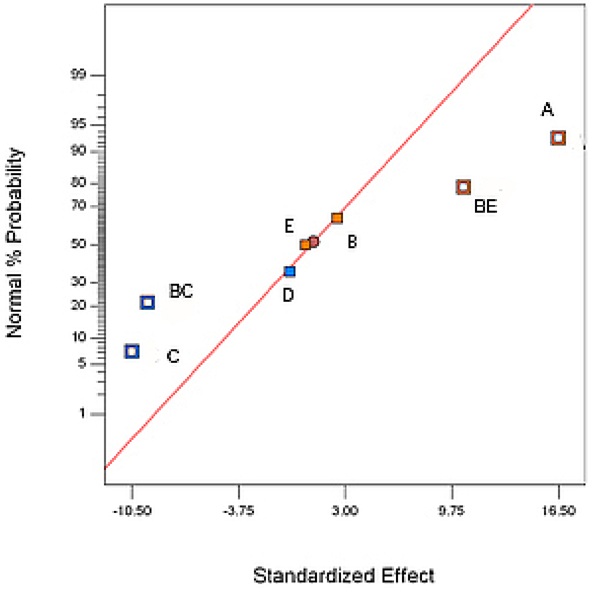


Figure 3. Normal probability plot of effects for the fractional factorial design (A: Pd%, B: Adsoption time (h), C: pH, E: Adsorption temperature (°C), BC: interaction effect between B and C, BE: interaction effect between B and E.

The factors and the interaction effects that show p-values less than 0.05 (P = 95%) in ANOVA are the most significant factors. It can be seen that two main effects, A and C, and also two two-factor interaction effects, BC and BE, are the most significant factors affecting the catalytic efficiency of the Pd−MWCNTs−OH catalyst.

A positive value for the estimated effect would indicate an increase in the reaction yield if the variable were increased to its higher level. A negative value indicates that a better reaction yield would be obtained at lower levels of the variables. Inspection of the ANOVA table and the normal plot shows that the greatest effect is due to the percent palladium, with a positive effect. An increase in BE would also increase the response. By contrast, the response is decreased by increasing the pH and the BC interaction. In addition, the effect of the precipitation temperature was not significant. Therefore, four factors, A, B, C, and E, were used in the next step for developing an accurate model, using CCD.

4.3 Response surface methodology

In this study a small-CCD, with a = 1.68, was used for optimization of the effective parameters. A small-CCD is the minimal-point design needed to estimate the terms in the second order model. Tables 4 and 5 show the level of the factors and the design matrix for the CCD, respectively.

Table 4. Factors and their levels for the central composite design

Variables	Levels				
	–1.68	–1	0	1	1.68
A : Pd, [%]	5	7.03	10	12.97	15
B: Adsorption time, [h]	1	1.81	3	4.19	5
C: pH	8	9	10.5	12	13
E: Adsorption temperature, [°C]	25	36.15	52.5	68.85	80

Table 5. Design matrix and the responses for the central composite design

Run	A	B	C	E	Response*
1	7.03	4.19	9	68.85	23
2	10	3	10.5	25	61
3	10	3	10.5	52.5	62
4	12.97	4.19	12	36.15	15
5	10	3	8	52.5	58
6	10	3	10.5	52.5	59
7	10	3	10.5	52.5	60
8	10	3	10.5	80	17
9	7.03	1.81	9	36.15	46
10	15	3	10.5	52.5	71
11	10	3	13	52.5	23
12	12.97	1.81	12	68.85	46
13	5	3	10.5	52.5	27
14	7.03	4.19	12	68.85	7
15	10	5	10.5	52.5	53
16	10	3	10.5	52.5	61
17	12.97	1.81	9	68.85	60
18	7.03	1.81	12	36.15	55
19	12.97	4.19	9	36.15	60
20	10	1	10.5	52.5	60

*Calculated after column chromatography using EtOAc/n-hexane (1:1).

Fitting of the data to various models (linear, quadratic and cubic) and their subsequent analysis of variance shows that the reaction is most properly described with a quadratic polynomial model. The ANOVA table for the model is shown in Table 6.

Table 6. Analysis of variances (ANOVA) table for the quadratic response surface model

Source	S.S.	d.f.	M.S.	F-Value	p-value	
Model	7269.9	13	559	114.7	< 0.0001	significant
A	968	1	968	198.6	< 0.0001	
B	24.5	1	24.5	5.03	0.0662	
C	1141	1	1141	234.2	< 0.0001	
E	968	1	968	198.6	< 0.0001	
AB	216	1	216	44.4	0.0006	
AC	338	1	338	69.3	0.0002	
AE	377	1	377	77.4	0.0001	
BC	392	1	392	80.4	0.0001	
BE	155	1	155	31.7	0.0013	
A^2	274	1	274	56.2	0.0003	
B^2	42.8	1	42.8	8.7	0.0252	
C^2	778	1	778	159.5	< 0.0001	
E^2	893	1	893	183.3	< 0.0001	
Residual	29.2	6	4.9			
Lack of fit	24.2	3	8.1	4.8	0.1137	not significant
Pure error	5	3	1.7			
Corrected Total	7299	19				

The F-value of 114.7 implies that the model is significant. A magnitude of the "p-value" less than 0.05 for a model term indicates that its effect is significant at the 95% confidence interval [43, 44]. The quadratic model was selected based on high values for R^2 and the F-value of the model and low values for the lack of fit and PRESS. The F-value of 4.8 for the lack of fit confirms the validity of the model and implies that the lack of fit is not significant relative to pure experimental error. The model generated consisted of the main effects, two-factor interactions and curvature effects in the coded format, and is shown in Equation 3.

$$\text{Yield}\,\% = 60.83 + 13.08A - 2.08B - 9.14C - 13.08E - 8.08AB - 6.5AC + 10.67AE - 7BC + 6.83BE - 4.39A^2 - 1.73B^2 - 7.39C^2 - 7.92E^2 \quad (3)$$

The statistical values of the model are presented in Table 7.

Table 7. Statistical parameters for the quadratic model in Equation 3

Std. dev.	2.21	R^2	0.996
Mean	46.20	R^2_{adj}	0.987
C.V.%	4.78	R^2_{pred}	0.905
PRESS	694.7	Adeq. precision	35.01

It can be seen from this table that the standard deviation of 2.21 and the coefficient of variation (C.V.) of 4.78 are reasonably low and acceptable [45]. The quantity of R^2 (0.996) is loosely interpreted as the proportion of the variability in the data that is explained by the model. The value of the adjusted coefficient of determination (R^2_{adj}) indicates that a high proportion of the variability (98.7%) in the response variable has been attributed to the predictor variables and a small amount of variability (1.3%) in the response variable is due to other uncontrollable factors. Additionally, the predicted R-square ($R^2_{pred} = 0.9048$), which is a measure of the amount of variation in the new data explained by the model, can be applied for the evaluation of the model. The R^2_{pred} and R^2_{adj} values should be within 0.20 of each other, otherwise there may be a problem with either the data or the model. The adequate precision is computed by dividing the difference between the maximum and minimum predicted responses by the average standard deviation of all predicted responses [46]. This statistic is a measure of the signal to noise ratio and a quantity greater than 4 is desirable. For the proposed model, this statistic is 35.01, indicating a good signal to noise ratio. The parity plot between the experimental and the predicted data is shown in Figure 4.

As can be seen, the predicted values match the experimental ones reasonably well, within the ranges of the experimental conditions. This result indicates the applicability and reliability of the equation in representing the reaction over a range of experimental conditions, with a sufficient degree of accuracy.

The 3-D representations of the interaction terms of the model are shown in Plot 1 in order to assess the graphical interpretation of the interaction terms of the model [47].

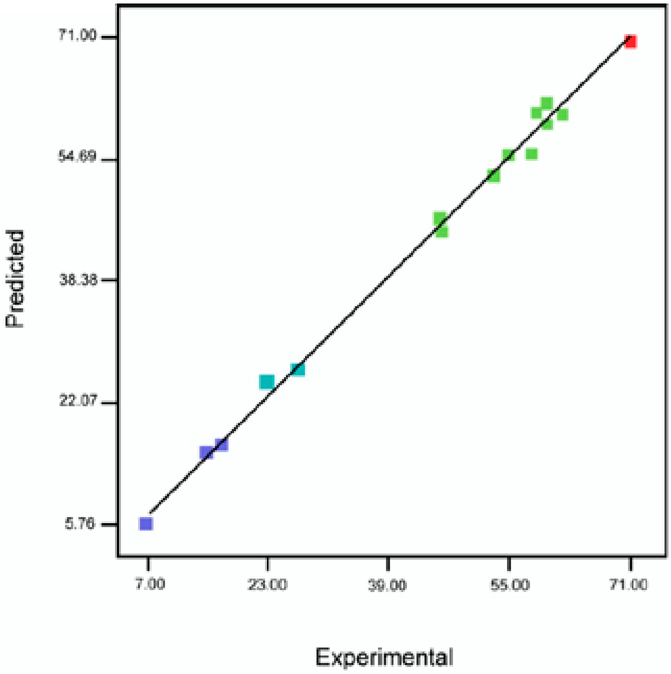
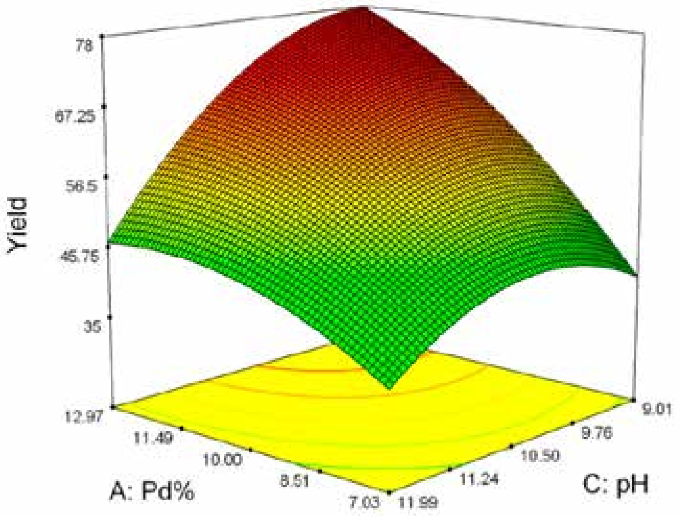


Figure 4. Experimental *vs*. predicted values of the reaction yield.



Plot 1. Three-dimensional (3-D) response surfaces for Pd%-pH.

As can be seen in this plot, the reaction yield increases considerably with increasing percent palladium. In contrast to the Pd percent, the solution pH represents a negative effect, especially at high values of Pd percent. In addition, low values for the adsorption time and temperature are more favourable. It should be noted that at low values of Pd percent, high values of the adsorption time are more desirable whilst at high values of Pd percent, this trend is reversed. The main objective of response surface methodology is to optimize the effective factors affecting the response. In order to optimize the process, values of the factors were considered in the range of ($\pm\alpha$) and the maximum value was obtained for the yield. According to this procedure, the optimum values of the factors were 12.97% for Pd percent, 1.81 h for the adsorption time, 9.61 for pH and 42.78 °C for the adsorption temperature. Considering that the palladium catalyst is the most expensive component of this reaction, the value of Pd percent was chosen as a compromise between the reaction yield and the price of the catalyst. The optimum and experimental values obtained for the yield were 81% and 76%, respectively. It should be noted that the value of 76% is the mean of three replicate experiments under the optimum conditions.

Considering our research program on the synthesis of HNIW and our experience on the use of other Pd supported catalysts, like Pearlman's catalyst, for the debenzylation of HBIW to TADB, we have obtained the same product (TADB), with the same purity (by the same extraction procedure (section 2.3)). In fact, MWCNTs could help us to enhance the reaction yield with reduced palladium consumption. However, all catalyst samples exhibited a low catalytic activity when recycled for the reductive debenzylation of HBIW to TADB. It is assumed that rapid deactivation of the Pd/MWCNTs in these experiments could be the result of agglomeration of Pd on the surface of the MWCNTs after a single use.

5 Conclusions

One of the challenging projects in the area of catalysis is the development of heterogeneous catalysts.

These types of catalysts have many advantages, such as easy separation from the products, easy recovery and re-usability of the catalysts, and lack of corrosion. In the present study, MWCNTs−OH supported Pd catalyst was used to effect the reductive debenzylation of HBIW. To assess the reactivity of the catalyst, catalyst preparation factors affecting the reaction efficiency were screened and optimized by using fractional factorial and central composite designs. Amongst other factors, percent palladium plays the most significant role. It has a positive effect on the reaction yield. The solution pH shows a negative effect on the reaction yield which might be due to a weak interaction of the support with Pd at higher pH values. The precipitation temperature makes no contribution to the yield. The experimental methodology can also be used for the optimization of factors affecting the debenzylation reaction, such as reaction temperature, hydrogen pressure, reaction time, catalyst to HBIW ratio, and the amount of Ac_2O.

6 References

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