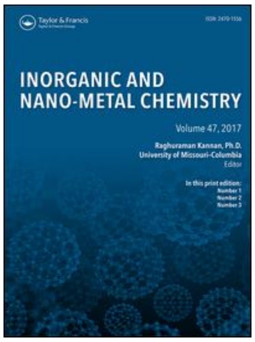

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Increment of activity of $Pd(OH)_2/C$ catalyst in order to improve the yield of high performance 2,4,6,8,10,12-hexanitrohexaazaisowurtzitane (HNIW)

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Abstract

CL-20 [2,4,6,8,10,12-hexanitrohexaazaisowurtzitane (HNIW)] is a well-known high performance explosive. The reductive debenzylation of hexaazaisowurtzitane (HBIW) over supported palladium catalyst produces 2,6,8,12-tetraacetyl-4,10-dibenzyl-2,4,6,8,10,12-hexaazaisowurtzitane (TADB). The effects of precipitation conditions of $Pd(OH)_2$ and the porosity of the activated carbon support on the activity of synthesized $Pd(OH)_2/C$ catalysts in the debenzylation of HBIW are investigated here. The activity of $Pd(OH)_2/C$ catalyst is considerably affected by the porosity of the activated carbon. The surface morphology of the synthesized catalysts is studied by X-ray diffraction (XRD) profile analysis and transmission electronic microscope (TEM). Metal dispersion of $Pd(OH)_2/C$ catalysts is changed by precipitation conditions of $Pd(OH)_2$.

Keywords

Precipitation; Hexanitrohexaazaisowurtzitane; Debenzylation; Heterogeneous catalysis; Palladium catalyst

1. Introduction

Among different nitramines, hexanitrohexaazaisowurtzitane (HNIW) or CL-20 (2, 4, 6, 8, 10, 12 -hexanitro-2, 4, 6, 8, 10, 12 hexaazatetracyclo [5.5.0.0^{3,11}.0^{5,9}] dodecane) contains high detonation performance [1]. Since CL-20 is superior oxidizer/explosive for using in conventional high-energy propellants and explosive formulations, some efforts have been used to develop its behaviors in the other fields, e.g. adsorption on a soil organic matter [2], thermal reactivity [3], fabrication of microcapsule [4] and corystal CL-20 and HMX (cyclotetramethylene-tetranitramine) [5]. Due to importance of CL-20, several methods [6] have been developed that are based on the condensation of glyoxal and benzyl amine (Figure 1). Among the synthesis steps of HNIW (Figure 1), the reductive debenzylation of hexabenzylhexaazaisowurtzitane (HBIW) over supported palladium catalyst is the most important step, which produces 2,6,8,12-tetraacetyl-4,10-dibenzyl-2,4,6,8,10,12-hexaazaisowurtzitane (TADB). Since the palladium catalyst rapidly deactivates in this step, the costs of the production of intermediates and the HNIW are high. However, it is important to increase the activity of catalyst. The activity of the supported catalysts depends on availability of active sites in supported metal catalysts, as metal dispersion, which participates in a desired catalytic reaction. Higher metal dispersion and more metal surface sites produce smaller metal particles, having higher surface to volume ratio, which generally relate to higher activity per mass of metal. The method of preparation of the catalyst and the nature of support can strongly influence the metal dispersion as well as the activity of the supported metal catalysts, which were demonstrated elsewhere [7].

Simonov et al. [7c] have done extensive research on the chemical processes, which occur when H_2PdCl_4 from aqueous solution is adsorbed on the surface of carbon materials. They found that adsorption proceeds through two competitive pathways: reduction to form metallic Pd particles and formation of π-complexes of $PdCl_2$ with C = C fragments of the carbon matrix:

$$\frac{PdCl_2}{C} + 2HCl \overset{2}{\Leftrightarrow} H_2PdCl_4 \overset{1}{\Leftrightarrow} \frac{Pd}{C} + \frac{2Cl^-}{2C^+} + 2HCl \quad (1)$$

They stated that Pd^{2+} (aq) ions are discharged by the “electron gas” of carbon accompanied by adsorption of Cl^- ions. The C^+ is a positively charged “hole” which appears at the carbon surface when Pd^{2+} (aq) is reduced. The Cl^- ions compensate the charge through the formation of an electric double layer on the carbon surface.

Koskin and coworkers [7f] studied the influence of the solvent nature, loadings of the reactants, catalyst and cocatalyst as well as reaction temperature on debenzylation of HBIW. Later they studied the influence of the synthesis methods and the nature of support of the Pd/C catalyst on the debenzylation of HBIW [7g].

The purpose of this work is to investigate the effects of precipitation conditions of $Pd(OH)_2$ including Pd content in catalyst, pH, temperature and time of $Pd(OH)_2$ precipitation and the porosity of the activated carbon support on the activity of catalyst in the reductive debenzylation of HBIW. It will be shown that optimization of these variables can provide higher yield of TADB. Moreover, the TADB yield will be considered as a criterion for assessing the activity of samples of $Pd(OH)_2/C$ catalyst.

2. Experiment

2.1. Pretreatment of activated carbon supports

The commercial activated carbons were supplied by Merck and used to prepare $Pd(OH)_2/C$ catalysts. Activated carbon samples were treated by HCl 20% solution at 80°C for 4 hours. They were treated with acid to remove probable metal impurities from activated carbons.

2.2. Synthesis of $Pd(OH)_2/C$ catalysts

$PdCl_2$ was supplied by Sigma-Aldrich. Na_2CO_3 and HCl were supplied by Merck. They were used without any form of purification. The $Pd(OH)_2/C$ catalyst or unreduced palladium catalyst was prepared via deposition-precipitation method [7a]. Acidic $PdCl_2$ or H_2PdCl_4 solution was used as precursor. To prepare H_2PdCl_4 solution, $PdCl_2$ was dissolved in concentrated HCl (37%), which was diluted with distilled water to the desired concentration. The mole ratio of Pd:Cl was adjusted to 1:10 in the precursor solution. The precursor solution was added to activated carbon, which was stirred with a magnetic stirrer at 30°C for 2 hours. While stirring was continued, the pH of the mixture was slowly increased by addition of Na_2CO_3 (10%) solution. H_2PdCl_4 was hydrolyzed in aqueous solution and converted to $Pd(OH)_2$ on the activated carbon supports. The $Pd(OH)_2/C$ catalyst or unreduced palladium catalyst was washed with distilled water that was filtered through a sintered glass funnel and dried in oven at 50°C for 6 hours. In each run about 2 grams of $Pd(OH)_2/C$ catalyst was synthesized.

2.3. Reductive debenzylation of HBIW

All solvents and reagents except HBIW were supplied by Merck, which were used without any form of purification. HBIW was produced and purified in our laboratory. Debenzylation of HBIW over $Pd(OH)_2/C$ catalyst was carried out according to the method of Wardle and coworkers [8] where their method was used in the related works[7f, 7g, 9]. The highest reported yield for this reaction was about 90% (desired product). To investigate the effects of $Pd(OH)_2$ precipitation conditions and the porosity of carbon support on catalyst activity, all catalytic reactions were performed in the same conditions. For all catalytic runs, the mole ratio of reactants and other conditions except $Pd(OH)_2/C$ catalysts were similar. HBIW (20 g), bromobenzene (0.8 ml) and dry $Pd(OH)_2/C$ catalyst (1.4g) were added to a mixture of DMF (156.5 g) and acetic anhydride (32.5 g) in a 1 liters semi batch stainless steel reactor. Pressure of H_2 gas and reactor temperature was adjusted respectively at 4 bar and 50°C during the reaction. After 5 hours, the reaction was terminated by stopping H_2 and the content of the reactor was drained. The solid was filtered and washed with ethanol. The highest TADB yield was obtained about 73%. After 4 hours from the beginning of the debenzylation reaction, the TADB yield remains approximately constant. The reaction was appeared to no longer progress probably due to deactivation of the active sites and the decreasing of HBIW surface concentration. The unreacted HBIW as substrate and synthesized TADB as desired product were characterized by spectroscopic (using FT-IR NICOLET 800 and H-NMR BRUKER 300 MHZ) and liquid chromatographic analysis (using HPLC Waters 600 with a C-18 column and an acetonitrile/water mixture in a ratio of 60: 40, as eluent). The relative standard deviation of TADB yield was examined by repeating procedure fifth times for $Pd(OH)_2/C$ catalyst samples and was ±3%.

2.4. Catalyst characterization

The palladium content in catalyst and precursor solution were determined by a Perkin Elmer 5300 DV inductively coupled plasma (ICP). To measure the palladium content in catalyst, the catalyst samples were burnt in a furnace under O_2 atmosphere at $900^{\circ}C$. Remaining catalyst sample was dissolved in aqua regia (a 1:3 mixture of nitric acid and hydrochloric acid) and the palladium content in leached solution was measured by ICP. The detection limits of the method was 3 mg/g and the relative standard deviation was lower than 2% (n = 5). The pH of the solutions was measured with a standard pH electrode. The specific surface area and pore volume of the synthesized palladium catalyst were measured by N_2 adsorption at 77 K with a quanta chrome gas sorption instrument. The chemisorption of H_2 over $Pd(OH)_2/C$ catalyst at 303 K was carried out by BEL Japan Inc. The samples were degassed in vacuum at 423 K for 4 hours before measurements. The morphology of the catalyst was studied by Philips CM30 transmission electronic microscope (TEM). Wide-angle X-ray diffraction (XRD) pattern of catalyst was recorded on a Philips PW 1830 with CuK radiation (λ of 0.154178 nm at 40 kV and 30 mA). The XRD scan was performed at ambient temperature with a 2θ range between 10^o and 90^o at a scanning rate of 0.04° (2θ/ sec).

3. Results and Discussion

3.1. Effect of palladium content on catalyst activity

Figure 2 shows the plot of TADB yield versus palladium content in catalyst. The TADB yield for the debenzylation reaction over catalyst with the palladium content of 3 wt% is negligible. The TADB yield is increased significantly by increment of the palladium content to 7 wt%,. There is no further change in the TADB yield by increasing the palladium content of catalyst to more than 13 wt%. When the active component is very expensive (as supported palladium catalyst), the objective is a maximum active surface area per unit weight of the active component. Therefore, active components will be applied to supports at low loadings [10]. The reaction over catalyst with palladium content less than 3 wt% does not proceed to produce

TADB. A probable reason is that HBIW molecules cannot be easily transferred to the active sites of catalyst. Previous studies [7g, 8] have shown that debenzylation of HBIW occur over catalyst with palladium content more than 5 wt%. Increasing the palladium content of catalyst to 7 wt% causes the increment of the active surface of catalyst, which gives higher yield of TADB. The probability of aggregation among palladium particles was increased by increment of the Pd content of catalyst to more than 13 wt%. Despite of the further increment of the palladium content of catalyst, the TADB yield has remained constant and therefore the activity of catalyst was decreased.

3.2. Effect of pH of $Pd(OH)_2$ Precipitate on catalyst activity

The activity of catalyst can be affected by the pH of precipitation [11]. Since all of the synthesis conditions were similar except the pH of $Pd(OH)_2$ precipitate, different acidic to basic pH ranges were examined for $Pd(OH)_2$ precipitate to prepare palladium catalyst. Figure 3 shows the TADB yield for debenzylation reaction over the synthesized palladium catalyst versus the pH of $Pd(OH)_2$ precipitate. Catalyst precipitation conditions are: Pd content in precursor solution/catalyst = 13 wt%, time = 5 hr, temperature = 50°C. As seen in Figure 3, the TADB yield is negligible for the $pH<3.0$ of $Pd(OH)_2$ precipitate. By increasing the pH of $Pd(OH)_2$ precipitate to 9, the TADB yield increased significantly. For the $pH>9.0$ of $Pd(OH)_2$ precipitate, the TADB yield approximately was remained constant. Since a part of Pd^{2+} (aq) ions was remained in the precursor solution for the $pH<3.0$ of $Pd(OH)_2$ precipitate, the palladium content in the catalyst can be decreased. By decreasing the palladium content in catalyst, the TADB yield can be reduced. However, low pH of the $Pd(OH)_2$ precipitate may raise the probability of co-precipitation of $Pd(OH)_2$ and $PdCl_2$. It was reported that the co-precipitation of $PdCl_2$ and

$Pd(OH)_2$ in low pH (<6) can enhance the reaction rate of debenzylation over the unreduced palladium catalyst [12].

3.3. Effect of temperature of $Pd(OH)_2$ precipitate on catalyst activity

Temperature of precipitation can affect the nucleation and growth of crystals, which may influence the metal dispersion in the catalyst as well as the catalyst activity. Therefore, the effect of the temperature of $Pd(OH)_2$ precipitate on the TADB yield was also studied. Figure 4 shows the TADB yield for the debenzylation of HBIW over the synthesized palladium catalyst at several temperatures of $Pd(OH)_2$ precipitate from 30 to 90°C. The results show that the TADB yield was slightly affected by the temperature of $Pd(OH)_2$ precipitate in this temperature range. Hydrolysis rate of Pd^{2+}(aq) ions in precursor is so high that the changes of $Pd(OH)_2$ precipitate temperature do not have major effects on the nucleation and growth of $Pd(OH)_2$ colloids. Then, $Pd(OH)_2$ colloids was deposited on carbon surface under the effects of mass transfer phenomena.

3.4. Effect of time of $Pd(OH)_2$ precipitate on catalyst activity

Palladium catalysts were synthesized at different precipitation times from 1 to 10 hours to determine the appropriate time of $Pd(OH)_2$ precipitate. Figure 5 shows the TADB yield for the debenzylation of HBIW over palladium catalyst versus the time of $Pd(OH)_2$ precipitate. As seen, the TADB yield is relatively low for the time of $Pd(OH)_2$ precipitate less than 1 hour. Meanwhile, the TADB yield is increased with an increment of the time of $Pd(OH)_2$ precipitate until 5 hours. For above 5 hours, the TADB yield is remained nearly constant. For precipitation reactions, hydrodynamic conditions have a major impact on the rates of nucleation as well as agglomeration and the product quality [13]. Higher numbers of $Pd(OH)_2$ particles are precipitated on activated carbon support by increasing the time of $Pd(OH)_2$ precipitate. Increment of palladium content of catalyst can increase the active surface of catalyst, which enhance the TADB yield.

3.5. Effect of the activated carbon porosity on the activity of catalyst

Since the surface functional groups of the activated carbon supports affect the yield of heterogeneous catalytic reactions, the differences in activity for catalysts on supports of different origin should be ascribed to differences in their porous structure [7e]. Therefore, it is important to study the effect of the porosity of the activated carbon supports on activity of the synthesized catalysts. Three types of commercial activated carbon were chosen as catalyst supports, which were used to prepare palladium catalysts. Table 1 shows the characteristics of the prepared catalysts. As seen in Table 1, the BET surface and cumulative micropore surface areas (m^2/g), respectively, for $Pd(OH)_2/C_1$ sample are considerably more than those for the other two catalysts. For three $Pd(OH)_2/C$ samples at 303 K, the amount of chemisorbed hydrogen was approximately equal (Table 1). In other words, the metal dispersion is the same in catalysts. However, in similar conditions, the TADB yield was considerably different for each $Pd(OH)_2/C$ samples. By assuming a similar metal dispersion for the three samples, decreasing TADB yield over $Pd(OH)_2/C_1$ and $Pd(OH)_2/C_3$ with respect to $Pd(OH)_2/C_2$ may attribute to their micropore surface area. Since HBIW is relatively large molecule, it cannot be easily transferred into micropores and a portion of mesopores in the catalyst. Hence, a fraction of the active sites on catalyst surface is not accessible in the catalytic debenzylation of HBIW.

3.6. Electron microscopy imaging and XRD analysis

Activity of the supported catalysts depends largely on metal dispersion. The wide-angle XRD patterns and TEM images were used to explain some effects of the $Pd(OH)_2$ precipitate conditions on the mean size of metal particles in catalyst and the activity of catalysts. Figure 6a and b show the XRD pattern of catalysts, which were prepared without and with the addition of Na_2CO_3 solution into the precursor slurry, respectively. The peaks positioned at $2\theta° = 34.26°$, 42.61°, 55.01°, 59.81° and 72.48° correspond to the lattice planes of the palladium oxide hydrate[14]. Meanwhile, the peaks positioned at $2\theta° = 40.42°$, 46.79°, 68.43° and 82.35° match to the lattice planes of the palladium metal [15]. These results show that Pd metal and $PdO.H_2O$ phases may exist in both catalyst samples. However, the peaks corresponding to the $PdO.H_2O$ and the Pd metal are very weak for the prepared catalyst without and with $Pd(OH)_2$ precipitate, respectively (Figures 6a and b). Thus, Pd^{2+} (aq) ions in acidic precursor solution, without the addition of Na_2CO_3 solution, were mainly deposited on the activated carbon surface in metallic phase[7a, 7c]. However, a main portion of Pd^{2+} (aq) ions was converted into $Pd(OH)_2$ by addition of Na_2CO_3 solution to the precursor slurry. Then, $Pd(OH)_2$ was precipitated on the activated carbon surface.

The evaluated crystallite dimension, that was deduced from Scherrer's equation [16], applied on the $PdO.H_2O$ (101) and Pd (111) diffraction peaks of XRD patterns for the prepared catalyst without and with $Pd(OH)_2$ precipitates, respectively (Figure 6a and b). According to the Scherrer's equation, the average crystallite size for the prepared catalyst without $Pd(OH)_2$ precipitate (>10 nm) is greater than that of with $Pd(OH)_2$ precipitate (<3 nm). Palladium dispersion for the supported Pd/C catalyst increases relatively when the Pd^{2+} (aq) ions are directly deposited on the activated carbon surface in the precursor solutions[7a].

Figure 7 shows the TEM images for both catalysts. The mean size of palladium particles for the prepared catalyst without $Pd(OH)_2$ precipitate (Figure 7a) is obviously larger than that of the prepared catalyst with $Pd(OH)_2$ precipitate (Figure 7b). The TEM images and XRD patterns of catalysts confirm that the mean diameters of palladium crystallites and particles are increased relatively when Pd^{2+} (aq) ions are directly deposited on the activated carbon surface. However, a large portion of Pd^{2+} (aq) ions is hydrolyzed to form $Pd(OH)_2$ with small particle size, which is well-dispersed on the activated carbon surface.

4. Conclusion

In this study, the $Pd(OH)_2/C$ catalyst was prepared using deposition-precipitation method. The palladium content in catalyst should be more than 7 wt% to obtain a considerable yield for the desired product TADB. Optimal values for pH and time of $Pd(OH)_2$ precipitate for the synthesis of palladium catalyst were found to be about 9 and 5 hours, respectively. The results showed that the TADB yield was slightly influenced by the temperature of $Pd(OH)_2$ precipitate in a temperature range of 30 to 90°C. It was also shown that the activity of $Pd(OH)_2/C$ catalyst was considerably affected by the porosity of activated carbon supports. The TEM images and XRD patterns of catalysts showed that the mean diameter of palladium crystallites and particles increased relatively when Pd^{2+} (aq) ions were directly deposited on activated carbon surface. After addition of Na_2CO_3 solution to the precursor solution, small size and well-dispersed palladium were precipitated on the activated carbon surface.

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Table 1. The characteristics of $Pd(OH)_2/C_1$, $Pd(OH)_2/C_2$ and $Pd(OH)_2/C_3$ catalyst

Characteristics of catalyst	**$Pd(OH)_2/C_1$**	**$Pd(OH)_2/C_2$**	**$Pd(OH)_2/C_3$**
The volume of monolayer (cm^3/g)	150	66	34
BET surface area (m^2/g)	630	286	149
Cumulative micropore surface area (m^2/g)	560	111	82
Cumulative wide pore surface area (m^2/g)	70	175	67
Ratio of cumulative micropore surface area to BET surface area	0.89	0.39	0.55
Pd content in catalyst (wt. %)	7.0	7.2	7.1
Chemisorbed hydrogen (cm^3(STP)/g) at 303 K	16.5	17.2	16.9
TADB yield (wt. %)	39.0	64.4	48.5

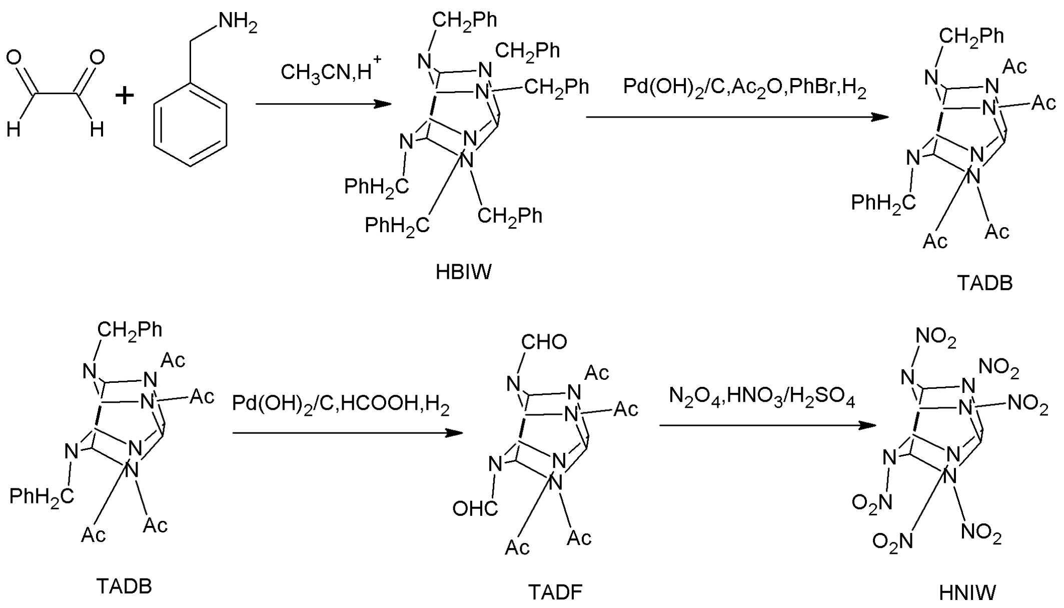


Figure 1. The synthesis process steps of hexanitrohexaazaisowurtzitane

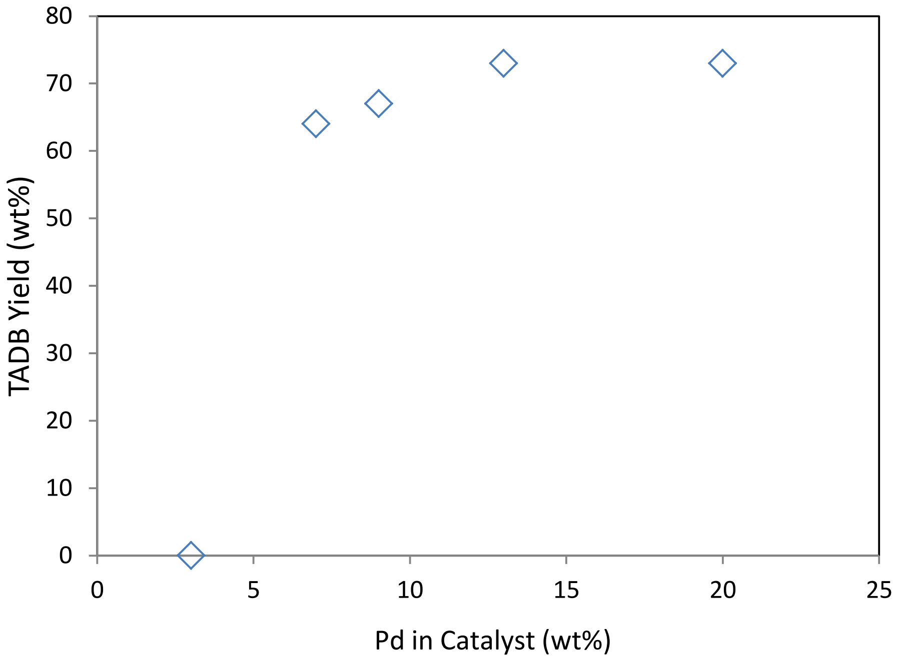


Figure 2. The TADB yield versus the Pd content in catalyst (catalyst precipitation conditions: pH = 12, time = 5 h, temperature = 50 °C)

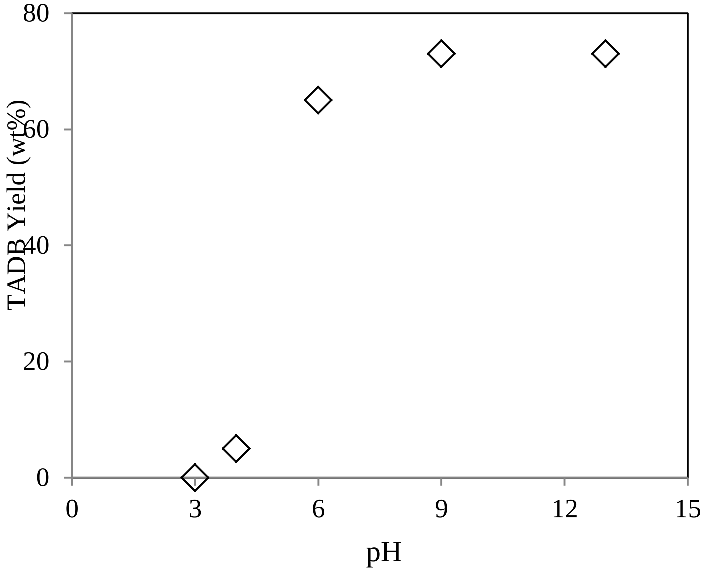


Figure 3. The TADB yield versus the pH of $Pd(OH)_2$ precipitate (catalyst precipitation conditions: Pd content in precursor solution/catalyst = 13 wt%, time = 5 h, temperature = 50°C)

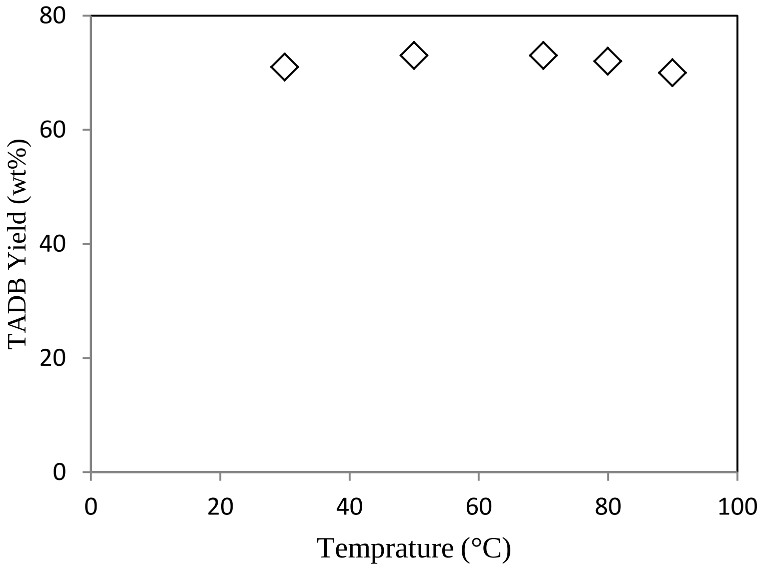


Figure 4. The TADB yield versus temperature of precipitation of $Pd(OH)_2$ (catalyst precipitation conditions: Pd content in precursor solution/catalyst = 13 wt%, time = 5 h, pH = 12)

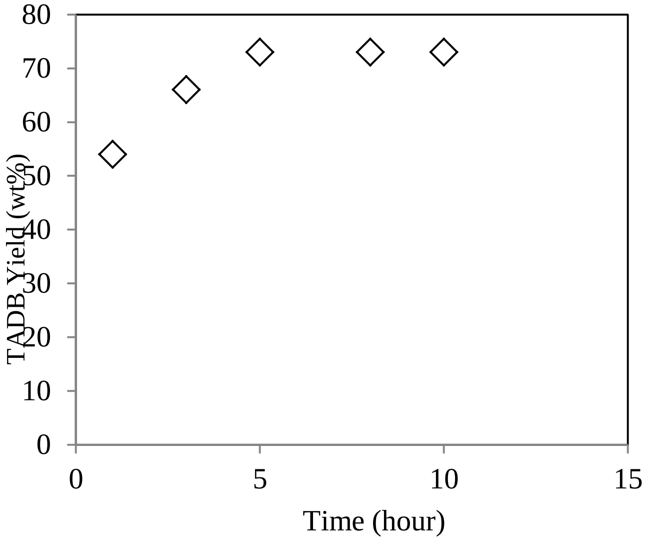


Figure 5. The TADB yield versus time of precipitation of $Pd(OH)_2$ (catalyst precipitation conditions: Pd content in precursor solution/catalyst = 13 wt%, temperature = 50°C, pH = 12)

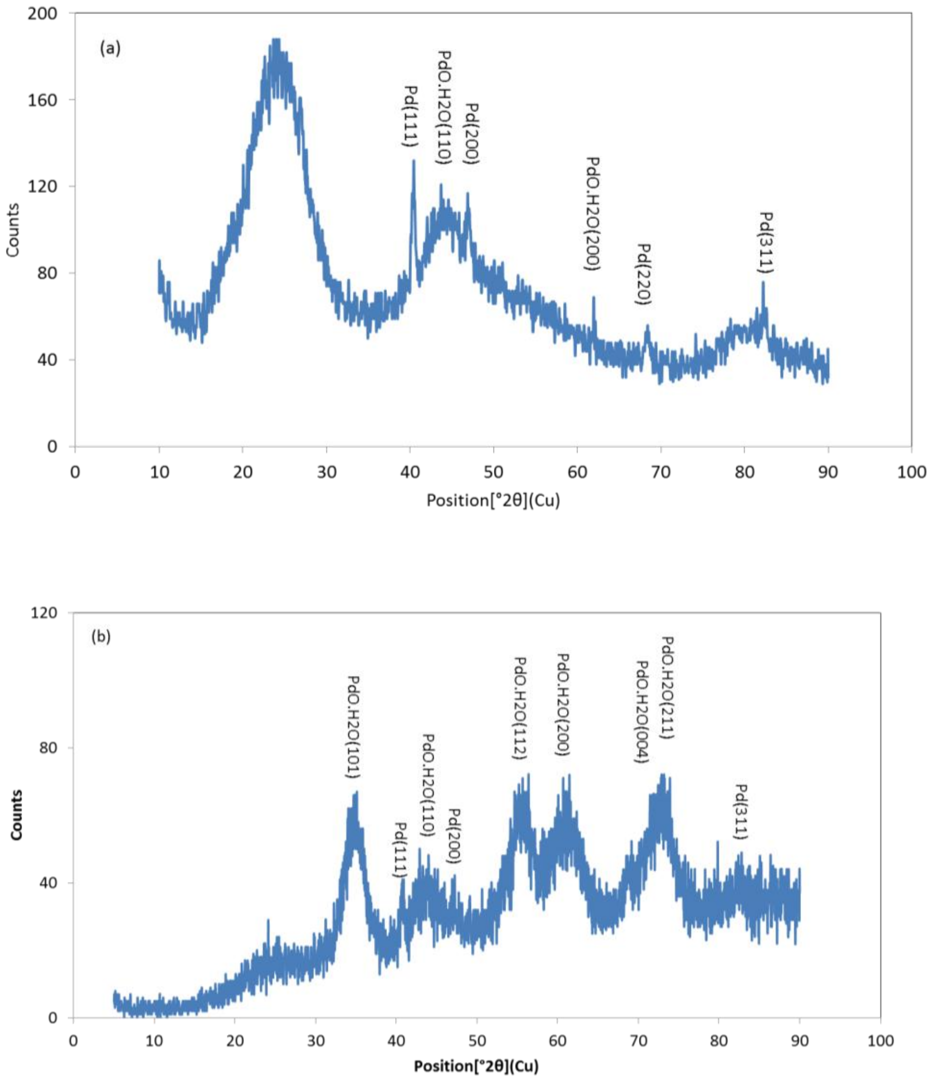
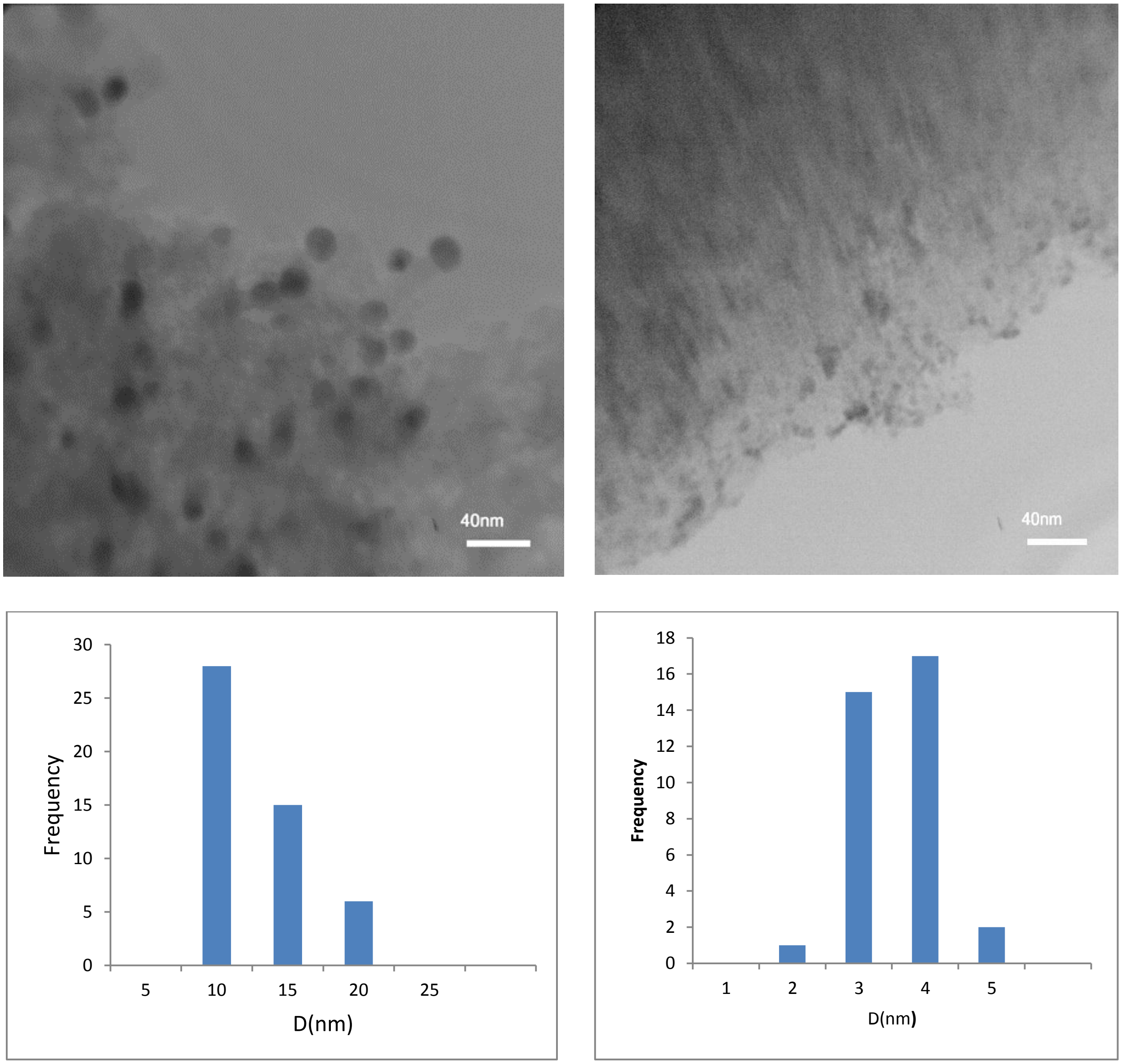


Figure 6. Wide-angle XRD patterns for: (a) the prepared catalyst without $Pd(OH)_2$ precipitate (Pd content in catalyst = 3.5 wt%) and (b) the prepared catalyst with $Pd(OH)_2$ precipitate (Pd in catalyst = 10 wt%)



(a) (b)

Figure 7. The TEM images for: (a) the prepared catalyst without $Pd(OH)_2$ precipitate (Pd content in catalyst = 3.5 wt %) and (b) the prepared catalyst with $Pd(OH)_2$ precipitate (Pd content in catalyst = 10 wt%)