



Palladium Catalyst in the HBIW Hydrodebenzylation Reaction. Deactivation and Spent Catalyst Regeneration Procedure

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Abstract: The polycyclic nitramine 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (HNIW, CL-20) is synthesized *via* hydrodebenzylation of 2,4,6,8,10,12-hexabenzyl-2,4,6,8,10,12-hexaazaisowurtzitane (HBIW) over a palladium-based catalyst. This process is the key step in the synthesis of CL-20, a compound with unique energetic and explosive characteristics. The use of CL-20 is restricted at present by the high cost of the hydrodebenzylation process, during which the palladium-based catalyst becomes rapidly deactivated. The catalyst deactivation has now been shown to consist of deposition of the reaction products on the carbon support with simultaneous blocking of the active centers by these products. The HBIW decomposition products can permanently combine with palladium, thereby reducing the number of the active centers on the catalyst. Other byproducts clog the pores of the active carbon and reduce both the surface area of the active carbon and the pore volume. The reaction yield is also reduced by aggregation of palladium particles. A palladium catalyst regeneration procedure which has now been developed, consists of heating the catalyst for a specific time at 350 °C in a nitrogen and water vapour stream, and allows partial recovery of the activity of the palladium catalyst in a subsequent HBIW hydrodebenzylation reaction. The specific area and overall pore volume of the regenerated catalyst are also enhanced. The yield from the HBIW hydrodebenzylation reaction using the regenerated catalyst was *ca.* 42%.

Keywords: HBIW hydrodebenzylation, palladium-based catalyst, Pd/C deactivation, spent Pd/C catalyst regeneration

1 Introduction

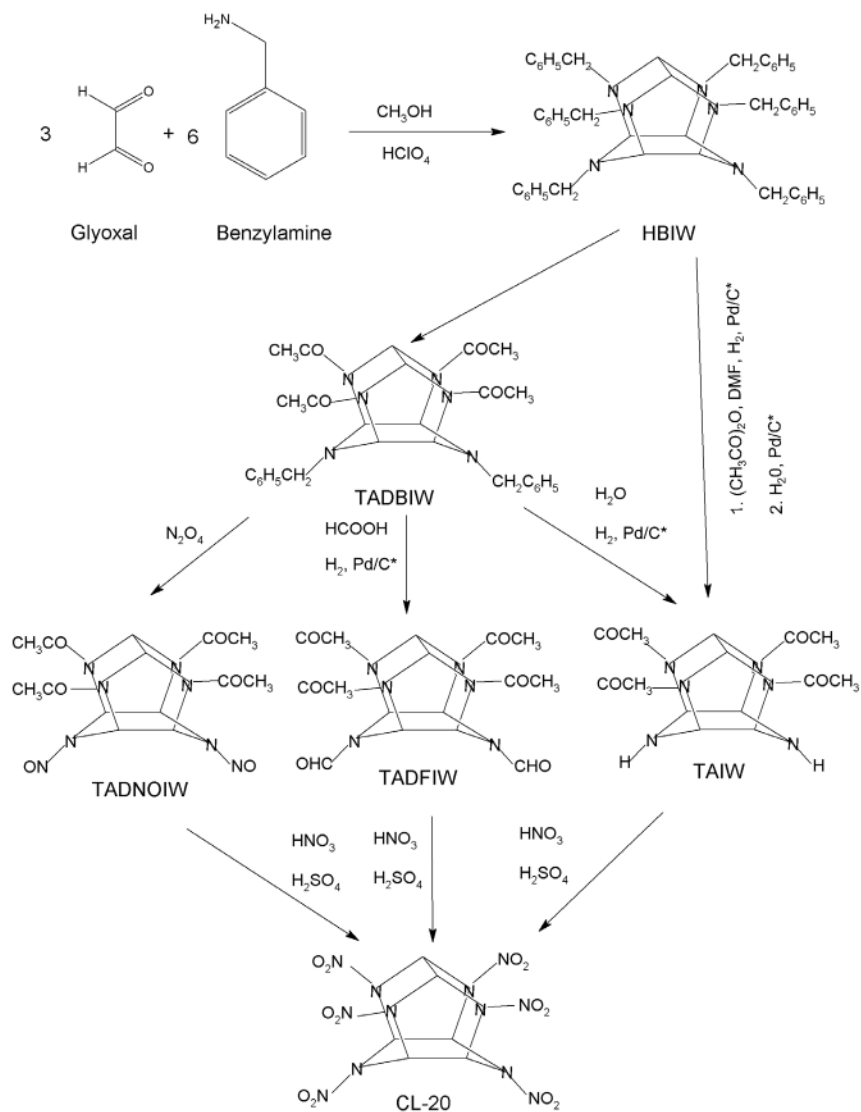


Figure 1. CL-20 synthesis.

High-density, highly energetic materials like polynitro cage compounds (CL-20, TEX [1]) are the subject of an extensive research effort in relation to the use of these compounds as components of rocket propellants, powders and formulations

of high-performance explosives. 2,4,6,8,10,12-Hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (HNIW, CL-20) is one of the major high-density high-energy materials. It features a higher energy and density than the commonly used monocyclic nitramines such as cyclotetramethylenetetranitramine (HMX) or cyclotrimethylenetrinitramine (RDX).

CL-20 synthesis comprises four steps (cf. Figure 1). The first step involves the preparation of the isowurtzitane cage with six benzyl substituents (2,4,6,8,10,12-hexabenzyl-2,4,6,8,10,12-hexaazaisowurtzitane, *i.e.* HBIW) in a condensation reaction of benzylamine with glyoxal in the presence of an acidic catalyst [2, 3]. Direct nitration of HBIW to CL-20 is unfeasible, as the compound is unstable in an acidic environment. Accordingly, the subsequent CL-20 synthesis step is the hydrodebenzylation reaction of HBIW to its acetyl, formyl, or amino derivatives, or the oxidative debenzylation reaction to a nitroso derivative [4]. The isowurtzitane derivative obtained may then be nitrated to CL-20 using typical nitrating mixtures.

The CL-20 synthesis step that is both the most challenging and expensive is the HBIW hydrodebenzylation reaction. The reaction is carried out in an autoclave filled with hydrogen under increased pressure in the presence of a palladium catalyst. The product of this reaction is 2,6,8,12-tetraacetyl-4,10-dibenzyl-2,4,6,8,10,12-hexaazaisowurtzitane (TADBIW). This synthesis step is illustrated in Figure 2.

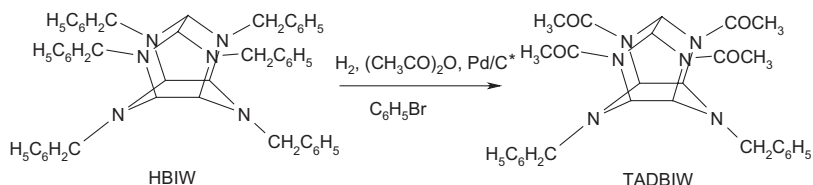


Figure 2. TADBIW synthesis.

Palladium catalysts are widely used for selective hydrogenolysis of C-N bonds. As shown in the pertinent literature, the process (cf. Figure 2) occurs only in the presence of palladium-based catalysts [5-7]. Their key advantage is the selectivity of the hydrogenolysis of the C-N bond between the cage nitrogen and the benzyl carbon, leaving the CN bonds in the hexaazaisowurtzitane cage intact. Unfortunately, the palladium catalyst in this process quickly becomes deactivated. To recycle the palladium from the spent catalyst, the latter has to be thoroughly incinerated and the palladium recovered from the residue, then purified and deposited again on the active carbon support. The process incurs palladium losses and a substantial increase in the cost of the intermediate product,

which is the CL-20 precursor.

A good catalyst for the HBIW hydrodebenzylation reaction should feature the largest possible specific surface area, a considerable quantity of mesopores (the quality that is required for the large volume of the HBIW molecule) and a uniform distribution of palladium over the entire catalyst surface. Minor differences in the conditions in which the palladium catalyst is prepared may significantly affect the fragile equilibrium between catalyst activity, its selectivity and life [8]. The literature recommendations for carrying out this hydrodebenzylation reaction are the commercial palladium catalysts of Pearlman or Degussa brand names.

The reductive debenzylation reaction is the most complicated and expensive step in the CL-20 synthesis. A reason for this is that in these reactions the expensive palladium catalyst must be used in considerable quantity. Therefore, the issue of developing a process for the recovery/regeneration of the catalyst employed is vital.

It was observed [9, 10] that the weight of the washed-off spent palladium catalyst sample is greater than that of the fresh catalyst. Comparative studies of the fresh and spent catalyst samples by means of nitrogen adsorption at low temperature (77 K) demonstrated that the pore specific surface and volume in the spent catalyst is clearly smaller than in the fresh catalyst. Rapid Pd/C catalyst deactivation during hydrodebenzylation was shown [9-11] to be independent of the catalyst preparation procedure. The reason for a reduced catalytic activity was believed to originate from blocking of the active palladium particles in the carbon pores by oligomerization products as well as by agglomeration of palladium particles.

In our laboratory a procedure has been developed for the preparation of a palladium catalyst, its characterization prior to and after the HBIW-hydrodebenzylation reaction, as well as development of a catalyst regeneration procedure.

2 Experimental

2.1 Materials

All of the reagents and chemicals were of AR grade. Active carbon, Carbo Medicinalis, from Gryf-Skand, was obtained by the vapour-gaseous activation of charcoal. The purity required was achieved by treatment with acid, followed by washing with distilled water. The final appearance was a powder with a particle-size distribution below 0.12 mm.

2.2 HPLC analysis

The quantitative composition of the synthetic products was determined on a Shimadzu (Japan) chromatograph (LC-10AD pumps, SPD-10A UV detector, CTO-10A oven) using detection at 220 nm. The separation was carried out on an analytical SUPELCOSIL ABZ+Plus 5 μm 150 \times 4.6 mm column (Sigma-Aldrich) and a 5 \times 4 mm precolumn packed with the same material. The mobile phase contained acetonitrile and water in the ratio 40/60 (v/v). The flow rate of the mobile phase was 1 mL/min, the column temperature 30 $^{\circ}\text{C}$ and the injection volume was 20 μL . The quantitative compositions of the prepared substances were calculated from calibration curves. The retention times of the acetylbenzyl derivatives of hexaazaisowurtzitane was: 4.4 min for 2,6,8,12-tetraacetyl-4,10-dibenzyl-2,4,6,8,10,12-hexaazaisowurtzitane (TADBIW); 7.3 min for triacetyl-tribenzyl-2,4,6,8,10,12-hexaazaisowurtzitane (TATBIW); 9.1 min for diacetyl-tetrabenzyl-2,4,6,8,10,12-hexaazaisowurtzitane (DATBIW).

2.3 Determination of specific surface area and porosity

The porosity and specific surface area were determined using a porosity and specific surface area analyzer, model Micromeritics ASAP 2020M. Nitrogen adsorption and desorption isotherms were measured for a $p/p_0 = 0.02\text{--}1.0$ range at 77 K by the static volumetric technique. Preliminary sample preparation involved heating of the material at 150 $^{\circ}\text{C}$ under vacuum (10^{-3} Torr) for 10 h. The specific surface area of the materials was found on the basis of a multipoint BET measurement for the range of $p/p_0 = 0.08\text{--}0.30$. The mesopore size distribution was calculated using the Barrett-Joyner-Halenda (BJH) procedure and the assumption of the adsorbate statistical thickness according to Halsey.

2.4 Thermogravimetry

The thermogravimetric analysis (TG/DTA) experiments were carried out using a SDT Q600 TA Instrument. The TG/DTA conditions were as follows: sample mass 15 mg; heating rate 10 $^{\circ}\text{C}/\text{min}$; nitrogen atmosphere flow rate 100 mL/min.

2.5 HBIW to TADBIW hydrodebenzylation reaction

HBIW (8 g) was placed in an autoclave. 10 wt.% Pd/C* (50% H_2O , 1.6 g) was weighed onto a Buchner filter funnel and then washed three times with DMF, the solvent being drawn through under reduced pressure. The catalyst was transferred into the autoclave and DMF (21 mL) and acetic anhydride (12 mL) admixed with bromobenzene (0.16 mL) were added. The reaction was carried out in the autoclave under an atmosphere of hydrogen at a pressure of 5 atm. The reaction mixture was stirred at ca. 1000 rpm. The reaction was conducted at 25 $^{\circ}\text{C}$ for

the first 0.5 h, then at 40 °C for 8 h. After that time the post-reaction product mixture was filtered off. The gray precipitate obtained was dispersed in acetic acid (10 mL AcOH per 1 g precipitate) and the resultant suspension was stirred at 60 °C for ca. 15 min. The catalyst was then filtered off on a Buchner filter funnel and the filtrate was concentrated until the TADBIW product separated. The solid was filtered off and was washed with acetone on the funnel to remove impurities. The TADBIW obtained was in the form of a white powder.

2.6 10% Pd(OH)₂/C* catalyst preparation

The catalyst was prepared using Gryf-Skand Carbo Medicinalis active carbon. In order to prepare 10 g (dry mass) of the catalyst with 10 wt.% Pd on the support surface, carbon (9.3 g) and water (46.7 mL) were added to a flask. Freshly prepared sodium carbonate solution (2 mL; 1.45 g in 7.7 mL water) was added to the suspension with stirring at room temperature. Stirring was continued for 15 min, an aqueous solution of sodium chloropalladate (50 mL, 2.77 g Na₂PdCl₄) was added, and the stirring was continued for another 15 min. After that time, the remaining sodium carbonate solution was added. The temperature was then raised to 70 °C with continuous stirring and was maintained at this temperature for 1 h. Subsequently, the stirring was continued at room temperature for 16 h. The catalyst obtained was filtered off on a Buchner funnel and washed with water until no Cl⁻ ions were present in the filtrate. The washed catalyst was transferred to a porcelain evaporating dish and dried in a drier at 120 °C until 50% moisture content. The partially dried catalyst was then transferred to a tightly sealed container.

2.7 Spent catalyst regeneration

The deactivated palladium catalyst from the HBIW to TADBIW hydrodebenzylation process was placed in a quartz tube which in turn was inserted into an electric furnace. Nitrogen or nitrogen mixed with water vapour was passed through the tube. Initially, the catalyst was heated to ca. 150 °C and after ca. 30 min the temperature was raised to 300-350 °C. The catalyst regeneration process was carried out in a stream of nitrogen or a nitrogen/water vapour mixture at a flow rate of 5 L/h (a stream of nitrogen at a flow rate of 5 L/h was introduced under the surface into a flask of boiling water and then transferred directly into the furnace, which contained the catalyst). The furnace temperature was maintained for 2 h and then the catalyst was cooled to room temperature under a flow of nitrogen. During the heating, the adsorbed impurities escaped from the catalyst surface by sublimation. An appropriate amount of water was added to the regenerated palladium catalyst to adjust the catalyst moisture content to 50%. At this stage the catalyst was stored for the next hydrodebenzylation.

3 Results and Discussion

The porous structure of the carbon support and the dispersion of the catalytically active metal, as well as its distribution are important characteristics of palladium-based catalysts. The microporous Norit SX carbon-containing material fails to yield the TADBIW product [10]. This lack of activity appears to be due to localization of the catalyst active centers in the micropores which are inaccessible to the bulky HBIW molecules. Use of a larger-pore support may secure better access for the HBIW molecules to the metallic palladium. This is why, for the preparation of the palladium catalyst, Carbo Medicinalis active carbon was used, as this material features a well-developed surface and pore system, with a low impurity level.

3.1 HBIW hydrodebenzylation reactions in the presence of palladium catalyst

A series of HBIW hydrodebenzylation reactions were performed in this laboratory with a Degussa catalyst, and with the catalyst obtained using Carbo Medicinalis. The results achieved are listed in Table 1.

Table 1. Results of the hydrodebenzylation reaction performed with various catalysts

No.	Catalyst (10 wt.% Pd/C)	Yield TADBIW [%]
1	Degussa, fresh catalyst	81
2	Degussa, after 1 st reaction	0
3	This work, fresh catalyst	79
4	This work, after 1 st reaction	0
5	This work, after regeneration	42

The activity of the Degussa catalyst and that made in this laboratory on the Carbo Medicinalis support, were similar (yields ca. 80%). No product was obtained in successive reactions with the re-use of the same catalysts. The HPLC chromatograms of the post-reaction filtrate shows that the catalyst is active at the early stage of reaction, as TADBIW is produced in minor quantities. However, as the reaction proceeds, the catalyst quickly loses its activity. The major products were di- and triacetyl intermediates, *i.e.* DATBIW and TATBIW.

3.2 Regeneration of the spent Pd/C* catalyst

In the subsequent developments of our research, attempts were made to recover/regenerate the deactivated HBIW hydrodebenzylation catalyst. Relevant trials

to achieve this objective included the following procedures applied to the spent catalyst:

- a. Prolonged heating in formic acid at 80 °C;
- b. Soaking in *aqua regia*, followed by driving off the acids, neutralization with sodium carbonate solution, separation by filtration and washing with distilled water;
- c. Soaking in saturated sodium hydroxide solution, filtration and washing with distilled water;
- d. Soaking in DMF, filtration and washing with distilled water;
- e. Stirring in an autoclave in a hydrogen atmosphere for 8 h in 50:50 water/acetic acid, filtration, neutralization with sodium carbonate solution, filtration and washing with distilled water;
- f. Prolonged heating above 300 °C in a furnace under a nitrogen or nitrogen and water vapour stream for 2 h, processes shown in Figures 3-5.

The catalyst recovery techniques listed were primarily intended to remove the products, absorbed from the previous reaction, from the catalyst surface and to increase the palladium dispersion on the catalyst surface. The catalyst regeneration techniques based on the removal of the absorbed reaction byproducts from the catalyst surface using a variety of reagents failed. The most successful approach for catalyst regeneration proved to be the one involving heating of the catalyst at 350 °C in a stream of nitrogen alone or combined with water vapour. It was found that if the process was run above 300 °C, sublimation of the products absorbed on the catalyst surface takes place. This observation was confirmed by gravimetric analysis of the catalyst samples after the HBIW hydrodebenzylation reaction. The results of the gravimetric measurements on the catalyst samples, before and after the regeneration process, are shown in Figures 3-5.

Figure 3 shows the results of gravimetric analysis of the catalyst samples after the HBIW hydrodebenzylation reaction. Samples “a” and “b” differ from each other in the way the catalyst was purified. Catalyst “a” was purified by triple heating in acetic acid, followed by thorough washing with water, whereas catalyst “b” was purified by a single heating in acetic acid with subsequent single washing with water. Each catalyst was compared with its corresponding fresh counterpart. A loss in mass visible in the figure commences above 300 °C for both ‘already used’ catalysts. For catalyst “a” the loss was ca. 18% and for catalyst “b” ca. 44%. The difference was due to how thoroughly the reaction products had been removed from the catalyst by acetic acid. Further washing of the catalyst no longer affects the “a” curve shape. This suggests that some of the products are more strongly bonded to the catalyst surface and are not washed out by a single treatment with acetic acid.

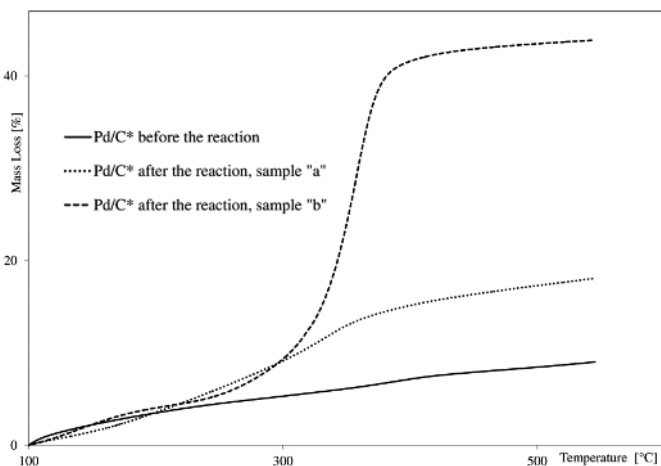


Figure 3. Gravimetric analysis of the catalyst samples before and after the HBIW hydrodebenzylation reaction.

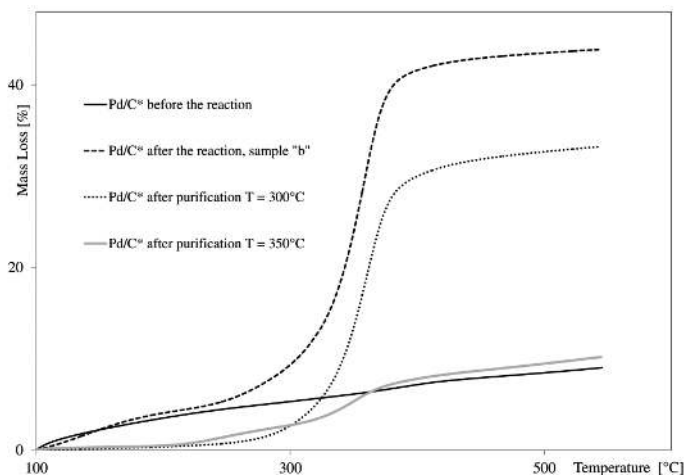


Figure 4. Gravimetric analysis of the catalyst samples before and after the HBIW hydrodebenzylation reaction. Influence of the heating temperature on the regeneration of the process spent catalyst.

Figure 4 shows the results of gravimetric analysis of catalyst samples treated by heating at 300 and 350 °C in a N₂ and water vapour stream, as compared to the catalyst after and before the hydrodebenzylation reaction. As seen from the graph, the higher the heating temperature, the less the products following the

hydrodebenzylation reaction remain on the catalyst surface. After 2 h heating in a N_2 and water vapour stream the mass loss from the catalyst processed at $300\text{ }^\circ\text{C}$ was ca. 33%, whereas the mass loss from the catalyst treated by heating at $350\text{ }^\circ\text{C}$ was only ca. 10%. The mass loss from the catalyst that was not processed by the regeneration procedure was ca. 44%.

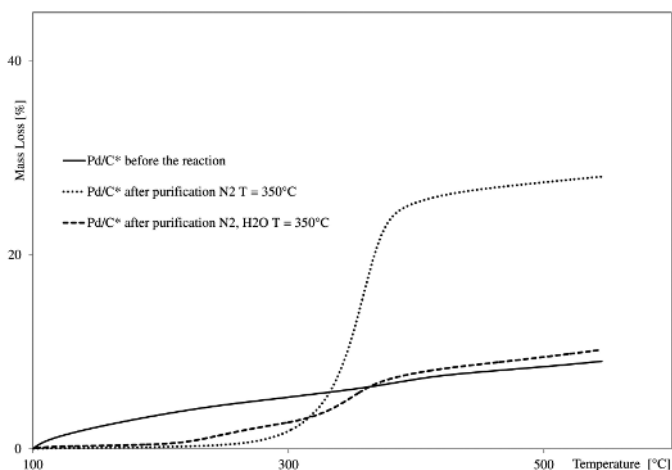


Figure 5. Gravimetric analysis of the catalyst samples before and after the HBIW hydrodebenzylation reaction. Influence of N_2 stream or N_2 with water vapour stream on the regeneration of the process spent catalyst.

Figure 5 shows the results of the gravimetric analysis of the catalyst samples treated by heating at $350\text{ }^\circ\text{C}$ in a N_2 stream or in a N_2 with water vapour stream. As seen from the graph, the use of water vapour improves the effectiveness of the spent catalyst regeneration process. After heating for 2 h at $350\text{ }^\circ\text{C}$ in the N_2 stream, the mass loss from the recovered catalyst was ca. 28%, whereas the corresponding mass loss for the process that employed nitrogen and water vapour was only ca. 10% and is greater than the value for the fresh catalyst by 1%.

3.3 Characteristics of the recovered catalysts

The porous structure of the carbon support and dispersion of the catalytically active metal, as well as its distribution, are significant properties of palladium-based catalysts.

To determine the characteristics of the prepared catalysts, examination of their surfaces and their SEM (Scanning Electron Microscope) photographs were

analyzed. The results of the study and determination of the specific surface area (BET model), the surface and volume of the pores (BJH model), and the surface and volume of the micropores (*t*-plot model) for the unused catalyst, the catalyst after HBIW hydrodebenzylation and for the recovered catalyst are collected in Table 2.

Table 2. Texture of the catalysts studied

Parameter	Units	Catalyst			
		Degussa	Made in this laboratory		
			Fresh	After reaction	After regeneration
BET Surface area		716.8	810.9	124.0	325.2
BJH Adsorption cumulative surface area of pores between 1.7 and 300 nm width	m ² /g	427.6	259.4	103.2	136.9
BJH Desorption cumulative surface area of pores between 1.7 and 300 nm width		366.4	152.6	80.3	97.6
<i>t</i> -plot Micropore area		298.2	487.4	30.5	168.1
BJH Adsorption cumulative volume of pores between 1.7 and 300 nm width	cm ³ /g	0.5101	0.2494	0.1434	0.1718
BJH Desorption cumulative volume of pores between 1.7 and 300 nm width		0.4781	0.1962	0.1269	0.1444
<i>t</i> -plot Micropore volume		0.1657	0.2679	0.0169	0.0928
Desorption average pore width (4V/A by BET)	nm	3.7	2.6	4.7	3.2
BJH Adsorption average pore width		4.8	3.8	5.6	5.0
BJH Desorption average pore width		5.2	5.1	6.3	5.9

A suitable catalyst for the HBIW hydrodebenzylation reaction should feature the largest possible specific surface area, a large number of mesopores (due to the large volume of the HBIW molecule) and uniform palladium distribution

over the whole catalyst surface.

For a comparison of the characteristics of the catalyst produced in this laboratory, a commercial Degussa catalyst was selected as it is generally recommended in the pertinent literature for this process. The commercial Degussa catalyst has a smaller specific surface area as compared with the catalyst made in this laboratory with Carbo Medicinalis as its support, yet it exhibits a greater overall void surface area and a greater overall volume of pores. These differences stem from the larger number of micropores in our Carbo Medicinalis-supported catalyst. The surface area of micropores in our Carbo Medicinalis-supported catalyst is greater by 63% and the micropore volume larger by 67% than in the Degussa catalyst (cf. Table 2). The mean diameter of the pores according to the BET and BJH models is greater in the Degussa catalyst; this is also due to a greater number of micropores in the catalyst made in this laboratory.

Figure 6 gives a comparison of the distribution of the mesopore size for both the Carbo Medicinalis-supported catalyst and the Degussa catalyst. The mesopore width of both catalysts is similar yet they differ substantially by volume. This suggests that the Degussa catalyst must have mesopores of greater depth.

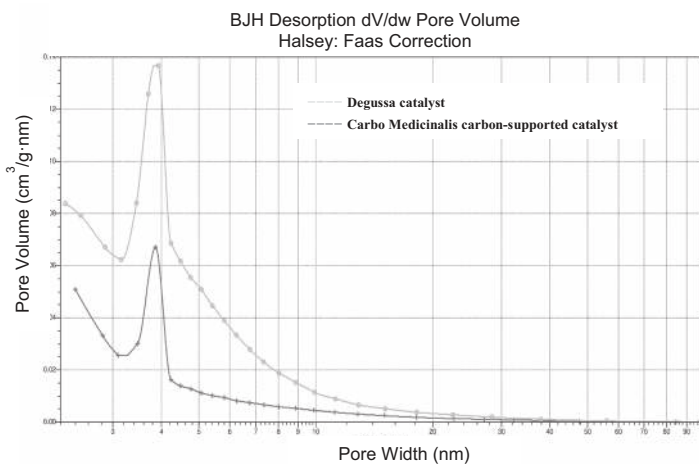


Figure 6. Comparison of the mesopore size distribution for the catalysts.

Figure 7 gives a comparison of the micropore distribution in both the Carbo Medicinalis carbon-supported catalyst and in the Degussa catalyst. The distribution curves are alike; therefore, the micropore size is similar in both catalysts. As pointed out earlier, micropores should not be critical in the HBIW hydrodebenzylation reaction.

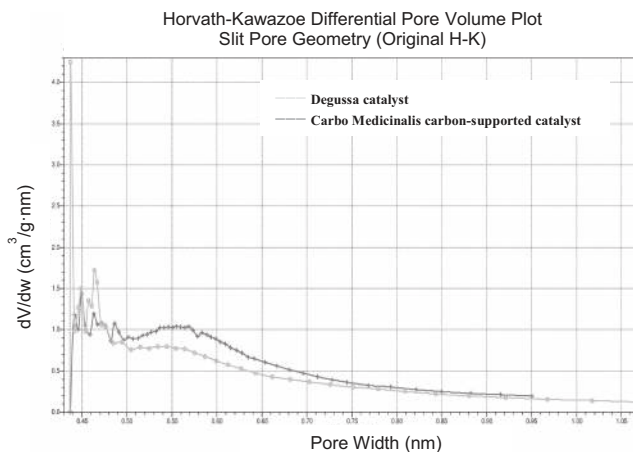


Figure 7. Comparison of the micropore size distribution for the catalysts.

After the HBIW hydrodebenzylation reaction both catalysts lose their activity. To find out which properties of the catalysts change, a study was made of the catalyst developed using Carbo Medicinalis as support, after its use in the HBIW hydrodebenzylation reaction. Prior to its examination the catalyst was dried in a vacuum dryer at 100 °C.

As a result of the hydrodebenzylation reaction, the catalyst lost its active surface. Also, the specific surface area (BET) was found to be reduced to 15% and the pore surface (BJH) to ca. 40% of the initial value. The pore volume dropped to ca. 60% of the initial value, with a rise in the mean diameter from a value of ca. 3.8 to 5.6 nm (BJH) and from 2.6 to 4.7 nm (BET). These effects can be explained by the pores of relatively small diameter vanishing first. This is confirmed by a considerable loss of micropores in the catalyst under study (*t*-plot). The volume and surface area of the micropores decreased to ca. 6% of their initial values (Table 2).

The following observations were made regarding the regenerated catalyst in relation to the corresponding values for the inactive catalyst after the hydrodebenzylation reaction: increases in the specific surface area by ca. 167% (BET), in pore surface area ca. 30% (BJH) and in pore volume ca. 20% (BJH), and reductions in the middle-size pores from 4.7 to 3.2 nm (BET) and 5.6 to 5.0 nm (BJH). These are the results of the removal of the reaction products from the catalyst surface and the clearing of the clogged pores. The regeneration of the spent catalyst procedure, however, fails to restore the initial parameters of the fresh catalyst.

An SEM study was employed to study the variations in the morphology of palladium particles on the carbon support surface during the HBIW hydrodebenzylation reaction. Figure 8 shows SEM photographs of the Degussa catalyst (A) and of our catalyst supported on Carbo Medicinalis (B), our catalyst after the HBIW hydrodebenzylation reaction (C), and our catalyst following regeneration (D). The brighter spots indicate the positions of palladium.

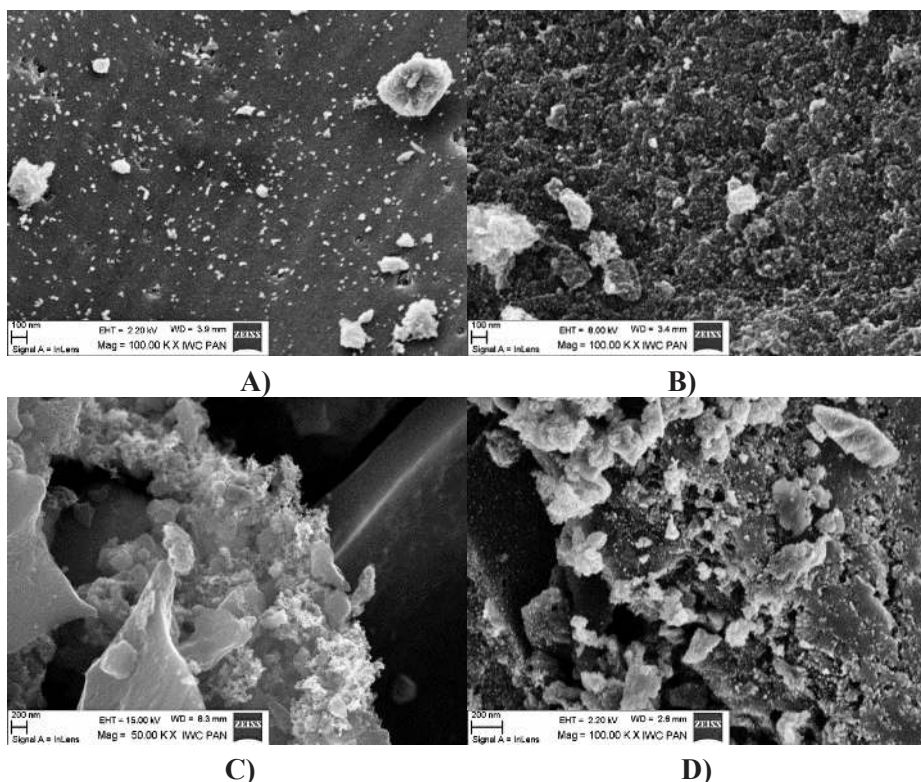


Figure 8. Scanning Electron Microscope photographs of the surface of the catalysts: A) Degussa. B) our catalyst, C) our catalyst after the reaction, D) our catalyst after regeneration.

The Degussa catalyst (Figure 8A) and our own catalyst (Figure 8B) exhibit the most uniform palladium distributions. The palladium particle size is ca. 100 nm. In the SEMs of the catalyst after the HBIW hydrodebenzylation reaction (Figure 8C) agglomeration of the Pd particles may be observed, which leads to a reduced area of active surface of the metal. The particles may be found to be of different sizes and to form larger agglomerates. The SEM of the distribution

of palladium particles on the regenerated catalyst surface remains unchanged (Figure 8D).

These observations allowed us to make the assumption that agglomeration of the palladium particles is one of the reasons for the loss of Pd/C catalyst activity. One of the conceivable routes for palladium agglomeration may be dissolution of support carbon-bonded palladium in the reaction solution, with subsequent re-adsorption of the metal in the form of large agglomerates.

4 Conclusions

During the HBIW hydrodebenzylation reaction the palladium catalyst used in the process becomes deactivated. The catalyst deactivation consists of the deposition of the reaction products on the carbon substrate with concomitant blocking of the active centers. The substrate used in the HBIW hydrodebenzylation reaction is unstable and at elevated temperatures it decomposes in a reaction with acetic anhydride. The decomposition products may permanently combine with palladium, thereby reducing the number of active centers on the catalyst. These products clog the pores present on the active carbon and reduce its active surface and pore volume. The reaction yield may also be decreased as a result of palladium particle agglomeration. The effect of the palladium particles growing in size, which brings about a lowering of the active surface area of the metal, is visible in the SEM photographs of the catalyst after the reaction. The palladium catalyst regeneration technique, by heating at 350 °C in a nitrogen gas with water vapour stream, allows partial restoration of the activity of the catalyst for a further HBIW hydrodebenzylation reaction. The catalyst specific surface area is increased from 124 to 325 m²/g, and the total pore volume from 0.143 to 0.172 m³/g. The yield of the HBIW hydrodebenzylation reaction using the regenerated catalyst was ca. 42%.

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References

- [1] Maksimowski P., Gołofit T., 4,10-Dinitro-2,6,8,12-tetraoxa-4,10-diazatetracyclo[5.5.0.05,9.03,11]dodecane Synthesis, *J. Energ. Mater.*, **2013**, 31(3), 224-237.
- [2] Krysztopa J., Maksimowski P., The Effect of the Conditions of Condensation of Benzylamine with Glyoxal Run in Methanol on the Yield of 2,4,6,8,10,12-Hexabenzyl-2,4,6,8,10,12-hexaazatetracyclo[5.5.0.05,9.03,11]dodecane, *Przemysł Chemiczny*, **2005**, 84(04), 260-263.
- [3] Jefimczyk J., Antczak A., Maksimowski P., Studies on Synthesis of Hexabenzylhexaazaisowurtzitane (HBIW) in the Menthol-sulfuric Acid System, *Przemysł Chemiczny*, **2008**, 87(03), 296-299.
- [4] Maksimowski P., Fabijańska A., Adamiak J., Tetraacetyl-dibenzyl-hexaazaisowurtzitane Nitrosation, *Propellants Explos. Pyrotech.*, **2010**, 35, 353-358.
- [5] Bellamy A.J., Reductive Debenzylation of Hexabenzylhexaazaisowurtzitane, *Tetrahedron*, **1995**, 51, 4711.
- [6] Nielsen A.T., Nissan R.A., Vanderah D.J., Coon C.L., Gilardi R.D., George C.F., Flippen-Andersen J., Polyazapolycyclics by Condensation of Aldehydes with Amines. Formation of 2,4,6,8,10,12-Hexabenzyl-2,4,6,8,10,12-hexaazatetracyclo[5,5,0,0^{5,9},0^{3,11}]dodecanes from Glyoxal and Benzylamines, *J. Org. Chem.*, **1990**, 55, 1459.
- [7] Wardle R.B., Edwards W.W., Hydrogenolysis of 2,4,6,8,10,12-Hexabenzyl-2,4,6,8,10,12-hexaazatetracyclo[5,5,0,0^{5,9},0^{3,11}]dodecanes, US Patent 5,739,325, **1996**.
- [8] Toebes M.L., Dillen J.A., Jong K.P., Synthesis of Supported Palladium Catalysts, *J. Mol. Cat. A*, **2001**, 173, 75.
- [9] Koskin A.P., Simakova I.L., Parmon, V.N., Reductive Debenzylation of Hexabenzylhexaazaisowurtzitane – the Key Step of the Synthesis of Polycyclic Nitramine Hexanitrohexaazaisowurtzitane, *Russian Chemical Bulletin*, **2007**, 56(12), 2370-2375.
- [10] Koskin A.P., Simakova I.L., Parmon V.N., Study of Palladium Catalyst Deactivation in Synthesis of 4,10-Diformyl-2,6,8,12-tetraacetyl-2,4,6,8,10,12-hexaazaisowurtzitane, *Reaction Kinetics and Catalysis Letters*, **2007**, 92(2), 293-302.
- [11] Klapötke T.M., Krumm B., Holl G., Kaiser M., Synthesis, Characterization and Quantum Chemical Computations of Hexanitrohexaaza-isowurtzitane, *Energetic Materials – Modeling of Phenomena, Experimental Characterization, Environmental Engineering*, Fraunhofer Institut, Karlsruhe, **1999**, P-120.