



Article Carbonized Melamine Cyanurate as a Palladium Catalyst Support for the Dehydrogenation of N-heterocyclic Compounds in LOHC Technology

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Abstract: In this work, the use of graphite-like carbon nitride (g-C₃N₄) with improved texture characteristics for the synthesis of supported palladium catalysts of dehydrogenation of nitrogen-containing heterocycles was studied. This process is key to the creation of liquid organic carrier technology (LOHC) using N-heterocycles as reversibly hydrogenated/dehydrogenated substrates. For the preparation of graphite-like carbon nitride supports with advanced textural characteristics, well-established technology of the melamine cyanurate complex carbonization and standard techniques of adsorption precipitation together with wet impregnation were used for the synthesis of Pd-containing systems. The activity of the synthesized catalysts was studied in decahydroquinoline dehydrogenation. The high weight content of extractable hydrogen (7.2 wt%) and the high extraction rate, respectively, make it possible to consider these substances as the most promising N-heterocyclic compounds for this technology. It was shown that an increase in the specific surface area of $g-C_3N_4$ allows for achieving a slightly lower but comparable fineness of palladium particles for the 1 wt% Pd/MCA-500 sample, compared to the standard 1 wt% Pd/C. In this case, the catalytic activity of 1 wt% Pd/MCA-500 in the dehydrogenation of both substrates exceeded the analogous parameter for catalysts supported by nitrogen-free supports. This regularity is presumably associated with the electron-donor effect of surface nitrogen, which favorably affects the dehydrogenation rate as well as the stability of catalytic systems.

Keywords: g-C₃N₄; melamine cyanurate; Pd catalysts; hydrogen storage; LOHC; dehydrogenation

1. Introduction

The development of hydrogen energy, as an alternative to the use of hydrocarbon fuels, implies the development of environmentally friendly methods for the synthesis of H₂ and the creation of technologies for its storage and transportation. One of the most promising hydrogen storage/transport technologies, at this moment, is the technology of liquid organic hydrogen carriers (LOHC) [1,2]. The LOHC technology is based on reversible catalytic hydrogenation/dehydrogenation reactions of cyclic hydrocarbons. Hydrogen storage is carried out by exothermic hydrogenation reaction of aromatic compounds. The resulting saturated compounds can be transported and stored for a long time using infrastructure for traditional liquid fuels. Further, chemically bound hydrogen can be released by an endothermic dehydrogenation reaction. Herewith, among the promising hydrogen carrier molecules, toluene [3] and mixtures of dibenzyltoluene [4] isomers are the most studied, at the moment, due to their relatively low price and technical availability. Nevertheless, N-containing heterocycles, such as indole [5,6], quinoline [7,8], and phenazine [9,10] derivatives, attract increasing attention due to their lower hydrogenation/dehydrogenation



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Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). enthalpy compared to cyclic hydrocarbons, which is more attractive from the point of view of the energy of the process.

In recent years, an environmentally friendly method of hydrogen production via photocatalytic water splitting has been actively studied [11,12] when considerable attention is paid to the use of graphite-like carbon nitride (g-C₃N₄) as a photocatalyst for this process [13]. Carbon nitride is a rare example of a non-metallic semiconductor material that has such important advantages as the relative ease of synthesis, as well as good biocompatibility and inexpensiveness [14]. Along with the photocatalytic applications of g-C₃N₄, other ones using carbon nitride as a support for metal-supported catalysts are also being actively developed. In this case, g-C₃N₄ has all the advantages of N-doped mesoporous carbonaceous materials [15].

In particular, the stabilization of the deposited metal component in a highly dispersed state and the resistance of metals to the leaching during the catalytic transformation are achieved due to the interaction of the metal with surface nitrogen [16,17]. In addition, supported catalysts containing palladium are currently being actively investigated in the dehydrogenation of H_2 -saturated N-heterocycles [18]. This process is a key one in a promising hydrogen storage technology using N-heterocycles as LOHC substrates. When implementing this technology, hydrogen is accumulated through the catalytic hydrogenation of an N-heterocycle (H₂-lean form of the LOHC substrate) and, subsequently, is being extracted as a result of dehydrogenation of the nH-N-heterocycle (H_2 -rich form). It has been repeatedly shown that the use of carbonaceous supports, compared to oxide ones, provides advanced catalytic properties [19]. However, the presence of nitrogen in a LOHCsubstrate molecule can lead to the leaching of active sites from the surface of the carbon support as a result of complexation of the Pd:N-heterocycle. Thus, to create catalysts for the dehydrogenation of N-heterocycles with a high stability, it is promising to use g- C_3N_4 as a support that has the content of surface nitrogen reaching 50 at.%. It should be noted that one of the main problems currently being solved in applications using carbon nitride is the development of techniques for the synthesis of $g-C_3N_4$ with a high specific surface area. This is due to the fact that ordinary carbon nitride synthesized through melamine pyrolysis is characterized by a low specific surface area $(3-5 \text{ m}^2/\text{g})$, and to solve a wide range of problems with its use, it is necessary to achieve the material with advanced textural characteristics. This process is realized during the exfoliation when the layers of graphite-like carbon nitride are separated. In this direction, at the moment, an intensive research is being carried out [20], and the obtained exfoliated $g-C_3N_4$ materials have been tested in many photocatalytic reactions [13]. The use of exfoliated-g- C_3N_4 materials as carriers for various supported catalysts has been less explored. Nevertheless, there are examples of transesterification [21,22], hydrogenation [23–25], etc. The reaction of dehydrogenation of H₂-rich N-heterocycles using Metal⁰/exfoliated-g-C₃N₄ catalysts has not been previously studied. The use of such promising supports providing the high dispersity of a supported metal is expected to allow for the successful development of highly effective catalytic systems for dehydrogenation in the LOHC technology and, potentially, for other similar reactions. Thus, the purpose of this work was to study the properties of palladium catalysts supported by the high surface area mesoporous carbon nitride in the dehydrogenation of a promising N-heterocyclic LOHC substrate.

2. Materials and Methods

2.1. Synthesis of the g- C_3N_4 and MCA-T Supports

The reagents melamine and cyanuric acid (all Alfa Aesar, >99.9%), hydrochloric acid, and aqueous ammonia (all Reakhim, 38 and 25%, respectively) were used as received.

For the synthesis of standard graphite-like nitride $(g-C_3N_4)$, melamine was calcined in a closed alumina crucible at a temperature of 550 °C (4 h), followed by the cooling of the sample for 1 h in an inert atmosphere. The synthesis of graphite-like carbon nitride with improved textural characteristics (MCA-T samples) from MCA adducts was carried out similarly. For the carbonization, the adducts obtained by mixing solutions of melamine and cyanuric acid with vigorous stirring were used. The adducts with various M:CA ratios and precipitated from various solvents were used, and the carbonization temperatures were also varied (T = 400–600 °C). The yield of the carbonization product was estimated as the percentage of the obtained solid product to the total mass of the initial adduct.

2.2. Synthesis of Pd-Containing Catalytic Systems

For the synthesis of 1 wt% Pd/g-C₃N₄ or 1 wt% Pd/MCA-T catalysts, the wet impregnation, and adsorption precipitation techniques were applied using H₂[PdCl₄] as the active component precursor. In the case of wet impregnation, the calculated volume of a solution of palladium salt with a concentration required for preparing 1 wt% of the catalyst was used. Next, the sample was dried at 100 °C (2 h) and reduced using a 1 M solution of sodium borohydride (Fluka). The resulting catalyst was washed with distilled water on a filter and dried at 100 °C (2 h).

Using the adsorption precipitation technique, 1 g of the support was dispersed in 20 mL of an EDTA water solution (56 mg) using a magnetic stirrer (600 rpm). Then, 1 M aqueous solution of $H_2[PdCl_4]$ of the required concentration was added dropwise and stirred for six hours (600 rpm). Thereafter, 5 mL of a 1 M sodium borohydride solution was added dropwise to the suspension, which further was stirred for 2 h, filtered, and dried at a temperature of 100 °C (2 h).

In addition, a 1 wt% Pd/C catalyst sample was used as a prototype, which was synthesized according to the technique developed at the Boreskov Institute of Catalysis [26–28].

2.3. Characterization Techniques

2.3.1. Dynamic Light Scattering (DLS)

Dynamic light scattering experiments were carried out using Photocor equipment (Photocor Instruments, Inc., Moscow, Russia) with a digital correlator (288 channels). The measurements were performed at a scattering angle of 90° and temperature of 24 °C. The wavelength of the light source was equal to 638 nm. The processing of the DLS raw data was performed using the DynaLS software (http://www.softscientific.com/science/WhitePapers/dynals1/dynals100.htm (accessed on 25 August 2023)) [29]. For the calculation of particle sizes, standard values of viscosity and refractive index H₂O and DMSO were used. To calculate the z-averaged hydrodynamic diameter, we used the Stokes–Einstein formula for spherical particles [30].

2.3.2. Electron Microscopy (SEM and TEM)

SEM measurements were performed using a Hitachi Regulus SU8230 (Hitachi Ltd., Tokyo, Japan) electron microscope with an electron beam energy of 30 keV in Secondary Electrons (SE) detection and Dark Field Scanning Transmission Electron Microscope (DF-STEM) modes.

The dispersion of metal particles and the microstructure of the catalysts were studied by transmission electron microscopy. The images were acquired with a JEM-2010 (JEOL Ltd., Tokyo, Japan) operating at an accelerating voltage of 200 kV and a resolution of 0.14 nm.

2.3.3. Adsorption Measurements (CO Chemisorption and BET)

The CO chemisorption was measured in a pulsed mode using a Chemosorb analyzer (MBE, Novosibirsk, Russia) equipped with a thermal conductivity detector. The catalyst (50 mg) was loaded into a U-shaped quartz reactor and treated with an H₂ flow (100 mL/min) at 20 and 100 °C with a heating rate of 10 °C/min. The reactor was kept at the final temperature for 20 min, then purged with argon and cooled to room temperature. After cooling, CO pulses (0.1 cm³) were injected into the reactor until the sample was saturated, and the amount of chemisorbed CO was estimated.

Single-point BET measurements of surface area were performed by dynamic adsorption of nitrogen at 77 K. The adsorption in the BET range was made by means of the dynamic adsorption analyzer Sorbtometr (Katakon LLC, Novosibirsk, Russia). Prior to the measurements, all samples were degassed in helium flow at 150 °C for 2 h.

The porous structure was studied by nitrogen adsorption-desorption at 77 K. The isotherms were measured by means of an automatic adsorption analyzer, Autosorb-6B (Quantachrome Instruments, Boynton Beach, FL, USA). Before the measurements, all samples were degassed in vacuum of less than 1 Pa at 150 °C for 16 h.

2.3.4. X-ray Diffraction (XRD)

Powder XRD measurements were carried out using an ARL X'TRA diffractometer (Thermo Electron Corporation, Reinach, Switzerland), equipped with the vertical theta-theta geometry (Bragg–Brentano), CuK α radiation (λ = 0.15418 nm) and a Peltier cooled Si(Li) solid state detector. A 2 θ range from 10° to 80° was scanned with a step of 0.05° and counting time of 5 s.

2.3.5. Small Angle X-ray Scattering (SAXS)

S3 MICRO (HECUS, Graz, Austria) small angle diffractometer (Cu K α , 50 W) with a point collimation of primary beam was used for measuring the scattering patterns of all samples. The scattering vector magnitude $q = 4\pi \times \sin(\theta)/\lambda$ (where 2 θ is the scattering angle and $\lambda = 1.541$ E is the radiation wavelength) was used as the scattering coordinate. The scattering intensity was measured in the range of the scattering vector magnitudes 0.01 < q < 0.60 E⁻¹. The data processing of the scattering curves was performed using the ATSAS software [31]. Structural invariants such as correlation length and Porod-specific surface have been calculated by using special formulas [32].

2.3.6. X-ray Photoelectron Spectroscopy (XPS)

The study of a sample composition was carried out by X-ray photoelectron spectroscopy (XPS) on a SPECS electronic spectrometer SurfaceNanoAnalysisGmbH (Berlin, Germany). The spectrometer is equipped with a PHOIBOS-150-MCD-9 hemispherical analyzer and an XR-50 X-ray source with a double Al/Mg anode. The spectra were recorded using non-monochromatized AlK α radiation ($h\nu$ = 1486.6 eV). The position of the C1s peak corresponding to the support was used to take into account the effect of sample charging. The relative concentrations of elements in the analysis zone are determined based on the integral intensities of XPS peaks, taking into account the photoionization cross-section of the corresponding terms [33]. For a detailed analysis, XPS spectra were decomposed into individual components. Accordingly, after subtracting the background according to the Shirley method [34], the experimental curve was deconvoluted into a series of lines corresponding to the photoemission of electrons from atoms in various chemical environments.

2.3.7. Elemental Analysis

The Pd concentration in the fresh and exhaust catalysts was determined using an ARL Advant'X 2247 X-ray fluorescence spectrometer (Thermo Fisher Scientific Inc., Waltham, MA, USA).

2.4. Catalytic Activity Tests

The catalytic activity of the synthesized Pd-containing catalysts, as well as the prototypical 1% Pd/C catalysts, was studied in the decahydroquinoline dehydrogenation reaction. Decahydroquinoline was preliminarily synthesized from a commercially available quinoline (Sigma Aldrich, St. Louis, MO, USA) according to the earlier described method [7]. Both 1H-NMR and GC-MS methods confirmed the purity of the obtained Nheterocyclic substrate (>99.7%). To study decahydroquinoline dehydrogenation, a reaction setup similar to those described earlier [7] was used.

The study of catalytic activity was carried out similarly to our previous reports [7,9]. In a standard test of the catalytic activity, the catalyst (50 mg) and a suspension of 1 mmol

decahydroquinoline in tetraglyme (3 mL) (Acros Organics, Geel, Belgium) were loaded into the reactor. The system was purged with argon (20 mL/min, 5 min, room temperature), the reactor was sealed and connected to the system for measuring the volume of released hydrogen. Next, the reaction mixture was heated to 240 °C with stirring (500 rpm) for 15 min (0–900 s), and the dehydrogenation reaction was carried out for 45 min (900–3600 s) before the reactor was removed from the heating zone. Then, the selected aliquot of the reaction mixture was separated from the catalyst particles by centrifugation and analyzed by the GC method. The GC analysis was performed using an Agilent-7890A gas chromatograph (Santa Clara, CA, USA) equipped with a ZB-5HT column.

The hydrogen yield characterizing the depth of dehydrogenation was calculated as follows:

$$Y_{H2} = Y_O + 0.6(Y_{4HOc} + Y_{4HOn}), \%$$

where Y_Q , Y_{4HQc} and Y_{4HQn} are the molar fractions of the product (Y_Q) and intermediates (Y_{4HOc} and Y_{4HOn}) obtained by gas chromatography.

3. Results and Discussion

3.1. Synthesis of Graphite-Like Carbon Nitride with a High Specific Surface

Along with photocatalytic applications, carbon nitride has attracted significant attention as a promising carbon support with a high content of surface nitrogen. The conventional synthesis of carbon nitride by melamine carbonization makes it possible to obtain a carbon nanomaterial with a deliberately functionalized surface, which provides many advantages compared to nitrogen-free analogs. However, the low specific surface area of $g-C_3N_4$ has long been a significant limitation both for the development of photocatalytic applications and for the use of $g-C_3N_4$ as a support for supported catalysts. The first implemented method for improving texture characteristics was the sulfuric acid treatment of $g-C_3N_4$ [35] by analogy with the Hummers' method for graphite [36]. However, the low manufacturability of this method initiated further research. Methodologies for hard template synthesis during melamine carbonization in the presence of SiO₂, MgO, and melting salts (NaCl-KCl) followed by washing out of the template [37–39] were successively studied. Nevertheless, soft-template methodologies attracted the most attention. Among them, the carbonization of the melamine:cyanuric acid adduct [40–42] is considered the most technologically advanced and scalable in the future [20].

Melamine cyanurate is an adduct compound having the composition $(M_x:CA_y)_n$ (Figure 1), which is poorly soluble in most solvents. The methodology for its synthesis consists of mixing solutions of commercially available melamine and cyanuric acid. Subsequent carbonization of the material at 400–550 °C temperatures results in the decomposition of oxygen-containing blocks of the MCA adduct with the formation of a material similar in composition and structure to the g-C₃N₄ materials obtained by pyrolysis of melamine and other precursors.

The specific surface area of the target carbon nitride significantly depends on the morphology of the starting (M:CA)_n, and the smaller crystallite size (<D>) of the adduct provides better textural characteristics [42]. This parameter, in turn, depends on the synthesis methodology. However, the solubility of melamine and cyanuric in water, DMSO, or other organic solvents is rather low. In a series of experiments, the influence of a solvent type and the deposition temperature on the characteristics of the resulting nanosols and the specific surface area of the final carbonized MCA was studied (Table 1). Herewith, the single-point BET method was used for the screening study of specific surface area of the synthesized samples of carbonized MCA adducts. Nanosols obtained from low-concentration solutions of M and CA in water and DMSO were studied using the dynamic light scattering (DLS) method, in which the hydrodynamic particle diameter was determined. As can be seen from the obtained data (Table 1), there is a certain correlation between the particle size in solution and specific surface area of the obtained carbon nitride. In Figure 2 as an example, typical particle size distributions for different solutions are given. In the case of a good sample, a small particle size and a minimum content of large aggregates in solution

are observed. With an increase in the particle size and/or an increase in the fraction of large aggregates, the values of the obtained specific surface area of the samples decrease during the synthesis.



Figure 1. The structure of the melamine: cyanuric acid adduct (melamine cyanurate).

Table 1. An effect of cyanurate-melamine synthesis methodology on the particle size of MCA and the specific surface area of MCA-derived carbon nitride.

Method	Solutions Used for Precipitation (Solvent, Concentration, Temperature)		<d> in MCA-Solvent Suspension *. nm</d>	SSA ** of Calcined	
	Melamine (M)	Cyanuric acid (CA)		(,pro, , g	
m1	H ₂ O,	H ₂ O,			
	~0.2%	~0.2%	194	61	
	25 °C	25 °C			
m2	H ₂ O,	H ₂ O,			
	~2.5%,	~2.5%,	366	24	
	90 °C	90 °C			
m3	DMSO,	DMSO,		72	
	~2.5%,	~2.5%,	130		
	25 °C	25 °C			
m4	DMSO,	DMSO,			
	~7.5%,	~7.5%,	288	34	
	25 °C	25 °C			
m5	HCl-H ₂ O (1 M),	NH ₄ OH-H ₂ O (1 M),			
	~2%,	~2%,	201	59	
	25 °C	25 °C			

* Particles diameter according to DLS method; ** by single-point N_2 adsorption.



Figure 2. Intensity distribution for the suspensions prepared by m2 (red line) and m3 (blue line) methods.

An elevated precipitation temperature enables to obtain large amounts of $(M:CA)_n$, which, taking into account the low solubility of the initial reagents, is important for the development of a technological synthesis method. However, it has been shown that an increased precipitation temperature leads to an increase in the MCA average crystallite size and, consequently, to a decrease in the specific surface area of the carbonized product.

The use of dimethyl sulfoxide instead supposedly provides better solubility, which favorably affects SSA. However, increasing the concentration of melamine and cyanuric acid in DMSO up to the solubility limits also led to the SSA decrease. In addition, it was shown that the use of ionic solutions of melamine and cyanuric acid containing, respectively, hydrochloric acid and ammonium hydrate makes it possible to increase the solubility of the starting compounds. When MCA was precipitated from this solution, <D> values comparable to those of the m3 method (Table 1) were achieved. The subsequent separation of the resulting adduct by centrifugation allows for obtaining a carbonized product with an SSA of 59 m²/g (carbonization temperature 450 °C).

At the next stage of research, using the method developed for m5, the influence of the carbonization temperature (Table 2, Figure 3) and M:CA ratio (Table 1) on the textural characteristics and the yield of the carbonization product was studied. As a result of the investigation, it was shown that despite a significant increase in the specific surface area at an elevated carbonization temperature, there is a significant decrease in the product yield [43,44]. In this case, a darkening of the carbonized sample from light to dark gray was noted, which is presumably associated with carburization.

According to the SEM data (Figure 3), an increase in carbonization temperature leads to a significant change in the surface morphology of the MCA. In this case, according to EDX data, oxygen-containing fragments are predominantly decomposed with the formation of a material similar in composition to the carbonization product of pure melamine.

It was shown (Table 3) that a gradual decrease in the content of cyanuric acid leads to an increase in the yield of the carbonization product up to the values typical for the pyrolysis of pure melamine [45].

Carbonization Temperature, °C	Yield of Carbonization Product, %	BET SSA *, m ² /g	
300	78	4	
400	47	3	
450	35	59	
500	21	71	
550	11	121	

Table 2. Effect of carbonization temperature on the support yield and the BET specific surface area(SSA) of carbon nitride prepared by m5 method.

* by single-point N₂ adsorption.



Figure 3. SEM images of samples carbonized at 400 $^{\circ}$ C (**A**) and 550 $^{\circ}$ C (**B**) demonstrating the effect on the resulting material morphology.

M:CA (mol:mol)	Temperature, °C	Yield of Carbonization Product, %	BET SSA *, m ² /g
1:0	550	34	3
0.9:0.1	500	29	12
0.67:0.33	500	24	41
0.5:0.5	500	21	71
0.6:0.4	500	9	65

Table 3. Effect of M:CA ratio on the carbon nitride BET SSA and material yield.

* by single-point N₂ adsorption.

The nitrogen adsorption-desorption isotherms on the samples with an M:CA ratio of 1:0 and 0.5:0.5 are given in Figure 4. One can see that the isotherms are very similar to each other except for the fact that the adsorption on the sample with M:CA = 0.5:0.5 becomes several times higher than that of the sample with M:CA = 1:0. Both isotherms are type II with hysteresis H3 according to the classification by IUPAC [46]. Figure 4 shows that despite the close yield of carbonization product, the addition of cyanuric acid enables to obtain a material with a significantly larger specific surface area even at a lower carbonization temperature. At the same time, the shape of the isotherms does not visually change, which indicates a similar shape of the pores of both supports. The type of hysteresis and the shape of the isotherm indicate that pores these samples are slit-like.

This type of isotherm is characteristic of macroporous and non-porous samples. Thus, the addition of cyanuric acid does not result in the formation of mesopores. The pore size distribution, calculated using the BJH method applied to the desorption branch of isotherms, does not show any mesopores as well (Figure 5). The maximum of the differential curve





Figure 4. The isotherms of nitrogen adsorption-desorption at 77 K on the samples with different content of cyanuric acid (for nomenclature, see Table 3) after calcination. (**A**)—the sample with M:CA = 1:0, (**B**)—the sample with M:CA = 0.5:0.5.



Figure 5. Pore size distribution dV/dlogD normalized to the maximum of this distribution in products of condensation of melamine and cyanuric acid. Calculation by BJH procedure using the desorption branch of isotherms. The peak at 4 nm should be ignored because it is the widely known artifact of nitrogen adsorption [47].

The larger pore size of the MCA-500 sample not only allows for supporting the active component in a more dispersed form due to the high specific surface area of this

material, but also provides an additional benefit due to the opportunity for higher catalytic conversion rates with less mass transfer restrictions.

In contrast to well-crystallized g-C₃N₄, MCA-550 materials obtained by $(M:CA)_n$ calcination differ significantly in morphology. According to scanning electron microscopy data, a greater disorder and a looser structure of the samples are observed upon passing from g-C₃N₄ to MCA-500 (Figure 6).



Figure 6. SEM images of g-C₃N₄ (A) and MCA-500 (B) supports.

This conclusion also agrees with the X-ray diffraction data (Figure 7). The diffraction patterns of the g-C₃N₄ and MCA samples show two main reflections at positions 13.2° and 27.3°, which correspond to peaks (100) and (002) in the C₃N₄ structure, respectively. However, the MCA sample is characterized by a more disordered structure, which is explained by a larger specific surface area. The most intense reflection (002) refers to the interplanar distances arising from the stacking of graphite-like conjugated heptazine aromatic fragments. The determined distance from the magnitude of this reflection is 0.32 nm, which is in good agreement with the data for standard carbon nitride (JCPDS 87–1526). Moreover, wide diffraction peaks for MCA samples in the range 22–25° resemble diffraction patterns from C₃N₄ nanosheets [48–50]. Apparently, in the case of the MCA sample, the heptazine layers are more disordered compared to usual g-C₃N₄ samples. They, most probably, can refer to residual heptazine structures. Earlier, the formation of such low-intensity reflections for C₃N₄ was found in [51–53].

According to the literature data [49,54,55], different ratios of the intensities of the (100) and (002) reflections are typical for carbon nitrides with different order degrees. For strongly disordered carbon nitrides, the intensity of the (100) reflection is strongly reduced compared to the (002) reflection or may even be completely absent. Therefore, the $I_{(100)}/I_{(002)}$ reflection intensity ratio can serve as a comparative test for assessing the disorder of the carbon nitride structure. In our case, for the g-C₃N₄ sample, the $I_{(100)}/I_{(002)}$ value is 0.19, while for the MCA sample, this value is 0.09. Based on these data, it can be assumed that the MCA sample is more disordered than g-C₃N₄.

According to the SAXS data (Figure 8), all C_3N_4 samples have typical disordered porous structures, such as usual porous supports without any peculiarities. In the Porod region towards higher q values, the power law $I(q) \sim q^{-x}$ gives a slope of x = 4.0 for the g-C₃N₄ sample and x = 3.7 for MCA, respectively. Powders with a uniformly smooth surface are characterized by Porod slopes of 4.0, whereas values of 3 < x < 4 correspond to the surface fractal structure. Therefore, the surface of MCA compared to the g-C₃N₄ has more defect character. Furthermore, the MCA sample is also characterized by smaller

values of structural parameters in comparison with the $g-C_3N_4$ sample. Thus, for MCA, the correlation length value determined from the SAXS data was 38.6 nm, while for the $g-C_3N_4$ sample, the analogous value was 47.2 nm. Moreover, the value of the radii gyration (R_G) for the MCA sample was 22.0 nm, while for the $g-C_3N_4$ sample, the same R_G value was 30.0 nm. The values of the specific surface area according to the Porod model were 77 m²/g for MCA-500 and 29 m²/g for the $g-C_3N_4$ sample. On the whole, this is in good agreement with the BET data. In general, the MCA sample, compared to the $g-C_3N_4$, has a more powerful and openwork porous structure.



Figure 7. X-ray diffraction patterns of samples ($g-C_3N_4$ (red line) and MCA (black line)). The inset shows a comparison of enlarged fragments of the diffraction patterns of 1%Pd/g-C₃N₄ (blue) and g-C₃N₄ (red). Weak reflections of metallic Pd are noted that correspond to the reference Pd structure (JCPDS 46-1043).



Figure 8. SAXS patterns of samples (g-C₃N₄ (red line) and MCA-500 (black line)).

Using high-resolution transmission electron microscopy, changes in the morphology of particles of the initial (M:CA)_n and graphite-like carbon nitride obtained on its basis were studied. According to the obtained data, elongated particles were found (length— 200–400 nm, thickness—30–50 nm) on micrographs of the original MCA (Figure 9A,B). After the heat treatment, these particles are destroyed via opening into sheets consisting of several layers of carbon nitride. (Figure 9C,D). According to EDX analysis of studied samples, quantities of C, N, and O were equal to $50.6 \pm 5.9\%$, 47.6 ± 5.6 , and $1.8 \pm 0.4\%$, respectively.



Figure 9. HRTEM images of (M:CA)_n (A,B) and MCA-500 (C,D) samples.

The samples of carbon nitrides were also studied by the XPS method. Figure 10 shows the C1s and N1s spectra for g-C₃N₄ and MCA, respectively. The C1s spectrum is well described by three peaks with binding energies around 285.1, 288.1, and 293.5 eV. The first peak is characteristic of carbon-containing impurities present on the surface of samples under study (often used to calibrate the binding energy scale). The second peak is characteristic of C1s g-C₃N₄ and corresponds to carbon forming bonds with nitrogen atoms in the g-C₃N₄ structure, and the last peak corresponds to π -excitation [56,57]. In the case of the N1s spectrum, four peaks are observed with binding energies in the region of 398.6, 400.0, 401.0, and 404.5 eV. According to the literature data, the first peak refers to nitrogen atoms forming the C-N=C bond, the second one to the N-(C)₃ bond with three carbon atoms, and the third peak to the N-H terminal groups [56,57]. The fourth peak corresponds to an excited π bond. The [N]/[C] atomic ratios calculated from XPS data were 1.27 and 1.40 for MCA and g-C₃N₄ may also indicate some disordering of this material compared to the initial carbon nitride.



Figure 10. XPS spectra C1s and N1s for MCA and g-C₃N₄ samples correspondingly.

3.2. Investigation of the Catalytic Activity in Decahydroquinoline Dehydrogenation, Pd Dispersity and Palladium Valence State for Pd/Carbon Nitride Systems

Figure 11 shows the reaction scheme for the stepwise dehydrogenation of decahydroquinoline using synthesized palladium-containing catalysts. The reaction takes place with the formation of intermediates—1,2,3,4-tetrahydroquinoline (4HQc) and 5,6,7,8- tetrahydroquinoline (4HQn). In this case, according to the GC data of the reaction mixtures, the contribution of the route through 4HQn is not significant and agrees with the previously obtained data for Pd/ γ -Al₂O₃ catalysts [7]. This is due to the significantly higher dehydrogenation rate of the nitrogen-containing quinoline ring ($\Delta G_f = 49.6 \text{ kJ/mol}$, according to the calculated data [7]), as compared to the carbon ring (64.5).



Figure 11. A scheme of decahydroquinoline dehydrogenation.

As the main parameter for evaluating the catalytic activity of the $Pd/g-C_3N_4$ samples under study and the Pd/C reference catalyst, the yield of hydrogen from the theoretically possible value for 1 h of reaction was used. Chromatograms of the reaction mixtures showed tetraglyme (solvent), decahydroquinoline (initial substrate), and dehydrogenation products, with insignificant (<1 mol.%) admixture of 1,2,3,4-tetrahydroquinoline. It should be noted that for all catalytic tests using carbon supports (g-C₃N₄, MCA, C), no by-products of decahydroquinoline decomposition, as well as products of substitution of the N-heterocycle by alkyl fragments, were detected on chromatograms of the reaction mixtures. In turn, when Pd/ γ -Al₂O₃ was used, the content of N-methyl- and N-ethyl-1,2,3,4-tetrahydroquinolines was noted in the reaction mixtures (less than 0.5 mol % in total). This is presumably related to the reaction of alkylation of the N-heterocycle by the decomposition products of the reaction solvent (tetraglyme), which occurs on the alumina acid sites.

It was shown that the use of the wet impregnation technique (wi, Table 4) generally results in less efficient catalysts for 10HQ dehydrogenation. Although the catalysts comparable in activity (ai-1%Pd/g-C₃N₄~wi-1%Pd/g-C₃N₄) were obtained using standard low-surface area g-C₃N₄, the ai-1%Pd/MCA-500 catalyst is significantly superior in activity wi-1%Pd/ISA-500. Presumably, in the case of the exfoliated support g-C₃N₄, wet impregnation does not allow one to obtain catalysts with a high dispersion of the supported metal. The hydrogen yield when using ai-1%Pd/MCA-500 (M:CA = 1) significantly exceeds those for 1%Pd/MCA-500 samples with a large M:CA ratio, which is probably due to the lower disorder of the exfoliated layers of carbon nitride.

Catalyst	Impregnation Method	M:CA Ratio (mol:mol)	D _{CO} , %	YH _{2,} %
g-C ₃ N ₄ or MCA-550	-	-	-	0
1%Pd/g-C ₃ N ₄	wi	1:0	17	45
1%Pd/g-C ₃ N ₄	ai	1:0	18	43
1%Pd/MCA-500	wi	(1:1)	20	58
1%Pd/MCA-500	ai	(1:1)	30	94
1%Pd/ MCA-400	ai	(1:1)	_ **	12
1%PdMCA-500	ai	(0.67:0.33)	22	71
1%Pd/MCA-500	ai	(0.9:0.1)	20	50
1%Pd/C	- *	-	41	78

Table 4. Catalytic activity of Pd-containing catalysts in dehydrogenation of decahydroquinoline.

* commercial catalyst; ** not measured.

According to high-resolution electron microscopy data, the ai-1%Pd/MCA-500 catalyst contains Pd nanoparticles with sizes from 0.5 to 4 nm (Figure 12). The presence of single palladium atoms fixed on the surface can also be seen in the TEM images. In this case, individual palladium atoms were not used in the construction of the particle size histogram due to the low contrast. The average particle size of palladium was 1.6 ± 0.6 nm. It is interesting to note that, according to the data of CO chemisorption, the dispersity of Pd supported on carbon nitride does not exceed 30% (Table 4). Such dispersion, in terms of CO chemisorption, should correspond to much larger metal particles with sizes of \approx 4 nm [58]. At the same time, it was shown that CO is not effectively adsorbed onto very small clusters and individual palladium atoms, which leads to an underestimation of the dispersion of supported palladium according to CO chemisorption data [59]. Therefore, such discrepancy between different methods only confirms the formation of extra small Pd nanoparticles, clusters, and single atoms on carbon nitride support. At the same time, much larger sizes of palladium particles are observed for the 1%Pd/g-C₃N₄ sample (Figure 13).



Figure 12. (A,B) HRTEM images of 1%Pd/MCA-500.



Figure 13. (**A**,**B**) HR SEM images of 1%Pd/g-C₃N₄.

According to microscopy data, the average size of Pd particles was 5.1 ± 3.6 nm. According to the XRD data for the 1% Pd/g-C₃N₄ sample, low-intensity reflections corresponding to the metallic Pd structure are also observed (Figure 7, inset). From this data, the CSR size of Pd nanoparticles can be estimated at \approx 3–4 nm. In the case of the 1%Pd/MCA-500 sample, no reflections corresponding to the palladium structure are observed in the diffraction patterns, which additionally confirms its high dispersity. It is necessary to note that the ratio of average sizes of palladium particles for the 1%Pd/g-C₃N₄ and 1%Pd/MCA-500 samples, according to the microscopy data and CO chemisorption, differs (3.2 vs. 1.8) that also indicates a possible underestimation of CO chemisorption for assessing the sizes of very small supported palladium particles.

Figure 14 shows the Pd*3d* spectra of the studied 1%Pd/g-C₃N₄ and 1%Pd/MCA-500 catalysts. In both cases, the Pd*3d* spectra show the presence of two different valence states of palladium. The first component with a Pd*3d*_{5/2} binding energy of 335.2 eV is characteristic of metallic palladium. The binding energy of the second component of the spectrum, equal to 337.5 eV, can be attributed to the valence state of Pd²⁺ [60,61]. In addition, an increased value of the Pd*3d* binding energy, which is close to the Pd²⁺ valence state, can also be attributed to individual Pd atoms on the support surface [62–64]. The Pd⁰/Pd²⁺ ratio, according to XPS data for the 1%Pd/g-C₃N₄ and 1%Pd/MCA-500 samples, was 1.51 and

1.07, respectively. Taking into account the significantly higher dispersion of palladium in the 1%Pd/MCA-500 sample, it can be assumed that the second component in the Pd3*d* spectrum for 1%Pd/MCA-500 refers not only to Pd²⁺ but also to individual atoms and small Pd clusters on the carbon nitride surface.



Figure 14. XPS spectra of Pd3*d* of 1%Pd/g-C₃N₄ (A) and 1%Pd/MCA-500 (B).

4. Conclusions

Thus, a series of exfoliated carbon nitrides MCA-T were synthesized from melamine cyanurate with a specific surface area of up to 121 m²/g. Based on the data on the yield of the carbonization product, the optimal support synthesis temperature and the M:CA ratio were selected. The MCA-500 support was used for the synthesis of a palladium-containing catalyst. It was shown that the use of the adsorption precipitation technique allows for obtaining 1 wt% Pd/MCA-500 catalysts with an ultrafine distribution of palladium, where this noble metal is represented by atomic and 1–2 nm Pd particles. The synthesized samples were studied in the dehydrogenation of decahydroquinoline and it was shown that the 1 wt% Pd/MCA-500 catalyst is significantly superior in activity (94% hydrogen yield per reaction hour) to the low-surface analog 1 wt% Pd/g-C₃N₄ (45%) and prototype 1 wt% Pd/C (78%) catalysts.

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