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CONVERSION OF CARBOHIDRATES ON MODIFIED GRAPHITE-LIKE CARBON NITRIDES

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The new efficient heterogeneous catalysts on the basis of modified polymer carbon nitrides are developed for the conversion of hexose carbohydrates to 5-hydroxymethylfurfural (HMF) – the most important basic compounds for the modern chemical industry. Carbon nitride was modified by interaction with HCl, PCl₅ and CrCl₃. The structure and composition of the modified carbon nitrides have been studied by IR spectroscopy and X-ray diffraction analysis. Established, that propounded catalysts provide the selective conversion of hexose carbohydrates into 5-hydroxymethylfurfural with a minimum yield of humic compounds under mild conditions.

Keywords: *vegetable carbohydrates, catalysis, graphite-like carbon nitride, 5-hydroxymethylfurfural.*

Introduction

The search for new renewable sources of raw materials for the chemical industry is a top priority for modern science. The conversion of the fastest-renewable source of organic carbon as cellulose and its derivatives into valuable chemicals such as fuels, polymers, agrochemicals etc., can be considered one of the promising directions in this field. 5-Hydroxymethylfurfural (HMF) – the product of dehydration of carbohydrates – are considered today as one of the versatile platform for the chemical technologies of the future [1, 2]. However, the selective production of HFM is complicated by the secondary processes of the formation of humic substances and oligomeric products during dehydration of carbohydrates and by the competitive rehydration reaction of the preliminarily formed HMF to levulinic acid (LA).

The traditional methods of carbohydrates dehydration are based on the application of strong mineral acids, as well as ion-exchange resins, zeolites and heteropolyacids as catalysts [3, 4]. The main difficulty in the realization of acid-catalyzed processes is a low selectivity at high substrate concentrations. High yields of the target products can be achieved only in the cases of using carbohydrates solutions with a concentration of no more than 1–2%. The challenges of regeneration of acid catalysts remain unresolved.

The aprotic solvents such as dimethylsulphoxide, dimethylformamide, polyethylene glycol, etc. were tested in order to increase the yield of HMF [5–7]. However, the aprotic solvents have a high boiling point and poorly dissolve the carbohydrates that adversely affect the synthesis of the desired products.

In recent years, the ionic liquids have been actively studied for the conversion of plant carbohydrates [8, 9]. They possess high thermal stability, excellent solubility, low melting point and demonstrate both as highly effective and selective solvents and as components of the various catalytic systems. A number of Lewis acids such as metal chlorides, especially CrCl₂, CrCl₃, LaCl₃, SnCl₄, etc., in the medium of ionic liquids allow to achieve high yields of HMF not only from fructose, but also from cheaper carbohydrates such as glucose, sucrose, starch, cellulose, lignocellulose biomass [5, 10–13]. The yield of the target products up to 60–90% on catalytic systems of this type in the temperatures range of 80–120⁰C and short reaction times with a quantitative conversion of the feedstock. However, scaling this method with the use of ionic liquids involves a number of difficulties, such as the high cost of reagents and catalysts, the difficulty in isolating the products and reusing the catalytic system. The negative impact on the environment of bioun-

degradable ionic liquids and heavy metal salts also limit the widespread application of these catalysts in practice.

The key problem is to achieve a high yield and selectivity of the target products with a reduced formation of humus substances at relatively low temperatures under conditions of heterogeneous catalysis with the possibility of catalyst recycling. In order to solve this problem, it was interesting to search the possibility of using graphite-type polymeric carbon nitride ($g-C_3N_4$) as solid organic catalyst for the conversion of carbohydrates. $g-C_3N_4$ possesses a high chemical and thermal stability, semiconducting properties and has been investigated intensively over the last decade as a multifunctional organic catalyst in many reactions [14]. However, low activity, a small specific surface area ($<10 \text{ m}^2/\text{g}$) and fast recombination of the photogenerated electron-hole pairs substantially limit the possibility of using $g-C_3N_4$ both in traditional chemical and in photo- and electrocatalysis. These problems are solved by modifying the surface and structure of $g-C_3N_4$ creating mesoporous morphology, using exfoliation and doping it by various functional groups and molecules. Based on these prerequisites, the polymeric carbon nitrides were functionalized by protonation and PCl_5 treatment followed by immobilization of $CrCl_3 \cdot 6H_2O$ into its structure. The prepared catalyst was tested in the dehydration reaction of D-fructose.

Experimental part

Fructose of food quality was used in the work.

The following reagents were also used: hydrochloric acid 37% concentration (Merck); chromium(III) chloride $CrCl_3 \cdot 6H_2O$ (Sigma-Aldrich Purum p.f.a., ≥ 98.0 , (RT); phosphorus(V) chloride PCl_5 (98%-Alfa Aesar).

Bulk $g-C_3N_4$ was obtained by stepwise thermal condensation of melamine in a corundum pot at $350\text{--}550^\circ\text{C}$ [14].

Melem was obtained by heating of melamine in a glass ampoule to 385°C . Heating to $385\text{--}390^\circ\text{C}$ was continued for 60 hours, after which the mass was cooled to room tempera-

ture. A light beige powder was obtained – pure melem – with a yield of 95.5%.

For protonation, grinded in mill $g-C_3N_4$ was stirred for 1 hour at room temperature with hydrochloric acid (1g/25 ml 37% HCl). The mixture was filtered, washed several times with deionized water, dried and thermally treated at 500°C .

The modification of the protonated $g-C_3N_4$ by PCl_5 was carried out by treating a carefully dried sample for 8 hours in a stream of argon under reflux. Residual PCl_5 was distilled off and the solid phase was stored in argon.

Immobilization of $CrCl_3 \cdot 6H_2O$ was carried out by impregnation. Protonated $g-C_3N_4$ was mixed with solutions of salts (6 mol%), stirred on a magnetic stirrer and then the precipitate was filtered off, washed with deionized water and dried.

The solvent – N-methylmorpholine-N-oxide (MMO) – was synthesized according to the well-known Eshweiler-Clark method with our own improvements [15].

The conversion process of fructose was carried out in stationary reactors at $100\text{--}120^\circ\text{C}$ for 2–5 hours. Then the solvent was distilled off from the reaction mixture on a rotary evaporator and HMF were extracted by toluene. The composition of the reaction products was determined chromatographically.

The following analysis methods were used:

- IR spectroscopy (Nicolet IS 10 Thermo Scientific),
- Fourier IR spectroscopy (Varian 660-IR),
- UV spectroscopy (SPECORD 1800 SHIMADZU),
- X-ray spectral analysis (X-ray diffractometer D2 Phaser, Bruker),
- gas-liquid chromatography (Agilent 7820A GC System, flame ionization detector, $0.32 \text{ mm} \times 30 \text{ m}$ HP-5 capillary column, temperature $60\text{--}325^\circ\text{C}$, using high purity ($>99.6\%$) He, H_2 and air).

Results and discussion

The process of acid conversion of hexoses can be represented by the scheme (Figure 1):

Fig. 1. Conversion of hexoses into HMF.

Obviously, the choice of solvent in this reaction is very important. Water is the most economical solvent for this purpose. However, in aqueous media the rehydration reaction of HMF into LA predominates, being the main reason for lowering the yields of target product [16]. To a large extent this is manifested at low temperatures – up to 100°C. The hydrolysis reaction of the obtained HMF can be suppressed, either by carrying out the process in an aqueous medium at high temperatures – over 200°C – to create an acceptable ratio of the rate constants (Figure 1), or by using aprotic solvents that do not form complexes and do not interact chemically with carbohydrates, while inhibiting the formation of by-products with the yield of HMF increasing. Preferring to aprotic solvents, we chose MMO – a solvent belonging to the group of true ("direct") solvents, in which the process of dissolution of plant carbohydrates occurs by the mechanism of direct solvation of molecules.

Preliminary studies have shown that g-C₃N₄ catalyses the conversion of carbohydrates at relatively low temperatures with a low yield of humic compounds. However, the activity of bulk g-C₃N₄ is low – the yield of HMF does not exceed 4–5%.

Protonation is a convenient way of modifying the properties of g-C₃N₄. Considering that g-C₃N₄ includes a large amount of nitrogen with potentially high basicity (–C–N–), the introduction of protons into structure should increase its acidity and, consequently, activity in the process of carbohydrates converting. The protonated adducts can be easily prepared by the interaction of polymeric carbon nitrides with strong mineral acids such as HClO₄, H₂SO₄ [17, 18]. The amount of introduced protons can be regulated by the use of acid of different concentrations. The addition of protons leads to better dispersity in aqueous solutions and, depending on the degree of protonation, even to a partial exfoliation of the structure. As a result of protonation, the surface area of g-C₃N₄ increases from 9–10 to 28 m²/g. Exfoliation of protonated samples by ultrasonic treatment can yield samples with a surface area of 300–380 m²/g [19]. The protonated g-C₃N₄ can be deprotonated to the initial state by heating in an inert atmosphere while maintaining a high surface area [20].

The protonation process can be represented by the scheme (Figure 2).

It should be noted that protonation occurs exclusively at the sites of the nitrogen atoms of the heptazine ring, while the NH₂ groups remain unchanged. As shown by IR, X-ray spectra, its structure remains intact after protonation. Fourier IR spectra of protonated g-C₃H₄(g-C₃N₄–H⁺Cl[–]) show the presence of typical bands responsible for C–N – heterocycled in the range 1100–1600 cm^{–1}; there are no peaks corresponding to amide or hydroxyl groups, which could be attributed to broken fragments.

Fig. 2. Protonation reaction of g-C₃N₄.

Fig. 3. The X-ray diffraction pattern of 1 – g-C₃N₄, 2 – protonated g-C₃N₄ (g-C₃N₄-H⁺Cl⁻).

Moreover, in X-ray spectra the presence of a completely preserved g-C₃H₄ structure was established (Figure 3). As can be seen from the comparison of these two X-ray patterns, the position of the (002) peak characteristic for g-C₃H₄ is conserved in g-C₃N₄-H⁺Cl⁻.

g-C₃N₄-H⁺Cl⁻ can easily be subjected to further postfunctionalization by exchanging anions in order to obtain new hybrid composites.

Doping with phosphorus-containing compounds is often used to modify both the texture and surface properties and the electronic structure of g-C₃N₄. The layers of g-C₃N₄ contain the fragments with nitrogen, having 6 unpaired electron pairs, available for alloying with non-metals, therefore phosphorus is an ideal dopant for adjusting its texture and electronic structure.

Doping by a phosphorus atom is carried out using various precursors and by various ways. Thus, the authors of [21] doped g-C₃N₄ with phosphorus by thermal copolymerization using hexachlorocyclotriphosphazene – triazine-like heterocyclic compound containing a double bond P=N – as a source of phosphorus and guanidine hydrochloride as a precursor. Doped with phosphorus g-C₃N₄ with improved photocatalytic activity was synthesized using dicyandiamide and ionic liquid – 1-butyl-3-methylimidazolium hexafluorophosphate – as a soft source of phosphorus [22]. A simple method with the use

of dicyandiamide and ammonium hydrophosphate – (NH₄)₂HPO₄ – as precursors was proposed in [23].

Since the location of the doped phosphorus atom should significantly influence the behavior of the resulting material in both chemical and photocatalysis, a special attention is paid to determining the locality of doping. Summarizing the data available in the literature, it is generally accepted today that the location of doping with phosphorus is determined by the nature of the precursor itself – the source of phosphorus. In the case of an ionic liquid, doping occurs by replacing the carbon atoms in the heptazine cycle and the phosphorus atom is bound to three nitrogen atoms. In the case of (NH₄)₂HPO₄, phosphorus is introduced into the space between the heptazine cycles forming the polymer network g-C₃N₄, while the phosphorus atom binds to two nitrogen atoms inside closed cycle of space in planar layers. Combining the doping process with the simultaneous condensation of precursors does not allow this practice to be extended to the unstable dopants at high temperatures.

We applied our own doping technique by introducing doped elements into the already formed g-C₃N₄ lattice. The modification of g-C₃N₄ was performed with the participation of PCl₅. The choice of the dopant is justified by

the fact that is shown in [24, 25], the presence of chlorine ions in the catalytic system for the conversion of carbohydrates has a positive effect on the dissolution and hydrolysis of di- and polysaccharides, on the isomerization of glucose and on the dehydration of fructose.

The modification process was studied on a model compound – melem (2,6,10-triamino-sim-heptazine) – the elementary building block of polymeric carbon nitride. A common scheme for obtaining phosphorus-containing triazines is the Kirsanov reaction [26]. In accordance with the concept put forward by him, the reaction of the melem with PCl_5 proceeds according to the following scheme (Figure 4):

Fig. 4. The reaction of iminophosphorylation of melem in the presence of PCl_5 .

The high activity of the P–Cl bond in the modified $\text{g-C}_3\text{N}_4$ was tested in the reactions of the product 1 with water, alcohols, phenols – it exothermically reacts with these compounds to form alkoxy- or aryloxy-iminophosphorane derivatives with evolution of gaseous HCl, certifying, a nucleophilic attack on phosphorus.

Relatively low melting point, good solu-

bility and high reactivity of the product 1 make it a good starting substrate for further modifications and synthesis of various $\text{g-C}_3\text{N}_4$ derivatives.

After recrystallization of the product 1 from 1,2-dichloroethane, the colorless crystals of the by-product – 2,5,8-*tris*-(trichlorophosphinimino)-*s*-heptazine hydrochloride (product II) (Figure 5) are obtained, as a result of protonation of one nitrogen atom in product I:

Fig.5. 2,5,8-*tris*-(trichloro-phosphinimino)-*s*-heptazine hydrochloride.

The HCl molecule can be removed under vacuum at 100°C , again forming product I. The fact that protonation takes place on the heptazine ring, leaving the P–N group intact, indicates the great basicity of the N-atoms of the ring and the high stability of the P=N bond and coincides with the conclusions that protonation of melem by protic acids occurs on the nitrogen atoms of the ring [17, 18].

The reaction products were identified by IR spectroscopy (Figure 6). In IR spectra, strong bands characterize the heptazine nuclei (1625 , 1435 , 1270 cm^{-1}), P = N-groups (1370 , 1395 cm^{-1}), P–Cl-group (579 cm^{-1}). The IR spectrum

Fig. 6. IR spectra (in films between KBr plates): 1 – product I, 2 – product II, 3 – H^+ - $\text{g-C}_3\text{N}_4/\text{PCl}_5$.

of the modified $g\text{-C}_3\text{N}_4$ (spectral line 3) is identical to that of product I, a markedly broadened absorption region $P=N$ is related to the polymer nature of the product.

Numerous studies of recent years have found that one of the most effective catalysts for the synthesis of HMP from plant carbohydrates are chromium chloride [11, 12, 27]. The reaction with their participation proceeds under mild conditions, with high conversion without formation of by-products (99% and higher) and good yields of HMF. In this connection, CrCl_3 was injected into the synthesized systems of the composition $\text{H}^+g\text{-C}_3\text{N}_4/\text{PCl}_5$ to improve the efficiency of the developed catalysts. It is a stronger Lewis acid, more stable, convenient for working in air, and therefore its use is more preferable compared to chromium (II) chloride. The experimental data on the developed catalytic fructose conversion systems into HMF are given in Table.

The process of formation and accumula-

tion of HMF was monitored by UV spectroscopy at 285 nm. In the initial period of the reaction, the optical density increases at 228 nm, which is due to the accumulation of intermediates. The intensity of the optical density at 228 nm decreases in the course of the reaction as the concentration of HMF increases.

The formation of HMF is confirmed by IR spectroscopic method in the frequency range $4000\text{--}500\text{ cm}^{-1}$ (Figure 7).

Thus, based on the results of the conducted studies, it can be concluded that the process of converting fructose on synthesized heterogeneous catalytic systems is characterized by high feed conversions and target products yield. Conversion at relatively low temperatures ($100\text{--}120^\circ\text{C}$) and short reaction times and short reaction times (1.5–2 hours) reaches 60–90%, yield of HMF – up to 70% with a minimum yield of humic resins. The developed catalytic systems are regenerated by simple filtrate ion and applied in 5–6 reaction cycles.

Hydrolysis of D-fructose on various catalytic systems *

Carbohydrate	Catalyst	$t, ^\circ\text{C}$	τ , hour	Carbohydrate conversion, %	HMF, % ^{a)}
D-Fructose	$g\text{-C}_3\text{N}_4$	100	1.5	31	5
	CrCl_3	100	5.0	68	45
	$\text{H}^+g\text{-C}_3\text{N}_4$	120	1.5	58	40
	$\text{H}^+g\text{-C}_3\text{N}_4/\text{PCl}_5$	120	1.5	72	63
	$\text{H}^+g\text{-C}_3\text{N}_4/\text{PCl}_5/\text{CrCl}_3$	100	2.0	92	75

* Solvent – MMO, 5 ml; D – fructose – 200 mg, 1.11 mmol; CrCl_3 0.022 mmol relative to fructose; solid catalysts – 100 mg.

^{a)} The yield of HMF after the extraction procedure is completed.

Fig. 7. IR spectrum of D-fructose conversion products on a catalytic system $\text{H}^+g\text{-C}_3\text{N}_4$ (in films between two KBr plates).

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KARBOHİDRATLARIN MODİFİKASIYA OLUNMUŞ KARBON NİTRİDLƏR ÜZƏRİNDƏ KONVERSİYASI

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Modifikasiya edilmiş polimer karbon nitrid əsasında heksoz karbohidratların bir sıra müasir kimya sənayesində universal xammal kimi nəzərdə tutulan 5-hidroksimetilfurfurala konversiyası üçün yeni effektiv heterogen katalizatorlar işlənilib hazırlanmışdır. Bu məqsədlə karbon nitrid HCl, PCl₅ və CrCl₃ vasitəsilə modifikasiya olunmuş və İQ və Rentgen spektroskopiyaya üsulları ilə tədqiq edilmişdir. Hazırlanmış katalizatorlar yumşaq şəraitdə karbohidratların yüksək selektivliklə 5-hidroksimetilfurfurala konversiyasını təmin edir.

Açar sözlər: bitki karbohidratları, kataliz, qrafit tipli karbon nitrid, 5-hidroksimetilfurfuröl.

КОНВЕРСИЯ УГЛЕВОДОВ НА МОДИФИЦИРОВАННЫХ НИТРИДАХ УГЛЕРОДА

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Разработаны новые эффективные гетерогенные катализаторы на основе модифицированных полимерных нитридов углерода для конверсии гексозных углеводов в 5-гидроксиметилфурфурол – важнейшее базовое соединение для современной химической промышленности. Нитрид углерода модифицировали взаимодействием с HCl, PCl₅ и CrCl₃. Структуры и составы модифицированных нитридов углерода изучены методами ИК-спектроскопии и рентгеноструктурного анализа. Установлено, что предложенные катализаторы обеспечивают селективную конверсию гексозных углеводов в 5-гидроксиметилфурфурол с минимальным выходом гуминовых соединений в мягких условиях.

Ключевые слова: растительные углеводы, катализ, графитоподобный нитрид углерода, 5-гидроксиметилфурфурол.