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CAFFEIC ACID COMPLEXES OVER ALUMINA SURFACE: FTIR, TPD MS AND DFT CALCULATIONS

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Caffeic acid (CA) is a phenolic, natural, biologically active compound with pronounced antioxidant and antimicrobial properties. It has a great potential for use in medicine and cosmetology and can also be used to obtain a number of other useful chemicals. Therefore, research aimed at improving the technologies for removing caffeic acid from plant raw materials and its processing is relevant. In our work, we have studied the complexes of caffeic acid with nanosized Al₂O₃, which is usually used in various plant biomass conversion technologies, using FT-IR spectroscopy, temperature-programmed desorption mass spectrometry (TPD MS), and DFT calculations. The FT-IR spectra analysis shows that CA can interact with aluminum oxide via both the carboxyl and phenolic groups. Based on the measured differences between carbonyl symmetric and asymmetric vibrational peaks ($\Delta\nu$), it was found that carboxylate complexes of CA on the Al₂O₃ surface can have bidentate and monodentate structures. The mass spectrometric data analysis made it possible to identify compounds of 4-vinyl catechol, pyrocatechol, and phenol, which are decomposition products of the formed carboxylate and phenolic complexes. It was found that on the surface of the studied CA/Al₂O₃ samples, CA chelate complexes, formed with the participation of both OH groups of the aromatic ring, predominate.

Keywords: biomass, carboxylate complexes, chelate complexes, 4-vinyl catechol, pyrocatechol, phenol, pyrolysis, biomass conversion technologies

INTRODUCTION

Caffeic acid is a C6-C3 phenolic natural biologically active compound, which has pronounced antioxidant, antimicrobial and other biological activities [1–5], and has great potential for use in medicine [6, 7]. It is often found in plants that are used in food, and is mainly found in them as ester or bound to biopolymers [8]. CA, both free and esterified, is usually the most abundant phenolic acid and accounts for 75 to 100 % of the total hydroxycinnamic acid content in most fruits [9]. It is mainly involved in the synthesis of lignin, as well as the regulation of cell expansion, turgor pressure, phototropism, water flow and growth [10]. At the same time, a significant part of the biomass, which is the waste of the agro-industrial complex, can be used to obtain caffeic acid for use in medicine, cosmetology and other areas. In particular, the source of CA can be pulp of apples [12–15], grapes [15–19], tomatoes *etc.* [20, 21], which are by-products of juice

production and wines and are obtained in large quantities. At the same time, this biomass can be processed into other useful chemicals [22–37].

Aluminum oxide is one of the oxides commonly used as a catalyst and carrier, including in various plant biomass conversion technologies [38–41]. Therefore, the study of caffeic acid complexes, which they form when interacting with aluminum oxide, is significant for the development and optimization of CA-obtaining technologies, as well as technologies for processing plant raw materials into various chemicals that involve the use of aluminum oxide. In particular, data on the type of complexes formed and their relative amount on the oxide surface combined with data on their stability, as well as an understanding of the mechanisms of the biomass components transformations under the influence of various physical factors (irradiation, heating, solvents, and others) [11, 19, 20, 25, 23, 29, 32, 33], will

allow determining the possibilities of using Al_2O_3 in those or other technologies.

Therefore, our work is devoted to determining the complexes formed by caffeic acid with nanosized aluminum oxide using FT-IR spectroscopy, temperature-programmed desorption mass spectrometry, and DFT calculations.

EXPERIMENTAL

The research used caffeic acid ($\geq 98\%$, Sigma-Aldrich) and alumina (99.5% , $S_{\text{Ar}} = 89 \text{ m}^2/\text{g}$, Evonic), which had previously been calcined at 500°C for two hours to remove any organic based impurities.

CA/ Al_2O_3 samples (0.3 and 0.6 mmol/g) were prepared by impregnating 100 mg of aluminum oxide with 2 ml of a solution of caffeic acid in ethanol (96%). The resulting suspensions were mixed and dried in the open air at room temperature.

IR-spectral studies were performed using a Fourier transform Thermo Nicolet NEXUS device in the diffuse reflectance mode. For research, samples of CA/ Al_2O_3 and pure Al_2O_3 were mixed with KBr in a ratio of 1:10, and pure CA – in a ratio of 1:100. All samples were thoroughly ground for the same amount of time. The spectra were recorded with a resolution of 4 cm^{-1} . The scanning speed was 0.5 cm/s , and the number of scans was 50.

Examination of the samples using the method of temperature-programmed desorption mass spectrometry (TPD MS) was performed on a monopole mass spectrometer MH-7304A (Sumy, Ukraine) with electron ionization, converted for conducting thermodesorption measurements [42]. A sample weighing 10–20 mg was placed in a quartz-molybdenum ampoule and pumped at room temperature to a pressure of $\sim 5 \cdot 10^{-5} \text{ Pa}$. The sample was heated at the rate of 0.17°C/s from room temperature to 750°C . Volatile decomposition products entered the ionization chamber of the mass spectrometer, where they were ionized and fragmented under the influence of electrons. The intensities of the ion currents of the products of desorption and thermolysis in the mass analyzer were recorded by a secondary electron multiplier BEU-6. The range of investigated masses was m/z 1–220. Registration and analysis of mass spectra were carried out by an automated computer system.

Density functional (DFT) calculations were performed using the wB97XD functional with Grimme's D2 dispersion corrections [43] and the 6-311++G(d,p) basis set. Gaussian 09 software version B01 [44] was used. For the studied molecular systems, full geometry optimization was performed. The total charge of the system was zero. The results of the calculations were visualized using the molecular graphics program MaSK v. 1.3.0 [45]. As the simplest model of aluminum oxide, a cluster of composition $\text{Al}_2\text{O}_6\text{H}_6$ [46] was used.

RESULTS AND DISCUSSION

FT-IR spectroscopic study. To find out which functional groups of CA are involved in the interaction with surface of aluminum oxide, a spectroscopic study of the CA/ Al_2O_3 sample (0.3 mmol/g) was carried out by the FT-IR method (Fig. 1).

For the CA/ Al_2O_3 sample, the absence of an absorption maximum at 1645 cm^{-1} , which corresponds to valence vibrations of the carbonyl group ($\nu(\text{C}=\text{O})$) [47], was found. This indicates the formation of carboxylate complexes. The new broad band at 1630 cm^{-1} , which was masked by intense absorption of $\nu(\text{C}=\text{O})$ in the CA spectrum, probably refers to $\nu(\text{C}=\text{C})$ vibrations. A shoulder appears around 1670 cm^{-1} for CA/ Al_2O_3 , which may correspond to $\nu(\text{C}=\text{O})$. Whereas the absorption detected in the spectra of the studied samples in the region of 1394 cm^{-1} probably corresponds to $\nu(\text{CO})$ vibrations. It has been demonstrated that the magnitude of " $\Delta\nu$ " the separation between the asymmetric and symmetric carboxylate stretches ($\Delta\nu = \nu_{\text{as}}(\text{COO}^-) - \nu_{\text{s}}(\text{COO}^-)$) or, in case of monodentate coordination, between the $\text{C}=\text{O}$ and $\text{C}-\text{O}$ stretches ($\Delta\nu = \nu(\text{C}=\text{O}) - \nu(\text{CO})$) can be used to determine the type of the carboxylate (and non-dissociated acid) binding [48, 49].

The absorptions at 1670 cm^{-1} $\nu(\text{C}=\text{O})$ and 1394 cm^{-1} $\nu(\text{CO})$ most likely correspond to monodentate complexes, since the value of $\Delta\nu$ is 276 cm^{-1} . The assignment of absorption bands to mono- and bidentate complexes was previously made on the example of surface complexes of valeric acid on the surface of metal oxide catalysts (SiO_2 , $\gamma\text{-Al}_2\text{O}_3$, $\text{CeO}_2/\text{SiO}_2$, $\text{Al}_2\text{O}_3/\text{SiO}_2$ and $\text{TiO}_2/\text{SiO}_2$) based on the values of $\Delta\nu$ [28]. The results of quantum chemical calculations and IR spectroscopy [50] supported such an interpretation. According to [50], the absorption

at $\sim 1680\text{ cm}^{-1}$ detected for valeric acid corresponds to monodentate carboxylate complexes. In addition, the CA/Al₂O₃ spectra contain absorptions in the region of 1400 and 1568 cm⁻¹, which apparently correspond to

symmetric ($\nu_s(\text{COO}^-)$) and asymmetric ($\nu_{as}(\text{COO}^-)$) valence vibrations of carboxylate complexes. The structure of these complexes is bidentate, since $\Delta\nu$ is 168 cm⁻¹.

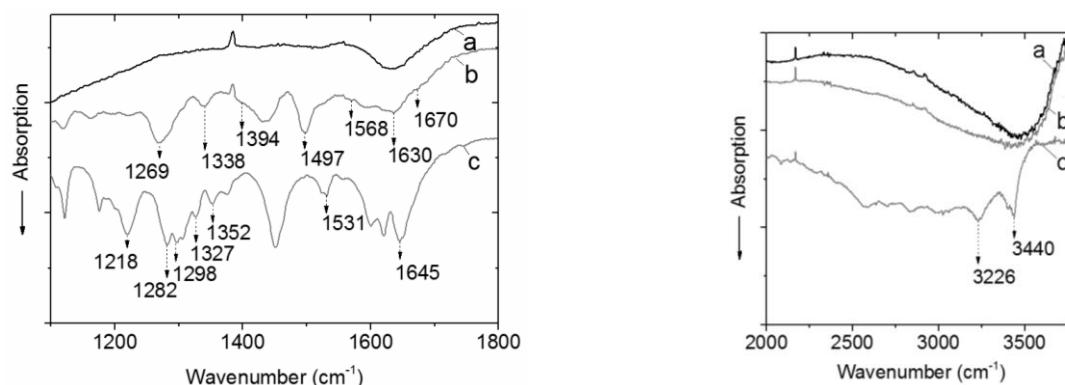


Fig. 1. FT-IR spectra in the regions 1100–1800 cm⁻¹ and 2000–3800 cm⁻¹: (a) pure Al₂O₃, (b) CA/Al₂O₃, (c) pure CA

Some changes were also detected in the region of valence vibrations of OH groups (Fig. 1 *b*). In particular, the maxima at 3226 and 3440 cm⁻¹ are not observed. There is only a broad band with a maximum of 3421 cm⁻¹. These bands belong to the valence vibrations of phenolic hydroxyls [47, 48]. The first maximum may correspond to phenolic groups forming intermolecular hydrogen bonds in CA associates. The maximum at 3440 cm⁻¹ is in the region where intermolecular hydrogen bonds in dimers of CA and intramolecular hydrogen bonds of CA are manifested [49]. Although the absorption of hydrogen-bonded OH groups of water, which may be present in the studied samples, may also appear here. The absence of a band at 3226 cm⁻¹ indicates the destruction of intermolecular hydrogen bonds between phenolic groups.

In addition, the part of the spectrum between 1000–1500 cm⁻¹ changes significantly for the CA/Al₂O₃ sample. Absorptions of COH-groups for phenolic and carboxyl groups appear here, so identifying bands in this part of the spectrum is challenging. The analysis of this area was performed based on a number of our own FT-IR spectroscopic studies of phenolic compounds [53, 54] and literature data [47, 55–57]. According to [47, 55], a broad intense band located around 1300 cm⁻¹, which often has several maxima, is due to the superimposition of COH vibrations of phenolic and carboxylic OH groups. For the CA/Al₂O₃ sample (0.3 mmol/g),

this band undergoes a transformation, in particular, its maximum shifts from 1282 to 1269 cm⁻¹. The peak at 1298 cm⁻¹, which may correspond to plane deformation vibrations of phenolic OH groups [47], practically disappears. In addition, the 1218 cm⁻¹ band, which is also attributed to COH vibrations [47], in the CA/Al₂O₃ spectrum (0.3 mmol/g) has a much lower relative intensity than for CA. The bands at 1327 and 1352 cm⁻¹ disappear, which can be manifested as plane deformation vibrations of OH groups [52]. Instead, absorption appears at 1338 cm⁻¹. Such changes may mean that not only the carboxyl OH group, but also phenolic groups participate in the interaction with the oxide. According to a number of literature data [58–60], the formation of CA complexes with the participation of phenolic groups can also be evidenced by the position of the two most intense bands in the CA/Al₂O₃ (0.3 mmol/g) spectrum - near 1269 and 1497 cm⁻¹. At the same time, the first of them is attributed to the C–OH valence vibrations of the aromatic nucleus, and the second to the $\nu(\text{C}=\text{C})$ vibrations of the benzene ring. This spectrum characteristic is a sign of chelate complexes forming phenolic groups of caffeic acid with various oxides [58–60].

DFT calculations. We calculated the possible structures of carboxylate complexes of caffeic acid on the aluminum oxide surface. Table 1 shows the value of the Gibbs free energy

at the temperature of 421 K (G421) for the calculated structures. The structures of CA complexes with a cluster of composition $\text{Al}_2\text{O}_6\text{H}_6$ are presented in Fig. 2.

According to the performed calculations, caffeic acid can form phenolate complexes (F1 and F2) and both monodentate carboxylate (C1-C3) and bidentate bridge (C4) complexes over alumina, Fig. 2.

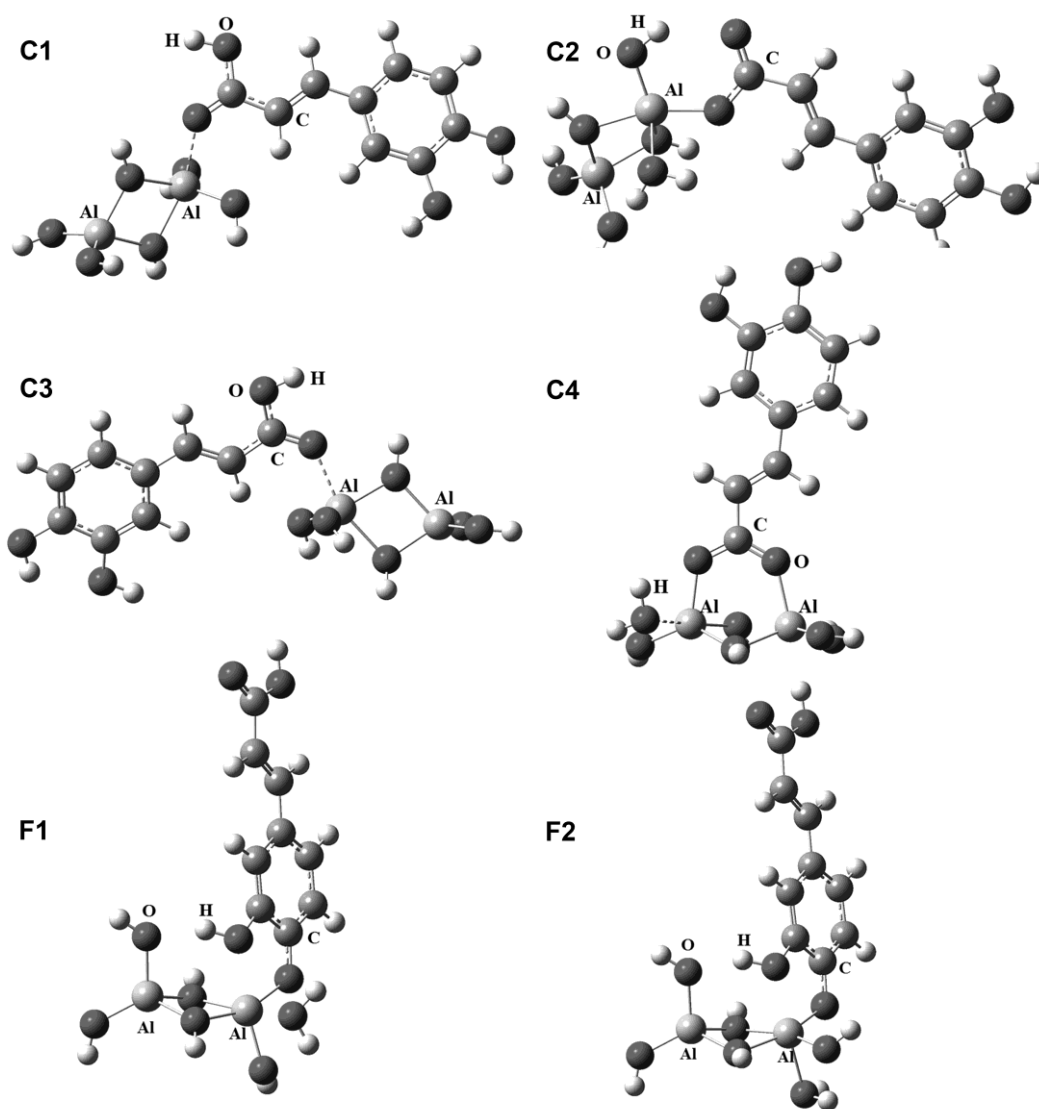


Fig. 2. Possible structures of caffeic acid complexes with alumina (carboxylate complexes: C1, C2, C3, C4 and phenolate complexes – F1, F2)

Table 1. Gibbs free energy values for the temperature 421K (G421) for the calculated structures of caffeic acid complexes over alumina

G_{421} , a.u.					
C1	C2	C3	C4	F1	F2
-1588.771629	-1588.778037	-1588.773954	-1588.774137	-1588.787403	-1588.786720

Study of the $\text{CA}/\text{Al}_2\text{O}_3$ sample by the TPD MS. The pyrolysis of CA occurred in the temperature range from 100 to 600 °C and was

accompanied by the formation of a large number of products with m/z from 3 to 178, which can be seen in the mass spectra obtained during the

TPDMS study of the sample of CA/Al₂O₃ (0.6 mmol/g) (Fig. 3). The main products of CA decomposition on the Al₂O₃ surface included: 4-vinyl catechol (m/z 136, 110–400 °C), catechol (m/z 110, $T_{\max} = 123$ °C), phenol (m/z 94, $T_{\max} = 409$ °C and others). In the process of pyrolysis, H₂O (m/z 18), CO₂ (m/z 44), and CO (m/z 28) were released intensively. Based on the analysis of the obtained TPD MS data (Fig. 3) and the results of studies of the thermal decomposition of cinnamic acids on the surface of ceria [53], certain conclusions can be drawn about CA complexes that form on the aluminum oxide surface.

From the results [53, 54, 61], it is clear that the destruction of carboxylate complexes of cinnamic acids on the CeO₂ occurs mainly by decarboxylation and the formation of the corresponding vinyl phenol (styrene). At the same time, it is shown that decarboxylation of various types of carboxylate complexes occurs at different temperatures. It is known that free phenolic acids, particularly caffeic, undergo decarboxylation both under the influence of temperatures [62] and in the metabolism processes of various microorganisms [63].

As shown in Figs. 3 and 4, 4-vinyl catechol (M.r. = 136 Da, m/z 136) belongs to the main decomposition product of CA pyrolysis over alumina. Its formation was registered in a wide range of temperatures (110–400 °C). Thus, its release is probably related to the destruction of various types of carboxylate complexes and associates of CA, which are formed when the CA amount increases on the surface of the oxide, whereas catechol (m/z 110) and phenol (m/z 94) (Figs. 3, 4) can be products of the destruction of complexes formed with the participation of phenolic OH groups [53]. The first compound may be a product of the decomposition of CA molecules bound to the Al₂O₃ surface through one aromatic hydroxyl. Phenol is probably released during the destruction of chelate complexes formed due to the interaction of both phenolic groups of CA with the oxide surface. Thus, the registration of these compounds in the mass spectra of CA/Al₂O₃ during heating can be a sign of the presence of a number of carboxylate and phenolic complexes on the Al₂O₃ surface, which was also revealed by FT-IR spectroscopic data.

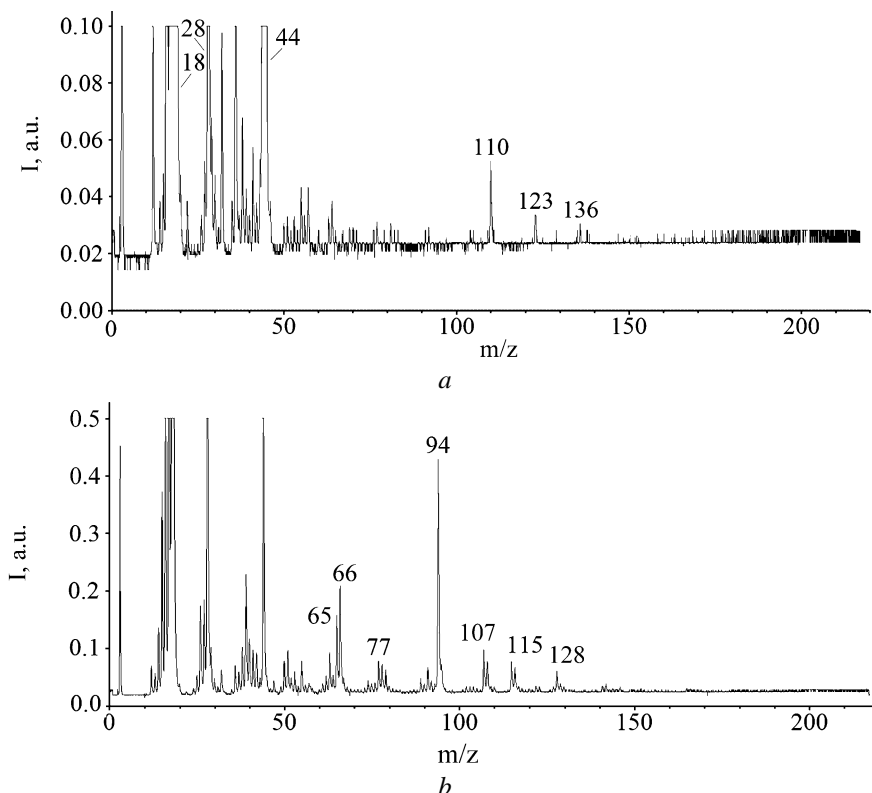


Fig. 3. Mass spectra of pyrolysis products of the CA/Al₂O₃ sample, obtained at temperatures of 194 °C (a) and 400 °C (b)

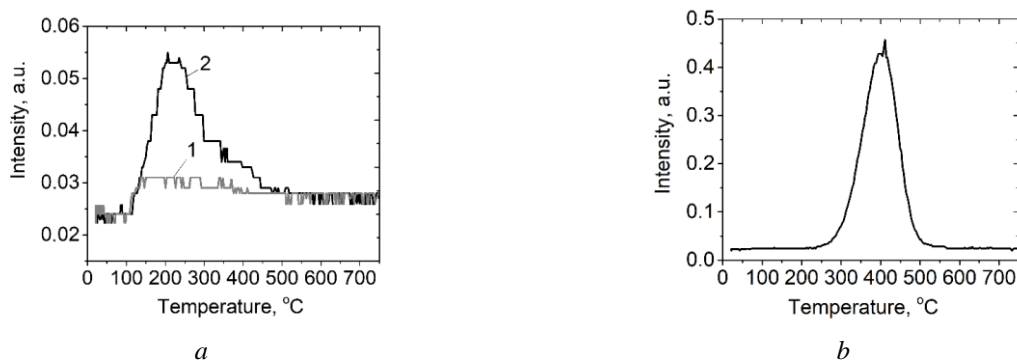


Fig. 4. TPD curves of molecular ions of (a) vinyl catechol (m/z 136, curve 1), catechol (m/z 110, curve 2); and (b) phenol (m/z 94), obtained during pyrolysis of the CA/ Al_2O_3 sample

At the same time, the high relative release intensity of phenol (m/z 94) compared to catechol (m/z 110) and vinyl catechol (m/z 136) may indicate a significant content of complexes that are formed with the participation of both phenolic groups. This is consistent with the results of the FT-IR spectroscopic study. As shown in Fig. 1, the relative intensity of the carboxylate bands is relatively low. In addition, it is known that caffeic acid, which has *o*-substituted hydroxyl groups in its structure, can form chelate phenolic complexes with metals [60, 64, 65].

CONCLUSIONS

Samples of CA over the alumina surface were investigated using FT-IR spectroscopy, TPD MS, and quantum chemical methods. From the obtained FT-IR spectroscopic data, it was found that the interaction of CA with aluminum oxide takes place with the participation of both carboxyl and phenolic groups. The formation of such products as 4-vinyl catechol (M.r. = 136 Da,

m/z 136), catechol (M.r. = 110 Da, m/z 110) and phenol (M.r. = 94 Da, m/z 94), which were registered by TPD MS in the study of CA/ Al_2O_3 samples, was associated with the destruction of a number of carboxylate and phenol complexes of CA. This can serve as confirmation of the presence of these complexes on the Al_2O_3 surface. The obtained data indicate that phenolic complexes predominate for the studied samples.

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Комплекси кавової кислоти на поверхні оксиду алюмінію: ІЧ спектроскопія, ТПД МС та DFT розрахунки

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Кавова кислота є фенольною природною біологічно активною сполукою з вираженими антиоксидантними та антимікробними властивостями, яка має великий потенціал застосування в медицині і косметології, а також може використовуватися для отримання ряду інших корисних хімікатів. Тому дослідження, спрямовані на вдосконалення технологій вилучення кавової кислоти з рослинної сировини, а також її переробки, є актуальними. В нашій роботі вивчалися комплекси кавової кислоти з нанорозмірним Al_2O_3 , який зазвичай застосовують в різних технологіях конверсії рослинної біомаси. Структуру та тип утворених комплексів СА досліджено за допомогою ІЧ-спектроскопії, температурно-програмованої десорбційної мас-спектрометрії (ТПД МС) та квантовохімічних методів. Аналіз отриманих ІЧ-спектрів свідчить, що СА може взаємодіяти з нанорозмірним оксидом алюмінію як карбоксильною так і фенольними групами. На основі розрахованих значень $\Delta\mu$ встановлено, що карбоксилатні комплекси СА на поверхні Al_2O_3 можуть мати бідентатну та монодентатну структури. Аналіз мас-спектрометричних даних дозволив ідентифікувати сполуки 4-вінілкатехолу, пірокатехолу та фенолу, які є продуктами розкладу утворених карбоксилатних та фенольних комплексів. Виявлено, що на поверхні досліджених зразків СА/ Al_2O_3 переважають хелатні комплекси СА, які утворюються за участі обох ОН-груп ароматичного кільця.

Ключові слова: біомаса, карбоксилатні комплекси, хелатні комплекси, 4-вінілкатехол, пірокатехол, фенол, піроліз, технології конверсії біомаси

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