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Silver Intercalation into Cellulose Matrix. An X-Ray Scattering, Solid-State ^{13}C NMR, IR, X-Ray Photoelectron, and Raman Study

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Abstract—Diffusion of silver ions into a cellulose matrix and their subsequent reduction both with the matrix itself and with specific reducers lead to preparation of cellulose materials containing silver(0). Most silver metal is intercalated into the cellulose matrix when glycerol is used as solvent and potassium hypophosphite or sodium boron hydrate are used as reducers.

At present a large number of polymeric materials exhibiting electric, magnetic, and catalytic properties have been obtained. Among them, polymeric compounds containing stabilized nanoparticles of metals, specifically silver, copper, nickel, etc., are of particular interest [1–3]. Synthetic polymers, such as polyethylene, polypropylene, polyethylene terephthalate, polyvinylpyrrolidone, etc., in solutions and gels are used as macromolecular matrices for metal particles [3–6]. The formation of associates between metal particles and macromolecular matrices consist of two main stages. The first of them involves formation of these particles directly in the matrix, and the second involves growth of these particles and their stabilization in the matrix. The first stage can be carried out if the polymer is in a highly disperse state. Thus, synthetic polymers should have a well-developed porous system. To this end, known methods of polymer drawing in active liquid media, leading to polymer deformation, are generally used [7]. Filling the porous polymer structure with metal particles is also important, since an optimum filling should be attained.

Intercalation of metal particles into polymer matrices has most commonly performed in solutions or gels of synthetic polymers. In recent years the authors of this study have investigated preparation of intercalates of a natural water-insoluble polymer, cellulose, and silver(0) metal nanoparticles obtained by reduction directly in the matrix [8, 9]. In contrast to synthetic polymers, cellulose is a highly porous system of conjugated fibers. Therefore, an essential advantage of its application as a polymer matrix is the fact that no additional treatment is required to increase its porosity and/or dispersity. Intercalates of metal nanoparticles and a cellulose matrix hold promise for many fields, including medicine, since nanodimensional metal particles acquire special properties [3].

The aim of this present study is to use a cellulose matrix, microcrystalline cellulose (MCC) as a basis for intercalating silver nanoparticles. Microcrystalline cellulose, a polymer of natural origin, is allowed for application in the manufacture of pharmaceutical forms of many drugs, both as a digestive additive and an independent means for treating some gastrointestinal diseases [10, 11], which is due to its high sorption properties. Silver(0) dispersed to nanoparticles in a polymer matrix exhibits high antimicrobial properties [3]. Bactericidal, specifically antimicrobial properties imparted to cellulose may extend its medical application.

The method we used for silver(0) intercalation involved diffusion of silver ions into the cellulose matrix and their chemical reduction in the matrix to silver(0). The present paper provides experimental evidence for the silver reduction and principal charac-

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Table 1. Characteristics of microcrystalline cellulose samples containing silver(0)

Sample no.	Sample	Reducer and/or additional treatment	MCC and silver(0) crystallite size, Å[a]			Elemental analysis, wt%			Silver(0) content, wt%	
			MCC	silver(0)		C	H	Ag	in bulk[b]	on the surface[c]
				[111]	[200]					
1	Initial cellulose	–	58	–	–	44.4	6.2	–	–	–
2	Cellulose–Ag	Cellulose	54	46	27	43.3	6.2	<1.0	0.6	<1.0
3	〃	Cellulose, heating (250°C)	54	34	11	43.6	6.4	1.0	1.3	1.2
4	〃	Cellulose, $NH_3 \cdot H_2O$	55	77	39	42.5	6.4	1.3	0.6	1.5
5	〃	Glycerol, $NH_3 \cdot H_2O$	61	127	78	41.0	6.4	5.9	6.1	12.6
6	〃	1,10-Phenanthroline, glycerol, $NaHCO_3$	57	–	–	39.9	6.0	3.0	4.1	3.0
7	〃	$NaBH_4$	54	102	68	40.6	6.1	4.9	5.3	2.2
8	〃	$NaBH_4$ (repeated treatment)	54	33	115	41.1	6.2	4.3	6.2	2.6
9	〃	KH_2PO_2, H_3PO_4	54	127	81	40.7	6.1	7.1	7.6	16.5
10	Ag(0)	–	–	–	–	–	–	100	100	

[a] X-ray phase analysis. [b] X-ray fluorescent analysis. [c] X-ray photoelectron spectroscopy.

teristics of MCC–silver(0) intercalates. The next paper will deal with the methods for obtaining the intercalates and the mechanisms of silver ions reduction in the cellulose matrix, discussed in accordance with the procedures used.

Table 1 lists the characteristics of the initial microcrystalline cellulose (sample no. 1) and materials obtained by silver ions reduction in the cellulose matrix [hereinafter, cellulose–Ag samples (sample nos. 2–9)].

As seen from Table 1, the maximum quantity of silver(0) obtained in bulk and on the surface of cellulose–Ag samples without specific reducers, owing to intrinsic reducing properties of the matrix is no more than 1.3–1.5 wt%. With various solvents and specific reducers (sodium boron hydrate or potassium hypophosphite), samples with different silver(0) contents were obtained. The greatest quantity of silver metal in bulk was 7.6 wt%. On the surface this quantity was much greater (up to 16.5 wt%).

Most emphasis in interpreting the results we will draw to samples with the highest silver(0) contents (sample nos. 5 and 9) and to their comparison with initial cellulose samples. The presence of silver(0) in bulk of cellulose–Ag samples was proved by X-ray phase analysis [wide-angle X-ray scattering (WAXS)] (Fig. 1). The X-ray scattering curves show that the samples are two-component crystalline systems comprising cellulose of structural modification I and silver(0). Since the X-ray scattering curves display no other features, mixed compounds are probably not formed. The cellulose crystallite sizes in these samples (54–55 Å) are mainly close to those of the initial cellulose (58–59 Å). However, in sample no. 5 obtained in aqueous-glycerol medium, these crystallites are slightly larger (61 Å) than in the initial cellulose. It is known that glycerol, like other alcohols, can form inclusion compounds with cellulose. The formation of inclusion compounds does not change the crystalline modification of cellulose but slightly increases the *d*-spacing and other cell parameters. This fact indirectly explains the result.

The sizes of silver crystallites obtained in the cellulose matrix are different and depend on reduction conditions and reducer type. Small silver crystallites are formed when reduction is performed in aqueous or aqueous-ammonia media without using specific reducers (sample nos. 2–4). The largest crystallites of silver(0) are formed when intrinsic reducing properties of the matrix are used and the reaction takes place in aqueous-glycerol medium (sample no. 5), or with a potassium hypophosphite reducer (sample no. 9). Reduction with sodium boron hydride gives smaller silver(0) crystallites (sample no. 7). Repeated treatment with the latter reducer favors formation of

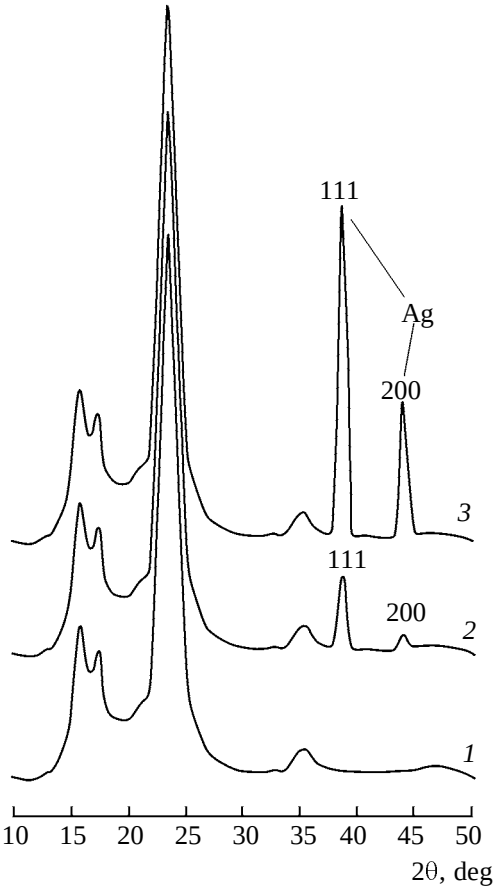

Fig. 1. X-ray scattering curves of (*1*) initial cellulose (sample no. 1) and (*2, 3*) cellulose–Ag intercalates (samples nos. 3 and 5, respectively), obtained by X-ray phase analysis.

silver(0) crystallites of another shape (sample no. 8), as evidenced by their lengths in directions [111] and [200].

The presence of silver(0) on the surface of cellulose–Ag samples was confirmed by X-ray photoelectron spectroscopy (XPS). Figure 2a shows the Ag3*d*5/2 XPS spectra of sample no. 5, compared with the spectrum of the silver metal obtained by reduction from $AgNO_3$ solution with sodium boron hydride (in the absence of cellulose). The identity of spectra *1* and *2* in Fig. 2a gives evidence for the presence of silver(0) in sample no. 5. Analogous silver(0) spectra were obtained for the other cellulose–Ag samples. As seen from Table 1, the results of elemental analysis and X-ray fluorescence (XRF) analysis for silver in sample bulk are mostly in good agreement. Taking into account the XPS data, we may conclude that the intercalation of a small amount of silver(0) into the MCC matrix gives rise to close

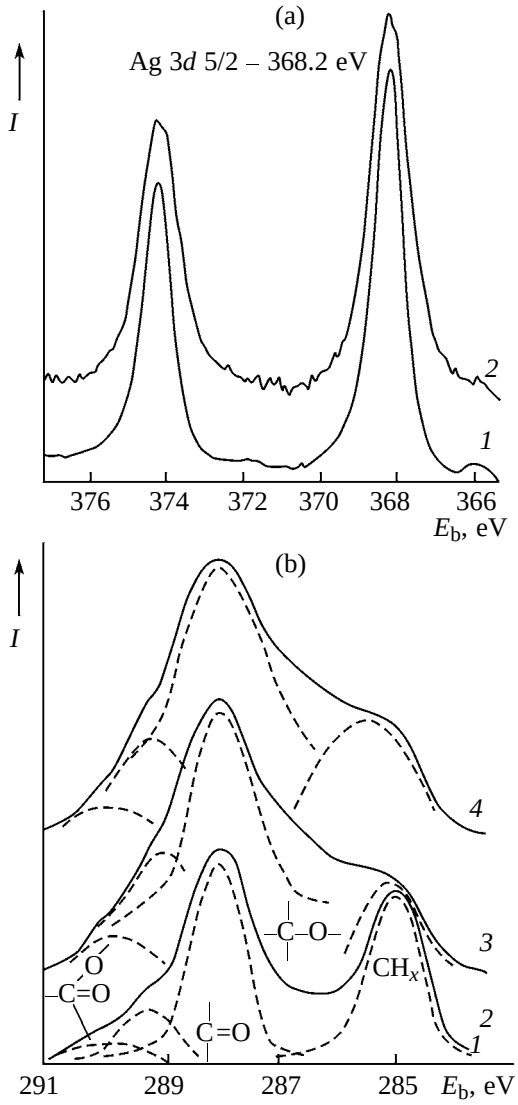

Fig. 2. X-ray photoelectron spectra. (a) Ag3*d*5/2 lines of (*1*) silver powder and (*2*) cellulose–Ag intercalate (sample no. 5). (b) C1*s* lines of (*2*) initial cellulose and (*3, 4*) cellulose–Ag intercalates (sample nos. 5 and 9, respectively), and (1) deconvolution of the C 1*s* line into four components.

silver concentrations in bulk and on the surface. The silver(0) concentrations in the samples with the highest silver(0) contents were higher on the surface that in bulk. Sample nos. 7 and 8 are exceptions. They were obtained by reduction with sodium boron hydride, and the silver concentration on their surface is lower than in bulk. Treatment with such a strong reducer evidently leads to loosening of cellulose structure, which facilitates reagent diffusion into the matrix, and silver reduction in it occurs in preference to that on the surface.

Table 2. Element contents on sample surface and characteristics of silver(0) particles

Sample no.	Concentration of functional groups, at%				Silver(0) content on sample surface, wt%	Characteristics of silver(0) particles	C/O ratio
	C–H, 285.0 eV	C–OH, C–O–C, 286.6 eV	O–C–O, C=O, 287.7 eV	COO^-, 289.1 eV			
1	28.6	26.6	8.8	3.0	0	–	1.77
2	28.9	25.8	7.8	2.3	<1.0	Disperse sizes	2.30
3	29.8	25.6	7.0	3.2	1.2	″	2.02
4	32.9	26.4	6.8	0.8	1.5	″	2.21
5	22.1	26.4	14.2	4.2	12.6	–	1.51
6	27.9	25.7	6.7	2.8	4.1	Small fraction of disperse sizes	1.80
7	33.2	27.6	5.1	1.2	2.2	–	2.26
8	22.5	26.7	15.3	2.6	2.6	–	1.59
9	26.0	24.1	14.4	2.6	16.5	–	1.58

Figure 2b provides an answer to the question whether the silver(0) intercalation changes the chemical composition on the MCC surface. The figure shows the C1s XPS spectra of sample nos. 1, 5, and 9. Deconvolution of the C1s line (spectrum *1*) revealed four components with binding energies corresponding to C–H (E_b = 285.0 eV), C–OH and C–O–C (E_b = 286.6 eV), O–C–O and C=O (E_b = 287.7 eV), and COO- carbons (E_b = 289.1 eV). According to these spectra, the surface of the initial cellulose sample contains mainly hydroxy, ether, and carbonyl groups, as well as a small amount of carboxy groups. Table 2 lists the atomic concentrations of separate functional groups on the surface of these samples. The C/O concentration ratio in the XPS spectrum is known to depend on the content of oxygen-containing groups [12]. Thus, it is 1.77 for the initial cellulose sample and higher for sample nos. 2–4 and 7, which is due to the appearance of a small quantity of silver(0) on the surface of the samples. This is accompanied by increase in the intensity of the C–H lines (E_b 285.0 eV) and characterizes the increase in the concentration of these groups from 28.6 to 33.2 at%. The decrease in the concentration of oxygen-containing groups is also confirmed by the decrease in the concentration of functional groups with E_b 287.7 eV (O–C–O and C=O) from 8.8 to 5.1 at%. The quantity of COO^- groups (E_b 289.1 eV) also decreases from 3.0 in the initial cellulose to 0.8–1.2 at% in the silver(0) samples. These findings suggest that silver intercalation into cellulose is a two-stage process. In the first stage, the β-glucoside bonds between glucopyranose units in the cellulose chain undergo partial scission. The aldehyde groups of initial MCC, whose amount is increased by chain scission and formation of shorter fragments, take part in silver ions reduction to silver(0) (in the second stage). Sample no. 3 is an exception from this series of experiments: Its C/O ratio decreases (compared to sample nos. 2 and 4), which is caused by cellulose oxidation upon heating to 250°C and formation of additional oxidized COO^- groups.

It is known that XPS can be used to characterize not only the degree of silver oxidation, but also the size of silver particles and their dispersity. Thus, sample nos. 2–4 obtained without specific reducers contain only small silver(0) particles dispersed on fiber surface (0.1–1.5 wt%).

With increasing silver(0) content in sample nos. 5, 6, 8, and 9 (on the surface and in bulk), the C/O ratio decreases (1.51–1.59 at%) and becomes lower than in the initial cellulose sample. This corresponds to decrease in the intensity of lines corresponding C–H groups, decrease in the content of these groups (from 22.1 to 26.0 at%), and increase in the content of oxygen-containing groups (to 15.3 at%), including aldehyde cellulose groups. The contents of hydroxyl groups and ether bonds C–O–C vary only slightly, implying that the chemical composition of glucopyranose cellulose units has underwent no changes. The content of carboxy groups in sample no. 5 markedly increases (by Raman spectroscopy; see below). Hence, the changes observed in the XPS spectra of cellulose–Ag samples reduced in aqueous-glycerol medium or with strong reducers are associated with processes involving end aldehyde and carboxy groups of cellulose and producing no considerable degradation of the cellulose chain. This conclusion is consistent with the occurrence of the chemical processes

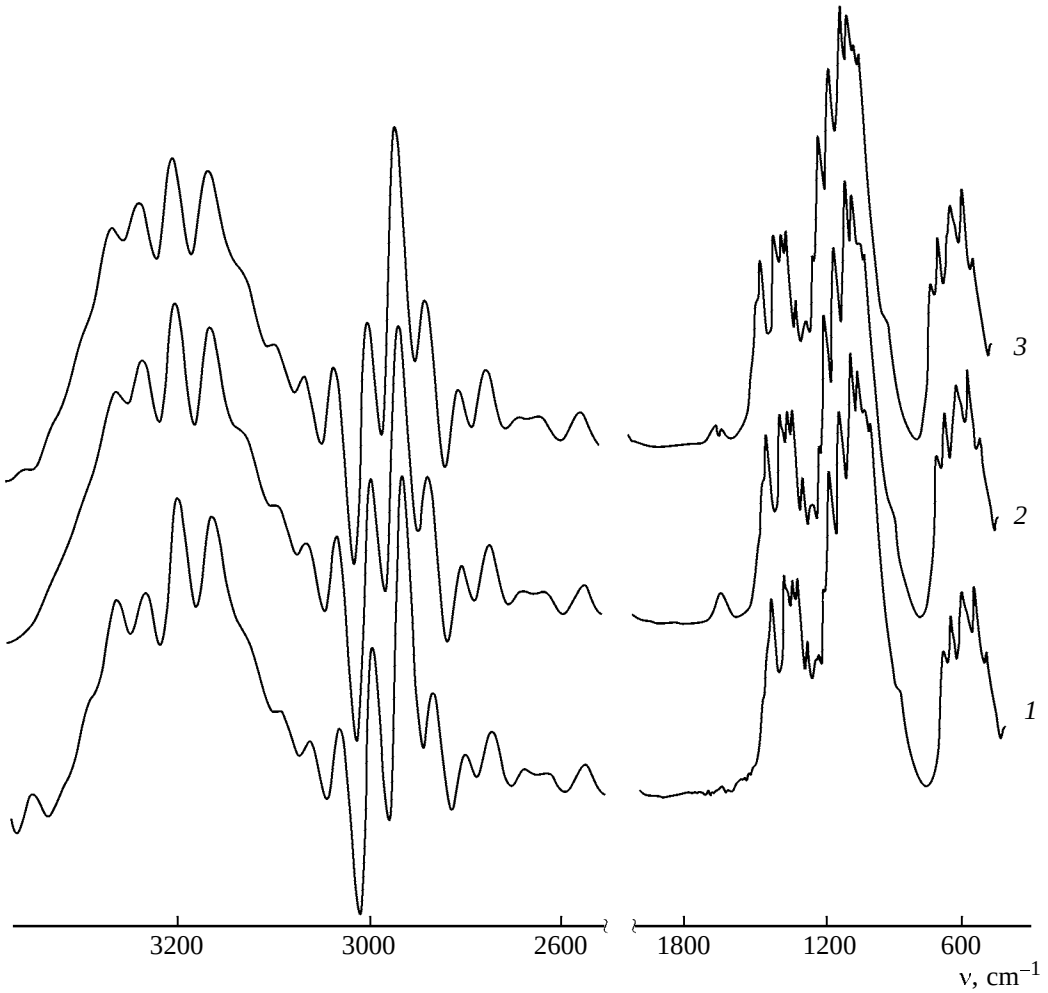

Fig. 3. Fourier-transform IR spectra of (*1*) initial cellulode (sample no. 1) and (*2, 3*) cellulose–Ag intercalates (sample nos. 5 and 9, respectively); deconvolution of the spectral range 2400–3700 cm^{-1}.

of diffusion of silver ions into the matrix and their subsequent reduction.

The IR spectra of cellulose–Ag samples containing intercalated silver(0) particles show no changes in the 400–1800 cm^{-1} range (Fig. 3, sample nos. 5 and 9). Deconvolution of the spectra in the 2400–3700 cm^{-1} range revealed intensity redistribution of the absorption bands of the O^2H and O^6H groups of cellulose, involved in intramolecular hydrogen bonding with each other (3410 and 3470 cm^{-1}). This evidence allows no conclusions as to any chemical interaction (i.e. chemical bond formation) between cellulose and silver(0). Comparison of the spectra of cellulose–Ag samples (sample nos. 5, 6, and 8) with those of the reducers and other compounds applied for treatments (glycerol, sodium boron hydride, and 1,10-phenanthroline) shows that the latter are completely removed from the samples [13].

Analysis of the ^{13}C NMR spectra of cellulose–Ag samples (Fig. 4) in comparison with the spectrum of initial cellulose shows that this method is more sensitive to chemical changes in cellulose, attendant on silver(0) intercalation. Thus, the shape of some signals changes and new signals appear. The new signal near 150 ppm in the spectrum of sample no. 5 is due to the formation of new –C–C=O and –O–R groups. In the spectrum of sample no. 9, this signal is shifted to 144–145 ppm. The most pronounced changes are observed in the spectral range related to structural rearrangements in samples subjected to chemical treatment. Thus, it is known that the che-mical shift of the C^6 atom is determined by the rotamer structure (changes in the rotational isomeric structure) of hydroxymethyl groups [14]. In some cases, diffusion and reduction produce chemical and structural modification of initial cellulose. For instance, broadening and

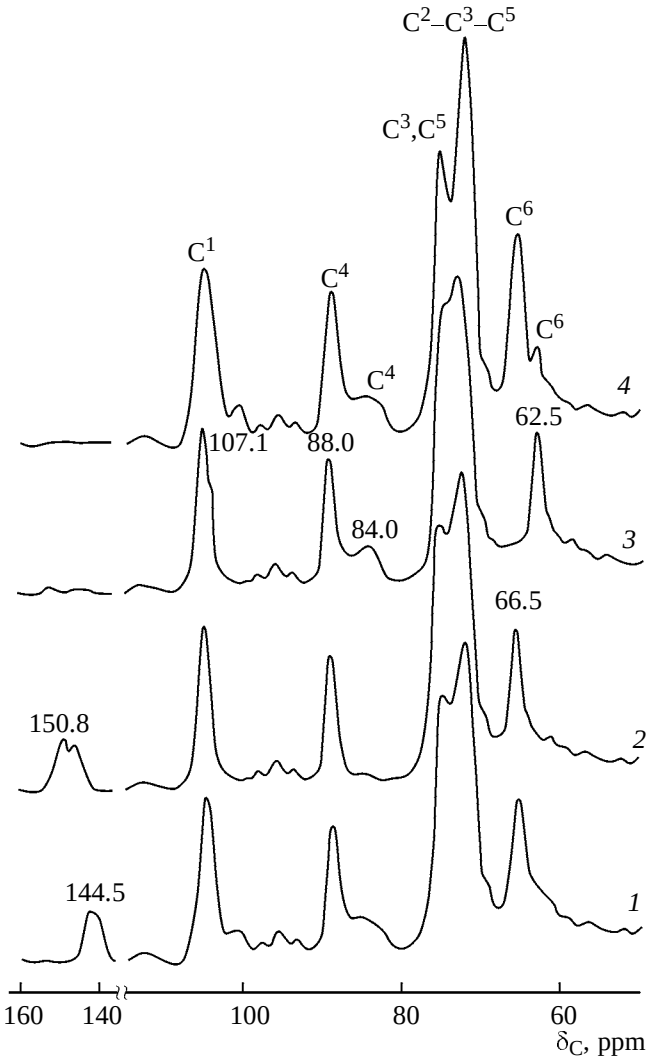

Fig. 4. Solid-state ^{13}C NMR spectra of (*1*) initial cellulose (sample no. 1) and (*2–4*) cellulose–Ag intercalates (sample nos. 7, 5, and 8, respectively).

intensity redistribution of the C^6 signals (shift from 66.5 to 62.5 ppm) are observed for sample nos. 4 and 7 treated with NH_4OH and $NaBH_4$ (Fig. 4, spectrum *2*). These changes are characteristic of the transformation of the initial cellulose modification I into modification II. Such transformation usually occurs after treatment of cellulose with NaOH or NH_4OH solutions or after its regeneration from solutions [14]. The changes in the shape and relative intensities of the C^2, C^3, and C^5 signals in the spectrum of sample no. 7, too, point to structural transformation of initial cellulose. In the spectra of sample nos. 5 and 7, changes in the C^4 chemical shifts are observed. It is known that in the ^{13}C NMR spectra of MCC, the chemical shift of the signal of the C^4 atom of glucose units is changed by rotation of glucopyranose cellulose units about the C^4–O^1 bond. The increased intensity of the low-field C^4 signal near 84 ppm in the spectrum of sample no. 7 suggests amorphization of the sample under chemical treatments. In contrast, in the spectrum of sample no. 5, the intensity of this signal considerably decreases (until it disappears completely), indicating increasing crystallinity of the sample. This result is not unexpected, if we take into account that the synthesis of sample no. 5 involves high-temperature heating in aqueous-glycerol medium.

Consequently, the results obtained by ^{13}C NMR spectroscopy allow us to estimate the degree to which diffusion and subsequent reduction of silver ions affect the structure of the initial MCC sample. In some cases, they can lead to partial modification of the cellulose structure I into II and/or to amorphization. In other cases, reduction takes place only on the cellulose surface. The apparent discrepancies between the results obtained by X-ray phase analysis and solid-state ^{13}C NMR indicate that the NMR method is more sensitive to fine structural changes in cellulose. It should also be borne in mind that for structural changes in cellulose I during its rearrangement into cellulose II to be detectable by X-ray phase analysis, no less than 10 wt% of cellulose should undergo this rearrangement. In sample nos. 4 and 7, probably, these changes have occurred to a lesser extent.

Raman spectroscopy is the most sensitive method we applied for characterization of changes in the chemical composition of cellulose, produced by silver intercalation. Thus, in the spectrum of sample no. 5 (Fig. 5b), strong changes are observed in the 1000–2000 cm^{-1} range as compared to the spectrum of initial cellulose (Fig. 5a): The bands in the 971–1151 and 1294–1478 cm^{-1} ranges increase in intensity and change shape and position, and new bands appear in the 1520–1558 cm^{-1} range. As a result, the bands at 1362, 1450, 1520, and 1558 cm^{-1} form a strong broad band with a complex structure. The integral intensity ratio of the bands at 1362 and 1450 cm^{-1} and new bands at 1520 and 1558 cm^{-1} is close to unity. The θ factor for bands in the 971–1151 cm^{-1} range is ~10 and for those in the 1294–1473 cm^{-1} range, ~30.

The absorption character in this range allows us to assign these bands to symmetric and antisymmetric COO^- vibrations. In other words, ionized and nonionized carboxy groups are present in the sample. We previously showed that MCC contains a small amount of COOH groups [15]. Moreover, additional quantity of these groups appears in cellulose during silver ions reduction to silver(0). Aldehyde cellulose groups are simultaneously oxidized to carboxy groups which participate in further complexation with silver ions.

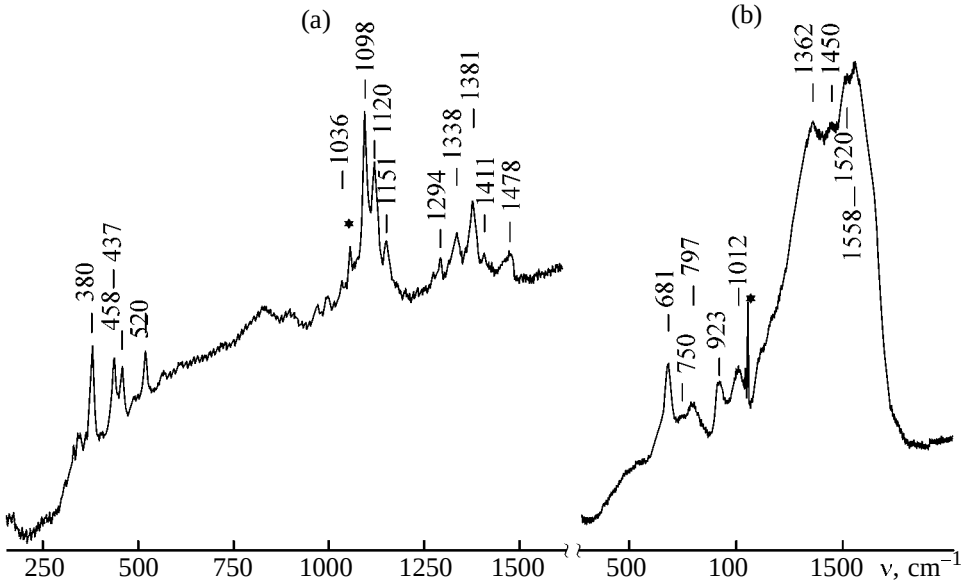

Fig. 5. Raman spectra of (a) initial cellulose (sample no. 1) and (b) cellulose–Ag intercalate (sample no. 5).

The high intensity of adsorption bands in this range may be due to interaction between oxidized cellulose and the surface of silver(0) particles. The θ factor for bands in the 1520–1558 cm^{-1} range is ~70. This result is important, because it shows that the silver(0) intercalation into cellulose gives rise to a silver(0) surface–enhanced Raman spectrum of the cellulose itself. Similar results were obtained by Laserna *et al.* [16] for silver reduction with sodium boron hydride on a filter paper matrix.

Hence, diffusion of silver ions into a cellulose matrix and their subsequent reduction both by the matrix itself or by specific reducers gives cellulose samples containing silver(0). In most cases, MCC preserves the structural modification I.

EXPERIMENTAL

Certain characteristics of sample nos. 2–9 are given in Table 1.

The bulk silver concentrations were determined by elemental and X-ray fluorescent analysis, and the surface silver concentrations, by X-ray photoelectron spectroscopy.

Elemental analysis was carried out on a Hewlett-Packard C, H, N analyzer.

X-ray fluorescent analysis was performed on an Oxford XR-500 spectrometer. The instrument parameters and analytical procedures are described in [17, 18]. The samples were placed on standard plastic cuvettes with a working diameter of 20 mm, closed from the butt end with a mylar film 4 μm thick. The standards with salt contents of 0.5–12 wt% were prepared by mixing (on a Specamill ball mill) pure $AgNO_3$ salt with MCC. The standard and sample weights were 0.5 g. The intensity of the AgK_α line (22.1 keV) excited in the material by an ^{241}Am ring isotope source (59.6 keV) was recorded. In this case, X-ray fluorescence analysis provides a volume-averaged concentration of the element being determined.

X-ray photoelectron spectra were obtained on a PHI-5400 Perkin-Elmer photoelectron spectrometer with excitation with Mg radiation. The samples were fixed on a standard holder, evacuated, and placed on a manipulator cooled with liquid nitrogen. The working vacuum during experiments was no higher than 5.1×10^{-8} mm. The surface chemical composition of the sample was determined from the review spectra taken at E_b 0–1000 eV. The chemical state of the elements and the relative atomic concentrations were determined from the spectra of individual photoelectron lines of the elements using standard software. The accuracy of binding energy determination was 0.1 eV and of quantitative analysis, 10%. The spectra were calibrated against the C1s line of hydrocarbon components (E_b 285 eV) [12].

The composition and properties of solid cellulose–Ag samples were studied by X-ray phase analysis (WAXS) and solid-state ^{13}C NMR, IR, and Raman spectroscopy.

The WAXS curves were obtained on a powder diffraction apparatus using monochromatic CuK_α radia-

tion. The measurements were carried out in the scattering angle range $5° < 2\theta < 40°$ with an angle step of 0.25°. Samples in the form of flat cakes about 1 mm thick were prepared. The samples were rotated in an evacuated chamber during the experiments.

The IR spectra were recorded as described in [19].

The solid-state 13C NMR spectra were recorded on a Bruker CXP-100 spectrometer, spinning the samples by a magic angle of 54° at a frequency of 3.6 MHz. The working frequency on ^{13}C nuclei was 26.16 MHz. The pulse duration along the ^{13}C channel was 1ms. The repetition period of pulse sequence was 2.6 s. The accumulation number ranged from 100 to 400. Cross polarization and proton decoupling were applied. The chemical shifts were measured in ppm relative to TMS [14].

The Raman spectra were recorded as described in [20, 21].

The microcrystalline cellulose prepared by mild acid hydrolysis by the procedure described in [10] had a particle size of < 0.06 mm; it was thoroughly dried and its moisture content was no more than 1 wt% (sample no. 1). Like cotton cellulose, it had the structural modification I (according to X-ray phase analysis) [10].

Silver intercalation into the MCC matrix was accomplished in two main steps: (1) diffusion and chemisorption of silver ions from $AgNO_3$ solutions into the MCC matrix, and (2) reduction of the silver ions to silver(0) directly in the MCC matrix. Cellulose itself can act as reducer. The role of MCC as reducer was studied both without its additional treatment and after heating at 250°C for 2 h, as well as by applying various solvents and complexing agents (ammonia, glycerol, and 1,10-phenanthroline). With specific reducers (sodium boron hydride and potassium hypophosphite), more silver ions reduced to silver(0).

The reduction mechanisms in various solvents and with various reducers are different. Detailed description of the procedures for obtaining cellulose–silver(0) intercalates and of the mechanisms of silver ions reduction will be given in the following publication.

The silver(0) powder prepared by direct reduction from an 0.1 N $AgNO_3$ solution with sodium boron hydride was applied as model sample (sample no. 10). All other reagents were pure or analytical grade.

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