Study of Platinum and Palladium Aggregates Intercalation into Cellulose by Waxs, Spectroscopic, and Microscopic Methods

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Abstract: The WAXS, SAXS, SEM, TEM, XPS were used to study methods of platinum and palladium aggregates intercalation into the cellulose matrix and changes of cellulose structure after this intercalation. As a result new microcrystalline cellulose - metal compounds containing aggregates of platinum, and palladium were synthesised for the first time using the redox interaction reaction.

INTRODUCTION

The incorporation of metallic species into polymers is an active area of research. Metal-containing polymers are numerous and highly diverse. The renewal of cellulose resources in nature makes cellulose one of the promising natural polymers. Therefore, the search for the paths of obtaining new modified cellulose materials is continuing in the cellulose research.

The aim of this contribution is to present some results of our study on cellulose metalization on surface and in bulk upon intercalation and reduction of cellulose-incorporated metal ions. The most valuable of them are silver, platinum, and palladium. This field of investigation can be referred both to the study of polymer complexes with metals and to the chemistry of coordination compounds of metals with organic ligands.

Earlier we have successfully carried out silver clusters intercalation into cellulose by the reduction of silver salts immobilised in the cellulose matrix using different reducers. The structure and properties of cellulose-silver complexes have been studied by WAXS, SAXS, spectroscopic (XPS), and microscopic (SEM and TEM) methods (Ref. 1).

EXPERIMENTAL PART

MCC used was applied as described elsewhere (Ref. 1). All other reagents used were analytical grade.

The intercalation of platinum into MCC was employed using the following steps:

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1 - chemisorption of complex metal compounds $K_2[PtCl_6]$ and $K_2[PdCl_4]$ by MCC from its solutions under different experimental conditions. The chemisorption kinetics was followed as a function of solution concentration, temperature, the reagent ratio, and solvent;

2 - direct reduction of metal ions in the MCC matrix. The effect of the reducer type, its solution concentration and temperature on the degree of metals oxidation was studied. Reducing agents include hydrazine sulfate, glycerol, etc. The role of cellulose itself as a reducing agent was also studied.

In some cases the new activation method was used to improve cellulose reactivity for metals intercalation. It consists in the treatment of cellulose samples by $TiCl_4$ in the gas phase (Ref. 2). This treatment leads to replacement of cellulose OH groups by TiO_2 groups, which are very active in further reactions. Treated samples were subjected to chemisorption and reduction of metals as described above.

The composition and properties of cellulose-metals compounds and the metal components distribution in cellulose fibres were determined by WAXS, SAXS as well as by XPS, EDXA, SEM and TEM.

MCC samples containing metals clusters and/or aggregates were observed in the SEM (Ref. 1, 3) and TEM (a Zeiss EM 10C transmission electron microscope) applying the usual preparation methods (Ref. 4). The metals content on the MCC surface was determined by XPS (Ref. 4).

RESULTS AND DISCUSSION

Some properties of the resulting compounds after platinum intercalation depending on the reducer type are listed in Table 1.

Table 1. Characteristics of MCC samples containing intercalated platinum aggregates

Characteristics	MCC initial	Reagents and reducers			
		MCC, hydrazine sulfate 1	MCC, KOH, K_2CO_3 2	MCC, KOH 3	MCC, $TiCl_4$, glycerol 4
MCC crystallite size, Å (WAXS)	74–75	72	73	72	–
Pt content in bulk, mass%	–	1.0	2.5	0.9	6.5
Platinum content on the surface, mass% (XPS)	–	0	8.4	2.1	–
Platinum crystals size, Å (directions 111 and 200) (WAXS)	–	48, 27	90, 60	71, 32	–

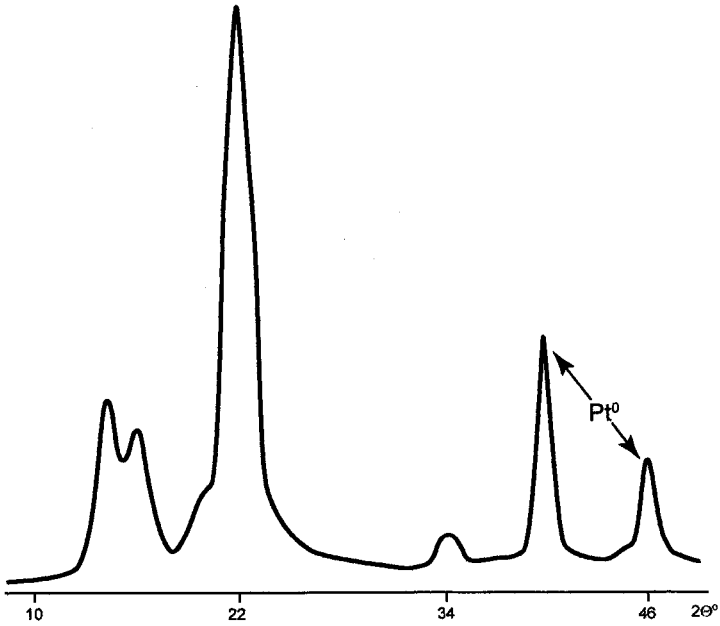

Fig. 1. The diffraction pattern of MCC--platinum compound (platinum content 2.5 mass% in bulk)

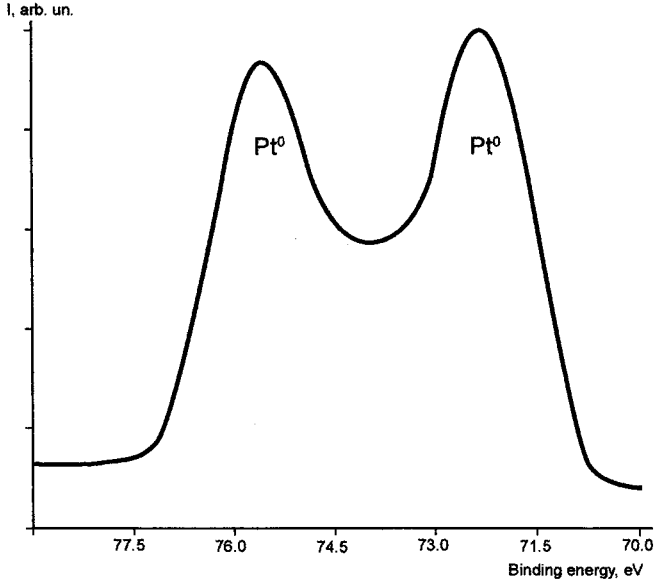

Fig. 2. XPS spectrum of platinum 4f line of the MCC-platinum compound (Pt content 8.4 mass% on the surface)

It can be seen that the content of platinum intercalated into the MCC matrix reaches 2.5 mass %. As in the case of silver clusters intercalation (Ref. 1), the resulting compounds exhibit the crystalline structure of cellulose I. The intensity curves of all samples indicate that these products are two-phase systems consisting of MCC and metallic platinum with zero degree of oxidation (Fig. 1). The size of cellulose crystallites in these samples is similar (72-73 Å) to that of initial MCC (74-75 Å). The platinum content as well as crystal sizes depend on the conditions of treatment, especially, on the MCC:$K_2[PtCl_6]$ molar ratio in the reaction. Thus, the largest Pt crystals (90x60 Å) were obtained when the molar ratio was the highest. It should be noted that the size of Pt crystals obtained is much larger than that known from the literature (19.88x23.12 Å). It is of interest that cellulose itself can reduce platinum from its compounds (samples 2, 3). Moreover, the crystals size is larger than in the case when specific reducers are used (sample 1). In this case a large amount of small crystals was obtained (SAXS results).

Fig. 2 shows the XPS spectra of Pt 4f line of the MCC-platinum compound (Pt content 2.5 mass% in bulk and 8.4 mass% on the surface) (sample 2). It can be seen that platinum is totally reduced on the surface of the MCC fibre. The same result was obtained for the samples 1 and 3. According to XPS data, platinum concentration on the surface of all samples is higher than in bulk. For instance, in the samples 2 and 3 platinum content is 2.5 and 0.9 mass% in bulk and 8.4 and 2.1 mass% on the surface, respectively. This means that only 30-40% of Pt is intercalated in bulk, and 60-70% is on the surface. Compared to the initial MCC, atom concentrations on the surface are changed. Thus, the C/O ratio (1.55) for these samples is lower than for the initial MCC sample (1.75). This corresponds to the changing of the shape of C 1s line and, probably, means that C-H bonds content decreases on the surface compared to the initial MCC.

In the case of palladium, its reduction is more difficult than that of platinum. In contrast to silver and platinum intercalation, cellulose itself can reduce only a small amount of palladium from its compounds. Thus, the presence of palladium after reduction was confirmed only by EDXA. The SAXS analysis confirms it contains a small amount of tiny Pd-crystals; it was not possible to estimate their size and distribution. Therefore, it was concluded that the specific reducers and the cellulose matrix itself are not sufficient for more complete reduction of Pt and Pd from their compounds. It is known that the intercalation of metals into cellulose requires heterogeneous reaction conditions. This limits the morphological distribution and concentration of the metal component (metal ions or clusters/aggregates) in the resulting material. To avoid this limitation, experiments on cellulose activation with the aim to add some reactive functional groups were carried out (see Experimental part).

SEM micrographs of MCC-Pt compounds (Fig. 3) provide a direct evidence of platinum aggregates intercalation onto MCC matrix surface. In some parts (mostly at the fibres ends) more particles can be observed (Fig. 3, left - Pt content 2.5 mass%). The EDXA analysis shows rather uniform platinum distribution on the surface. Treatment of microcrystalline cellulose by $TiCl_4$ leads to partial destruction of MCC and to additional intercalation of platinum (Fig. 3, right - Pt content 6.5 mass%).

An analogous result was obtained when palladium was intercalated into the cellulose matrix. Fig. 4 present SEM and TEM micrographs of MCC-palladium compound (palladium content 3.5 mass%). Palladium aggregates on the surface of MCC fibre can be easily seen (Fig. 4, left). In some places on the surface they

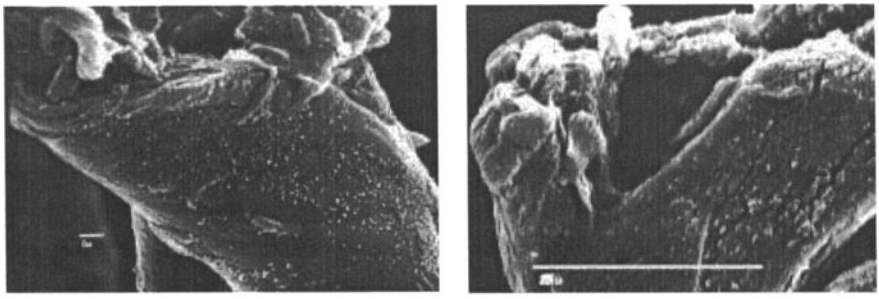

Fig. 3. SEM micrographs of MCC-platinum compounds. Left - platinum content 2.5 mass%. Right – after preliminary treatment of MCC by $TiCl_4$ – platinum content 6.5 mass %. Light spots correspond to platinum aggregates on the MCC fibre surface.

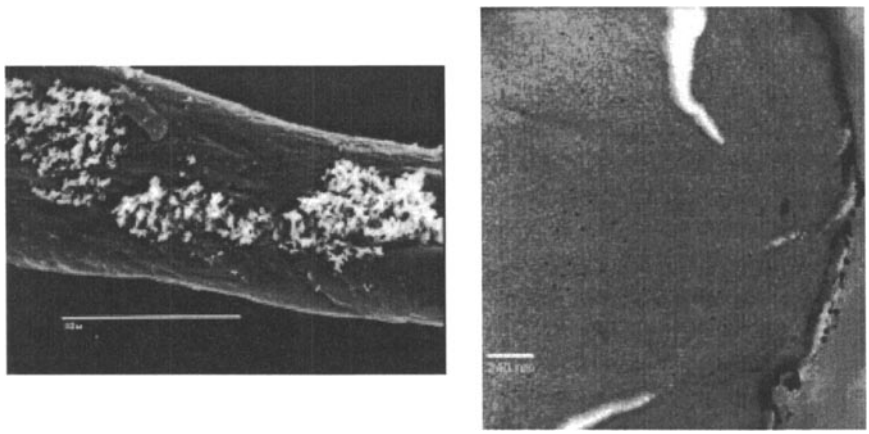

Fig. 4. SEM (left) and TEM (right) micrographs of MCC – palladium compounds (palladium content 3.5 mass%). Light spots (left) correspond to palladium aggregates on the MCC fibre surface; dark spots (right) – to palladium aggregates intercalated into the fibre and on the fibre surface (method of fibre cutting – perpendicular to fibre axis). MCC was preliminary treated by $TiCL_4$.

form large agglomerates. A few of small palladium particles can be also seen inside the fibre (Fig. 4, right). The distribution of these aggregates along the fibre and on the surface is not uniform. It is of interest that all particles of Pt and Pd have a regular globular form; their average size is 0.1 and 0.2 mcm on the surface and 0.05 and 0.07 mcm in bulk, respectively. It should be noted that these results present the first example of metallic platinum and palladium intercalation (on the surface and in bulk) into the natural cellulose matrix. Therefore, the synthesis of these compounds represents a new synthetic paradigm in cellulose-metal chemistry.

CONCLUSIONS

1. New MCC-metal compounds containing aggregates of platinum, and palladium intercalated into cellulose were synthesised for the first time using the above reaction conditions. The concentration and size of these aggregates and their distribution on the surface and inside the fibres were estimated by WAXS, XPS, SEM, and TEM.

2. The treatment of cellulose samples by $TiCl_4$ partially leads to fibres destruction. Cellulose samples are activated under this treatment and exhibit higher reactivity in interaction with metals compounds than the untreated samples.

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