THERMAL STABILITY OF COMPOUNDS FORMED BY THE ADSORPTION OF COPPER(II) ION ON MoO₃ MODIFIED WITH AMINES

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Due to their application in the formation of inorganic–organic nanocomposites, in promising electronic devices, as well as in heterogeneous catalysts, the intercalation of organic molecules in lamellar inorganic solids has a great interest. The copper(II) incorporation process was undertaken by forming suspensions of the materials in aqueous solutions of the metal. The affinity of the materials to the Cu^{2+} ion exhibits the following sequence: octyldiamine>3-aminopyridine>piperazine. Due to the presence of Cu^{2+}, after calcinations, the material recovers the initial characteristics, with a small displacement in the bands of infrared spectra.

Keywords: amine, copper(II), intercalation

Introduction

The intercalation of organic molecules in lamellar inorganic solids has been attracting considerable interest, because such intercalation compounds present promising applications as nanocomposites and in electronic devices and heterogeneous catalysts [1–5]. Among the inorganic host materials, lamellar MoO₃ forms stable intercalation compounds. This oxide does not present a high reactivity and the syntheses are quite often time consuming and demand high temperatures. It is believed that the electron transfer from the guest species toward MoO₃ is the first step of the intercalation reaction.

It has been reported that the reduction of MoO₃ results in the formation of inorganic intercalation compounds [2]. Most of these compounds were formed by the intercalation of metallic ions, although the electrochemical intercalation of organic cations has been described in the case of transition metal dichalcogenides [6–9]. The aim of the present work is to evaluate the Cu^{2+} ion incorporation in molybdenum trioxide modified with amines.

Experimental

Samples

The process of adsorption was undertaken by the addition of about 0.3 g of the amine-incorporated materials in polyethylene recipients, in which 15 mL of copper acetate aqueous solutions were added at the concentration of 0.01, 0.04, 0.07 and 0.1 mol L⁻¹. The system was maintained under orbital mechanical agitation for 6 h in a bath at 25ºC. Then the solid material was decanted, washed with distilled water and dried between 30–40ºC temperature range for 48 h. The concentrations of the solutions before and after the adsorption of Cu^{2+} were determined by EDTA complexometric titration.

X-ray diffraction

The diffraction patterns were obtained using Siemens model D5000 X-ray diffractometer at the range of 2θ=3–50º, with a 0.02º step and a step time of 2.0 s, using CuK$_\alpha$ radiation.

Infrared spectroscopy

The infrared spectra were obtained in the 400–4000 nm⁻¹ range by means of a Bomem MB-series spectrophotometer, using KBr pellets. All the samples were characterized before and after the intercalation and Cu^{2+} pillar formation.

Thermal analysis

The thermogravimetric curves (TG/DTG) were recorded using TA Instruments SDT 2960 simultaneous TG-DTA equipment between 25–950ºC, at a heating rate of 10ºC min⁻¹, under a dynamic nitrogen purging (flow rate: 50 mL min⁻¹).

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Results and discussion

Copper(II) complexation in the amine-intercalated lattice

By the evaluation of the X-ray diffraction patterns of the MoO₃/3-aminopyridine lattices with different concentrations of the copper(II) ion (Fig. 1a) indicate that the complexation of the metal ions did not modify the structure or the interlamellar distance of the intercalation compound. Another fact with was noticed that the diffraction patterns indicate the $Cu_3(MoO_4)_2(OH)_2$ phase when the concentration of copper(II) is 0.07 mol L^{-1} or even higher. The complexometric titration confirms the incorporation of Cu^{2+} into the structure of the intercalation compound.

The insertion of copper(II) ions at different concentrations does not alter the lattice structure intercalated with piperazine, as observed in the diffraction patterns (Fig. 1b). The interlamellar distances remain practically the same at the values of 95, 87 and 72 nm for MoO₃ lattice intercalated with 3-aminopyridine, piperazine and octyldiamine, respectively. Similarly to the lattice inserted with 3-aminopyridine, the

$Cu_3(MoO_4)_2(OH)_2$ phase appears, but no for initial copper concentration as low as 0.04 mol L^{-1}. The concentrations of Cu^{2+} in the structure were of 0.0042, 0.012, 0.028 and 0.035 mol L^{-1} for the initial solutions, whose copper concentration were 0.01, 0.04, 0.07 and 0.10 mol L^{-1}, respectively.

The insertion of copper(II) ions at different concentrations into the lattice intercalated with octyldiamine leads to the changes of the diffraction patterns (Fig. 1c), starting with the interlamellar distance of the materials upon the copper(II) insertion. A decrease in the number of peaks was observed, indicating that after the copper insertion only one interlamellar distance exists. These changes can be explained by the approximate linear configuration of the octyldiamine molecule. This leads to an increase of the interlamellar area organization, what is the disclosure of only one interplanar distance. Another observed fact was the appearance of the $Cu_3(MoO_4)_2(OH)_2$ phase starting from 0.04 mol L^{-1} Cu(II) concentration in the solution. Besides, the concentration of Cu^{2+} in the structure has increased with the increase of the copper(II) concentration in the starting solution.
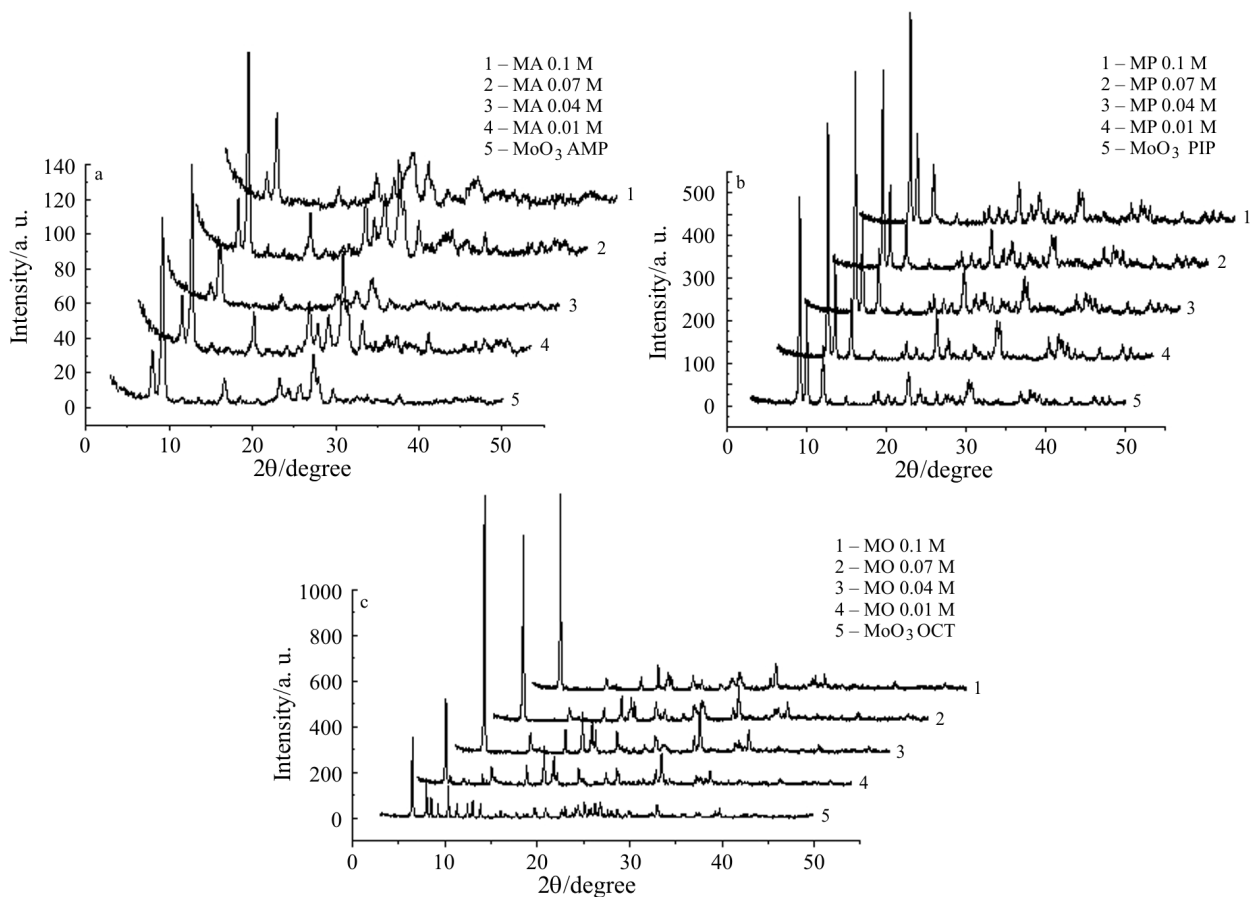
Fig. 1 X-ray diffraction patterns of the lattices with copper(II) ion at different compositions: a – MoO₃/3-aminopyridine, b – MoO₃/piperazine and c – MoO₃/octyldiamine

The infrared spectra of the amine-intercalated lattices, without and with the presence of copper(II), reveals that the Cu^{2+} ion complexation did not cause changes in the FTIR spectrum of MoO_3/3-aminopyridine (Fig. 2a). The spectrum of the MoO_3/piperazine complexed with the copper(II) ions (Fig. 2b) was shown to be similar to the one without the presence of copper. The main difference is the presence of a new band, peaked at 816 cm^{-1}, probably due to the interaction O–Cu–O. The spectrum of the material MoO_3/octyldiamine/Cu^{2+} (Fig. 2c) reveals small changes in relation to the material without copper. These changes occurred in the whole spectrum, with the appearance of bands with peaks at 2620 and 2026 cm^{-1}. An increase in the intensity of the band peaked at 1397 cm^{-1} was observed, due to the presence of the ammonium ion. The enlargement of the band peaked at 880 cm^{-1} (Mo–O) and the displacement of the Mo–O–Mo band peak from 664 to 626 cm^{-1} were also noticed.

According to the TG/DTG curves of MoO_3/3-aminopyridine complexed with copper(II) (Fig. 3a), the initial mass loss step is related to the release of coordina-

tion water. It begins at 191ºC and ends at 355ºC (DTG temperature is 310ºC) causing 10% of mass loss. The second stage is related to the amine evolution and occurs between 355–677ºC with a DTG peak temperatures of 398 and 519ºC. The corresponding mass loss is 21%. After the second stage, an oxidation of the compound between 697–839ºC was noticed, with a mass gain of 2.8%. Over 859ºC another mass loss step was verified, due to the decomposition of MoO_3.

The TG curve of MoO_3/piperazine complexed with copper(II) (Fig. 3b) displays four mass loss steps. The first one (release of water) starts at 75 and ends at 123ºC, with a peak temperature of 86ºC and the corresponding mass loss is 4.5%. The second and the third stages are related to the evaporation of coordination water and amine presenting a step between 254–338ºC (DTG peak temperature is 326ºC) and another one between 370–447ºC (DTG peak temperature is 412ºC), causing 12.5 and 6.3% mass losses, respectively. Over 448ºC an oxidation starts and completes at 613ºC giving a 3% of mass gain. At 722ºC the decomposition of the oxide starts followed by its sublimation.
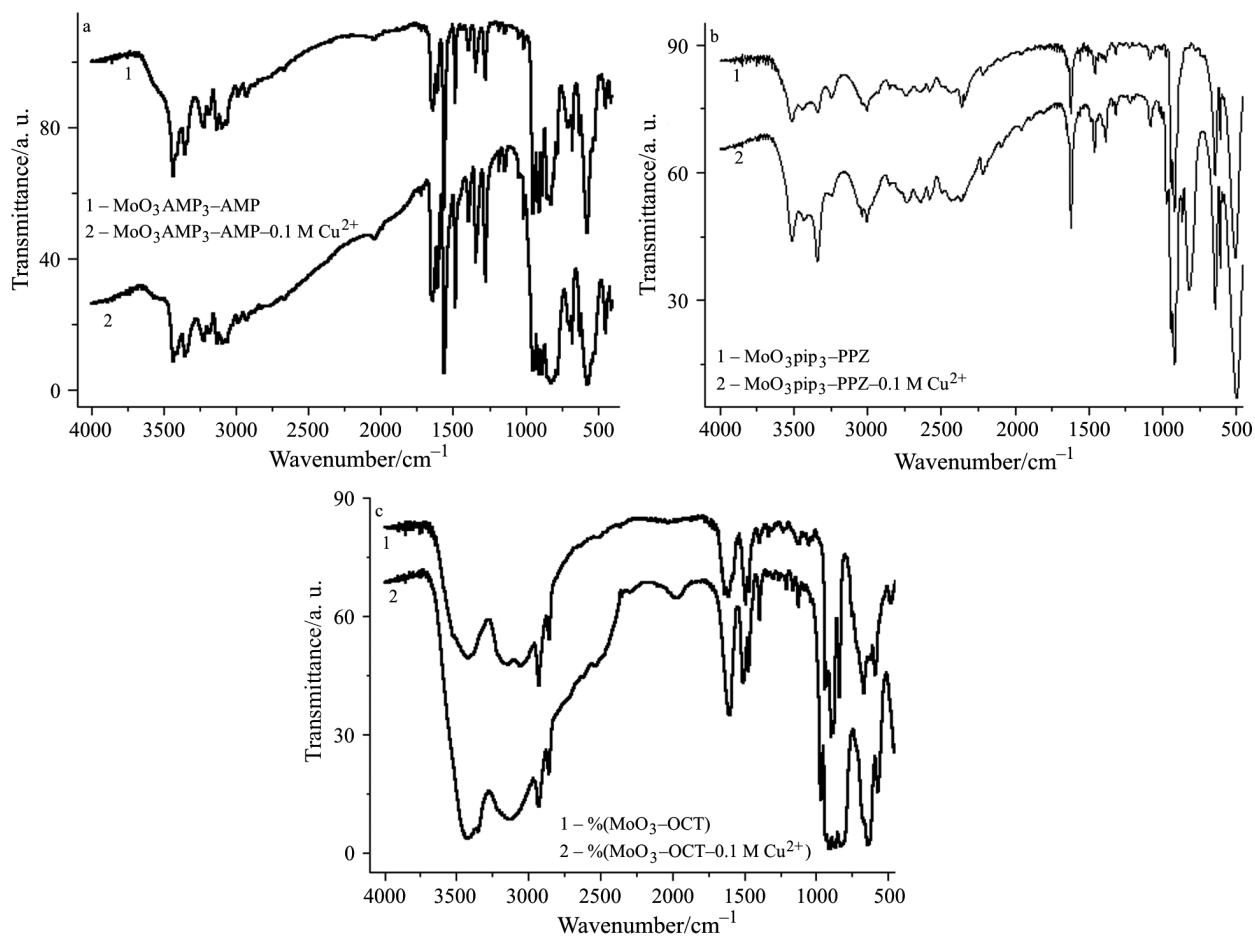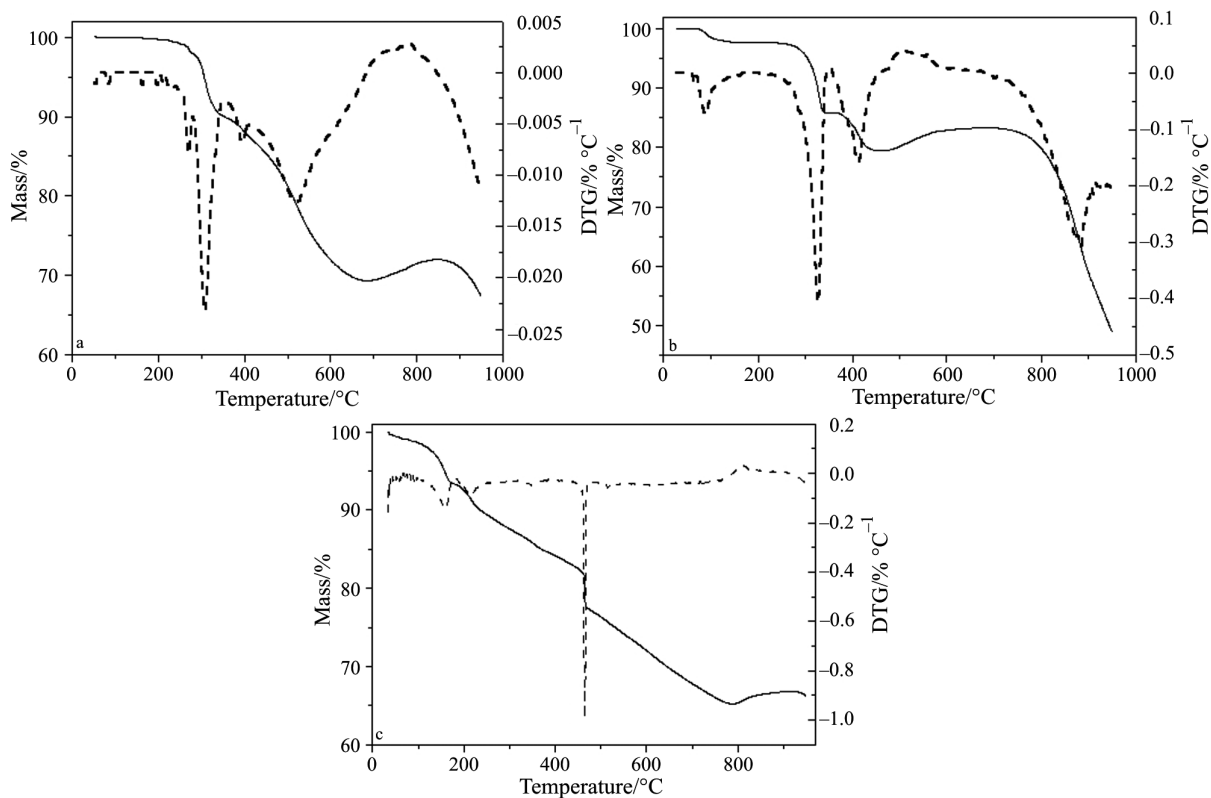

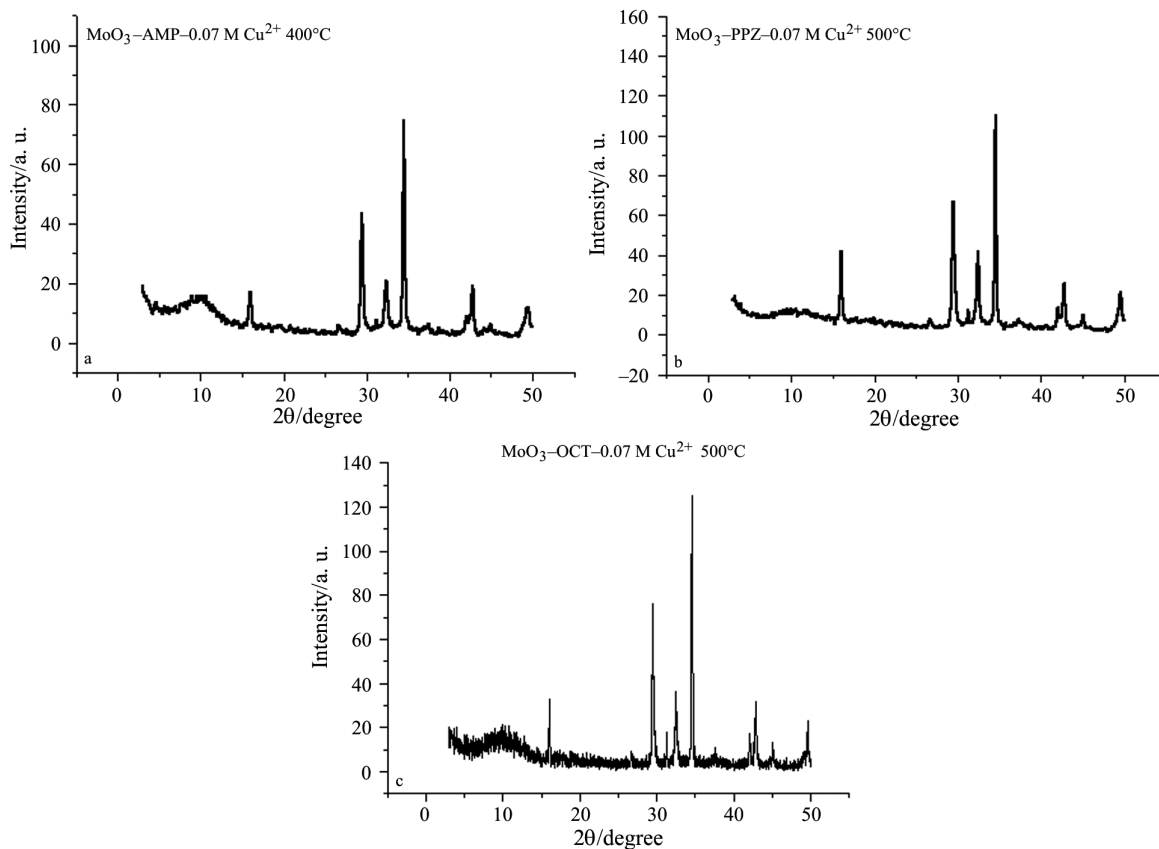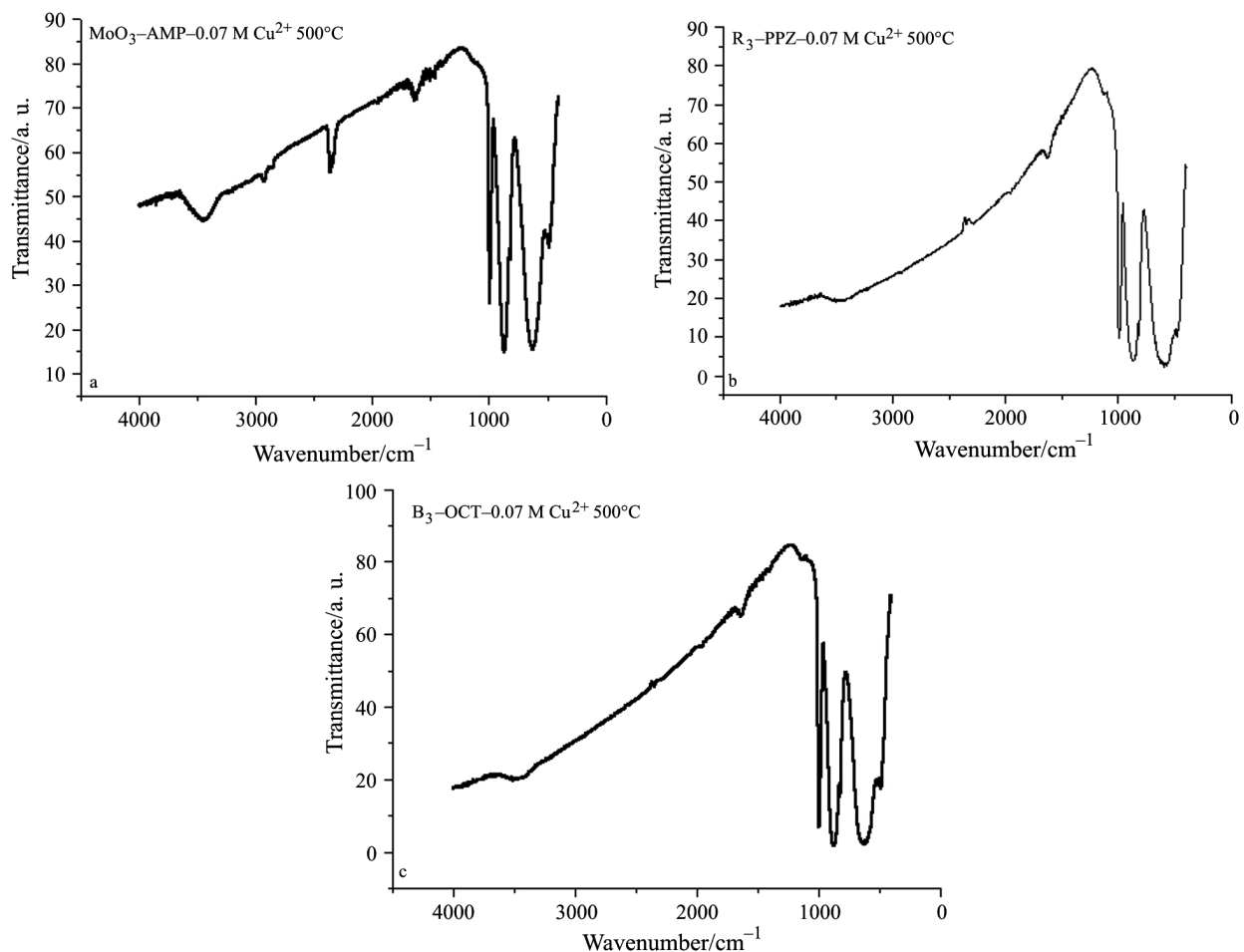**Fig. 2** Infrared spectra of the lattices with and without Cu^{2+}

Fig. 3 TG/DTG curves of a – MoO$_3$/3-aminopyridine, b – MoO$_3$/piperazine and c – MoO$_3$/octyldiamine complexed with 0.1 M Cu^{2+}

Fig. 4 X-ray diffraction patterns of the calcined compounds

Fig. 5 Infrared spectrum of a – MoO_3/3-aminopyridine, b – MoO_3/piperazine and c – MoO_3/octyldiamine complexed with Cu^{2+} heat-treated at 500°C

Similarly to the copper(II)-free compound, the TG curve of the MoO_3/octyldiamine lattice complexed with Cu^{2+} (Fig. 3c) presents the overlapped mass loss stages, indicating that the release of water and amine takes place in a more complexed way.

Calcination of the amine-intercalated lattices complexed with a 0.07 M Cu^{2+} solution

The X-ray diffraction patterns of MoO_3/3-aminopyridine/0.07 M Cu^{2+} calcined at 400°C presents a peak related to the lamellar distance (*d*) at $2\theta=16.71°$ (Fig. 4a), which corresponds to *d*=69.6 nm. It shows that the calcined material practically exhibits the same structure of MoO_3, as its oxide has *d*=70 nm. The analysis of the X-ray diffraction pattern of MoO_3/piperazine complexed with the copper(II) ion (Fig. 4b) shows that the lamellar distance of the material calcined at 500°C is the same than that of the lamellar molybdenum trioxide. Thus it can be characterized the similarity to the original material. The X-ray diffraction patterns of MoO_3/octyldiamine/Cu^{2+} (Fig. 4c) calcined at 500°C and the pure

oxide are very similar denying the determinative role of Cu^{2+} which are present in the compound.

The infrared spectrum for the compound MoO_3/aminopyridine complexed with Cu^{2+} heat-treated at 500°C (Fig. 5a) shows the bands of molybdenum trioxide at 993, 872 and 620 cm^{-1}. The band related to the Mo–O–Mo side bond, which was located in the initial compound at 581 cm^{-1}, underwent a displacement. It is suggested that such a displacement takes place due to the presence of Cu^{2+} at the surface and not between the lamellae of the material. The infrared spectrum of the MoO_3/piperazine complexed with Cu^{2+} calcined at 500°C (Fig. 5b) presents characteristic bands of MoO_3 at 996, 865 and 579 cm^{-1}, with a small displacement of the first band, which previously was placed at 988 cm^{-1}, and an enlargement of the other bands. Therefore, it is believed that the Cu^{2+} ion is present in the compound without interfering in the interlamellar distance. The infrared spectrum of MoO_3/octyldiamine/Cu^{2+} (Fig. 5c) was shown to be similar to the one of the starting oxide. The difference is related to the

Mo–O–Mo band shifts from 580 to 620 cm^{-1}, without indicating any changes. Thus, the obtained results are similar to the ones coming from other studies of other amines: after the release of the amine, copper remains in the MoO_3 structure, without altering the interlamellar distance.

Conclusions

It can be verified that the compound MoO_3/octyldiamine retains the largest amount of the Cu(II) ion, followed by the compounds MoO_3/3-aminopyridine and MoO_3/piperazine. The X-ray diffraction patterns for the copper-containing samples do not reveal meaningful changes concerning the structure or the interlamellar distance of the intercalation compound. This could be proven by the lack of change or small change of the positions of the interlamellar distance peaks of the complexed materials, as related to the intercalation compound. Only for the compound MoO_3/octyldiamine complexed with copper, changes could be noticed in the X-ray diffraction pattern, including the interlamellar distance of those materials, that undergo alteration. Therefore, it can be stated that the insertion of copper(II), along with octyldiamine, within the lattice, alters the structure of the compound. Also for this same lattice, a decrease in the number of interlamellar peaks was observed, indicating that after insertion of copper only one interlamellar distance exists.

The TG curves of the materials complexed with copper presented very peculiar changes. In the compound intercalated with 3-aminopyridine no mass loss step corresponding to the evaporation of free water was observed. In case of the compound intercalated with piperazine, the release of the amine molecules takes place in two stages. For the compound interca-lated with octyldiamine, the mass loss stages are similar to the ones of the copper-free compound. Few changes were observed in the infrared spectra of the copper-containing materials, as compared to the copper-free samples.

After the calcination, no meaningful changes in the diffraction patterns were observed, in relation to the original material. In the infrared spectra of the samples band displacements were observed. It is believed that copper remains in the structure, without changing the interlamellar distance of the compounds.

Acknowledgements

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