

Lamellar molybdenum oxide as a molecular sieve towards nitrogen containing molecules: intercalation compounds with pyridazine, acrylamid and tris(hydroxymethyl)aminomethane

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Received: 18 October 2007 / Accepted: 7 December 2007 / Published online: 25 December 2007
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Abstract The synthesis and characterization (by CHN elemental analysis, FTIR spectroscopy, XRD diffractometry, thermogravimetry and SEM microscopy) of MoO₃ intercalation compounds with pyridazine (pdz), acrylamid (ald) and tris(hydroxymethyl)aminomethane (tham) is reported. Such investigation was performed taking into account the possible uses of molybdenum trioxide as a molecular sieve towards nitrogen containing compounds. It is verified that the affinity of MoO₃ towards the investigated species follows the sequence: ald \cong tham > pdz.

Keywords Molybdenum oxide · Intercalation · Molecular sieve · Amides

Introduction

The inorganic–organic hybrids obtained through the intercalation of organic molecules into inorganic substrates have been extensively explored, since they could exhibit the properties of both, the inorganic and organic phases, with adsorptive, catalytic and transport properties, for example.

Molybdenum trioxide (α -MoO₃) has a lamellar structure, being insoluble in water. Its layered structure is constituted of parallel rows of distorted MoO₆ octahedra as shown in Fig. 1.

Due to its many applications for catalytic purposes, redox effects on MoO₃ have been studied [1, 2], by deposition of conducting polymer on its surface. Furthermore, taking into account that its sheets are separated by a Van der Waals gap, lamellar MoO₃ can be used as host species to produce intercalation compounds. The most recent studies of such compounds involves MoO₃-pyrazine [3], MoO₃-pyrrolidinedithiocarbamate [4], MoO₃-1,10-phenanthroline [5], nicotinamide and hexamethylenetetramine [6], as well as MoO₃ organosilanes [7] hybrids. The obtained results suggest that lamellar MoO₃ can be successfully employed as a molecular sieve towards a series of nitrogen containing organic species. Therefore, following our previous studies, the aim of this paper is to report the synthesis and characterization of MoO₃ intercalation compounds with pyridazine (pdz), acrylamid (ald) and tris(hydroxymethyl)aminomethane (tham), whose formulas are shown in Fig. 2, taking into account the possible uses of molybdenum trioxide as a molecular sieve towards nitrogen containing compounds.

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Experimental

All employed reagents were of analytical grade (Aldrich) and were used without further purification. The MoO₃ intercalation compounds with pyridazine (pdz), acrylamid (ald) and tris(hydroxymethyl)aminomethane (tham) were synthesized as by suspension of MoO₃ into aqueous solutions (40 cm³ of deionized water) of the organic species at room temperature (28 °C) under magnetic stirring for

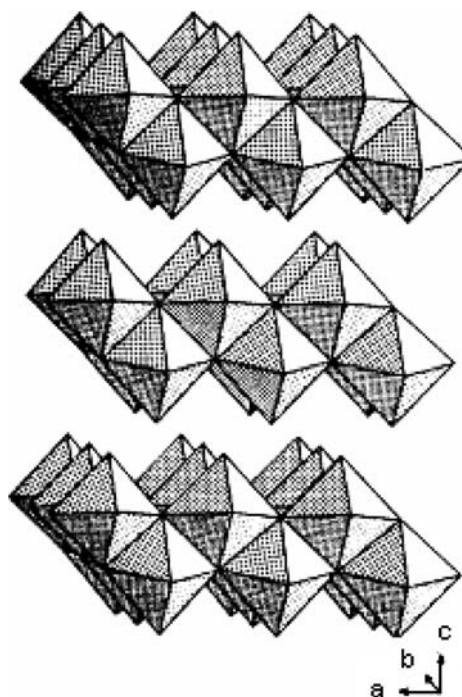
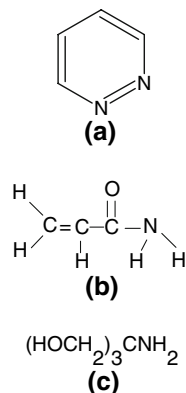


Fig. 1 Schematic representation of the network structure of lamellar MoO_3

Fig. 2 Structural/molecular formulas for (a) pyridazine, (b) acrylamid and (c) tris(hydroxymethyl)aminomethane



3 min. The obtained suspensions were then aged for 5 days, and then, the remaining solvent was slowly evaporated at 30 °C for another 2 days. The employed stoichiometric ratios were:

- MoO_3 (0.50 g) + ald (0.15 g) = Mo(ald)1
- MoO_3 (0.50 g) + ald (0.30 g) = Mo(ald)2
- MoO_3 (0.50 g) + tham (0.20 g) = Mo(tham)1
- MoO_3 (0.50 g) + tham (0.40 g) = Mo(tham)2
- MoO_3 (2.0 g) + pdz (0.50 cm³) = Mo(pdz)1
- MoO_3 (2.0 g) + pdz (1.0 cm³) = Mo(pdz)2

Hereafter, the six obtained hybrid matrices will be named as indicated from (a) to (f) respectively.

Carbon, nitrogen and hydrogen elemental analysis were performed in a Perkin-Elmer, model PE 2400,

microelemental analyzer. The X-ray diffraction patterns were obtained in a Shimadzu XD-3A equipment, using $\text{CuK}\alpha$ radiation (35 kV, 25 mA). Infrared spectra were recorded in a Gengis II FTIR apparatus in the 4,000–400 cm^{-1} range, with a resolution of 4 cm^{-1} . All I.R. spectra were obtained from powders in KBr discs. Thermogravimetric curves were obtained using a Shimadzu TG-50H apparatus under N_2 atmosphere with a heating rate of 15 °C min^{-1} . The SEM micrographs were taken in a Jeol equipment, model JSM T-300, with an accelerating voltage of 15 kV.

Results and discussion

The obtained elemental analysis results are summarized in Table 1. As can be verified, the lamellar MoO_3 exhibits its lower affinity towards pdz, since the formed compound, despite the fact that the ligand/oxide ratio is doubled from Mo(pdz)1 to Mo(pdz)2, is the same, in both cases: $\text{MoO}_3 \cdot (\text{pdz})_{0.5}$. Furthermore, based on analogous arguments, it can be concluded that the oxide exhibits its higher affinity towards acrylamid and an intermediary affinity towards tham. So, in using lamellar MoO_3 as a molecular sieve towards the studied species, the affinity sequence is: ald \cong tham > pdz.

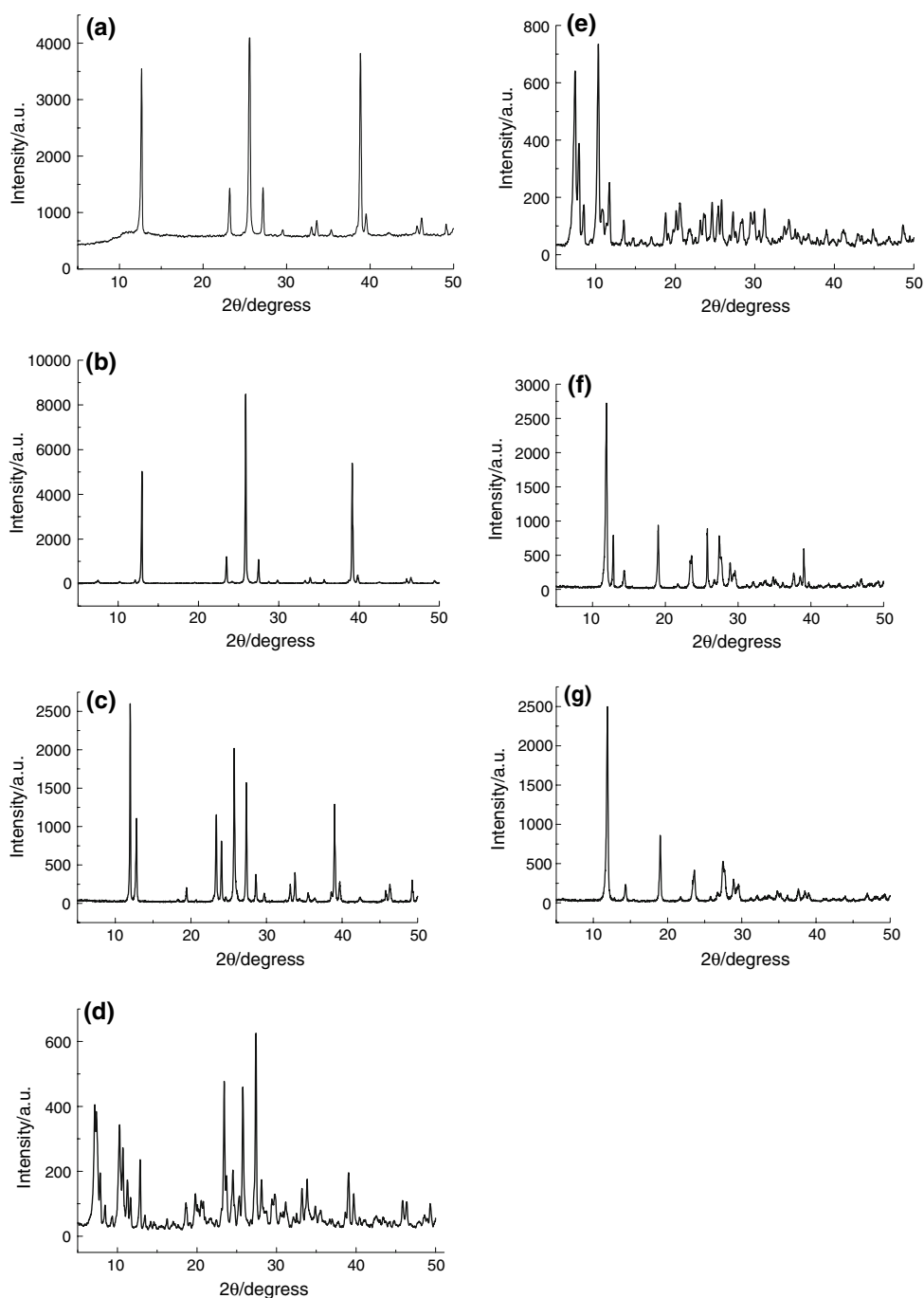
The obtained X-ray diffraction patterns for MoO_3 and hybrid matrices are shown in Fig. 3. In the oxide diffraction pattern, Fig. 3a, peaks at 12.6° and 25.2°, are associated with the 001 and 002, diffraction planes (10,11). Taking into account the 001 diffraction peak position, the interlayer distance can be calculated as 0.70 nm.

For Mo(ald)1, Fig. 3b, only the diffraction peaks of pure MoO_3 are observed, showing that the interaction between acrylamid and the oxide occurs only at the grain surfaces, with no intercalation. On the other hand, for Mo(ald)2, Fig. 3c new diffraction peaks at 11.9° (0.74 nm) and 23.3°, associated to the 001 and 002 diffraction peaks of a new crystalline phase are observed, besides the peaks for pure MoO_3 at 12.6° and 25.2°. Hence, it is verified that an increase on the relative amount of acrylamid have “pushed in” the amide molecules inside the interlayer cavity of

Table 1 Elemental analysis results for MoO_3 hybrids with pyridazine (pdz), acrylamid (ald) and tris(hydroxymethyl)aminomethane (tham)

Matrix	C/(%)	H/(%)	N/(%)	Proposed formula
Mo(ald)1	8.8	1.6	3.4	$\text{MoO}_3 \cdot (\text{ald})_{0.4}$
Mo(ald)2	17.8	3.6	6.9	$\text{MoO}_3 \cdot (\text{ald})_{1.1}$
Mo(tham)1	12.1	3.3	2.8	$\text{MoO}_3 \cdot (\text{tham})_{0.5}$
Mo(tham)2	18.2	4.2	4.2	$\text{MoO}_3 \cdot (\text{tham})_{1.0}$
Mo(pdz)1	12.7	1.5	7.6	$\text{MoO}_3 \cdot (\text{pdz})_{0.5}$
Mo(pdz)2	13.1	1.7	7.5	$\text{MoO}_3 \cdot (\text{pdz})_{0.5}$

Fig. 3 X-ray diffraction patterns for (a) MoO₃ (b) Mo(ald)1, (c) Mo(ald)2 (d) Mo(tham)1 (e) Mo(tham)2, (f) Mo(pdz)1 and (g) Mo(pdz)2



MoO₃. The minor increase of the interlayer distance (0.04 nm = 40 pm) suggests that acrylamid have penetrated the interlayer cavity in a “parallel” orientation to the inorganic layer.

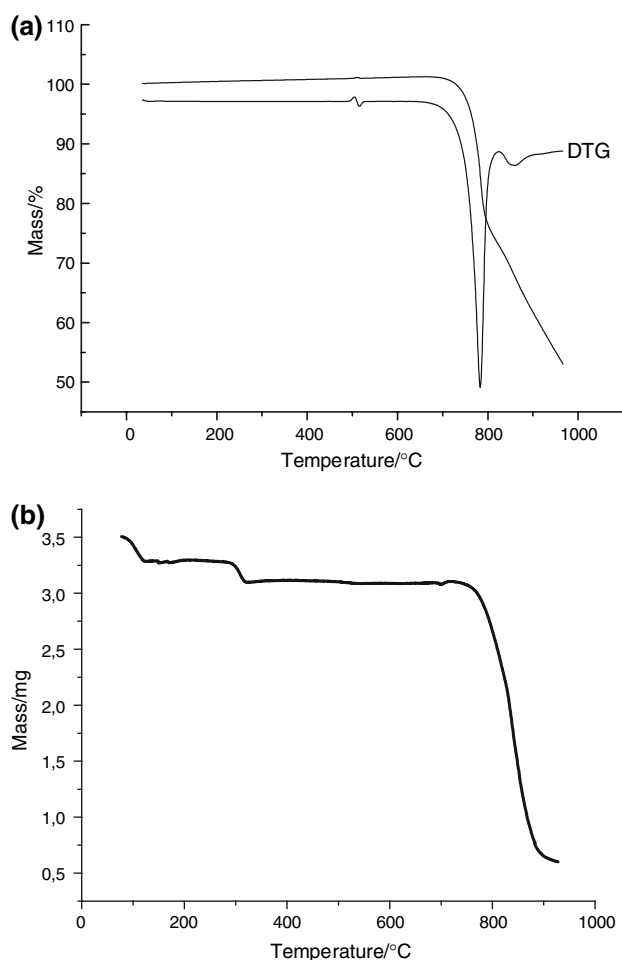
For Mo(tham)1 and Mo(tham)2, Fig. 3d and e, respectively, is observed a new (in comparison with MoO₃) diffraction peak at 7.3° (1.2 nm) that could be supposed to be the 001 diffraction peak of a formed intercalation compound. However, the obtained X-ray pattern suggests that interaction between tris(hydroxymethyl)aminomethane

and MoO₃ have provoked the disruption of the lamellar structure of the inorganic substrate, with the formation of a MoO₃-tham compounds which are not lamellar. The increase in the total amount of tham has provoked the total disruption of the oxide regular backbone.

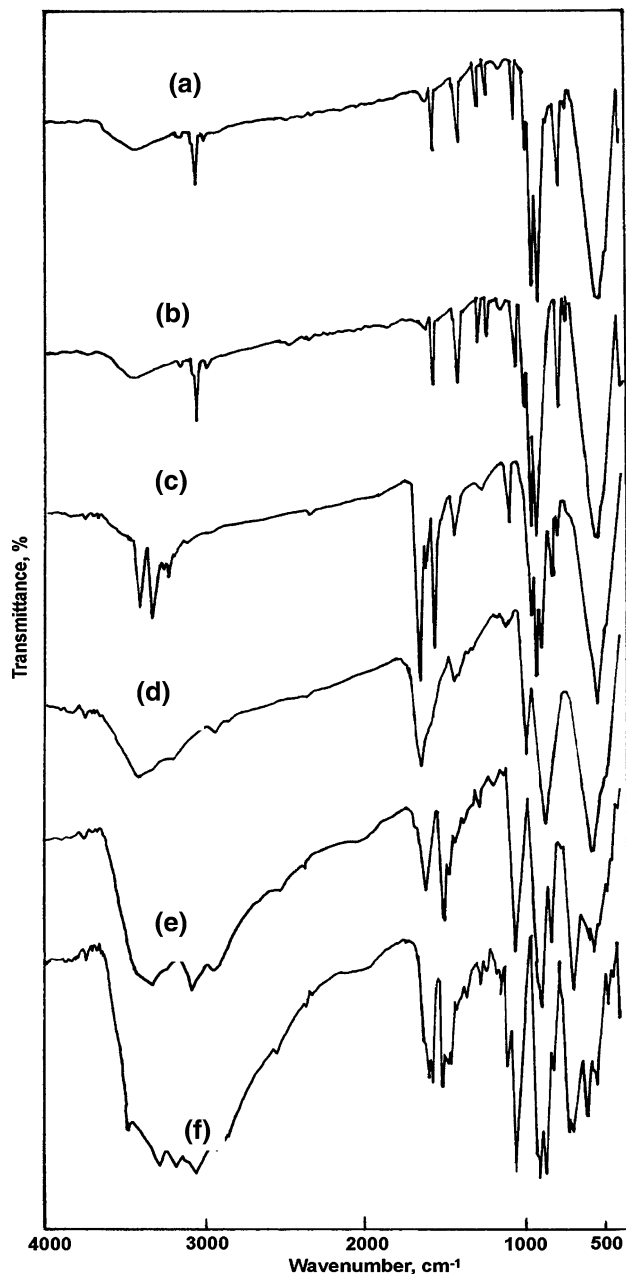
For Mo(pdz)1, Fig. 3f, new diffraction peaks at 11.8° (0.75 nm) and 23.6° that can be associated with the 001 and 002 diffraction peaks of a new crystalline phase are observed, besides the diffraction peaks of the pure oxide at 12.6° and 25.2°. On the other hand, for Mo(pdz)2, Fig. 3g,

Table 2 Main thermogravimetric data for MoO₃ and its compounds with pyridazine (pdz), acrylamid (ald) and tris (hydroxymethyl) aminomethane (tham)

Compound	$\Delta T/(^{\circ}\text{C})$	Mass loss/(%)
MoO ₃	25–750	0
	750–800	25 (sublimation)
	800–1,000	25 (sublimation)
MoO ₃ · (ald) _{0,4}	85–125	6.6 (water)
	290–320	5.2 (organic moiety)
MoO ₃ · (ald) _{1,1}	65–130	16.7 (water)
	390–680	9.6 (organic moiety)
MoO ₃ · (tham) _{0,5}	45–100	2.3 (water)
	190–420	17.3 (organic moiety)
MoO ₃ · (tham) _{1,0}	40–95	3.6 (water)
	160–520	26.5 (organic moiety)
MoO ₃ · (pdz) _{0,5}	25–350	0
	350–400	18 (organic moiety)
MoO ₃ · (pdz) _{0,5}	25–350	0
	350–400	19.6 (organic moiety)

**Fig. 4** Thermogravimetric curves for MoO₃ (a) and MoO₃ · (ald)_{0,4} (b)

only the diffraction peaks at 11.8° and 23° are observed, showing that an increase on the pyridazine/MoO₃ ratio have caused the formation of a pure intercalation phase, despite the fact that the number of intercalated molecules increased only in a minor amount as shown by CHN elemental analysis (Table 1). As observed for Mo(ald)₂, the minor increase of the interlayer distance (0.05 nm = 50 pm) suggests that the guest molecule have penetrated the interlayer cavity in a “parallel” orientation to the inorganic layer.

**Fig. 5** Infrared spectra for Mo(pdz)₁ (a), Mo(pdz)₂ (b), Mo(ald)₁ (c), Mo(ald)₂ (d), Mo(tham)₁ (e) and Mo(tham)₂ (f)

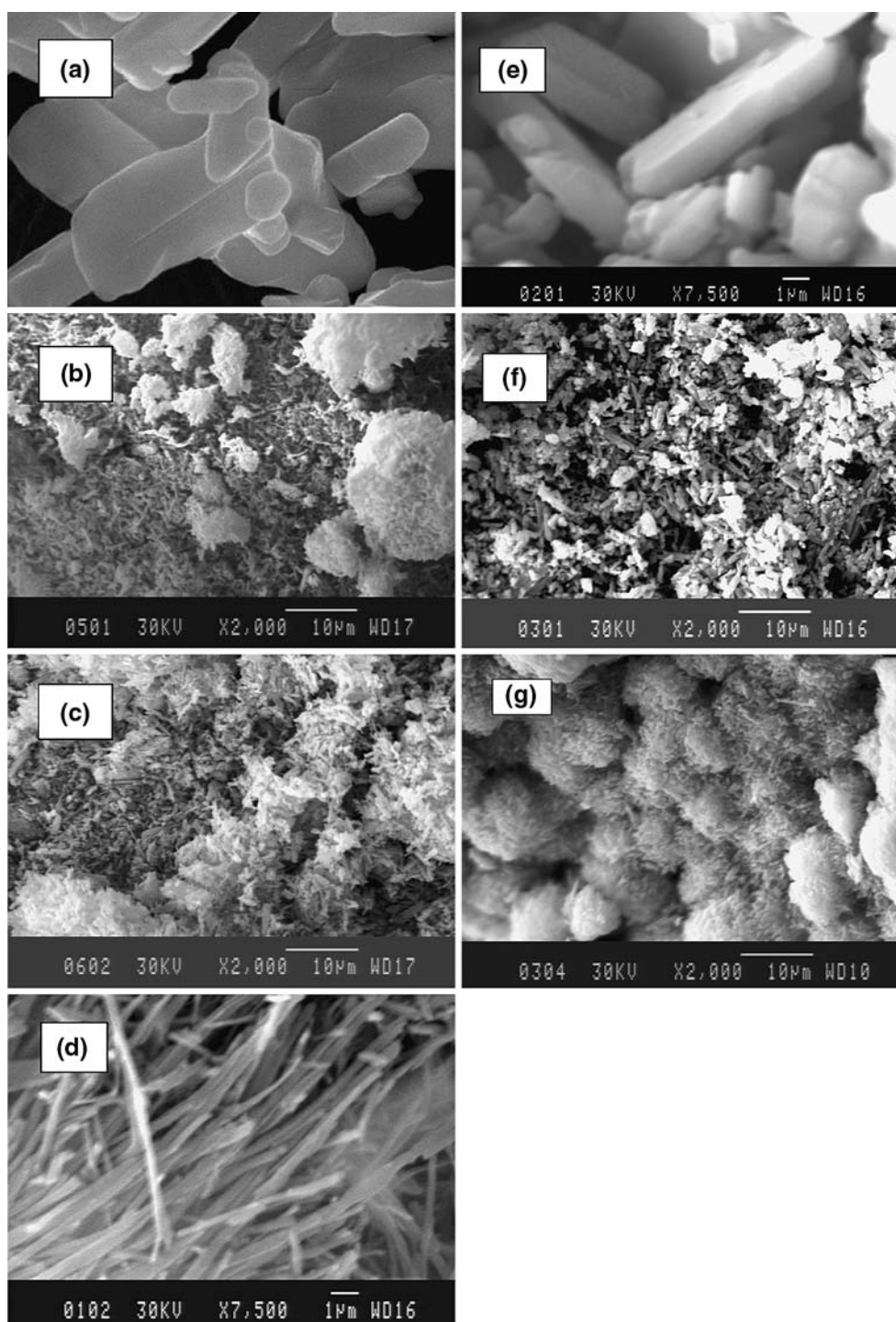


Fig. 6 SEM micrographs for MoO_3 $\times 500$ (a), $\text{Mo}(\text{pdz})1$ $\times 2,000$ (b), $\text{Mo}(\text{pdz})2$ $\times 2,000$ (c), $\text{Mo}(\text{ald})1$ $\times 7,500$ (d), $\text{Mo}(\text{ald})2$ $\times 7,500$ (e), $\text{Mo}(\text{tham})1$ $\times 2,000$ (f) and $\text{Mo}(\text{tham})2$ $\times 2,000$ (g)

The main thermogravimetric data are summarized in Table 2. To MoO_3 compounds only the mass losses due to the organic moiety are considered since, after that, there is only the pure oxide, which exhibits the same behavior in all cases. As illustrative examples, the TG curves for MoO_3 and $\text{MoO}_3 \cdot (\text{ald})_{0.4}$ are shown in Fig. 4. As can be verified

from Table 1 data, the minor difference in organic content observed for pdz compounds by CHN elemental analysis is confirmed by the TG data.

The obtained infrared data are in agreement with the hypothesis that there are chemical interactions between the acidic sites on the inorganic substrate and the organic

species, with interactions through nitrogen for tham and pdz and through oxygen for ald. Such interactions are the main ones, besides some other possible interactions, including hydrogen bonding. The obtained spectra are shown in Fig. 5.

Not only the nanostructure, as verified by DRX data, but also the microstructure of the lamellar oxide was affected by the interaction with the studied organic species. The obtained SEM micrographs for MoO₃ and the hybrid matrices are shown in Fig. 6. As can be verified, the MoO₃ grain size and morphology are greatly affected by the reaction with the investigated organic species. It is worth noting the Mo(ald)1 compound, for which fibers can be observed.

Conclusions

Based on the obtained experimental results, it can be concluded:

- (1) It is possible to form MoO₃ intercalation compounds with acrylamid and pyridazine, and an increase of the organic species/oxide ratio “pushed in” the host molecules into the interlayer space. Or, in another words, an increase of the guest molecule amount turns the intercalation process most favorable from a thermodynamic and/or kinetic point of view. On the other hand, the interaction between MoO₃ and tris(hydroxymethyl)aminomethane provokes the disruption of the

lamellar nanostructure of the inorganic substrate, with the formation of a salt. Such behavior is probably related with the acidity of the tham molecule.

- (2) The affinity of MoO₃ towards the investigated species follows the sequence: ald \cong tham > pdz.
- (3) The nano and microstructure of lamellar MoO₃ is greatly affected by the interaction with the studied organic species.

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