Journal of Thermal Analysis and Calorimetry, Vol. 61 (2000) 625–636

STUDIES ON WATER AND AMMONIA PROGRAMMED THERMODESORPTION OF MIXED M(III)-VANADYL PHOSPHATES

G. Bagnasco[1], *G. Busca*[2*], *P. Galli*[3], *M. A. Larrubia*[2], *M. A. Massucci*[3*], *L. Benes*[4], *R. Ramis*[2] *and M. Turco*[1*]

[1]Dipartimento di Ingegneria Chimica, Università 'Federico II', P. le Tecchio, 80. 80125 – Naples
[2]Dipartimento di Ingegneria Chimica e di Processo 'G. B. Bonino', Università di Genoa
P. le J. F. Kennedy, 1, 16129 – Genoa
[3]Dipartimento di Chimica. Università 'La Sapienza', P. le Aldo Moro, 5, 00185 – Rome, Italy
[4]Joint Laboratory of Solid State Chemistry, Academy of Sciences of the Czech Republic and University of Pardubice, Studenska 84, 530 09 Pardubice, Czech Republic

Abstract

Hydrated M(III)-vanadyl phosphates (*M*(III)=Mn, Fe, Ga, Al) have been prepared and studied for water and ammonia adsorption properties by TG/DTA, NH_3 TPD, FTIR and XRD techniques. The compounds have the same tetragonal layered structure of $VOPO_4 \cdot 2H_2O$, but shorter interlayer distances. Ammonia adsorption leads to intercalation of large amounts (0.19–0.39 mol/mol) of base between the layers of the materials, without displacement of water. The ammoniated phases obtained from these compounds have interlayer distances shorter than that of the corresponding precursors. In this connection an interaction mechanism NH_3-host is proposed. Treated at 450°C the materials adsorb ammonia only on the external surface because of the large decrease of the interlayer distance that prevents NH_3 from entering the interlayer space. All M(III)-vanadyl phosphates present a wide distribution of strength of ammonia adsorbing sites.

Keywords: intercalation, M(III)-vanadyl phosphates, NH_3 adsorption, NH_3 thermodesorption, surface acidity

Introduction

Mixed M(III)-vanadyl phosphates are formally derived from the phase $VOPO_4 \cdot 2H_2O$ (VOP) by partial substitution of VO groups with trivalent metal ions [1, 2]. It is expected that such substitution influences adsorption properties of VOP, that are related to the presence of coordinatively unsaturated vanadium atoms acting as Lewis acid sites [1, 3]. This effect should lead to materials with new catalytic properties. This has been already observed for Fe(III)-vanadyl phosphate (FeVOP) showing very interest-

* Authors for correspondence: e-mails: icibusca@csita.unige.it; massucci@axrma.uniroma1.it; turco@irc.na.cnr.it

1418–2874/2000/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

ing catalytic activity for NH_3 oxidation [4] and selective NO reduction [5]. A structural and thermal characterization of this material has also been reported, together with a thorough investigation of NH_3 adsorption properties [6]. Vanadyl phosphates substituted with other trivalent metals (Al. Ga, Cr, Mn) have recently been investigated for structural and thermal properties [7] but their adsorption or catalytic properties have not yet been considered. In this work we extend previous characterization studies by considering adsorption properties of VOP substituted with trivalent Al, Ga or Mn. Adsorption of water and ammonia on these compounds is studied by means of TG/DTA and NH_3 thermodesorption (TPD) techniques. FT-IR and XRD are also employed in order to study the nature of adsorbing sites and of phases resulting from ammonia adsorption.

Experimental

Materials

The compounds $[M(H_2O)]_x(VO)_{1-x}PO_4{\cdot}nH_2O$ (*M*=Mn, Fe, Ga and Al) were prepared as described previously [6–8] by refluxing for 16 h a suspension of vanadium pentoxide in diluted phosphoric acid to which was added the proper amount of metal(III) nitrate [6, 7] except for the manganese derivative for which potassium permanganate was used [8]. All of the compounds were air dried. The formulation of the as prepared compounds, as determined by chemical analysis [6–8] and TG measurements, is reported in Table 1. The short expression to denote them in the text (MVOP) is also indicated.

Table 1 Chemical composition, specific surface area (*S. A.*) and interlayer distance (d_i) of the as prepared and treated at 450°C compounds

Material	Abbreviation	*S. A.*/$m^2\ g^{-1}$)	d_i/Å	
$[Mn(H_2O)]_{0.25}(VO)_{0.75}PO_4{\cdot}1.90H_2O$	MnVOP	3.8	6.88	4.32*
$[Fe(H_2O)]_{0.20}(VO)_{0.80}PO_4{\cdot}2.20H_2O$	FeVOP	5.3	7.16	4.19*
$[Ga(H_2O)]_{0.18}(VO)_{0.82}PO_4{\cdot}1.85H_2O$	GaVOP	3.3	6.83	4.23*
$[Al(H_2O)]_{0.15}(VO)_{0.85}PO_4{\cdot}1.95H_2O$	AlVOP	5.9	6.95	4.21*

*after treatment at 450°C

Physical characterization

Scanning electron microscopy (SEM) was performed on a Philips XL30 apparatus. BET surface areas were measured by N_2 adsorption at –196°C on a Quantachrom CHEMBET 300 instrument.

A Philips diffractometer PW 1100 model was employed for taking the X-ray diffraction patterns (XRD) at room temperature (r.t.). A computer-controlled Philips diffractometer 1710 model provided with a HT-A.Paar diffraction camera was used for the XRD taken at 450°C. For both diffractometers Ni-filtered CuK_α radiation was

employed and the 2θ measurements were accurate to 0.05°. A Stanton Redcroft STA-801 model simultaneous TG/DTA thermoanalyzer was used to study the thermal behaviour of the as prepared and NH_3-treated materials and evaluate their water and ammonia content (heating rate 10°C min^{-1}, ignition up to 1000°C in an air flow, Pt crucibles, Pt-Pt/Rh thermocouples).

NH_3 temperature programmed desorption measurements (TPD) were carried out in a flow apparatus with a TCD detector and performed both on hydrated materials and on materials pretreated at 450°C for 12 h (MVOP-450). The sample (0.05–0.5 g) was treated at r.t. with a 5% NH_3/He mixture for 4 h and after purged in He flow for 3 h. Then NH_3 thermodesorption was effected by heating to 600°C at a rate of 10°C min^{-1}. A water trap (anhydrous KOH) was inserted during NH_3 desorption.

FT-IR spectra were recorded at *r.t.* with Nicolet Protégé 460 Fourier Transform spectrometers (4 cm^{-1} resolution) using self-supporting pressed disks of the pure catalyst powders calcined in the IR cell at 400°C for 2 h and outgassed in dynamic vacuum (10^{-4} torr) at 400°C for 30 min. Ammonia was from commercial cylinders from SIAD (Milano, Italy).

Results and discussion

Structural and thermal characterization

SEM micrographs of the MVOP compounds are reported in Fig. 1, that of VOP [6] is also given for comparison (Fig. 2). All samples show lamellar square shaped crystals, as expected from the tetragonal structure of vanadyl phosphate [9], however the crystal sizes of metal-vanadyl phosphates, being about 2x2x0.2 μm, are markedly smaller than that of VOP, leading to geometrical specific surface area of about 4 $m^2 g^{-1}$. This value is in good agreement with those of MVOP measured by N_2 adsorption (Table 1) and larger than 1 $m^2 g^{-1}$ of VOP.

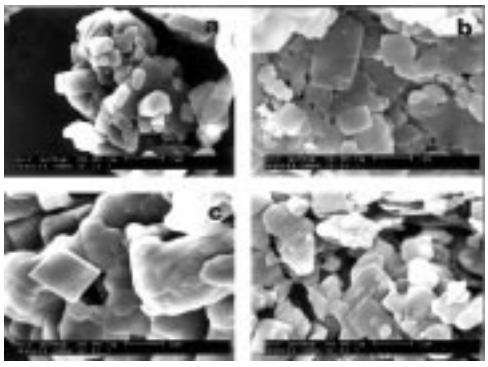

Fig. 1 SEM micrographs of MVOP compounds: a – MnVOP, b – FeVOP, c – GaVOP, d – AlVOP

The XRD patterns of the as prepared compounds are reported in Fig. 3 together with that of VOP [7] for comparison. All the compounds have the same tetragonal,

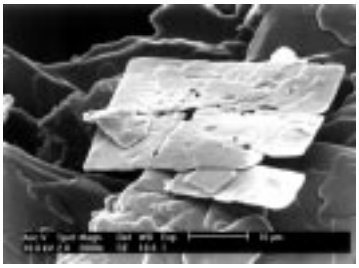

Fig. 2 SEM micrograph of VOP

layered structure as VOP, with, however, a lower degree of crystallinity. Their interlayer distances (Table 1), obtained from the first diffraction line in the respective diffraction patterns, are in the range 6.83–7.16 Å, a little shorter than VOP (7.41 Å). This suggests that the substitution of VO with trivalent metal ions enhances the interaction between the layers, leading to a decrease of the interlayer distance. In Fig. 4 are reported the XRD of the samples heated at 450°C. The loss of the hydration water does not affect the layered structure of the materials and the interlayer distances of the anhydrous compounds are in the range 4.19–4.32 Å (Table 1). Left in air the heated compounds slowly regain the crystal water and the interlayer distances of the hydrated compounds are restored. The thermal behaviour of the MVOP compounds has been already described [7]. It is useful to remember, however, that for MnVOP,

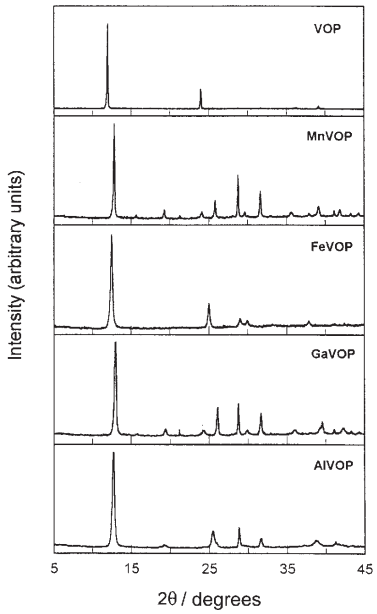

Fig. 3 XRD patterns of MVOP and VOP

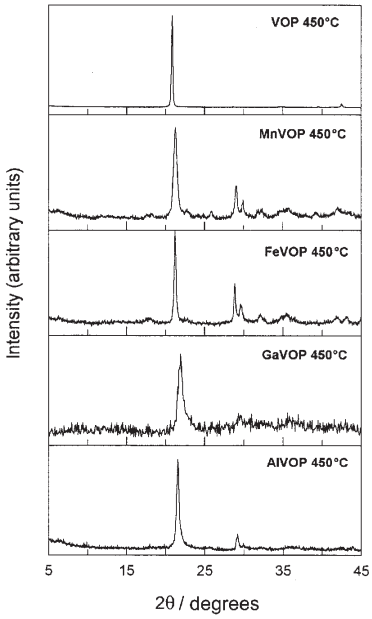

Fig. 4 XRD patterns of MVOP-450 and VOP-450

as for pure VOP, the hydration water is lost in two neat steps in the range 20–90 and 90–150°C, each corresponding to about one mole per mole of compound. For the other three MVOP materials the crystal water is also lost in two steps, the first is neat as for MnVOP and ends around 100°C, while the second, concluded at 230–250°C, is accompanied by broad and composed endothermic effects. The X-ray diffraction patterns of the four materials taken at regular temperature intervals of 15°C up to the conclusion of their dehydration process [7], lead to suppose that the different thermal behaviour of MnVOP is probably to be connected to the higher degree of crystallinity of this compound in comparison with that of the other three materials [7]. All compounds lose the water coordinated to the substituting trivalent metals in the range 550–650°C and, after 700°C, they begin to slowly decompose.

FT-IR study of ammoniated compounds

Ammonia adsorption has been investigated by FT-IR technique in order to obtain information on the nature of NH_3-adsorbing sites interactions. FT-IR measurtements were effected on anhydrous and hydrated materials.

The FT-IR spectra of the surface species formed after contacting the dehydrated MVOP with NH_3 gas at room temperature are very similar for all the sample and are reported in Fig. 5. In the spectral region 2000–1000 cm^{-1} the broad band between 1400–1500 cm^{-1} is due to N-H asymmetric ($\delta_{as}NH_4$) deformation mode of ammonium

ions [10, 11], indicating the presence of surface Brönsted acid sites. The corresponding associate stretchings, in the 3100–2600 cm^{-1} region, are not detectable because the scattering of the powders cuts the transmittance above 2500 cm^{-1}. Another very weak and broad absorption can be observed between 1600-1700 cm^{-1}. In this spectral region fall the bands due to the symmetric deformation mode ($\delta_{sym}NH_4$), characterised by a lower intensity with respect to the corresponding $\delta_{as}NH_4$. However we cannot exclude also the presence of trace of coordinated ammonia on surface Lewis acid sites, that present an asymmetric deformation mode ($\delta_{as}NH_3$) near 1605 cm^{-1}, so superimposed to $\delta_{as}NH_4$, and a symmetric deformation ($\delta_{sym}NH_3$), that fall near 1200 cm^{-1}, not detectable because obscured by the cut-off of the transmittance of the

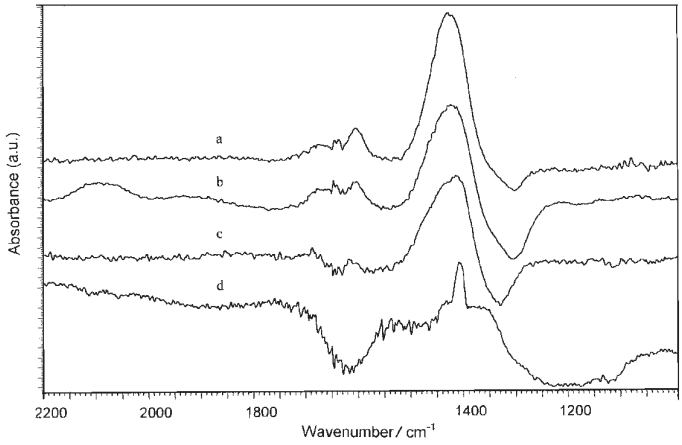

Fig. 5 FT-IR spectra of MVOP-450-4 compounds: a – FeVOP-450-4, b – MnVOP-450-4, c – AlVOP-450-4, d – GaVOP-450-4

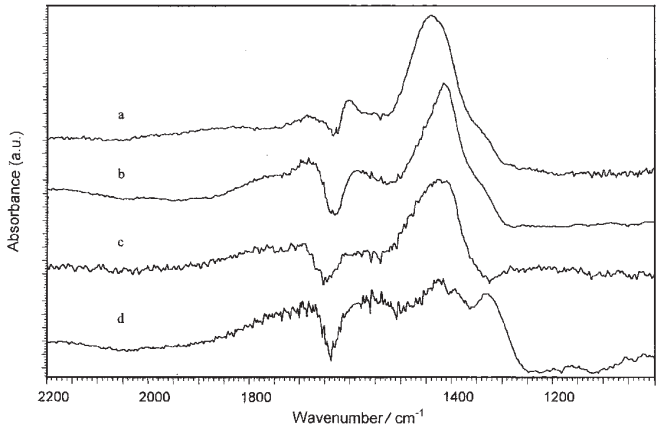

Fig. 6 FT-IR spctra of MVOP compounds: a – FeVOP-4, b – MnVOP-4, c – AlVOP-4, d – GaVOP-4

sample due to the absorption of the bulk. Outgassing at progressively higher temperature the bands associated to ammonium ions slightly shift towards lower frequencies and decrease in intensity up to completely disappear after evacuation at 250°C. The above data indicate that ammonia adsorbs over –OH surface groups of MVOP-450 materials in the form of ammonium ions, although the presence of molecularly coordinated species cannot be excluded. These results suggest that on the anhydrous MVOP materials Brönsted and Lewis acid sites are present. The presence of the –OH groups, acting as Brönsted sites, in the dehydrated materials could be due to the water molecules coordinated to the M(III) ions that are released at temperature higher than 550°C [7]. Lewis sites can be the coordinatively unsaturated $M(H_2O)$ and VO groups [6]. It must be observed that the spectrum of adsorbed ammonia over FeVOP-450 shows the band at 1610 cm^{-1} of coordinated ammonia slightly more relevant with respect to those observed on the other sample.

The adsorption of ammonia has also been investigated on the hydrated MVOP materials. The spectra (Fig. 6) are similar to those observed on MVOP-450 compounds, giving evidence of the formation of NH_4^+ ions. Few differences can, however, be observed. In particular, in all the spectra a negative signal near 1620 cm^{-1} gives evidence of interaction between coordinated water and ammonia. Therefore the protonation of ammonia by coordinated water can be hypothesized.

On the base of these results the following interaction mechanism between NH_3 and adsorbing sites, already hypothesized for VOP and FeVOP [6], can be extended to the MVOP materials:

$$\begin{array}{c} \text{H} \\ | \\ \text{-L --- O–H} \end{array} + NH_3 \Leftrightarrow \text{-L --- } O^-\text{–H} + NH_4^+ \qquad (1)$$

In the hydrated materials NH_3 is protonated by H_2O which is made more acidic due to coordination to $M(H_2O)$ and VO groups, while in the anhydrous materials only the $M(H_2O)$ groups must be taken into account.

Thermodesorption of the ammoniated compounds

NH_3 TPD measurements have been carried out both on hydrated (MVOP) and treated at 450°C for 12 h in He flow (MVOP-450) materials. MVOP and MVOP- 450 materials submitted to ammonia adsorption for 4 h are named MVOP-4 and MVOP-450-4 respectively. The spectra obtained with hydrated materials are reported in Fig. 7 together with that of VOP, in the same NH_3 adsorption conditions [6], for comparison. All spectra show peaks with maxima at rather high-temperatures, indicating that NH_3 is strongly adsorbed. MVOP-4 materials desorb NH_3 mainly as one large peak, while VOP-4 gives two main desorption peaks. The amounts of desorbed NH_3, calculated by integration of TPD curves (Table 2), are of the order of 10^{16} molecules cm^{-2}, higher than that admissible only for surface adsorption. Therefore NH_3 intercalation between the layers of the crystals can be hypothesised, as already observed with other basic molecules, strongly retained between the layers of VOP [12]. In agreement with the above interaction mechanism

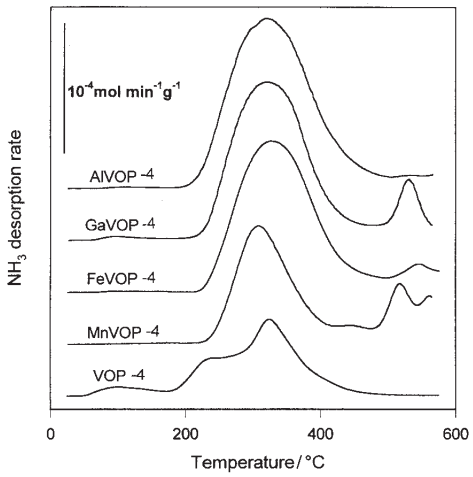

Fig. 7 TPD spectra of MVOP-4 compounds

(Scheme 1) a 1:1 stoichiometry between NH_3 and adsorbing VO or M groups can be assumed. The amounts of adsorbed NH_3 lower than one mole per mole of MVOP (Table 2) indicate that the materials are far from saturation. This behaviour can be explained by the slow rate of NH_3 intercalation in the interlayer space, due to diffusive resistances [6], that do not allow to reach saturation in 4 h of adsorption time employed in TPD experiments. Previous results showed that saturation is not achieved even after 24 h adsorption time [6]. It can be observed that MVOP materials adsorb NH_3 amounts higher than VOP, probably because the smaller crystal sizes lead to a reduced importance of diffusive resistances on NH_3 adsorption rate. Diffusive resistances can also affect the desorption rate, leading to some delay of the TPD peaks. Therefore the maximum temperatures may not be indicative of the strength of the NH_3-acid sites interactions. As observed above, VOP-4 gives two main desorption peaks, unlike MVOP-4 materials. This could be explained because intercalation of NH_3 in VOP leads to the formation of at least two different ammoniated phases [6], the deammoniation of such phases giving rise to the desorption of NH_3 in two steps. This does not occur for mixed phosphates probably because the substitution of M for VO induces a structural disorder that does not allow the formation of two distinct ammoniated phases. The TPD signals at high temperature (abt. 500°C) that appear in the spectra of MnVOP-4, FeVOP-4 and GaVOP-4 materials, is indicative of very strong NH_3 adsorption. It can be hypothesized that during thermodesorption ammonia replaces the water molecules strongly coordinated to the trivalent metal ion and is desorbed at higher temperature. This signal is absent in the spectrum of AlVOP-4 probably because the high affinity of Al(III) for H_2O prevents the replacement of H_2O by NH_3.

The MVOP-450 materials show different behaviour towards NH_3 adsorption as shown by TPD spectra reported in Fig. 8. Broad TPD peaks are obtained, having maxima at rather low temperatures (150–180°C), in agreement with FT-IR data showing the ammonia desorption occurring within 250°C. However tails extending to high temperatures

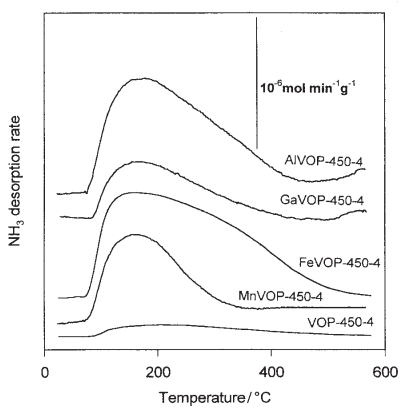

Fig. 8 TPD spectra of MVOP-450-4 compounds

(450–500°C) are present in all spectra. NH_3 amounts adsorbed by heat treated materials are two order of magnitude lower than those adsorbed by hydrated materials (Table 3). The concentrations of NH_3, if referred to unit surface area, correspond to the theoretical surface concentrations of VO and M groups (about $3 \cdot 10^{14}$ cm^{-2}), suggesting that only surface adsorption occurs on MVOP-450 materials. This is confirmed by the observation that NH_3 adsorption is much faster with heat treated than with hydrated materials: in fact the saturation is reached in a few minutes, giving evidence that no limitation due to diffu-

Table 2 Interlayer distances (d_i) and desorbed NH_3 and H_2O amounts for MVOP-4 materials

Material	d_i/Å	NH_3		H_2O	
		10^3 mol g^{-1}	mol mol^{-1}	10^3 mol g^{-1}	mol mol^{-1}
VOP-4	7.20	0.74	0.14	9.82	1.90
MnVOP-4	6.68	0.98	0.19	9.63	1.94
FeVOP-4	6.52	1.48	0.29	9.18	1.85
GaVOP-4	6.58	1.67	0.34	8.90	1.82
AlVOP-4	6.68	2.00	0.39	10.14	2.05

Table 3 Results of NH_3 TPD measurements for MVOP-450-4 materials

Material	T_{max}/°C	Desorbed NH_3	
		10^5 mol g^{-1}	10^{-14} mol cm^{-2}
VOP-450-4	180	0.16	1.1
MnVOP-450-4	155	0.99	1.6
FeVOP-450-4	150	2.10	2.4
GaVOP-450-4	167	0.84	1.5
AlVOP-450-4	175	2.05	2.0

sion affects the adsorption rate. The absence of ammonia intercalation in MVOP-450 is due to the large decrease of interlayer distance as a consequence of dehydration, that prevents NH_3 from entering the interlayer space. It is expected that diffusive limitations are also absent during desorption of NH_3 leading to lower temperature desorption peaks in comparison with the hydrated materials. On the base of FT-IR results, the mechanism of adsorption of ammonia by MVOP-450 should be similar to that of MVOP materials, although the coodination to VO groups can not be excluded. The shape of TPD peaks appearing in Fig. 8 points to a wide distribution of strength of NH_3 adsorbing sites, that can be attributed to surface heterogeneity. From the extension of peak tails it seems that MnVOP has a smaller fraction of strong adsorption sites in comparison with the other materials. This could be explained by the higher degree of crystallinity of MnVOP, that leads to a lower concentration of structural defects. Moreover FeVOP-450 sample shows a higher concentration of strong adsorbing sites probably related to a higher concentration of coordinative sites, as observed in FT-IR measurements.

Thermal behaviour and XRD patterns of ammonia treated compounds

The thermal behaviour of MVOP-4 is reported in Fig. 9. By observing TG curves of the compounds, the mass losses seem to occur in two large steps up to 500°C. However, a careful examination of the corresponding DTA profiles indicates a series of at least four endothermic effects for each compound, thus suggesting that the total loss

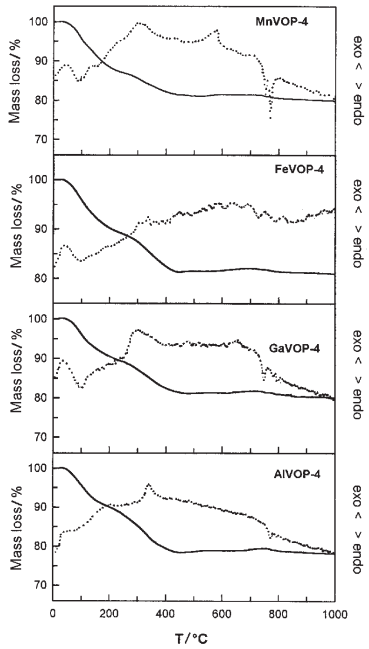

Fig. 9 TG (—) and DTA (···) curves of MVOP-4 compounds

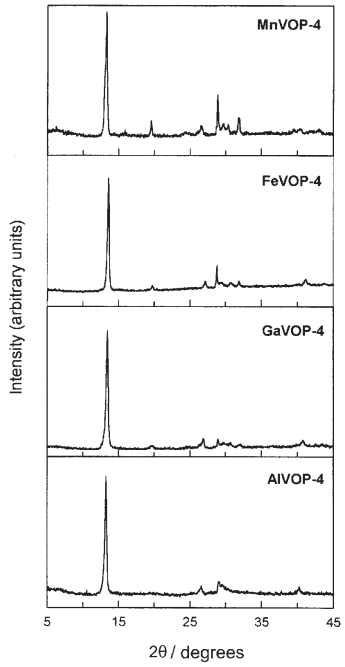

Fig. 10 XRD patterns of MVOP-4 compounds

process, involving water and ammonia release, is rather complicated. The endothermic effect and mass losses observed up to 150°C are due to elimination of hydration water, about 1 mole per mole of material, that does not interact with ammonia. DTA and TG signals occurring at higher temperature (up to 500°C) can be related to the simultaneous loss of the remaining water and ammonia. Such process occurs *via* the decomposition of ammonium ions, leading to ammonia desorption, and subsequent removal of water. From NH_3-TPD and TG data the amount of water released from ammonia treated compounds have been calculated (Table 2). It can be observed that the amounts of water are very close to those of the MVOP materials (Table 1), suggesting that ammonia adsorption does not cause the removal of hydration water from the solids. Therefore these results are a further confirmation to the hypothesized mechanism of NH_3 adsorption (Scheme 1).

X-ray diffraction patterns of MVOP-4, reported in Fig. 10, show that all compounds retain the layered structure and have a degree of crystallinity comparable with that of the respective MVOP. It is interesting to note that, notwithstanding the slightly larger amount of species in the interlayer region of the NH_3-treated compounds, the interlayer distances (Table 2) are shorter than that the simply hydrated analogues (Table 1). The reduction of the interlayer space after ammonia adsorption, can be due to strong interaction between

NH_4^+ ions and negatively charged layers.. Moreover, as it was expected, for as concerns compounds MVOP-450-4, the very small amounts of adsorbed ammonia (Table 3) do not give rise to significant differences in the XRD patterns in comparison with those of the MVOP-450 materials reported in Fig. 4.

Conclusions

NH_3 adsorption properties of different M(III)-vanadyl phosphates have been studied by means of thermal and spectroscopic techniques. The different behaviour of hydrated and anhydrous compounds has been described. The hydrated materials are able to intercalate large amounts of ammonia, without displacement of hydration water. Heat treatment leading to the dehydration causes a marked decrease of interlayer distances, preventing ammonia intercalation and allowing only surface adsorption. Adsorbing sites of widely different strength are found on the external surface of crystallites. FT-IR measurements suggest an interaction mechanism involving protonation of ammonia by water coordinated to M or VO groups.

* * *

The authors thank the Ministero della Ricerca Scientifica e Tecnologica (Murst) for financial support. The authors also thank Mrs. Clelia Zucchini and Mr. Sabatino Russo of Istituto di Ricerche sulla Combustione, CNR, Napoli (Italy) for performing SEM measurements. M. A. Larrubia acknowledges MEC for an FPI grant.

References

1 K. Melanova, J. Votinsky, L. Benes and V. Zima, Mat. Res. Bull., 30 (1995) 1115.
2 K. Richtrova, J. Votinsky, J. Kalousova, L. Benes and V. Zima, J. Solid State Chem., 116 (1995) 400.
3 L. Benes, J. Votinsky, J. Kalousova and J. Klikorka, Inorg. Chim. Acta, 114 (1986) 47.
4 G. Bagnasco, L. Benes, P. Galli, M. A. Massucci, P. Patrono, G. Russo and M. Turco, Studies in Surface Science and Catalysis, 119 (1998) 653.
5 G. Bagnasco, P. Galli, M. A. Massucci, P. Patrono, G. Russo and M. Turco, Atti de 11° Congresso Nazionale di Catalisi, Villasimius (CA), June 1998, p. O10.
6 G. Bagnasco, L. Benes, P. Galli, M. A. Massucci, P. Patrono, M. Turco and V. Zima, J. Therm. Anal. Cal., 52 (1998) 615.
7 L. Benes, P. Galli, M. A. Massucci, K. Melanova, P. Patrono and V. Zima, J. Thermal Anal., 50 (1997) 355.
8 L. Benes, K. Richtrova, J. Votinsky, J. Kalousova and V. Zima, Powder Diffr., 8 (1993) 130.
9 H. R. Tietze, Austral. J. Chem., 34 (1981) 2035.
10 A. A Tsyganenko, D. V. Pozdnyakov and V. N. Filimonov, J. Mol. Struct., 29 (1975) 299.
11 K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, 4th ed., Wiley, New York 1986.
12 L. Benes, R. Hyklova, J. Kalousova and J. Votinsky, Inorg. Chim. Acta, 177 (1990) 71.