Journal of Thermal Analysis, Vol. 50 (1997) 355-364

THERMAL, STRUCTURAL AND ACIDIC CHARACTERIZATION OF SOME VANADYL PHOSPHATE MATERIALS MODIFIED WITH TRIVALENT METAL CATIONS

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(Received December 6, 1996)

Abstract

A set of new materials with general formula $[M(H_2O)]_x(VO)_{1-x}PO_4{\cdot}2H_2O$ (M^{3+}= Al, Cr, Ga, Mn), isomorphous with layered tetragonal $VOPO_4{\cdot}2H_2O$ and having potential catalytic properties, have been characterized by TG and DTA, X-ray diffraction and surface acid strength. During heating the compounds transform in the monohydrated and anhydrous phases, all maintaining a layered structure, with a proper interlayer spacing. Catalytic tests performed with 1-butene show that the M^{3+}-vanadyl phosphates greatly improve the conversion of the olefine with respect to pure vanadyl phosphate.

Keywords: 1-butene isomerization, M^{3+}-substituted vanadyl phosphates, structural characterization, thermal characterization, vanadyl phosphate

Introduction

In recent years much attention has been paid to vanadium-phosphorus containing compounds for their possibility to be used as catalysts in oxidative hydrocarbon reactions [1, 2]. Many of these materials have their precursors in layered vanadyl phosphate dihydrate ($VOPO_4{\cdot}2H_2O$) and some related compounds such as $VOHPO_4{\cdot}0.5H_2O$, from which the catalysts are prepared by thermal treatment at a suitable temperature [3]. Vanadyl phosphates are used in oxidation of propane to acetic and acrylic acid [4], in ammoxidation of picolines [5] and toluenes [6–8] to nitriles, in the preparation of aminocyanopyridines from aminomethyl-pyridines [9] or, mixed with titanium phosphate, for the prepara-

0368–4466/97/ $ 5.00

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tion of acrylic acid and methacrylate from acetic acid [10]. With the aim of disposing of a larger number of vanadium-phosphorus based materials to be used as potential catalysts in oxidative reactions, a set of recently prepared [11–13] layered compounds derived from vanadyl phosphate with general formula $[M(H_2O)]_x(VO)_{1-x}PO_4{\cdot}2H_2O$ (M^{3+}= Al, Cr, Ga, Mn) are here considered. According to previous studies [13], it is reasonable to assume that these compounds maintain the tetragonal structure of the layered $VOPO_4{\cdot}2H_2O$ [14], which consists of sheets of $(VOPO_4)_\infty$ connected to each other through molecules of water located in the interlayer space. The $(VOPO_4)_\infty$ sheets are composed of highly distorted VO_6 octahedra sharing four oxygen atoms with four different PO_4 tetrahedra groups. One of the two water molecules is coordinated to the vanadium atom in an axial position, thus completing the VO_6 vanadium octahedron; the other is anchored more loosely through H-bonds to the oxygens of the tetrahedral phosphate groups [14]. In the case of the $[M(H_2O)]_x(VO)_{1-x}PO_4{\cdot}2H_2O$ compounds, the $M(H_2O)^{3+}$ ions partially replace equivalent amounts of VO^{3+} oxocations, in a random distribution all along one layer. The hydration water of the new compounds is 2 moles of water per mole of compound, probably intercalated in the same fashion as in $VOPO_4{\cdot}2H_2O$.

Since these new mixed M^{3+}-vanadyl phosphates will be tested as heterogeneous catalysts in the oxidative hydrocarbon reactions, the purpose of this investigation is that of a preliminary characterization of the diierent materials by studying their thermal properties as a function of the nature of the M^{3+}, following the structural changes they undergo due to thermal treatments, and by evaluating their acid strength at temperatures close to those usually employed for the catalytic reactions cited.

Experimental

The vanadyl phosphate dihydrate was prepared according to the Ladwig method [15] by refluxing a suspension of V_2O_5 in diluted H_3PO_4.

The compounds $[M(H_2O)]_x(VO)_{1-x}PO_4{\cdot}2H_2O$ (M= Al, Cr, Ga, Mn; $x = 0.18$–0.25) were similarly prepared by suspending vanadium pentoxide in diluted phosphoric acid containing the trivalent metal salt. The preparation of the various compounds and their chemical analysis have been reported in detail pre-

Table 1 Chemical composition of the obtained compounds with their abbreviations

Materials	Abbreviations
$VOPO_4{\cdot}2H_2O$	VOP
$[Al(H_2O)]_{0.15}(VO)_{0.85}PO_4{\cdot}2H_2O$	AlVOP
$[Cr(H_2O)]_{0.17}(VO)_{0.83}PO_4{\cdot}2H_2O$	CrVOP
$[Ga(H_2O]_{0.18}(VO)_{0.82}PO_4{\cdot}2H_2O$	GaVOP
$[Mn(H_2O)]_{0.25}(VO)_{0.75}PO_4{\cdot}2H_2O$	MnVOP

viously [11–13]. All the materials obtained are listed in Table 1, together with short expression used to denote them in the text.

Before submission to X-ray diffraction analysis all the compounds as prepared, except CrVOP, were kept in a dessicator over a saturated solution of K_2CO_3 (relative humidity=43%) for one week up to constant weight. In these conditions CrVOP possesses 2.2 moles of water per mole of compound. This form changes into the dihydrated phases on long standing in air or by heating at 30°C. The X-ray diffraction patterns (XRDs) were taken on a Freiberg Präzisionsmechanik X-ray diffractometer model HZG-4, using CuK_{α}, radiation with discrimination of CuK_{β} radiation by a nickel filter. The CuK_{α_2} intensities were removed from the original data. Diffraction angles (2θ) were measured from 8 to 35°. Silicium (a=5.43055 Å) was used as an external standard. The diffractograms were taken at different temperatures (from 20 to 250°C). The powder samples were placed on a corundum plate (with thermocouple), heated up to the desired temperature value and the XRD recorded.

The thermal behaviour of the different solids was followed using a Stanton Redcroft STA-801 model simultaneous TG-DTA thermoanalyzer with ignition up to 1000°C (heating rate 10°C min^{-1}, Pt crucible, Pt-Pt/Rh thermocouples) in an air flow. The water content of the solids was also determined using TG methods.

The acid strength measurements of the M^{3+}-vanadyl phosphates were performed utilizing 1-butene isomerization as test reaction [16, 17]. The catalytic tests were carried out in a fixed bed flow microreactor at 450°C and atmospheric pressure. The reaction products were first condensed in a trap at different times on stream and later analyzed by injection into a Carlo Erba model 4200 gas-chromatograph equipped with a 50 m capillary Al_2O_3/KCl column.

Results and discussion

Thermal behaviour

The TG-DTA curves of all of the derived M^{3+}-vanadyl phosphates are reported in Fig. 1 together with those of pure VOP for comparison.

MnVOP behaves like VOP [18]. The TG curves of the two compounds show that all the hydration water is lost between 20 and 150°C. The process occurs in two steps, each corresponding to the loss of one mole of water per mole of compound. Two endothermic effects are correspondingly observed in the respective DTA curves and are evidenced by sharp and well resolved peaks. AlVOP and GaVOP also have similar thermal behaviours. Both materials lose the hydration water in two steps. However, while the first occurs in the same temperature range as for VOP and MnVOP and is accompanied by a sharp endothermic peak, the second needs a larger temperature interval to bring the process to completion and is accompanied by a broad and composite endothermic effect. Unlike the other M^{3+}-substituted analogues that lose their less bounded water in one, well-defined step, CrVOP loses this water into two steps that are clearly evidenced in

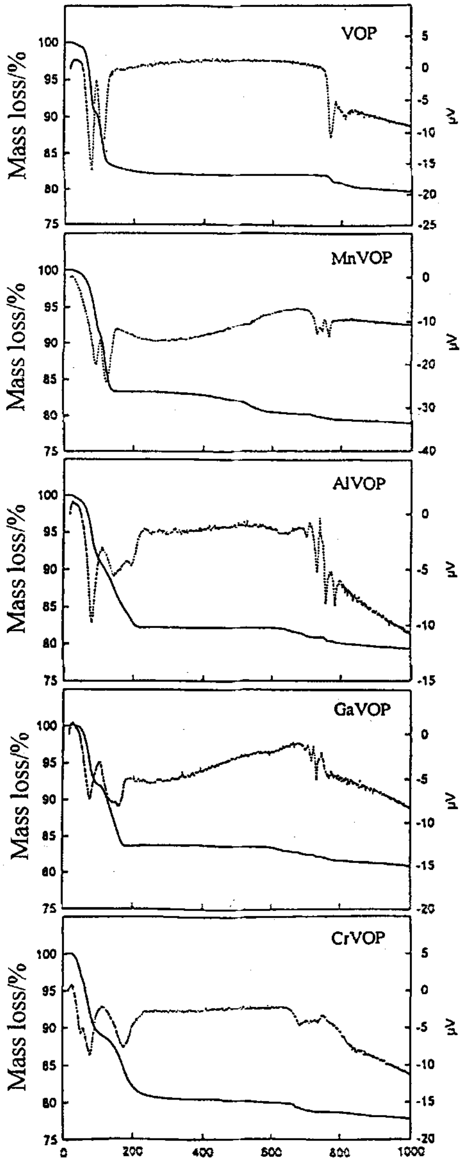

Fig. 1 Simultaneous TG-DTA curves of VOP, MnVOP, AlVOP, GaVOP and CrVOP

both TG and DTA curves. As for AlVOP and GaVOP, the last mole of hydration water is lost over a somewhat larger temperature interval than VOP and MnVOP.

For all the compounds the water coordinated to the substituted metal is lost between 250 and 600°C and the residual solids can be formulated as $M_x(VO)_{1-x}PO_4$.

After 600°C the presence of a new series of endothermic peaks indicates the beginning of the decomposition of the anhydrous materials.

X-ray characterization

The XRD patterns of VOP and the M^{3+}-substituted compounds were recorded over the temperature range 20–250°C. For VOP [18] and MnVOP [12, 13] three distinct phases corresponding to the dihydrated, monohydrated and anhydrous compound, are singled out during heating. The transition from one phase to the other occurs over divide intervals of temperature in which two phases, the di- and monohydrated or the monohydrated and anhydrous phases, are simultaneously present, each one with its own, well-defined interlayer distance. These characteristics are clearly illustrated in Fig. 2a and b in which the

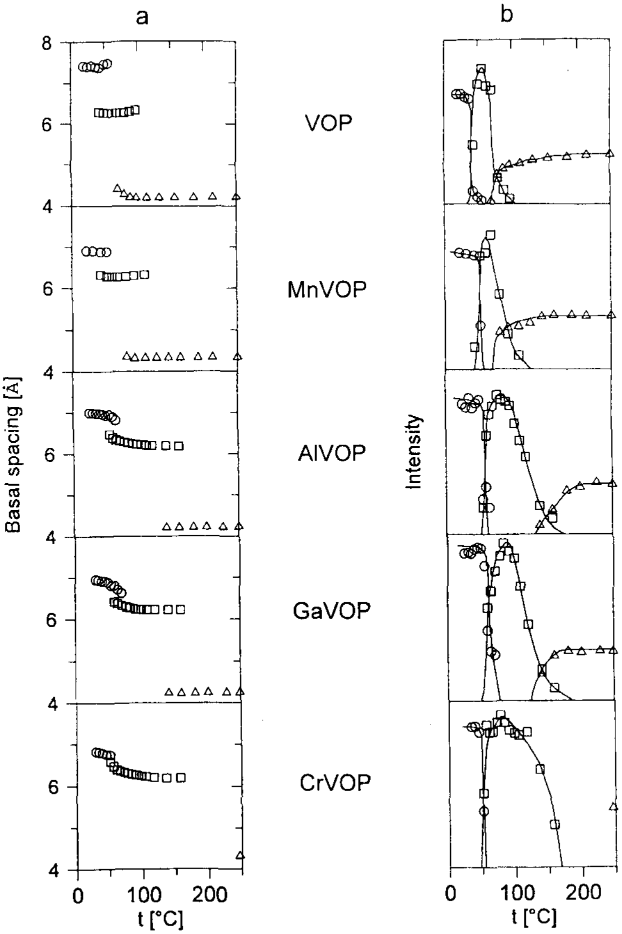

Fig. 2 a) basal spacings and b) intensities, corresponding to the (001) diffraction lines of VOP, MnVOP, AlVOP, GaVOP and CrVOP

interlayer spacings (Fig. 2a) obtained from the basal (001) diffraction lines, and the corresponding integral intensity values (Fig. 2b) of the differently hydrated phases of all the studied compounds, are respectively shown as a function of the temperature. Fig. 2a shows that each hydrated or anhydrous phase of VOP or MnVOP maintains its own, constant, interlayer distance until it disappears, while Fig. 2b, which is closely related to Fig. 2a, shows that the intensities of the basal reflexions of the anhydrous phases, even when they are alone in the solids, strongly decrease with respect to that of the di- or monohydrated phases. This behaviour, which is observed also for the other compounds studied (see below), is probably related to a certain amorphization of the solid on complete dehydration.

AlVOP and GaVOP show trends similar to VOP and MnVOP. However, by comparing the two couples of compounds in Fig. 2a, it can be observed that on going from the dihydrated to the monohydrated phase under heating, AlVOP and GaVOP continuously change their interlayer spacing. The shift of the (001) lines towards higher 2θ angles is accompanied by a broadening of the diffraction peaks, both features that can be caused by a slightly disordered stacking of the layers [19]. A similar phenomenon has been observed for VOP when the rehydration process of the anhydrous compound was studied [20]. By carefully examining Fig. 2a and b, the transition from the dihydrated to the monohydrated phase for the four compounds occurs over a temperature range of about 10–15 degrees, around 50°C for VOP and MnVOP and 70°C for AlVOP and GaVOP.

A peculiar behaviour is shown by CrVOP, in which the transition from the dihydrated to the monohydrated phase occurs through a "continuum" of a somewhat disordered phase that changes its interlayer distance as the water content decreases (Fig. 2a), except for a very short range of temperatures located around 51–52°C, in which two phases are simultaneously present (Fig. 2b).

The range of temperatures in which the monohydrated and anhydrous phases coexist is confined to about 20–30 degrees for VOP, MnVOP, AlVOP and GaVOP. For the AlVOP and GaVOP this range is shifted towards higher temperatures in comparison with VOP and MnVOP. Furthermore the anhydrous phases alone appear around 140°C, as if water could be more tightly retained by Al and Ga. In view of the fact that the metal ions of the III A group interact strongly with water (Al^{3+} more than Ga^{3+}) this could account for the large second exothermic effect observed in the DTA curves of AlVOP and GaVOP (Fig. 1), an effect that ends around 190°C for GaVOP and is even larger (it almost could be split into two endothermics) in the case of AlVOP for which water is definitely lost around 230°C.

In the case of CrVOP, the monohydrate and anhydrous phase never coexist, and although the monohydrate phase disappears completely around 157°C, the anhydrous phase is observed only at 250°C. This material actually has a very low degree of crystallinity with respect to the other compounds and displays very broad and somewhat indistinct diffraction lines.

The values of the interlayer distance of the di-, monohydrated and anhydrous compounds are reported in Table 2. The temperatures at which the monohydrate and anhydrous phases begin to form are indicated by t_1 and t_0, while t_{2d} and t_{1d}

Table 2 Basal spacing (d_{001}) of the different M^{3+} vanadyl phosphate phases

Materials	Dihydrate		Monohydrate			Anhydrous	
	d/Å	t_{2d}/°C*	d/Å	t_1/°C**	t_{1d}/°C*	d/Å	t_0/°C**
VOP	7.41	56	6.26	43	98	4.20	70
AlVOP	6.99	65	6.27	55	159	4.21	140
CrVOP	6.81	51	6.30	51	157	4.32	250
GaVOP	6.91	71	6.27	60	160	4.23	141
MnVOP	6.91	53	6.28	44	110	4.32	82

*t_{2d} and t_{1d}: temperature at which the dihydrated and monohydrated phases disappear respectively
**t_1 and t_0: temperature of formation of monohydrate and anhydrous phases respectively.

indicate the temperatures at which the dihydrate and monohydrate phases disappear completely.

It is immediately apparent that the basal spacings of the anhydrous compounds are very similar. This means that the replacement of part of the vanadyl groups by the metal ions does not significantly influence the way adjacent layers are bonded. The interlayer distance of all the compounds studied is a sum of the thickness of the layer itself and the length of the coordination bond between the vanadium and the axial oxygen of the vanadyl group of adjacent layers [13]. The basal spacings of the monohydrate phases (i.e. the interlayer distance taken at the temperature at which the highest intensity of the diffraction line was found) are also very close together. In this case the basal spacing is increased, compared with the anhydrous compounds, by the value corresponding to the steric demand of the molecule of water coordinated by its oxygen to the vanadium atom. It follows from these considerations that the molecule of water coordinated to the substituted M^{3+} ions has the same, or a slightly smaller, sterical demand as the water molecule coordinated to vanadium and does not influence the interlayer distance. The basal spacing values found for the dihydrates of the M^{3+}-modified compounds are significantly lower than for VOP. It is assumed that in VOP the second water molecule is bonded to the PO_4 tetrahedron by a weak H-bond [13]. If a similar bonding is supposed for the modified compounds, the difference compared with the basal spacing of VOP is rather surprising. Investigations on the subject are under way.

Catalytic tests

In order to probe the nature and the strength of the surface sites of the M^{3+}-vanadyl phosphates, all the material were investigated in the catalytic reaction of 1-butene isomerization, a reaction known to be catalyzed by acidic materials proceeding via the carbenium ion [21, 22].

Before any catalytic test, VOP and the M^{3+}-vanadyl phosphates were previously thermally treated at 500°C for two hours in air flow. This treatment was necessary to completely eliminate any water and to ensure reproducible materials.

Table 3 Molar percent of the outflowing gases in the catalytic conversion of 1-butene at 723 K and τ (g cat/g 1-butene/h)=2.4 h

Samples	Working time/	1-butene/	Isobutene/	*trans* 2-butene/	*cis* 2-butene/	1-3-butadiene/	1-butene conversion/
	min	%					
VOP	15	84.16	–	6.88	7.10	1.86	15.84
	60	84.74	–	6.59	6.85	1.82	15.26
	120	85.13	–	6.49	6.78	1.58	14.87
AlVOP	15	55.41	0.02	20.12	19.51	4.94	44.59
	60	61.75	0.01	17.93	16.84	3.47	38.25
	120	75.15	–	11.90	11.35	1.60	28.85
MnVOP	15	35.63	0.28	31.72	28.37	4.00	64.37
	60	44.29	0.22	27.77	25.36	2.35	55.71
	120	53.22	0.17	23.60	21.51	1.50	46.78
GaVOP	15	34.66	0.24	31.48	26.44	7.18	65.34
	60	38.10	0.23	31.49	26.40	3.78	61.90
	120	41.38	0.21	30.78	25.93	1.70	58.62
CrVOP	15	24.20	1.60	40.10	28.87	5.23	75.80
	60	24.95	1.55	41.25	29.83	2.42	75.05
	120	25.53	1.53	41.72	30.27	0.95	74.47

The catalytic tests were perfomed at a temperature of 450°C, atmospheric pressure and a time on stream of τ= 2.4 h. These operating conditions were chosen in order to correctly correlate the reactivity of 1-butene with the strength of the acid sites. The results are reported in Table 3.

The catalysts were active towards 1-butene conversion and the reactions were the followings: double bond isomerization, with the formation of *cis*- and *trans*-2-butene; skeletal isomerization with the formation of isobutene and dehydrogenation, giving 1-3-butadiene.

Conversion of 1-butene on M^{3+}-vanadyl phosphates is much higher than on VOP and follows the order: CrVOP>GaVOP>MnVOP>AlVOP>VOP (last column of Table 3). This clearly indicates that the partial substitution of VO^{3+} with M^{3+} gives rise to an increased reactivity of 1-butene and that the nature of the trivalent cation also plays an important role in the isomerization reaction. However, for all the catalysts the conversion decreases with time on stream because of coke formation on their surface, a feature that strongly reduces the catalysts' performance, except for CrVOP for which the 1-butene conversion is almost constant.

On the basis of the analyses of the reaction products, the predominant reaction at the stationary stage was ascertained to be double bond isomerization with the formation of 2-butene in the *cis* and *trans* isomeric species. It can be seen from Table 3 (columns 5 and 6) that for VOP, AlVOP, MnVOP and GaVOP the reaction reaches a maximum after 15 min time on stream, in parallel with the maximum of the conversion of 1-butene. For CrVOP, on the other hand, notwithstanding the slight decrease in the total conversion, the 2-butene formation (*cis*+*trans*) still increases after 2 h.

Whatever the time on stream, the *cis*/*trans* molar ratios have constant values for each material, thus indicating that the two isomers are always in kinetic equilibrium. Their values range from 1 to 0.72 and follow the order VOP>AlVOP>MnVOP>GaVOP>CrVOP. Apart from CrVOP, which gives a *cis*/*trans* molar ratio of 0.72, the other values are far from thermodynamic equilibrium which, in our operating conditions (450°C), should be 0.67 [23]. Furthermore, it is evident that while *cis* ↔ *trans* geometric isomerization is in kinetic equilibrium, double bond migration is not because, as said above, the 2-butene formation continuously decreases. This is in agreement with the fact that the double bond migration occurs on acid sites stronger than those for the *cis* ↔ *trans* isomerization [16, 24].

Table 3 shows that the yield of isobutene is very low and very far from thermodynamic equilibrium (48% at 450°C), thus indicating that the reaction is kinetically limited under our working conditions. This is in accordance with the stronger acid sites needed for skeletal isomerization with respect to double bond migration and geometric isomerization [16].

A significant amount of the dehydrogenation product 1-3-butadiene (column 7) was also formed over the M^{3+}-vanadyl phosphate with respect to VOP. Since Lewis acid sites are known to be able to catalyze dehydrogenations, among other reactions, it can be supposed that the M^{3+} ions present in the structure of the vanadyl phosphate act as stronger Lewis sites than in pure VOP and, consequently, improve 1-3-butadiene formation.

Dehydrogenation approaches kinetic equilibrium over all the catalysts after a short time on stream. However, the reaction is progressively inhibited as the 1-butene conversion decreases, probably as a consequence of the poisoning by coke of the acid sites involved in the dehydrogenation reaction.

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This work was carried out in the framework of the Agreement for scientific cooperation between the National Research Council of Italy and the Academy of Sciences of the Czech Republic. V.Z. and L.B. wish to thank the Grant Agency of the Czech Republic for financial support (Grant no. 203/95/1321). Funds from Ministero dell'Universita e della Ricerca Scientifica (MURST) are also acknowledged by M.A.M.

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