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On the synthesis of monovalent, divalent and trivalent element vanadates†

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A *chimie douce* method has been used to prepare vanadates (V^{5+}) of various elements, trivalent (Al, Cr, Fe, In, Y, Bi), divalent (Co, Ni), monovalent (Li, Tl), and a combination of nickel and lithium. By varying several parameters, especially the pH during the synthesis, several types of vanadates have been obtained ranging from orthovanadates ($VO_4{}^{3-}$) to decavanadates ($V_{10}O_{28}{}^{6-}$). The pH conditions required to prepare the various vanadates fall nicely within the expectations of the previously reported cation charge–pH diagram.

Introduction

Vanadates (with vanadium in the +5 oxidation state) present a wide range of interesting properties; for instance, they have excellent catalytic properties, and recently they were shown to be potential candidates for anodes in lithium-ion batteries.[1] However, most of these compounds are synthesized at high temperatures *via* a ceramic route. Among the main synthesis routes used for the preparation of vanadium-based oxides are the sol–gel,[2] hydrothermal,[3] insertion reaction,[4] and coprecipitation[5] routes. The former that allows a good control of the synthesis is mainly used for the synthesis of V_2O_5 xerogels. The hydrothermal method allows microporous vanadium-based compounds to be obtained as well as the synthesis of vanadates containing nitrogen-based groups. Insertion reactions are mainly used to form $M^{n+}{}_xV_2O_{5+nx/2}$ vanadates and vanadium bronzes of general formula $M_xV_2O_{5-\delta}$. Finally, coprecipitation methods, under specified pH conditions, were successfully applied to the synthesis of vanadates such as, for instance, thallium polyvanadates.[5]

Herein, we report on the synthesis of various vanadates using either monovalent (Tl, Li), trivalent (In, Cr, Fe, Al, Y, Bi), or divalent (Co, Ni) elements. Details of the synthesis conditions are given in order to emphasize the importance of pH in controlling the resulting phases of this low temperature process. Structural evolutions are reported for some of these phases.

Experimental

Synthesis methods

Four different synthesis methods, denoted A, B, C and D, with a different vanadium source as starting material, have been used (Fig. 1).

Method A. A measured amount of vanadium pentoxide was suspended in boiling water. After a few hours, a solution (nitrate or chloride) containing the selected cation, *i.e.* divalent or trivalent element, was added in stoichiometric proportions, according to the compound to be prepared. However, for the synthesis of some lithium- and thallium-based vanadates, $LiOH{\cdot}H_2O$ and Tl_2CO_3 were used. Usually, the precipitation of a solid is linked to a change in color of the suspension.

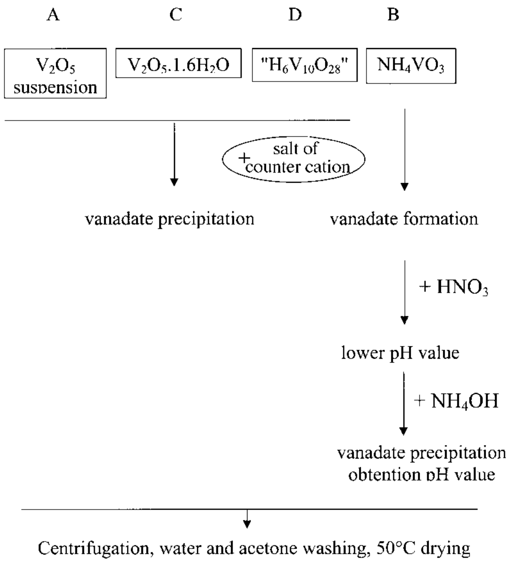

Fig. 1 Various procedures for the synthesis of vanadates.

Method B. This method, which is derived from the method used by Roth and Waring to prepare $BiVO_4$,[6] was that mainly used in this study. This method consists of mixing ammonium metavanadate (NH_4VO_3) with the nitrate of the selected element at a given concentration, and then controlling the pH. Initially a 3 M HNO_3 solution was added to lower the pH to a value denoted as 'lower pH'. Then, the pH was adjusted to favor the precipitation process. This pH value turns out to be strongly dependent on the nature of the counter cation as shown later.

Method C and D. Common to these two methods is the preparation of a 0.5 M sodium metavanadate solution which was passed through a cation-exchange resin. For the method C, the resulting solution was left to stand, leading to the formation of the xerogel $V_2O_5{\cdot}1.6H_2O$. Alternatively, the solution can be diluted leading to a decavanadic acid solution (method D). Then the synthesis steps are the same as for method A with the addition of a nitrate solution. Independently of the method used, the precipitate was washed several times with water and acetone, recovered by centrifugation, and dried in air overnight.

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Characterization

Thermal analyses were performed using a Setaram (TG-DTA92) apparatus. X-Ray diffraction measurements were performed on a Philips diffractometer (PW1710) using Cu-Kα radiation ($\lambda = 1.5418$ Å). The X-ray pattern refinement was performed using the NBS*AIDS80 program.[7] Temperature resolved X-ray powder diffraction was performed with a Guinier–Lenné camera (Cu-Kα, $\lambda = 1.5418$ Å) at a rate of 0.1 °C min^{-1}. For all the obtained compounds the metal/V ratio was measured using an EDS analyzer (Link, Oxford).

Results

Monovalent element-based vanadates

Several thallium-based vanadates, TlV_3O_8, $Tl_3V_5O_{14}$, $TlVO_3$, $Tl_4V_2O_7$ and Tl_3VO_4,[8] have been obtained using methods A and B, in both anhydrous and crystallized forms. It is interesting that TlV_3O_8, which is richer in vanadium, is only obtained using method A (*i.e.* using V_2O_5) whereas conversely, Tl_3VO_4 is prepared *via* method B. Zurkova *et al.*[5] synthesized their thallium-based vanadates through a cation exchange reaction from sodium-based vanadates, at a pH ranging from 14 for the orthovanadate to 12 for the divanadate, and 4 for the thallium decavanadate $Tl_6V_{10}O_{28}{\cdot}4H_2O$. On the other hand, for lithium-based compounds, only two compounds Li_3VO_4 and $LiVO_3{\cdot}1.5H_2O$ were obtained using method A. For the latter compound, the solution must be partly evaporated to initiate precipitation due to its high solubility. Finally, $LiVO_3$ is obtained by simple dehydration of $LiVO_3{\cdot}1.5H_2O$. Other lithium vanadates, such as LiV_3O_8 cannot be prepared in aqueous media because a gel is formed for V/Li ratios >1.[9]

Divalent element vanadates

Our work was mainly concerned with the synthesis of nickel and cobalt based vanadates through method B.[10] Several new hydrates of the orthovanadates $M_3(VO_4)_2{\cdot}xH_2O$ (pH = 8), divanadates $M_2V_2O_7{\cdot}xH_2O$ (pH = 6.5) and metavanadate tetrahydrate $M(VO_3)_2{\cdot}4H_2O$ (pH = 6) families with M = Ni and Co were synthesized. Usually, upon dehydration, we mainly obtained anhydrous compounds with X-ray powder patterns similar to those of the same composition prepared by the classical ceramic route. However, occasionally the dehydration step is not as straightforward as, for example, for the cobalt decavanadate $(NH_4)_2Co_2V_{10}O_{28}{\cdot}16H_2O$.[11] Here dehydration leads to the destruction of hydrogen bonds in the structure (as determined by structural analysis), destabilizing the $V_{10}O_{28}{}^{6-}$ group. In order to study structural evolution during dehydration, we have performed temperature resolved X-ray powder diffraction measurements. Fig. 2 shows that below about 150 °C, three transitions occurred leading to four different intermediate compounds. If we compare these results with the thermal analysis (Fig. 3) and the scenario we proposed earlier,[11] we can ascribe the successive phases to $(NH_4)_2Co_2V_{10}O_{28}{\cdot}16H_2O$, $(NH_4)_2Co_2V_{10}O_{28}{\cdot}12H_2O$, $(NH_4)_2Co_2V_{10}O_{28}{\cdot}4H_2O$ and $(NH_4)_2Co_2V_{10}O_{28}$, respectively. A detailed structural study of each of these phases is presently under way. Upon further dehydration of the material, it becomes amorphous to X-rays, which is in agreement with our assumption that the decomposition is linked to the removal of ammonium ions which trap an oxygen in the $V_{10}O_{28}{}^{6-}$ group leading to $Co_2V_{10}O_{27}$ between 240 and 380 °C. The final observed transformations involve crystallization of V_2O_5 and α-$Co(VO_3)_2$, followed by the well known polymorphic transformation of α-$Co(VO_3)_2$ into γ-$Co(VO_3)_2$.[10] Finally, we find at 662 and 705 °C two endothermic peaks in agreement with the binary system V_2O_5–CoO for a 71.5 mol % V_2O_5 composition. The slight discrepancy between the temperatures observed in the thermal analysis and the temperature resolved X-ray powder diffraction measurements can simply be explained from the differences in the heating rate of the two experiments, which were 10 and 0.1 °C min^{-1}, respectively. Based on the similarity of the synthesis of cobalt and nickel compounds, we tried to obtain a nickel decavanadate using similar conditions, *i.e.* with an initial ratio Ni/V equal to 0.2, a 'lower pH' value of 2.5 and 5.3 as the final pH. The Ni/V ratio of the resulting compound was checked by EDX, and the X-ray diffraction pattern was similar to that for the above cobalt-based compound. Together with the thermogravimetric measurement this leads to a formulation $(NH_4)_2Ni_2V_{10}O_{28}{\cdot}16H_2O$. XRPD pattern refinement using NBS*AIDS80[7] software led to the indexation of the X-ray diffraction pattern (Tables 1 and 2). A dehydration study, similar to that carried out for the cobalt compound is shown in Fig. 4 and 5. At the beginning of the process, they show similar behavior except that removal of water occurs in two steps and correspond to removal of 13 and 3 water molecules, respectively (Fig. 5). These three phases, *i.e.* the initial phase,

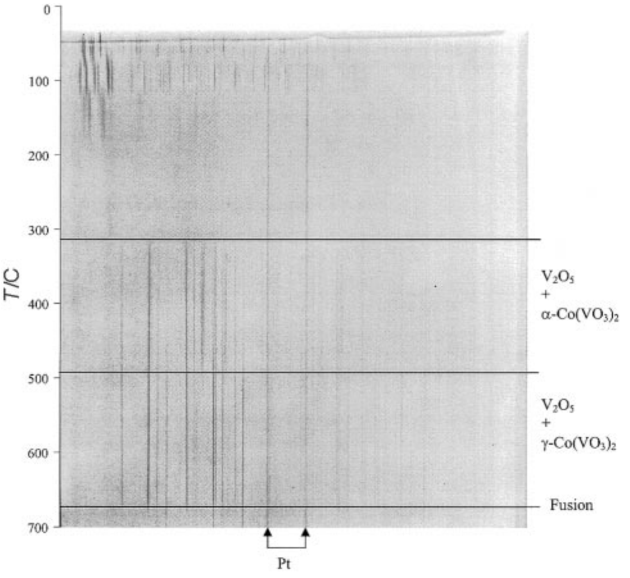

Fig. 2 Temperature resolved X-ray powder diffraction patterns (heating rate 0.1 °C min^{-1}) using a Guinier–Lenné camera for $(NH_4)_2Co_2V_{10}O_{28}{\cdot}16H_2O$.

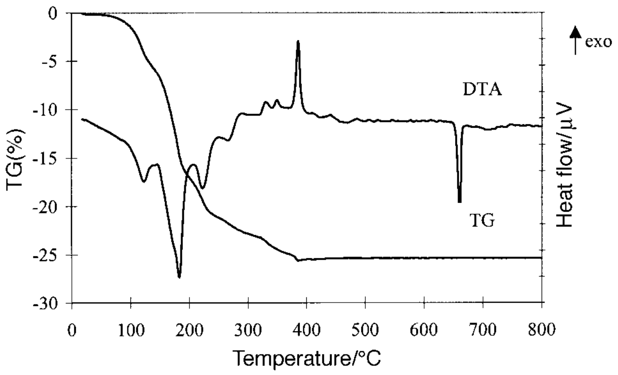

Fig. 3 DTA and TG (heating rate 10 °C min^{-1}) curves for $(NH_4)_2Co_2V_{10}O_{28}{\cdot}16H_2O$.

Table 1 Crystal data for $(NH_4)_2Ni_2V_{10}O_{28}{\cdot}16H_2O$ from X-ray powder diffraction analysis

Space group	$P\bar{1}$ (no. 2)
2θ range/°	8–70
Unit cell parameters	$a = 8.834(4)$ Å, $b = 10.897(5)$ Å, $c = 11.116(4)$ Å $\alpha = 65.03(3)°$, $\beta = 74.44(3)°$, $\gamma = 70.86(4)°$
$M(20)$[12]	17.2
$F(30)$[13]	29.4 (0.0152, 67)

Table 2 X-Ray diffraction pattern of $(NH_4)_2Ni_2V_{10}O_{28}\cdot16H_2O$

h	k	l	$2\theta_{obs}/°$	$2\theta_{calc}/°$	$d_{obs}/Å$	I_{obs}
0	0	1	8.883	8.878	9.954	71
0	1	0	9.230	9.236	9.581	62
0	1	1	10.191	10.196	8.679	48
1	0	0	10.712	10.724	8.259	97
1	1	1	11.886	11.895	7.446	100
1	0	1	12.865	12.854	6.881	2
−1	0	1	14.924	14.946	5.936	12
−1	1	0	15.801	15.809	5.608	19
1	1	2	17.030	17.035	5.206	7
0	0	2	17.817	17.810	4.978	29
0	2	0	18.530	18.533	4.788	25
1	−1	1	19.033	19.017	4.663	7
1	2	2	19.454	19.449	4.563	3
0	2	2	20.477	20.473	4.337	3
2	1	0	21.278	21.256	4.176	2
2	0	0	21.510	21.543	4.131	19
−1	1	2	22.491	22.514	3.953	7
−1	2	1	23.393	23.390	3.803	1
2	2	2	23.906	23.921	3.722	21
1	3	1	24.760	24.782	3.596	2
1	2	3	25.061	25.078	3.553	6
1	3	2	25.340	25.335	3.515	14
−2	1	0	25.543	25.527	3.487	13
2	0	2	25.875	25.873	3.443	4
0	2	3	26.440	26.461	3.371	2
0	0	3	26.886	26.853	3.316	13
0	3	2	27.094	27.086	3.291	5
1	3	0	27.350	27.372	3.261	4
2	3	2	28.023	28.068	3.184	10
−2	−2	1	29.626	29.680	3.015	14
3	1	1	30.457	30.416	2.935	4
2	3	3	30.820	30.827	2.901	11
−1	3	1	31.282	31.267	2.859	2
−2	−1	2	31.973	31.985	2.799	1
−1	3	0	32.471	32.471	2.757	7
−1	3	2	32.683	32.659	2.740	21
0	1	4	33.717	33.700	2.658	8
−1	−1	3	34.050	34.054	2.633	2
3	0	2	34.825	34.794	2.576	2
−3	0	1	35.162	35.147	2.552	1
3	1	3	35.758	35.791	2.511	1
−2	−2	2	36.302	36.314	2.475	5
0	4	3	37.391	37.383	2.405	23
2	−1	3	37.477	37.495	2.340	19
−1	0	4	39.349	39.349	2.290	4

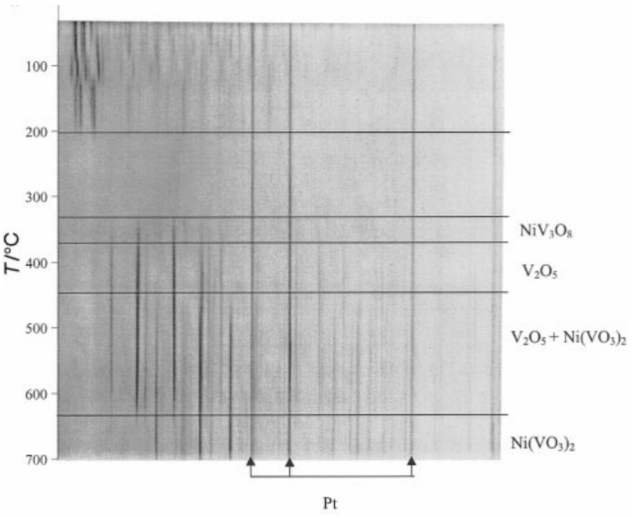

Fig. 4 Temperature resolved X-ray powder diffraction patterns (heating rate 0.1 °C min^{-1}) using a Guinier–Lenné camera for $(NH_4)_2Ni_2V_{10}O_{28}\cdot16H_2O$.

and the compounds obtained after each water loss, appeared also on the temperature resolved X-ray photograph (Fig. 4). The main difference is the appearance at about 330 °C of the bronze α-NiV_3O_8, which was also confirmed by annealing the powder at 400 °C during 24 h. At this temperature the bronze is contaminated by V_2O_5. This is in agreement with the loss of an oxygen atom from the $V_{10}O_{28}{}^{6-}$ group during the simultaneous departure of the ammonium ions and a water molecule. Above 390 °C, we note the disappearance of this phase, followed at 550 °C by oxidation in air, leading to the only known anhydrous nickel metavanadate $Ni(VO_3)_2$. Finally, the three endothermic peaks appearing at 670, 770 and 910 °C are consistent with the V_2O_5–NiO binary system. We can summarise the thermal behavior as follows:

$$(NH_4)_2Ni_2V_{10}O_{28}\cdot16H_2O \xrightarrow{105\text{–}250\,°C} (NH_4)_2Ni_2V_{10}O_{28}\cdot3H_2O$$

$$\xrightarrow{250\text{–}350\,°C} (NH_4)_2Ni_2V_{10}O_{28} \xrightarrow{350\text{–}390\,°C} 2\alpha\text{-}NiV_3O_8 + 2V_2O_5$$

$$\xrightarrow{550\,°C} 2Ni(VO_3)_2 + 3V_2O_5$$

Finally, concerning the vanadates containing divalent elements, we recently synthesized a new amorphous hydrated compound $LiNiVO_4\cdot2.6H_2O$ [14] that upon dehydration led to the well known anhydrous spinel $LiNiVO_4$.[15] It should be noted that such a phase can only be obtained using an excess of lithium (Li : Ni : V = 15 : 1 : 1). The 'lower pH' was 3 and the final pH was 8.5.

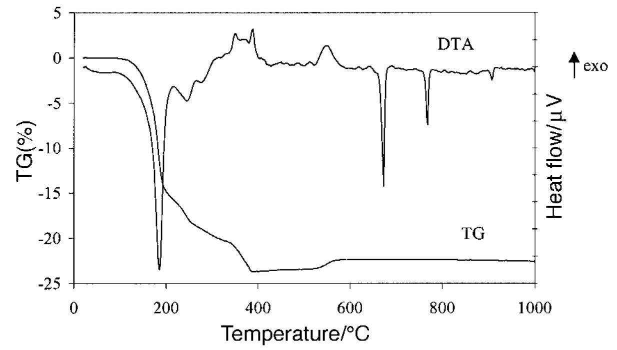

Fig. 5 DTA and TG (heating rate 10 °C min^{-1}) curves for $(NH_4)_2Ni_2V_{10}O_{28}\cdot16H_2O$.

Trivalent element-based vanadates

Two types of compounds have already been reported: MVO_4 and $M_2V_4O_{13}$ (M being a trivalent element). Orthovanadates of general formula $MVO_4\cdot xH_2O$ (M = In, Cr, Fe, Al)[16] were obtained using method B. After mixing the two precursors [NH_4VO_3 and nitrate $M(NO_3)_3$ solutions] spontaneous precipitation occurred. The pH was then lowered to 1 to induce complete dissolution, and then raised to 4 in order to obtain pure phases. This method was also implemented to the successful preparation of mixed trivalent element based vanadates of $M_xM'_{1-x}VO_4$ (M, M′ = In, Cr, Fe) formula;[17] all these compounds were hydrated. The use of method B also led to an yttrium-based vanadate $YVO_4\cdot2H_2O$[18] which is poorly crystallized. Finally, well crystallized anhydrous MVO_4-type compounds can also be synthesized for bismuth.[19] Two $BiVO_4$ polymorphs, monoclinic fergusonite and the high temperature tetragonal $BiVO_4$ can be directly obtained by the *chimie douce* process. The fergusonite $BiVO_4$ is obtained using method B (bismuth nitrate must be dissolved in concentrated nitric acid), whereas monoclinic $BiVO_4$ can be prepared by method A. This shows that the hydration state and the degree

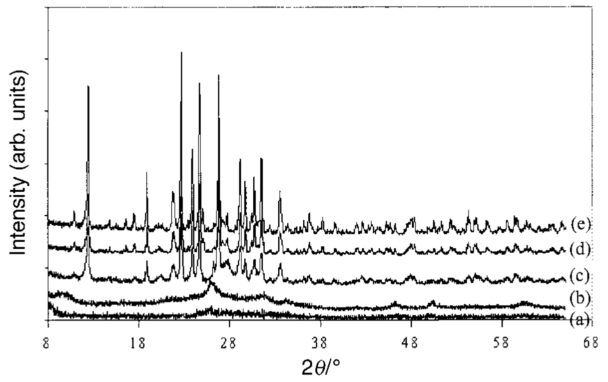

Fig. 6 Evolution of the X-ray diffraction patterns of $Fe_2V_4O_{13}{\cdot}4.4H_2O$ annealed at different temperatures for 24 h under air. (a) 50 °C, (b) 300 °C, (c) 400 °C, (d) 500 °C, (e) 600 °C.

of crystallization depend on the trivalent element as discussed below.

The second type of compound of general formula $M_2V_4O_{13}$ (M = Cr, In, Fe)[20–22] was prepared by methods C and D. However, one of the disadvantages of these methods is that large amounts of precipitates are not obtained (owing to the low solubility of the xerogel, and the need for using low vanadium concentrations for method D). Therefore, we tried to alleviate this problem using method B. A solution of 0.08 M ammonium metavanadate was mixed with 0.2 M iron nitrate in stoichiometric proportions (Fe/V = 1/2) and the resulting pH was 1.7. The 'lower pH' value was 1, and this value was adjusted to 2.8 to induce precipitation. An amorphous brown precipitate (as determined by X-ray diffraction) was obtained. Upon annealing at different temperatures (Fig. 6) $FeVO_4$ was always observed alongside the main product $Fe_2V_4O_{13}$ as observed previously.[23] To our knowledge, this is the first time that a hydrated precursor of $Fe_2V_4O_{13}$ has been obtained by such a method. As deduced by thermal analysis (Fig. 7), this was very similar to indium- and chromium-based compounds, and has the formula $Fe_2V_4O_{13}{\cdot}4.4H_2O$. Dehydration occurs in two steps: from ambient temperature to 210 °C and from 210 to 410 °C. The end of the dehydration is characterized by an exothermic peak on the DTA curve which corresponds to crystallization of the material. Finally the endothermic peak at 710 °C corresponds to the peritectic decomposition of $Fe_2V_4O_{13}$.

Discussion

We have seen that method B can be successfully used for the preparation of a large number of vanadates ($M{-}V{-}O{\cdot}nH_2O$) based either on monovalent, divalent or trivalent elements.

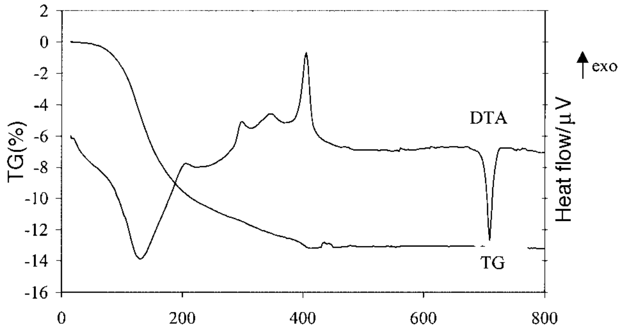

Fig. 7 DTA and TG curves of the amorphous $Fe_2V_4O_{13}{\cdot}4.4H_2O$ (heating rate: 10 °C min^{-1}).

We can now compile our results so that general trends can be drawn.

The formation of oxides in solution, while being a complex phenomenon, has been extensively studied. Few papers dealing with this topic have been published besides a very complete study by Livage *et al.* on the sol–gel process.[24] They have modeled the condensation of ions in solution to form simple oxides on the basis of a partial charge model. However, with respect to the formation of polymetallic oxides the problem is even more complicated owing to the increasing number of parameters that must be simultaneously compatible.[25] From a thermodynamic point of view, the polyelement oxide must be more stable than the two separate oxides, and kinetically it must form as quickly as these. Thus, synthesis conditions, in particular, the pH must be finely tuned to favor the formation of each type of compound.

For reasons of clarity, we will split the discussion in two parts starting with the role of vanadate anion type, and ending with the role of the cation.

If we fix the cation, *e.g.* cobalt or nickel, we have seen that depending on the experimental conditions (Table 3), different classes of vanadates can be obtained. In solution it is well known that vanadium can exist in various polyanion forms. More specifically, when the pH of an orthovanadate (VO_4^{3-}) solution is lowered, several isopolyanions are successively formed: the divanadate ($V_2O_7^{4-}$), metavanadate (VO_3^-) and decavanadate ($V_{10}O_{28}^{6-}$) ions. So, the more acidic the solution is, the more condensed are the vanadium polyanion species (*i.e.* they are formed by an increasing number of molecular units). We can see that the pH at which the solid vanadate is obtained follows the same evolution. The results obtained for monovalent (Tl) and trivalent (Fe) metals followed the same trend as divalent Co and Ni.

Secondly, if we fix a specified anion, *e.g.* orthovanadate VO_4^{3-} (Table 4), then the pH at which the vanadates are obtained is a function of the nature of the counter element. As an attempt to understand this trend, once again, we can refer to the work on sol–gel synthesis. The first coordination sphere of a cation in aqueous solution can be composed of aqua, hydroxo and oxo species. Their relative proportions are a function of the cation charge and of the pH of the media as shown by the charge–pH diagram.[24] With the present synthesis, aqua species are initially present and must become deprotonated in order to condense, hence the importance of adjusting the pH. Based on the cation charge–pH diagram, hydroxo groups would be expected to form at lower pH upon increasing the charge of the cation, in good agreement with our results, as shown in Fig. 8.

Another noteworthy point is the discrepancy between the range of existence of orthovanadate in solution and the pH at which the solid orthovanadates are obtained. In solution, VO_4^{3-} is predominant in highly alkaline solutions. However,

Table 3 Synthesis parameters for M vanadates (M = Co, Ni)

Compound	Initial M : V ratio	Lower pH value	pH of obtention
$(NH_4)_2M_2V_{10}O_{28}{\cdot}16H_2O$	1 : 5	2.5	5.3
$M(VO_3)_2{\cdot}xH_2O$	1 : 2	3	6
$M_2V_2O_7{\cdot}xH_2O$	1 : 2	3	6.5
$M_3(VO_4)_2{\cdot}xH_2O$	3 : 2	3	8

Table 4 pH values for the synthesis of several orthovanadates

Compound	pH of obtention
$RVO_4{\cdot}xH_2O$ (R = Cr, In, Fe, Y, Al)	4
$Co_3(VO_4)_2{\cdot}xH_2O$	8
$LiNiVO_4{\cdot}2.6H_2O$	8.5
Li_3VO_4	≈12

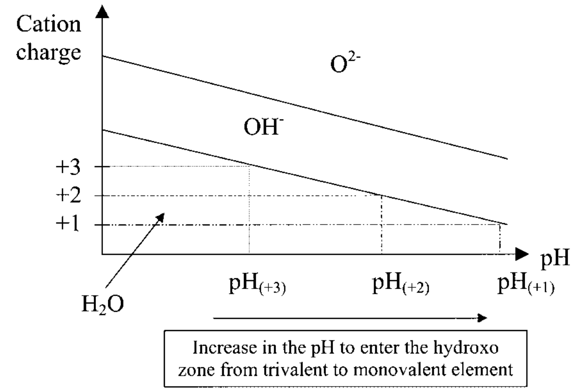

Fig. 8 Cation charge–pH diagram showing the obtention pH evolution for one vanadate type.

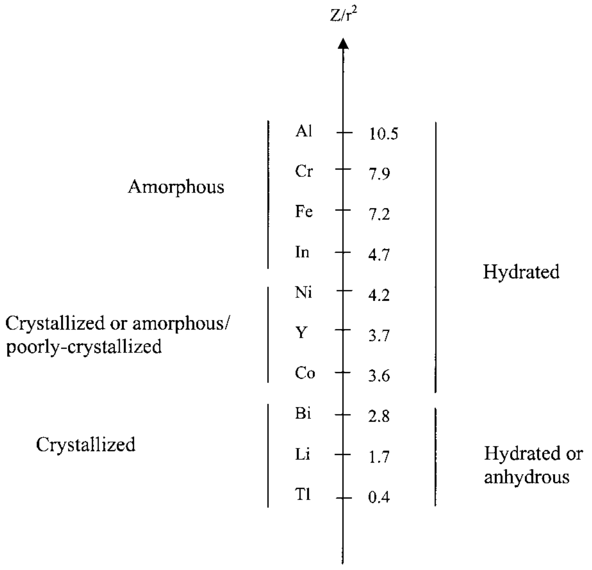

Fig. 9 Evolution of the degree of crystallization and hydration as a function of the polarizing power Z/r^2; Z is the cation charge and r is its ionic radius.

solid vanadates were obtained at a lower pH. If we make a comparison with the distribution diagram of isopolyvanadates[26] we see that this pH zone corresponds to the presence of HVO_4^{2-} and $H_2VO_4^-$ which are oxohydroxo vanadium species, consistent with our results. It should also be noted that a too low pH value led to the presence of V_2O_5 or ammonium vanadates as impurities whereas for a high pH value mono-element oxides formed. The requirement to lower the pH value even when no precipitation occurred (for instance in the synthesis of divalent element-based vanadates) is, as yet, unclear and further investigations are required. Suitable conditions have been determined for the synthesis of divalent transition element vanadates (M = Co, Ni) but some differences may arise for non-transition elements.

Finally turning to the crystallization degree of the different compounds obtained it is seen that vanadates containing monovalent counter ions (Li, Tl) are all crystallized either in hydrated or anhydrous forms. When divalent elements are used the two vanadium-rich compounds are crystallized (decavanadate and metavanadate) while the divanadate and the orthovanadate are amorphous. Finally, the trivalent element-based vanadates are well or poorly crystallized for some elements (Bi and Y), and amorphous for other elements (In, Cr, Fe, Al). An interesting tentative correlation with the polarizing power of a cation, proportional to Z/r^2 can be made. It can be seen (Fig. 9) that low polarizing power leads to crystallized compounds while a high value leads to amorphous compounds. For the calculation of the polarizing power, the ionic radius used corresponds to an octahedral environment of the different elements.[27] On the same basis we can also account for the anhydrous or hydrated states of the obtained compounds. Indeed, the anhydrous compounds are obtained for the three elements with the lowest polarizing power. Is this correlation purely coincidental? We are presently addressing this point in order to understand the degree of crystallinity of our compounds.

Conclusion

A *chimie douce* method to prepare various vanadates is reported. It was shown that these compounds exhibited a very rich solid state chemistry, and investigations of crystal chemical aspects are in progress. Method B presents great advantages over the three other methods, in particular, a better control of the synthesis (once the pH conditions are determined), and the possibility of obtaining a larger amount of compound, which is of interest for energy storage application (*e.g.* lithium batteries). Understanding the formation of these types of compounds requires a clear identification of the species existing in solution, and thereby the need for *in situ* measurements of the solutions during the course of the reaction.

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