

Vanadate-Inserted Layered Double Hydroxides: A ^{51}V NMR Investigation of the Grafting Process

M. Ménétrier,* K. S. Han, L. Guerlou-Demourgues, and C. Delmas

Institut de Chimie de la Matière Condensée de Bordeaux-CNRS and Ecole Nationale Supérieure de Chimie et Physique de Bordeaux, Av. Dr. A. Schweitzer, 33608 Pessac Cedex, France

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The reduction of mixed nickel–cobalt γ -oxide–hydroxides in an $\text{NH}_4\text{VO}_3/\text{H}_2\text{O}_2$ medium ($\text{pH} = 4$) leads to layered double hydroxides (LDH's) in which vanadate species are inserted in order to compensate for the excess positive charges brought by Co^{III} ions. Static ^{51}V NMR spectra have been recorded on such LDH's after various treatments, showing that the hyperfine magnetic interaction exerted by unpaired electrons of Ni^{II} on the inserted vanadium nuclei allows us to determine whether the latter are grafted to the layer or not. For materials kept for a long time in the $\text{NH}_4\text{VO}_3/\text{H}_2\text{O}_2$ solution, a partial grafting of the inserted metavanadate chains is evidenced which leads to a full occupancy of the interlayer space by vanadate species and water molecules. Upon thermal or vacuum treatment, a further grafting and a fragmentation of the chains are evidenced, accompanied by a decrease of the interlayer spacing. For materials removed very early from the reducing solution, the initial polycondensation step of the vanadate species can be followed by NMR, which again also shows a simultaneous partial grafting.

1. Introduction

Layered double hydroxides (LDH's) are intensively studied for their well-known anionic exchange properties and their potential use as precursors for new catalytic materials.^{1,2} The general formula of these lamellar materials, i.e. $[\text{M}^{\text{II}}_{1-y}\text{L}^{\text{III}}_y(\text{OH})_2]^{y+}\text{X}_{y/p}^{p-} \cdot z\text{H}_2\text{O}$ ($\text{X}^{p-} = \text{CO}_3^{2-}$, NO_3^- , Cl^- , OH^- , SO_4^{2-} , etc.), shows that their structure consists of stacked brucite-type $[\text{M}^{\text{II}}_{1-y}\text{L}^{\text{III}}_y(\text{OH})_2]$ slabs, with water molecules and X^{p-} anions inserted within the interslab spaces.² The role of the interlamellar anions is to compensate for the excess positive charge due to the partial substitution of trivalent cations (L) for the divalent ones (M) within the slabs. The inserted anions also take part in the stabilization of the structure by acting as pillars.

The role of vanadium oxides in the field of catalysis is well known,³ and pillaring of various LDH's with $\text{V}_{10}\text{O}_{28}^{6-}$ decavanadate anions has already been reported by several authors.^{4–9} These materials were prepared by ion exchange from organic anion, carbonate, or chloride precursors obtained by coprecipitation methods.

Among our general studies devoted to the preparation of LDH's by chimie douce methods,^{10–13} we recently reported the preparation and characterization of a new LDH constituted by packed $\text{Ni}_{0.70}\text{Co}_{0.30}(\text{OH})_2$ slabs with interlamellar $(\text{VO}_3)_n^{n-}$ metavanadate chains made of corner-sharing VO_4 tetrahedra,^{14,15} the main results are very briefly sketched out hereafter.

Investigations of the intercalation process have shown that the metavanadate chains are not directly inserted into the interslab space but rather result from an in situ polycondensation of diperoxovanadate anions within the LDH. Such peroxovanadate species are primarily inserted during the initial preparation of the LDH. However, the changes in the overall characteristics of the material (as studied by X-ray diffraction, IR spectroscopy, chemical analysis, and TGA) cannot be interpreted exclusively in terms of a polycondensation of the interlamellar species and suggest a spontaneous partial grafting of the vanadate interlamellar ions to the slab. After thermal or vacuum treatments, an extensive grafting of the vanadate species, associated with a chain segmentation, has also been evidenced by X-ray diffraction.

Since Ni^{II} ions are present within the layers, one can expect that they will exert a magnetic interaction on vanadium nuclei when a $\text{Ni}-\text{O}-\text{V}$ bond exists, as it was demonstrated for lithium in related materials.^{16,17} ^{51}V NMR studies were thus performed in order to further investigate the polycondensation and grafting phenomena.

2. Experimental Section

2.1. Material Preparation. The materials were obtained by the reduction of cobalt- substituted γ -oxyhydroxides¹⁸ in an $\text{NH}_4\text{VO}_3/\text{H}_2\text{O}_2$

* Corresponding author. E-mail: menetri@chimsol.icmcb.u-bordeaux.fr.
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- (10) Chimie douce reactions differ from classical solid-state chemistry ones in that lower energies are involved, so that they often occur at room temperature. The final material exhibits a structure that closely resembles that of the starting material. In the peculiar case of the nickel hydroxides, the NiO_2 slab is maintained during the various chimie douce reactions (exchange, hydrolysis, and reduction) that lead to the reduced phase.
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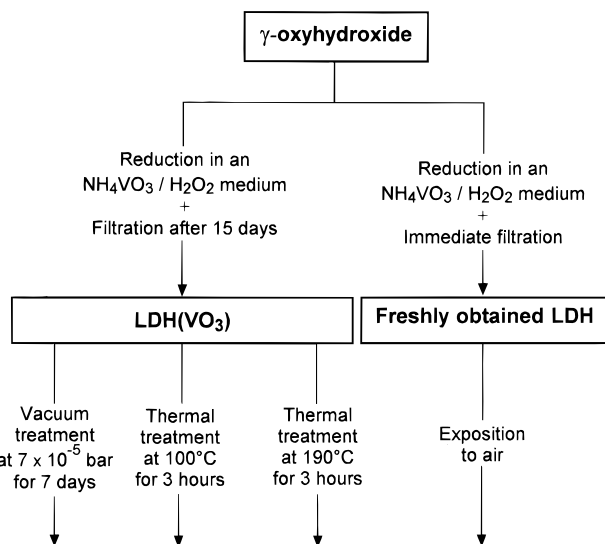


Figure 1. Preparation scheme of the two sets of materials characterized by ^{51}V NMR.

medium (pH = 4).^{14,15} Two different sets of materials were obtained, depending on the preparation conditions, as schematized in Figure 1. The pristine material of the one set, which was designated as LDH(VO_3) in a previous paper, was obtained after 15 days in the reducing solution.¹⁴ It was shown to contain interlamellar $(\text{VO}_3)_n^{n-}$ metavanadate chains. This material was then treated either thermally (100 or 190 °C) or in vacuum. The pristine material of the other set, which is designated as “freshly obtained LDH”, was prepared by dropping the $\text{NH}_4\text{VO}_3/\text{H}_2\text{O}_2$ solution onto the γ -oxyhydroxide present on a mesh (in air). It was dried under vacuum and then exposed to air and characterized vs. aging time.¹⁵ As indicated above, the preparation conditions of the LDH(VO_3) and of the material obtained after an aging in air of the “freshly obtained LDH” are different, although they both contain intercalated metavanadate chains: The aging is performed in the liquid reaction medium in the first case and in air in the second case.

2. 2. NMR. ^{51}V NMR ($I = 7/2$) spectra were recorded on a Bruker MSL 200 spectrometer at 52.6 MHz. VOCl_3 was used as an external reference set at 0 ppm. A solid echo sequence with an 8-step phase cycling was utilized. The length of the two pulses was 1.8 μs . Indeed, a 90° pulse length would have corresponded to 3.3 μs and resulted in too narrow an irradiated zone, considering the width of the spectra recorded. The echo sequence used thus results in overemphasizing the quadrupolar satellites with respect to the central transition. No analysis of the quadrupolar part of the spectra was therefore performed. Furthermore, even with such short pulses, the width of the spectra prevents any quantitative analysis, so that only qualitative changes are discussed from these data.

3. Results and Discussion

3.1. Evolution of LDH(VO_3) upon Vacuum or Thermal Treatment. Two different compositions of LDH(VO_3) with different Ni/Co ratios were investigated: One corresponds to an $\text{Ni}_{0.69}\text{Co}_{0.31}(\text{OH})_2$ slab formula, and the other, to $\text{Ni}_{0.62}\text{Co}_{0.38}(\text{OH})_2$. For simplicity, an LDH(VO_3) type material with a given γ cobalt composition is designated hereafter as $\text{LDH}_\gamma(\text{VO}_3)$.

The X-ray diffraction patterns of $\text{LDH}_{0.31}(\text{VO}_3)$ after the various treatments are reported in Figure 2. The $(10l)$ and $(11l)$ diffraction lines present in the X-ray diffraction pattern of an LDH crystallizing in the 3R polytype are replaced, for the LDH(VO_3) phase, by two large asymmetric bands in the 35–45° and 60–65° $2\theta_{\text{Cu}}$ ranges. Such a behavior is characteristic of a disorder in the periodicity of both the $(10l)$ and $(11l)$ planes

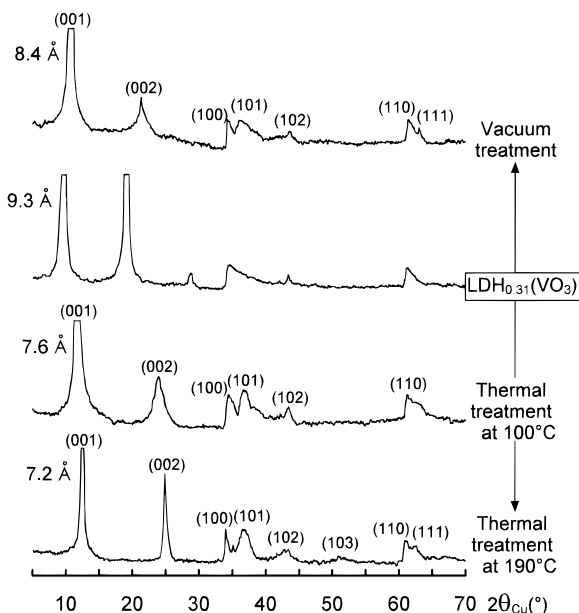


Figure 2. X-ray diffraction patterns of $\text{LDH}_{0.31}(\text{VO}_3)$ before and after the various treatments.¹⁴

and does not allow any indexation. After the thermal treatment, the large bands are replaced by narrower separate lines. Indexation has been performed by considering only one slab per unit cell, which may be surprising since LDH’s generally possess two or three slabs per cell.² However, in the patterns shown in Figure 2 (which exhibit a relatively poor quality), all lines are indexed using this small unit cell; therefore, there is no need nor justification for using a larger one. Furthermore, in the case of the three slab hypothesis, a rhombohedral space group would be expected; this would imply extinction conditions which are not compatible with an indexation of the experimental pattern under such a hypothesis.

Figure 2 shows a significant decrease of the interslab distance (diffraction line in the 5–15° $2\theta_{\text{Cu}}$ range) when a thermal or vacuum treatment is performed. Although not reported here, the evolution observed for $\text{LDH}_{0.38}(\text{VO}_3)$ is quite similar. Since the observed interslab distance of 7.2 Å allows for only one layer of oxygen atoms, this behavior was assigned in a previous paper to a grafting/fragmentation of the metavanadate chains to the slabs, which proceeds via a slab dehydroxylation and deprotonation and leads to the release of water.¹⁴ In addition to the decrease in the c parameter, Figure 2 also shows a significant change in the line shape, which can again be interpreted in terms of a grafting/fragmentation of the metavanadate chains. First, the low-angle diffraction lines are broad and asymmetric for the starting material, because of local structural distortions due to electrostatic interactions between the intercalated chains and the slab.¹⁴ These lines are replaced by separate ones after the treatments, which shows a decrease in the magnitude of those distortions because of the fragmentation of the inserted entities. Second, the $(00l)$ lines tend to broaden after a mild treatment (i.e. vacuum or 100°C), for which an interstratified-type material must be obtained since it contains various types of intercalated vanadate species (grafted and nongrafted; chains or segmented entities). After the more severe 190°C treatment, relatively narrow lines are recovered, which suggests that a single, well-defined type of inserted entity is present.

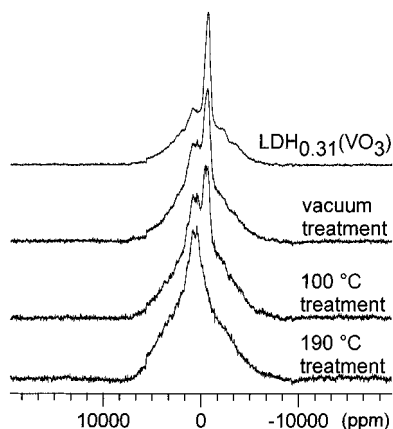


Figure 3. Static ^{51}V NMR spectra of $\text{LDH}_{0.31}(\text{VO}_3)$ before and after the various treatments. (The reference is VOCl_3 .)

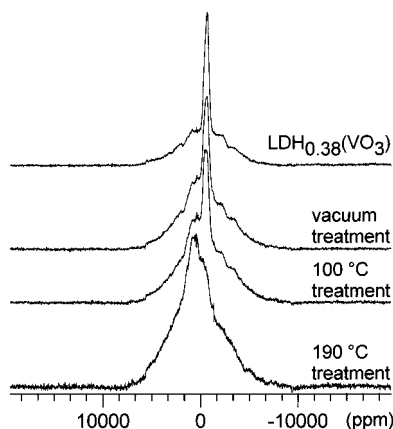


Figure 4. Static ^{51}V NMR spectra of $\text{LDH}_{0.38}(\text{VO}_3)$ before and after the various treatments.

In the case of inserted sulfate ions, a simple grafting process has previously been observed by Besse et al.¹⁹ and in our laboratory.¹⁸

The ^{51}V NMR spectra of these various materials are presented in Figures 3 and 4 for $y = 0.31$ and $y = 0.38$, respectively. The pristine materials spectra (particularly the $y = 0.38$ one) are dominated by a narrow signal at -600 ppm with quadrupolar satellite transitions at the base. Upon vacuum or thermal treatment, another signal at 850 ppm grows gradually at the expense of the former. This new signal is less defined (both in the quadrupolar base and the central peak which seems to contain two contributions) and broader than the former one; since a grafting process is assumed in those conditions, it is attributed to vanadium atoms which are grafted via oxygen to the nickel atoms of the $\text{Ni}_{1-y}\text{Co}_y(\text{OH})_2$ slabs. This assignment is comforted by the position of the signal: While vanadate species are usually found in the -400 to -800 ppm range (such is the case for the ungrafted species at -600 ppm), the new signal is shifted by nearly 1500 ppm toward positive ppm values. This implies that a new kind of interaction occurs; indeed, the existence of $\text{V}-\text{O}-\text{Ni}$ bonds allows the transfer of unpaired electrons (or, strictly speaking, of a density of presence probability thereof) from the Ni^{II} ($t_{2g}^6 e_g^2$) to the vanadium atoms via the orbitals overlap. This hyperfine magnetic interaction causes a broadening and a shift (the so-called Fermi contact shift) of the NMR signal vs. that due to vanadium atoms with no $\text{V}-\text{O}-\text{Ni}$ bond (850 ppm vs. -600 ppm). The grafting is thus seen by NMR through the unpaired electrons of Ni^{II} , which

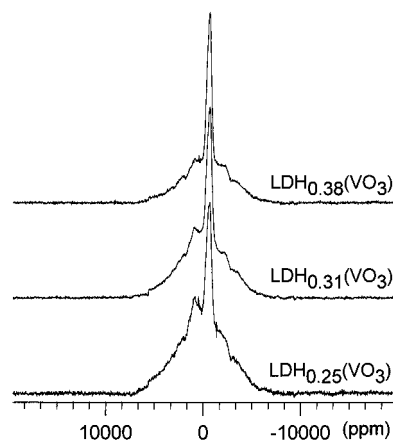


Figure 5. Static ^{51}V NMR spectra of various $\text{LDH}_y(\text{VO}_3)$ ($y = 0.25, 0.31, 0.38$).

Table 1. Chemical Analyses Results of Various $\text{LDH}_y(\text{VO}_3)$ ($y = 0.25, 0.31, 0.38$)

A	A/(Ni + Co) molar ratio		
	$\text{LDH}_{0.25}(\text{VO}_3)$	$\text{LDH}_{0.31}(\text{VO}_3)$	$\text{LDH}_{0.38}(\text{VO}_3)$
Ni	0.75	0.69	0.62
Co	0.25	0.31	0.38
V	0.41	0.38	0.39
H	3.20	3.38	3.26

means that no magnetic interaction would be expected for vanadium atoms grafted to an oxygen bonded only to diamagnetic Co^{III} ions.

Figures 3 and 4 show that the relative amount of grafted vanadium ions for the variously treated materials ranges (inversely) with their respective interslab distances deduced from the X-ray diffraction patterns of Figure 2. Furthermore, the disappearance of the narrow signal at -600 ppm in the NMR spectrum recorded after the 190 °C thermal treatment suggests that virtually all vanadium ions are grafted; this is in agreement with the shape of the X-ray diffraction lines discussed above, as well as with the presence of V_2O_7 entities deduced from TGA results.¹⁴ Thus, this ^{51}V NMR characterization constitutes, to our knowledge, the first direct evidence of the grafted or nongrafted character of the inserted vanadate ions in an LDH.

Comparing the NMR spectra of the pristine $\text{LDH}_{0.31}(\text{VO}_3)$ and $\text{LDH}_{0.38}(\text{VO}_3)$ materials from Figures 3 and 4, respectively, reveals that the relative magnitude of the two signals is significantly different in the two materials. Indeed, the relative magnitude of the 850 ppm signal grows with the Ni/Co ratio, as shown in Figure 5 for $y = 0.38$, $y = 0.31$ and $y = 0.25$. Since vanadium ions grafted to an oxygen ion with only Co as neighbors would contribute to the -600 ppm signal, the changes observed might be influenced by the number of nickel atoms present. The existence of such vanadium atoms would indeed require a nonstatistical distribution of the nickel and cobalt ions. However, such a situation cannot be excluded a priori, since a tendency to cobalt clusterization had been evidenced by ^7Li NMR in the case the $\text{LiNi}_{1-y}\text{Co}_y\text{O}_2$ solid solution.^{16,17}

In order to eliminate that ambiguity, chemical analyses have been carried out and are reported in Table 1. If all vanadium ions present were in nongrafted $(\text{VO}_3)_n^{n-}$ chains, the achievement of the charge compensation would require the presence of one vanadium ion per cobalt ion. Instead, the values of the $\text{V}/(\text{Ni} + \text{Co})$ molar ratio, which are quite similar (close to 0.4) whatever the cobalt content (Table 1), imply that not all inserted vanadium atoms bring a negative charge. This may arise from a partial grafting to the slab but in a way slightly different from the one mentioned above (which occurred during vacuum or

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thermal treatments of the material after its removal from the reducing solution). Indeed, in the present case, only a slab dehydroxylation must occur, which does not result in the fragmentation of any vanadate entity. The OH^- ions produced in the process must be released into the acidic medium, and the corresponding charges need then be compensated for by the intercalation of additional vanadate species from the solution. According to this interpretation, the cobalt and vanadium molar ratios reported in Table 1 imply that 0.16 VO_4 tetrahedra per $(\text{Ni} + \text{Co})$ ion are grafted for $y = 0.25$, 0.07 for $y = 0.31$, and 0.01 for $y = 0.38$ (which leads to the presence of 1.84, 1.93, and 1.99 OH groups per $(\text{Ni} + \text{Co})$ ion, respectively, vs 2 in the case of the $(\text{Ni},\text{Co})(\text{OH})_2$ nickel hydroxide). This is in very good agreement with the increase in relative magnitude of the signal for vanadium ions grafted to nickel ions observed in Figure 5 when y decreases. Chemical analyses results given in Table 1 show that the grafting/overintercalation process seems to go on until approximately 0.4 vanadium ion per $(\text{Ni} + \text{Co})$ is present, whatever the value of y . Through the determination of the hydrogen content by elemental analysis, a rough estimate of the amount of water can be made; it amounts to about 0.7 H_2O molecule per formula unit. One can consider that most of this water is intercalated since the particle size of these chimie douce materials is rather large as compared to the case of coprecipitated LDH's.²⁰ Therefore, the total number of oxygen atoms present in the interslab space is close to two per formula unit, whatever the value of y . Besides, the interslab distances observed correspond to two layers of oxygen; it therefore seems that the grafting/overintercalation process goes on until the interslab space is fully occupied.

Note that this grafting process implies that vanadium ions belonging to the same chain can be grafted to the layers, which must participate in creating the local structural distortions responsible for the shape of the X-ray diagrams of the $\text{LDH}_y(\text{VO}_3)$ material (Figure 2), in addition to the electrostatic interactions mentioned earlier.^{14,15}

3.2. Evolution of the "Freshly Obtained Vanadate-Inserted LDH" Exposed to Air. As mentioned just above, a partial grafting occurs during the polycondensation step. In order to characterize it more fully, we have recorded ^{51}V NMR spectra during this step, starting as early as possible after the reduction process (see the Experimental Section for details).

The X-ray diffraction patterns upon aging in air of the "freshly obtained vanadate-inserted LDH" with $y = 0.3$ are shown in Figure 6. Their changes have already been discussed in details in a previous paper¹⁵ and correlated with the results of IR spectroscopy and chemical analysis. The large decrease of the interslab distance from 10.1 Å for the "freshly obtained LDH" to 8.6 Å after 4 days in air must be related to the polycondensation of the diperoxovanadate ions inserted primarily into metavanadate chains, as stated in the introduction of the present paper. The modification of the inserted vanadate species also shows up through a change in the shape of the (10 l) and (11 l) lines, which are well-separated for the "freshly obtained LDH" and tend to broaden into large asymmetric bands upon aging in air. This behavior, which was characterized as a loss of the local structural order within the slab, is due to the evolution of the isolated diperoxovanadate species into metavanadate chains, which tend to create strains within the slab lattice.¹⁵ Furthermore, the presence of different inserted entities leads again to the appearance of a (00 l) line shape characteristic of an interstratified material.

The ^{51}V NMR spectra for the same set of materials ("freshly obtained" and after aging) are reported in Figure 7. Right after

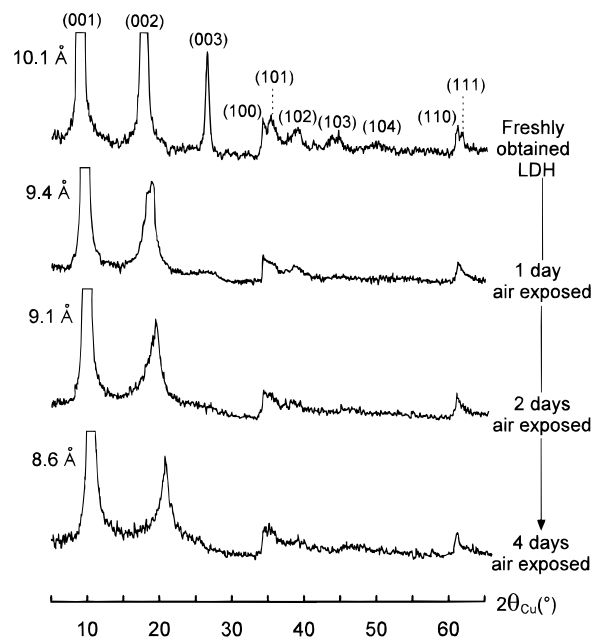


Figure 6. X-ray diffraction patterns of the "freshly obtained LDH" ($y = 0.3$) and after aging in air.¹⁵

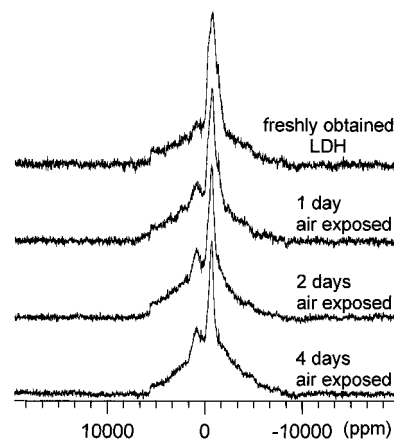


Figure 7. Static ^{51}V NMR spectra of the "freshly obtained LDH" ($y = 0.3$) and after aging in air.

the filtration, the signal at -600 ppm is rather broad and ill-defined with a negligible contribution at 850 ppm, which may correspond to the presence of several vanadate species not grafted to the layers, diperoxovanadate ions and also intermediate species arising from partial and gradual polycondensation of the diperoxovanadate ions into metavanadate chains.¹⁵ That asymmetric broad line, centered around -600 ppm, tends to lose its feature upon aging and to give rise after 4 days of exposure in air to a narrow line identical to that of $\text{LDH}_y(\text{VO}_3)$, which can therefore be attributed to vanadium ions from metavanadate chains. Simultaneously, the signal at 850 ppm, which was attributed in the previous section to vanadium atoms grafted to the slab, grows in relative magnitude (this is not clearly apparent at first sight on the figure because of the narrowing with time of the line at -600 ppm). This shows that a grafting phenomenon simultaneously occurs during the polycondensation step. This grafting (as well as the polycondensation) occurs while the material is kept outside the medium containing vanadate species, so that the OH^- ions extracted from the slab cannot be replaced by more vanadate ions. Consequently, the total amount of vanadium ions intercalated is 0.23 per $(\text{Ni} + \text{Co})$ whereas it was around 0.4 for the former case. Actually, this value is too small for compensating for the charge of the $0.30 \text{Co}^{\text{III}}$ ions, but it does fit if one takes into account

the additional presence of carbonate ions coming from the atmosphere, as identified by IR spectroscopy.¹⁵ As to the OH⁻ ions produced by the grafting, they can either remain within the interslab space or combine with protons if a dehydroxylation (and consequently a segmentation of the chains) occurs. Since this involves anyway a small fraction of the vanadate ions present, it is impossible to assert which of the two hypotheses is true.

After the initial modification of the NMR spectra during the first 4 days just described, no more change of the -600 ppm signal shape occurs. The relative magnitude of the signal at 850 ppm increases extremely slowly with time under ambient conditions, showing that negligible grafting of the vanadate ions goes on spontaneously after the polycondensation step. However, an extensive grafting and fragmentation is obtained after a thermal or vacuum treatment of the material, as discussed in the first part of this paper.

4. Conclusion

Through the magnetic interaction exerted by Ni^{II} ions, ⁵¹V NMR is able to distinguish vanadium atoms which are grafted to the layer from those which are not in vanadate-inserted LDH's resulting from the reduction of mixed nickel-cobalt γ -oxyhydroxides in an NH₄VO₃/H₂O₂ medium. It thus appears that this overall reaction involves rather complex phenomena.

As soon as they are inserted (in order to compensate for the excess positive charges due to the presence of Co^{III} ions), the isolated diperoxovanadate ions undergo a competition between polycondensation and grafting processes.

When the material is kept in the reducing solution containing vanadate species, a partial grafting occurs during the polycondensation and causes a dehydroxylation of the slab. In order to maintain the required charge compensation, more vanadate ions are inserted until the interslab space is filled.

When it is removed and filtered very early from the solution, only as many vanadate ions are inserted as are necessary for the charge compensation. The polycondensation then occurs in air and can be followed by NMR, which also evidences a partial simultaneous grafting.

In both cases, after the polycondensation step, partially grafted metavanadate chains are present. Then, further grafting and fragmentation occur, which involve both a dehydroxylation and a deprotonation of the slab, and thus lead to the formation of water. This process is negligible under ambient conditions but is significant and even brought to completion by heating or applying vacuum (i.e. helping to remove the water produced). Such a grafting causes a collapse of the interlayer spacing.

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