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Preparation and Study of Decavanadate-Pillared Hydrotalcite-like Anionic Clays Containing Transition Metal Cations in the Layers. 1. Samples Containing Nickel−Aluminum Prepared by Anionic Exchange and Reconstruction

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For the first time, the nickel−aluminum layered double hydroxide (LDH) $[Ni_{1-x}Al_x(OH)_2]\ (CO_3)_{x/2}\cdot mH_2O$ containing carbonate anions in the interlayer, has been pillared with polyvanadate in aqueous solution at pH = 4.5 by anionic exchange without the assistance of any swelling agent. Making use of the so-called *memory effect* of these materials, synthesis of similarly pillared compounds through recovery of the structure from calcined LDH in contact with an aqueous solution of sodium metavanadate was also achieved. Characterization of the materials obtained so far has been carried out by chemical analysis, X-ray diffraction, Fourier-transform infrared spectroscopy, and thermal analysis. The influence of experimental conditions during the calcination−reconstruction process of the pillared−layered structure, such as calcination temperature and pH during the reaction, as well as the temperature during hydrothermal treatment (to improve crystallinity), is reported; purity of the product depends on the calcination temperature of the starting precursor, and at pH values higher than 4.5, a $(VO_3)_n$ polyvanadate chainlike pillared material is obtained. Exchange of carbonate anions depends on the pH of the solution, total exchange being only attained at pH = 4.5−5.5. Thermal stability of the pillared materials and the microstructure properties are also reported.

Introduction

The so-called layered double hydroxides (LDH), formally hydroxycarbonates, are a family of compounds with increasing interest in the last few years, because of their applications in different fields.[1] They are usually referred as "hydrotalcite-like" materials, because of the relationship existing between their structures and that of hydrotalcite, a magnesium−aluminum hydroxycarbonate with the formula $Mg_6Al_2(OH)_{16}CO_3\cdot4H_2O$; its structure corresponds to brucite-like layers $[Mg(OH)_2]$ where a partial Mg^{2+}/Al^{3+} substitution has taken place, the positive charge in excess being compensated by carbonate anions in the interlayers. When other cations exist in the hydroxide layer, they receive different names (e.g., takovite for Ni, Al). These materials show an interest by their own, and also because of the different compounds that can be obtained therefrom, upon exchange of the interlayer anions with, specially, polyoxones.

Previous studies on the exchange properties of hydrotalcite-like materials with polyoxones deal mainly with materials containing carbonate, chloride or nitrate.[2−4] The nature of the anion initially present in the LDH plays a significant role on the ion-exchange properties of the solid; thus, anions weakly held between the hydroxide layers are more appropriate as they can easily be replaced by the pillaring anions. The exchange facility decreases in the order $NO_3^- > Cl^- > SO_4^{2-} > CO_3^{2-}$. Alternatively, the use of swelling agents, such as organic molecules has been also proposed[5,6] to improve exchange by bulk anions, and recently the method has been also applied to introduce Keggin anions in the interlayer space[7,8] of this kind of material.

Calcination of LDHs leads to a mixture of metal oxides,[9] which, upon being hydrated in solutions containing a given anion, are able to recover the layered structure but incorporate such an anion in the interlayer space.[10] Recently, this method has been reported to be a facile route for preparation of pillared LDHs by exposing these metal oxides to the appropriate organic or inorganic anion solutions.[11−14] However, the ability of the mixture of metal oxides obtained upon calcination of LDHs to recover the layered structure strongly depends on the experimental conditions, and also on the nature of the metal cations existing originally in the layers.[10,15]

A systematic study is reported in the present paper on the pillaring of nickel−aluminum hydroxycarbonate (takovite-like) with decavanadate, $V_{10}O_{28}^{6-}$, anions. On one side, the exchange method has been used, studying the pH during exchange and the wetting state of the solid (as it will be shown below, no exchange is achieved by simply pouring the solid in the vanadate solution). On the other side, reconstruction of the layered

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structure by immersion of calcined nickel–aluminum hydroxycarbonate in an aqueous vanadate solution has been also studied. In this case, the following experimental variables were studied: calcination temperature of LDH, pH of solution during reconstruction, and temperature during hydrothermal treatment. The solids obtained have been characterized by chemical analysis, X-ray diffraction, thermal analysis (differential and thermogravimetric), and FT-IR spectroscopy.

Experimental Section

Preparation of Parent Nickel–Aluminum Hydroxycarbonate. Preparation of the Ni–Al LDH (hereafter NiAlCO3) has been carried out following the method described by Reichle.[16] All chemicals were from Fluka (Germany). A 250 mL aliquot of an aqueous solution containing 0.1 mol of nickel nitrate and 0.05 mol of aluminum nitrate was added dropwise to a vigorously stirred aqueous solution, kept at 65 °C formed by dissolving 0.7 mol of NaOH and 0.2 mol of Na_2CO_3 in 200 mL water (pH *ca.* 11). Addition extended along *ca.* 30 min. The obtained gel was aged overnight, then separated by centrifugation and washed with distilled water. The obtained slurry was hydrothermally treated for 48 h at 120 °C and then dried at 70 °C overnight.

Samples Prepared by Anionic-Exchange. A 3 g sample of the dried NiAlCO3 LDH was suspended in 300 mL of water overnight to ensure complete wetting of the LDH's particles, and then the pH was adjusted to a given pH by adding a 0.5 M HCl solution.

A 6 g sample of sodium metavanadate was dissolved in 100 mL distilled water, the pH of the solution was also adjusted at the same pH value by adding 0.5 M HCl. The metavanadate solution was added dropwise to the NiAlCO3 suspension. The orange-yellow solid was separated by centrifugation, washed, and then dried at 70 °C.

In all cases the pH of the LDH suspension was adjusted to the same value than that of the metavanadate suspension before the anion exchange, using a Metrohm Dosimat 725.

The samples will be labeled as NiAlV-E.

Samples Prepared by Reconstruction. A 1 gram amount of the NiAlCO3 sample, calcined at 300, 400, and 500 °C for 3 h, was added to a solution (6 g of vanadate in 100 mL of water) of sodium metavanadate at 70 °C and at a given pH between 4.5 and 8.5, previously stirred for 1 h. During the stirring process, the pH was controlled and adjusted at the same pH value of the sodium metavanadate solution using a Metrohm Dosimat. The suspension was then submitted to hydrothermal treatment at 120 °C overnight. The precipitate was separated by centrifugation, washed and dried at 65 °C in air.

The samples will be labeled NiAlV-R.

In order to assess the effect of calcination temperature on reconstruction of the layered structure, portions of NiAlCO3 were calcined at 300, 400, and 500 °C for 3 h in air. The oxides mixtures were put into suspension in hot distilled water and then hydrothermally treated (THT) in a stainless steel, lined with teflon cell, under autogenous pressure at 120 °C, overnight. The solid was separated by centrifugation and washed and then dried at 65 °C.

Characterization. Ni, Al, and V analyses were carried out by atomic absorption after dissolution of the solid in a HCl solution; a Perkin Elmer atomic absorption spectrometer, Model 3100, was used. Powder X-ray diffraction (PXRD) was obtained using a Siemens diffractometer with Cu Kα radiation and a graphite monochromator. Differential thermal analysis (DTA) and thermogravimetric analysis (TG) of the samples were carried out in Perkin–Elmer DTA 1700 and TGS-2 apparatuses, respectively, coupled to a Perkin–Elmer 3600 data station at a heating rate of 10 °C/min. The FT–IR spectra were recorded on a BOMEN MB-100 spectrometer in the 4000–400 cm^{-1} range using pressed KBr pellets. Microstructural characterization of the materials was carried out by transmission electron microscopy on a JEOL 200CX instrument. Full nitrogen adsorption/desorption isotherms at −196 °C for surface area and porosity assessment were recorded in a conventional Pyrex high-vacuum system equiped with a MKS pressure transducer, grease-free stopcocks, an APV-DD4 rotatory pump and a silicon oil diffusion pump, after outgassing the samples *in situ* at 150 °C for 2 h.

Table 1. Chemical Analyses of Parent NiAlCO3 and of Decavanadate-Pillared Samples Obtained at pH = 4.5

sample	% Ni	% Al	% V	Ni/Al[a]	V/Al[a]
NiAlCO3	55.0	7.3		3.44	
NiAlV-E	24.9	5.0	19.3	2.31	2.04
NiAlV-R	27.0	6.1	17.8	2.03	1.54

[a] Atomic ratio.

Results

Chemical Analysis. Chemical analyses for the parent NiAlCO3 sample and for those containing decavanadate obtained at pH = 4.5, are given in Table 1. As will be shown below, attempts carried out at other pH values did not lead to well-crystallized, fully exchanged layered materials.

It is observed that in both cases the Ni/Al ratio is lower than in the parent LDH. This decrease is due to the easier dissolution of nickel compared to that of aluminum. Also in the same table, values for the V/Al atomic ratio are given. Assuming the intercalated anion is being $V_{10}O_{28}{}^{6-}$, the V/Al atomic ratio should be 1.66. Of course, some other polyoxovanadate species (e.g., $V_4O_{12}{}^{4-}$, $V_2O_7{}^{4-}$) could be located in the interlayer space, cancelling the positive charge in the layers because of the presence of Al^{3+} ions; however, such species are stable only at pH values rather higher than that used in the present work for preparation of the samples,[17] and also the PXRD and FT-IR data below discard the presence of these species. This value results to be 2.04 for sample NiAlV-E and 1.54 for sample NiAlV-R. It can be assumed that such decavanadate species should exist in the sample obtained by reconstruction (expected V/Al ratio 1.67; found 1.54), while in the case of sample NiAlV-E (found V/Al = 2.04) an excess of vanadium should exist.

Powder X-ray Diffraction. Figure 1 shows the PXRD diagrams of parent NiAlCO3 and of several decavanadate-containing samples prepared by ionic exchange.

The PXRD diagram for sample NiAlCO3, Figure 1a, shows well-defined peaks at 7.58, 3.78, 2.55 Å, etc. This is typical of well-crystallized LDH, and the value of *c*/3 coincides with *d*(003) at 7.58 Å; this value is comparable to that of natural takovite, 7.53 Å.[18,19] The position of the (110) peak at 1.51 Å coincides with half of the *a* unit cell parameter.[1]

When a sample of NiAlCO3 was added to a vanadate solution at pH = 4.5, the solid thus obtained exhibited the PXRD diagram shown in Figure 1b. Despite the low quality of the diagram, due to the low crystallinity of the sample, it is clearly concluded that no exchange has been achieved, as a weak, broad peak is still recorded at 7.6 Å, i.e., a position coinciding with that expected for a layered hydroxide containing carbonate anions in the interlayer. (The weak, sharp peaks close to 2θ = 40, 45, and 65° are due to the aluminum sample holder.)

On the contrary, if the NiAlCO3 is maintained in suspension overnight and then the vanadate solution (pH = 4.5) is dropwise added, exchange takes place (the peak due to (003) planes of carbonate containing LDH at 7.58 Å has been completely removed), leading to a powder whose PXRD diagram is shown in Figure 1c.

A new phase is, however, formed, with relevant peaks at 11.7, 5.85, and 3.93 Å that are ascribed to diffraction by planes (003),

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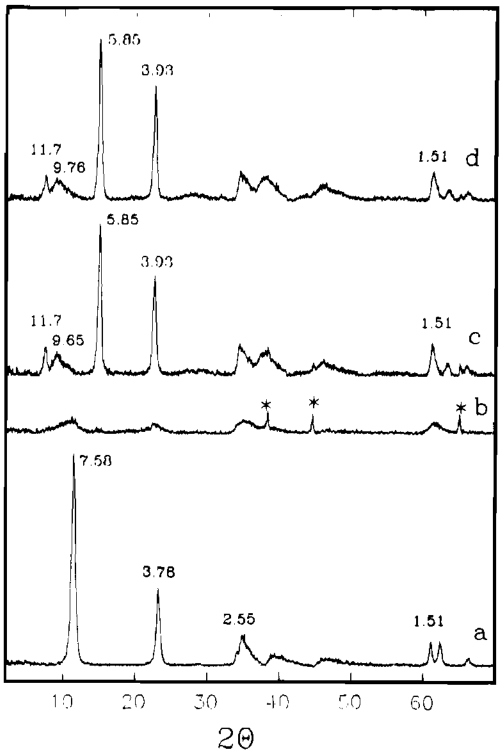

Figure 1. PXRD diagrams: (a) parent NiAlCO3 anionic clay; (b) sample prepared upon immersion of parent NiAlCO3 in decavanadate solution; (c) sample NiAlV-E prepared by addition of decavanadate solution to a suspension of the anionic clay; (d) sample NiAlV-E prepared by addition of decavanadate solution to the slurry of the anionic clay. (pH = 4.5 in all cases.) (* = peaks due to the Al sample holder.)

(006), and (009), respectively; the (110) peak, whose position is related to parameter *a* and then to the sizes of the cations and anions existing in the layers, is again recorded at 1.51 Å. Inversion in the expected relative intensities of the (00l) peaks has been previously reported for materials similar to those here synthetized.[6] The position of peak (003) coincides with the sum of the thickness of the brucitelike layer (4.8 Å[20]) and the height of the $V_{10}O_{28}^{6-}$ species, located with its main C_2 axis parallel to the host layers,[3,21] 6.9 Å.

However, in addition to all these peaks, ascribed to the presence of a $NiAlV_{10}O_{28}$ pillared, layered material, a broad feature is recorded at 9.65–9.8 Å. The origin of this peak is rather unclear, although it has been also reported by other authors for materials obtained through intercalation of polyoxones in hydrotalcite-like materials. So, Narita *et al.*[22] report a peak at 10.2–10.9 Å upon intercalation of $(\alpha\text{-SiW}_{11}O_{39})^{8-}$, and $(\alpha\text{-1,2,3-SiV}_3W_9O_{40})^{7-}$ into Zn,Al LDH, and this peak has been attributed to Zn^{2+} and Al^{3+} salts of the polyoxone. Clearfield *et al.*[7] have reported a broad PXRD peak at 11–13 Å upon intercalation of anions possessing the Keggin structure into several LDHs, and it was also reported in the case of Mg–Al pillared by decavanadate anions.[14] Development of this broad peak seems to be independent on the nature of the divalent and trivalent cations in the brucite layers, neither on the nature of the polyoxone anions, nor on the way of the synthesis.

It should be stressed that despite many previous papers report the broad feature, it always covers the weak peak due to diffraction by planes (003), and this is the first report on decavanadate-exchanged materials (the report by Clearfield *et al.*[7] refers to anions with the Keggin structure) where the (003) peak is clearly recorded, independent on the broad feature.

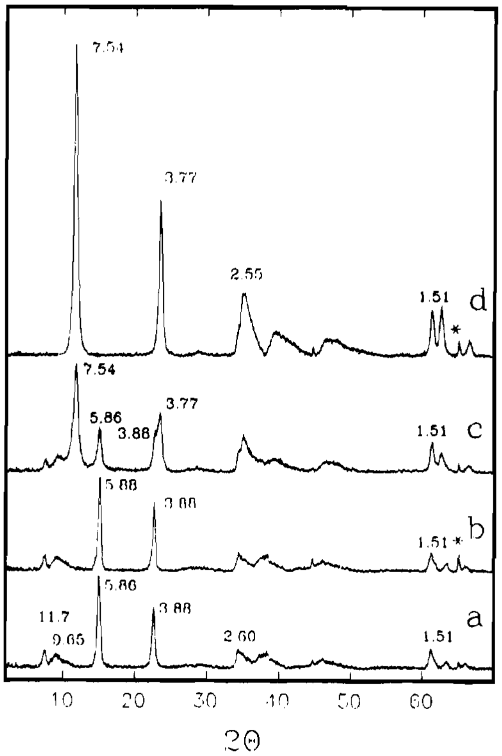

Figure 2. PXRD diagrams of samples NiAlV-E prepared by addition of decavanadate solution to the slurry of the anionic clay at different pH: (a) 4.5; (b) 5.5; (c) 6.5; (d) 8.5. (* = peaks due to the Al sample holder.)

Finally, Figure 1d shows the PXRD diagram of a sample obtained similarly to that responsible for Figure 1c, but from the slurry obtained during preparation of parent NiAlCO3 not being submitted to drying. It should be noted that in this case the suspension was not maintained overnight before addition of the vanadate solution. The similarities between profiles c and d in Figure 1 indicate that the use of the slurry permits a faster synthesis of a layered material with similar crystallinity properties.

As mentioned above, when exchange was performed at pH = 4.5 a good yield of decavanadate-pillared material was obtained. A detailed study of the effect of pH is shown in Figure 2. Profiles in this figure correspond to the material obtained when exchange was performed at the pH values indicated. For pH values between 4.5 and 5.5 the PXRD were identical, indicating a good exchange, leading to a totally exchanged material. On the contrary, at pH = 8.5 or higher no exchange occurs, the material showing the (003) peak at 7.54 Å, due to carbonate-containing LDH. However, for intermediate pH values (specially at pH = 6.5) a partial exchange takes place, the PXRD diagram showing (003) peaks for decavanadate- (weak peak at 11.7 Å) and carbonate-containing (7.54 Å) materials. This behavior at high pH values could be originated by two (non exclusive) facts: first, that the carbonate anion is not replaced, and, second, that vanadate does not polymerize to decavanadate under these experimental conditions. In order to check this behavior, the following experiments were carried out: A vanadate solution at pH = 6.5 was added to a LDH suspension at pH = 4.5, and after reaction, the solid was isolated. Its PXRD diagram is shown in Figure 3a, where it can be clearly seen that almost total exchange to a decavanadate-containing material has been achieved, i.e., under these pH conditions, vanadate has already polymerized to $V_{10}O_{28}^{6-}$. However, when

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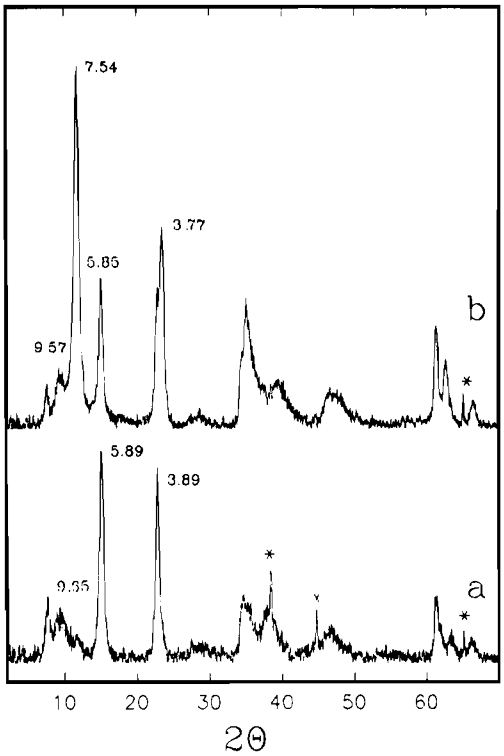

Figure 3. PXRD diagrams of samples NiAlV-E prepared by addition of decavanadate solution (pH = 6.5) to the slurry of the anionic clay at pH (a) 4.5 and (b) 6.5. (* = peaks due to the Al sample holder.)

the vanadate suspension at pH = 6.5 was added to a LDH suspension *also* at pH = 6.5, only a partial exchange, Figure 3b, was attained. So, it should be concluded that a pH value of 4.5 should somewhat facilitate a carbonate/chloride exchange in the interlayer space,[23] the chloride anion being immediately substituted by decavanadate, while at higher pH values the carbonate is only partially exchanged for chloride and thus only a partial substitution for decavanadate exists.

Powder XRD diagrams of samples prepared by reconstruction of the layered structure are shown in Figures 4 −6. Each figure corresponds to the study of the effect of one of the experimental factors. It should be stressed that rehydration of the precursor calcined at 300 °C led to reconstruction of the carbonate-containing specimen, but starting form the precursor calcined at 400 °C or above, only partial reconstruction was achieved.

First of all, PXRD diagrams of samples prepared by reconstruction starting from LDHs previously calcined at different temperatures are shown in Figure 4. Although in all cases a solid with the hydrotalcite-like structure is obtained, as the precalcination temperature is increased, peaks due to diffraction by NiO planes (2.07 Å) are also observed. According to Clause *et al.*,[24] as the precalcination temperature is increased, Al^{3+} ions migrate from the mixed oxide phase to the crystallite surface, wherefrom they are dissolved when the solid is suspended at pH = 4.5. So, the nickel in excess does not enter the reconstructed LDH structure but remains as an independent NiO phase. So, all reconstruction studies have been carried on solids precalcined at 300 °C.

The effect of pH during reconstruction on the PXRD diagrams of the solids is shown in Figure 5. As mentioned above, at pH = 4.5 a decavanadate-containing LDH is obtained, Figure 5a, with *d*(006) = 5.89 Å, in addition to the broad feature close to 10 Å. As the pH during reconstruction is increased, the broad feature disappears and the main diffraction peak shifts from 7.48 Å (at pH = 5.5) to 7.28 Å (at pH = 8.5), indicating the synthesis of a single phase. In all cases, the value is too low to be due to carbonate-containing LDH, and (*vide infra*) the FT−IR spectra confirm the absence of carbonate anions. The basal

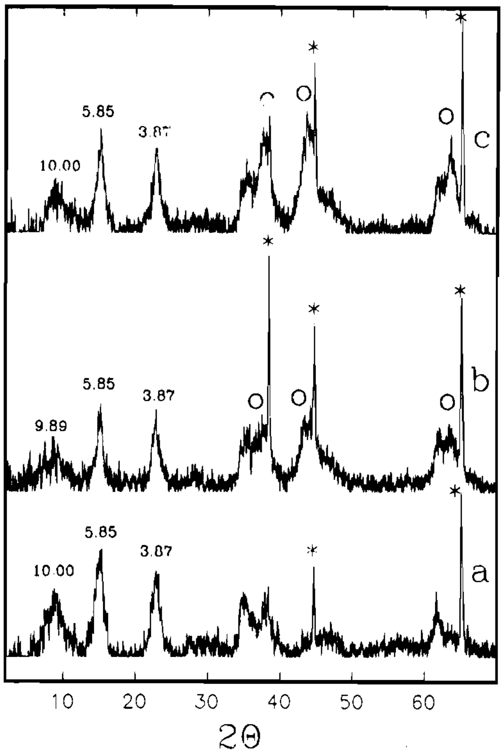

Figure 4. PXRD diagrams of samples NiAlV-R prepared by reconstruction at pH = 4.5 of the solids precalcined at (a) 300; (b) 400 and (c) 500 °C. (* = peaks due to the Al sample holder; (O = peaks due to NiO.)

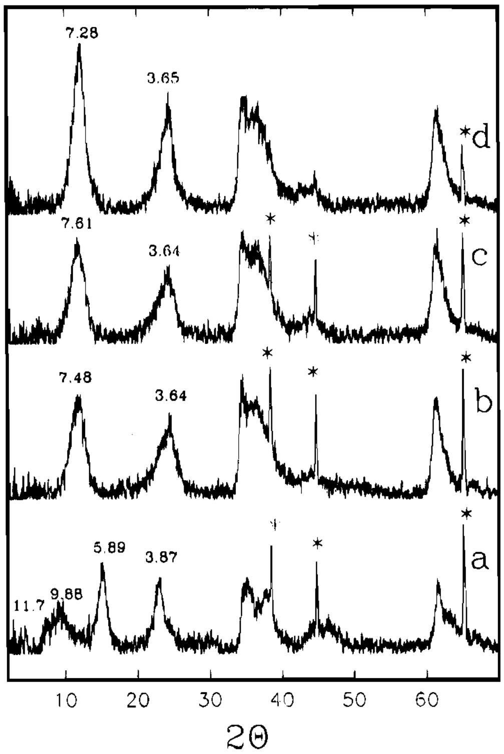

Figure 5. PXRD diagrams of samples NiAlV-R prepared by reconstruction of the solid calcined at 300 °C with decavanadate solution at pH (a) 4.5; (b) 5.5, (c) 6.5, and (d) 8.5. (* = peaks due to the Al sample holder.)

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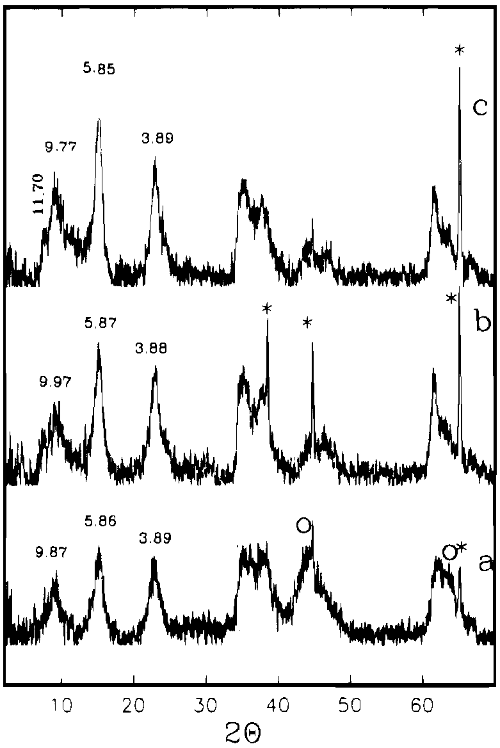

Figure 6. PXRD diagrams of samples NiAlV-R prepared by reconstruction at pH = 4.5 of the solid precalcined at 300 °C and hydrothermally treated at (a) 80; (b) 120 and (c) 150 °C. (* = peaks due to the Al sample holder; O = peaks due to NiO.)

spacing of 7.3 Å (d(003) = 7.3 Å) corresponds to a gallery height of 2.5 Å, which can be due to the formation of $(VO)_3$ chainlike polymeric metavanadate, composed of the (VO_3) tetrahedra with C_{2v} symmetry, and with the longitudinal chain axis (*a* axis) parallel to the host layers.[25]

Finally, the effect of temperature during hydrothermal treatment of the samples on the crystallinity and nature of the phases obtained is shown in Figure 6. It should be noted that the LDH structure is not recovered if the sample is not submitted to hydrothermal treatment. As the temperature during hydrothermal treatment is increased, the intensity of diffraction peaks due to NiO decreases, while those of the decavanadate-containing LDH is increased. In other words, increasing of the hydrothermal treatment temperature favors formation of the layered structure.

Thermal Analysis. The TG diagram of the starting material (NiAlCO3), Figure 7a, shows the presence of two weight losses, the first one up to ca. 260 °C and the second one up to ca. 470 °C. The pattern is similar to that reported for different hydrotalcite- and takovite-like solids, and from mass spectrometric analysis of the gases evolved during decomposition,[26] the first weight loss should correspond to removal of molecular water from the interlayer, while the second corresponds to evolution of carbon dioxide (from interlayer carbonate anions) and water (from condensation of layer hydroxyl groups). Total weight loss up to 750 °C is 34% and, taking into account that the final solids formed upon calcination at this temperature (from comparison with similar materials) are a mixture of NiO and $NiAl_2O_4$, the formula of the starting solid can be calculated as $[Ni_{0.78}Al_{0.22}(OH)_2](CO_3)_{0.11}\cdot 0.72H_2O$. The corresponding DTA profile for this sample, Figure 7b, shows two endothermic minima at 271 and 371 °C, coincident with the above mentioned weight losses.

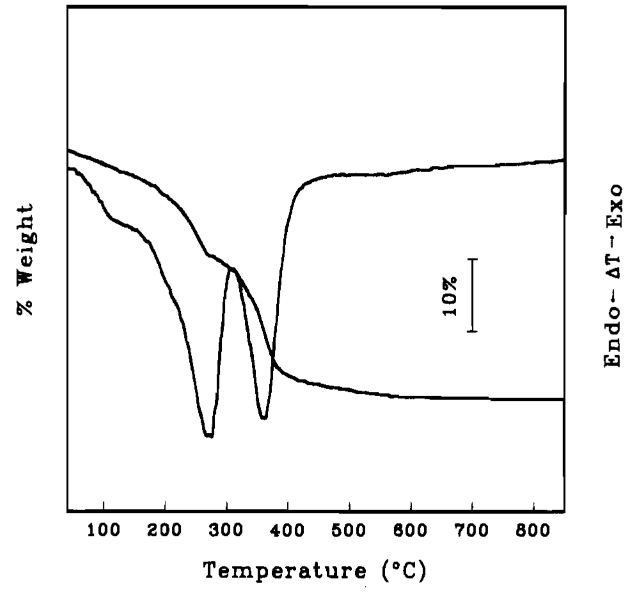

Figure 7. (a) Thermogravimetric and (b) differential thermal analysis curves for parent NiAlCO3.

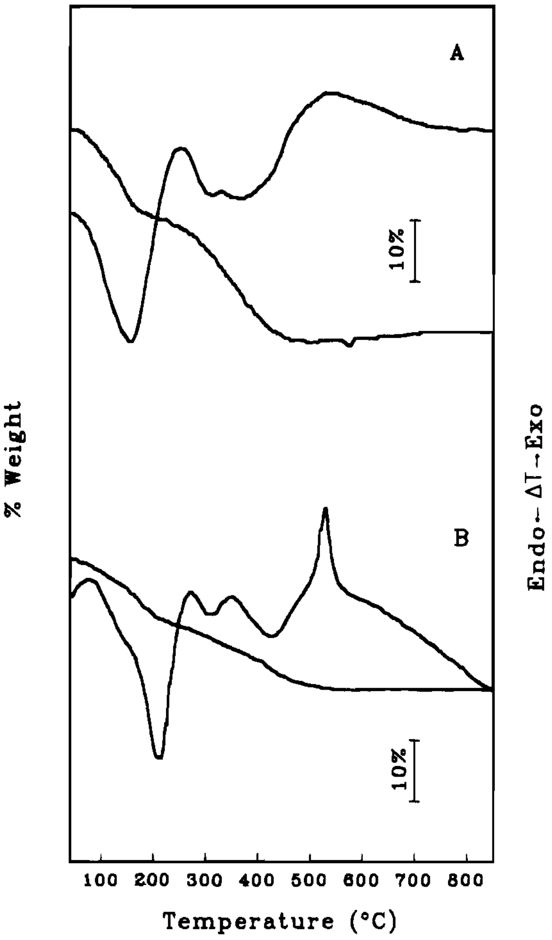

Figure 8. Thermogravimetric and differential thermal analysis curves for samples (A) NiAlV-E and (B) NiAlV-R.

After pillaring *via* anion-exchange at pH = 4.5, the TG diagram for sample NiAlV-E, Figure 8A, shows three weight losses. The first one corresponds to 9% of the initial weight of sample and extends from room temperature to 210 °C; from comparison with the pattern for sample NiAlCO3 and other decavanadate-containing solids,[14] it should be ascribed to

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removal of interlayer water molecules. The second weight loss extends from 210 to *ca.* 550 °C, with a change in the slope close to 330 °C , and represents 8.3% of the initial weight. This value is markedly lower than that recorded for parent NiAlCO3 (16%), but this is due to the fact that in decavanadate-containing LDHs only hydroxyl groups are removed (as water molecules) in this temperature range, while in sample NiAlCO3, carbonate is also removed as carbon dioxide. The change in the slope of the TG curves simply suggests that two types of hydroxyl groups exist in this sample, different temperatures being needed to remove them.

The DTA profile for this sample, Figure 8A, is rather different from that for parent NiAlCO3. The first, intense, endothermic minimum at 203 °C coincides with the main weight loss up to 210 °C. However, at higher temperatures, two weak minima are recorded at 315 and 429 °C; it should be noted that the average temperature between these two temperatures is 372 °C, coincident with the position of the second minimum (371 °C) in the DTA profile of sample NiAlCO3. As sample NiAlV-E does not contain carbonate anions, these two minima should correspond to removal of differently held hydroxyl groups (probably interacting with different strength with other lattice components), although this fact cannot be observed in the DTA profile of sample NiAlCO3 due to overlapping with the peak corresponding to removal of carbonate species.

In addition, a sharp, exothermic peak is recorded at 532 °C. This temperature is higher than that at which any weight loss is recorded, and should then correspond to a non-weight-loss process, such as a recrystallization. This peak should then be ascribed to formation of binary and/or ternary Ni−Al−V oxide species, as confirmed by X-ray diffraction (*vide infra*).

Thermal analysis curves for sample NiAlV-R, prepared at pH = 4.5 with precursor precalcined at 300°C, are shown in Figure 8B. The TG curve is rather similar to that for sample NiAlV-E, with two main weight losses up to ca. 200 and 530 °C, with weight losses of 10 and 10.5%, respectively. Peaks in the corresponding DTA curve are badly defined, probably because of the low crystallinity of this sample, if compared to those of samples NiAlCO3 and NiAlV-E. Removal of interlayer water molecules is attained at temperatures somewhat lower, the minimum being recorded in the DTA curve at 152 °C (cf. 278 and 203 °C for samples NiAlCO3 and NiAlV-E, respectively). It should be also noted that the broad feature in the PXRD peak of this sample is more intense in this case than for sample NiAlV-E. It can be tentatively concluded that thermal stability of sample NiAlV-R is somewhat similar to that of sample NiAlV-E, but the lack of crystallinity leads to bad resolution of the peaks.

FT-IR Spectroscopy. FT-IR spectra for samples NiAlCO3, NiAlV-E and NiAlV-R, as well as for sample NiAlCO3 calcined at 300 °C (i.e., the solid used for preparation of sample NiAlV-R) are shown in Figure 9. The broad peak at 3800−3600 cm^{-1} in all four samples corresponds to ν_{OH} of hydrogen-bonded hydroxyl groups. The shoulder slightly above 3000 cm^{-1} in the spectrum of sample NiAlCO3 corresponds to ν_{OH} of water molecules hydrogen-bonded to carbonate ions in the interlayer;[27,28] its absence in the spectra of samples NiAlV-E and NiAlV-R indicates the lack of carbonate species in these two samples. A definitive confirmation of this absence comes from the lack in these two spectra of the intense peak at 1373 cm^{-1} (recorded at 1376 cm^{-1} for sample NiAlCO3 calcined at 300 °C), due to mode ν_3 of carbonate species.[29] Restricted geometry within the interlayer region shifts this band from its position in free carbonate at 1450 cm^{-1}. The peak at *ca.* 1620 cm^{-1} is due to δ_{H_2O} of molecular water. The bands at 964, 810, 748, 598, and 520 cm^{-1} are due to decavanadate species in the gallery space.[30,31] The band at 964−960 cm^{-1} can be assigned to the symmetric stretching mode of VO_2 species,[32] the 750 cm^{-1} band is attributed to V−O stretching vibration. The bands near 800 and 500 cm^{-1} are attributed to antisymmetric and symmetric modes of V−O−V chain, respectively.[33]

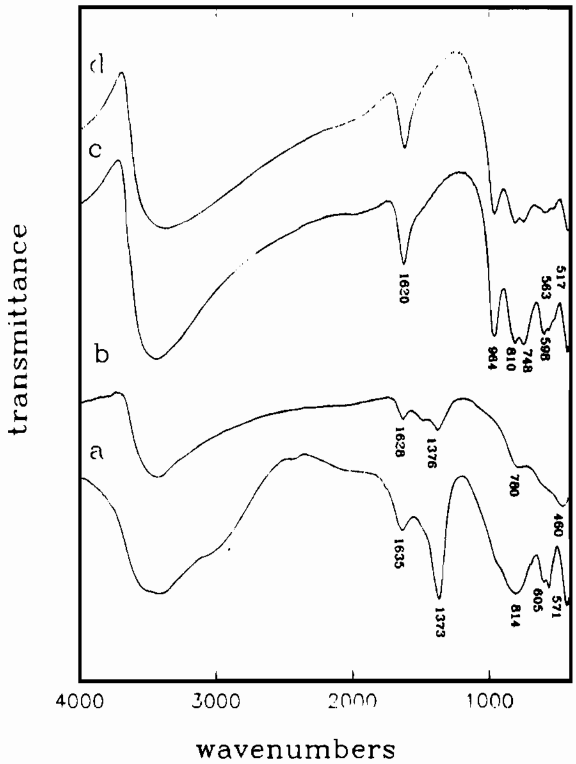

Figure 9. FT-IR spectra of (a) the parent NiAlCO3 anionic clay, (b) the parent NiAlCO3 calcined at 300 °C, (c) sample NiAlV-E, and (d) sample NiAlV-R.

Calcination of sample NiAlCO3 at 300°C leads to the decrease of the bands originated by mode ν_{OH} of hydroxyl groups and ν_3 mode carbonate anion. The bands at low wavenumbers are due to lattice metal−oxygen bonds of the amorphous material obtained upon calcination.

After reconstruction at pH = 4.5 the spectrum for sample NiAlV-R is almost coincident with that for sample prepared by anionic exchange, NiAlV-E. Only when reconstruction is carried out at pH = 6.5, is a very weak absorption band recorded at 1377 cm^{-1}, confirming that no total exchange of carbonate has been attained.

Decomposition Products. The current interest in LDHs and in their pillared-derivatives comes not only from their possible role by them but also because of the use of their decomposition products after calcination at different temperatures, a treatment leading to a mixture of metallic oxides, useful as catalysts in several oxidation processes. In this work we have studied the development of new crystalline phases when the solids prepared have been calcined at increasing temperatures.

PXRD patterns of sample NiAlV-E calcined in air for 3 h at increasing temperatures are shown in Figure 10. Calcination

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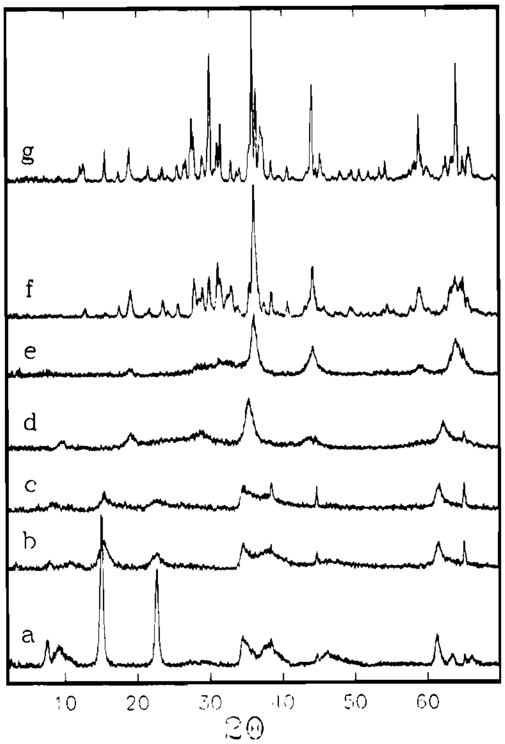

Figure 10. PXRD diagrams fo sample NiAlV-E calcined at (a) 25, (b) 150, (c) 200, (d) 300, (e) 400, (f) 500, and (g) 850 °C. (* = peaks due to the Al sample holder.)

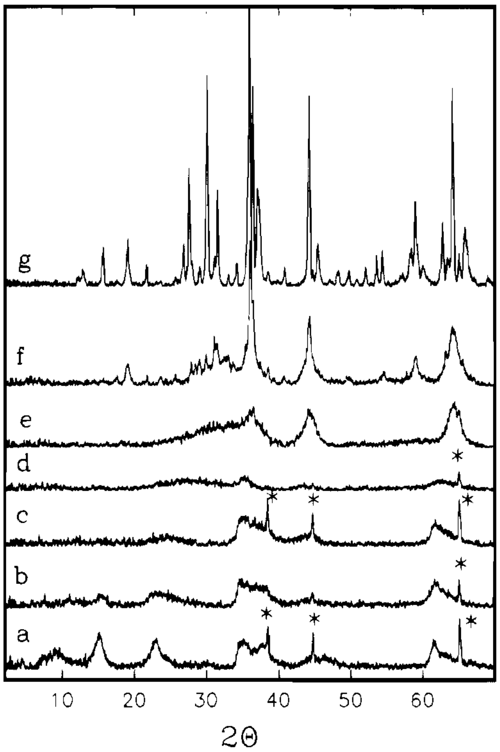

Figure 11. PXRD diagrams of sample NiAlV-R calcined at (a) 25, (b) 150, (c) 200, (d) 300, (e) 400, (f) 500, and (g) 850 °C.

at 150 or 200 °C gives rise to a general broadening of the diffraction peaks, although their positions remain unchanged. When the sample is calcined at 300 °C the peaks originated by the decavanadate-intercalated material vanish and, instead, two broad, weak peaks develop at 9.22 and 4.62 Å. This can be originated by a depolymerization of the decavanadate species[34] as dehydroxylation of the host layers occurs and a Ni−Al−O solid solution starts being formed.[10,34] It should be mentioned that the (110) peak close to 1.50 Å remains in the same position, although it broadens, up to 300 °C.

Calcination at 400 °C gives rise to strong changes in the PXRD profile. Peaks due to the layered material are absent, and strong peaks develop at 2.49, 2.04, and 1.46 Å. The second peak is due to NiO. Calcination at 500°C leads to development of new peaks and sharpening of those already existing. From comparison with PXRD files, the new peaks can be ascribed to $Ni_3V_2O_8$ and $Ni_2V_2O_7$, the second existing as a minor impurity. Aluminium should exist forming a $NiAl_2O_4$ spinel, but its detection is rather difficult, as the positions of its diffraction coincide, within experimental error, with many of the peaks shown by $Ni_3V_2O_8$.

The behavior shown by sample NiAlV-R when it is submitted to calcination at increasing temperatures is rather similar to that observed for sample NiAlV-E, although changes are observed generally at lower calcination temperatures; so, decavanadate exists only up to 150 °C, Figure 11. Calcination at 200 °C still keeps the layered structure (the (110) peak is still recorded at 1.51 Å), but basal spacings have been changed, only a broad, weak peak being observed at 3.65 Å that can be tentatively ascribed[26] to (009) reflexion of $[V_3O_9]$-intercalated LDH. Calcination at 300 °C destroys the layered structure (the 1.51 Å maximum is absent) and calcination at increasing temperatures again develops peaks due to NiO and $Ni_3V_2O_8$ and, to a minor extent, $Ni_2V_2O_7$, their crystallinity increasing upon calcination at 850°C.

According to the results here obtained, thermal stability of decavanadate species seems to be different in the bulk, when supported, or in the interlayer space of a LDH material. The decavanadate structure is maintained up to 450°C when supported on alumina.[36,37] When intercalated in Mg,Al LDH decomposition takes place even upon calcination at 100 °C.[30,34] For the nickel−aluminum-LDH intercalated solids here studied, stability seems to be also dependent on the way the sample has been obtained (ionic exchange or reconstruction); so, decomposition takes place upon calcination at 200°C for the exchanged material, but at 150 °C for the reconstructed one. According to Twu and Dutta,[34] such a behavior could be related to hydrolysis of decavanadate species by water molecules remaining in the interlayer space: with increasing water loss (DTA peaks for water removal were recorded at 203 and 152 °C for samples NiAlV-E and NiAlV-R, respectively) from the interlayers, the decavanadate ion, due to its high charge density, promotes polarization and hydrolysis of the remaining water molecules, resulting in the formation of hydroxyl groups and protons, the former favoring decomposition of decavanadate into lower charge density cyclic metavanadate species.

Changes occuring in samples NiAlV-E and NiAlV-R during calcination at increasing temperatures have been also followed by FT-IR spectroscopy, leading to conclusions similar to those above given from the PXRD study.

Transmission Electron Microscopy. Transmission electron micrographs for selected samples are shown in Figure 12. For parent sample NiAlCO3, Figure 12a, crystallites show an hexagonal shape, that change to compact aggregates when the sample is calcined in air at 300 °C, Figure 12b. The shape of

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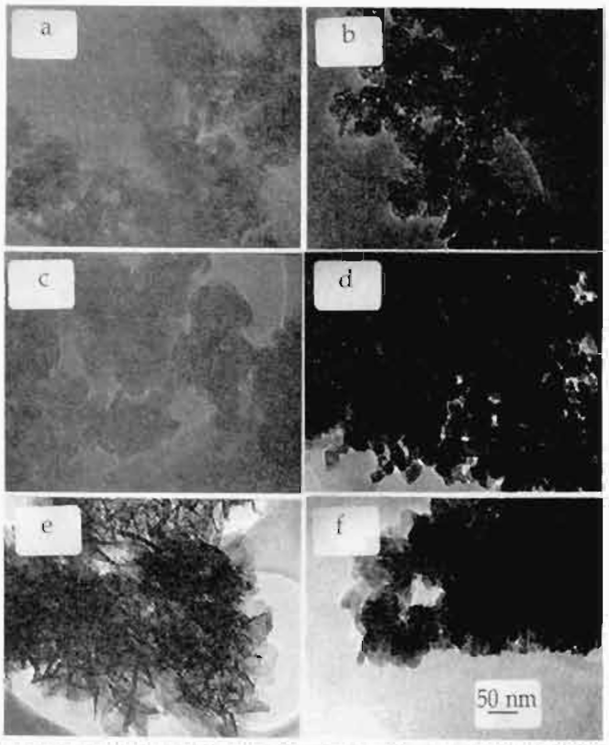

Figure 12. Transmission electron micrographs: (a) the parent NiAl-CO3; (b) sample NiAlCO3 calcined at 300 °C; (c) sample NiAlV-E; (d) sample NiAlV-E calcined at 700 °C; (e) sample NiAlV-R; (f) sample NiAlV-R calcined at 700 °C.

the original crystallites is not affected by anionic exchange, again leading to hexagonal-shaped crystallites for sample NiAlV-E, Figure 12c; calcination of this sample at 700 °C leads to a sintering of the crystallites, and square shaped crystallites are formed, Figure 12d.

After reconstruction with decavanadate, sample NiAlV-R in Figure 12e, the particles are different with respect to both size and morphology than for the starting material. The particles have now nodular appearance and are oblong with long dimension, the nodules being embedded on plate particles; the hydrothermal treatment results not only in an increase in particle size but also in a change in the particle shape. Calcination at 700 °C leads to a change in the morphology of the particles, all particles with nodular form have disappeared, and aggregates of transparent particles are observed.

Surface Area and Porosity. The nitrogen adsorption isotherm for sample NiAlV-E corresponds to type II in the IUPAC's classification, originated from adsorption on nonporous or mesoporous samples.[38] The specific surface area of this sample, as determined by the BET method, was 76 m^2/g, fairly similar to that measured for sample NiAlCO3, 86 m^2/g, suggesting that the pores in both materials originate primarily from inter-particle packing rather than from within the galleries; it is expected that if the pores were those arising from the gallery surface, the surface areas of nonpillared materials and pillared would be significantly different.[3]

When sample NiAlV-E was calcined at increasing temperatures, a steady decrease in the specific surface area was observed, Figure 13, that sharpens when the sample is calcined at ca. 500 °C, i.e., the temperature at which PXRD data indicated formation of new, crystalline Ni−V−O phases. Final surface area, when calcination is carried out at 600−700 °C, was ca. 10 m^2/g.

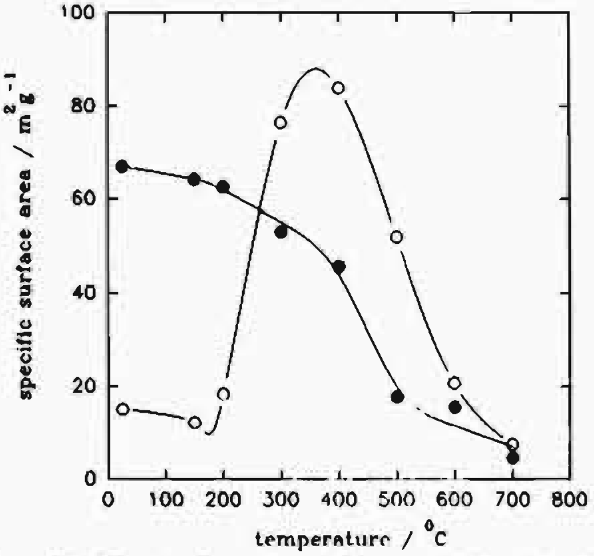

Figure 13. Change in the specific surface area with the calcination temperature for sample NiAlV-E (solid symbols) and NiAlV-R (open symbols).

The surface area of sample NiAlV-R is, however, much lower, and amounts only 14 m^2/g, less than one-tenth of the specific surface area for precursor NiAlCO3 calcined at 300 °C (160 m^2/g). It is evident that reconstruction of the precursor results in significant changes indicating the formation of new material. When the sample was calcined at increasing temperatures, an increase in the specific surface area was observed, reaching a maximum (ca. 90 m^2/g) upon calcination at ca. 400 °C, i.e., when PXRD data indicate formation of intermediate amorphous materials, before crystallization of new Ni−V−O phases.

Conclusions

Pillared hydrotalcite-like materials with decavanadate were attained at pH = 4.5 both by anionic exchange and by reconstruction of the mildy decomposed Ni−Al−O oxides. While by anionic exchange the nature of the interlayer, polymerized material does not depend on the pH during synthesis, a chainlike material was obtained at pH > 4.5 following the reconstruction method. Hydrothermal treatment of both series of samples led to an improvement in crystallinity. The interlayer space of the hydrotalcite-like material develops a reactive environment for the decavanadate moiety, specially for the samples prepared by reconstruction. However, the brucite-like layers are more stable than the original carbonate-containing nickel−aluminum material.

Calcination at increasing temperatures lead to formation of intermediate amorphous phases; the specific surface area increase with the calcination temperature (reconstructed samples), then decreasing upon calcination above 500 °C, while for the samples prepared by anionic exchange a steady decrease of the specific surface area as the calcination temperature increases is observed. At high temperature, ternary Ni−V−O materials are formed, with a sharp decrease in the specific surface area.

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