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Thermal Transformation of a Layered Double Hydroxide Pillared with Decavanadate Isopolyanions

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$V_{10}O_{28}^{6-}$ anions, intercalated by anion-exchange into the interlayer gallery of a Mg–Al layered double hydroxide, undergo chemical transformation and reduction in the valence state when subjected to thermal treatment. XRD and IR analyses indicate that $V_{10}O_{28}^{6-}$ breaks up into smaller species at 473 K, which then rearrange to form polymeric vanadate species of the type $[-VO_3-]_n^{n-}$ at 573—623 K. Concomitant with the disarrangement of the decavanadate anion, reduction of V(V) to V(IV) species takes place even when heat treated under air, as evidenced by ESR analysis. The number of V(IV) species increased steadily from 2.4×10^{18} to 2.2×10^{19} spin g^{-1} when the temperature of heat treatment rose from 393 to 473 K. Higher temperatures decreased gradually the number of V(IV).

Layered double hydroxides (LDHs) with hydrotalcite-like structure can be synthesized by coprecipitation of the metal salts.[1-3]

They are represented by the general formula

$$[M(II)_{1-x}M(III)_x(OH)_2][A^{n-}]_{x/n}\cdot yH_2O$$

where M(II) and M(III) are metal ions which occupy octahedral positions in the hydroxide layers, and A^{n-} is the gallery anion.

Recently, various attempts have been reported for increasing the interlayer distance by incorporating large anions in the gallery. Thus, the intercalation of iso- and heteropolyanions such as $Mo_7O_{24}^{6-}$, $V_{10}O_{28}^{6-}$, α-$SiW_{11}O_{39}^{8-}$, α-$H_2W_{12}O_{40}^{6-}$, and $SiV_3W_9O_{40}^{7-}$ has been carried out.[4-6] The interest on metalate-exchanged LDHs originates from their potential application to adsorption and catalysis. In fact, LDHs intercalated with $Mo_7O_{24}^{6-}$ and $V_{10}O_{28}^{6-}$ anions were tested as catalysts for the decomposition of 2-propanol and dehydrogenation of *p*-butylethylbenzene.[7] However, the exact state of the polyoxometalate pillars under the reaction conditions has not been clearly established. Twu and Dutta reported the thermal transformation of $V_{10}O_{28}^{6-}$ isopolyanions intercalated into a Mg–Al LDH (Mg/Al=3) by XRD and Raman spectroscopy.[8] However, they did not examine whether the valence state of the vanadium atoms changed in the course of the thermal treatment. Idemura et al. have reported that the host layer may strongly influence the electronic state of guest metal complexes.[9]

In order to obtain a better understanding on the state of the intercalated isopolyanions, we have prepared a Mg–Al LDH (Mg/Al=2) intercalated with $V_{10}O_{28}^{6-}$ anions with a view to examine not only the chemical transformation of the anions, but particularly to detect any possible variation in the valence state of the vanadium atoms caused by the thermal treatment of the LDH.

Experimental

Preparation of V10-LDH. A hydrotalcite clay containing NO_3^- as the interlayer anion (hereinafter called NO3-LDH) was synthesized by essentially following the method described by Miyata.[3]

To the aqueous solution containing $Mg(NO_3)_2\cdot6H_2O$ and $Al(NO_3)_3\cdot9H_2O$ (Mg/Al=2), the NaOH solution was added dropwise. The resulting white slurry was stirred at 348 K for 18 h. Thoroughly washing and drying at 393 K under vacuum yielded white glassy crystals. Deionized and decarbonated water was used througout all the experiments.

A 1.5 g portion of NO3-LDH thus obtained was suspended in 50 ml of water and the pH was adjusted to 4.5 by adding 2 M HNO_3 (1 M=1 mol dm^{-3}). Separately, 2.27 g of $NaVO_3$ was dissolved in 88 ml of water and the pH adjusted to 4.5 by adding 2 M HNO_3, since $V_{10}O_{28}^{6-}$ anion is stable at pH lower than 6.[10]

The orange solution containing $V_{10}O_{28}^{6-}$ was added dropwise to the NO3-LDH suspension at 313 K. Further addition of 2 M HNO_3 in order to mantain the pH 4.5 and vigorous stirring for 15 min yielded a deep orange solid. As pointed out elsewhere, a short time of ion-exchange does not cause any significant dissolution of Mg^{2+} away from the LDH layers.[4] The solid thus obtained was thoroughly washed with water and dried in the oven at 333 K for 12 h.

Characterization. X-Ray powder diffraction (XRD) analysis was carried out with a Rigaku Geigerflex apparatus using monochromatic Cu $K\alpha$ radiation, operating at 30 kV and 20 mA. Infrared (IR) spectra were recorded on a Shimadzu IR-460 spectrophotometer in an ambient atmosphere by the KBr method. The disks were prepared by pressing at 600 kg cm^{-2} for 1 min a 50 mg of KBr powder containing 1.5 wt% of a sample. Electron spin resonance was recorded on a conventional X-band spectrometer (JEOL JES RE-1X) with a TE_{102} mode microwave cavity. Absolute number of spins were determined by using DPPH in toluene as the standard. Thermogravimetric analysis was performed with a Shimadzu TGA-50 thermogravimetric analyzer. A constant heating rate of 5 K min^{-1} and an air flow rate of 10 cm^3 min^{-1} were used throughout the analyses. The specific surface area was determined by a nitrogen adsorption method using a conventional static adsorption apparatus.

Results and Discussion

Identification of the Intercalation Product. The anion-exchange of NO3-LDH by an aqueous solution of $NaVO_3$ at pH 4.5 proceeded smoothly to yield an orange product. The IR spectra of NO3-LDH and the anion-

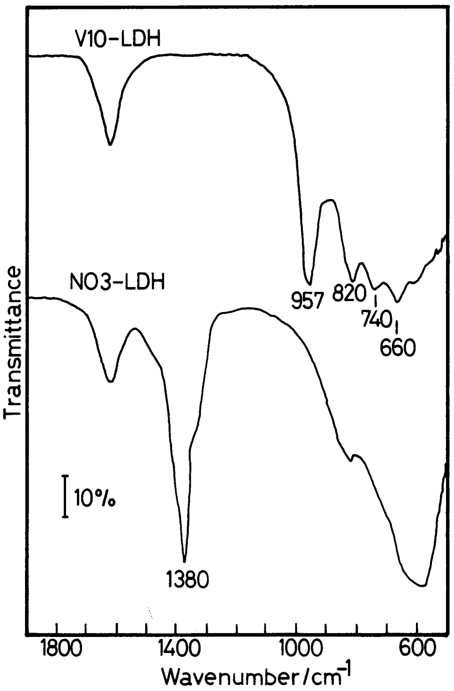

Fig. 1. IR spectra of NO3-LDH and V10-LDH.

exchanged product are shown in Fig. 1. The IR spectrum of NO3-LDH shows a strong band at 1380 cm^{-1}, characteristic of the ν_3 mode of NO_3^-,[11] and a broad band at 600 cm^{-1}. The peak at 1640 cm^{-1} is due to the presence of water.

Anion-exchange of NO3-LDH with a isopolyvanadate solution yielded a significantly different IR spectrum. The band at 1380 cm^{-1} due to NO_3^- ions was completely eliminated and new absorption bands appeared at 557, 598, 660, 740, 820, and 957 cm^{-1}. The complete absence of the band at 1380 cm^{-1} in the V10-LDH indicates that all the interstitial NO_3^- were exchanged by decavanadate anions. The new strong bands at 740, 820, and 957 cm^{-1} indicate the presence of decavanadate species in the LDH.[12] The presence of the band at 660 cm^{-1} (ν_{V-O-V} bridged) suggests that the exact species is $H_xV_{10}O_{28}^{6-x}$ (x=1—3) rather $V_{10}O_{28}^{6-}$ anions.[12]

The complete absence of NO_3^- in the V10-LDH indicates that decavanadates occupy all the interlayer space (33.3 wt. % V_2O_5), in agreement with reported results.[4]

Thermogravimetric Analysis and Surface Area Measurements. The TGA patterns of NO3-LDH and V10-LDH are shown in Fig. 2. Both NO3-LDH and V10-LDH lose most of physically adsorbed water below 470 K. Further weight loss occurs between 550 and 820 K. The second water loss in NO3-LDH agrees well with that expected from the dehydroxylation and expulsion of the interstitial NO_3^- anions, while the weight loss in V10-LDH corresponds to the dehydroxylation.

The surface area of NO3-LDH dried at 423 K for 4 h was 27 m^2 g^{-1}, and the intercalation product, V10-LDH, dried under the same conditions had the surface area of 64 m^2 g^{-1}. Heating V10-LDH at 773 K resulted in a slight increase in the surface area (69 m^2 g^{-1}).

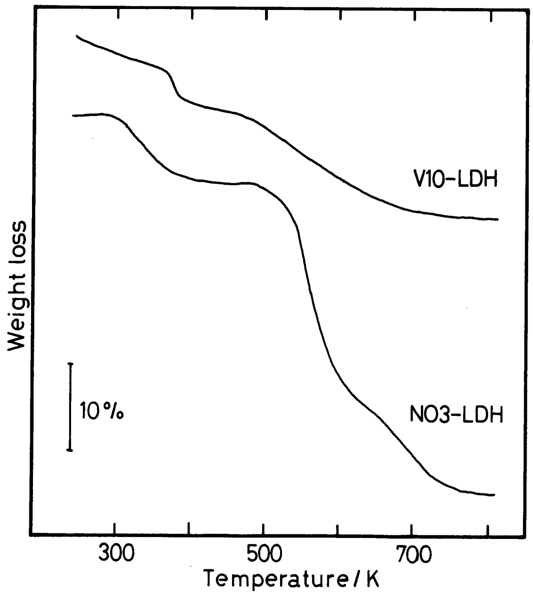

Fig. 2. TGA weight loss patterns of NO3-LDH and V10-LDH.

XRD Analysis. The change in the XRD pattern of V10-LDH upon heating at various temperatures for 2 h is shown in Fig. 3. The sample dried at 333 K shows an XRD pattern typical of a layered material with three harmonics, d_{003}, d_{006}, and d_{009}, shifted to lower angles in comparison with the corresponding peaks of the precursory NO3-LDH. The basal spacing of the material determined from the angle for d_{006} line is 1.21 nm. Since the thickness of the brucite layer is 0.48 nm,[1] the interlayer spacing occupied by the $V_{10}O_{28}^{6-}$ anions is 0.73 nm. This indicates that the $V_{10}O_{28}^{6-}$ ions are accomodated with the C_2 axis perpendicular to the brucite layers. Drying at 393 K did not yield any significant change in the XRD pattern.

When the sample was heated at 473 K, the d_{006} line, which is the sharpest of the three harmonics in V10-LDH, shifted to higher angle. The interlayer spacing at this stage is 0.43 nm, indicating the formation of a new phase by the decomposition of $V_{10}O_{28}^{6-}$ anions. By this treatment, the sample lost its initial orange color and turned brown suggesting some chemical transformation occurring to the decavanadate anions.

A new phase developed by heating the sample at 573 K. A gradual loss in the crystallinity of the sample was recognized after it was heated at 623 and 673 K, indicating the dehydroxylation of the brucite layers.

Heating the V10-LDH at 673—773 K resulted in the appearance of a new broad line at 43.5° which can be assigned to a magnesium–aluminium solid solution,[13] and several weak peaks between 27 and 34°. Calcination at 873 K resulted in the formation of a crystalline

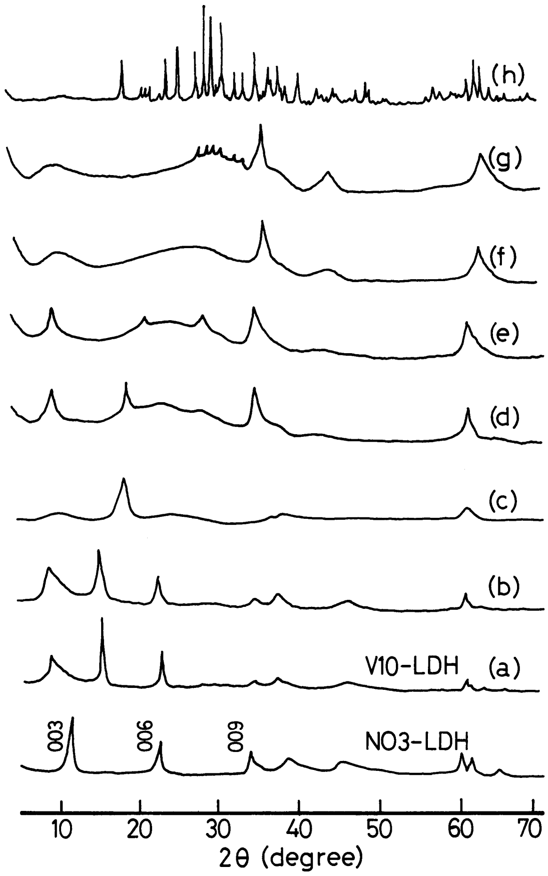

Fig. 3. XRD patterns of NO3-LDH and V10-LDH heat treated in air at: a) 333 K, b) 393 K, c) 473 K, d) 573 K, e) 623 K, f) 673 K, g) 773 K, and h) 873 K.

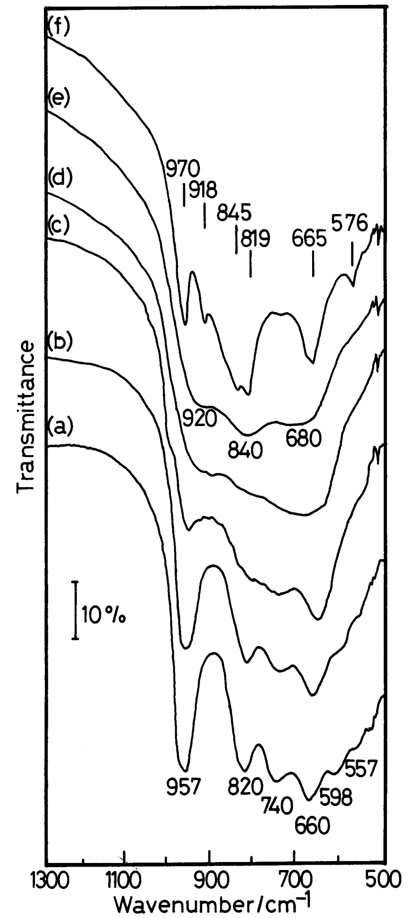

Fig. 4. Effect of thermal treatment on the IR spectra of V10-LDH. a) 333 K, b) 393 K, c) 473 K, d) 573 K, e) 673 K, and f) 873 K.

material with sharp peaks, which match the XRD pattern of α-$Mg_2V_2O_7$.[14] This shows that the reaction between the vanadate species and the Mg–Al-oxide occurs in the temperature range of 773—873 K.

Similar XRD study has been reported for a LDH with Mg/Al=3 intercalated with $V_{10}O_{28}^{6-}$ anions.[8]

Infrared Absorption Spectroscopy. The X-ray analysis shows that V10-LDH undergoes a series of transformations upon thermal treatment above 473 K. Infrared spectroscopy was used in order to identify changes in the chemical structure of the intercalated isopolyvanadates upon thermal treatment. Figure 4 shows the infrared spectra of V10-LDH in the range of 500—1300 cm^{-1}. The samples were heated at the indicated temperature for 2 h prior to the preparation of the KBr disk. As described earlier, the spectrum of the sample heated at 333 K shows strong bands at 557, 598, 660, 740, 820, and 957 cm^{-1}, indicative of the presence of decavanadate ions. The spectrum of the sample heated at 393 K is essentially identical to that of the sample dried at 333 K.

When the sample was heated at 473 K, the bands due to the vanadate ions decreased considerably. The spectrum of the sample heated at 573 K showed no evidence of the decavanadate ions, indicating that the decavanadate ions are transformed to another vanadate species. However, the broadness of the bands impedes the identification of the newly formed species. When the sample was heated at 673 K, four bands appeared at 550, 680, 840, and 920 cm^{-1} in the spectrum. Metavanadates of the type MVO_3 (M=K, Rb, Cs, and NH_4) in which VO_3 groups link to constitute long chains, give infrared bands at 850—863, and 920—935 cm^{-1} for terminal V=O stretching and 475—495 and 685—693 cm^{-1} for V–O stretching in bridging V–O–V bonds.[15] A comparison of the new vibrational bands with the bands arising from the metavanadates indicate that newly formed vanadate species are polymeric vanadate chains, $(-VO_3-)_n^{n-}$.

Calcination at 873 K yielded distinct bands with 576, 665, 680, 819, 845, 918, and 970 cm^{-1}. These bands are in agreement with those found for α-$Mg_2V_2O_7$,[14] and confirm the conclusion deduced from X-ray diffraction analysis.

Electron Spin Resonance. A recent study of LDH materials intercalated with iron complexes indicates that the host layer may exert a strong influence on the electronic state of the metal complexes.[9] These results

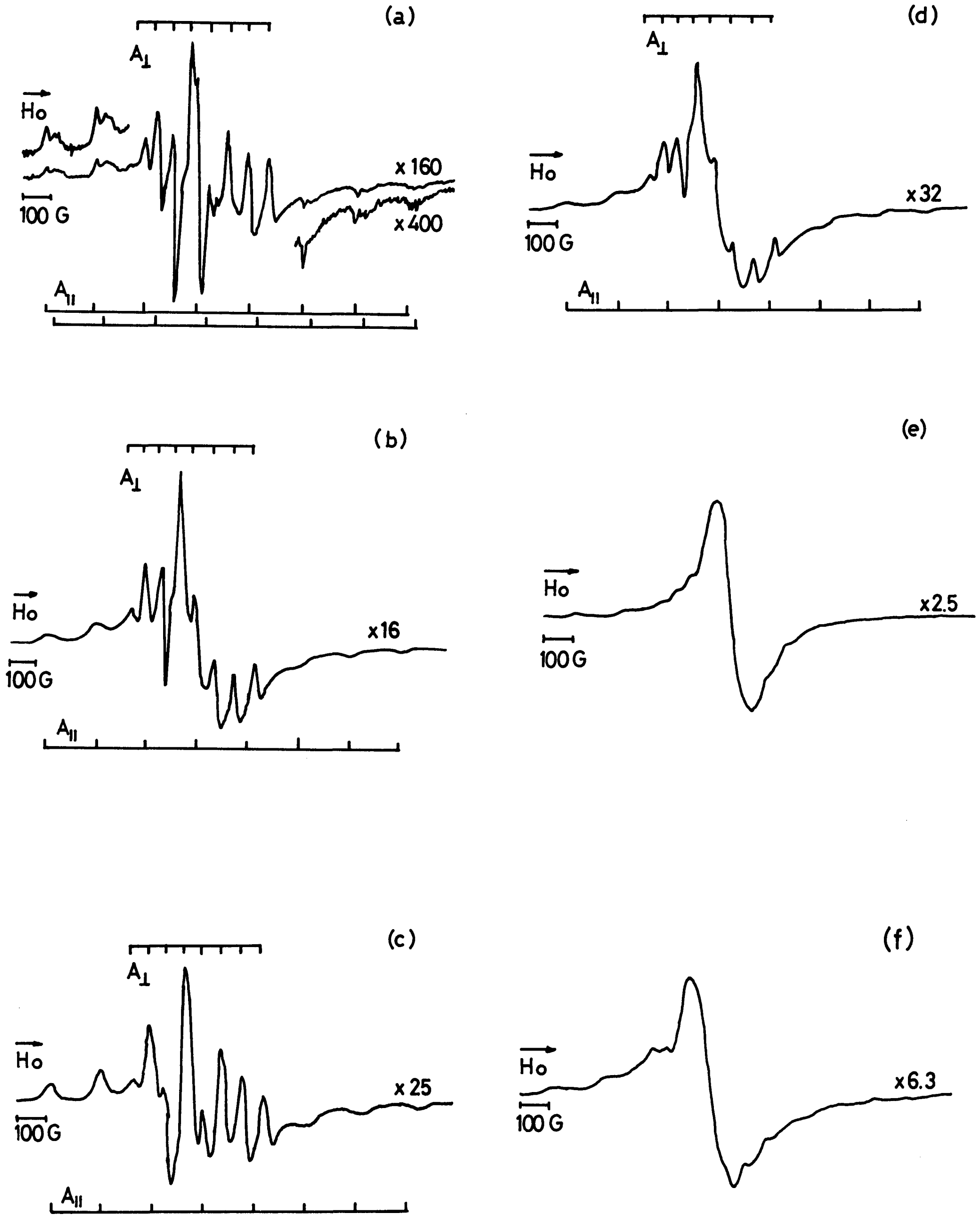

Fig. 5. ESR spectra of V10-LDH heat treated in air at: a) 393 K, b) 473 K, c) 573 K, and under vacuum at d) 393 K, e) 473 K, and f) 573 K.

prompted us to undertake an ESR study on the V10-LDH in order to examine the effect of the thermal treatment on the valence and coordination state of the interlayer vanadate species.

The ESR spectra of the V10-LDH treated at various temperatures in air were measured at room temperature and are shown in Fig. 5 (a), (b), and (c). The spectra measured at liquid nitrogen temperature gave essentially same line shapes. The *g*-values and hyperfine splitting constants are listed in Table 1, and the number of spins after heat treatment are shown in Fig. 6.

The ESR-analysis of V10-LDH dried in air at 333 K indicated no ESR-signal at all. In other words, V(IV) species were completely absent from the as-prepared V10-LDH.

The spectrum of the sample dried at 393 K consists of well resolved lines, which can be assigned to two different V(IV) species. The hyperfine splitting shows that each unpaired electron is interacting with a single vanadium, which is in the tetragonal or square-pyramidal environment. This is supported by the indifference of the line shape to the temperature of measurement. The estimated amount of spins was about 2.4×10^{18} spin g^{-1}, which corresponds to 0.1% of the total vanadium atoms in the interlayers.

The ESR spectrum of V10-LDH heated at 473 K gives a more simple spectrum, which can be assigned to a single V(IV) species on the tetragonal or square-pyramidal

Table 1. Spin Hamiltonian Parameters of V(IV) Formed in V10-LDH (Mg/Al=2) at Various Calcination Temperatures

Temperature K	$g_\perp$	$g_\parallel$	$A_\perp\times10^4$ cm^{-1}	$A_\parallel\times10^4$ cm^{-1}	Δg
393[a)]	—	1.954	—	156	—
	1.982	1.928	55	151	0.05
473	1.986	1.930	53	152	0.06
573	1.983	1.931	63	156	0.05
673	1.980	1.934	65	159	0.05
773	1.986	1.937	68	151	0.05

V10-LDH was calcined in a static atmosphere for 2 h at a given temperature. ESR analyses were carried out at room temperature. a) Two V(IV) species were detected.

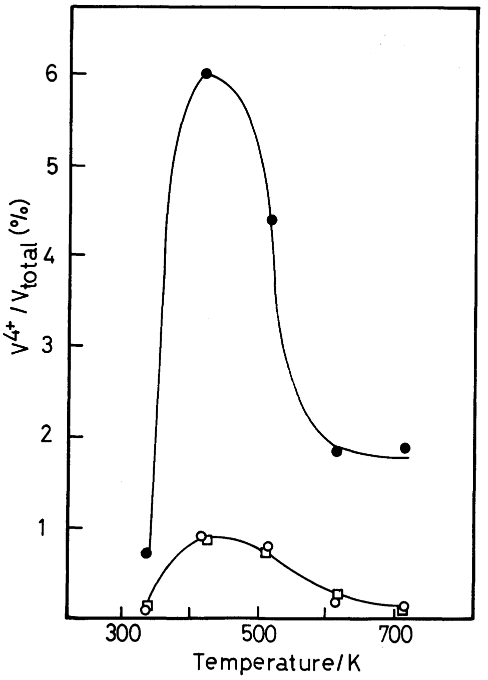

Fig. 6. Effect of heat treatment temperature on the amount of V(IV) species formed in V10-LDH. (●) V10-LDH (Mg/Al=2) heat treated under vacuum. (□), (○) V10-LDH (Mg/Al=2, 3) heat treated in air.

environment. The number of spins in the sample was larger than that in the sample dried at 393 K and about 0.9% of the total vanadium.

By calcining V10-LDH at 573—773 K, the intensity of the signal decreased, indicating that a part of V(IV) species is converted into V(V) species, which are ESR insensitive.

The ESR spectra of the V10-LDH heated at various temperatures under vacuum were also measured and shown in Fig. 5 (d), (e), and (f). The ESR spectrum of the sample evacuated at 393 K has the hyperfine structure characteristic of V(IV) species. The number of spins corresponds to 0.7% of the total vanadium atoms. This is about 7 times greater compared with that of the sample dried in air at the same temperature.

When the sample was evacuated at 473 K, the ESR spectrum changed to a single broad line with increased intensity. The number of spins is about 6% of the total vanadium atoms. The change in the line shape may be caused by the dipolar interactions between the spins due to the increased number of spins.

Figure 6 shows the effect of the heating temperature on the amount of V(IV). It is clear from this figure that the formation of V(IV) species, in a sample heat treated in air or in vacuum, occurs at 393—473 K. Though reduction of V(V) to V(IV) species does not occur to a great extent (6% in the evacuated sample at 473 K), it occurs at relatively low temperatures (<473 K). Further increase of the evacuation temperature to 573—773 K decreased the intensity of the signal, indicating that the V(IV) species are converted into ESR insensitive species such as V(V).

A sample evacuated at 473 K was exposed to 40 kPa of oxygen at room temperature or at 473 K for 1 h. This oxidative treatment gave no influence on the spectrum. The ESR spectrum of the sample evacuated at 473 K did not change either by exposing the sample to 27 kPa of hydrogen. This is probably because of the impossibility of small molecules to access the interlayer space due to very close adjacent isopolyanions.[4)]

General Discussion

The XRD and IR studies have revealed that the $H_xV_{10}O_{28}^{6-x}$ anions are easily intercalated in the gallery of the interlayers of the double layered hydroxide. The isopolyanions remain unchanged up to 393 K, when heated. At 473 K the interlayer spacing of the material diminishes considerably indicating that the isopolyanions decompose to smaller species at this temperature. This is also supported by the almost complete disappearance of the absorption bands characteristic of the isopolyanions in the IR spectrum. Twn and Dutta[8)] suggest the formation of $V_3O_9^{3-}$ species from Raman spectroscopy by treating the hydrotalcite containing $V_{10}O_{28}^{6-}$ ions at 433—553 K. However, positive evidence for $V_3O_9^{3-}$ species was not obtained from the IR spectra.

The calcination at 573—623 K leads to the formation of polymeric vanadate species of the type $[-VO_3-]_n^{n-}$. The layered structure still maintained, though the brucite layers are completely dehydroxylated.

At 673—723 K, the original brucite layers are turned into a magnesium–aluminium solid solution with MgO structure. The chemical reaction between the interlayer vanadate and the host oxide takes place around 873 K, resulting in the formation of crystalline α-$Mg_2V_2O_7$.

ESR spectroscopy revealed that a part of the pentavalent vanadium is reduced to tetravalent vanadium, even in air, during the thermal treatment of V10-LDH. The formation of V(IV) species takes place between 393 and 473 K. Since the decomposition of the $V_{10}O_{28}$ species occurs in this temperature range, the reduction of V(V) to V(IV) seems related to this chemical transformation of the isopolyanions. The maximum concentration of V(IV) species was observed by heating the V10-LDH at 473 K under vacuum and corresponds to 6% of the total vanadium in the V10-LDH.

This work clearly demonstrated that, though the intercalation of the isopolyanions into layered double hydroxides is a rather facile process, the anions are not very stable towards thermal treatment and easily transform to other chemical species. Thermal treatment causes also, as clearly indicated in this work, reduction in the electronic state of the intercalated metal species. Therefore, careful consideration is required on the real chemical and physical structure of the interstitial species for discussing adsorptive and catalytic properties of the materials.

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