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A Kinetic Study of the Effect of Water on the Nitrogen-Fixing Ability of the $Mg(OH)_2$–$V(OH)_2$ System

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Abstract—An increase in the limiting oxidation number of V^{2+} ions in the presence of nitrogen in the $Mg(OH)_2$–$V(OH)_2$ system was found. This phenomenon was interpreted from the standpoint of the existence of a critical size of vanadium clusters in an ion layer of the mixed hydroxide. The attainment of this critical size is necessary for the reduction of N_2 and the release of H_2. This hypothesis also explains the specific activity of the system as an extremal function of the concentration of vanadium(II) at a constant Mg : V ratio. The effect of solvent (methanol–water) composition on the rate of nitrogen reduction supports the idea that the concentration of free water in the system plays a decisive role in this process. An increase in the intensity of H/D exchange in the presence of nitrogen, which is similar to that observed in biological systems, was found.

INTRODUCTION

The magnesium–vanadium hydroxide system is one of the best studied systems used for the reduction of molecular nitrogen in protic media under mild conditions [1]. A study of the effects of various parameters on the rate of nitrogen reduction demonstrated that the structure of active centers in this system exhibits some special features. The coprecipitation of Mg^{2+} and V^{2+} ions by an excess of an alkali is required for the formation of a system highly active toward nitrogen (reaction rate constant $k \sim 10^6$ l mol^{-1} s^{-1} [1]). The magnesium ions affect the occurrence of all conceivable reactions. These facts indicate that in this case a double hydroxide is formed (rather than a mechanical mixture of hydroxides), which exhibits almost no activity in the reduction of nitrogen[1]. The appearance of an orange color at the instant of mixing solutions of the reactants at $[Mg^{2+}] \gg [V^{2+}]$ is indicative of the formation of double hydroxide. The life span of this color increased with an excess of magnesium ions, and the color was retained at reduced temperatures (~270 K) for ~1 min. This color is not due to individual hydroxides because $Mg(OH)_2$ is white and $V(OH)_2$ is black. It is reasonable to suggest that this color results from the initial formation of a metastable mixed hydroxide phase, in which vanadium ions are statistically distributed and that these ions primarily occur as mononuclear species. Data on the magnetic susceptibility of the freshly precipitated hydroxide support this idea: as the Mg : V ratio was increased up to 50, the magnetic moment μ approached the Bohr magneton value 3.8, which is close to the magnetic moment of $V(OH)_2$ [4]. It is likely that, even in a considerable excess of magnesium ions, the initial mixed hydroxide is thermodynamically unstable and can decompose to $Mg(OH)_2$ and $V(OH)_2$ phases. The diffusion mobility of ions is responsible for the phase separation; however, aging processes, which result in the formation of fragments of three-dimensional crystal lattices, terminate the decomposition at the stage of the formation of $[V(OH)_2]_n$ clusters incorporated into the lattice of $Mg(OH)_2$. Evidently, the value of n depends on the ratio between the ions and on other conditions of precipitation.

Studies performed by electron microscopy and electron diffraction demonstrated that even 30 s after precipitation magnesium hydroxide developed a crystal structure; however, in the presence of only 10 mol % V^{2+}, it remained amorphous to X-rays for 3 min. Thus, the addition of vanadium ions prevents $Mg(OH)_2$ microcrystals from growing to >40 Å. The association of vanadium ions in primary hydroxide globules is also indicative of a deceleration in the structural ordering of $Mg(OH)_2$.

Like a number of bivalent metal hydroxides, crystalline magnesium hydroxide contains a hexagonal close-packed lattice of OH^- ions ($a = 3.116$ Å; $c = 4.78$ Å), and metal cations are arranged in the octahedral cavities of the lattice. It is believed that the main structural unit of the double magnesium and vanadium hydroxide is a fragment of the cation layer of magnesium ions with a linear dimension of 15–20 Å with incorporated vanadium ions; the vanadium ions tend to accumulate in separate layers of the double hydroxide. The association of vanadium ions was complete in 1 to 2 min at 293 K, as follows from experimental data on the reduc-

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[1] It is well known that under similar conditions magnesium ions form substitutional solid solutions with Ni^{2+} and Co^{2+} ions [2, 3], whose ionic radii, as well as the ionic radius of V^{2+}, are close to the ionic radius of magnesium (r = 0.74, 0.78, 0.74, and 0.72 Å for Mg^{2+}, Co^{2+}, Ni^{2+}, and V^{2+}, respectively).

tion of nitrogen to hydrazine on varying the time of nitrogen admission to the system after its formation [5].

The following data are indicative of the progressive increase in the average size of the hydroxo clusters of V(II) with time: only the two-electron reactions $N_2H_4 \longrightarrow 2NH_3$ and $C_2H_2 \longrightarrow C_2H_4$ occur immediately at a high Mg : V ionic ratio, whereas the occurrence of an induction period is typical of the four-electron processes $N_2 \longrightarrow N_2H_4$ and $C_2H_2 \longrightarrow C_2H_6$ [6]; an active vanadium center with $n \geq 4$ is formed during this induction period. Thus, it is reasonable to suppose that initially formed magnesium–vanadium hydroxo polymers, in which metal atoms are joined by bridging OH groups, undergo conversion into disordered microcrystalline particles of magnesium hydroxide in the subsequent processes of aging. In these particles, separate groups of Mg^{2+} ions in the cationic layers are replaced by vanadium(II) ions. The size of these clusters primarily depends on the initial ratio between the metal ions and on the initial concentration of vanadium ions.

A very interesting special feature of the magnesium–vanadium system is the weak effect of methanol additives on this system. This feature, which remains unexplained, differentiates the above system from other nitrogen-fixing systems. Whereas the addition of methanol to all of the systems studied previously increased their activity by a factor of 5–10, the yield of products in the magnesium–vanadium system increased by only ~20–30% as compared with the yield in a purely aqueous medium [7]. Studies of the effect of water on the rate of hydrazine formation in protium and deuterium solvents were favorable for an understanding of the mechanism of the action of molybdenum nitrogen-fixing systems [8], $Cr(OH)_2$ [9], and $Nb(OH)_3$ [10].

This work, which is a continuation of these studies, was devoted to the effect of water concentration in alkaline water–methanol solutions on the rates of formation of hydrazine and hydrogen and to the H/D exchange in the $Mg(OH)_2$–$V(OH)_2$ system.

EXPERIMENTAL

The reduction of nitrogen was performed in a two-chamber glass vessel placed in an autoclave according to the previously published procedure [11]. The autoclave was thoroughly purged with nitrogen, a pressure of 40.5×10^5 Pa was adjusted, and the autoclave was cooled to 284 K. Thereafter, the water–methanol solutions of $MgCl_2$–VCl_2 and KOH were mixed. The reaction was performed with vigorous shaking. The reaction rate was determined by the yield of reaction products in 1 min because under these conditions the kinetic curves of product formation were linear [5]. The solutions had the following concentrations: $[VC1_2] = 1.5 \times 10^{-2}$, $[MgC1_2] = 7.5 \times 10^{-2}$, and [KOH] = 4 mol/l.

The total amount of oxidized vanadium(II) (V_Σ) was determined by titration with ammonium vanadate in an argon atmosphere in the presence of phenylanthranilic acid. The amount of vanadium(II) that took part in the reduction of nitrogen (V_{N_2}) was calculated from the total reaction products (hydrazine and ammonia), taking into account stoichiometric coefficients. The amount of vanadium(II) that took part in the formation of hydrogen was found by the difference V_Σ–V_{N_2}. Hydrazine was determined by photocolorimetry using the reaction with *para*-dimethylaminobenzaldehyde, and ammonia was determined by the indophenol method [11].

Deuterium exchange was performed in a two-chamber Rittenberg vessel; degassed components of the reaction mixture were introduced into the chambers. The degree of exchange was evaluated by the mass-spectrometric analysis of a gas phase. The background HD concentration in the initial D_2 was 0.37 ± 0.01%, and the results of deuterium exchange are given below with consideration for this value. The experimental conditions were as follows: temperature of 313 K, reaction time of 15 min, $[V^{2+}] = 1.5 \times 10^{-2}$ mol/l, [KOH] = 4 mol/l, $[H_2O] = 40$ mol/l, $Mg^{2+} : V^{2+} = 20$, and $P_{D_2} = 0.4 \times 10^5$ Pa.

RESULTS AND DISCUSSION

All nitrogen-fixing hydroxide systems are almost completely inactive in the absence of water. As water was added, the activity increased and reached a maximum value at a certain concentration of water. The effect of water concentration in alkaline water–methanol solutions in the range of 17 to 55 mol/l on the initial rate of hydrazine formation in the magnesium–vanadium system was studied in detail. This study demonstrated that maximum activity was attained only at $[H_2O] = 45$–48 mol/l and this maximum was preceded by a plateau at $[H_2O] = 25$–40 mol/l (Fig. 1).

According to our ideas [8–10], the rate of nitrogen reduction significantly depends on the concentration of free water in the system, that is, water unincorporated into the tightly bound solvate shells of cations and anions. According to published data, the numbers of water molecules in the strong solvate shells of K^+ and OH^- ions are equal to 4 and 3, respectively. Consequently, a deficiency in free water appears when the total water content of the CH_3OH–H_2O–KOH system is less than 7[KOH]. The role of this circumstance is illustrated in Fig. 1, which compares the nitrogen-fixing activities of various hydroxide systems as functions of water content. Although concentrations of the alkali in these systems differ by a factor of eight, the total concentrations of water in these systems at the maximums are close to each other and deviate from the values of 7[KOH] (the corresponding positions are indicated by arrows in Fig. 1) by a factor of no more than 1.6. Moreover, the shapes of activity curves at $[H_2O] > [H_2O]_{max}$ are approximately identical for all of the systems. Thus,

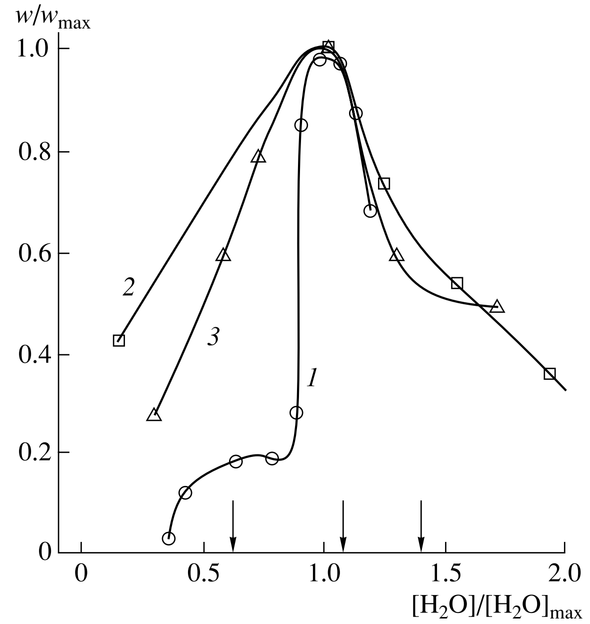


Fig. 1. Relative rates of nitrogen reduction to hydrazine as functions of relative water contents of hydroxide systems: (*1*) Mg(II)–V(II), [KOH] = 4 mol/l, 284 K; (*2*) Mg(II)–Ti(III)–Mo(III), [KOH] = 0.5 mol/l, 293 K; (*3*) Nb(III), [KOH] = 1 mol/l, 288 K [10]. Arrows indicate the positions that correspond to the concentrations [KOH] × 7 in different systems.

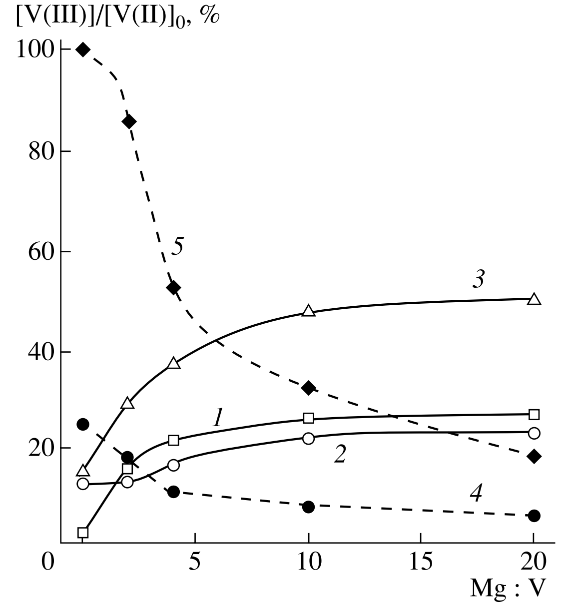


Fig. 2. Characteristics of reactions occurring in the $Mg(OH)_2$–$V(OH)_2$ system as functions of the Mg : V ratio: (*1*) fraction of V(II) consumed in nitrogen reduction for 10 min, (*2*) fraction of V(II) consumed in hydrogen liberation for 10 min, (*3*) degree of overall reaction in the presence of nitrogen for 10 min, (*4*) degree of overall reaction in the absence of nitrogen for 10 min, and (*5*) the same for 24 h [14].

it is best to evaluate the nitrogen-fixing activity of aqueous and water–alcohol systems at water concentrations from $[H_2O]_{max}$ to 55 mol/l, that is, on going from a water–alcohol medium with a maximum activity to a purely aqueous medium. The wider the range between $[H_2O]_{max}$ and 55 mol/l, the more dramatically the activities differ.

A shift of the activity maximum of the magnesium–vanadium system to higher water concentrations in comparison with other systems results from the higher alkali concentration in this system (higher by a factor of 5–8 than that in the Mo-containing system) [7]. At the same time, the region of low concentrations of free water ($[H_2O] < [H_2O]_{max}$), in which a sufficient number of alcohol molecules are replaced by H_2O in a reaction center, is strongly extended in the case of the magnesium–vanadium system. In other systems, the activity increases within a very narrow range of water concentrations, so that this phenomenon practically cannot be studied experimentally.

The process of hydrogen liberation competes with the reaction of nitrogen reduction. This process can be represented schematically as follows:

$$2V^{2+} + 2H_2O \longrightarrow 2V^{3+} + H_2 + 2OH^-.$$

In this study, we found that, at [V(II)] = const, magnesium ions exert different effects on the degrees of nitrogen reduction and hydrogen liberation, which were evaluated by the amounts of consumed V(II). It can be seen in Fig. 2 that, as the Mg : V ratio increased from 0 to 20, the fraction of the reductant oxidized in the reaction with nitrogen increased by a factor of 11, whereas that in the parallel reaction of hydrogen liberation increased by a factor of only two. A comparison of these results with analogous data that a change in the Mg : V ratio from 0 to 20 in the oxidation of V(II) in an Ar atmosphere [4] decreased the degree of reaction of H_2 liberation from 100 to 18% is indicative of the opposite effects of magnesium ions on the degrees of both reactions under consideration.

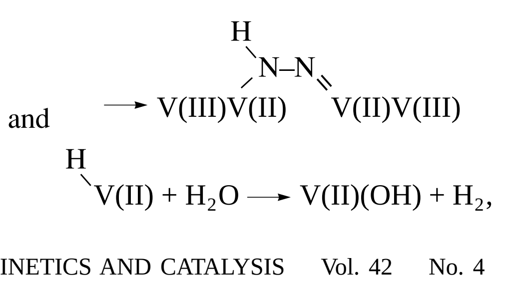
In this case, as follows from Fig. 2, magnesium–vanadium hydroxide of the same composition (Mg : V > 1) can consume more electrons in the simultaneous reduction of nitrogen and water for 10 min than in the reduction of only water. The shape of curve *5* in Fig. 2, which corresponds to the liberation of hydrogen in 24 h in the absence of nitrogen, suggests that the inactive V(II) ions accumulated in the system as the Mg : V ratio increased. If only single V(II) ions, which lack the required amount of electrons, in the lattice of magnesium hydroxide belonged to these inactive ions, the degree of reaction in the presence of two substrates (water and nitrogen) could not be higher than that in the presence of only water. Thus, we believe that only vanadium clusters, the number of metal atoms in which is at least as great as a critical value of n_0, can reduce both of the substrates. Then, taking into account the stoichiometry of hydrazine and hydrogen formation, which require 4 and 2 equiv of a reducing agent, respectively, we may expect that active centers will lose more electrons in the combined reduction than in the reduction of only water to hydrogen. If these centers are predominant in the system, the degree of reaction can increase because a four-electron process is added to a two-electron reduction process.

On the one hand, the hypothesis of the existence of a critical cluster size is consistent with an increase in the reduction potential of the system as the number of atoms in a cluster increases [13]. On the other hand, this hypothesis makes it possible to use the hydride mechanism of nitrogen reduction and hydrogen liberation, which was proposed for other hydroxide systems [8–10]. It is reasonable to suppose that the formation of a hydride intermediate

$$[LV_n(H_2O)]^m \longrightarrow [LV_nH]^{m-1} + OH^-,$$

which is the same for the reactions of nitrogen reduction and hydrogen liberation, is thermodynamically possible only after the clusters reach a certain size. This is supported by data on isotope exchange. The formation of 0.28% HD was detected when the reaction of hydrogen liberation was performed in a protium solvent in the presence of D_2 (0.4 atm). After the addition of 0.56 atm nitrogen under the same conditions, 2.36% HD was formed. Such an increase in the yield of HD in the presence of nitrogen in other hydroxide systems was not detected previously in analogous experiments.

It is likely that the anticymbatic effects of the concentration of magnesium ions on the degrees of nitrogen reduction and hydrogen liberation reactions can be associated with a number of causes. On the one hand, the concentration of water in the system is high, as compared with the concentration of nitrogen. Therefore, the hydrogen liberation reaction occurs at a higher rate, all other factors being the same, because of a low concentration of active centers and diffusion limitations. With the incorporation of magnesium ions into the nitrogen-fixing active centers, they can exert a combined electrophilic effect, for example, because of the direct interaction between the N atom and Mg^{2+} (complexes of this kind are known [15]). Evidently, this electrophilic effect of magnesium ions facilitates hydride-ion transfer to the coordinated nitrogen molecule. Because of this, the ratio between the times of reactions of an active hydride complex via the two routes



$$\overset{H}{\diagdown}V(III)V(III) + N{\equiv}N \longrightarrow V(III)V(III)\overset{H}{\diagdown}N{-}N{=}V(II)V(III)$$

$$\text{and}\quad \overset{H}{\diagdown}V(II) + H_2O \longrightarrow V(II)(OH) + H_2,$$

can be changed significantly. Indeed, the latter reaction of hydride-ion transfer to the solvent proton is responsible for the formation of ions in the system and, hence, for an increase in the energy of rearrangement of the medium, as compared to the energy of intramolecular hydride-ion transfer.

For theoretical modeling, let us consider a simpler case when the total concentration of metals is changed at a fixed ratio between magnesium and vanadium ions. It can be seen in Fig. 3 that this results in a nonlinear relationship between the activity of the system and the V(II) content. The absolute concentration of V(II) affects the nitrogen-fixing ability of the magnesium–vanadium system because the size-distribution function of vanadium(II) clusters in the cationic layer of the magnesium hydroxide lattice is changed. Under conditions of rapid hydrolysis of magnesium and vanadium salts by the action of an excess of an alkali, a single amorphous $V(OH)_2$–$Mg(OH)_2$ phase is formed, although it is thermodynamically unstable. This circumstance makes the V–V ion association more favorable than the Mg–V ion association, which, in turn, depends on the ratio between the ions in the system. Therefore, clusters containing no less than four vanadium(II) atoms are formed in a sufficient amount even at a great excess of magnesium ions. This is evident from a relatively high yield of hydrazine (at a purely statistical distribution, the fraction of these clusters would be $1/X^4$, where X = Mg : V, i.e., negligible). In this case, an amount of nonreactive single vanadium(II) ions is present in an amorphous lattice. This is evident from a decrease in the limiting yield of hydrogen as the $Mg^{2+} : V^2$ ratio increased.

We use a universal distribution function for quantitatively describing the size distribution of clusters. A study of the growth of associates in terms of the model of diffusion-limited aggregation of particles [16] demonstrated that the size distribution of associates at different times could be adequately described by the universal function

$$x_n = \frac{1}{\langle n \rangle^2} f\left(\frac{n}{\langle n \rangle}\right),$$

where $\langle n \rangle = \Sigma n x_n(t)/\Sigma x_n(t)$ is the average associate size at time t.

Function f can be approximated by the expression $f(y) = 1.9846y^{1.2105}\exp[-(0.9419y)^2]$. In this approximation, the size distribution of vanadium clusters depends on the sole parameter $\langle n \rangle$, which depends on the concentration of vanadium.

In the consideration of the nitrogen-fixing activity of the system, it should also be taken into account that vanadium clusters become capable of reducing molecular nitrogen to hydrazine only starting from a critical size of $n_0 \geq 4$. Thus, an extremal character of the experimental dependence of specific activity on the Mg : V ratio can be explained naturally because the fraction of clusters with $n > n_0$ is small at a low concentration of

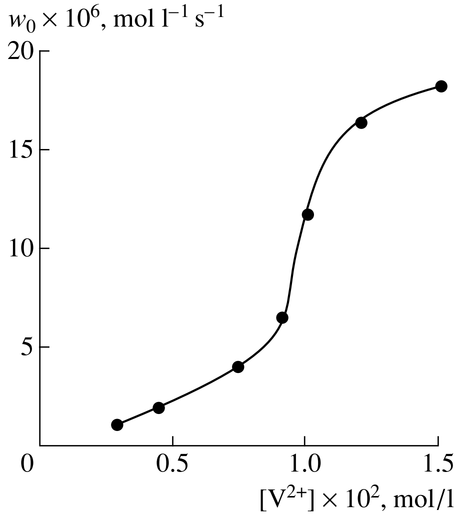


Fig. 3. Initial rate of nitrogen reduction to hydrazine as a function of vanadium concentration under the following conditions: Mg : V = 20, [KOH] = 5 mol/l, temperature of 293 K, and 20% CH_3OH [14].

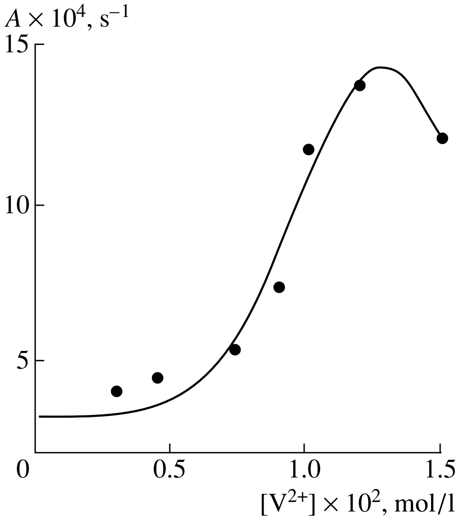


Fig. 4. Specific activity (*A*) of the $Mg(OH)_2$–$V(OH)_2$ system in the reaction of nitrogen reduction as a function of vanadium concentration. Points indicate the experimental data, and the curve represents the calculated data.

vanadium(II), whereas the total number of clusters begins to decrease at a high vanadium concentration when $n > n_0$ for the majority of clusters. Thus, the initial rate of reaction can be described by the expression

$$w_0 = n \sum_{n \geq n_0} \frac{k_0}{\langle n(C) \rangle^2} f\left(\frac{n}{\langle n(C) \rangle}\right)^2,$$

where $C = [V]$, k_0 is a constant, and the activities of all clusters with $n \geq n_0$ are taken to be equal for simplicity. We describe the initial dependence of $\langle n(C) \rangle$ on the concentration of vanadium by the simplest two-parameter function $\langle n(0) \rangle / n_0 = a + bC^\rho$, where $\rho = 4$, as demonstrated by analysis. With consideration for all experimental data, an optimization of constants a and b at $n_0 = 4$ gave the values $a = 0.544$ and $b = 0.283 \times 10^{-8}$ l^4/mol^4. Figure 4 compares the calculated and experimental data.

The above consideration demonstrated that the nonlinear character of the effect of vanadium concentration on the nitrogen-fixing ability of the Mg–V system can be explained by a change in the ratio between active centers with different numbers of nuclei. It is likely that the active center of a critical size contains four V(II) atoms. Hence, it follows that at high Mg : V ratios, when it is reasonable to neglect the concentration of V(II) clusters with $n > n_0$, the limiting degree of reaction of nitrogen reduction can be twice as high as the limiting degree of reaction of hydrogen liberation in the absence of N_2. Experimental data (see Fig. 2) demonstrate that this proportion is almost valid at Mg : V = 20. However, an interesting phenomenon was observed in this case: the degree of vanadium(II) oxidation with water with the liberation of hydrogen in the presence of nitrogen was higher than in the absence of nitrogen. This observation correlates with an increase in the intensity of H/D exchange in the presence of nitrogen, as is also the case in biological systems [17]. The stoichiometry of the process, which takes place in nitrogenase [17],

$$D_2 + 2H^+ + 2e \longrightarrow 2HD$$

corresponds to the reductive hydrolysis of hydrogen in the presence of nitrogen. The reason for this effect of nitrogen is not completely understood. It is believed that, on the coordination to a polynuclear vanadium cluster, the nitrogen molecule, as a potential multielectron oxidant, induces a decrease in the electron density of the active center and this decrease is sufficient for initiating a redox process of electron transfer from the neighboring low-nuclearity vanadium(II) clusters with $n < n_0$. For example, the coordination of a nitrogen molecule to a cluster containing $n_0 + 1$ ions of V^{2+} results in electron transfer from a neighboring cluster containing $n_0 - 1$ ions of V^{2+}. In turn, an electron is also transferred to the latter from another low-nuclearity cluster within the lifetime of the nitrogen complex. Under these conditions, an excessive electron remains on the $(n_0 + 1)$-nuclear cluster upon the dissociation of the nitrogen complex. Then, after hydrogen formation in the reaction of a hydride derivative with a solvent, an electron will be deficient for the reduction of nitrogen. It may be assumed that this deficiency is compensated for in the course of the subsequent coordination of the nitrogen molecule by the same mechanism because of the above electron processes. The idea of the concerted processes of hydrogen liberation and nitrogen reduction can also explain the fact that the degrees of these reactions as functions of the Mg : V ratio are symbatic in an excess of Mg ions.

Thus, new data on an increase in the limiting oxidation state of V^{2+} ions in the $Mg(OH)_2$–$V(OH)_2$ system in the presence of nitrogen were obtained in this work. It is our opinion that these data are indicative of the existence of a critical size of V_n clusters in the ionic layer of the mixed hydroxide. This critical size is required for the combined occurrence of the processes of N_2 reduction and H_2 liberation. An increase in the intensity of H/D exchange in the presence of nitrogen was found. The dependence of the rate of nitrogen reduction on the composition of a solvent supported our previous idea of the crucial importance of the concentration of free water for this process.

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