Initial stages of the formation of the structure of metal hydroxides

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Based on the data for the initial stage of aging of metal hydroxides that exhibit nitrogen fixation properties and the exact solution of the model kinetic problem for the association of aqua and hydroxo complexes, the regularities of the formation of the structure of primary amorphous particles of metal hydroxides have been revealed. The primary particles consist of chain hydroxo polymers that contain *ca.* 10 units and are chemically bound to each other by μ_3-OH bridging groups in sites at chaotically arranged intersections.

Key words: hydroxo polymers, clusters, phases of structure formation.

The study of the reduction of molecular nitrogen by Ti^{3+}, V^{2+}, Nb^{3+}, Ta^{3+}, and Cr^{2+} [1] hydroxides and their systems involving Mo^{3+} [2] and Mg^{2+} [3] ions made it possible to draw the conclusion that the reactivity of these systems is determined not only by peculiarities of the structure of the N_2 molecule, but also by some specific features of the hydroxides mentioned that have a universal character. Along with the dependence of the reaction rate on the reductive properties of the metal and the conditions of precipitation (the concentration of the metal salt and base, the composition of the solvent, *etc.*), there is one other general regularity: maximum reactivity is always observed at the initial moment of hydroxide precipitation.

In this work, the formation of primary amorphous particles of metal hydroxides is studied.

All aforementioned metal ions are unstable in alkaline aqueous and aqueous-alcoholic solutions. In these solutions, they are oxidized by the solvent to evolve hydrogen in a disproportionation reaction[4] or *via* a hydride mechanism.[5] It is precisely the fast formation of hydrogen which is the reason, *e.g.*, for the low nitrogen-fixation activity of $Ta(OH)_3$.[6] However, as the kinetic data testify, in other cases the fast decrease in the activity is due not to the side reaction of oxidation of the metal ion by the solvent, but to some other processes that occur without changing the oxidation state of the metal. For example, when a N_2 molecule is reduced to hydrazine and ammonia by Nb^{III} hydroxide, the reaction is completed in 5 min (308 K), while only 6—7% of the reducing agent is oxidized during this time.[7] The activity of the system determined by the amount of niobium(III) that reacted with nitrogen, taking into account the stoichiometry of the reactions of formation of hydrazine and ammonia, decreases from 38% in 1 min to 15% in 5 min. The $Mg(OH)_2$—$V(OH)_2$ system also loses its nitrogen-fixation activity with time, and the lower the $Mg^{2+} : V^{2+}$ ion ratio, the higher the deactivation rate. This is most pronouncedly exhibited for the reaction of N_2 with $V(OH)_2$ in the absence of Mg^{2+} ions. In this case, the reaction is completed in 5—10 s (293 K) and the degree of oxidation of V^{II} is ~1%.[7] A similar regularity is observed when the hydroxide is oxidized by the solvent. For example, a kinetic study of the hydrogen evolution by Mo^{III} hydroxide showed that the reaction rate decreases rapidly even 15 s after the beginning of the reaction, and the reaction rate constant decreases[8] from $7 \cdot 10^{-2}\ s^{-1}$ to $7 \cdot 10^{-4}\ s^{-1}$.

The examples presented make it possible to consider that the fast change in the reactivity of hydroxide is related to its aging, by which is meant all of the processes that occur spontaneously and result in the end, as a rule, in the formation of a crystalline phase.[9,10]

The electron microscopic and electron diffraction studies of $Ti(OH)_3$, $V(OH)_2$, and $Mo(OH)_3$ revealed no evidence of their crystallinity after short aging time (1—3 min). Therefore, it seems reasonable to relate these changes to processes of molecular organization that occur at the earliest stages of the evolution of hydroxides preceding their crystallization.

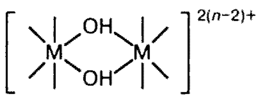
In several cases, hydroxo complexes are formed even in an acidic medium due to the equilibrium reaction of the metal aqua complex with a base

$$M(H_2O)_m^{n+} + OH^- \rightleftharpoons [M(H_2O)_{m-1}OH]^{(n-1)+} + H_2O\ .$$

Increasing the pH results in the further deprotonation of the coordinated water molecules and the appearance first of dimeric complexes

$$2[M(H_2O)_{m-1}OH]^{(n-1)+} \rightleftharpoons 2[M(H_2O)_{m-2}(OH)_2]^{(n-2)+} \rightleftharpoons$$

$$\rightleftharpoons$$



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and then of polynuclear forms with a great number of metal atoms mainly linked by μ_2-OH bridges.[11] When mixing solutions of the metal salt and the base, these processes occur very rapidly so that already during the time of mixing the reagents the hydroxo polymers precipitate as amorphous particles ~40 Å in size, depending slightly on the nature of the metal and the conditions of precipitation.[12,13]

Due to the very low solubility product of the majority of $M(OH)_n$ hydroxo complexes, their formation in reactions of metal salts with bases is almost irreversible.

$$[M(OH)_n]_i + [M(OH)_n]_j \xrightarrow{k_{ij}} [M(OH)_n]_{i+j}$$

(The coordination of solvent molecules is not indicated for simplicity).

Let us consider an idealized situation in which only particles with $i = 1$ are present at the initial moment. Mononuclear complexes have the maximum reactivity since they are the most mobile particles. In addition, hydroxo clusters $[M(OH)_n]_i$, even dimers, due to their anisotropy, have sites for both the less and more probable addition of monomeric particles. From this viewpoint, mononuclear complexes are the most isotropic particles, which means they add faster than clusters, other conditions being equal. Based on these grounds, we can consider that $k_{i1} \gg k_{jl}$ (j, $l > 2$), and all association processes except cluster growth one unit at a time can be neglected at the initial stage of the formation of clusters. Taking $k_{i1} = k$, one can conclude that this association results in a fairly narrow and universal size distribution of clusters: the average powers of the number of particles in the cluster $<n^k>$ are the following: $<n> = e$, $<n>^2 = 3e$, and $<n>^3 = 10e$ (see Supplement).

Moreover, since the function of the size distribution of clusters $p_i = (i - 1)/i!$ is very steep, all di-, tri-, tetra-, and pentamers ($p_2 + p_3 + p_4 + p_5 = 0.992$) are formed over a very short time τ of the order of $10/(k[M(OH)_n]_0)$ (Fig. 1). Thus, the primary processes are mainly completed before the time when association processes involving particles larger than monomers become kinetically significant. There is a hypothesis in the literature about primary plankton[10] from which amorphous hydroxides are also formed. The analysis presented unambiguously shows that the process occurs in two stages, and low-nuclear hydroxo complexes formed due to the complete association of monomers act as the plankton. Low-nuclear Pd^{II} hydroxo complexes have previously been observed experimentally.[14]

These hydroxo complexes also have advantages over mononuclear hydroxo complexes with respect to the rate of their addition to growing hydroxo polymers. Therefore, the kinetic consideration of the next stage of association can be similar, if one assumes that an abstract particle, an e-nuclear hydroxo complex (e is the base of the natural logarithm), acts as a monomer. Using this approximation, the average size of the cluster after the second cycle of association becomes equal to e^2. Then, if the e-particle subunit in the abstract size distribution is replaced by the primary size distribution of particles, the secondary size distribution of particles can be estimated (Fig. 2).

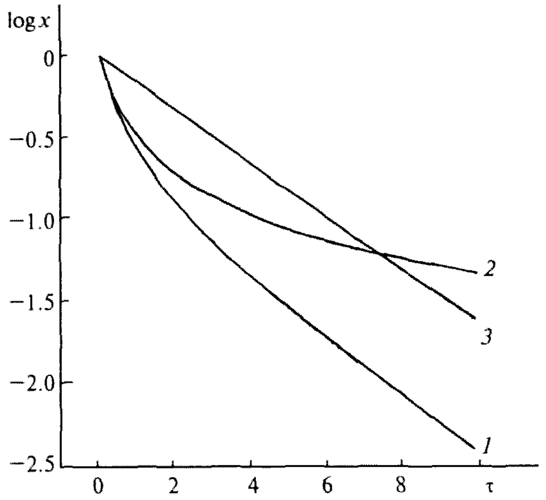


Fig. 1. Kinetics of the change in the reduced concentration of monomeric particles $x = [a]/[a]_0$ (*1*) and its asymptotic kinetic curves of the second (*2*) and first (*3*) orders corresponding to short and long times, respectively. Dimensionless time $\tau = tk[a]_0$.

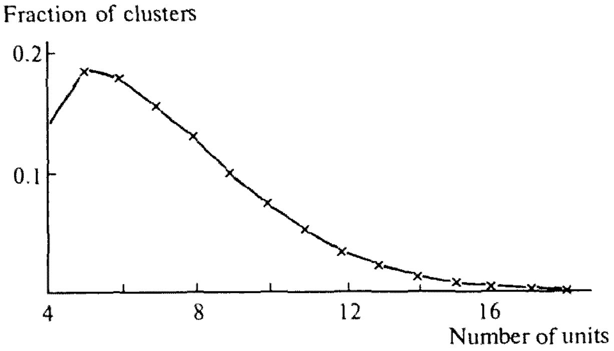


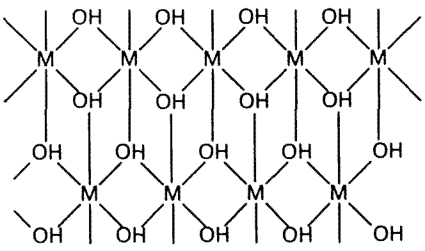
Fig. 2. Function of size distribution of clusters.

When growth of the polymer is linear, it seems evident that beginning from some size, different growing hydroxo polymers begin to contact each other. For the average number of contacts per hydroxo polymer, which is equal to 2, their intrinsic mobility is completely frozen, and after complete consumption of the low-nuclear hydroxo complexes the primary processes of the formation of amorphous metal hydroxides can be considered to be completed. It can be assumed that this moment nearly coincides with the completion of the second stage of association. This assumption is based on the following considerations. The main fraction of particles in the size distribution are multinuclear hydroxo complexes with $i > 6$. During their motion in solution, before the mutual orientation favorable for their association through the points of linear growth appears, they are capable of contacting each other many times to form thermodynamically favorable μ_3-OH bonds. Each of these bonds means the incorporation of a OH group of one polymer into the coordination sphere of another polymer accompanied by the simultaneous displacement of a coordinationally bound water molecule from that coordination sphere. This interaction is confirmed by the structural data for the crystalline dimeric molybdenum hydroxo complex,[15] which testify that it associates into a tetranuclear complex *via* the transformation of μ_2-OH bonds to μ_3-OH bonds. Thus, the size of the chains of hydroxo polymers forming the primary amorphous globule takes a fixed value of $i \approx 10$ due to the universal character of the primary size distribution of low-nuclear hydroxo complexes. This conclusion is in line with experimental observations. For example, the study of primary amorphous particles of Fe^{3+} hydroxide showed[11] that they consist of hydroxo polymers containing 15—20 iron atoms, and the function of the size distribution of polynuclear Pd^{II} hydroxo complexes drops sharply in the region of ~25 Å.[13]

It is likely that the chemical linkage of hydroxo polymers through OH bridge groups is preceded by weaker interactions through labile hydrogen bonds. The formation of these bonds between the chains occurs according to a random law, which causes the particles to have isotropic properties. The external size of the amorphous particles of the hydroxide is greater than the average size of the chains due to their random arrangement within a globule. For typical metal—metal distances ~3 Å in the chain, a globule size of ~40 Å corresponds to a chain of ~15 units.

Specific differences between mononuclear complexes depending on the nature of the incorporated metal atoms and their concentration determine only the time required for the formation of the primary amorphous particles. Although this time can vary within wide limits due to kinetic regularities, it remains short due to the small value of the volume of the solution containing the metal ions that form one globule.

The authors of several works[8,16,17] believe that the crystallization of amorphous particles consisting of low-soluble hydroxides cannot occur *via* their dissolution, as required by the classical theory of crystallization from solutions,[18] but occurs *via* the rearrangement of the amorphous structure and the appearance at first of nucleation forms in which crystallization has partially occurred. This rearrangement should result in the formation of a regular lattice, whose dimeric fragment can be presented schematically as follows.



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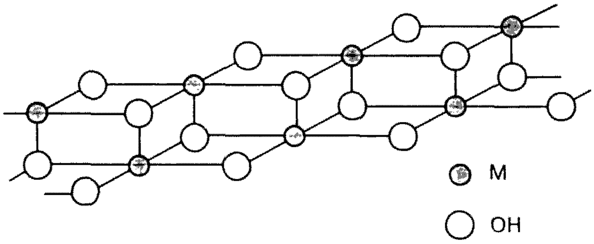
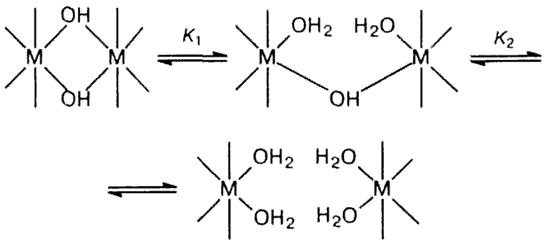


A simple mechanism of rearrangement by cleavage of the previously formed bridging bonds between hydroxo polymers is likely improbable for two reasons: the simultaneous cleavage of many bonds is thermodynamically unfavorable and the orientation of strongly anisotropic particles in a small space is difficult, because it leads necessarily to an initial amorphous structure. As far as we know, this problem has not yet been considered.

The mechanism of the rearrangement can be understood by considerating the properties of the bridging OH bond between the metal atoms. This bond possesses a very important (from the viewpoint of the reactivity of hydroxides) property: it can undergo step-by-step protonation.*



These processes occur when fresh precipitates of hydroxides are dissolved in acidic media. In alkaline media, the bridging hydroxo group can act as a base and capture (in equilibrium) the proton of a water molecule. The cleavage of two bridging bonds is equivalent to the dissolution of hydroxide, which is virtually impossible due to the low value of the solubility product, SP $\approx K_1 \cdot K_2$, but the concentration of binuclear fragments with one cleaved bridging bond is substantially greater than the SP value. A single bridging bond provides several units of a polymeric particle with the rotational degree of freedom that allows them to be orientationally linked to the adjacent polymer. Distortion of the linear structure of palladium(II) hydroxo polymers caused by the cleavage of one of the two bridging OH bonds was shown by the EXAFS method.[13] The initial stage of ordering of the amorphous species, which begins with the formation of double polymeric chains, is presented

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* The existence of an equilibrium between binuclear complexes linked by one and two μ-OH bonds has been shown,[19,20] *e.g.*, for Cr^{3+} compounds.

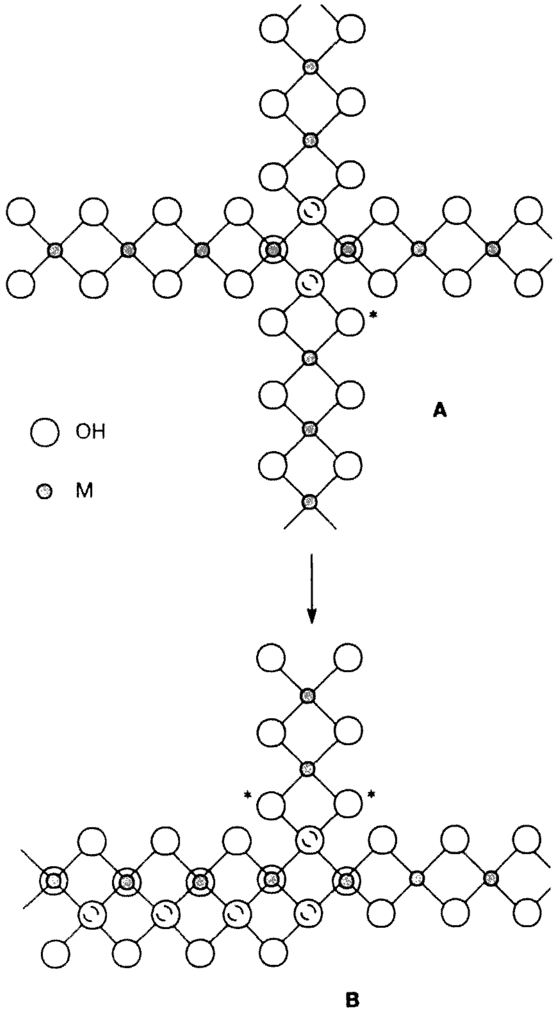
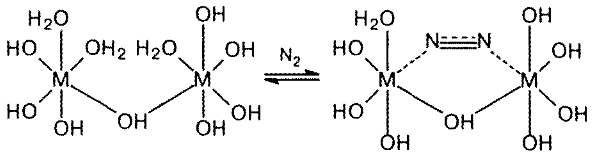


Fig. 3. Initial phases of ordering of the structure of amorphous hydroxides. Cleaving μ-OH bonds are marked by the symbol "*."

schematically in Fig. 3. This mechanism determines the orientation of free ends of intersecting polymers (see Fig. 3, **B**).

The formation of μ_3-OH bonds at the sites of the intersection of hydroxo polymers increases the number of OH ligands in the coordination sphere of the metal, which can increase strongly the K_1 and K_2 constants for the μ_2-OH bridging groups adjacent to the μ_3-OH groups. This results in the possibility of cleavage of two μ_2-OH bonds at the sites of distortion of the regularity, where the character of the arrangement of an individual chain relative to the growing phase of the hydroxide violates the layered character of its structure (see Fig. 3, **B**). Thus, a free end of the hydroxide chain appears again. The considered elementary stages of ordering of the regular hydroxide structure in the primary amorphous globule cause the formation of a regular structure.

The concepts presented are confirmed by the results of our study of the regularities of the reduction of a N_2 molecule by metal hydroxides. Thus, the first stage of the reaction is the incorporation of a N_2 molecule into the coordination sphere of the binuclear fragment of a (μ-OH) cluster accompanied by the replacement of two water molecules in this cluster.[8]



At the second, limiting stage, a hydride ligand is formed from the coordinationally bound water in the anionic aquahydroxo cluster. This ligand is transferred to a N_2 molecule, forming a N—H bond within the coordination sphere of the hydroxo polymer.[5] The sensitivity of the reduction of N_2 to the structure of amorphous metal hydroxides made it possible to formulate general conclusions about the primary stages of their formation. It can be assumed that a purposefully organized study to select and compare structurally sensitive reactions will make it possible to obtain further detailed information on the formation of the structure of metal hydroxides.

Supplement

Kinetic model

The kinetic equations that describe the successive growth of clusters one subunit at a time

$$
\begin{aligned}
&a + a \xrightarrow{k} a_2,\\
&a_2 + a \xrightarrow{k} a_3,\\
&\ldots\ldots\ldots\ldots\ldots\ldots\\
&a_n + a \xrightarrow{k} a_{n+1},\\
&\ldots\ldots\ldots\ldots\ldots\ldots
\end{aligned}
$$

can be written in the dimensionless form, if one takes $x = [a]/[a]_0$, $x_i = [a_i]/[a]_0$, and $\tau = t \cdot k \cdot [a]_0$, where $[a]_0$ is the total concentration of particles that form the cluster. Then the dimensionless kinetic equations take the form

$$
\begin{aligned}
&\dot{x} = -2x^2 - xx_2 - \ldots - xx_n - \ldots,\\
&\dot{x}_2 = x^2 - xx_2,\\
&\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\\
&\dot{x}_n = xx_{n-1} - xx_n,
\end{aligned}
$$

where the point denotes differentiation with respect to τ with the initial conditions $x(0) = 1$, $x_i(0) = 0$. For our purposes, it is enough to know the kinetic regularities for the functions x and $z = x_2 + x_3 + \ldots + x_n + \ldots$ (the total number of clusters). The average size of the clusters after association processes are completed is the following

$$
<n> = \frac{\sum_i i[a_i]}{\sum_i [a_i]} = \frac{1}{x(\infty) + z(\infty)} = \frac{1}{z(\infty)}.
$$

The x and z functions are determined by the system of nonlinear equations

$$\dot{x} = -2x^2 - xz, \qquad (1)$$
$$\dot{z} = x^2$$

with the initial conditions $x(0) = 1$, $z(0) = 0$. It can be shown by standard procedures that the solution satisfies the condition $x + z = \exp[-z/(x + z)]$, from which we obtain that $z(\infty) = \exp(-1)$ and $<n> = \mathrm{e}$. Using these functions, one can determine the mean square size of a cluster

$$<n^2> = \frac{\sum_i i^2[\mathrm{a}_i]}{\sum_i [\mathrm{a}_i]} = \frac{1 + 2\int_0^\infty x\mathrm{d}\tau}{z(\infty)} = 3\mathrm{e},$$

if it is noted that

$$\dot{w} = \sum_{i=2} i^2\dot{x}_i = 2x^2 + xx_2 + xx_3 + \ldots + $$
$$+ 2[x^2 + 2xx_2 + 3xx_3 + \ldots] = -\dot{x} + 2x, \qquad (2)$$

and

$$\int x^2\left(y^n - \frac{y^{n+1}}{n+1}\right)\mathrm{d}\tau = \frac{1}{n+1}\left[xy^{n+1} + \frac{zy^{n+2}}{n+2} + \right.$$
$$\left. + \int\left(y^{n+1} - \frac{y^{n+2}}{n+2}\right)x^2\mathrm{d}\tau\right] \qquad (3)$$

where $y = \int x\mathrm{d}\tau$, $y(0) = 0$.

Then it follows from Eq. (2) that

$$< n^2 > = \frac{x(\infty) + w(\infty)}{x(\infty) + z(\infty)} = \frac{1 + 2\int_0^\infty x\mathrm{d}\tau}{z(\infty)},$$

and from Eq. (3) we determine that

$$\int_0^\infty x^2(1 - y)\mathrm{d}\tau = \left[x\sum_{n=1}^\infty \frac{y^n}{n!} + z\sum_{n=2}^\infty \frac{y^n}{n!}\right]\Bigg|_0^\infty =$$
$$= z(\infty)\{\exp[y(\infty)] - 1 - y(\infty)\}. \qquad (4)$$

On the other hand, direct calculation taking into account the system of equations (1) leads to the expression

$$\int x^2(1 - y)\mathrm{d}\tau = \int(1 - y)\mathrm{d}z = -z - yz - x,$$

whose comparison with Eq. (4) gives the final result

$$z(\infty)\exp[y(\infty)] = 1 \text{ or } y(\infty) = \int_0^\infty x\mathrm{d}\tau = 1.$$

The average cube of the number of particles in the cluster $<n^3> = u(\infty)/z(\infty) = 10\mathrm{e}$ can be determined in a similar way using the fact that

$$\dot{u} = \sum_{i=2} i^3\dot{x}_i = -\dot{x} + 3x + 3x^2 + 3xw.$$

The $<n^k>$ values calculated make it possible to estimate the function of the size distribution of clusters if it is approximated that beginning from $i = 4$, $i \cdot x_{i+1}(\infty)/x_i(\infty) = \mathrm{const}$; $x_2(\infty) = 0.5002$, $x_3(\infty) = 0.3327$, $x_4(\infty) = 0.1258$, $x_5(\infty) = 0.0330$, and $x_6(\infty) = 0.0069$. Using this distribution function, $<n^4> = 37.002\mathrm{e}$ can be estimated, while analytical calculations give $<n^4> = 37\mathrm{e}$. Thus, the fractions of individual clusters determined differ slightly from the exact values. It is noteworthy that the initial terms of the distribution function are very close to simple correlations: $x_2(\infty) = 1/2$, $x_3(\infty) = 1/3$, $x_4(\infty) = 1/8$, and $x_5(\infty) = 1/30$, which, as can easily be seen, are described by the general law

$$x_i(\infty) = (i - 1)/i!$$

This law is exact, because it allows all $<n^k>$ values to be reproduced.

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