

Defect Magnesium Oxides Containing Acetate and Nitrate Ion Fragments Incorporated in the Oxide Structure

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Abstract—The results of studies on the synthesis of defect magnesium oxides by MgO hydration in salt solutions are summarized. The incorporation of oxygen-containing salt anions into the anionic hydroxide/oxide framework is described. In this case, the anion residue whose oxygen atoms belong to the oxygen framework of the oxide is incorporated in the octahedral oxygen cell of the oxide to occupy the place of a virtual magnesium cation. A portion of cationic vacancies remains free, whereas a portion is occupied by the transformed anion residue with a positive charge other than 2+. As a result, defect magnesium oxides are formed as substitutional solid solutions. The structure and charge heterogeneity of defect oxides is responsible for their high catalytic activity.

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INTRODUCTION

Magnesium oxide is widely used as a catalyst constituent, a support for an active phase, and an independent catalytic system. In the last-named case, either a standard (reactive) oxide or an oxide doped with impurity ions for the formation of required active centers is a catalyst. Catalysts based on MgO are commonly used in one-electron-transfer reactions, such as photoreactions, oxidative methane dimerization, and hydrocarbon pyrolysis. Studies on heterogeneous catalysts for the radical chain pyrolysis of hydrocarbons are scanty. The catalysts are empirically chosen because the science of catalyst preparation for radical chain pyrolysis is still in its infancy. Previously [1, 2], a mechanism was proposed for the pyrolysis of hydrocarbons on heterogeneous catalysts; this mechanism demonstrated the participation of surface sites in radical chain-propagation reactions and hence predetermined the radical nature of active centers.

The appearance of active centers that affect radical reactions on the surface of magnesium oxide has been repeatedly discussed in studies of other processes, for example, oxidative methane dimerization [3–5]. (Unlike pyrolysis, oxidative methane dimerization occurs in the presence of oxygen.) Catalysts based on magnesium oxide for oxidative methane dimerization have been most frequently synthesized by impregnation or coprecipitation with the use of aqueous solutions of metal salts (carbonates, nitrates, or chlorides) or by mixing pastes followed by drying and thermal treatment [6–8]. However, as a rule, modification with the use of these methods affects only near-surface layers containing structural distortions, which facilitate the introduction of a modifier. In this case, regular crystals of cubic magnesium oxide remain almost unaffected

and serve as a kind of support for an active phase as defect magnesium oxide. At high temperatures, the catalysts are rapidly deactivated in an atmosphere containing free radicals.

The greatest number of fundamental studies (both theoretical and experimental) was performed with lithium-doped magnesium oxide catalysts for oxidative methane dimerization [9, 10]. It is believed that Li⁺ replaces Mg²⁺ ions at the lattice points; in this case, the active surface center [Li⁺O⁻], which was detected by EPR spectroscopy, is formed [11]. However, the question of whether this center takes part in the reactions of methyl radical formation under conditions of oxidative methane dimerization or the presence of lithium in the lattice facilitates the formation of a surface radical center as O⁻ is still an open question [12–14]. Note that these catalysts are short-lived.

We performed a series of studies on the synthesis and characterization of catalysts for radical chain pyrolysis as defect magnesium oxides, which were stable up to 1000°C and did not lose activity in radical chain pyrolysis at 700–750°C after operation for ~90 h. In this case, the nature of active centers was beyond the scope of our studies; the knowledge of the radical nature of these centers under conditions of pyrolysis was sufficient. The proposed synthetic method depended on the properties of MgO and the problems of its use.

The aim of this work was to summarize studies on the synthesis of catalysts based on magnesium oxide for radical chain processes, such as the pyrolysis of hydrocarbons.

CAUSES OF THE ACTIVITY OF MgO

Magnesium oxide has a face-centered cubic lattice of the NaCl type with the parameter $a = 4.212 \text{ \AA}$. The melting temperature is 2800°C. At room temperature, MgO is a dielectric with a band gap of 7.8 eV [15]; this is responsible for a low rate of relaxation of appearing near-surface charges, which affect the formation of active centers. As in the majority of oxides, the catalytic activity of standard MgO is often related to the presence of active centers as surface defects. They can be of morphological nature (angles, steps, edges, etc.); oxide ions at these defects exhibit a low coordination and, consequently, an increased activity [16]. Surface dehydroxylation occurs in polycrystalline magnesium oxide at high temperatures, and surface defects as anion vacancies appear. When MgO was thermally activated in a vacuum and then cooled to room temperature and the adsorption of substances capable of adding electron (electron-deficient compounds) was performed, the formation of radical anions was observed [17]. These electron-donor defects are reducing active centers [18].

Defects on an oxide surface can also be formed in the case that cation vacancies (V centers) occur in the oxide structure. The point is that O^{2-} is a rather unstable state of oxygen. This follows from data on the electron affinity of oxygen atom and ion: $\text{O} + \text{e} = \text{O}^-, -1.4 \text{ eV}$; $\text{O}^- + \text{e} = \text{O}^{2-}, +8.9 \text{ eV}$. That is, in a vacuum, the O^{2-} ion will be spontaneously converted into O^- with the release of an energy of 8.9 eV. In an oxide crystal, the state O^{2-} is stabilized by the Coulomb interaction with surrounding Mg^{2+} cations [19]. In magnesium oxide, each oxygen ion is surrounded by six magnesium cations. Energy released because of the Coulomb interaction is higher than the negative electron affinity of O^{2-} . A cation vacancy in an oxide crystal is the site at which the Coulomb interaction field is strongly disturbed. Two of the nearest six O^{2-} ions gave an electron each to the cation vacancy to form two O^- ions. In the oxygen framework of the oxide, O^- is an electron defect (F center). Its wave function can be delocalized over more than one O^{2-} position to cause valence fluctuations, which transform O^- into a charge carrier. As a result, O^- migrates as a hole in the crystal, and it can be stabilized on the surface to form an active center [20]. The hole site O^- is an oxidative site; chemically, it is a radical, which can become an active center in heterogeneous-homogenous radical reactions of chain propagation.

Consequently, synthetic techniques that facilitate the formation of cation and anion vacancies in the bulk or in a near-surface layer of the oxide are of interest because either catalysts or supports with an active phase immobilized at surface vacancies can be prepared in this case. Along with the above cases, anion vacancies in oxide catalysts can be formed as a consequence of changes in the crystal structure due to the addition of dopants [20–23].

Thus, the appearance of structure and charge heterogeneities in the oxide can be responsible for the formation of radical surface centers.

SYNTHESIS OF DEFECT MgO

As mentioned above, currently available techniques for the synthesis of catalysts based on MgO affect only the near-surface layers of microcrystallites. In essence, well-crystallized MgO is a support for an unstable active phase. Impurity additives should be introduced immediately into the structure cell of the oxide in order to produce charge heterogeneity and increase the thermal and reaction stability of defect magnesium oxide. However, because magnesium oxide is a very thermodynamically stable compound, the impurity can be incorporated into the structural unit of the oxide only at the instant of its formation or rearrangement. The methods of coprecipitation, impregnation, or paste mixing do not meet this requirement. Therefore, we proposed an original synthetic method, in which parent MgO, which was calcined at 1073 K, was subjected to hydration in concentrated solutions of corresponding salts until its complete conversion into magnesium hydroxide. Next, this magnesium hydroxide was dried and calcined at high temperatures. The embedding of anions and cations took place at the stages of oxide–hydroxide–oxide transition [24–27]. We studied the samples of defect magnesium oxides prepared by the hydration of parent magnesium oxide in the concentrated solutions of magnesium acetate, lithium acetate, magnesium nitrate, lithium nitrate, and lithium chloride. The salts were chosen so that the cation or anion sublattice of the oxide was affected. Hydration occurred at room temperature for eight days with stirring at regular intervals; the completeness of hydration was monitored using X-ray diffraction (XRD) analysis and differential thermal analysis (DTA). Next, the precipitate was filtered off, washed, and air-dried. The samples were kept in a desiccator. The dried and calcined samples were studied by thermogravimetry (DTA), IR spectroscopy, diffuse-reflectance electron spectroscopy, electron microscopy, and diffractometry with the use of ordinary X-rays and synchrotron radiation. A mechanism was proposed for the structure formation of the resulting oxides, and their catalytic activity was tested in radical chain pyrolysis [24–28]. The results are summarized below.

EFFECT OF THE ANION

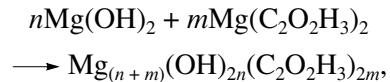
Acetate ion. The samples prepared by the hydration of parent magnesium oxide in a magnesium acetate solution are denoted as $\text{MgO}/\text{Mg}(\text{Ac})_2$. First, we qualitatively evaluated the interaction between components on keeping MgO in an aqueous solution of MgAc_2 [24]. It was found that the activity ($a_{\text{Mg}^{2+}}$) is much higher than the solubility ($S_{\text{Mg}^{2+}}$); therefore, the release of

Mg^{2+} from the resulting $Mg(OH)_2$ into solution was completely suppressed. In contrast, in accordance with the Peskov–Fajans rule, Mg^{2+} ions are chemisorbed from solution to remove defects from the cationic framework of $Mg(OH)_2$. The activity of hydroxyl ions (a_{OH^-}) is lower than their solubility (S_{OH^-}) by a factor of 2.3; therefore, OH^- passes from a solid phase of $Mg(OH)_2$ into solution. To maintain electric neutrality, hydroxyl ions are replaced by acetate ions from solution. Thus, it is believed that the chemisorption of magnesium ions and the partial replacement of hydroxyl groups by acetate groups occur as MgO is kept in a concentrated solution of $MgAc_2$.

The hydration of MgO is associated with the rearrangement of the close-packed cubic structure into the hexagonal layer structure of magnesium hydroxide. These structures (MgO and $Mg(OH)_2$) are based on close-packed anionic layers of oxygen or OH^- ions, respectively, with various spatial arrangements. In the oxide, the layers are arranged in accordance with a cubic close packing (ABC, ABC...), and the direction of the closest packing corresponds to the [111] orientation in the cubic unit cell. In the hydroxide, the closely packed layers form two-layer stacks (AB, AB...) in the [001] direction of the hexagonal unit cell. The two-layer stacks are joined by weak hydrogen bonds. On the structural rearrangement of MgO into $Mg(OH)_2$, the [111] direction of the close packing of O^{2-} ions in the cubic unit cell is changed to the [001] direction of OH^- ions in the hexagonal unit cell [29]. Taking into account the high capacity of acetate groups for complexation, the deep replacement of hydroxyl groups would be expected in the hydration of the oxide. The radius of the acetate ion is greater than the radius of the hydroxyl ion by a factor of about 3. This results in an increase in the interlayer distance in the hydroxide structure; according to XRD data, brucite (001) diffraction lines were shifted [24, 25]. However, the structure of magnesium hydroxide was retained in this case. Thus, it is believed that, under mild hydration conditions in salt mother liquor, an unusual compound with the hydroxide structure is formed, in which a portion of hydroxyl groups is replaced by acetate groups. It occurs in equilibrium with the mother liquor for an arbitrarily long time under these conditions. In a dried state, this compound was identified as an individual phase of defect magnesium hydroxide.

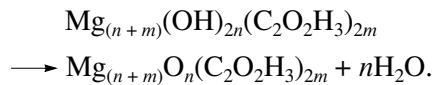
According to DTA data [24], the transition of standard magnesium hydroxide into the oxide occurs at 410°C. Defect magnesium hydroxide is unstable, and it undergoes a rearrangement into a hydroxoacetate structure of variable composition, which depends on the degree of substitution of acetate groups for hydroxyl groups, at 235°C. The transition to defect magnesium oxide occurs in two steps at 335 and 370°C. A doubled peak due to an endo effect suggests the formation of at least two hydroxoacetate phases, in which the rates of

solid-phase transformations on heating are different, from a defect hydroxide phase. At 370°C, a transition to defect magnesium oxide occurs. Spatial hindrances, which can appear upon the displacement of the bulky acetate ion from the MgO lattice formed, result in that not all of the ions have managed to leave the lattice. Magnesium acetate ($T_{decomp} = 323^\circ C$) or magnesium carbonate ($T_{decomp} = 350^\circ C$) phases were absent from defect magnesium oxides. In the general form, the process can be represented as



where $n \gg m$.

On calcination, hydroxoacetates are converted into the defect oxide:



Surface compounds formed on the surface of MgO upon the adsorption of carbon dioxide from air were adequately characterized by IR spectroscopy. The signals of these compounds were much different from the signals of incorporated carbon compounds. According to data obtained by IR spectroscopy and diffuse-reflection electron spectroscopy, a portion of distorted acetate groups remained in the lattice of MgO above 485°C and partially decomposed to carbonate ions and carbon as the temperature was further increased [24]. The presence of impurities immediately in the structure of magnesium oxide affects the nearest environment of magnesium ions. According to IR-spectroscopic data, the contour of a sample calcined at 700°C was significantly broadened and more asymmetrically shaped than the standard spectrum of MgO , and an absorption maximum was considerably shifted (by 60 cm^{-1}) to the low-frequency region [24]. Because the microcrystallites of MgO exhibit a high cubic symmetry, any changes in the parameters of a fundamental absorption band suggest local changes in the nearest environment of MgO . Thus, for example, the formation of lattice vacancies changes the vibration conditions of particles arranged in the immediate vicinity of them. The occurrence of a void in the neighborhood increases the amplitude and, consequently, decreases the vibration frequency of particles in neighboring vacancies [30]. In our case, the frequency of $Mg-O$ vibrations significantly decreased; this is indicative of the presence of not only impurity ions but also vacancies due to them in the lattice of magnesium oxide (Figs. 1, 2).

The calcination of a sample at 1000°C resulted in a slight decrease in the halfwidth of the spectral contour and a shift of the absorption maximum to the high-frequency region by $10-20\text{ cm}^{-1}$ [24]. However, the main differences between the spectra of the sample and standard MgO were retained. This fact suggests that structure defects in magnesium oxide were retained even at such a high temperature; however, their concentration

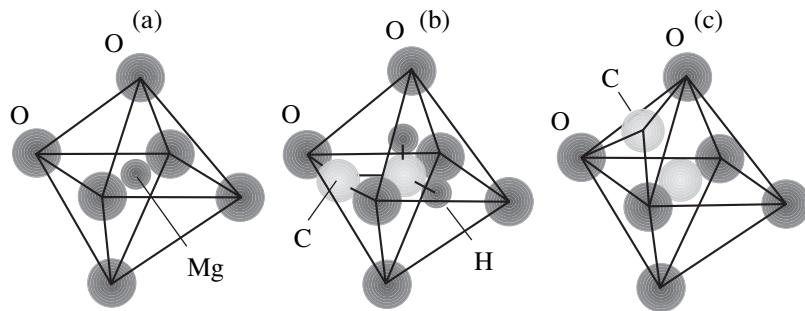


Fig. 1. Structure of the oxygen octahedra of MgO: (a) a standard oxygen octahedron with the central localization site of the magnesium cation, (b) the magnesium cation is replaced by an incorporated acetate ion, and (c) the magnesium cation is replaced by C⁰ and an incorporated carbonate ion.

was lower than that in a sample calcined at a lower temperature (according to diffuse-reflectance electron-spectroscopic data [24]). The defect structure of MgO was retained after the calcination of a sample at $T = 1000^\circ\text{C}$ for 6 h.

The unusual results obtained stimulated us to refine the real structure of magnesium oxide modified with acetate groups. Data obtained by IR and diffuse-reflectance electron spectroscopy are indirect; they indicate the presence of impurities and changes in the bond lengths and angles of incorporated CO_x fragments, which were retained in the oxide structure even at 1000°C. Only XRD and synchrotron radiation data can be direct evidence for the occurrence of structural

changes. Because a thorough analysis of the integrated intensities and profiles of diffraction peaks is required for seeking for real models, the structure of magnesium oxide modified with acetate groups was refined with the use of a precision diffractometer mounted at a synchrotron radiation beam at the Siberian Synchrotron Radiation Center [25].

As a result of structure refinement, a conclusion was drawn [25, 30–32] that defect magnesium oxide prepared by calcination at 700°C exhibited the increased lattice parameter $a = 4.22$, as compared with the value of $a = 4.212$ for standard oxide. Defect MgO can be described by the stoichiometric formula Mg_{0.88}□_{0.04}O_{0.84}(C₂H₃O₂)_{0.08}, where the symbol □ denotes a free cation vacancy. The charge of the acetate ion is -1 . In this case, the oxygen of the acetate ion is simultaneously incorporated in the oxygen framework of the magnesium oxide structure; this changes in principle the nature of parent acetate groups (Fig. 1).

To understand how acetate groups can be trapped by magnesium oxide, let us consider the structures of MgO and the acetate ion. The oxygen framework of MgO is a closely packed cubic structure of oxygen ions in the octahedral voids of which Mg²⁺ ions are arranged. The Mg–O and O–O distances are 2.1105 and 2.9842 Å, respectively. The chains of octahedra occupied by Mg²⁺ ions in a layer are vertex-shared, whereas the layers are edge-shared octahedra. A comparison between the interatomic distances and geometries of the acetate ion and MgO demonstrates that, in principle, the oxygen ions of the acetate ion can be incorporated in the oxygen framework of the MgO structure. However, small molar amounts of acetate ions (0.08 per formula unit of MgO) did not allow us to localize the positions of carbon atoms, which are lighter than Mg. It is believed that the carbon atom (bound to two oxygens of the acetate ion rather than to hydrogen atoms) is arranged between oxygen ions in the edge of an octahedron or near this position. In this case, the minimum C–O distance was 1.49 Å, which is somewhat greater than distances in the acetate ion (1.43 Å). Moreover, the OCO angle should be considerably changed. In this case, the most probable location of the CH₃ group belonging to the

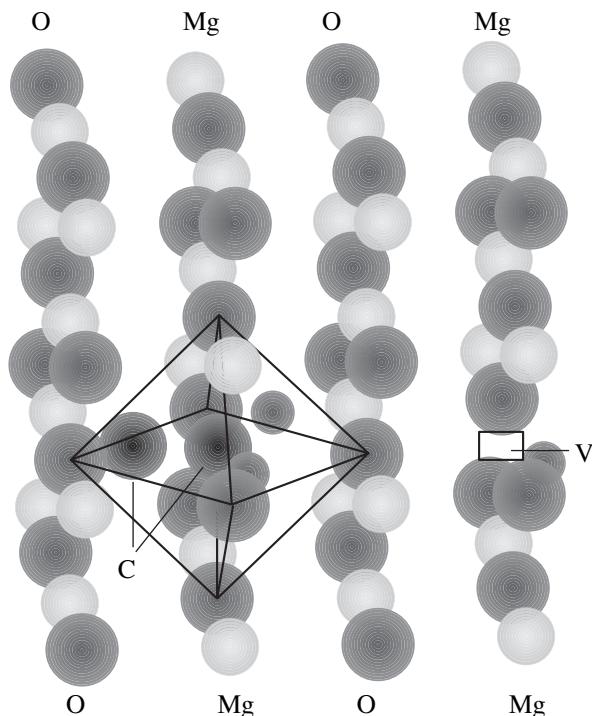


Fig. 2. Structure of defect magnesium oxide with an incorporated acetate ion and a cation vacancy V; $n = 2$. An oxygen octahedron is marked in accordance with Fig. 1b.

acetate ion is the center of an octahedron unoccupied by a magnesium ion (Fig. 1b). It is likely that the C–H distance (1.00 Å), which is greater than the ionic radius of Mg (0.74 Å), is responsible for the observed increase in the unit cell parameter of MgO.

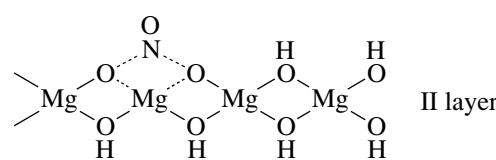
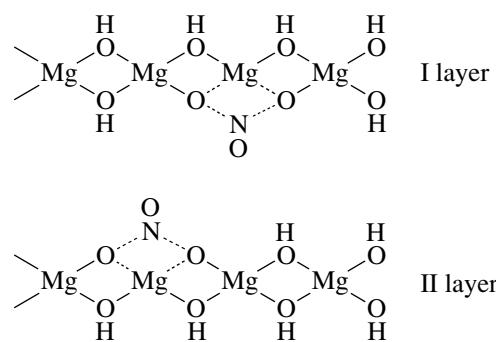
Note that the resulting formula of defect oxide indicates a deficiency of magnesium ions. The building units of the oxygen framework of defect MgO are oxygen ions that belong to acetate, which is incorporated in the oxygen framework and arranged in the interlayer space of the hydroxide. Therefore, dried samples had the magnesium hydroxide structure with an increased interlayer distance because of incorporated acetate groups. Upon going into the oxide, the oxygen ions of incorporated acetate groups belong to the oxygen octahedron of MgO as well. The residue of a transformed acetate anion as the C_2H_3 group with an effective charge of 3+ is enclosed within such an oxygen octahedron. Thus, as compared with the above formula, the refined stoichiometric formula has the form $[Mg_{0.88}\square_{0.04}(C_2H_3)_{0.08}]O_1$ (Fig. 1b). Thus, the compound obtained upon calcination to 700°C can be considered as the lattice of MgO in which each eleventh Mg²⁺ cation is replaced by the $C_2H_3^{3+}$ cation. This is an unusual case of the formation of a substitutional solid solution.

It was noted that a cubic structure is thermodynamically most stable. The $C_2H_3^{3+}$ cation clamped in this microcrystal explains the wide temperature range (to 700°C) of the existence of the resulting compound. However, a further deformation and rearrangement of incorporated cations to the pseudocarbonate group and free carbon occurred on calcination above 700°C in air because of $C_2H_3^{3+}$ decomposition. It is likely that the hydrogen of the methyl group diffused as H₂ to the microcrystal surface; the C–C bond became weaker, and the “acetate” group underwent a rearrangement into elemental carbon and the “carbonate” group. This was supported by IR-spectroscopic and diffuse-reflection electron-spectroscopic data [24], which indicated that distorted carbonate groups and elemental carbon appeared in the sample.

Based on the crystal chemistry of other compounds containing carbonate groups [33], the CO₃ group is usually a planar triangle of oxygen ions at the center of which carbon is arranged. The C–O distances are usually equal to 1.4–1.5 Å. In the structure of MgO, the faces of oxygen octahedra are these triangles of oxygen ions. Thus, on the decomposition of acetate, one of the carbon atoms from the edge of an octahedron goes to the plane of its face with the formation of the carbonate ion structure. In this case, an increase in the lattice parameter of MgO can be explained by the presence of C⁰ carbon atoms, which were formed from C₂H₃ groups, in the octahedra. The resulting compound can be represented by the stoichiometric formula $[Mg_{0.85}\square_{0.09}(C_2)_{0.06}]O_1$ (Fig. 1c). Here, the cation (C)

exhibits a formal charge of 2.5+. A decrease in the positive charge, as compared to 3+ in the former case, is responsible for a decrease in the deficiency of Mg ions in the latter compound, as compared with the former compound. This compound can also be considered as a substitutional solid solution that is stable even upon calcination at 1000°C for many hours.

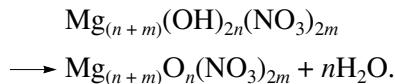
Nitrate ion. The possibility of preparing defect magnesium oxide was tested with another oxygen-containing anion, the nitrate ion. The samples of MgO/Mg(NO₃)₂ were prepared by the hydration of parent magnesium oxide in a magnesium nitrate solution. Studies analogous to those with MgO/Mg(Ac)₂ were performed. As in the case of magnesium acetate, the formation of a defect structure of magnesium oxide occurred even at the step of hydration. This follows from a temperature shift of the hydroxide–oxide phase transition toward lower temperatures and a change in the shape of the curve, which suggests the occurrence of at least two phases crystallizing at 380 and 430°C [26]. The defect magnesium hydroxide having a layer structure of the brucite type was formed as described below. Hydroxide layers were built of edge-shared Mg(OH)₆ octahedra. The coordination numbers of Mg and OH groups are 6 and 3, respectively. The layers were bound by van der Waals forces. Because the hydration of MgO took place in a magnesium nitrate solution, NO₃[–] ions were incorporated into the resulting hydroxide structure (to maintain electric neutrality) at the most accessible sites: in the interlayer space. The IR-spectroscopic studies demonstrated that the absorption bands of the nitrate ion incorporated into the hydroxide can be attributed to a chelate bidentate complex of the nitrate ion. The formation of this complex was accompanied by embedding two oxygen atoms of the NO₃ group at the position of the OH group in the brucite layer and entering into the coordination sphere of the metal [34]:



Thus, the dried sample was defect magnesium hydroxide modified with nitrate ions or magnesium hydroxonitrate: $nMg(OH)_2 + mMg(NO_3)_2 \rightarrow Mg_{(n+m)}(OH)_{2n}(NO_3)_{2m}$.

According to IR-spectroscopic data, sample calcination at 330 and 395°C resulted in the almost complete removal of hydroxyl groups from the interlayer

space. The observed changes in the spectra were due to both the effects of the nearest environment and structural distortion of NO_3^- in approaching layers and the appearance of the NO_2^- ion in the structure. The NO_3^- ions and then the NO_2^- ions (which were formed as the temperature was increased and the system ordered) in the first coordination sphere of Mg^{2+} prevent the complete structural transition $\text{Mg}(\text{OH})_2 \rightarrow \text{MgO}$:



The modified oxide cannot be described by cubic symmetry, and it more likely exhibits the structure of a distorted cube, which is intermediate between magnesium oxide and magnesium hydroxide.

Indeed, structural studies (XRD and synchrotron radiation analysis) demonstrated that the diffraction patterns of a sample calcined at 500°C exhibited diffraction peak splitting. This splitting suggests that the structure of modified magnesium oxide exhibits a rhombohedral distortion along the main diagonal line of the cubic unit cell [27]. Evidently, the rearrangement of the anion framework of the hydroxide (two-layer hexagonal) into a face-centered cubic structure causes a redistribution of magnesium ions over all of the octahedra of the new oxygen packing. In this case, the [001] direction of the close packing of oxygen layers of the hydroxide structure is changed to the [111] direction of the close packing of the oxide structure. It is likely that the complete displacement of NO_3^- groups is hindered because at least one oxygen ion in each of the NO_3^- groups enters into a closely packed oxygen layer [26] and retains a portion of NO_3^- groups in the oxygen framework of magnesium oxide. Thus, as in the case with magnesium acetate, the oxygen of the nitrate ion completes the oxygen framework of magnesium oxide formed on calcination to retain the transformed NO_3^- group in the oxide structure. Structurally, the NO_3^- group is a triangle of oxygen ions at the center of which the nitrogen ion is arranged. The O–O distances in the group are ~ 2.4 Å, which is somewhat shorter than the O–O distances in closely packed structures (2.7–3.0 Å) [35]. All of the NO_3^- groups in the structure of magnesium hydroxide are ordered parallel to [001]. Thus, if the [001] direction is changed to [111] in the hydroxide \rightarrow oxide transition, the orientation of NO_3^- along the [111] direction in MgO , that is, along the spatial diagonal line of the cubic lattice of MgO , is retained. This shortened the spatial diagonal line of the unit cell and lowered the symmetry of the structure to rhombohedral. This was supported by IR-spectroscopic data [26, 36]. The presence of NO_3^- groups resulted in the appearance of cation vacancies \square in the structure. The general formula of defect magnesium oxide has the form $[\text{Mg}_{0.925}\square_{0.045}(\text{N})_{0.03}]\text{O}_1$. Here, nitrogen acts as a cation. According to IR-spectroscopic data, the effec-

tive charge of the cation in an octahedral oxygen cell can vary depending on the retained bonds of the nitrogen atoms with oxygen, which belongs to the oxygen framework of the oxide more than to the nitrate ion: N^{5+} for NO_3^- , N^{3+} for NO_2^- , and N^{2+} for NO^- . The resulting substitutional solid solution was also stable on high-temperature calcination.

According to diffuse-reflectance electron-spectroscopic data [24, 26], the occurrence of impurity levels reflects the charge heterogeneity of the resulting defect magnesium oxides and suggests that the presence of these levels facilitates one-electron transitions in the course of radical chain pyrolysis.

Note that the hydration of magnesium oxide in chloride solutions did not result in the formation of defect oxides. This fact supports the conclusion that a defect structure can be formed only in the case of oxygen-containing anions whose oxygen atoms participate in the formation of the oxygen framework of the oxide.

EFFECT OF THE CATION

To study the effect of the nature of the salt cation on the formation of defect magnesium oxide, we performed the hydration of parent magnesium oxide in a solution of lithium nitrate. We examined the resulting samples in accordance with a standard procedure. According to XRD and IR-spectroscopic data, a rhombohedral distortion of the cubic oxide structure was also observed in MgO/LiNO_3 . A comparative analysis with the $\text{MgO}/\text{Mg}(\text{NO}_3)_2$ sample led us to conclude that, if the hydration occurs in a salt solution with the lithium cation, the presence of this cation facilitates the exit of magnesium ions from the cation framework and replacement with lithium ions. The NO_3^- ions were incorporated into the interlayer space in the cases of both magnesium nitrate and lithium nitrate. The ionic radius of lithium is smaller than the ionic radius of magnesium, and the cation framework in the case of MgO/LiNO_3 is more labile than that in the case of $\text{MgO}/\text{Mg}(\text{NO}_3)_2$. This facilitates the diffusion of and gradual removal of modifier anions. This takes place until defect oxide is completely converted into standard magnesium oxide. These processes occur slowly. However, the formula of the substitutional solid solution cannot be determined because the concentration of modifier substances slowly changed.

Thus, we can conclude that thermally stable substitutional solid solutions are formed only in the case that the cation framework of the oxide is strengthened by the same cation from solution. At the instant of the rearrangement of the oxide into the hydroxide (and reversely into the oxide), the oxygen-containing anion is incorporated into the hydroxide and oxide structures and transformed into a cation to form a substitutional solid solution.

CATALYTIC ACTIVITY OF DEFECT MgO

The synthetic defect magnesium oxides exhibited not only structural but also charge heterogeneity. However, defect MgO did not contain F centers in the bulk in a classical sense: oxygen ions were added rather than removed. (Of course, classical F centers can appear on the surface of MgO as a result of dehydroxylation.) Note that defect magnesium oxides contained V²⁺ cation vacancies (denoted by the symbol \square in structural formulas) and cations with a charge higher than 2+ in the bulk. The presence of these species decreased the effective negative charge of neighboring oxygen ions to form O^{δ-}. The diffusion of hole centers to the surface was responsible for the appearance of active centers, whose activity depended on the value of δ- and the degree of electron localization. It is believed that defect magnesium oxides exhibit higher activity in radical chain pyrolysis than standard MgO.

Indeed, studies on the activity of defect MgO in the pyrolysis of *n*-undecane and *n*-butane demonstrated that they can be arranged in the following order of activity: quartz < MgO < MgO/Mg(NO₃)₂ < MgO/MgAc₂ [28, 37]. An analogous order was obtained in a study of the generation of alkyl radicals in the pyrolysis of *n*-undecane. The radicals were frozen immediately in the resonator of an EPR spectrometer [38]. The more active the catalyst, the greater the amount of radicals generated in the bulk. These data provide support for the statement that active centers on the surface of magnesium oxides in the course of pyrolysis are of a radical nature and the formation of these centers was due to the charge heterogeneity of substitutional solid solutions.

CONCLUSIONS

In the synthesis of defect magnesium oxides by the hydration of parent oxide in a magnesium salt solution followed by drying and calcination to oxide, the incorporation of oxygen-containing salt anions into the anion framework of the hydroxide/oxide was found. In this case, the anion residue whose oxygen atoms belong to the oxygen framework of the oxide is incorporated in the oxide structure to occupy the place of a virtual magnesium cation. A portion of cation vacancies remains unoccupied, and a portion is occupied by the transformed anion residue with a positive charge other than 2+. The structural rearrangement occurs in the temperature range of the formation of defect magnesium oxide.

At $T \geq 700^\circ\text{C}$, defect magnesium oxide was formed as a substitutional solid solution. This structurally homogeneous compound existed even after the calcination of samples at 1000°C for 6 h and after tests for many hours (from 60 to 90 pyrolysis-regeneration cycles 1.5 h each). A decrease in the activity was practically not observed.

The structure and charge heterogeneity of defect oxides facilitates the formation of active radical centers on the surface. The resulting catalysts are highly active in radical chain pyrolysis.

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REFERENCES

1. Vasil'eva, N.A. and Buyanov, R.A., *Kinet. Katal.*, 1993, vol. 34, no. 5, p. 835.
2. Vasil'eva, N.A. and Buyanov, R.A., *Khim. Interes. Ust. Razv.*, 1998, vol. 6, no. 4, p. 311.
3. Arutyunov, V.S. and Krylov, O.V., *Okislitel'nye pre-vrashcheniya metana* (Oxidative Conversion of Methane), Moscow: Nauka, 1998.
4. Nada, R., Hess, A.C., and Pisani, C., *Surf. Sci.*, 1995, vol. 336, no. 3, p. 353.
5. Stiakaki, M.A.D., Tsipris, A.C., Tsipris, C.A., and Xanthopoulos, C.E., *J. Chem. Soc., Faraday Trans.*, 1996, vol. 92, no. 15, p. 2765.
6. Kolts, J.H. and Delzer, G.A., *Science*, 1986, vol. 232.
7. Burch, R. and Grabb, E.M., *Appl. Catal., A*, 1993, vol. 97, p. 49.
8. Podro, C.L., Gross, W.E., Baronetti, G.T., Castro, A.A., and Scelza, O.A., *II World Congr. IV European Workshop Meeting*, Benalmadena, Spain, 1993, p. 47.
9. Shi, C.L., Xu, M.T., Rosinek, M.P., and Lunsford, J.H., *J. Phys. Chem.*, 1993, vol. 97, no. 1, p. 216.
10. Cant, N.W., Kennedy, E.M., and Nelson, P.F., *J. Phys. Chem.*, 1993, vol. 97, no. 7, p. 1445.
11. Wang, J.-H. and Lunsford, J.H., *J. Phys. Chem.*, 1986, vol. 90, no. 22, p. 5883.
12. Matsuura, I., Utsumi, Y., Doi, T., and Yoshida, Y., *Appl. Catal.*, 1989, vol. 47, no. 2, p. 299.
13. Anpo, M., Sunamoto, M., Doi, T., and Matsuura, I., *Chem. Lett.*, 1988, no. 4, p. 701.
14. Ming-Cheng, Wu., Truong, C.M., Coulter, K., and Goodman, D.W., *J. Catal.*, 1993, vol. 140, no. 2, p. 344.
15. Roessler, D.M. and Welker, W.C., *Phys. Rev.*, 1967, vol. 159, p. 733.
16. Klabunde, K.J. and Nieves, I., *J. Phys. Chem.*, 1988, vol. 92, no. 5, p. 2521.
17. Morris, R.M. and Klabunde, K.J., *Inorg. Chem.*, 1983, vol. 22, p. 682.
18. Tanabe, K., *Solid Acids and Bases*, New York: Academic, 1970.
19. Friedemann, F., *J. Geophys. Res.*, 1993, vol. 98, no. B12, p. 22209.
20. Hargreaves, J.S.J., Hutchings, G.J., and Joyner, R.W., *Catal. Today*, 1990, vol. 6, p. 481.
21. Lehmann, L. and Baerns, M., *J. Catal.*, 1992, vol. 135, no. 2, p. 467.
22. Hargreaves, J.S.J., Hutchings, G.J., Joyner, R.W., and Kiely, C.J., *J. Catal.*, 1992, vol. 135, no. 2, p. 576.

23. Efstatiou, A.M., Boudouvas, D., Vamvouka, N., and Verikios, X.E., *Appl. Catal., A*, 1992, vol. 92, no. 1, p. 1.
24. Kuz'mitskaya, S.Yu., Odegova, G.V., Vasil'eva, N.A., Plyasova, L.M., Kriger, T.A., and Zaikovskii, V.I., *Kinet. Katal.*, 1997, vol. 38, no. 6, p. 921.
25. Plyasova, L.M., Vasilieva, N.A., Cherepanova, S.V., Shmakov, A.N., and Chuvilin, A.L., *Nucl. Instrum. Methods Phys. Res., Sect. A*, 1998, vol. 405, nos. 2–3, p. 473.
26. Odegova, G.V. and Vasil'eva, N.A., *Zh. Neorg. Khim.*, 2000, vol. 45, no. 6, p. 928.
27. Plyasova, L.M., Vasil'eva, N.A., Kriger, T.A., Shmakov, A.N., and Litvak, G.S., *Kinet. Katal.*, 2000, vol. 41, no. 4, p. 612.
28. Kuzmitskaya, S.Yu. and Vasilieva, N.A., *React. Kinet. Catal. Lett.*, 1996, vol. 58, no. 2, p. 335.
29. Kasimov, G.G., Manurin, Yu.N., Seleznev, V.D., and Zhelonkin, N.A., *Zh. Neorg. Khim.*, 1986, vol. 31, no. 4, p. 842.
30. Kovtunenko, M., *Fizicheskaya khimiya tverdogo tela: Kristally s defektami* (Physical Chemistry of Solids: Imperfect Crystals), Moscow: Vysshaya Shkola, 1993.
31. *Powder Diffraction File*, Swarthmore: Joint Committee on Powder Diffraction Standards, 1986, set 4, no. 829.
32. Warren, B.E. and Averbach, B.L., *J. Appl. Phys.*, 1952, vol. 23, no. 1, p. 497.
33. Wells, A.F., *Structural Inorganic Chemistry*, Oxford: Oxford Univ. Press, 1986.
34. Sokolova, M.M. and Vol'khin, V.V., *Zh. Neorg. Khim.*, 1997, vol. 42, no. 10, p. 1631.
35. Povarennykh, A.S., *Kristallokhimiya i klassifikatsiya mineral'nykh vidov* (Crystal Chemistry and Classification of Mineral Species), Kiev: Naukova Dumka, 1966, p. 547.
36. Kravchuk, L.S. and Ivashchenko, N.I., *Zh. Fiz. Khim.*, 1997, vol. 71, no. 10, p. 1781.
37. Vasil'eva, N.A. and Zarutskaya, N.L., *Sib. Khim. Zh.*, 1992, no. 2, p. 131.
38. Vasil'eva, N.A., Ermolaev, V.K., and Kuz'mitskaya, S.Yu., *Kinet. Katal.*, 1999, vol. 40, no. 1, p. 111.