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Structure of MgO-Based Catalysts Modified with $Mg(NO_3)_2$ and $LiNO_3$

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Abstract—The structure of magnesium oxide prepared by hydration in lithium nitrate and magnesium nitrate solutions and further thermal treatment is examined by X-ray analysis on a precision diffractometer using synchrotron irradiation. Magnesium oxide with a distorted lattice is formed when this preparation procedure is used, and the symmetry is reduced from cubic to rhombohedral. Distortions were more pronounced in the case of a sample treated with magnesium nitrate. The distortions are due to NO_3 groups incorporated into the oxygen framework of the oxide. Such a structure is stable up to 1000°C. The defects formed lead to the structure and charge inhomogeneity of the crystalline lattice. It is likely that these defects are responsible for the high catalytic activity of the samples.

INTRODUCTION

The catalytic activity of magnesium oxide essentially depends on the modification procedure. This is most frequently done by the impregnation and coprecipitation methods with of aqueous metal salts or by mixing pastes, drying, and thermal treatment [1–3]. A new procedure was proposed earlier for preparing defect magnesium oxide by hydrating a magnesium oxide reagent in a magnesium acetate solution, followed by the drying and calcination of the samples [4]. It was found that defect magnesium hydroxide was produced even at the stage of hydration; the defect oxide was formed from this hydroxide in the course of thermal treatment. Oxygen atoms of the acetate group took part in the formation of the oxygen framework of the oxide; in this case, the distorted residues of acetate groups remained in the structure of magnesium oxide, being transformed into cations with an effective positive charge and forming a substitutional solid solution [5]. The defect structure was retained upon calcination above 1000°C. The catalyst exhibited high activity and stability in chain-radical reactions of hydrocarbon pyrolysis [6].

The goal of this work was to examine the structure of magnesium oxide prepared by the hydration in a lithium nitrate or magnesium nitrate solution.

EXPERIMENTAL

A weighed portion of MgO precalcined at 800°C was immersed in a calculated amount of a concentrated lithium nitrate or magnesium nitrate solution. All the reagents used were of analytical grade. The hydration was performed for 8 days with stirring at regular intervals. The completeness of hydration was monitored by X-ray diffraction analysis. Next, the sediment was filtered off, washed, dried at 110°C, and calcined at some temperatures. The samples were designated as $MgO/LiNO_3$ and $MgO/Mg(NO_3)_2$, respectively. For comparison, a magnesium oxide reagent and magnesium hydroxide prepared by hydrating the initial MgO in water were used in the study.

Dried and calcined samples were examined by thermal analysis (DTA and TG) and diffraction analysis using X-rays and synchrotron irradiation. DTA and TG curves were recorded on a Q 1500D derivatograph (Hungary).

X-ray diffraction patterns were obtained on a D 500 diffractometer (Siemens) using CuK_α radiation and a graphite monochromator for the reflected beam. The diffraction patterns were obtained in the range of diffraction angles $2\theta = 5°–130°$. A precision diffractometer mounted on a synchrotron radiation beam at the Siberian Center of Synchrotron Radiation was used for the structure refinement. The diffraction patterns were obtained by scanning in the range of angles $2\theta = 35°–115°$ at a step of 0.04° using radiation with the wavelength $\lambda = 1.54$ Å and a Ge(III) analyzing crystal in the reflected beam. A Si (99.99999) powder was used as the reference sample. The lattice parameters were determined to within ±0.001 Å.

RESULTS AND DISCUSSION

A study of the phase composition of modified samples demonstrated that different hydroxide phases were formed even at the hydration stage, depending on the nature of the promoter. The thermal analysis curves of dried $Mg(OH)_2$ and $MgO/LiNO_3$ samples (Fig. 1) are almost identical, whereas the curves of the $MgO/Mg(NO_3)_2$ sample exhibit two dehydration effects that correspond to the thermal decomposition of $Mg(OH)_4(NO_3)_2$ and $Mg(OH)_2$, respectively [7]. In this

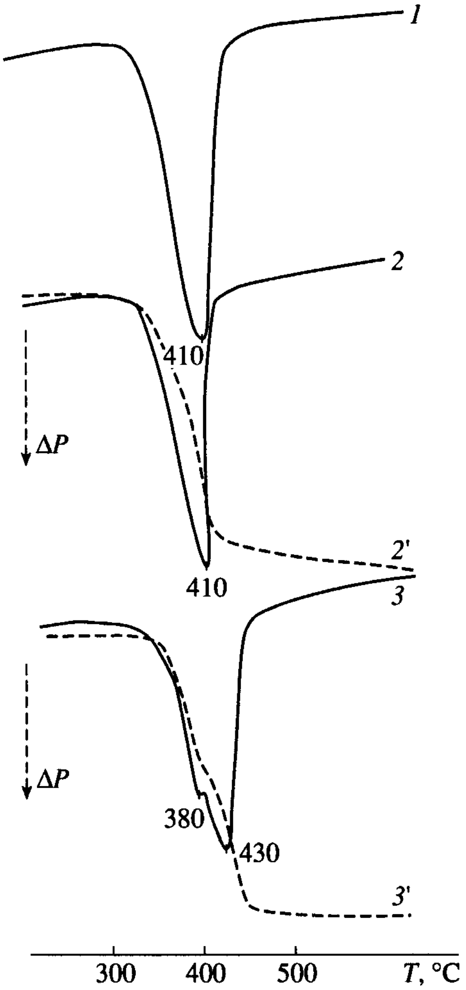

Fig. 1. Fragments of thermal analysis curves: (*1–3*) DTA curves of the $Mg(OH)_2$, $MgO/LiNO_3$, and $MgO/Mg(NO_3)_2$ samples, respectively; (*2'* and *3'*) TG curves of the $MgO/LiNO_3$, and $MgO/Mg(NO_3)_2$ samples, respectively.

case, the temperature of thermal decomposition of the modified magnesium hydroxide shifted toward higher temperatures as compared to pure magnesium hydroxide. Above this temperature, the sample is defect magnesium oxide. The TG curves indicate that in the course of calcination the $MgO/LiNO_3$ sample continued to suffer weight loss after the transformation of the hydroxide into the oxide, whereas the $MgO/Mg(NO_3)_2$ sample after its transformation into the oxide form exhibited no weight loss up to 800°C. To estimate more precisely the weight loss by the $MgO/Mg(NO_3)_2$ sample, we increased the weighed portion up to 300 mg and improved the sensitivity of balance. The weight loss was ~3 wt % in the temperature range 560–1000°C. According to IR-spectroscopic data, distorted NO_3 groups remained in the structure of magnesium oxide after the 4-h calcination of the sample at 1000°C.

A phase of the approximate composition of the hydroxide nitrate $Mg_3(OH)_4(NO_3)_2$ was formed upon the hydration of magnesium oxide in a magnesium nitrate solution. Upon the hydration of magnesium oxide in a lithium nitrate solution, a phase of $Mg(OH)_2$ with a somewhat decreased interlayer distance was formed, and a phase of the initial magnesium oxide was retained. Thus, the hydration of the initial magnesium oxide in a lithium nitrate solution was much slower than that in pure water and a magnesium acetate or magnesium nitrate solution.

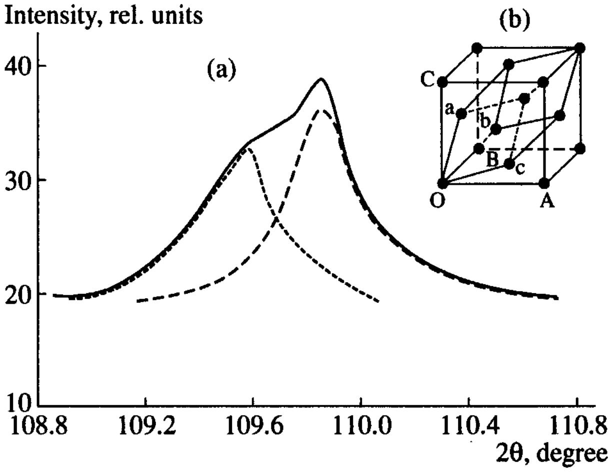

Fig. 2. (a) Fragment of the diffraction pattern of the $MgO/Mg(NO_3)_2$ sample in the region of the MgO 420 reflection ($\lambda = 1.54$ Å; synchrotron radiation) and (b) face-centered cubic cell (ABC) and the corresponding rhombohedral primitive cell (abc).

Because the magnesium oxide prepared by hydration in salt solutions differs from the ordinary oxide prepared by thermal decomposition of the hydroxide in the catalytic properties, we examined the former in detail. Samples calcined at 500°C were used for this purpose. The diffraction patterns for these samples were measured on a precision diffractometer using synchrotron irradiation. Figures 2 and 3 demonstrate the fragments of diffraction patterns in the range of angles $2\theta = 106°–112°$ for the $MgO/Mg(NO_3)_2$ and $MgO/LiNO_3$ samples, respectively.

$MgO/Mg(NO_3)_2$. The diffraction pattern of the sample calcined at 500°C at the diffraction angles $2\theta > 90°$ exhibits diffraction splitting (Fig. 2a). Note that this effect is difficult to reveal in the range of medium angles and with the use of polychromatic $\mathrm{Cu}K_{\alpha_1+\alpha_2}$ irradiation, which is commonly used in X-ray diffraction analysis. The diffraction splitting indicates that the structure of modified magnesium oxide exhibits rhombohedral distortion along the main diagonal of the cubic unit cell. Figure 2b shows the ratio between the axes of cubic and rhombohedral cells. The table summarizes the rhombohedral cell parameters. As can be seen, the angle α differs only slightly from the corresponding angle in a regular rhombohedron inscribed in a close-packed fcc lattice ($\angle\alpha = 60°$). However, this deviation ($\Delta\alpha = 0.08°$) is large enough for the reflex splitting at the angles $2\theta > 90°$ to be detected in diffraction patterns. For example, it is well known that the cubic structure of NiO is rhombohedrally distorted due to the discrepancy between the size of octahedral interstices of the oxygen packing and the ionic radius of Ni^{2+} [8]. In this case, it is likely that this structural distortion can be due to the presence of residual NO_3 groups in the oxygen framework of magnesium oxide.

To understand the mechanism of magnesium oxide modification with NO_3 groups, let us consider the structure of standard magnesium hydroxide [9]. It is well known that the brucite-like structure of $Mg(OH)_2$ consists of packs of double oxygen layers, and that magnesium ions are located in the octahedral interstices (Fig. 4a). The packs are bound together by weak hydrogen bonds. The close-packed oxygen layers are perpendicular to the [001] direction.

An analysis of the structure of hydroxide salts of bivalent metals and the data on the lattice parameters of magnesium hydroxide nitrate [10] allowed us to conclude that $Cu_2(OH)_3NO_3$, along with the known structure [11], is a structural analog of $Mg_3(OH)_4(NO_3)_2$. Packs of double oxygen layers, in the octahedral interstices of which magnesium ions are located, also form the basis of the magnesium hydroxide nitrate structure. These packs are joined together primarily by hydrogen bonds and partly by NO_3 groups, which are arranged so that one oxygen atom of the group is in a pack, and the other two, in the interlayer space (Fig. 4c). The NO_3 groups represent a triangle of oxygen atoms at the center of which a nitrogen atom is placed. The other oxygen atoms shown in Fig. 4c belong to hydroxyl groups. With an increase in the temperature during dehydration, water and a portion of NO_3 groups are released, and the anionic framework of the hydroxide (a double-layer hexagonal framework) is rearranged to form the oxide structure (an fcc lattice) with a redistribution of magnesium ions throughout all octahedrons of the new oxygen packing. In this case, the [001] direction of the closest packing of oxygen layers of the hydroxide structure is changed to the [111] direction of the closest packing of the oxide structure (Fig. 4b). It is likely that the complete displacement of NO_3 groups is hindered because at least one oxygen ion in each of these groups is incorporated into a close-packed oxygen layer; thus, a portion of NO_3 groups is retained in the anionic framework of magnesium oxide. As in the modification of magnesium oxide with magnesium acetate, oxygen of the anion completes the oxygen framework of magnesium oxide formed in the course of calcination, retaining the anionic NO_3 group in the oxide structure.

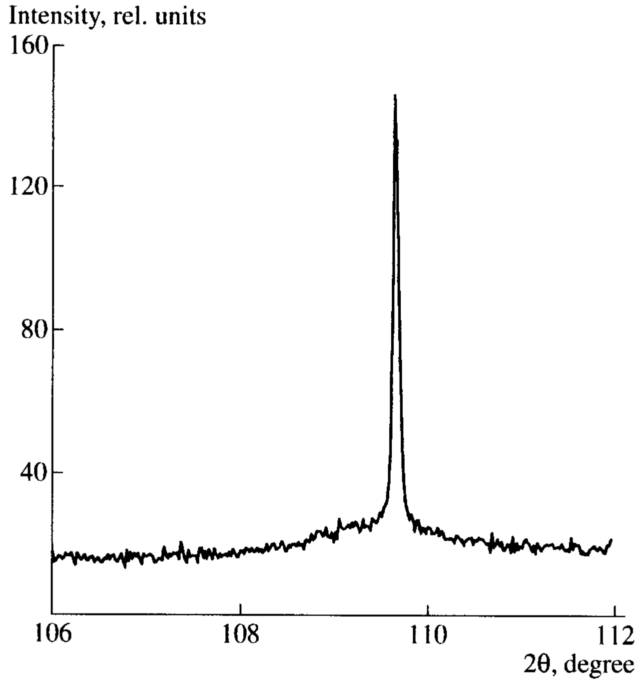

Fig. 3. Fragment of the diffraction pattern of the $MgO/LiNO_3$ sample in the region of the MgO 420 reflection ($\lambda = 1.54$ Å; synchrotron radiation).

The structure of the NO_3^- group is a triangle of oxygen ions at the center of which a nitrogen ion is located. The O–O distances in the group are ~2.4 Å; this value is somewhat shorter than the O–O distances in close-packed structures (2.7–3.0 Å) [9]. All NO_3 groups in the structure of modified magnesium hydroxide are orderly, arranged parallel to the [001] direction. Thus, the [001] direction changes to [111] in the hydroxide ⟶ oxide transition, whereas the orientation of NO_3 was retained in MgO along the [111] direction, that is, the body diagonal of the cubic lattice of MgO (Figs. 4d and 2b). This results in shortening the body diagonal of the unit cell and in lowering the symmetry to a rhombohedral structure. The presence of NO_3groups results in the occur-

X-ray diffraction characteristics of samples

T, °C	$MgO/Mg(NO_3)_2$	$MgO/LiNO_3$
110	$Mg(OH)_2 + Mg_3(OH)_4(NO_3)_2$	$Mg(OH)_2$ + MgO
500	MgO (rhombohedral): $a = 2.975(3)$ Å $\alpha = 59°55'$ (59.92°), Coherent-scattering region ≈ 100 Å	$MgO^{(1)}$: $a = 4.219(4)$ Å, Coherent-scattering region ≈ 100 Å $MgO^{(2)}$: $a = 4.213(4)$ Å, Coherent-scattering region ≈ 1000 Å

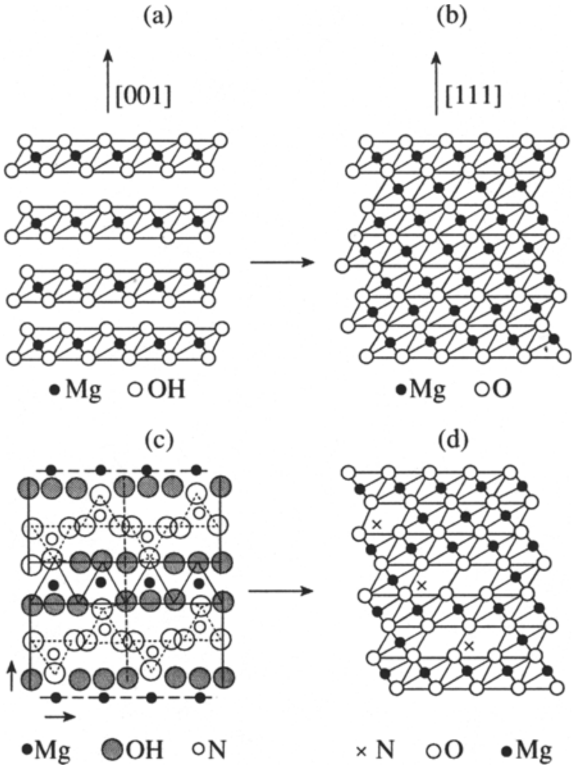

Fig. 4. Relationship between the structures of Mg hydroxides and oxides: (a) [001] $Mg(OH)_2$, (b) [111] MgO, (c) [001] $Mg_3(OH)_4(NO_3)_2$, and (d) [111] MgO.

rence of cation vacancies (□) in the structure. Taking into account that the weight loss due to a loss of NO_3 groups is ~3%, the empirical formula of the defect magnesium oxide can be presented as $Mg_{0.925}\square_{0.045}(NO_3)_{0.03}O_{0.91}$ or, more precisely, $(Mg_{0.925}N_{0.03}\square_{0.045})O$. This structure is stable up to 1000°C. The deviation of the structure of defect magnesium oxide from perfect and the retention of NO_3 groups in the structure are consistent with the IR-spectroscopic data, which will be published elsewhere.

$MgO/LiNO_3$. The diffraction pattern of magnesium oxide modified with lithium nitrate is different from that of $MgO/Mg(NO_3)_2$. As can be seen from Fig. 3 using the 420 line as an example, each diffraction line of the lithium-containing sample exhibits a rather extended halo. Thus, two phases different in the dispersities can be distinguished. One of them is well-crystallized cubic MgO with the parameter $a = 4.213$ Å, which is close to the tabulated data [12], and the other is a highly dispersed phase ($D \approx 100$ Å) with the somewhat greater parameter $a = 4.219$ Å (in the cubic packing). We cannot conclude whether this phase is defective and distorted, much like $MgO/Mg(NO_3)_2$, because it occurred in a small amount in the presence of ordinary magnesium oxide. Judging from the data of IR spectroscopy, this highly dispersed phase of MgO also exhibits structural distortions due to the presence of NO_3 groups, and these distortions are similar to distortions in the $MgO/Mg(NO_3)_2$ sample.

Thus, magnesium oxide with a distorted lattice resulted from the hydration of the initial magnesium oxide in solutions of magnesium nitrate or lithium nitrate followed by drying and calcination of the samples. The distortion was more pronounced in the case of $MgO/Mg(NO_3)_2$ and less pronounced in the case of $MgO/LiNO_3$. The distortion resulted from NO_3 groups incorporated into the oxygen framework of the oxide. The extensive defects formed produce the structure and charge inhomogeneity of the crystal lattice and they are apparently responsible for the high catalytic activity of the samples.

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