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Electrical Conductivity of Magnesium Oxide as a Catalyst for Radical Chain Hydrocarbon Pyrolysis Reactions

N. A. Vasil'eva*[,a] and N. F. Uvarov[b]

[a] *Boreskov Institute of Catalysis, Siberian Branch, Russian Academy of Sciences, Novosibirsk, 630090 Russia*
[b] *Institute of Solid State Chemistry and Mechanochemistry, Siberian Branch, Russian Academy of Sciences, Novosibirsk, 630128 Russia*
* *e-mail: nel@catalysis.nsk.su*

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Abstract—The electrical conductivity of polycrystalline MgO between 350 and 750°C is determined by the transport of surface electronic and hole defects and depends on the applied voltage. Near 620°C at low applied voltages, the conductivity decreases by 1–2 orders of magnitude in a narrow temperature range (ΔT = 75°C), and this is accompanied by a change of the sign of the surface charge carriers. The "ignition" of the catalytic activity of magnesium oxide in free radical generation in radical chain hydrocarbon pyrolysis is observed in the same temperature range. It is assumed that the change of the sign of the charge carriers is due to the existence of an isoelectric temperature T_i and that, at $T > T_i$, $O_O^{\cdot}$ defects come out to the magnesium oxide surface.

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Magnesium oxide is widely used as a catalyst for one-electron processes, such as photochemical reactions and methane oxidative dimerization [1], and in nonbranched-chain hydrocarbon pyrolysis [2–5]. It was demonstrated theoretically that the activity of the catalyst and its role in the nonbranched-chain process depend on the active site concentration and on the active site–adsorbed radical binding energy [2, 5]. When the binding energy is comparable with the bond energies in the hydrocarbon molecules, the role of the catalyst is to generate an additional amount of chain carrier radicals and to release them into the gas phase. This accelerates the homogeneous steps of the heterogeneous–homogeneous process. The number of radicals approaches its thermodynamic limit. In practice, this raises the hydrocarbon conversion at lower temperatures and alters the proportions of pyrolysis products, increasing the yield of α-olefins and light paraffins—$^{\cdot}CH_3$, $^{\cdot}C_2H_5$, and $H^{\cdot}$ recombination products.

Direct experimental evidence of the generation of extra radicals was obtained by an EPR study of *n*-undecane pyrolysis on various catalysts at a reduced pressure followed by freezing out the free radicals in the resonator of the EPR spectrometer [4, 6]. Magnesium oxide is among the catalysts capable of generating free radicals. Conventional pyrolysis with a typical activation energy of E_a = 335 kJ/mol takes place in the reactor up to a certain temperature in spite of the presence of magnesium oxide. The amount of the resulting radicals is in agreement with the theoretical value obtained using the kinetic scheme of the chain process. At $T \approx 630$°C, the amount of radicals increases sharply, approaching the thermodynamic limit, and the activation energy of generation of radicals decreases to 63 kJ/mol. This effect can be called the "ignition" of catalytic activity.

Two causes of this "ignition" are possible. High temperature is always favorable for the appearance of free radicals in the gas phase. These radicals interact with the catalyst surface to generate active sites. The lifetime of these sites is sufficiently long for heterogeneous–homogeneous chain propagation.

The "ignition" effect can also arise from the specific features of the catalyst. Charge carriers are injected in the catalyst bulk under the above-specified experimental conditions, and they diffuse to the surface to generate stable radical surface sites active in radical chain processes. The steady-state concentration of these sites is determined by the ratio of the charge carrier injection and relaxation rates in the catalyst bulk on the one hand and by the gas-phase radical generation and disappearance reactions on the other hand.

The catalytic activity of ordinary MgO, like that of most oxides, is usually due to the presence of surface defects [7]. It is hypothesized that $O_O^{\cdot}$ hole sites can appear on the magnesium oxide surface. Chemically, these sites are radicals, so they can serve as catalytic sites initiating heterogeneous–homogeneous radical chain reactions of hydrocarbons.

In order to verify this assumption, it is necessary to elucidate the nature of the active sites on the magnesium oxide surface that are potential charge carriers.

For this purpose, we studied the electrical conductivity of magnesium oxide in the temperature range in which this compound shows high catalytic activity.

EXPERIMENTAL

Electrical conductivity (σ) was measured in commercial polycrystalline MgO (reagent grade). The samples were 280-mg pellets 1.2 cm in diameter and 0.15 cm in thickness with silver electrodes pressed into them at a pressure of 500 MPa. Measurements were performed in a vacuumized quartz cell with two pressure contacts and platinum leads. The heat removal system in the cell was asymmetric: one of the electrodes was entirely deep in the cell, while the other was in contact with the cell wall. This design allowed a small temperature gradient (~1 K) to be maintained between the electrodes so as to generate a thermal emf and, accordingly, a thermostimulated current. Before each series of measurements, the sample was conditioned according to the following protocol: (1) heat treatment at $T = 750$°C and $P = 5 \times 10^{-4}$ Torr for 2 h, (2) admission of oxygen at 750°C up to 40 Torr followed by pumping and holding at $P = 5 \times 10^{-4}$ Torr for 20 min, (3) admission of hydrogen at 750°C up to 40 Torr followed by pumping and holding at $P = 5 \times 10^{-4}$ Torr for 20 min, and (4) admission of oxygen at 750°C and pumping at $P = 5 \times 10^{-4}$ Torr for 2 h.

The gases were purified to remove the moisture and other possible impurities by passing them through purifying columns. This treatment ensured good data reproducibility. Electrical conductivity was measured at reduced pressures (10^{-1}–10^{-4} Torr) between 450 and 720°C using a two-electrode technique. Current intensity in the 10^{-11}–10^{-7} A range was measured with a V7-30 electrometric voltmeter. A constant voltage in the 0–15 V range was maintained using a B5-47 dc power supply or an autonomous battery. Electrical conductivity was calculated via the equation $\sigma = (I/U)(L/S)$, where I is the current intensity, U is the voltage, L is the thickness of the pellet, and S is the electrode surface area. Thermostimulated current was measured in the same cell with the power supply switched off. "Fresh," nonpolarized samples were used in these measurements. For same samples, we measured ac conductivity. In this case, current intensity was derived from the voltage drop across a standard resistor connected in series with the sample. The voltage drop was measured with a Unipan-237 selective nanovoltmeter. The ac power supply was a G3-112 voltage generator.

RESULTS AND DISCUSSION

Electrical Conductivity of MgO

Figure 1a plots typical temperature dependences of the electrical conductivity of MgO at $P = 5 \times 10^{-4}$ Torr under heating and cooling conditions. At temperature ramp rates of 3 K/min and above, the conductivity

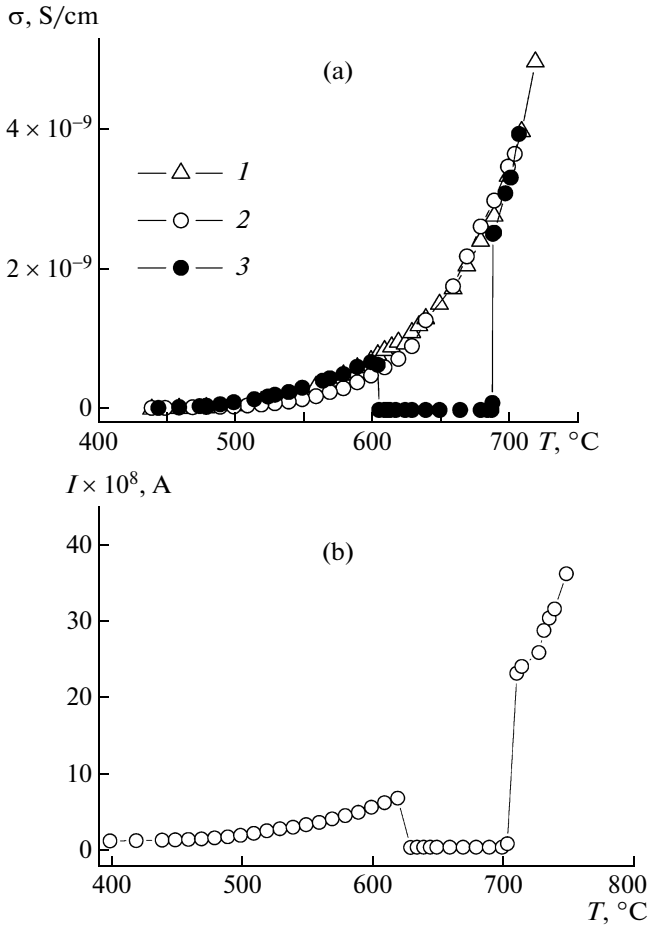

Fig. 1. (a) Temperature dependence of the electrical conductivity of MgO under (*1*) rapid (3–10 K/min) heating, (*2*) rapid cooling, and (*3*) slow (0.5 K/min) heating. The measurements were taken at $P = 3 \times 10^{-4}$ Torr and $U = 3$ V. (b) Intensity of the ac current in magnesium oxide as a function of temperature. The ac frequency is 113 Hz; $U = 3$ V.

curves recorded in the heating and cooling modes coincide closely (curves *1*, *2*). Under slow heating (<1 K/min), the conductivity curve has a crevasse (curve *3*): σ first falls abruptly and then, as the temperature is raised, increases equally sharply to reach the curve recorded at the higher heating rate.

The electrical conductivity shows an Arrhenius temperature dependence (Fig. 2). At a fixed voltage, the conductivity drop temperature T_0 varies from one experimental series to another within 40 K, but in all cases T_0 increases as the applied voltage U is raised. For example, $T_0 = 560$°C at $U = 1$ V, 600°C at $U = 5$ V, and 700°C at $U = 7$ V. The crevasse width ΔT also varies, narrowing as the voltage is increased: at $U = 1$, 5, and 7 V, ΔT is ~70, 40, and 10 K, respectively. No conductivity crevasse is observed at $U = 8$–15 V. The activation energy of conduction (E_a) measured at a fixed voltage outside the crevasse is independent of the heating rate. At T = 450–720°C and U = 3 V, $E_a \approx$

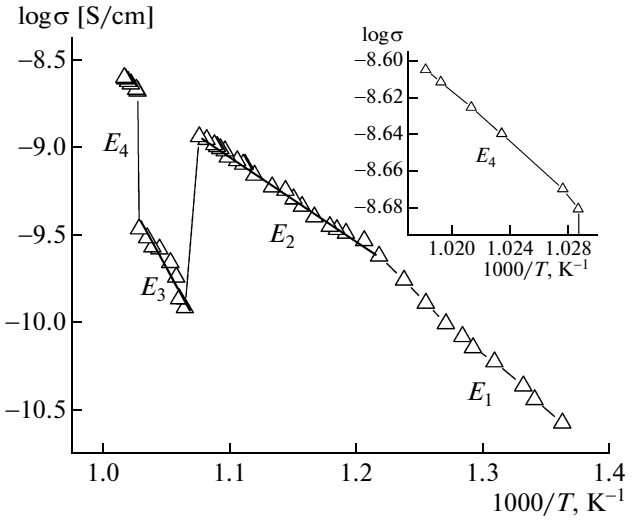

Fig. 2. Arrhenius plots of the electrical conductivity of MgO obtained at $U = 3$ V and $P = 5 \times 10^{-4}$ Torr under slow heating conditions. Inset: high-temperature range ($T > 700$°C). The activation energies in the temperature ranges indicated here are $E_1 = 129 \pm 10$ kJ/mol, $E_2 = 100 \pm 8$ kJ/mol, $E_3 = 270 \pm 30$ kJ/mol, and $E_4 = 130 \pm 6$ kJ/mol.

130 kJ/mol. To rule out all artifacts, including the appearance of the conductivity crevasse as a result of electrode polarization, we measured the ac conductivity of magnesium oxide (ac frequency of 113 Hz, $U =$ 3 V) at a low sample heating rate. In this experiment, a conductivity crevasse was observed as well (Fig. 1b). Therefore, this crevasse is an inherent property of magnesium oxide showing itself only at low sample heating rates.

The values of σ and E_a depend considerably on the applied voltage U. Figure 3 plots the activation energy of conduction as a function of the applied voltage for a high sample heating rate. This kind of dependence is characteristic of electron or hole conductivity, when space charge–limited currents are induced, and is unnatural for ion conductivity.

The electrical conductivity at the "bottom" of the crevasse is also temperature-dependent. However, because of the extremely low current intensity ($I < 10^{-11}$ A), it was only possible to estimate the conductivity value. The activation energy at different U values was estimated to be 270–400 kJ/mol, much higher than E_a outside the crevasse.

Thermostimulated Ion Current

Figure 4 demonstrates how the thermostimulated current intensity depends on temperature when the external power supply is switched off. Under slow heating, a sharp decrease in the thermostimulated current intensity in magnesium oxide is observed about 620°C. Between 620 and 730°C (where the conductivity versus temperature curve shows a crevasse), the current intensity almost falls to zero ($|I| < 10^{-12}$ A). As the temperature is further raised, the thermostimulated current changes its sign and grows in magnitude. As the sample is cooled, the reverse abrupt change in current intensity and current reversal take place at 620°C, and the temperature interval in which $I \approx 0$ is rather narrow. Recall that, at ~630°C, the catalytic activity "ignition" effect is observed in radical generation.

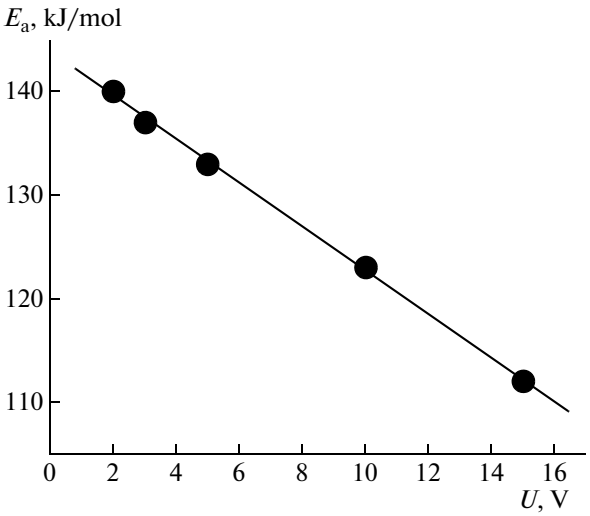

Fig. 3. Activation energy of conduction at low temperatures as a function of the applied voltage. The measurements were taken under rapid heating at 5×10^{-4} Torr.

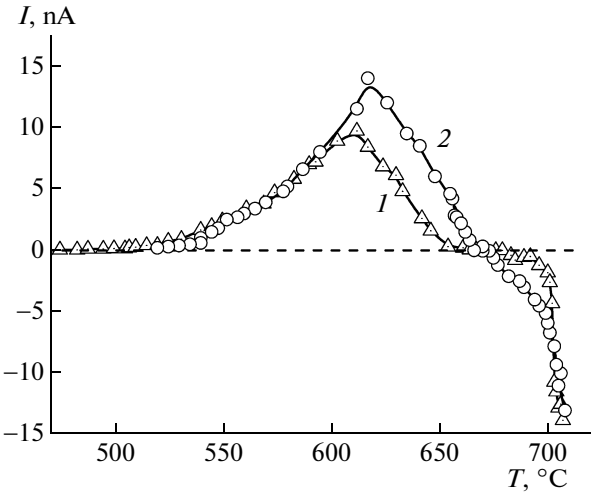

Fig. 4. Temperature dependence of the thermostimulated current in the sample not subjected to prepolarization: (*1*) slow heating and (*2*) cooling. The measurements were taken in the absence of external voltage at $P = 5 \times 10^{-4}$ Torr. The sign of the current corresponds to the polarity of the colder electrode.

Point Defects and Transport Properties of Magnesium Oxide

There are only a few publications dealing with the electrical conductivity of magnesium oxide [7–10]. At 1200–2000°C, this compound possesses mixed, ion–electron conductivity. At atmospheric pressure, the dominant electron carriers are holes. The conductivity of MgO in a reductive medium is largely due to electrons. The quasi-chemical reactions yielding intrinsic Schottky defects and intrinsic electron–hole pairs can be represented, using Kröger's notation, as the following equations:

$$0 \longleftrightarrow V''_{Mg} + V^{\bullet\bullet}_{O}, \quad \text{(I)}$$

$$0 \longleftrightarrow n' + p^{\bullet}, \quad \text{(II)}$$

where the symbols 0, V''_{Mg}, $V^{\bullet\bullet}_{O}$, n', and $p^{\bullet}$ stand for an ideal crystal, cationic vacancy, anionic vacancy, electron, and hole, respectively. In the localized electronic states model, a hole $p^{\bullet}$ is a defect electron or a hole site $O^{\bullet}_{O}$ (singly charged oxygen anion in the MgO lattice). This site travels in the crystal and, upon stabilization on the surface, forms a surface hole site $[O^{\bullet}_{O}]_S$, which can serve as a catalytic site. Calculations demonstrate that the formation energy of a point defect (E_S) and the band gap (E_g) in MgO are fairly large (~7.4 eV [9] and 6.7 ± 0.4 eV [11], respectively). It can, therefore, be assumed that the observed conductivity is extrinsic and is due to extrinsic cationic vacancies and donor–acceptor sites.

Polycrystalline magnesium oxide (reagent grade) always contains Cr^{3+}, Mn^{3+}, and Fe^{3+}, whose total concentration can be up to several hundreds of parts per million. When the impurities are triply charged cations (M^{3+}), the dominant defects are cationic vacancies generated according to the equation

$$0 \longleftrightarrow 2M^{\bullet}_{Mg} + V^{\bullet\bullet}_{Mg}, \quad \text{(III)}$$

which cancel out the extra charge associated with the impurity cations ($M^{\bullet}_{Mg}$).

Cationic vacancies have low mobility, and the activation energy of their formation is 2.2 eV. The conductivity due to the magnesium and oxygen ions can be calculated from experimental self-diffusion coefficients using the Nernst–Einstein relationship, $\sigma/D \sim 4e^2N/kT$, where e is the electron charge and $N = 10^{22}$ cm^{-3}. Because of the low mobility of the ionic charge carriers, the total conductivity of magnesium oxide is largely due to electrons (at low oxygen pressures) and hole sites (at high oxygen pressures). The latter result from the following redox quasi-chemical reactions:

$$O^{\times}_{O} + V''_{Mg} \longleftrightarrow 1/2O_2 + 2n', \quad \text{(IV)}$$

$$1/2O_2 + 2M^{\bullet}_{Mg} \longleftrightarrow O^{\times}_{O} + 2p^{\bullet}, \quad \text{(V)}$$

where $O^{\times}_{O}$ is an effectively uncharged oxygen ion in its normal position. Equations (I)–(V) provide a satisfactory description for the experimental conductivity data for iron oxide–containing MgO at 1200–1600°C and oxygen partial pressures of 10^{-1}–10^{-12} MPa.

Calcination of magnesium oxide dehydrates its surface, which always contains hydroxyl groups, $OH^{\bullet}_{O}$. This process can be viewed as the following quasi-chemical reaction [12]:

$$V''_{Mg} + 2OH^{\bullet}_{O} \longrightarrow [O^{\bullet}_{O}–V''_{Mg}–O^{\bullet}_{O}]^{\times} + H_2, \quad \text{(VI)}$$

which yields metastable $[O^{\bullet}_{O} - V''_{Mg} - O^{\bullet}_{O}]^{\times}$ complexes. These complexes are sources of hole sites:

$$[O^{\bullet}_{O}–V''_{Mg}–O^{\bullet}_{O}]^{\times} \longleftrightarrow [O^{\bullet}_{O}–V''_{Mg}]' + O^{\bullet}_{O}. \quad \text{(VII)}$$

On being heated above 600–800°C, these complexes decompose to release gaseous oxygen:

$$[O^{\bullet}_{O}–V''_{Mg}–O^{\bullet}_{O}]^{\times} \longrightarrow O^{\times}_{O} + V''_{Mg} + V^{\bullet\bullet}_{O} + 1/2O_2. \quad \text{(VIII)}$$

According to the literature [12, 13], the low-temperature conductivity of single-crystal magnesium oxide is due to the above metastable hole sites. The activation energy of conduction is reported to be 1 eV at low temperatures and to increase to ~3.2 eV near the decomposition temperature of the complex.

The $[O^{\bullet}_{O} - V''_{Mg} - O^{\bullet}_{O}]^{\times}$ hole complexes were also described by other authors [14]. They result readily from X-ray or UV irradiation of magnesium oxide. This is accompanied by the generation of *F*-sites—electrons captured by $[n' - V^{\bullet\bullet}_{O} - n']^{\times}$ anionic vacancies. These *F*-sites have been studied in greater detail [15] than the hole sites.

Note that processes (VI)–(VIII) occur in the temperature range in which the catalytic activity of magnesium oxide increases. Unfortunately, surface conductivity data for magnesium oxide are lacking in the literature. For example, Kathrein and Freund [12] did not specify the locus of the metastable hole complexes (crystal bulk or surface) and did not consider the specific features arising from surface properties.

The data obtained in this study enabled us to distinguish between the bulk and surface conductivities. The activation energy of low-temperature conduction is 1–2 eV, far below the activation energies characteristic of ion and electron transport in MgO single crystals. It can, therefore, be assumed that the conductivity measured in this study is due to "biographical" metastable

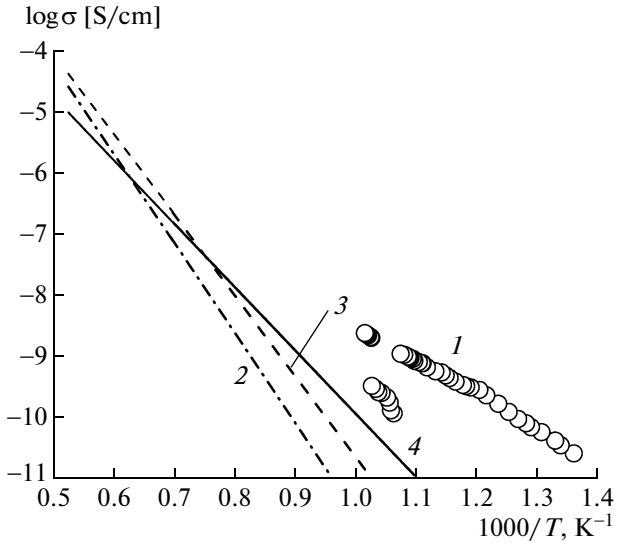

Fig. 5. Comparison of the MgO conductivities (*1*) measured in this study with the (*2*) electron, (*3*) hole, and (*4*) ion conductivities of single-crystal MgO containing 300 ppm Al^{3+} [7, 9]. The straight lines were obtained by extrapolating high-temperature (1200–1600°C) data to the temperature range examined in this study.

defects in the sample bulk or surface defects (surface conductivity). When the conductivity is determined by the metastable defects, it varies with time as successive heating–cooling cycles are performed, because these defects are progressively annealed and annihilate. Just this effect was observed by Kathrein and Freund [12]: above 600°C, the metastable defects, namely, the $[O_O^{\bullet} - V_{Mg}'' - O_O^{\bullet}]^{\times}$ hole complexes and $O_O^{\bullet}$ sites underwent annealing, and this reduced the observed conductivity to the level typical of "normal" single crystals heat-treated at a high temperature for a long time.

In our experiments, no irreversible decrease in conductivity was observed and the character of conductivity did not change over several heating–cooling cycles throughout the 450–750°C range. Therefore, the defects responsible for conduction in our samples are stable. It is very likely that they are localized on the surface or in the subsurface layer and the samples are surface-conducting. Figure 5 compares the experimental MgO conductivities measured in this work to the electron, hole, and ion conductivities of an MgO single crystal containing 300 ppm Al^{3+} [7, 9]. The straight lines plotted in Fig. 5 were obtained by extrapolating high-temperature data (1200–1600°C) to the temperature range in which our measurements were taken. Our conductivity values are several orders of magnitude higher than the conductivity of the single-crystal oxide, indicating that our samples are surface-conducting rather than bulk-conducting.

Defect Equilibrium on the Surface and Interpretation of Experimental Data

The surface conductivity of an ionic crystal is determined by the defects forming the electrical double layer on the crystal surface. The double layer is enriched with point defects, and conduction is usually due to the location of charge carries in the diffuse layer under the crystal surface [16–20]. Model calculations [12] demonstrated that the concentration of extrinsic ion defects (impurity cations and cationic vacancies) in magnesium oxide is 5–10 orders of magnitude higher than the concentration of electrons and holes. Nevertheless, according to experimental data [9, 10], conduction in MgO above 1000°C is due to electrons or hole sites, depending on the oxygen partial pressure. This is explained by the fact that the electrons and holes are much more mobile than the ions.

Therefore, the double layer potential on the oxide surface at the temperatures examined in this study is determined by the equilibrium of ionic, not electronic, defects. The formation of the electrical double layer is due to the difference between the energies of internal adsorption of bulk defects on oppositely charged surface defects of the crystal. For example, if the energy of adsorption on the surface cationic vacancy V_{Mg}'' in MgO is negative and its absolute value is larger than the corresponding energy for the anionic vacancy $V_O^{\bullet\bullet}$, the surface will be negatively charged. The diffuse layer under the surface will be enriched with $V_O^{\bullet\bullet}$ defects. The surface conductivity of ionic crystals is determined by the sum of the contributions from the defects located just on the surface and the defects located in the bulk of the diffusion layer. The surface charge of ionic crystals containing heterovalent impurities is determined both by the balance of the energies of adsorption on intrinsic and extrinsic defects (in the case of extrinsic $M_{Mg}^{\bullet}$ defects, the segregation energy of the M^{3+} cation) and by the impurity concentration. As a rule, the surface potential at low temperatures is determined by the charge of the extrinsic defects (in the case considered, $M_{Mg}^{\bullet}$ or $OH_O^{\bullet}$). As the temperature is increased, the concentration of intrinsic defects increases, and, at some $T = T_i$ (isoelectric temperature), the surface charge changes its sign.

According to the data presented in Fig. 3, the charge carriers in the samples are electronic and hole defects. The sign of the charge on the electrodes at a preset temperature gradient in the sample allows the polarity of the charge carriers to be determined unambiguously. As judged from the polarity of the thermostimulated current, the charge carriers below the conductivity crevasse temperature are positive and are likely $O_O^{\bullet}$ hole sites located in the diffuse surface layer, the activation energy of conduction being ~130 kJ/mol.

The surface charge is negative and is due to adsorption on the cationic vacancies V''_{Mg}. Apparently, the crevasse region (Fig. 1) contains the isoelectric temperature $T_0 \approx T_i \approx 620$°C. As this temperature is approached, the surface potential falls to zero and then changes its sign. This is proved by the thermostimulated current data (Fig. 4). Because the concentration of charge carriers (electrons n' and holes $p^{\bullet}$) is very low, a decrease in the number of carriers is accompanied by a disproportionately large decrease (or increase) in conductivity. This is the cause of the abrupt drop in conductivity near the T_i point and of the formation of the crevasse. At the bottom of the crevasse, the surface potential and surface conductivity are low and, accordingly, the total electrical conductivity is determined by the ionic defects in the crystal bulk. These can be holes and cationic vacancies. The activation energy of conduction for these carriers must be higher, equal to the activation energy for an MgO single crystal, and this is actually observed experimentally.

Above T_i, the surface potential changes its sign. The cationic vacancies V''_{Mg} pass into the diffusion layer, and the anionic vacancies $V_O^{\bullet\bullet}$ and hole sites $O_O^{\bullet}$ come out to the surface. The holes form a dense layer on the surface, and the electrons n' accumulate in the diffuse layer, giving rise to electron conductivity with an activation energy close to that of $p^{\bullet}$-conduction. Because the recharging of the surface occurs slowly, during rapid heating or cooling this process can be detected only as a slight change in the activation energy. When strong local electric fields are appear as a result of charge carrier injection, the double layer structure can be disturbed, causing a hysteresis and crevasse smearing and disappearance. Therefore, our observation of the conductivity crevasse, not a conventional change in the slope of the Arrhenius plot, is due to the appropriately chosen experimental conditions, which allowed the electrical properties of magnesium oxide to be studied in greatest possible detail in the temperature range in which the oxide shows catalytic activity in free radical generation.

Thus, polycrystalline magnesium oxide is surface-conducting between 350 and 750°C. The isoelectric temperature T_i, at which the surface of the oxide changes its sign, has been determined. Near T_i, the charge carrier concentration decreases sharply and the electric conductivity falls by 1–2 orders of magnitude. Above T_i, $O_O^{\bullet}$ defects come out to the surface, which serve as active sites in free-radical processes. The temperature interval of the conductivity crevasse coincides with the temperature range in which MgO is catalytically active in hydrocarbon pyrolysis [2–5]. Therefore, the catalytic activity of magnesium oxide in radical chain processes and the catalytic activity "ignition" effect [3] are likely due to the recharging of the surface at the isoelectric temperature T_i and to the $O_O^{\bullet}$ active sites emerging on the surface.

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