

Hydrogen Release during the Thermal Decomposition of Magnesium Hydroxide to Magnesium Oxide

R. MARTENS,¹ H. GENTSCH² AND F. FREUND¹

¹ *Mineralogisches Institut der Universität zu Köln, Zülpicher Strasse 49, 5000 Köln 1, Germany.*

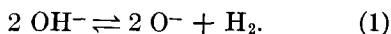
² *Institut für Physikalische Chemie, Callin Strasse 36, 3000 Hanover, Germany*

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Hydrogen and oxygen evolution from MgO prepared by thermal decomposition of high purity Mg(OH)₂ was studied mass spectroscopically. Hydrogen is evolved in the temperature range 300–600°C (maximum at 450°C) and again between 600 and 900°C (maximum at 750°C). The amount of H₂ evolved is of the order of 10¹⁹–10²⁰ molecules g⁻¹ MgO. An equivalent amount of oxygen appears to be evolved predominantly as atomic oxygen between 600 and 900°C. The first H₂ evolution is assigned to the formation of H₂ molecules within cation vacancies [Mg][•] in the MgO neighbored by two OH⁻ groups, leading to the formation of O⁻ ions: 2 OH⁻ ⇌ 2 O⁻ + H₂. The second H₂ evolution is assigned to the dissociation of residual OH⁻ groups: OH⁻ → O⁻ + ½H₂. The oxygen evolution is probably due to decomposition of O⁻: 2O⁻ → O²⁻ + O. The O⁻ concentration in the MgO calculated on the basis of these experiments is 10⁴–10⁶ times higher than the concentration of V_I centers achieved by thermal activation and measured by esr. This indicates that only a very small fraction of the O⁻ ions present in the sample is able to form V_I centers.

INTRODUCTION

Recently, in an *ab initio* calculation of the linear atomic chain [Mg–O–H...H–O–Mg]²⁺ Derouane *et al.* (1) have evaluated the possibility of the formation of molecular hydrogen within a cation vacancy [Mg][•] in MgO neighbored by two residual OH⁻ groups. The results predict that there exists an arrangement [Mg–O...H–H...O–Mg]²⁺ which is metastable at a H–H distance of 0.80 Å, close to the H–H value, 0.746 Å, in the free H₂ molecule. The underlying reaction can be written as:



For each hydrogen molecule evolved two O⁻ ions are formed which are positive holes with respect to the surrounding O²⁻ sublattice.

This reaction is of prime importance for the understanding of the formation of V-

type centers by thermal activation in MgO. Such V-type centers are trapped-hole centers in different steric arrangements either at the surface or in the bulk of the oxide.

Hydrogen-containing hole centers in irradiated MgO single crystals were first reported by Wertz *et al.* (2) and Kirklin *et al.* (3). The esr spectrum of O⁻-containing centers on magnesium oxide powder surfaces has been observed by Smith and Tench (4), Nelson and Tench (5), Williamson *et al.* (6), and Wong and Lunsford (7) after uv-irradiation and subsequent reaction with N₂O or after γ-irradiation in the presence of hydrogen gas (8, 9). MgO powder first heated in vacuum and then exposed to ionizing radiation (10) is long known to be catalytically active for the hydrogen-deuterium exchange reaction H₂ + D₂ ⇌ 2 HD even at 77 K. This

activity was first related to the presence of a V_I center consisting of an O^- ion associated to a cation vacancy (10). More recently Boudart *et al.* (11) have established that by thermal activation alone, i.e., without ionizing radiation, paramagnetic V-type centers can be produced in MgO which are catalytically active for the H/D exchange reaction. This center was called V_I . It is believed to consist of a triangular array of three O^- ions on an MgO (111) surface plane with a nearby cation vacancy. The catalytic site then consists of an OH-group adjacent to the V_I center. The V_I center can be transformed reversibly into the related V_I^* center by thermal treatment and into six other centers by adsorption of various gases (12).

In order to observe the V_I center in thermally activated MgO extremely pure samples are needed. If transition metal impurities are present, the esr signal of the V_I center is reduced in intensity or lost. Derouane and Indovina (13) have been able to show that transition metal ions, mainly Mn^{2+} , readily react with the O^- ions giving trivalent cations and O^{2-} ions.

The highest V_I center concentration reached in thermally activated MgO was of the order of $10^9/cm^2$ or $10^{15}/g$ MgO (11), slightly more when deuteroylated MgO powders were used (14).

All V-type centers have in common O^- ions. While the V_I center and others of rather complex structure with electronically interacting O^- ions have discernible esr signals, single O^- ions in MgO powders in low concentration have not been detected by esr. For this reason the total concentration of O^- in MgO is unknown. It is probably much higher than the V_I center concentration. From the observation that the V_I center takes a rather long time to form thermally (11)—typically several hours at 800 K—one might conclude that diffusional processes, involving O^- ions, play an important role: the positive holes must first migrate to certain favorable

lattice or surface sites—such as a (111) face—where they may form the stable clusters which give rise to the well-defined esr signals. In order to obtain quantitative information about the total concentration of O^- ions in thermally activated MgO we have undertaken a mass spectroscopic study of the hydrogen release during the thermal decomposition of $Mg(OH)_2$.

EXPERIMENTAL METHODS

A hydrocarbon-free, mercury-sealed, all-glass ultrahigh vacuum line, bakeable to 450°C, with two mercury diffusion pumps staged in tandem and liquid nitrogen traps was used in the present experiments. The base pressure was in the range of 10^{-9} Torr. The $Mg(OH)_2$ samples were prepared separately in a conventional vacuum line by vapor phase hydration of high purity MgO (supplied by Johnson Matthey Chemicals Ltd. with a stated impurity content (ppm): Fe < 3, Ag < 1, Ca < 1, Cu ~ 1).

Microgram quantities of the $Mg(OH)_2$ samples were contained in a small fused-silica tube sealed to the vacuum system and externally heated in a nitrogen atmosphere at a rate of about 2°C/min up to 1000°C. The sample compartment was connected to the main vacuum line either by a wide tubing during drying and rapid pumping periods or—for the determination of absolute partial pressures—by a set of calibrated capillaries of known conductances. The gases evolved from the sample were analyzed with a memory-free, all-platinum (Pt/10Ir alloy) Omegatron mass spectrometer built by Gentsch (15) and Gentsch *et al.* (16) and kept at 200°C during the experiment to avoid adsorption on the metal surfaces. All electrical feedthroughs and connections in the mass spectrometer tube were made of noble metal as well, and a ThO_2 -coated iridium wire was used as relatively inert hot cathode of only 0.5 mm² surface area. Thus the equipment allowed the determination of all gases of

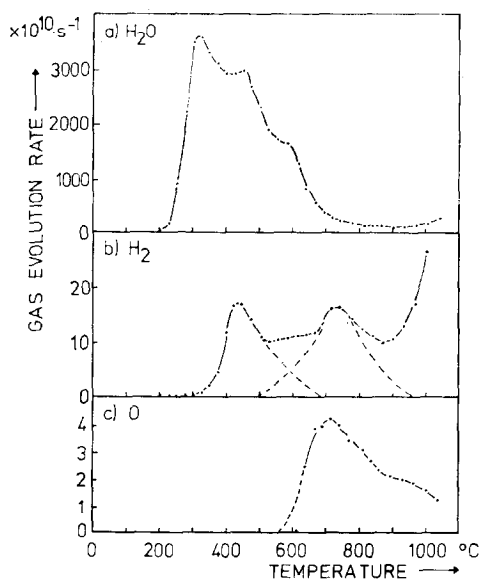


Fig. 1. Gas evolution curves as a function of the dehydration temperature for $38\mu\text{g Mg(OH)}_2$ (heating rate: 2°C min^{-1}): (a) water, (b) hydrogen, (c) atomic oxygen.

interest here, even hydrogen and oxygen in the presence of excess water, minimizing the danger of side reactions.

RESULTS AND DISCUSSION

The evolution of water, hydrogen and oxygen from a $38\mu\text{g}$ sample of Mg(OH)_2 between room temperature and 1000°C is shown in Fig. 1. The rate values are given as number of molecules or atoms evolved per second. Traces of methane ($m/e = 16$ for CH_4^+) detected in the reaction gas could be separated from atomic oxygen ($m/e = 16$ for O^+) on the basis of the ratio of the mass spectrometer ions $\text{CH}_3^+:\text{CH}_2^+$, etc., using the Mass Spectral Data tables (17). The methane results from the decomposition of organic trace impurities carried into the Mg(OH)_2 during the preparation of the Mg(OH)_2 sample in a conventional vacuum line. Earlier experiments (18) with absolutely grease-free Mg(OD)_2 samples prepared *in situ* in the ultrahigh vacuum system by deuteroxylation of high purity MgO showed that the deuterium and oxygen

evolution from the sample is not altered by the presence or absence of traces of organic volatile impurities.

Mg(OH)_2 starts to dehydrate at about 250°C . The evolution rate of H_2O quickly rises and reaches a first maximum at about 325°C , then drops and rises again to a second maximum at 450°C . A third maximum was often observed around 600°C . This variation in the gas evolution rate had already been observed in earlier experiments (18). It is attributed to recrystallization effects (19): a high defect concentration reaction layer first formed at the surface of the Mg(OH)_2 crystallites by the initial loss of the H_2O molecules from the trigonal hydroxide structure (20) recrystallizes into cubic MgO exposing fresh, unreacted hydroxide surface. The cubic MgO thus formed includes numerous defects, mainly residual OH^- groups and cation vacancies, and gives rise to weak superstructure lines in the X-ray diffraction diagram (21).

Figure 1 clearly shows that the hydrogen evolution starts only after the first recrystallization has taken place. This indicates that the first formation of molecular hydrogen is connected with the cubic MgO and the particular defects therein: the first maximum of the H_2 evolution rate at 450°C coincides with the second maximum in the H_2O evolution curve.

As shown in Fig. 1 there is a second maximum of the H_2 evolution rate at about 750°C . This maximum parallels the evolution of oxygen. It should be noted that, while hydrogen is evolved in molecular form from the MgO , oxygen appears to come off the sample as atomic oxygen. This is inferred from the fact that the mass spectrometer ion $m/e = 16$ (corresponding to O^+) greatly prevails over the species $m/e = 32$ (corresponding to O_2^+), much more than one would expect on the basis of the ionization rates of molecular oxygen gas or gas mixtures given in the Mass Spectral Data (17) and verified for the

Omegatron mass spectrometer (15, 16). On the basis of the earlier experiments using $\text{Mg}(\text{OH})_2$ free of any hydrocarbon impurities and of the accuracy of the quantitative analysis achieved here it can be excluded that the small CH_4 content observed in the present experiments is mistaken for atomic oxygen.

The areas under the curves shown in Fig. 1 yield the total number of molecules or atoms evolved from the sample over the temperature range investigated. Table 1 contains the values for the experiment shown in Fig. 1 and of another experiment using a partially deuterioxyated sample. The numbers in parentheses give the amount of hydrogen and oxygen evolved per gram MgO . The accuracy of the determination can be estimated from the numbers in line 3, where the measured amounts of H_2O have been used to recalculate the sample weights. The calculated sample weights are too low but by not more than 20%. Considering that some of the H_2O molecules may well stick to the glass walls before reaching the mass spectrometer, the agreement is excellent. The present experiments confirm earlier results (18) that molecular hydrogen and atomic oxygen are indeed evolved from MgO formed by the dehydration of $\text{Mg}(\text{OH})_2$.

One outstanding result of the present study is the fact that there seem to be two different processes leading to the evolution of molecular hydrogen, one operative between 300–700°C, the other above 500°C. The first hydrogen evolution is probably to be assigned to the mechanism suggested earlier (22) involving two OH^- groups neighboring a cation vacancy in the defect MgO structure or on the MgO surface. As Derouane *et al.* (1) have shown, the formation of a molecular H_2 species is energetically possible within such a cation vacancy in the MgO structure. This requires OH^- groups occluded in the MgO .

It has been shown recently (20) that when $\text{Mg}(\text{OH})_2$ is carefully heated in

vacuum in experiments involving step-wise heating of the sample over many days the trigonal hydroxide structure is retained up to 470°C. A hexagonal defect MgO is formed which can be written as $\text{Mg}(\text{OH})_{2-x}\text{Q}_{x/2}\text{O}_{x/2}$ using the symbol Q for a neutral vacancy created by an H_2O molecule expelled from the $\text{Mg}(\text{OH})_2$ structure (23). The value for x may well reach 1.80, or 90% dehydration, before recrystallization to cubic MgO takes place. The remaining 10% of the initial OH^- groups, also predicted by Monte Carlo calculations (24, 25), will partly be included into this cubic MgO structure. The degree of disorder in the cubic MgO thus formed is quite high and gives rise to superstructure reflections in the X-ray diffraction diagrams (21). Hence, the concentration of defects of the type $[\text{Mg}-\text{OH}\dots[\text{Mg}]''\dots\text{HO}-\text{Mg}]^{2+}$ as used by Derouane *et al.* (1) will surely be sufficiently high to permit the assignment of the first H_2 evolution maximum to the formation of H_2 within such $[\text{Mg}]''$ vacancies. Concomitantly two O^- ions will be formed as indicated by Eq. (1).

According to Boudart and co-workers (11) V_I centers can first be observed in MgO samples thermally activated for several hours at 450°C. Their concentration increases with the temperature of treatment, then reaches a maximum at 550°C and decreases again, due to the one-to-one conversion of the V_I centers into the V_I^* centers (12).

There exists a close correlation between the temperature dependence of the V_I center formation and the first hydrogen evolution and the oxygen evolution observed in the present experiments. The gas evolution, however, is nearly instantaneous (heating rate 2°C/min), while the V_I centers take hours to form. Also the V_I center concentration is much less than one would expect on the basis of the hydrogen evolution assuming that for each H_2 molecule evolved two O^- ions are formed. The

TABLE 1
Gas Evolution during the Thermal Decomposition of $\text{Mg}(\text{OH})_2$ and $\text{Mg}(\text{OD})_2$

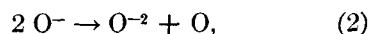
Line	Sample	$\text{Mg}(\text{OH})_2$	$\text{Mg}(\text{OD},\text{OH})_2$
1	Sample (μg)	38	69
2	Total number of water molecules evolved during dehydration	3.3×10^{17}	1.6×10^{17} H_2O 2.3×10^{17} HDO 2.7×10^{17} D_2O
			Total 6.6×10^{17}
3	Sample wt (μg) calculated from line 2	32	65
4	Number of hydrogen molecules evolved between 300–700°C	8×10^{14} ($3.1 \times 10^{19} \text{ g}^{-1} \text{ MgO}$)	5×10^{14} H_2 14×10^{14} HD 11×10^{14} D_2
			Total 30×10^{14} ($6.5 \times 10^{19} \text{ g}^{-1} \text{ MgO}$)
5	Number of hydrogen molecules evolved between 500–1000°C	9×10^{14} ($3.4 \times 10^{19} \text{ g}^{-1} \text{ MgO}$)	5×10^{14} H_2 13×10^{14} HD 5×10^{14} D_2
			Total 23×10^{14} ($5 \times 10^{19} \text{ g}^{-1} \text{ MgO}$)
6	Total number of hydrogen molecules evolved	17×10^{14} ($6.5 \times 10^{19} \text{ g}^{-1} \text{ MgO}$)	53×10^{14} ($11.5 \times 10^{19} \text{ g}^{-1} \text{ MgO}$)
7	Number of oxygen atoms evolved between 500–1000°C	3.2×10^{14} ($1.2 \times 10^{19} \text{ g}^{-1} \text{ MgO}$)	2.5×10^{14} ($0.5 \times 10^{19} \text{ g}^{-1} \text{ MgO}$)

O^- concentration in the MgO at about 550°C calculated on the basis of Eq. (1) should be in the order of 0.5 to $1 \times 10^{20} \text{ g}^{-1}$, while the highest V_I center concentration found by Boudart *et al.* (11) is in the order of 10^{15} g^{-1} . Using deuterioxyated MgO as a starting material, V_I concentrations of the order of 10^{16} g^{-1} may be reached (14).

The present results suggest that only a very small fraction, 10^{-4} to 10^{-5} , of all O^- ions formed by the first H_2 evolution leads to the formation of V_I centers. The reason for this is probably the very special nature of the V_I center, requiring three O^- ions on a (111) surface plane of the MgO crystallites. The relatively long time needed to build up a detectable V_I -center concen-

tration in MgO (typically several hours at 550°C) is an indication for the need of diffusion processes by which the O^- ions must first migrate from the sites where they were formed to the sites where they can cluster to give V_I centers.

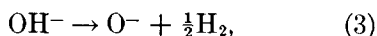
The second H_2 evolution, which leads to the maximum at 750°C appears to be simultaneous with the evolution of atomic oxygen reaching its maximum around 700°C. The oxygen evolution is probably due to the thermal decomposition of O^- ions by



as one might anticipate on the basis of the thermal instability of magnesium peroxide

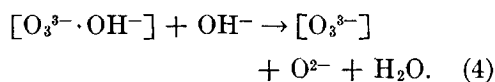
(26). The quantity of oxygen found (see Table 1) is less than expected. Considering the very high reactivity of atomic oxygen and its sticking probability during wall collisions in the vacuum line the low oxygen value is not in contradiction with Eq. (2).

As to the second hydrogen evolution process shown in Fig. 1 it should be noted that above 700°C the fused-silica tubing used as a sample container starts to emit increasing amounts of hydrogen as well. This blank value had to be subtracted in the appropriate way in order to obtain the H₂ evolution from the MgO sample alone. Probably the source of this hydrogen is all the residual OH⁻ groups still retained irrespective of their particular surroundings. This leads to the assignment of the high temperature maximum in the hydrogen evolution curve to the thermal dissociation of residual OH⁻ groups:



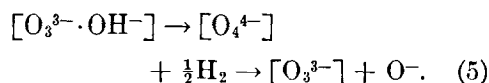
followed by the oxygen evolution as described in Eq. (2). This interpretation agrees with results obtained by Henderson and Sibley (27) during annealing experiments with H-doped MgO single crystals in the temperature range 800–1000°C, indicating a decay of the OH⁻ groups and an increase of the amount of hydrogen dissolved in the MgO structure.

Whether or not the transformation of the V_I center including the OH⁻ group, [O₃³⁻·OH⁻], into V_I^{*}, [O₃³⁻], is accompanied by the evolution of H₂O molecules, as proposed by Boudart *et al.* (11), or by the simultaneous evolution of molecular hydrogen and atomic oxygen cannot be decided on the basis of the present experiments, due to the low concentration of V_I centers. The mechanism leading to the formation of H₂O (11) requires an additional OH⁻ group:



The second mechanism does not require any

additional OH⁻ group nearby:



The intermediate cluster of four O⁻ ions would be unstable and lose one O⁻ ion by diffusion, which subsequently yields atomic oxygen according to Eq. (2). The observation that, while the V_I center is lying flat in a (111) MgO surface, the V_I^{*} center is tilted into the surface (11, 12) suggests that the transformation V_I → V_I^{*} is not solely achieved by the loss of a proton but also by an oxygen exchange. Equation (5) appears to be the more likely mechanism for this transformation since it readily permits the oxygen exchange.

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