Crystalline Structure of MgO Prepared by the Sol–Gel Technique with Different Hydrolysis Catalysts

Bokhimi[1] and A. Morales

Institute of Physics, National University of Mexico (UNAM), a.p. 20-364, 01000 México D. F., Mexico

and

T. Lopez and R. Gomez

Departamento de Química, Universidad Autónoma Metropolitana–Iztapalapa, a.p. 55-534, 09340 México D. F., Mexico

We have prepared MgO by the sol–gel technique using different hydrolysis catalysts that control the size of the particle and its evolution with temperature. The phases in the sample were identified by X-ray diffraction. The evolution in the temperature range between 150 and 900°C of the MgO crystalline structure was studied by Rietveld refinement technique. As a profile for the diffraction peaks we used a modified pseudo-Voigt function with the average particle size as one of its fitting parameters. This allowed us to follow the evolution of particle size with temperature for the different hydrolysis catalysts. From the Mg deficiency in the MgO lattice we find Mg:O molar ratios between 3.56(2):4.00 and 3.85(3):4.00 depending on the average particle size. © 1995 Academic Press, Inc.

1. INTRODUCTION

The need for new materials with specific physical and chemical properties, controlled by the initial reaction conditions, has prompted many research groups to develop new preparation techniques. They have developed some techniques which are, nowadays, an alternative to the traditional ones (1–5), as for example the sol–gel technique. This technique involves a colloidal solution which transforms into a gel, producing high purity and chemically homogeneous materials which makes them very attractive from an industrial point of view, especially in biology, the membrane industry, optical fibers, and catalysis.

Magnesium oxide (MgO) is found in nature in its periclase form (the only crystalline form of magnesium oxide). Periclase can be synthesized by calcination of a large variety of salts, and by dehydration of brucite $(Mg(OH)_2)$ (6).

Due to its low specific area, magnesium oxide has seldom been used as a support in metal catalysts. This situation has been changed by preparing MgO by the sol–gel technique which produces powders with larger specific areas. Hydration of the powder and a heat treatment at 673 K produces even higher specific areas (7). MgO is also of interest because it has the capability of stabilizing metals in unusual oxidation states, and avoids sintering and evaporation of the metal atoms (8, 9). There are many examples where metal reactivity is affected when MgO is used as the support (10–12), one of which is the hydrogenation reaction of CO. In this reaction the catalyst has a higher selectivity than when it is prepared with a SiO_2 support. Logan and Datye (13) have proposed four different causes that could help in understanding the peculiar behavior of the MgO as compared to other oxides. These causes are: (i) changes in morphology and structure of the surface, (ii) changes in particle size, (iii) different ways of surface dehydroxylation, and (iv) a large electron mobility as well as the presence of defects (14, 15). Holt *et al.* (7) have studied the effect of chlorine on MgO morphology. They propose that Cl^- ions in periclase and brucite affect the specific area and the crystallinity of the system. Leofanti *et al.* (16) correlate the dehydroxylation in brucite with temperature, and observe changes in the lattice parameter through the effect of chlorine in the system.

In the present work we report the preparation of MgO by the sol–gel process, starting with a metal alkoxide (magnesium ethoxide). Particle size and surface hydroxylation are controlled from the beginning of the reaction by adding acid or basic hydrolysis catalysts (pH 3 to 9) (17).

We have made a detailed study of the crystalline structure of the MgO system prepared with different hydrolysis catalysts: pH 3 (HCl), pH 5 $(C_2H_4O_2)$, pH 5 $(C_2H_2O_4)$,

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[1] To whom correspondence should be addressed.

pH 7 (H_2O), and pH 9 (NH_4OH). The study was performed with X-ray powder diffraction together with refinement of the crystalline structure by the Rietveld technique. From the refinement it has also been possible to obtain information about the average particle size for each system and temperature.
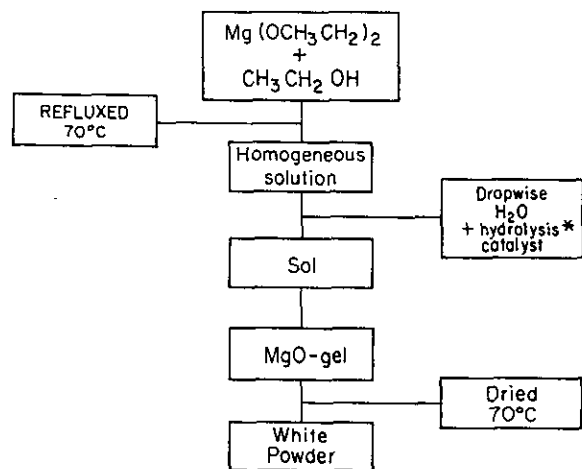
2. EXPERIMENTAL

2.1. Sample Preparation

Figure 1 shows a diagram that describes the method used to prepare the samples for each one of the hydrolysis catalysts (17). The samples for each system were heated in air for 12 hr at temperatures of 150, 300, 600, and 900°C.

2.2. X-Ray Diffraction Characterization

Powder diffraction data were obtained at room temperature with a Siemens D-5000 diffractometer, with Cu$K\alpha$ radiation and a graphite diffracted beam monochromator. Each XRD specimen was prepared by packing the sample powder in a glass sample holder. The intensity was determined by step scanning in the 2θ range between 35° and 130°, with a 2θ step size of 0.02° and a measuring time of 1.5 sec per point. Atomic scattering factors for neutral atoms from the "International Tables for X-ray Crystallography" (18) were used. Rietveld analysis was done with the DBWS-9006PC program (19). As a profile we have used a pseudo-Voigt function modified by Thompson et al. (20), allowing one to use average particle size and microstrain as two of the profile-breadth fitting parameters (21). In the range of particle sizes obtained in
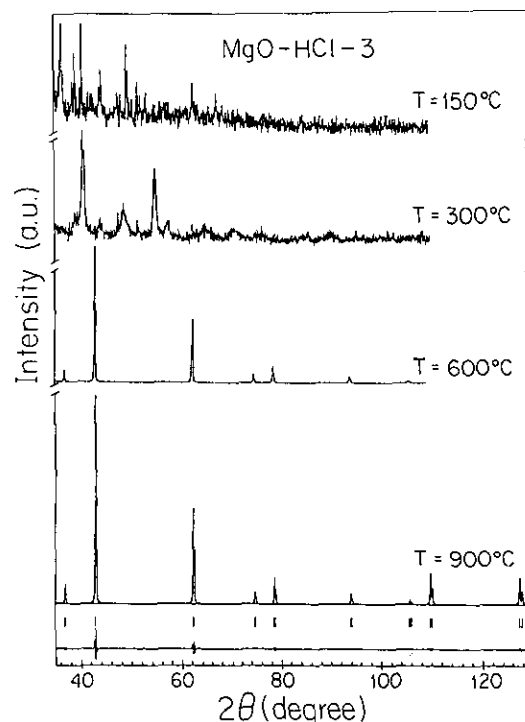

FIG. 2. X-ray diffraction patterns of the sample prepared at pH 3 with HCl as the hydrolysis catalyst. They were obtained after annealing the sample for 12 hr in air at 150, 300, 600, and 900°C. For $T = 900$°C, the results of the Rietveld refinement are also included, $R_F = 0.011$.

the present work, it is found that the particle size is isotropic. X-ray diffraction patterns were well fitted assuming $Fm3m$ as the space group.

3. RESULTS AND DISCUSSION

We have used HCl as the hydrolysis catalyst to prepare the samples at low pH values. Figure 2 shows the X-ray diffraction patterns for pH 3 after heating the samples at temperatures of 150, 300, 600, and 900°C. After heating the sample at 150°C the predominant phase is amorphous. While the sample is heated at 300°C the amorphous phase is transformed into crystalline MgClOH (magnesium chloride hydroxide). No MgO is formed at this temperature. HCl, the hydrolysis catalyst, causes chlorine ions to be incorporated into the lattice. When the sample is heated at 600°C the only phase observed is MgO (periclase) with an average particle size of 1518(25) Å and a lattice parameter of 4.21032(2) Å. Standard deviations, indicating the variation of the last figures of the corresponding number, are given in parentheses. From the Rietveld refinement we find a Mg:O molar ratio of 3.82(2):4.00 which corresponds to a deficiency of nearly 5% in the occupation of the Mg cation sites. Mg cation deficiency is characteristic of MgO as has been shown by

* hydrolysis catalysts: HCl, $C_2H_4O_2$, $C_2H_2O_4$, H_2O, NH_4OH

FIG. 1. Diagram describing the sample preparation.

TABLE 1

Parameters Obtained from the Rietveld Refinement of the MgO Crystalline Structure as a Function of Temperature for the Different Hydrolysis Catalysts

Hydrolysis catalyst	pH	T (°C)	Average particle size (Å)	Lattice parameter (Å)	Mg occupancy
HCl	3	600	1518(25)	4.21032(2)	3.79(2)
HCl	3	900	1555(26)	4.21022(2)	3.78(2)
$C_2H_2O_4$	5	600	160(3)	4.2161(2)	3.56(2)
$C_2H_2O_4$	5	900	430(7)	4.2119(6)	3.69(1)
$C_2H_4O_2$	5	150	331(5)	4.21704(6)	3.68(1)
$C_2H_4O_2$	5	300	332(7)	4.21663(7)	3.69(1)
$C_2H_4O_2$	5	600	396(8)	4.21149(5)	3.75(1)
$C_2H_4O_2$	5	900	634(10)	4.21058(4)	3.79(1)
H_2O	7	150	186(4)	4.2179(1)	3.59(2)
H_2O	7	300	198(4)	4.2170(1)	3.64(2)
H_2O	7	600	348(6)	4.2121(1)	3.75(2)
H_2O	7	900	776(15)	4.21064(4)	3.71(1)
NH_4OH	9	600	644(15)	4.21179(9)	3.82(2)
NH_4OH	9	900	874(28)	4.21014(8)	3.85(3)

Note. Standard deviations are also obtained from the refinement. The ideal Mg occupancy is 4.00.

Figure 3 shows the X-ray diffraction patterns obtained by preparing the sample with oxalic acid as the hydrolysis catalyst. When the sample is heated at 150°C it contains $C_2MgO_4 \cdot 2H_2O$ (Glushinskite) as the only phase which is crystalline with an average particle size smaller than 200 Å. This is because oxalate ligand is strong (monodentate and bidentate) and easily bonds to the lattice. We have not intended to refine this crystalline structure because this is outside of the scope of the present work. Due to the weak ligands, the Glushinskite is transformed into $Mg(OH)_2$ (brucite) and MgO, by heating the sample at 300°C, with brucite as the majority crystalline phase, the peak breadth indicates that the crystalline phase has a small average particle size. When the sample is heated at 600°C it is totally transformed and only the MgO crystalline phase is observed. From the Rietveld refinement we obtain a lattice parameter of 4.2161(2) Å for this phase, an average particle size of 160(3) Å, and a Mg deficiency in the lattice of 11.0(5)%, which is the highest Mg deficiency observed in our study. When the sample is heated at 900°C the particle size increases to 430(7) Å and the Mg deficiency in the lattice decreases to 7.8(3)% (Table 1). If one is interested in synthesizing small MgO particles at high temperature, oxalic acid will be an adequate hydrolysis catalyst.
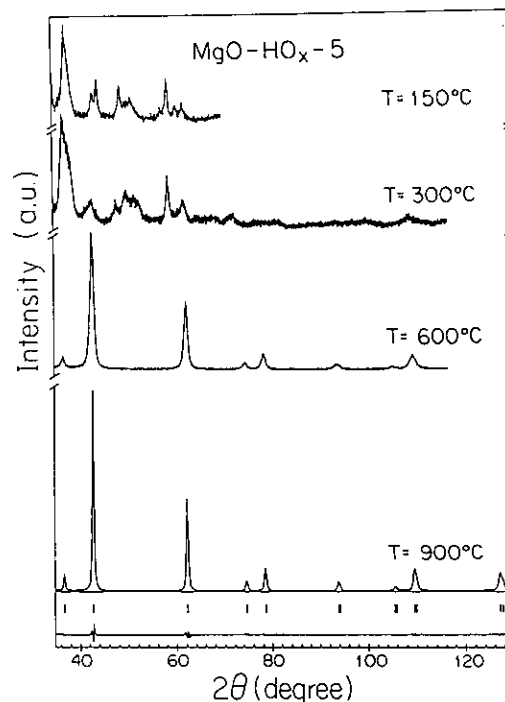
Derouane *et al.* (22) who report the formation of molecular hydrogen within a cation vacancy neighbored by two residual OH⁻ groups. They propose the arrangement $[Mg-O \cdots H-H \cdots O-Mg]^{2+}$. This is important in order to understand the formation of V-type centers by thermal treatment. Table 1 gives the corresponding values for all samples and temperatures. Heating the sample at 900°C does not produce any significant change in the average particle size and crystalline structure parameters.

It is important to remark that when the gelation process is carried out at an acid pH, the hydrolysis reaction is enhanced while the polymerization reaction is decreased (23), producing solid particles that have the tendency toward ramification. $Mg(OH)_2$ with a cubic structure is obtained as an intermediate compound and polymerizes in all directions according to the equation

$$\text{Hydrolysis: } Mg(OCH_2CH_3)_2 + H_2O \xrightarrow{\text{HCl}} Mg(OH)_2 \xrightarrow{\Delta} MgO \text{ (ramified)}.$$
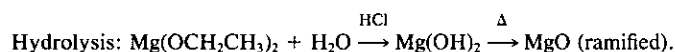
Two different hydrolysis catalysts were used for preparing the samples at pH 5, acetic acid $(C_2H_4O_2)$ and oxalic acid $(C_2H_2O_4)$. We have found that the evolution of the crystalline structure with temperature depends on the type of hydrolysis catalyst that is used. Therefore, we will separately describe each one.

FIG. 3. X-ray diffraction patterns of the sample prepared at pH 5 with $C_2H_2O_4$ as the hydrolysis catalyst. They were obtained after annealing the sample for 12 hr in air at 150, 300, 600, and 900°C. For $T = 900$°C, the results of the Rietveld refinement are also included, $R_F = 0.012$.
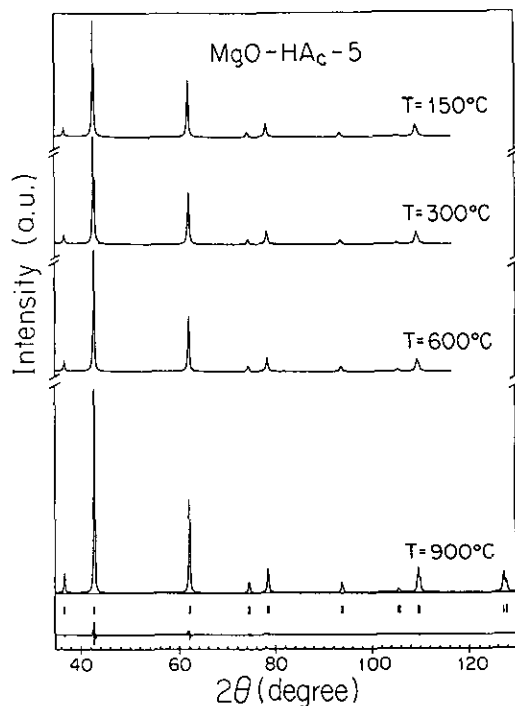
FIG. 4. X-ray diffraction patterns of the sample prepared at pH 5 with $C_2H_4O_2$ as the hydrolysis catalyst. They were obtained after annealing the sample for 12 hr in air at 150, 300, 600, and 900°C. For T = 900°C, the results of the Rietveld refinement are also included, R_F = 0.011.
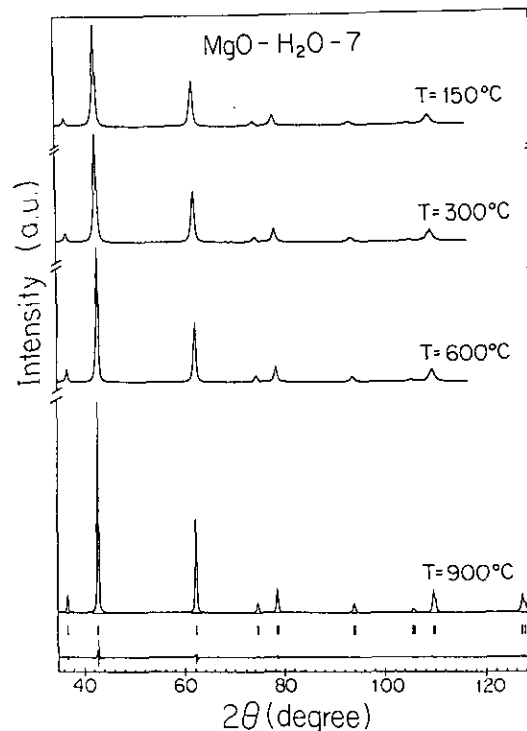

FIG. 5. X-ray diffraction patterns of the sample prepared at pH 7 with H_2O as the hydrolysis catalyst. They were obtained after annealing the sample for 12 hr in air at 150, 300, 600, and 900°C. For T = 900°C, the results of the Rietveld refinement are also included, R_F = 0.014.

Figure 4 shows the results obtained when acetic acid is used as the hydrolysis catalyst. When the sample is heated at 150°C the composition is of crystalline MgO with an average particle size of 331(5) Å, a lattice parameter of 4.21704(6), and a Mg deficiency in the lattice of 8.0(3)%. In this case $C_2MgO_4 \cdot 2H_2O$ (Glushinskite) is not formed because acetate ligand is very weak and it does not bond to the brucite lattice. When the sample is heated at higher temperatures the particle size increases; it is about two times larger at 900°C, while the lattice parameter and the Mg deficiency decrease. Table 1 gives details about this variation with temperature.

When the sample is prepared at pH 7 and heated at 150°C, the resulting phase is crystalline MgO with an average particle size of 198(4) Å and a lattice parameter of 4.2170(1) Å. Figure 5 gives the X-ray diffraction patterns taken after annealing the sample at different temperatures. We observe that the only effect of temperature is to change the average particle size, which has a value of 776(15) Å when the sample is heated at 900°C.

To prepare the sample at pH 9, NH_4OH was used as the hydrolysis catalyst (Fig. 6). After heating the sample at 150°C, an amorphous phase is observed with a small amount of crystalline $Mg(NO_3)_2 \cdot H_2O$ (nitromagnesite) due to the presence of NH_3 in the gelation reaction; this
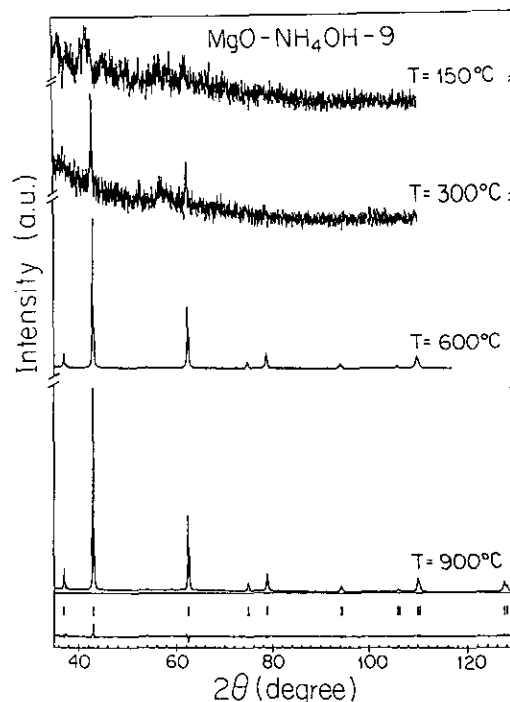

FIG. 6. X-ray diffraction patterns of the sample prepared at pH 9 with NH_4OH as the hydrolysis catalyst. They were obtained after annealing the sample for 12 hr in air at 150, 300, 600, and 900°C. For T = 900°C, the results of the Rietveld refinement are also included, R_F = 0.028.

amorphous phase is stable even when the sample is heated at 300°C. At this temperature the crystalline nitromagnesite is transformed into MgO, with a large average particle size. When the sample is heated at 600°C the crystalline MgO phase increases considerably and coexists with the amorphous phase. The MgO phase has an average particle size of 644(15) Å, a lattice parameter of 4.21179(9) and a Mg : O molar ratio of 3.85(3) : 4.00 which corresponds to a Mg deficiency in the lattice of only 4.5(5)%, the smallest observed Mg deficiency. As the temperature of the sample is increased to 900°C the average particle size increases to 874(28) Å, but the amorphous phase is still present. At basic pH 9, the polymerization rate increases and the hydrolysis is only partial, therefore, the solids tend to be one-dimensional with a large particle size (23). In the Rietveld refinement, the amorphous phase is included as part of the background.

4. CONCLUSIONS

We have shown that the hydrolysis catalyst used in the preparation of MgO by the sol–gel technique is responsible for the initial phases present in the sample. They control the transformation of these phases into MgO, and determine the evolution of the MgO crystalline structural properties and particle sizes with temperature. We have shown the usefulness of the crystalline refinement technique by the method of Rietveld to characterize the evolution of the parameters involved in the crystalline structure of MgO prepared by the sol–gel technique, including the average particle size. We propose that the parameter reported in the present work will be very useful to those research groups involved with the applications of MgO. Our results not only supply new data for the characterization of the MgO system but they also generate many questions related to the role of the different components of the hydrolysis catalysts in the formation of the crystalline structure.

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