Hydrolysis of Magnesium Methoxide. Effects of Toluene on Gel Structure and Gel Chemistry

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The hydrolysis of magnesium methoxide in methanol or methanol–toluene solvents with a water-to-methoxide molar ratio of 2 has been studied. The gel obtained from the hydrolysis of magnesium methoxide appears to be polymeric based on the mass fractal dimensions and TEM micrographs. The presence of toluene accelerates the hydrolysis and gelation processes. The fractal dimensions of the wet gels obtained in the absence and in the presence of toluene were 2.22 and 1.80, respectively. Both of these observations indicate that the presence of toluene changes the fractal growth from a reaction-limited to a diffusion-limited growth. In either case, the hydrolysis is only completed partially and produces an intimate gel of $MgO–Mg(OH)_2–Mg(OH)(OCH_3)$. The N_2 BET surface area of the dry gel, obtained with a toluene to methanol volume ratio of 1.60, is 1011 m^2/g, which is 1.74 times as large as that of the gel obtained in the absence of toluene.

Introduction

There is considerable interest in the synthesis of nanoscale magnesium oxide (MgO) and magnesium hydroxide $Mg(OH)_2$ particles via the magnesium alkoxide $Mg(OR)_2$ route. Generally, an alkoxide is hydrolyzed in an alcohol solvent to yield the hydroxide, which is followed by isolation and thermal dehydration.[1,2] Techner and co-workers[3] have described the preparation of magnesium hydroxide aerogels on the basis of the hydrolysis and condensation reactions of the alkoxide. They carried out the hydrolysis of $Mg(OCH_3)_2$ in a water–methanol–benzene mixture and, after autoclave hypercritical drying, obtained magnesium hydroxide aerogels with surface areas of about 400 m^2/g.

A modified autoclave hypercritical drying procedure has been developed to prepare nanoscale MgO particles.[4,5] These nanoscale materials exhibit unusual surface chemistry and catalytic properties and, compared to other MgO samples, are more chemically reactive. They have been extensively studied as destructive adsorbents for a variety of toxic substances. Examples are chemical warfare agents such as VX, GD, and HD,[6] organophosphorus compounds and chlorocarbons,[7,8] and chlorinated hydrocarbons and benzenes.[9] Moreover, they have shown superior adsorption capacity for some inorganic compounds such as HCl, HBr, NO, and SO_3,[10] and SO_2 and CO_2.[11,12]

The modified autoclave hypercritical drying procedure has four steps: preparation of $Mg(OCH_3)_2$ by the reaction of magnesium metal with methanol, hydrolysis of $Mg(OCH_3)_2$ in the presence of toluene, hypercritical drying, and thermal activation.[4,5] The hydrolysis was conducted in a water–methanol–toluene mixture, and

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Table 1. Effect of Toluene on the Hydrolysis of Mg(OCH₃)₂ (Temperature: 18 °C)

sample ID	TM000	TM032	TM094	TM160
H₂O in methanol/toluene	0.8 M, 5 mL	0.8 M, 5 mL	0.8 M, 5 mL	0.8 M, 5 mL
Mg(OCH₃)₂ in methanol/toluene	0.4 M, 5 mL	0.4 M, 5 mL	0.4 M, 5 mL	0.4 M, 5 mL
toluene/methanol (vol) in water solution	0	0	0.94	2.93
toluene/methanol (vol) in Mg(OCH₃)₂ solution	0	0.94	0.94	0.94
toluene/methanol (vol) for mixture	0	0.32	0.94	1.60
gelling start time[a] (s)	88	42	seconds	instant
gelling end time[b] (s)	114	50	seconds	instant
gel or solution	clear gel	clear gel	clear gel	clear gel

[a] Gelling start time was the time when the solution became very viscous. [b] Gelling end time was the time when the gel became rigid.

consequently, the subsequent hypercritical drying was done in the presence of toluene. The surface areas of thus-obtained magnesium hydroxide aerogels were about 1000 m²/g, more than twice the values reported by Techner and co-workers. The reasons for such great improvement in surface areas are still not clear, although it has been postulated that excess toluene could affect the hydrolysis and condensation process and the incorporation of hydrophobic solvent could reduce the surface tension at the pore walls.[4]

When water is added into a methanolic Mg(OCH₃)₂ solution, hydrolysis occurs. According to the following reaction, the stoichiometric molar ratio of water to methoxide is 2

$$Mg(OCH_3)_2 + 2H_2O \rightarrow Mg(OH)_2 + 2CH_3OH \quad (1)$$

The work reported herein was carried out to investigate the effects of toluene on the hydrolysis of Mg(OCH₃)₂ by observing the gelling process and by determining the structure of the obtained wet gels. The wet gels were then dried by allowing solvent evaporation in air (hypercritical drying was not used) followed by vacuum, and the obtained dried gels were studied to gain information on the hydrolysis step. Throughout the study, the concentration of Mg(OCH₃)₂ was kept constant at 0.4 M and the water to methoxide molar ratio was fixed at 2.

Experimental Section

A. Materials. Commercially available Mg(OCH₃)₂ solution (Aldrich, 8.0 wt % in methanol, stored under nitrogen), methanol (Fisher Scientific, certified A. C. S. spectranalyzed), and toluene (Fisher Scientific, certified A. C. S.) were used. Water was triply distilled and deionized.

B. Preparation of Wet Gels. Two 0.4 M Mg(OCH₃)₂ solutions in methanol and methanol−toluene solvents were prepared with toluene to methanol volume ratios of 0 and 0.94, respectively. Three 0.8 M H₂O solutions in methanol and methanol−toluene solvents were prepared with toluene to methanol volume ratios of 0, 0.94, and 2.93, respectively. In each experiment, 5 mL of a H₂O solution was first transferred into a vial. Then, 5 mL of a Mg(OCH₃)₂ solution was added to the vial. In this way, while allowing different toluene to methanol volume ratios in the mixture, the Mg(OCH₃)₂ concentration and water to methoxide molar ratio were all kept constant. Shown in Table 1 are four combinations of the above-prepared Mg(OCH₃)₂ and H₂O solutions, which give the toluene to methanol volume ratios of 0, 0.32, 0.94, and 1.60, respectively. These four samples were identified with sample IDs of TM000, TM032, TM094, and TM160, respectively.

After the Mg(OCH₃)₂ solution was rapidly mixed with the water solution, the vial was placed on a benchtop at room temperature. The gelling process was visually monitored by tilting the vial from time to time to observe the change in the viscosity of its contents. The time when the contents became very viscous and stuck to the wall was recorded as gelling start

time. The time when the contents refused to pour was recorded as the gelling end time. The gelling start and end times are also shown in Table 1.

C. Preparation of Dried Gels. To obtain dried gels, the caps of the vials containing wet gels were loosened for 12 days to allow slow evaporation of the solvents. Then, the vials were put in a desiccator, which was connected to a vacuum pump, and vacuum-dried for 3 days. Finally, the vials were transferred to an oven and heated at 60 °C until constant weight was obtained.

D. Characterization of Wet Gels. *1. Transmission Electron Microscopy (TEM).* TEM samples were prepared by spreading a piece of wet gel directly on a TEM grid with a spatula. After being dried, the sample was observed under a Philips CM100 electron microscope at the Kansas State University Biology Research Microscope and Image Processing Facility.

2. Small-Angle X-ray Scattering (SAXS). SAXS samples were prepared by transferring the wet gels, by using a syringe, to 1.5 mm i.d. thin-wall quartz capillary tubes. The tubes were sealed with 5 min epoxy. SAXS data was collected on the University of New Mexico/Sandia National Laboratories 5 m pinhole instrument in short (15 min) geometry.[13] An empty capillary was used as background. The scattering intensity, I, was plotted as a function of the Fourier spatial frequency, q, on a log−log plot, where q is given by

$$q = \frac{4\pi}{\lambda} \sin\left(\frac{2\theta}{2}\right) \quad (2)$$

Here, λ is the wavelength of the incident radiation and 2θ is the scattering angle. Power laws, i.e., $I(q) = Cq^p$ will be rendered as straight line segments in such log−log plots. The inverse of q can be thought of as a yardstick for the structure of the material in question.[14]

E. Characterization of Dried Gels. *1. X-ray Diffraction (XRD).* For XRD studies, dried gel was ground into powder and loaded onto the sample holder provided with a Scintag XDS-2000 instrument, which uses a Cu Kα radiation ($\lambda = 0.1544$ nm). The diffractometer was set at a voltage of 40 kV and a current of 40 mA. The scan was a step scan from 10 to 85° (2θ) with a step size of 0.05° and a counting time of 0.8 s.

2. Fourier Transform IR (FTIR) Spectroscopy. FTIR experiments were conducted on a Mattson RS-1 FTIR spectrometer with a liquid nitrogen cooled detector. The dried gel was ground into powder and then mixed with a small amount of KBr. The mixture was pressed into a thin disk under a load of 10 000 lbs. The disk was quickly transferred to the spectrometer chamber, which was purged with nitrogen, and the spectra were collected after purging for 15 min.

3. Elemental Analyses. For elemental analysis, the samples, which were sealed in vials under nitrogen, were sent to Galibraith Laboratories (Knoxvill, TN). Elemental analyses were performed for magnesium, carbon, and hydrogen. The amount of oxygen was obtained by difference.

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4. Nitrogen Adsorption. The adsorption measurement was carried out on the dried gel at the boiling point of liquid nitrogen by using a Quantachrome AUTOSORB-1-MP gas sorption analyzer. The BET nitrogen surface area, S_{BET}, was obtained by applying the BET (Brunauer, Emmett, and Teller) equation to a relative pressure range of 0.05–0.3 on the adsorption isotherm. The total pore volume, V, was evaluated from the amount of nitrogen adsorbed at the highest relative pressure examined, which was 0.995. The micropore volume, V_0, was determined by applying the D–R (Dubinin–Radushkevich) equation[15,16] to a relative pressure range of 0.00005–0.009 on the adsorption isotherm. The pore-size distribution was estimated by applying the BJH (Barrett, Joyner, and Halenda) method[17] to the desorption isotherm.

Results and Discussion

With different combinations of the above-prepared H_2O and $Mg(OCH_3)_2$ solutions, different toluene to methanol volume ratios were obtained. Table 1 shows the results from four combinations, which gave toluene to methanol volume ratios of 0, 0.32, 0.94, and 1.60, respectively. It has been found that gelling time is relatively short and decreases with an increase in the toluene-to-methanol ratio. The longest gelling time is less than 2 min, which occurs when there is no toluene present. In all cases, hydrolysis resulted in the formation of clear rigid gels.

The gel structure was studied with the aid of TEM. Figure 1a displays the TEM micrograph for the gel formed in the absence of toluene. The micrographs suggest the existence of a polymer network which appears under the microscope as a multitude of thin strands to give a porous web-like matrix. There is no indication of particles. This is also the case for the samples prepared in the presence of toluene (see Figure 1b).

To further investigate the morphology of the wet gels, SAXS studies were conducted on gel samples prepared in the absence as well as in the presence of toluene. Figure 2 presents the scattering patterns for the wet gels prepared in the absence and presence of toluene. The gel obtained in the absence of toluene appears to be a power law scatterer ($I(q) \sim q^{-p}$) over the range of $0.03 < q < 0.2$ Å^{-1}. The power law has a slope of -2.22. The scattering patterns for the wet gels prepared in the presence of toluene were similar with power law slopes of -1.80 and -1.81 for toluene-to-methanol ratios of 0.32 and 1.60, respectively. These slopes are consistent with the formation of mass fractal aggregates with fractal dimensions of 2.22, 1.80, and 1.81, respectively.[18,19] The fractal nature extends up to a q value of about 0.2 Å^{-1}, which implies that it extends down to length scales of q^{-1} of about 5 Å (essentially molecular

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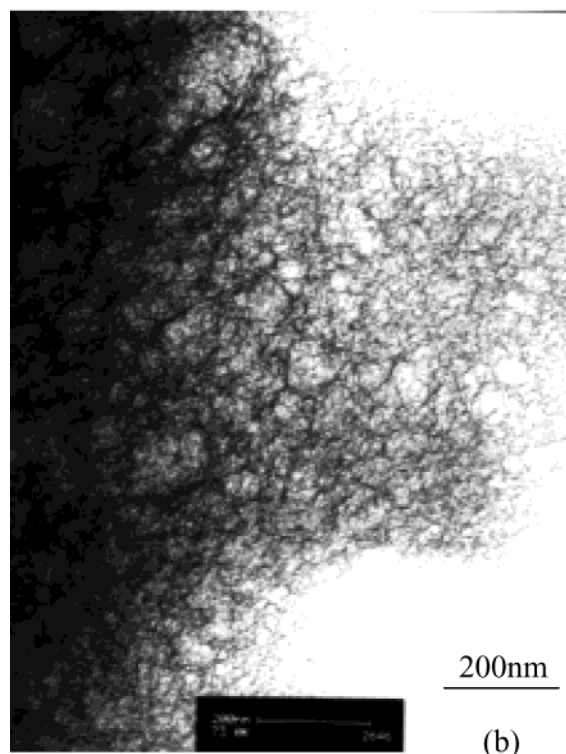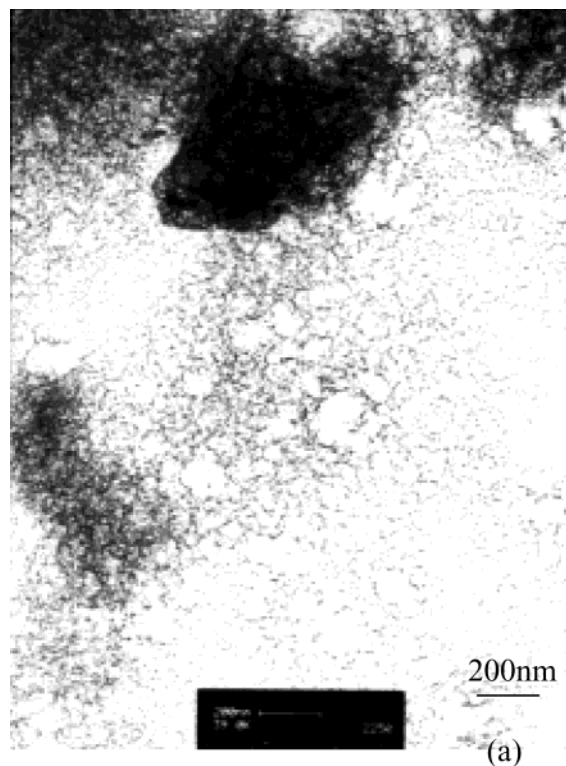

Figure 1. TEM micrograph of wet gel: (a) toluene/methanol = 0 and (b) toluene/methanol = 1.60. Note the more uniform but highly porous material formed under rapid gelation conditions in b.

dimensions). There is no indication of the formation of smooth dense particles that one would expect to demonstrate a q^{-4} power law.[14,20] The amount of toluene seems to have little influence on the mass fractal

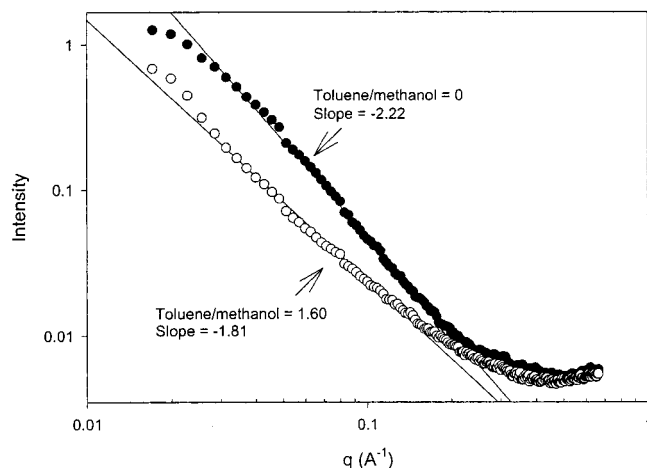(20) JCPDS XRD reference file (Joint Committee for Powder Diffraction Standards).
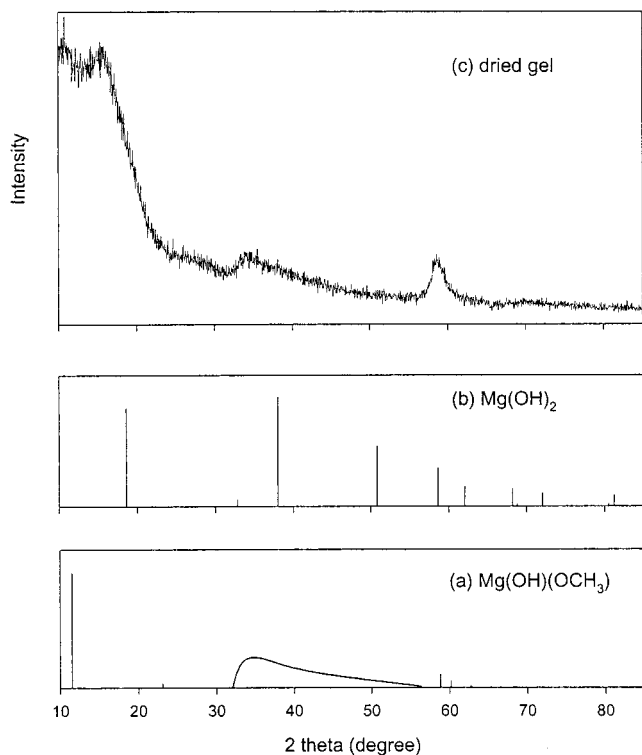
Figure 2. SAXS patterns for wet gels.

Figure 3. XRD patterns for (a) Mg(OH(OCH$_3$)), (b) Mg(OH)$_2$, and (c) dried gel obtained with toluene/methanol = 1.60.

dimension of the formed gel as long as there is some toluene in the system.

To obtain more information on the hydrolysis products, the wet gel was dried according to the previously mentioned drying procedure. Figure 3 shows the XRD pattern of the dried gel derived from hydrolysis with a toluene-to-methanol ratio of 1.60. The decaying peak at 2θ of 33.5° indicates the presence of Mg(OH)(OCH$_3$). However, the peaks at 17, 37, and 59°, although broad and somewhat distorted, indicate that Mg(OH)$_2$ is also present in large amounts.[20] The IR spectrum of the same gel is displayed in Figure 4. The bands at 1100, 2792, 2840, and 2931 cm^{-1} are all indicative of the presence of −OCH$_3$ groups.[10−12] The broad band at 3450 cm^{-1} indicates a large amount of hydrogen-bonded −OH groups, while the bands near 1480 cm^{-1} indicate surface carbonates.[10−12] Mg−O bonds appear at 540 cm^{-1}. There is no indication of ring vibrations that one would expect
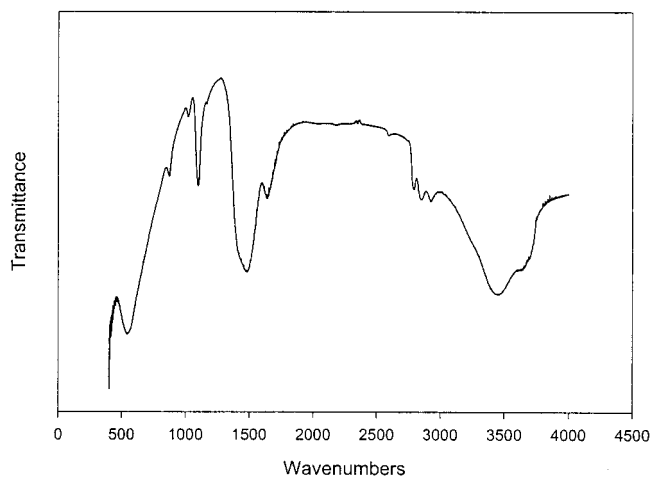

Figure 4. IR spectrum of the dried gel. Toluene/methanol = 1.60.

to see with toluene present in the gel; this suggests that toluene has been completely removed by the drying procedure. The XRD patterns and IR spectra for other dried gels in this series are similar to those for this sample. Elemental analyses were performed on the dried gels, and the results are given in Table 2. It shows that the dried gels contain about 8 wt % carbon, due to a combination of OCH$_3$ and CO$_3$.

The dried gels were characterized by N$_2$ adsorption. Figure 5 shows the adsorption isotherms for the dried gels obtained with toluene-to-methanol ratios of 0 and 1.60. The adsorption isotherms for other gels are similar. These isotherms exhibit broad hysteresis loops, which are characteristic of adsorbents possessing a high proportion of mesopores. Table 3 presents the properties derived from the adsorption isotherms. It is seen that the BET surface area increased from 581 to 1011 m^2/g with the increase of toluene-to-methanol ratio from 0 to 1.60; the total pore volume increased from 1.03 to 1.50 cm^3/g. It is also noted that the ratio of micropore volume (up to 2 nm pore-size opening) to total pore volume remained fairly constant with values between 10 and 13%. Displayed in Figure 6 are the pore-size distributions of the dried gels whose isotherms are shown in Figure 5. The peak positions are at 48 and 38 Å for the samples obtained with toluene-to-methanol ratios of 0 and 1.60, respectively. The peak positions for samples obtained with toluene-to-methanol ratios of 0.32 and 0.94 are the same as that for the sample obtained with toluene-to-methanol ratio of 1.60. Figure 6 also shows that the sample obtained without toluene had a broader pore-size distribution.

The results demonstrate that the hydrolysis of Mg(OCH$_3$)$_2$ does not go to completion according to eq 1 even if an adequate amount of water is added to the system. There are still some −OCH$_3$ groups left unhydrolyzed. The XRD patterns of the hydrolysis product show the presence of some Mg(OH)(OCH$_3$). This suggests that the hydrolysis proceeds stepwise as shown below

$$Mg(OCH_3)_2 + H_2O \rightarrow Mg(OH)(OCH_3) + CH_3OH \quad (3)$$

$$Mg(OH)(OCH_3) + H_2O \rightarrow Mg(OH)_2 + CH_3OH \quad (4)$$
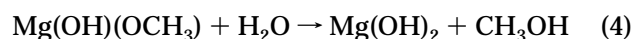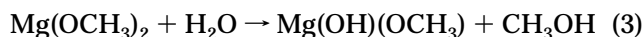
where eq 4 is considerably slower than eq 3 under the

Table 2. Elemental Analyses for the Dried Gels

sample ID[a−f]	TM000	TM032	TM094	TM160
toluene/methanol (vol)	0	0.32	0.94	1.60
% Mg	32.00	35.60	36.61	33.85
% C	8.57	7.90	7.36	7.19
% H	3.92	4.23	4.25	4.09
% O	55.51	52.27	51.78	54.87
empirical formula	$MgO_{2.64}C_{0.54}H_{2.95}$	$MgO_{2.23}C_{0.45}H_{2.87}$	$MgO_{2.15}C_{0.41}H_{2.80}$	$MgO_{2.46}C_{0.43}H_{2.91}$

[a] Weight percentage of oxygen, % O, is obtained by difference. [b] For pure $Mg(OCH_3)_2$, % Mg = 28.1, % C = 27.8, % H = 6.95, and % O = 37.1. [c] For pure $Mg(OH)(OCH_3)$, % Mg = 33.6, % C = 16.6, % H = 5.55, and % O = 44.3. [d] For pure $Mg(OH)_2$, % Mg = 41.6, % H = 3.43, and % O = 54.9. [e] For pure MgO, % Mg = 60.3 and % O = 39.7. [f] For pure $MgCO_3$, % Mg = 28.8, % O = 56.9, and % C = 14.2.
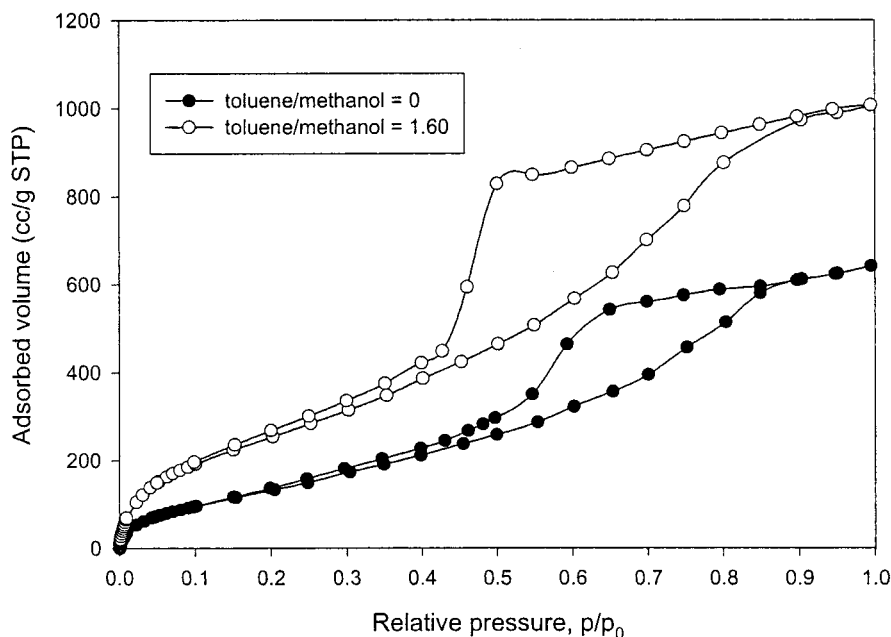

Figure 5. Nitrogen adsorption isotherms for dried gels.

Table 3. Properties of the Dried Gels

sample ID	TM000	TM032	TM094	TM160
toluene/methanol (vol)	0	0.32	0.94	1.60
BET N_2 surface area, S_{BET}, (m²/g)	581	715	893	1011
total pore volume, V, (cc/g)	1.03	1.04	1.46	1.50
micropore pore volume, V_0, (cc/g)	0.10	0.13	0.17	0.19
V_0/V (%)	10	13	12	13

conditions used in this study. The work of Utamapanya et al.,[4] Rywak et al.,[21] and Chadwick et al.[22] also indicated that one of the hydrolysis products was $Mg(OH)(OCH_3)$, although different water-to-methoxide ratios and different water addition methods were applied; these parameters appeared to have a great influence on the hydrolysis and gelling process. Rywak et al.[21] explored water-to-methoxide ratios of 1 and 4, which represented substoichiometric water and excess water according to eq 1, respectively; and they obtained essentially similar hydrolysis products in both cases. Utamapanya et al.[4] added pure water drop-by-drop by using a syringe into a stirred methanolic $Mg(OCH_3)_2$ solution. They observed a white cloudy precipitate upon addition of each drop of water and the mixture trans-

formed into a clear syrup-like solution after a few minutes. In this study, the mixture remained clear throughout the process; it became more and more viscous and eventually gelled. To explain the differences in reaction behavior, one may consider eq 4 as a reversible reaction. We speculate that when water droplets were added into the methoxide solution, $Mg(OH)_2$ particles were initially formed due to local high water concentration. However, methanol was in large excess and water was still less than stoichiometric; subsequently, eq 4 could be shifted to the left and $Mg(OH)_2$ was transformed into $Mg(OH)(OCH_3)$. In this study, methanol-diluted water was mixed with a methoxide solution in methanol. This allowed a good mixing between the reactants, and thus, a local high water concentration did not exist. Consequently, the reaction proceeded to completion according to eq 3 but did not reach completion with eq 4.

The formation of a polymeric gel from the hydrolysis of alkoxides generally involves simultaneous hydrolysis and polycondensation reactions. With the goal of obtaining crystallized MgO directly from the hydrolysis and supercritical drying without further thermal activation, Znaidi and co-workers[23] investigated the relative importance of the hydrolysis and polycondensation reactions on magnesium methoxide at different water-to-

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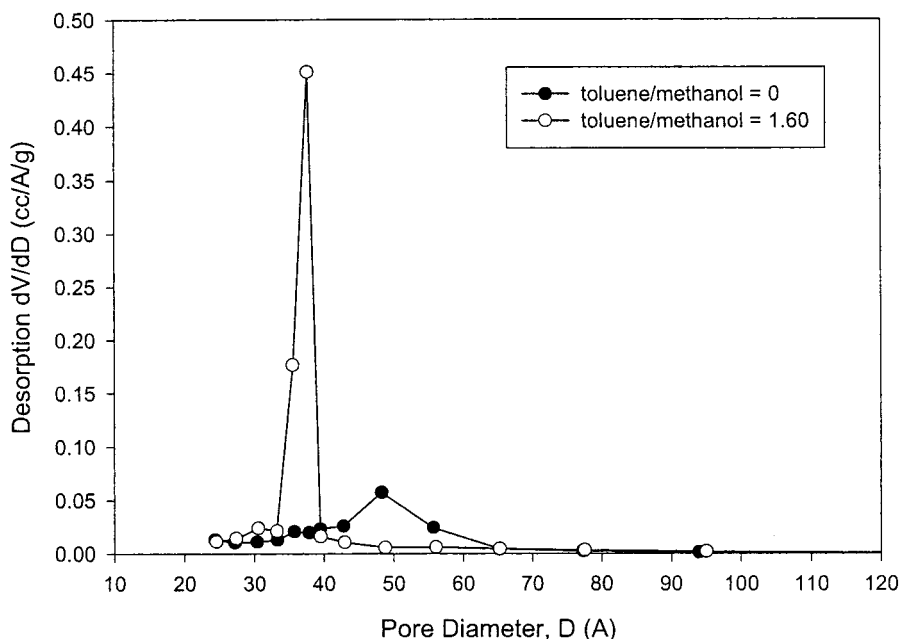
Figure 6. Pore-size distribution of the dried gels.

methoxide ratios. They found that lower water-to-methoxide ratios, e.g., 5 or less, favor hydrolysis reactions while higher water-to-methoxide ratios promote poly-condensation reactions. In our study, the water-to-methoxide ratio was kept constant at 2, which is much lower than what Znaidi and co-workers had used. Therefore, the polycondensation reactions were not expected to occur to a large extent. If we ignore surface carbonates, according to the elemental analysis results listed in Table 2, the recovered powders have mean chemical compositions of $MgO_{0.76}(OH)_{1.33}(OCH_3)_{0.54}$, $MgO_{0.26}(OH)_{1.52}(OCH_3)_{0.45}$, $MgO_{0.16}(OH)_{1.58}(OCH_3)_{0.41}$, and $MgO_{0.41}(OH)_{1.62}(OCH_3)_{0.43}$ for toluene-to-methanol ratios of 0, 0.32, 0.94, and 1.60, respectively. Note that the above formulas are not charge-balanced; and the same is true for those obtained by Znaidi and co-workers.[23] However, such formulas are in accordance with the presence of $-OCH_3$, $-OH$, and $Mg-O$ bonds which are evidenced from the IR spectrum. The results show that there exists substantial content of MgO in the recovered powders. This suggests that the following polyconden-sation reactions occur between the hydrolysis products

$$-Mg-OCH_3 + HO-Mg- \rightarrow$$
$$-Mg-O-Mg- + CH_3OH \quad (5)$$

$$-Mg-OH + HO-Mg- \rightarrow -Mg-O-Mg- + H_2O \quad (6)$$
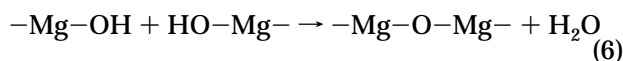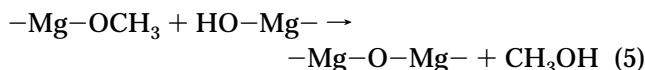
The formed polymeric chains of $-Mg-O-Mg-$ are consistent with the polymeric nature of the obtained gels. The existence of $Mg(OH)(OCH_3)$ in the gels is also consistent with the polymeric nature of the obtained gels. As shown in Figure 7, $Mg(OH)(OCH_3)$ and $Mg(OH)_2$ molecules can be interconnected through hydrogen bonding ($H \cdots O$) or $Mg \cdots O$ bonding.

Gels can be formed either through the condensation of polymers or through the aggregation of particles. In both cases, growing clusters collide, thus forming links between them to produce a single spanning cluster, i.e., gel. Several kinetic models have been proposed to
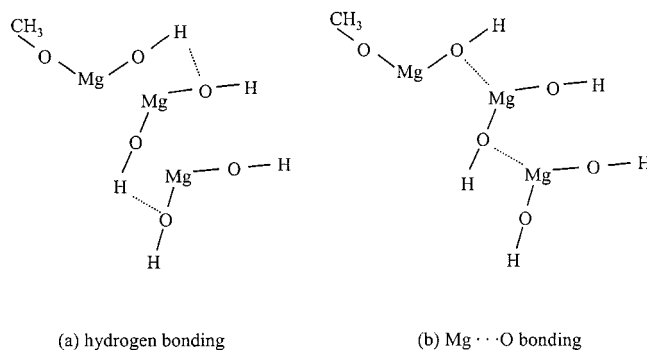

(a) hydrogen bonding   (b) Mg $\cdots$ O bonding

Figure 7. Examples of interconnected gel molecules.

describe polymer growth[24] and particle aggregation.[18] According to cluster–cluster growth models, clusters randomly stick together with a certain probability upon colliding.[25] Under diffusion-limited conditions, the stick-ing probability for clusters is close to unity, whereas under reaction-limited conditions, the sticking prob-ability is much less than unity. Both growth processes produce mass fractal objects. The results of computer simulations and experiments have revealed that the fractal objects in the diffusion-limited and reaction-limited regimes are characterized by fractal dimensions of about 1.80 and 2.15,[18,19,24] respectively. The presence of toluene clearly accelerates the hydrolysis and gelling process. Also, the faster reaction in the presence of toluene produces a mass fractal gel with fractal dimen-sion of about 1.80, whereas the slower reaction in the absence of toluene yields a mass fractal gel with fractal dimension of 2.22. Therefore, we believe that the addi-tion of toluene caused a change in the hydrolysis and gelling process from reaction-limited aggregation to diffusion-limited aggregation.

(24) Znaidi, L.; Chhor, K.; Pommier, C. Batch and Semi-continuous Synthesis of Magnesium Oxide Powders from Hydrolysis and Super-critical Treatment of Mg(OCH₃)₂. *Mater. Res. Bull.* **1996**, *31*, 1527.
(25) Brinker, C. J.; Scherer, G. W. *Sol–Gel Science: The Physics and Chemistry of Sol–Gel Processing*; Academic Press: Boston, 1990 and references therein.

As demonstrated by their low mass fractal dimensions, the wet gels formed in the presence of toluene are much less dense than those formed in the absence of toluene. Gels with lower mass fractals end up with higher surface area when dried. The surface area of the dried gels increases rapidly with increase in the amount of toluene in the system. The same is true with the hypercritical drying procedure.[4] This suggests that toluene does have a significant effect in producing gels with higher surface area. As the toluene-to-methanol ratio increases to 1.60, the surface area of the dried gel increased to 1011 m^2/g; this is comparable to the surface areas of gels obtained through the autoclave hypercritical drying procedure.[4] This suggests that the autoclave procedure, which is an expensive one, may not be necessary for producing dried gels with high surface areas in this case.

Conclusions

When large amounts of CH$_3$OH are present, the hydrolysis of Mg(OCH$_3$)$_2$ does not go to completion even if stoichiometric amounts of water are present. The way the water is introduced into the hydrolysis system does influence the hydrolysis process. The wet gels that are obtained are polymeric and are mass fractals. They are most likely composed of polymeric chains of $-$Mg$-$O$-$Mg$-$, which result from polycondensation reactions, and Mg(OH)(OCH$_3$) and Mg(OH)$_2$ molecules interconnected through hydrogen bonding (H$\cdots$O) and/or Mg$\cdots$O bonding. Toluene accelerates the hydrolysis and gelation process when added in the hydrolysis system. It changes the fractal growth kinetics from a reaction-limited into a diffusion-limited growth, thus producing gels with a mass fractal dimension of about 1.80 instead of 2.22. This much lower mass fractal dimension eventually yields dried gels with much higher surface areas. It is worth noting that with more toluene in the system, the faster are hydrolysis and gelation and higher is the surface area of the dried gel. This suggests that the presence of more toluene helps form and maintain a less dense, more porous structure. Thus, we conclude that the beneficial effect of toluene is due to its ability to change the kinetics of gelation thereby causing the onset of a rapid (diffusion-limited) process leading to a less dense, more porous structure. The underlying reason for this change in kinetics is not known and is the driving force for further studies.