Solvent Effects in the Hydrolysis of Magnesium Methoxide, and the Production of Nanocrystalline Magnesium Hydroxide. An Aid in Understanding the Formation of Porous Inorganic Materials

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The hydrolysis of magnesium methoxide in various solvent−methanol mixtures with a water-to-methoxide ratio of 2 has been studied. Solvents having low dielectric constants such as toluene, benzene, and anisole were found to accelerate the gelation process, while solvents having high dielectric constants such as acetonitrile, *N*,*N*-dimethylformamide, and dimethyl sulfoxide did not have a significant effect in the gelation process. A correlation between the gelation time and the dielectric constant of the solvents employed was found, which suggests that the solvation of the alcohol−alkoxide mixture is an important parameter which influences the gelation time and hence the resulting properties of the dry gel. This has important implications in the synthesis of porous oxide materials with high surface area.

Introduction

Mesoporous materials have been the subject of intense research since the discovery of the M41S class of materials by Mobil scientists.[1,2] Generally, they are characterized by large pores, high specific surface areas, and narrow pore-size distributions. The mesoporous silicate materials are often synthesized by a surfactant templating process, and these materials are useful in selective adsorption and catalysis because their large and uniform sized pores ensure a facile diffusion of reactants.[3−5] However, in recent years, wormhole-like mesoporous materials have been the focus of attention of several scientists.[6,7] These materials are more active heterogeneous catalysts in comparison to their ordered hexagonal analogues. Their enhanced reactivity has been partly explained based on the framework connectivity in three dimensions, thus allowing the guest molecules to more easily access active sites. Thus, the synthesis of porous materials with controlled morphology and size is of significant importance in fields such as catalysis, sensors, and solid-state electrochemistry.[8,9]

Magnesium hydroxide is used as flame-retardant filler in composite materials but is more commonly used as a precursor for the preparation of magnesium oxide. Magnesium oxide finds applications in catalysis, as an additive in refractories and paint, and is finding applications in the semiconducting industry as a thin film intermediate for other metal oxide layers.[10−12] The most conventional method for the synthesis of MgO is the decomposition of various magnesium salts or magnesium hydroxide.[13] However, the MgO powders obtained in this manner exhibit small surface areas, inhomogeneous morphologies, and varied grain (crystallite) sizes, all of which are disadvantageous for their use.

A modified autoclave hypercritical drying procedure has been developed to prepare nanoscale MgO.[14,15] The modified autoclave hypercritical drying procedure has four steps: preparation of $Mg(OCH_3)_2$ by reaction of Mg metal with methanol, hydrolysis of $Mg(OCH_3)_2$ in the presence of toluene, hypercritical drying, and thermal activation. The surface areas of the resulting magnesium hydroxide dry powders are as high as 1100 m^2/g, more than twice the values reported earlier.[16] The reasons for the dramatic improvement in the surface areas are not clear, although it has been suggested that the presence of toluene could affect the hydrolysis and condensation process, and the hydrophobic solvent could reduce surface tension at the pore walls. The subsequently prepared (by dehydration) high surface area MgO nanoparticles possess unique and different morphologies as compared to conventionally prepared MgO and are extremely good as adsorbents and catalysts.[17−19]

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In a recent study, we found that with the addition of increasing amounts of toluene in a $Mg(OCH_3)_2$−methanol−toluene mixture, the faster are the hydrolysis and gelation, the higher is the surface area of the resulting dry gel.[20] Also, when substantial amounts of toluene solvent were present in the gel, the wet gel was more uniform and highly porous having a weblike porous appearance. The beneficial effect of toluene was attributed to its ability to change the kinetics of the gelation causing the onset of a diffusion-limited process leading to a less dense and more porous gel structure. Still, the role of the "spectator solvent", toluene, was not entirely clear. The driving force for the study described herein was to understand the "toluene effect" in the gelation process. Another important question that is to be addressed is whether the hypercritical drying procedure is really necessary in the preparation of large surface area $Mg(OH)_2$. It is widely believed that the hypercritical drying step in which the solvent employed is stripped off in a fluid state so that the gel structure is preserved is the most important step. However, a recent study indicates that the gelation step may be the most important one.[20] For industrial scale-up preparations, high temperature and high pressure conditions (hypercritical drying step) are rather inconvenient and not economically feasible. Hence, an inexpensive method to produce $Mg(OH)_2$ with controlled structure and morphology, narrow size distribution, and large surface area is necessary.

The preparation of glasses and ceramics by the sol−gel method is affected by a number of factors such as reaction temperature, catalyst concentration, nature of the metal ion precursor, amount of water, and type of solvent. Various shapes (powder, monolith, fiber) can be obtained by controlling these factors. The hydrolysis of $Si(OR)_4$ has been the subject of numerous investigations, and several reviews and books pertaining to the chemistry of silica have been published.[21−25] On the other hand, only few reports exist in the literature regarding the hydrolysis and gelation of $Mg(OR)_2$.[26−29] No report exists in the literature on the effect of different solvents in the hydrolysis of $Mg(OCH_3)_2$.

In the present work, we have investigated the effect of various solvents (in addition to toluene) on the hydrolysis of magnesium methoxide to have a better understanding of the gelation process. The gelation process was followed for a series of solvents, the wet gels were dried by solvent evaporation in air followed by vacuum, and the properties of the resulting dry gel were investigated.

Experimental Section

A. Materials. Commercially available $Mg(OCH_3)_2$ solution (Aldrich, 8.0 wt % in methanol, stored in nitrogen), $Zr(OPr)_4$ (Aldrich, 70 wt % in propanol), $Ti(OPr)_4$ (Aldrich, 98%), methanol (Aldrich, 99.93%, A. C. S. HPLC grade), propanol (Aldrich, 99.5 +%, HPLC grade), toluene (Aldrich, 99.8%, anhydrous), benzene (Fluka, 99.5%), hexane (Fisher Scientific A. C. S. certified), ethyl benzene (Aldrich, 99.8%), propyl benzene (Aldrich, 98%), mesitylene (Aldrich, 98%), *N*,*N*-dimethyl aniline (Aldrich, 99.5 +%), anisole (Aldrich anhydrous, 99.7%), acetone (Fisher A. C. S. certified, dried over molecular sieves), acetonitrile (Riedel de Haën, AMD chromasolv), *N*,*N*-dimethylformamide (Fisher Scientific A. C. S. certified), and dimethyl sulfoxide (DMSO) (Fisher Scientific A. C. S. certified) were used. Water used was deionized.

B. Preparation of Wet Gels. Six 0.4 M $Mg(OCH_3)_2$ solutions in methanol and methanol−solvent mixtures were prepared with varying solvent to methanol volume ratios of 0, 0.39, 0.88, 0.94, 1.11, and 1.67. Six 0.8 M H_2O in methanol and methanol−solvent mixtures were prepared with solvent to methanol volume ratios of 0, 0.25, 0.68, 1.55, and 2.94. In each experiment, 5 mL of a water solution was first transferred into a vial. In a separate vial, 5 mL of $Mg(OCH_3)_2$ solution was prepared. Next, 5 mL of $Mg(OCH_3)_2$ solution was rapidly added to the water solution. Throughout the study, the concentration of $Mg(OCH_3)_2$ was kept at 0.4 M, and that of water was kept at 0.8 M. In this manner, while varying the methanol and solvent ratios in the mixture, the water-to-methoxide ratios were kept constant. Combinations of the above-prepared solutions in the mixture gave solvent to methanol volume ratios of 0, 0.1, 0.4, 0.8, 1.6, and 1.96. These samples are identified as MM000, MM010, MM040, MM080, MM160, and MM196.

The gelling process was visually monitored by gently tilting the vial from time to time to observe any changes in the viscosity of the gel. The time when the contents became very viscous was recorded as the gelling start time. The time when the contents in the vial refused to pour was recorded as the gelling end time. In certain instances, in the cases of $Zr(OPr)_4$ and $Ti(OPr)_4$ hydrolysis, it was difficult to accurately determine the gelling start time and hence only the gel end times were recorded.

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. Next, the vials were placed in a vacuum desiccator and vacuum-dried for 3 days. Finally, the vials were transferred to an oven and heated at 60 ± 4 °C until constant weight was obtained. It was observed that for the gels prepared using toluene, benzene, anisole, and acetone, 2 days of drying at 60 ± 4 °C was sufficient, whereas for the gels prepared using acetonitrile and *N*,*N*-dimethylformamide, 3 days was necessary to obtain constant weight. Gels prepared using *N*,*N*-dimethylaniline (bp 193 °C) and dimethyl sulfoxide (bp 189 °C) were very difficult to dry under these conditions. These gels were not dry even after 45 days at 60 ± 4 °C, and hence further studies were not undertaken using gels prepared from these two solvents.

Barium methoxide was prepared by the reaction of Ba metal with methanol in a manner similar to that reported previously.[14]

D. Characterization of Dried Gels. *1. X-ray Diffraction (XRD).* For XRD studies, the dried gel was ground into powder and loaded onto the sample holder of a Bruker D8 Advance Series 2 instrument that uses Cu Kα radiation ($\lambda = 0.1544$ nm). The diffractometer was operated at a voltage of 40 kV and 40 mA. The scan was a step scan from 10° to 70° (2θ) with a step size of 0.025°.

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Table 1. Effect of Solvents on the Hydrolysis of $Mg(OCH_3)_2$[a]

solvent	time (s)	MM000 solvent/CH_3OH = 0.00	MM010 solvent/CH_3OH = 0.10	MM040 solvent/CH_3OH = 0.40	MM080 solvent/CH_3OH = 0.80	MM160 solvent/CH_3OH = 1.60	MM196 solvent/CH_3OH = 1.96
toluene	gel start	30	20	17	10	9	instant
	gel end	35	25	22	20	12	8
hexane	gel start	30	18	15	[b]	[b]	[b]
	gel end	35	27	20	[b]	[b]	[b]
benzene	gel start	30	19	15	10	10	instant
	gel end	35	28	20	16	16	8
ethyl benzene	gel start	30	18	15	10	10	[b]
	gel end	35	23	20	15	14	[b]
propyl benzene	gel start	30	24	17	17	9	[b]
	gel end	35	33	23	21	15	[b]
mesitylene	gel start	30	16	16	11	[b]	[b]
	gel end	35	27	22	18	[b]	[b]

[a] MM000, MM010, MM040, MM080, MM160, and MM196 refer to samples prepared with solvent/methanol ratios of 0, 0.10, 0.40, 0.80, 1.60, and 1.96, respectively. [b] Forms an immiscible mixture.

Table 2. Effect of Solvents on the Hydrolysis of $Mg(OCH_3)_2$[a]

solvent	time (s)	MM000 solvent/CH_3OH = 0.00	MM010 solvent/CH_3OH = 0.10	MM040 solvent/CH_3OH = 0.40	MM080 solvent/CH_3OH = 0.80	MM160 solvent/CH_3OH = 1.60	MM196 solvent/CH_3OH = 1.96
N,*N*-dimethyl aniline	gel start	30	22	20	20	instant	instant
	gel end	35	30	28	25	22	12
anisole	gel start	30	22	15	16	6	instant
	gel end	35	26	25	24	16	10
acetone	gel start	30	18	16	13	10	5
	gel end	35	25	20	17	15	15
acetonitrile	gel start	30	30	18	14	8	16
	gel end	35	36	23	18	14	21
N,*N*-DMF	gel start	30	34	25	27	24	19
	gel end	35	43	38	42	32	24
DMSO	gel start	30	29	24	16	16	20
	gel end	35	39	28	23	18	27

[a] MM000, MM010, MM040, MM080, MM160, and MM196 refer to samples prepared with solvent/methanol ratios of 0, 0.10, 0.40, 0.80, 1.60, and 1.96, respectively.

2. Nitrogen Adsorption. The nitrogen adsorption measurements were carried out on the dry gel at 77 K using a Quantachrome Nova 1000 series gas adsorption analyzer. The BET (Brunauer, Emmett, and Teller) surface area, S_{BET}, was obtained by applying the BET equation to a relative pressure range of 0.05−0.35 in the adsorption isotherm. The total pore volume, V, was evaluated from the amount of nitrogen adsorbed at the highest relative pressure of 0.99. The pore-size distribution was estimated by applying the BJH (Barrett, Joyner, and Halenda) method to the desorption isotherm.

3. Fourier Transform-Infrared (FT-IR) Spectroscopy. FT-IR experiments were conducted on a Nicolet Nexus 670 FT-IR spectrometer. The dried gel powder was mixed with a small amount of KBr (Acros, IR grade, 99+%). The mixture was pressed into a thin disk under a load of 7000 lbs. The disk was quickly transferred to the spectrometer sample holder to record the IR spectrum.

4. Scanning Electron Microscopy (SEM). SEM experiments were conducted on a Hitachi S-3500 N instrument. The SEM samples were prepared by spreading a small amount of the dried gel on a double-coated tape fixed onto the aluminum specimen mount stub for the electron microscope study. Elemental analyses were performed with the S-3500N instrument equipped with an Oxford detector for energy-dispersive X-ray analysis (EDXA) coupled with the Oxford Inca Energy Microanalysis system. For the EDXA analyses, a gold film of about 30 nm thickness was coated atop the specimen to make the specimen surface electrically conductive. The metal overlayer is too thin to be seen by the SEM and usually does not cause loss of detail.

5. Transmission Electron Microscopy (TEM). TEM samples were prepared by spreading a small amount of the dry gel directly on a TEM grid. The sample was observed under a Philips CM100 electron microscope at the Kansas State University Biology Research Microscope and Image Processing Facility.

6. Thermal Gravimetric Analysis (TGA). TGA studies were carried out under a flow of air. The dry gel was placed in the Pt mini balance and heated from room temperature to 700 °C at a heating rate of 10 °C/min in a flow of air using a thermogravimetric Shimadzu TGA-50 analyzer.

Results and Discussion

Using different combinations of water (0.8 M) solution and $Mg(OCH_3)_2$ solutions (0.4 M), six different solvent to methanol volume ratios were obtained. Table 1 shows the results from the six combinations which have solvent-to-methanol ratios of 0, 0.1, 0.4, 0.8, 1.6, and 1.96. In all cases, hydrolysis resulted in the formation of rigid gels. Clear gels were formed when the solvents employed were toluene, benzene, anisole, and acetone, while gels prepared using DMSO solvent were found to be translucent and gels prepared using acetonitrile and *N*,*N*-DMF were found to be rigid but opaque. From Table 1, we can see that the gelling time is relatively short and decreases in general with an increase in the ratio of solvent to methanol. The longest gelling time is less than a minute, which occurs when there is no toluene present. Each measurement is an average value of three experiments. On the basis of the data presented in Tables 1 and 2, a correlation can be made between the gelation time and the dielectric constant of the solvent. For example, in case of solvents (solvent/methanol volume ratio = 1.96) having low dielectric constant such as toluene, benzene, and anisole, the formation of gel is instant on addition of water solution to $Mg(OCH_3)_2$ solution and the gel end times are very short, that is, 8, 8, and 10 s,

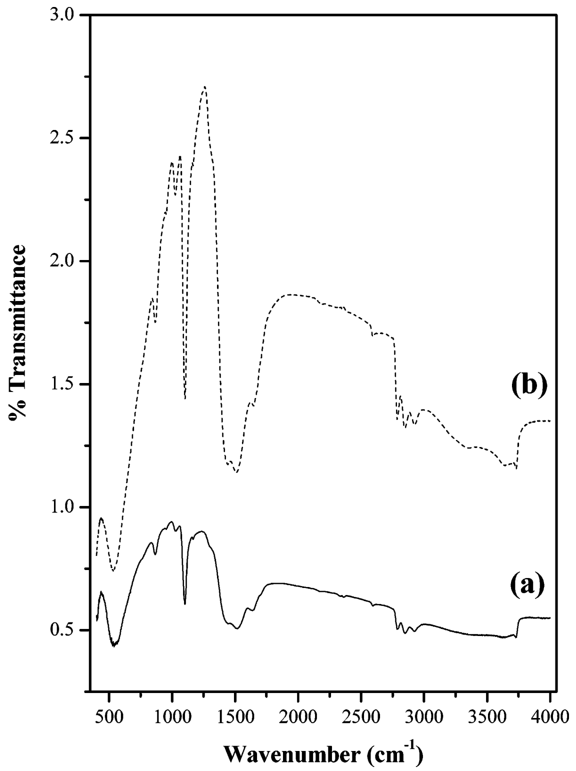

Figure 1. FT-IR spectra of the dried gels derived from hydrolysis of $Mg(OCH_3)_2$ with (a) toluene/CH_3OH = 1.96 and (b) CH_3CN/CH_3OH = 1.96.

respectively. Other low dielectric constant solvents such as hexane, ethyl benzene, propyl benzene, and mesitylene were not miscible with methanol at high volume ratios (solvent/methanol = 1.6 and 1.96), and hence no further studies were carried using the above-mentioned solvents. Thus, the time required for gelation is strongly dependent on the ratio of solvent/alcohol. However, in the case of the gels prepared using higher dielectric constant solvents such as acetonitrile, *N*,*N*-dimethylformamide, and DMSO (solvent/methanol volume ratio = 1.96), no clear trend in the gelation time with variation in the solvent/methanol ratio was observed. The gel end times are 21, 24, and 27 s, which are not significantly different in the absence of these solvents.

To obtain detailed information on the hydrolysis products, the wet gels were dried as stated in the Experimental Section. The XRD pattern (not shown) of the dried gel derived from the hydrolysis of $Mg(OCH_3)_2$ and having a volume ratio of toluene/methanol of 1.96 showed broad and distorted peaks at 2θ values near 17°, 37°, and 59° indicative of the presence of amorphous $Mg(OH)_2$. In addition to these three peaks, a small decaying peak starting at a 2θ value of ca. 33° is seen. This peak indicates the presence of $Mg(OH)(OCH_3)$, suggesting that the hydrolysis is only completed partially even when a stoichiometric amount of water is used. The XRD patterns for all of the remaining other dried gels were all similar to the one described above.

IR spectra were further recorded for the dried gels. The IR spectrum of the dried gel derived from the hydrolysis of $Mg(OCH_3)_2$ and having a volume ratio of toluene/methanol of 1.96 is shown in Figure 1a. The sharp band at 3735 cm^{-1} is indicative of isolated $-OH$ groups, while the broad band in the region of $\sim$3400 cm^{-1} indicates the presence of hydrogen-bonded $-OH$ groups.[14] The bands at 2920, 2846, and 2788 cm^{-1} and at 1100 cm^{-1} are all indicative of the presence of $-OCH_3$ groups.[14] Similar results have been obtained by us previously for samples prepared in this manner as well as samples prepared by the hypercritical drying procedure.[14,20] The presence of surface carbonates can be discerned from the bands observed at 1654, 1515, and 1440 cm^{-1}.[14] The band near 1030 cm^{-1} is assigned to the ν_{C-O} stretch.[20] The IR results show no indication of ring vibrations due to the presence of toluene. This clearly suggests that the solvent, toluene, has been completely removed by the drying procedure employed. In addition, a band near 540 cm^{-1} appears which is indicative of the Mg$-$O bond.[14] The IR spectra of all other dried gels were similar, and Figure 1b shows the FT-IR spectrum of $Mg(OCH_3)_2$ prepared using acetonitrile. The IR spectrum is similar to that of Figure 1a, indicating that the solvent, acetonitrile, is completely removed. The FTIR spectra of other dry gels were similar to those prepared using toluene solvent, indicating the facile removal of the solvents by relatively mild drying conditions. The FTIR results are consistent with the XRD results, which suggest the presence of some $-OCH_3$ groups left unhydrolyzed. This suggests that the hydrolysis proceeds in two steps as shown by eqs 1 and 2:

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

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

where eq 2 is slower than eq 1 under the experimental conditions employed in the present investigation.

The presence of $-OCH_3$ groups has been observed previously in the works of Utamapanya et al.,[14] Diao et al.,[20] Chadwick et al.,[27] and Rywak et al.[30] Rywak et al.[30] studied the hydrolysis of $Mg(OCH_3)_2$ with water-to-methoxide ratios of 1 and 4 and found that even when excess water (i.e., $H_2O/Mg(OCH_3)_2 = 4$) was used, $Mg(OH)(OCH_3)$ was formed as one of the hydrolysis products. Similarly, Chadwick et al.[27] inferred from NMR studies that, despite extensive hydrolysis, $-OCH_3$ groups persist until extensive calcinations have been performed. The XRD patterns of their samples heated to 300 °C showed the presence of both $Mg(OH)_2$ and $Mg(OH)(OCH_3)$. Only after calcining at 500 °C did the XRD patterns show peaks due to MgO. Utamapanya et al.[14] and Teichner and co-workers[16] too detected the presence of $-OCH_3$ groups after the hypercritical drying procedure. This was attributed to the esterification of the hydroxyl groups by the alcoholic solvent under the autoclave treatment conditions. Utamapanya et al.[14] observed a white cloudy precipitate upon addition of water to a stirred mixture containing $Mg(OCH_3)_2$ and toluene. After a few minutes, the solution turned into a white syrup-like solution. In the present study, the methoxide$-$methanol$-$toluene solution was added to a water$-$methanol$-$toluene mixture. This allowed a good mixing of the reactants, and consequently the mixture remained clear. The gel was however found to be opaque when acetonitrile and *N*,*N*-DMF were used as solvents.

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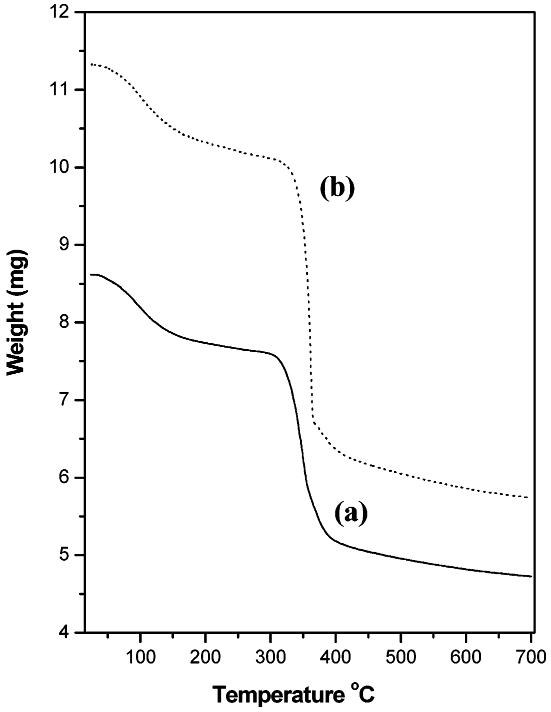

Figure 2. TGA of the dried gels derived from hydrolysis of $Mg(OCH_3)_2$ with (a) toluene/CH_3OH = 1.96 and (b) toluene/CH_3OH = 0.

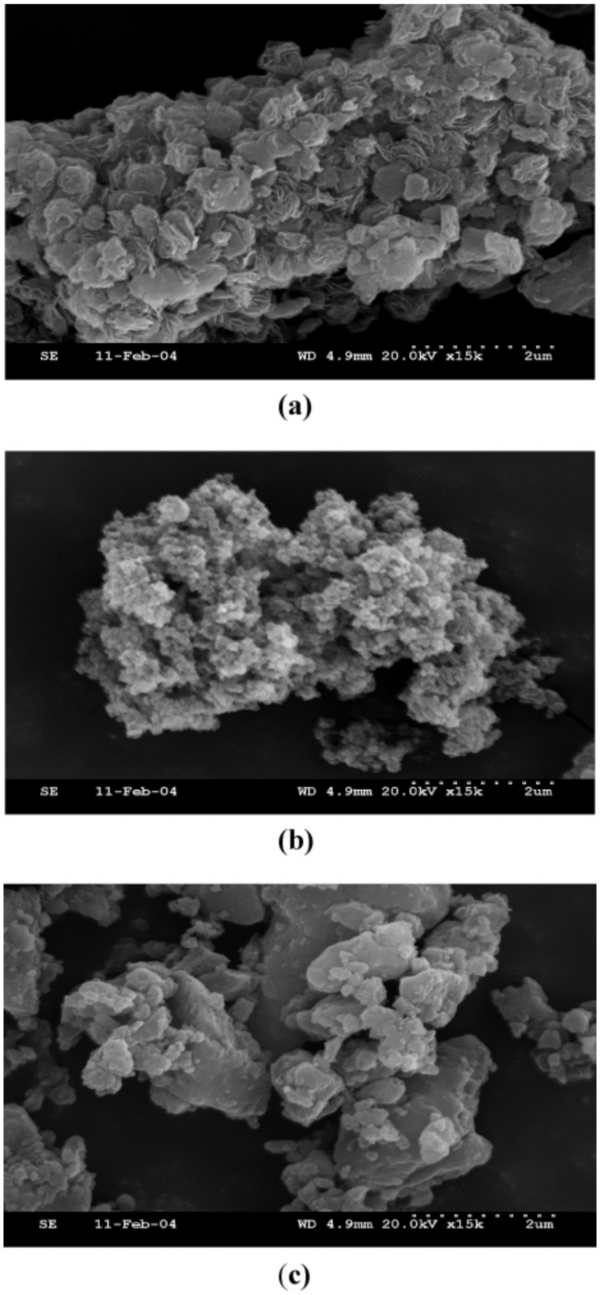

Figure 3. SEM pictures of gels derived from hydrolysis of $Mg(OCH_3)_2$ with (a) toluene/CH_3OH = 0, (b) anisole/CH_3OH = 1.96, and (c) DMF/CH_3OH = 1.96.

Figure 2 shows the weight loss for the dry gel prepared from the hydrolysis of $Mg(OCH_3)_2$ with toluene/methanol ratios of 0 and 1.96. The total weight loss was 49% and 45.2%, respectively, for these two samples. There are two major weight losses, from room temperature to 150 °C (loss of physisorbed water) and from 300 to 400 °C due to loss of chemisorbed water and decomposition of $-OCH_3$ groups. The conversion of $Mg(OH)_2$ to MgO should yield a weight loss of 31%. The SEM-EDXA analysis of all of the dried gels showed that they contained 8−10 wt % C. Such high residual C content was also encountered by Utamapanya et al.[14] and Teichner and co-workers.[16]

The structure of the dried powders was further studied by SEM and TEM studies. Figure 3 shows the SEM pictures of dry gel prepared from the hydrolysis of $Mg(OCH_3)_2$ with toluene/methanol ratios of 0 and gel prepared with anisole/methanol = 1.96 and *N*,*N*-DMF/methanol = 1.96. The striking differences in the morphology between the three samples are evident. The gel prepared with only methanol as the solvent shows hexagonal platelets of brucite, while the gel prepared with anisole/methanol = 1.96 shows no clear structure. The SEM photograph shows a highly porous weblike structure. The SEM of $Mg(OH)_2$ prepared with toluene and benzene also shows a highly porous weblike matrix. In stark contrast, the gels prepared from solvents such as acetonitrile and *N*,*N*-DMF display mixed morphologies, with large clusters of small particles and large irregular-shaped particles. To further probe the morphology of the dry gels, TEM studies were undertaken. Figure 4 shows the TEM of the dry gel prepared from the hydrolysis of $Mg(OCH_3)_2$ with toluene/methanol ratios of 0 and 1.96. The TEM micrograph of $Mg(OH)_2$ prepared without any toluene shows a multitude of strands with a polymer-like network. However, the micrograph of the gel prepared with toluene/methanol = 1.96 shows a more uniform and porous material. The SEM and TEM studies thus reveal that rapid gelation in case of solvents such as toluene, benzene, and anisole leads to the formation of more uniform and highly porous materials, while solvents such as acetonitrile and *N*,*N*-DMF lead to the formation of large irregular particles.

The dried gels were characterized by nitrogen adsorption studies. Adsorption on mesoporous materials proceeds via multilayer adsorption followed by capillary condensation. Thus, the amount adsorbed gradually increases as the relative pressure increases, and then at higher pressures, the amount adsorbed increases steeply due to capillary condensation in the mesopores. Once these pores are filled, the adsorption isotherm levels off. Capillary condensation and capillary evaporation do not take place at the same pressure, and hence

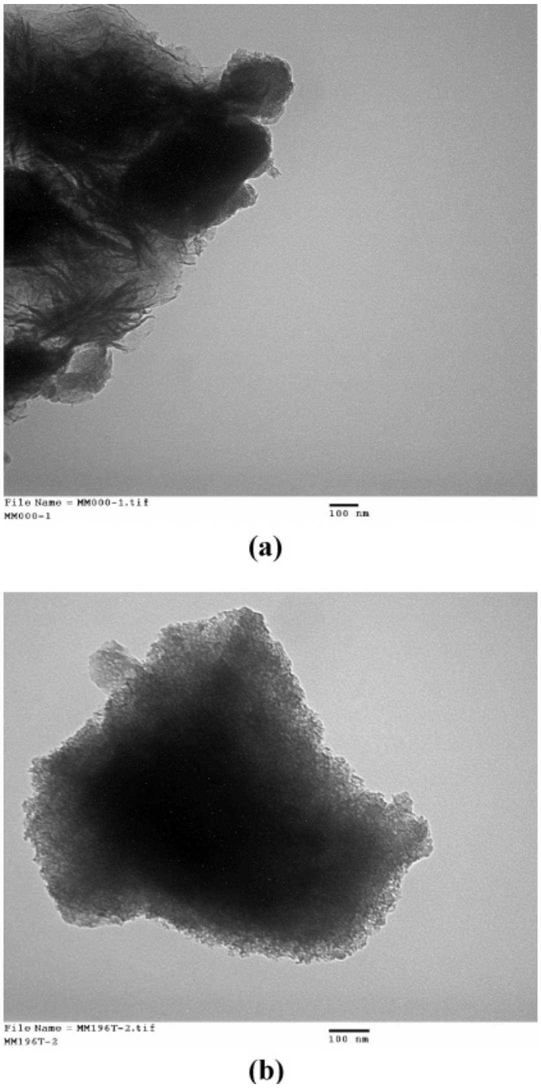

Figure 4. TEM pictures of gels derived from hydrolysis of $Mg(OCH_3)_2$ with (a) toluene/CH_3OH = 0 and (b) toluene/CH_3OH = 1.96.

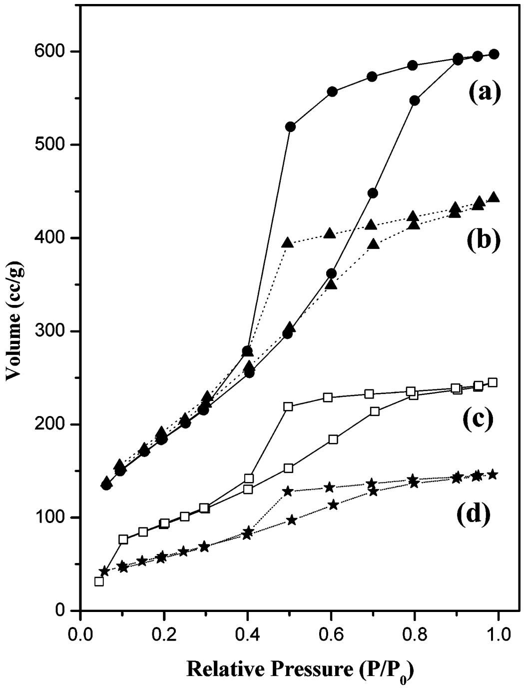

Figure 5. Nitrogen adsorption isotherms for the dried gels from hydrolysis of $Mg(OCH_3)_2$ with (a) toluene/CH_3OH = 1.96, (b) anisole/CH_3OH = 1.96, (c) toluene/CH_3OH = 0, and (d) *N*,*N*-DMF/CH_3OH = 1.96.

Table 3. Textural Properties of the Dried Gels Derived from the Hydrolysis of $Mg(OCH_3)_2$[a]

sample	solvent	S_{BET} (m^2/g)	pore volume (cm^3/g)	pore diameter (BJH) (Å)
MM000	toluene	348	0.38	37
MM196	toluene	687	0.91	36
MM196	benzene	579	0.73	36
MM196	anisole	705	0.68	36
MM196	acetone	524	0.62	34
MM196	methyl ethyl ketone	528	0.51	34
MM196	acetonitrile	425	0.38	36
MM196	*N*,*N*-DMF	220	0.22	36

[a] MM000 and MM196 refer to $Mg(OH)_2$ samples prepared with solvent/methanol ratios of 0 and 1.96, respectively.

this leads to the appearance of hysteresis loops. Figure 5 shows the nitrogen adsorption isotherms for the dried gels obtained with various solvent-to-methanol ratios. These isotherms exhibit broad hysteresis typical of adsorbents possessing mesopores. The hysteresis loop has a triangular shape and a steep desorption branch. This is classified as type H2 according to the IUPAC nomenclature.[31] Such behavior has been observed in many porous inorganic oxides and was attributed to pore connectivity effects.[32] These have been traditionally attributed to the presence of pores with small openings (ink bottle pores). However, in recent years, H2 hysteresis loops were observed for materials even with uniform pores when the desorption branch happened to be located at relative pressures in the vicinity of a lower pressure limit of adsorption−desorption hysteresis.[33] This lower limit is characteristic of a given adsorbate at a given temperature. We can see from Figure 5 that the lower pressure limit of the hysteresis loop is at P/P_0 = 0.4 irrespective of the adsorbent. The TEM and the SEM pictures clearly suggest that the gels prepared with a toluene/methanol ratio of 1.96 are highly porous. Thus, the appearance of a H2 hysteresis loop in the proximity should not be regarded as evidence of pore connectivity or ink-bottle pore shape. The gel prepared with a volume ratio of toluene/methanol = 1.96 shows a very steep adsorption isotherm as compared to the other samples, indicating the highly porous nature of the sample. Table 3 shows the results obtained from the nitrogen adsorption studies. The BET surface area of the dried gels progressively increased with an increase in the toluene/methanol ratio from 348 to 687 m^2/g; the total pore volume too increased from 0.38 to 0.91 cm^3/g. The BET surface areas of the dried gels prepared from low dielectric constant solvents such as toluene, benzene, and anisole (volume ratio of solvent/methanol of 1.96) are ∼600 m^2/g, and decrease when high dielectric constant solvents such as acetonitrile and *N*,*N*-DMF are used. However, the pore diameters calculated from the BJH desorption isotherms were found to be similar irrespective of the solvent employed in the study. Figure 6 shows the pore-size distribution of the dried gels prepared with volume ratios of toluene/methanol = 1.96

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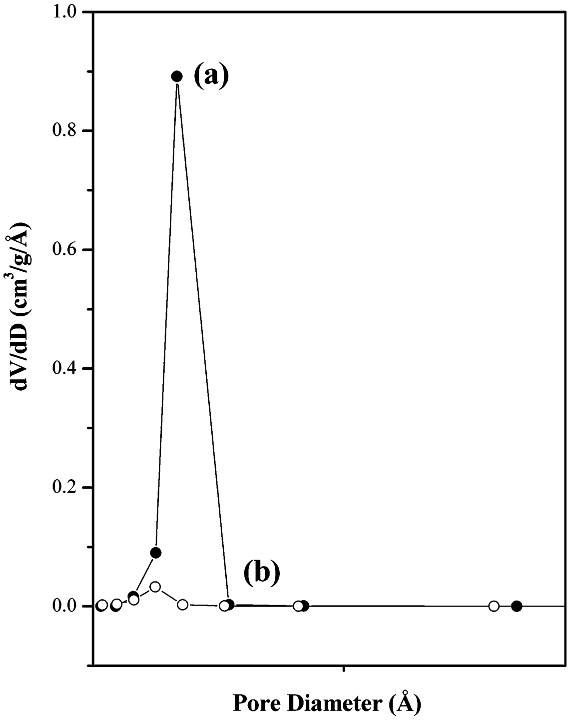

Figure 6. Pore-size distribution of the dried gels from hydrolysis of $Mg(OCH_3)_2$ with (a) toluene/CH_3OH = 1.96 and (b) toluene/CH_3OH = 0.

and 0. The sample containing toluene has a sharper pore-size; gels prepared from solvents such as benzene and anisole too showed a narrow pore-size distribution, while gels prepared from solvents such as *N*,*N*-DMF and acetonitrile showed a broad pore-size distribution. The surface areas of the dried gels prepared with a high ratio of toluene/anisole/benzene to methanol are quite comparable to the surface areas of the gel produced by the autoclave hypercritical drying procedure. This suggests that the autoclave procedure, which is an expensive method especially for large-scale production, is not necessary for producing high surface area inorganic hydroxides, in this case, $Mg(OH)_2$. From the surface area analysis and TEM studies, the mean particle size (fundamental building block of aggregates and strands, not necessarily the crystallite size) of the dry gels is estimated to be ~5 nm when toluene is used as the solvent. Similarly, when benzene and anisole were used as the solvents, the mean particle sizes were estimated to be ~6 and ~5 nm, respectively. When only methanol was used as the solvent, the mean particle size is ~10 nm, while using *N*,*N*-DMF as the solvent led to particle size of ~15 nm. Solvents such as toluene/benzene or anisole lead to the formation of particle sizes similar to the ones prepared by the hypercritical autoclave procedure (3−5 nm).

To understand the role of the solvent, a plot of the dielectric constant of the solvent and the surface area and the pore volume of the resulting dried gels was made. Figure 7a and b shows the correlation obtained between the dielectric constant of the solvent (ϵ) and the surface area and pore volume of the resulting dry gels. A linear correlation is observed, suggesting that the solvation of the alkoxide−alcohol mixture by the solvents employed is important in the gelation process and in the subsequent formation of the dry gel. Figure 8 shows the plot of gelation time and the dielectric constants of the solvent used in the study. It can be seen that the gelation time increases with an increase in the dielectric constant of the solvent. This suggests that the degree of solvation of the alkoxide−methanol−water mixture is different for different solvents and increases with increasing dielectric constants. Hence, use of solvents of higher dielectric constants would result in stronger solvation of the alkoxide, resulting in the lowering of the hydrolysis rate and thus increasing the gelation time. The effects of solvents have been studied mainly in the context of “drying control chemical additives” (DCCA) in the sol−gel process of silica.[34,35] These are used as cosolvents with alcohol to facilitate rapid drying of monoliths and help in the formation of crack-free monoliths. Solvents such as methanol, acetone, acetonitrile, dioxane, formamide, glycerol, and *N*,*N*-dimethylformamide are some of the solvents that were found to affect the rate of hydrolysis and condensation of tetraethyl (methyl) orthosilicate.[36−40]

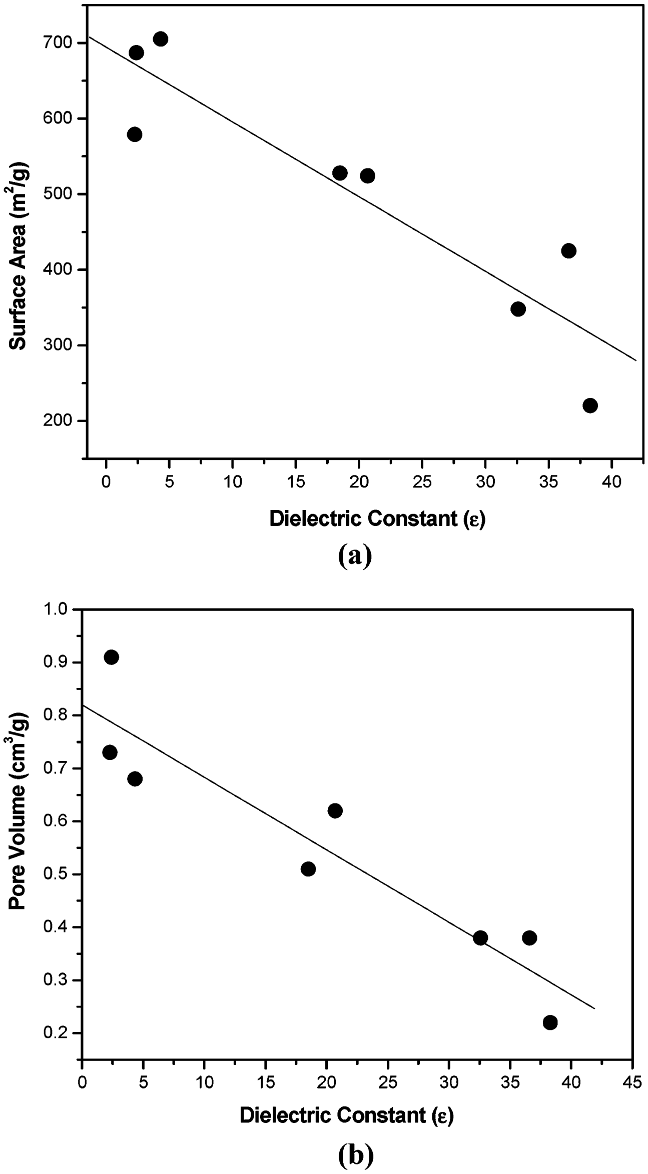

Figure 7. Plot of dielectric constant of solvent and (a) surface area (m^2/g) of the dried gels and (b) total pore volume (cm^3/g).

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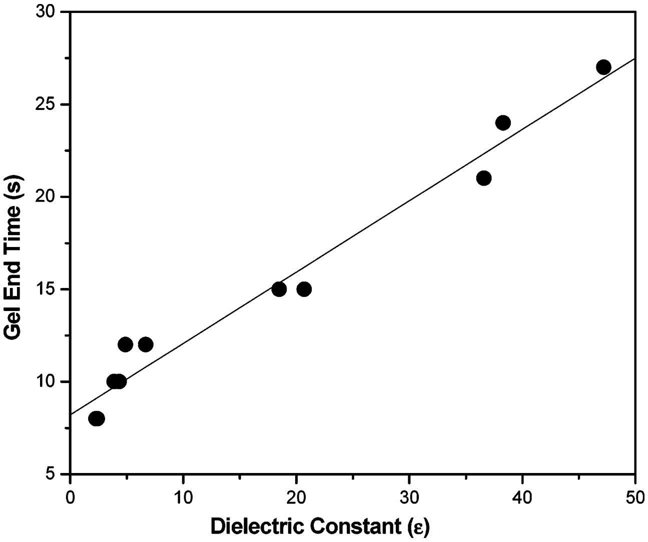


Figure 8. Plot of gel end time and dielectric constant (ϵ) of solvents employed (volume ratio of solvent/methanol = 1.96) in the hydrolysis of $Mg(OCH_3)_2$.

Table 4. Partial Charge on M(δ) for Various Alkoxides and Gelation Time in the Presence and Absence of Toluene[a]

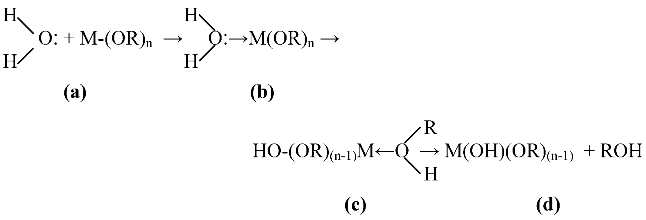
alkoxide precursor	partial charge on M(δ)	gelation time ROH/toluene = 0	 ROH/toluene = 1.6
$Ba(OCH_3)_2$	+0.97	no gel formation	no gel formation
$Mg(OCH_3)_2$	+0.72	35 s	8 s
$Zr(O(CH_2)_2CH_3)_4$	+0.65	2160 s	25 s
$Ti(O(CH_2)_2CH_3)_4$	+0.61	gel formation started after 3 days[b]	11 s

[a]From ref 44. [b] The gel end time was difficult to determine because a very soft gel was obtained.

The sol−gel processing of silicates from silicon alkoxides has been the subject of numerous investigations. However, the hydrolysis of metal alkoxides has not been studied extensively. Metal alkoxides are generally very reactive species, which is due to the presence of electronegative alkoxy groups (−OR) making the metal atom prone to nucleophilic attack. The lower electronegativity of metallic elements as compared to Si leads to a much higher electrophilic character of the metal ion. The reaction of metal alkoxides with water leading to the formation of hydroxides or hydrous oxides can be described by reaction 3:

$$M(OR)_n + nH_2O \rightarrow M(OH)_n + nROH \qquad (3)$$

The formation of an oxide network involves two chemical processes, hydrolysis and condensation. Hydrolysis of each alkoxide is thought to occur through a three-step mechanism as described below:[41,42]



The species $M(OH)(OR)_{(n-1)}$ undergoes further hydrolysis to eventually give $M(OH)_n$. The first step (a) is the nucleophilic addition of a water molecule to the positively charged metal ion leading to the formation of a transition state (b). The second step involves proton transfer within the transition state (b) to the leaving alkoxy group leading to intermediate (c). Finally, the third step involves the departure of the leaving group (ROH). The whole process (a) to (d) follows a nucleophilic substitution mechanism, and the reaction will be highly favored when the nucleophilic character of the entering molecule and the electrophilic character of the metal atom are strong, that is, when $\delta(O) \ll 0$ and $\delta(M) \gg 0$. On the other hand, the nucleophilic substitution also depends on the coordinative unsaturation of the metal alkoxide and on the ability of the proton to be transferred within the intermediate (b). The more acidic the proton, the faster the transfer will be. If the proton-transfer step is the rate-limiting step, using a metal ion of higher Lewis acidity would cause the toluene effect (dielectric constant decrease) to be lessened.

A more accurate description of the chemistry involved in the above reactions requires knowledge of the charge distribution of the atoms. This could be done with the partial charge model.[41] This model allows the calculation of the partial charge distribution of any complex to predict its chemical reactivity. According to the model, the electronegativity (χ_i) of an atom varies linearly with the partial charge (δ_i), and electron transfer stops when the electronegativities of all atoms become equal to the mean electronegativity.[43] The partial charge model corresponds to a thermodynamic approach and gives a reasonable estimate of the enthalpy changes involved in these chemical reactions. However, is does not take into account steric hindrance effects, resonance effects, and entropy variations. Nevertheless, the partial charge model has been applied successfully to describe the chemical reactions involved in sol−gel processes and provides a useful guide for inorganic reactions.[44]

To understand the effect of toluene in the hydrolysis of magnesium methoxide, the hydrolysis of other alkoxides was studied. A main limitation, however, was the insolubility of several alkoxides. Hence, the hydrolysis of calcium methoxide, strontium methoxide, aluminum isopropoxide, and zinc *tert*-butoxide could not be followed. The other alkoxides that were studied are barium methoxide, titanium propoxide, and zirconium propoxide. $Zr(OPr)_4$ (Aldrich, 70 wt % in propanol) and $Ti(OPr)_4$ (Aldrich, 98%) were used as received. The gelation time and the partial charge (δ) on M for the alkoxides are shown in Table 4.

From Table 4, we can see that the toluene effect is lessened when the electrophilic power (measured by δ(M)) is more

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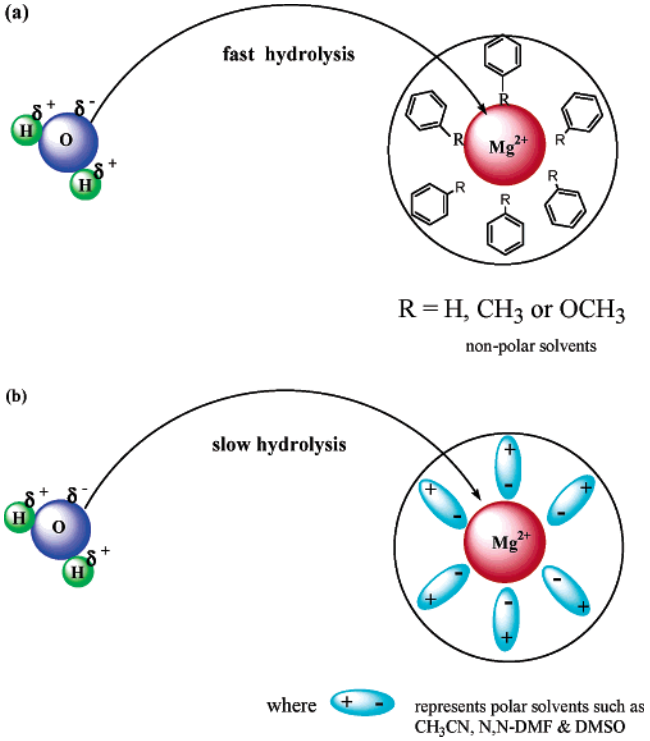
positive. As stated earlier, the hydrolysis of $Mg(OCH_3)_2$ proceeds in two steps as shown previously by eqs 1 and 2. If eq 2 is actually an equilibrium, then the equilibrium constant K would be increased with an increase in added toluene, because the toluene–water incompatibility would be minimized. This may explain why the hydrolysis rate is enhanced with increasing amounts of toluene. Also, one can expect lower solubility of $Mg(OH)_2$ in nonpolar solvents such as toluene. Because of the insolubility of $Mg(OH)_2$ in toluene, eq 2 would be pushed to the right. The resulting high supersaturation could promote nucleation. Low solubility would inhibit subsequent digestion of the nuclei and formation of larger crystallites. Hence, the observed high surface area and porosity are consistent with undigested nuclei (nanocrystallites). Increase in solubility of $Mg(OH)_2$ in polar solvents would reduce supersaturation and promote digestion with the formation of larger particles. A third explanation could be that solvents such as toluene, benzene, or anisole may force the water molecules to complex with Mg^{2+} rapidly (to minimize water incompatibility) and that structure (b) is formed in high concentration and subsequent proton transfer is the rate-limiting step. If the proton-transfer step is assumed to be the rate-limiting step, then the toluene effect should be most significant for $Ti(OCH_2CH_2CH_3)_4$ and least for $Ba(OCH_3)_2$. Consider that the positive charge on $\delta(M)$ decreases in the order $\delta(Ba) > \delta(Mg) > \delta(Zr) > \delta(Ti)$. Therefore, the rate of nucleophilic addition of water to the metal alkoxides is normally in the order $Ba(OCH_3)_2 > Mg(OCH_3)_2 > Zr(OCH_2CH_2CH_3)_4 > Ti(OCH_2CH_2CH_3)_4$. In fact, in the work at hand, in the case of $Ba(OCH_3)_2$, which is more electrophilic as compared to $Mg(OCH_3)_2$, the addition to toluene did not cause any increase in the rate of gel formation. The results shown in Table 4 thus suggest that the proton-transfer step as depicted in step (b) → (c) is the rate-determining step for the following reasons. The use of nonpolar aprotic solvents such as toluene, benzene, and anisole could force the water molecules to complex with the metal ion more quickly, and structure (b) is formed in high concentrations. Using a metal ion of higher electrophilicity should then cause the toluene effect to be lessened (it does not need toluene to force the hydrolysis reaction). This is indeed the case as is evidenced from Table 4.

When highly polar solvents such as methanol, *N*,*N*-DMF, acetonitrile, and DMSO are used, the alkoxides are solvated to give $M(OR)_x\cdot$solvent solvates. Metal alkoxides behave as Lewis acids and react with Lewis bases leading to solvate formation. This reaction seems to be favored when the electrophilic power $\delta(M)$ of the metal atom is high. Stable $M(OR)_4\cdot$solvent solvates have been observed for alkoxides such as $Ti(OEt)_4$ ($\delta(Ti) = +0.60$), $Zr(OPr^i)_4$ ($\delta(Zr) = +0.65$), and $Ce(OPr^i)_4$ ($\delta(Ce) = +0.75$).[45] Livage et al. have reported that the stability of such solvates increases with the positive charge of the metal atom.[42] Similarly, because Mg is highly electrophilic ($\delta(Mg) = +0.72$), the formation of stable $Mg(OCH_3)_2\cdot$solvent solvates (where solvent = acetonitrile, *N*,*N*-DMF, or DMSO) would be favorable. Because of solvate formation, they would be stable toward hydrolysis, and hence the gelation times would be longer when these solvents are used. In fact, stable addition compounds between alkoxide and nucleophilic molecules such as DMF, DMSO, or even ROH have been isolated.[46,47] The hydrolysis of magnesium methoxide in the presence of nonpolar solvents such as toluene, benzene, and anisole and polar solvents such as acetonitrile, *N*,*N*-DMF, or DMSO is depicted in Scheme 1.

Scheme 1. Diagrams Representing the Hydrolysis of Magnesium Methoxide in the Presence of (a) Low Dielectric Constant Solvents and (b) High Dielectric Constant Solvents



Conclusion

The hydrolysis of $Mg(OCH_3)_2$ depends on the solvent used. When low dielectric constant solvents are employed, the faster are the hydrolysis and gelation and the higher is the surface area of the dried gel. The presence of such solvents helps in the formation of a more open porous structure and high surface area materials. However, when solvents having high dielectric constants are used, the gelation is slower due to the possible formation of alkoxide–solvent solvates. The partial charge model was invoked to explain the hydrolysis of metal alkoxides in the presence of toluene. Also, the study demonstrates that, with the appropriate choice of solvents (such as toluene, benzene, or anisole), high surface area porous inorganic oxides can be obtained. High-temperature hypercritical procedure does not seem to be necessary for the preparation of nanoscale $Mg(OH)_2$.

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