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Effects of Temperature and Solvent on the Hydrolysis of Alkoxysilane under Alkaline Conditions

Hongmei Jiang, Zhen Zheng, Zhiming Li, and Xinling Wang*

School of Chemistry and Chemical Technology, Shanghai Jiaotong University, Shanghai 200240, China

Fourier transform infrared (FTIR) spectroscopy was employed to study the hydrolysis reaction of methyltriethoxysilane (MTES) in an alkaline catalyzed system. The effects of reaction temperature and solvent on the hydrolysis rate were investigated. The hydrolysis rate constants, activation energy, and Arrhenius frequency factor were achieved by linear regression analysis for MTES hydrolysis in the alkaline system. The results showed that the hydrolysis reactions were obviously affected by the reaction temperature and solvents, and had larger activation parameters in the alkaline system than those in an acid system. It is possible that hydrogen-bonding characteristics and "hydrophobic interaction" resulted in the different hydrolysis rates of MTES in the various solvents of MeOH, EtOH, DOX, and DMF.

Introduction

The sol−gel technique is a method for synthesis through hydrolysis and condensation of metal organic and inorganic compounds.[1] The advantages of the technique over the melting process, chlorosilane hydrolysis, or silane pyrolysis are the homogeneity and high purity of the gels and a relatively low sintering temperature. Materials that can be prepared by this technique include functional ceramics, monodisperse dense colloids, zeolites and related molecular sieves, amorphous silicon resins, and molecular crystals composed of cagelike species.[2−4] It has been found that the structure and properties of these products are governed by the dynamic process.[5] To understand how to control the silicon structure and properties through processing conditions, it is essential to investigate the subtle interplay of all factors influencing the rates of processes and contributing to structure evolution.

The pH of the silicate system causes major qualitative changes in the behavior of sol−gel systems.[6−10] In general, under moderately acidic conditions with sufficient ethanol present, alkoxysilane produces transparent, homogeneous gels; as the pH is raised, the gels become cloudy, and as the pH is raised still further (in alkaline systems), monodisperse silica particles are formed.[2] In previous studies, the studies of alkoxysilane hydrolysis and condensation focused mainly on acid catalyzed systems and ^{29}Si NMR was the most frequently used tool.[2−9] However, there are few studies related to the hydrolysis of alkoxysilane in an alkaline catalyzed system since the system would show serious phase separation during the hydrolysis process, resulting in the great difficulty of following the hydrolysis process. The serious phase separation would lead to loss of NMR signal, which makes ^{29}Si NMR no longer considered to be a very powerful tool to study the sol−gel process.[11]

Solvents may have considerable influence on the hydrolysis−condensation behavior of the alkoxysilane compounds. Kinetic studies of acid catalyzed polycondensation of silanols was performed in a polar or weakly polar solvent, which affected the course of the reaction.[12−14] Bernards and co-workers investigated the effect of alcoholic solvents on the hydrolysis kinetics of alkoxysilane under acid systems. They found the

different hydrolysis rates in the different alcohols and explained them as the different dissociation degrees of HCl.[15] In formamide and methanol solutions, the rates of hydrolysis were different because of the different viscosity and hydrogen-bonding characteristics.[11] The role of formamide during condensation was also investigated, and it was found that it had a large influence on the gelation time.[16] Hendricks found that the solvents had a great effect on the distribution of silicate oligomers at hydrolysis−condensation equilibrium.[17]

Trialkoxysilane compounds are important to the silicone industry, for their hydrolysis is often viewed as the initial reaction in the moisture curing—the process produces polysiloxane elastomers, coatings, adhesives, and sealants.[7] This study focused on the reaction process of methyltriethoxysilane (MTES) hydrolysis in alkaline systems. Ethoxysilane was chosen over methoxysilane because of appropriate reaction rates and avoiding libration of toxic methanol. As mentioned above, these systems would not be good candidates for ^{29}Si NMR to study the reaction kinetics. Therefore, we will explore the analytical capabilities of vibration spectroscopy for the "in situ" study of these systems. In acid systems, Fourier transform infrared (FTIR) spectroscopy can be regarded as a powerful tool to study the hydrolysis process.[5,18−19] In this study, FTIR was used to "in situ" monitor the hydrolysis process of MTES in alkaline systems with a 1:11 molar ratio of H_2O to silane at several temperatures. The rate constants and the activation energy parameters were obtained by linear regression analyses. The effect of solvent structure on the hydrolysis process of MTES in alkaline systems was also studied.

Experimental Section

Materials. Methyltriethoxysilane (MTES), used as a precursor, was purchased from Shanghai Resin Factory Co. Ltd. and used as received. Methanol (MeOH), ethanol (EtOH), 1,4-dioxane (DOX), and *N,N*-dimethylformamide (DMF) were used as solvents. Distilled water was used for hydrolysis, and sodium hydroxide was used as catalyst.

Hydrolysis of MTES at Different Temperatures. MTES was added to a solvent to form a solution. The solution and an alkaline solution with pH 12.10 were put in a reactor at a given temperature and mixed quickly after both solution temperatures were same. The mixture was transferred into the liquid cell of the FTIR spectrometer with an injector and continually scanned

* To whom correspondence should be addressed. Tel.: +86-21-54745817. Fax: +86-21-54741297. E-mail: xlwang@sjtu.edu.cn.

at different times. The hydrolysis reaction rate can be affected by the amount of NaOH. In this system, the hydrolysis reaction is moderate when the molar concentration of NaOH is about 0.01 M. The hydrolysis of MTES was conducted at 20−50 °C. The molar ratio of alkoxysilane/H_2O/1,4-dioxane was 1:11:8.2 (volume ratio was 1:1:5). The reaction mixture was transparent and homogeneous at first, and separated into two phases with the progress of the hydrolysis reaction. The upper transparent phase was monitored.

Hydrolysis of MTES in Different Solvents. For different solvents, the sol−gel systems from alkaline catalyzed MTES were prepared at room temperature (23 ± 2 °C). The volume ratio of alkoxysilane/H_2O/solvent was 1:1:5, and the pH value was 12.90. Typically, the reaction system was obtained by quickly mixing the MTES organic solutions with an appropriate amount of NaOH aqueous solution, and then the mix solution was immediately transferred into the liquid cell of the FTIR spectrometer with an injector. The mixture was "in situ" monitored and scanned by FTIR spectroscopy at different times.

Standards Used in the Preparation of Calibration Curve. Samples of known concentration were used to establish the relationship between the intensity of the absorption band and the concentration for MTES in 1,4-dioxane. The basic principle of quantitative IR spectroscopy was described in a previous paper.[20]

Data Analysis. Linear regression analyses were performed using the data analysis software of Origin 7.0, which uses the Levenburg−Marquardt minimization algorithm. The tolerance for convergence was set to 1×10^{-6}.

Technique. Infrared (IR) spectra were obtained by a Perkin-Elmer 1000 FTIR spectrometer from 700 to 4000 cm^{-1}. The spectral resolution was 2 cm^{-1} and collection time was about 1 min. An infrared liquid cell with BaF_2 windows was employed, which was suitable for aqueous systems and worked as a reactor. Therefore, the hydrolysis of alkoxysilane could be "in situ" monitored. Teflon film with a thickness of 0.05 mm was used as spacer.

Results

For the different systems of MTES under alkaline conditions, two phases were obtained (liquid and solid). The solid phase appeared as white particles which stuck to the walls of the flask. All results on the hydrolysis of MTES were related to the liquid phases in this paper. The solid particle was considered to be silica of condensation products, which would not affect the hydrolysis process.[5]

Representative FTIR spectra from the alkaline catalyzed hydrolysis of methyltriethoxysilane (MTES) at 50 °C are shown in Figure 1. Table 1 listed the assignments of all characteristic peaks observed in Figure 1.[5,16,19]

From the moment of mixing, the hydrolysis of MTES started. As seen in Figure 1, the intensity of the absorption peak at 960.0 cm^{-1}, which was attributed to Si−OCH_2CH_3, decreased with reaction time and finally disappeared after 1 h. The absorption band at 1650.0 cm^{-1} was assigned to the deformation vibration of O−H in H_2O, and its intensity decreased with reaction time but was still strong after 1 h due to excess water in the system. Broad absorption bands were observed between 1000.0 and 1200.0 cm^{-1}, and their positions, intensities and shapes changed with hydrolysis progress. The shoulder peak at 1127.0 cm^{-1}, attributed to Si−O−C vibration, decreased with reaction time. The band at 1053.0 cm^{-1}, identified as absorption bands of Si−O−Si and C−O vibration of alcohol, increased with reaction time. The band at 1370.7 cm^{-1} belonging to C−H vibration of
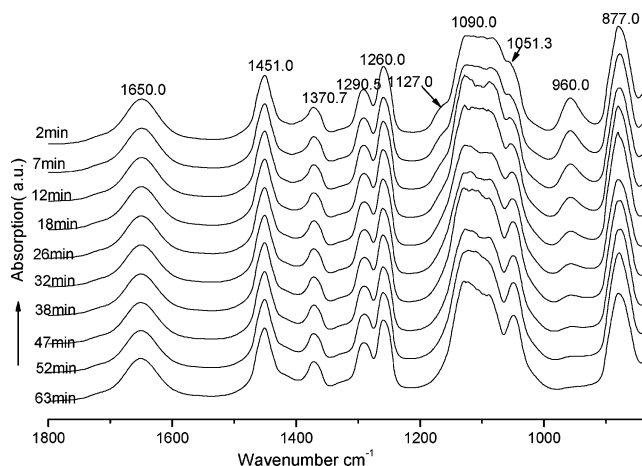

Figure 1. Evolution of IR spectra with time during hydrolysis for the MTES alkaline catalyzed system at 50 °C.

Table 1. Assignment of IR Bands in the Alkaline Catalyzed System between 800.0 and 1850.0 cm^{-1}

freq at max (cm^{-1})	assignment	vibration mode[a]
877.0	CH_3CH_2OH	v(C−C/C−O)
960.0	$CH_3Si(OCH_2CH_3)_3$	v(Si−O−C)
1051.3	silica network, CH_3CH_2OH, 1,4-dioxane	v(Si−O−Si/C−O)
1090.0	silica network, $CH_3Si(OCH_2CH_3)_3$	v(Si−O−Si/Si−O−C)
1127.0	$CH_3Si(OCH_2CH_3)_3$	v(Si−O−C)
1260.0	$CH_3Si(OCH_2CH_3)_3$	v(Si−C)
1290.5	$CH_3Si(OCH_2CH_3)_3$, CH_3CH_2OH	$\delta_{as}(CH_2)$
1370.7	$CH_3Si(OCH_2CH_3)_3$	$\delta_s(CH_2)$
1451.0	$CH_3Si(OCH_2CH_3)_3$, CH_3CH_2OH	$\delta_{as}(CH_2)+ \delta_{as}(CH_3)$
1650.0	H_2O	v(O−H)

[a] v, stretching vibration; δ_s, symmetry bending vibration; δ_{as}, antisymmetry bending vibration.

methylene could be used as the internal reference peak in quantified analysis because its intensity remained constant during the whole hydrolysis process.

The bands around 1086.0 and 1045.0 cm^{-1} were attributed to the C−C−O skeleton vibration for pure ethanol.[5] However, the two bands were overlapped with the symmetric vibration of the Si−O−C and Si−O−Si of condensation products. Therefore, the broad band between 1100.0 and 1000.0 cm^{-1} indicated the decrease of MTES concentration and the simultaneous formation of partially hydrolyzed monomer species, as well as the formation of EtOH during the hydrolysis reaction. However, since the broad band at 1090.0 cm^{-1} was from multiple origins, the variation of its intensity would not provide quantitative information on the hydrolysis reaction.

Effect of Temperature on Hydrolysis of MTES. Though MTES hydrolysis reactions showed similar IR spectra under different temperatures, their reaction rates were very different. The hydrolysis rate obviously decreased with the decrease of temperature. It took about 1 h at 50 °C and 1.5 h at 40 °C for MTES to be completely consumed. At 20 °C, the hydrolysis reaction was much slower, and did not finish after 4 h. Evolution of the IR spectra of MTES hydrolysis reactions at 20, 30, and 40 °C was similar to that shown in Figure 1. The intensities of the bands at 960.0 and 1168.0 cm^{-1} that were associated with MTES and of the band at 1647.3 cm^{-1} of H_2O were decreased while the intensities of the bands of EtOH increased with reaction time. The change in the intensity of MTES absorption at 1100.8 cm^{-1} was difficult to follow due to the bands overlapping with those of hydrolyzed products.

FTIR spectroscopy can be used as a quantitative tool to measure species in solution or suspension. The basic principles
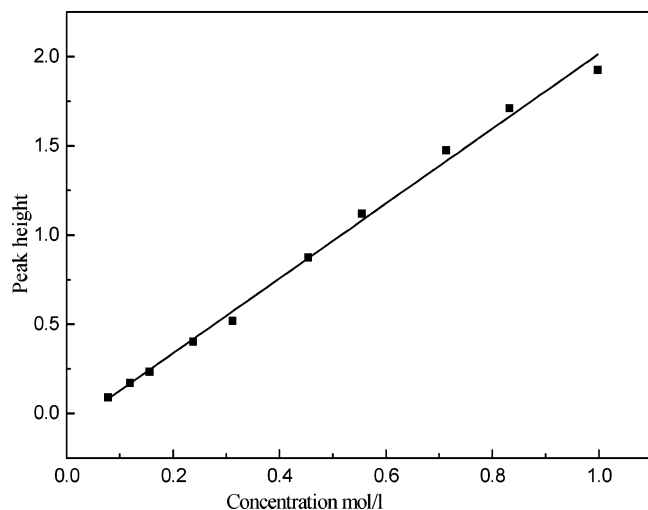
Figure 2. Calibration curve for MTES in 1,4-dioxane: using the height of the peak at 960.0 cm^{-1}.
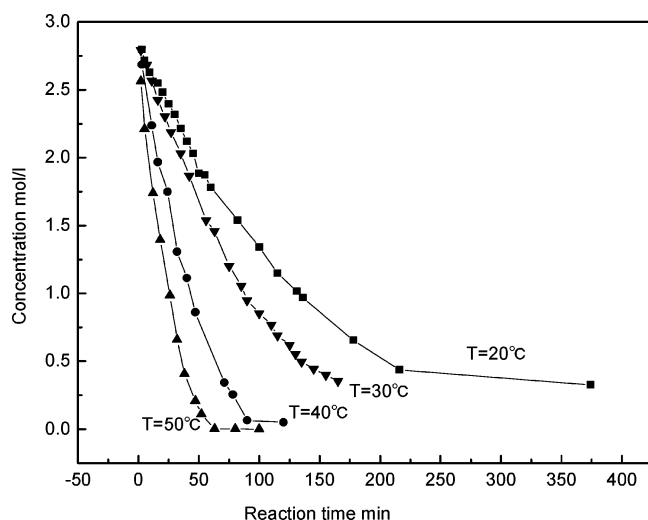

Figure 3. Kinetics of hydrolysis for alkaline MTES system at different temperatures, inferred from the height of peak at 960.0 cm^{-1}.
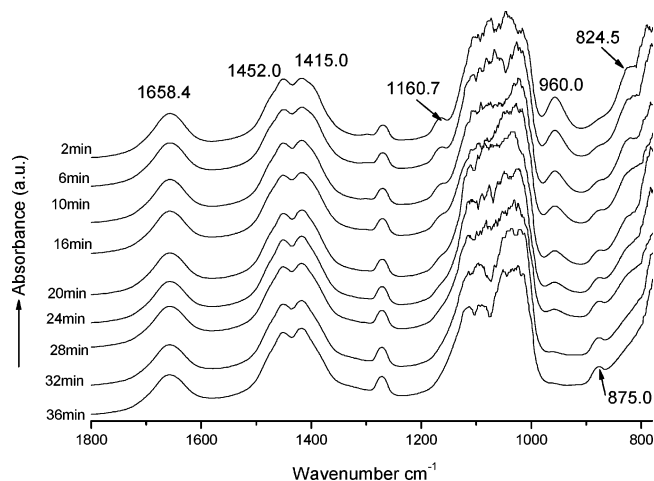

Figure 4. FTIR spectra of MTES in alkaline system at different times, MeOH as solvent. The interval of each spectrum is 2 min.

were described in a previous paper.[20] For a given set of sample parameters, as far as the refractive index of the sample does not change with concentration, the plot of the absorbance of IR band (*A*) vs concentration (*C*) should be a straight line. To get quantitative information from IR spectra, a standard curve was needed to calibrate the system. The calibration curve of MTES in 1,4-dioxane is shown in Figure 2. The characteristic peak of MTES at 960.0 cm^{-1} was followed since it was strong and was not overlapped by any other bands.

A fit straight line of the type $y = kx$ ($k = 2.099$) through the experiment points was obtained by linear regression with Origin 7.0. The proportion of total variation as given by the square of the multiple correlation coefficient, R^2 (0.9955), was excellent.

The kinetics of MTES hydrolysis can be expressed by the changes of MTES concentration in the reaction system. Figure 3 shows the results of the hydrolysis of MTES at 20, 30, 40, and 50 °C. In the system at 50 °C, the change of MTES concentration exhibited a typical exponential decay, which suggested that the reaction followed first-order law. The concentration reached a minimum after approximately 1 h, which indicated that the hydrolysis of MTES was finished. In the systems at 20, 30, and 40 °C, the changes of MTES were very similar to that in the system at 50 °C. The hydrolysis of MTES was finished after 1.5 h in the system at 40 °C. However,

the system showed a much lower hydrolysis rate at 20 °C. The concentration of MTES decreased slowly and reached a minimum of about 0.4 M after 4 h. The results indicate that temperature greatly affected the hydrolysis of MTES, especially at lower temperature.

Effect of Solvent on Hydrolysis of MTES. Solvent is an important factor on the hydrolysis−condensation behavior of alkoxysilane compounds. To study the solvent effect on the hydrolysis of MTES, FTIR spectroscopy was used to study the hydrolysis rate of MTES in methanol (MeOH), ethanol (EtOH), 1,4-dioxane (DOX), and *N*,*N*-dimethylformamide (DMF), respectively. In this paper, all reactions were carried out at pH 12.90, *T* (temperature) = 23 ± 2 °C, and the ratio of MTES/H$_2$O = 1:11 (mol). Figure 4 shows the FTIR spectra of MTES hydrolysis in MeOH. The FTIR spectra of MTES hydrolysis in DOX were similar to those in Figure 1 except for a slower hydrolysis rate. The FTIR spectra in EtOH and DMF were also similar to those in MeOH.

In Figure 4, the IR bands of MTES at 1160.7, 960.0, and 824.5 cm^{-1} are observed. Their intensities decreased with reaction time. A new absorption band at 875.0 cm^{-1} appeared, which was attributed to EtOH, and its intensity increased with time. Its intensity change could also provide qualitative information on hydrolysis. MTES hydrolysis in MeOH was fast, and the characteristic bands of MTES disappeared after about 30 min. In the EtOH system, similar IR spectra were obtained. However, the hydrolysis rate was lower than that in the MeOH system.

N,*N*-Dimethylformamide (DMF) was used as a drying control chemical additive in preparing homogeneous glasses, which could significantly reduce fracturing. DMF was found to inhibit the hydrolysis of tetramethyl orthosilicate (TMOS) in an acid catalyzed system.[11] In alkaline systems, similar results were obtained. The hydrolysis of MTES in DMF was much slower than that in MeOH, EtOH, and DOX. After 150 min, the concentration of monomer was large and decreased at a lower rate. The IR variations of the hydrolysis process in DMF were similar to that in Figure 4. However, the change of IR bands related to hydrolysis and condensation was more clearly observed, since DMF, itself, had no IR band between 1100.0 and 1000.0 cm^{-1}. According to the hydrolysis reaction, the intensities of IR bands related to ethanol (1050.0, 1023.0, 881.5 cm^{-1}) increased with reaction time. The band at 1090.0 cm^{-1}, attributed to the vibration of Si−O−Si in MTES condensation products, could be observed with the reaction progress.
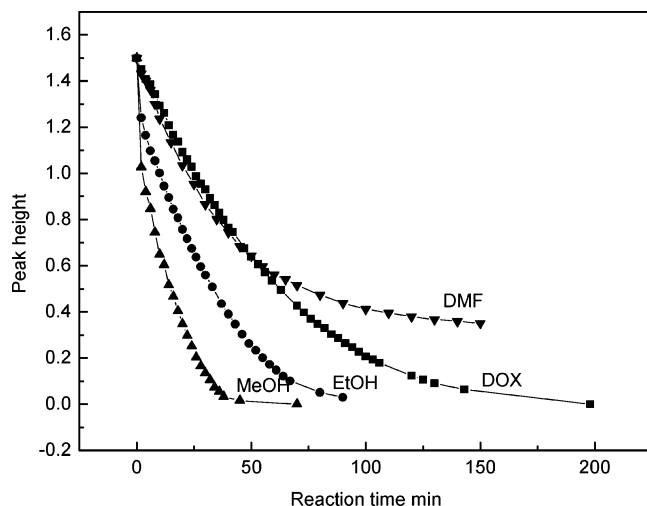
Figure 5. Kinetics of hydrolysis for MTES in alkaline system at different solvents, inferred from the peak height of MTES at 960.0 cm^{-1}.
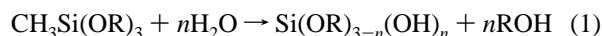
The kinetics of MTES hydrolysis can be expressed by the increase in concentration of EtOH or the decrease of MTES in the reaction solution. The concentration change is relational with the characteristic peak height in an FTIR spectrum.[11] In this paper, the kinetics of hydrolysis of MTES were studied through following the decrease of the MTES peak at 960.0 cm^{-1} since this peak was a strong single peak. The kinetics of hydrolysis of MTES at different solvents is shown in Figure 5.

The results indicate that the rate of MTES hydrolysis was obviously affected by the solvents. The time of complete consumption of monomer was defined as hydrolysis finished time (t_H). The t_H values were 30, 60, 120, and >150 min for MTES hydrolysis to be finished in MeOH, EtOH, DOX, and DMF, respectively.
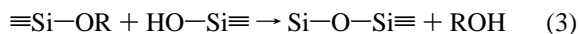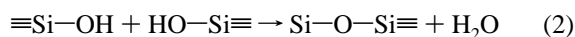
Discussion

In alkoxysilane hydrolysis, the alkoxy groups on the silicon atom are replaced by hydroxyl groups. The replacement may not occur on all alkoxy units at the same time, and the hydrolysis and condensation reactions are shown below.[11]

hydrolysis:

$$CH_3Si(OR)_3 + nH_2O \rightarrow Si(OR)_{3-n}(OH)_n + nROH \quad (1)$$

condensation:

$$\equiv Si-OH + HO-Si\equiv \rightarrow Si-O-Si\equiv + H_2O \quad (2)$$

$$\equiv Si-OR + HO-Si\equiv \rightarrow Si-O-Si\equiv + ROH \quad (3)$$

Under alkaline conditions, condensation of partially hydrolyzed species may occur prior to complete hydrolysis. In contrast, hydrolysis in most cases is faster than condensation reaction in acidic medium.[21]

Figure 1 indicates that the intensity of peak at 960.0 cm^{-1} decreased but that at 1050.0 cm^{-1} attributed to EtOH increased with reaction time since the hydrolysis of MTES started after the alkaline solution was added. However, the peak at 940.0 cm^{-1} assigned to SiOH was not observed in these studies.[19] This showed that the hydrolyzed SiOH was consumed immediately by condensation since the condensation rate was much faster than the hydrolysis rate. It suggested that the hydrolysis reaction of alkoxysilane under alkaline conditions should be rate-limiting for the overall reaction. The dimethyldiethoxysilane hydrolysis under alkaline conditions showed a similar result
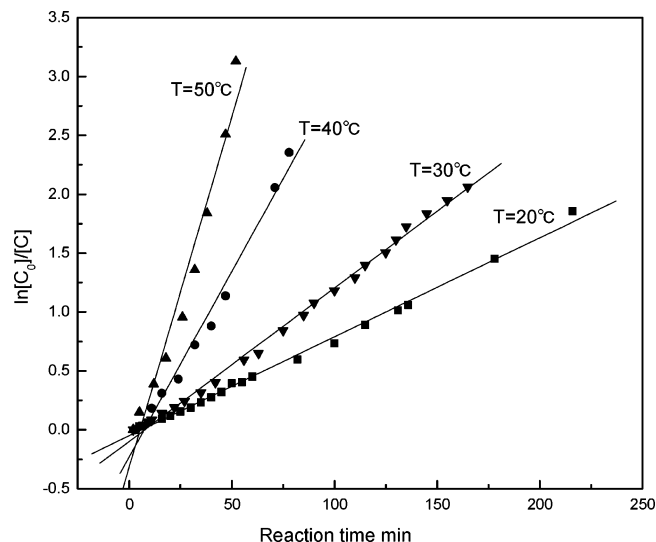

Figure 6. Results of fitting eq 4 to all measured experiment data in Figure 4.

Table 2. Reaction Rate Constants for MTES Hydrolysis at Different Temperatures

temp (°C)	rate const ($\times 10^4$ s^{-1})	dependence
20	1.401 ± 0.021	$R^2 = 0.9979$
30	2.453 ± 0.283	$R^2 = 0.9966$
40	5.245 ± 0.258	$R^2 = 0.9916$
50	8.960 ± 0.626	$R^2 = 0.9907$

characterized by ^{29}Si NMR.[2] The results indicate that monitoring the change of MTES is an effective method for studying the hydrolysis dynamics.

In Figure 1, the intensity of the characteristic peak of Si–OCH$_2$CH$_3$ decreased with reaction time. The evolution was in agreement with the decrease of MTES concentration with the proceeding hydrolysis. Figure 3 shows the evolution of MTES concentration with time at different temperatures. The concentration of monomer showed an exponential decrease with reaction time. This indicates that temperature had a great influence on the hydrolysis of MTES under alkaline conditions. At higher temperature, the hydrolysis of MTES proceeded faster. The hydrolysis of MTES finished after 1 h at 50 °C, 1.5 h at 40 °C, and over 4 h at 20 °C until the absorption band at 960.0 cm^{-1} almost disappeared, respectively.

In this study, MTES can only participate in the hydrolysis reaction via eq 1 and the rate constant is K_h. Water was largely excessive compared with MTES in these systems. The reaction was determined to have a first-order dependence on the monomer. Therefore, the initial slope of the ln [MTES] vs time curve can be used to predict the magnitude of K_h. The integrating equation of hydrolysis can be described as follows.

$$\ln \frac{[T_0]}{[T_0]_0} = -K_h t \quad \text{or} \quad \ln \frac{[T_0]_0}{[T_0]} = K_h t \quad (4)$$

In eq 4, $[T_0]$ and $[T_0]_0$ refer to the MTES molar concentration in hydrolysis progress and the initial concentration, respectively. K_h denotes the hydrolysis rate constant. Figure 6 shows the results. The fitted line from linear regression analysis was based on all measured data in Figure 3. It was successful so that there was good linear fitting for the experimental data in all cases, $R^2 \approx 0.990$. The slope of the lines indicated that the rate constant was a function of reaction temperature. Table 2 shows all the rate constants. The proportion of total variation is given by the square of the multiple correlation coefficients. From Table 2, it
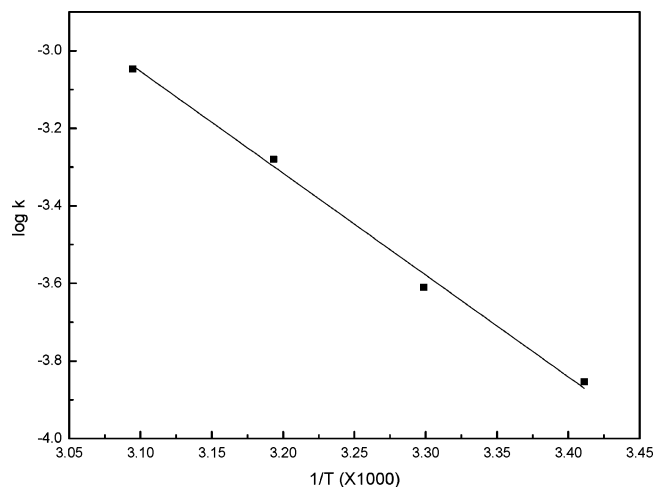
Figure 7. Plot of log k as a function of $1/T$.

is noted that the reaction rate constants are different at varied reaction temperatures, which reflects a great temperature dependence of the MTES hydrolysis.

Activation energies and the Arrhenius frequency factor of the hydrolysis reaction of MTES can be calculated through the least-squares method. The applicable Arrhenius equation is[22]

$$\log k = \log A - \frac{E_a}{2.303RT} \qquad (5)$$

where k is the rate constant, A is the Arrhenius frequency factor, E_a is the activation energy, R is the gas constant, and T is the reaction temperature. Theoretically, the plot of log k vs $1/T$ should give a straight line. The slope and intercept of the line could be used to predict the magnitude of E_a and A. Figure 7 shows the linear regression results based on the data in Table 2.

In Figure 7, the plot of log k vs $1/T$ shows good linearity. According to the slope and intercept of the line, the values of the activation energy (E_a) and the Arrhenius frequency factor are 50.09 kJ/mol and 12.24×10^4 mol^{-1}·s^{-1}, respectively.

The activation parameters for MTES alkaline catalyzed hydrolysis were in general agreement with other reports but larger than those with acid catalysis.[7] K. A. Smith has reported that the E_a value of methyltrimethoxysilane (MTMS) hydrolysis is 10.3 kcal/mol for an alkaline system and 6.4 kcal/mol for an acid system, respectively.[7] This indicates that alkoxysilane hydrolysis under alkaline conditions has a greater dependence on temperature. The activation energy (E_a) of MTES hydrolysis (11.93 kcal/mol) is slightly larger than that of MTMS hydrolysis (10.3 kcal/mol) with alkaline catalysis. The reason is that steric effect on the nucleophilic substitution reaction plays an important role and influences the overall rate of hydrolysis consisted of a nucleophilic substitution reaction wherein the hydroxyl attacks the silicon atom.[1,9,11] The MTES has a larger steric effect than MTMS to block the hydroxyl attacking Si atom, which results in larger activation energy and decreases the reaction rate.[1,24]

In Figures 4 and 5, the results clearly show that organic solvents had a great influence on the hydrolysis of alkoxysilane in alkaline systems. The hydrolysis rates decreased in the order MeOH, EtOH, DOX, and DMF. The hydrolysis rate of MTES in DMF was slower than that in MeOH, and showed results similar to those of tetramethyl orthosilicate (TMOS) hydrolysis.[11]

The organic solvents could affect the existing state of water, and then the hydrolysis rate. The influence of organic solvents on the structuring of water was commonly attributed to "hydrophobic interaction".[17] It was assumed that water molecules existed in a two-state equilibrium:

$$H_2O_{free} \rightleftharpoons H_2O_{H\text{-bonded}} \qquad (6)$$
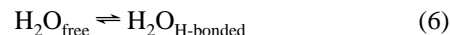
Generally, the organic solvent conduced to produce more hydrogen-bonded water molecules.[17]

Based on the equilibrium of reaction 6, the influence of hydrophobic interaction on the hydrolysis of MTES could be understood. The hydrolysis rate would decrease since the organic solvent can cause the equilibrium (6) to shift to the right and result in less free H_2O participating in the hydrolysis reaction. The ability of the functional group of solvent in polarizing the alkyl of the molecule is different; thus the water molecular structuring effect or "hydrophobic interaction" is different. In MeOH or EtOH system, the oxygen atom in hydroxyl has a higher withdrawal of electron density from the alkyl group or a weaker "hydrophobic effect" than that in DOX or DMF, which produced more free water molecules to participate in the hydrolysis or show a higher hydrolysis rate. The presence of organic solvents would promote forming a three-dimensional hydrogen-bonded structure of water, which becomes more pronounced as the organic species chain length increases due to the steric effect.[25] Compared with MeOH and EtOH, DOX has a symmetrical ring structure and larger steric effect, which probably blocks the oxygen atom in DOX from forming a strong hydrogen bond with the water molecule and results in fewer free water molecules or a lower hydrolysis rate. The hydrolysis rate in DMF was lower than those in MeOH, EtOH, and DOX, since the electron-withdrawing capacity of the oxygen atom in DMF is decreased somewhat by the presence of π electrons and the electronegativity of nitrogen is lower than that of oxygen.

Alcohol is a special solvent for alkoxysilane hydrolysis, since it may participate in the sol−gel reaction. There may be other reasons for the different hydrolysis rates of MTES in MeOH or EtOH except for the steric effect. Therefore, it should be discussed separately. It has been found that exchange reaction of alkoxy groups occurs when an alcohol solvent is used with an alkoxy group different from the alkoxy groups of the silane.[26,27] The exchange reactions are strong for a tetra-1-propoxysilane (TPOS)−methanol mixture but negligible for a TMOS−1-propanol mixture.[12] In this study, when MeOH was used as a solvent, the exchange reaction between ethoxyl group and MeOH would occur, which would increase the hydrolysis reaction. Though EtOH is one of the hydrolyzed products, large amounts of EtOH in the solution would result in reverse reaction of hydrolysis. In an acid system, the different proton activities of catalyst in various solvents plays an important role in the differences of alkoxysilane hydrolysis rates for different alcohols. The activity of the catalyst in MeOH is larger than that in EtOH.[15] In an alkaline system, a similar result was observed since hydroxyl have different activities in MeOH and EtOH. To explore the effect of catalyst activity on the hydrolysis reaction, other alkoxysilane hydrolysis reactions are being studied in various solvents.

Conclusion

In this work, FTIR spectroscopy was used to characterize the kinetic behavior of MTES hydrolysis in an alkaline system through following the change of the characteristic peak, which

decreased with time and disappeared at the end of the hydrolysis reaction. The peak height is lined with the concentration of the species being probed. In our study, the condensation reaction was very fast and the hydrolysis of monomer was rate-limiting for the overall reaction. The influences of temperature and solvent were investigated under alkaline conditions. From experimental data at different temperatures, the reaction rate constants were achieved by linear regression analysis. The results showed that the reaction rates were different at varied reaction temperatures and solvents, which reflected a great dependence of the MTES hydrolysis on temperature and solvent. In the MTES hydrolysis, its activation energy and Arrhenius frequency factor were 50.09 kJ/mol and 12.24×10^4 mol^{-1} s^{-1}, respectively.

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