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PROCEEDINGS

KUSTEM 5TH ANNUAL SEMINAR ON
Sustainability Science and Management

"Creating Wealth with Pristine Environment via Biotechnology"

2nd - 3rd May 2006

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Kolej Universiti Sains dan Teknologi Malaysia

Effect of dimethylformamide on the gels structure of SiO_2-gels materials from TMOS and TEOS

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Abstract

The effect of dimethylformamide (DMF) on the gelation processes of tetramethoxysilane (TMOS) and tetraethoxysilane (TEOS) were investigated by Polarization Microscope. The hydrolysis and polycondensation reactions are carried out at 50°C, with ammonium fluoride catalysts. The sol-gel was investigated on the SiO_2-gels formed using CP MAS ^{29}Si NMR spectroscopy, BET and XRD. The results have shown that the hydrolysis rate are as a function of the quantity DMF; the highest concentration of DMF produces the fastest gelation time[3, 4]. Both products showed the same textural properties. N_2 adsorption-desorption isotherms have indicated that at higher quantity DMF an increase in particle sizes and greater increase in the mean pore size. Micrographs have shown that sols are made of primary particles of about 10-20 Å in diameter. These primary structural units organize to form the secondary particles with diameter about 40-70 Å at the agglomeration solid.

Keywords --- **TMOS; TEOS; Gelation time; Dimethylformamide; Lamelar structure; Porous size.**

1. Introduction

The sol-gel process has become useful in preparing of some materials by means of hydrolysis and polycondensation reaction of alkoxides as glasses, glass-ceramic, protecting electronic materials [1] and an encapsulation of some biological object (bio-encapsulation) [2]. The useful alkoxide gels from silicone has been developed in the last decade, using source of liquid of alkoxysilane as the organic-inorganics hybrid materials. Hybrid materials usually posses some flexibility due to organic modifier present in the composition. The order of the flexibility depends on the length of carbon chains and amount of the organic and inorganic elements.

In the present work the influence of the solvent dimethylformamide (DMF; C_3H_7NO) on the gelation processes and organization structure of SiO_2-gels of alkoxysilane has been studied.

Tetramethyl octylsilicate or tetramethoxysilane (TMOS; $C_4H_{12}O_4Si$) of silica network and *tetraethyl orthosilicate* or tetraethoxysilane (TEOS; $C_8H_{20}O_4Si$) as an organic with one and two chains carbon have been selected for this work. TMOS and TEOS are most popular sources for build matrices of SiO_2 network in solid state. Its have difference reactivity with different carbon chain to contribute some degree of flexibility to the silica network in the encapsulation activity.

The equipment used, are; ^{29}Si- and ^{13}C-NMR to monitor the production of these intermediate 'silica' species. This information was combined with the results from Polarization Microscope, BET and X-rays diffraction (XRD) to determine if there is a correlation between the soluble silica concentrations and the detection of the primary particles to link the reactions in the liquid-phase to the first detection of colloids in the solid phase.

2. Materials and Methods

2.1. Materials

Quality of reagents; ammonium hydroxide (30% NH_4OH), ammonium fluoride (40% NH_4F), methanol, TMOS (99% purity) and TEOS (99% purity) were purchased from Fluka. The ethanol (99%) was purchased from Fluka. Water was produced by aquadestilation filtering system at Corriu Laboratory, UM-II, France.

The following data densities (ρ) and MWs were used to calculate the concentrations of the various chemicals: ρTMOS=1.032 kg/l, ρTEOS=0.93 kg/l, ρDMF=1.4305 kg/l MW_{TMOS}=152.22 g/mol; MW_{TEOS}=208.3 g/mol; MW_{DMF}=73.10 g/mol; $\rho_{methanol}$=0.79 kg/l, g/mol; $\rho_{ethanol}$=0.78 kg/l, $MW_{ethanol}$=46.07 g/mol; MW_{water}=18 g/mol; $\rho_{ammonia}$=0.89 kg/l (30% NH_3), $MW_{ammonia}$=17 g/mol; ρNH_4F =1.11 kg/l (40% NH_3), $MW_{ammoniumfluoride}$=37.4 g/mol..

2.2. Hydrolysis-polycondensation reaction and observation

The gelation process without DMF as the blank samples are carried under temperature of 50°C. The reactions hydrolysis and condensation of TMOS taken in absolute ethanol (EtOH) with ammoniumfluoride (NH_4F 1-4%). (The same methods are use for TEOS). However, for study of the influence solvent of dimethylformamide (DMF), the SiO_2-gel from TMOS or TEOS was prepared by mix of these alkoxysilane with variation quantitative molar volume of DMF in the presence of 1% NH_4F, under the same temperature of 50°C. The mixture was quickly introduced into the reactor tube under inert atmosphere and edges are sealed before observation, the thermostat is used for controlling temperature on 50°C. The gelation time was investigated within gelation process after mix and shake. (The same methods are use for TEOS).

2.3. Observation and characterization

Observation is used by microscope polarization for the gelation process on the mixture of the alkoxysilane with alcohol and alkoxysilane with with DMF in presence ammoniumfluoride 1%. These mixtures are injected rapidly into Teflon cells by 1.5 μm diameter, observation are passed time by time until gels formed and fracture begins [8].

The scanning electron microscope are use to know there are texture and morphology. The dimensions grain of fractal and the other possibility artifacts can be determine. The samples scanning are prepared by 1 μg dried gels in alcohol solution under ultrasound vibration for 2 hours. Data of the surface area specific and porosity of 1.0 mgr dried gels can be collected by the N_2 adsorption-desorption isotherm using Micromeritic BET equipment under the constant temperature of 120°C [8].

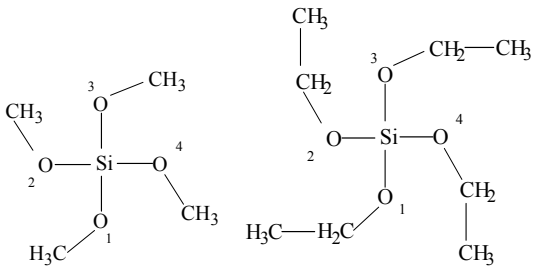
For characterizations of CP MAS ^{29}Si NMR, the SiO_2-gels were prepared by firing process in the oven at 120 ˚C. The observation were performed using a Bruker 400 MHz NMR spectrometer with a spectral width of 4100 Hz. The experiments were conducted at 298 K and were controlled to ± 2 K [8].

X-RD measurements were taken at the Phillipou Laboratory UM-II, CNRS-5636, France. The instrument was operated under low vacuum (50 mTorr) with a 4 kW power incident beam of wavelength 1.54 Å (CuKα). The (2×2 cm^2) specimen holder was placed on position sensitive detector 20 cm away from the sample to detect all of organization structure in the small gels aggregate [8].

3. Results and Discussion

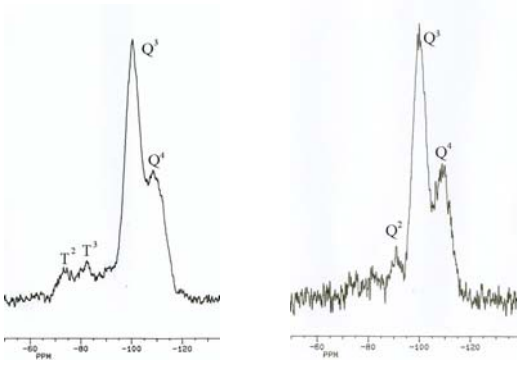
The NMR spectra information was used to determine the effect of DMF solvent, NH_3 and H_2O. Fig.1 shows the structure of TMOS and TEOS with the appropriate labels for its oxygen on the carbon backbone. Figure 2 shown that hydrolysis and polycondenzation of TMOS and TEOS in DMF produce a different spectra of ^{29}Si-O [8]. The T^1 and T^2, Q^3, Q^4 appear in the dried gels of TMOS, whereas are there are not detect on the TEOS. Reactivity of TEOS is less than TMOS due the different long chain carbon

influenced in the nucleus reaction mechanism [3, 4]. Appearing of the Q^2, Q^3, and Q^4 on dried gels TEOS shown that there are effect of DMF solvent in the liquid phase reaction.



(a) (b)

Fig. 1. The structure of TMOS (a) and TEOS (b).



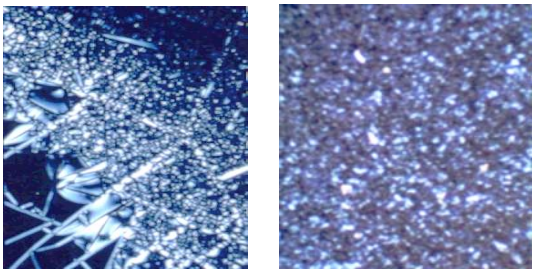
(a) (b)

Fig. 2. ^{29}Si CP MAS NMR Spectra for the SiO_2 dried gels formed in Etanol (a) and DMF (b).

Fig. 2 shows a comparison of the time gelation of a reaction mixture containing 1.0 mol alkoxysilane (TMOS or TEOS) in *fractionmole* of DMF/EtOH. The effect 1% M [NH_4F] has very little on the disappearance of Q^1; however, Q^1 was rapidly hydrolyzed to Q^3, whereas Q^2 had chance to build of peak Q^4, shown that the hydrolysis reaction are rapidly change to condense as Q^3 [8].

The intermediate product of TMOS or TEOS appeared peak on the T^2 and Q^2, which was previously identified by Brinker and Scherer in ethanol [3]. In this observation this peak as an intermediate reaction were detected at −85.4 ppm as the same peak in gels from TMOS or TEOS in *fractionmole of DMF*/EtOH. Effect of solvents on the gelation time and physical properties of gel products have been studied both as medium function and catalyst [1, 2, 3, 4 and 8].

Figure 3. shown the polarization micrograph (magnification; 20,000) of the solvent effect in the gelation of TMOS. Fractals in TMOS/EtOH are more rapid than in DMF [3, 4, 8].



(a) (b)

Fig. 3. The Polarization Micrograph of the SiO_2-gels from TMOS in EtOH (a) and in DMF (b)

Fig.4 shown that concentration of DMF influenced on the porosity of gels produced. The higher quantity DMF an increase in particle sizes and greater increase in the mean pore size.

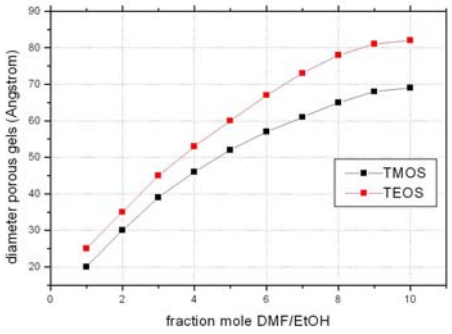
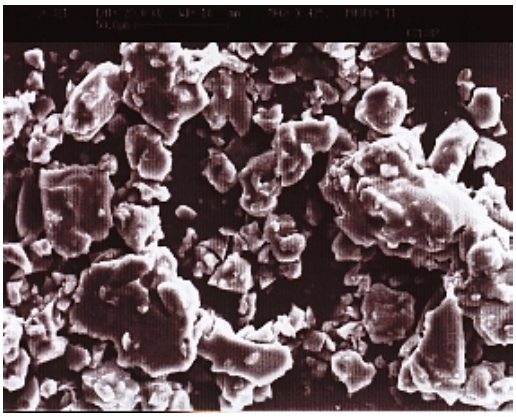
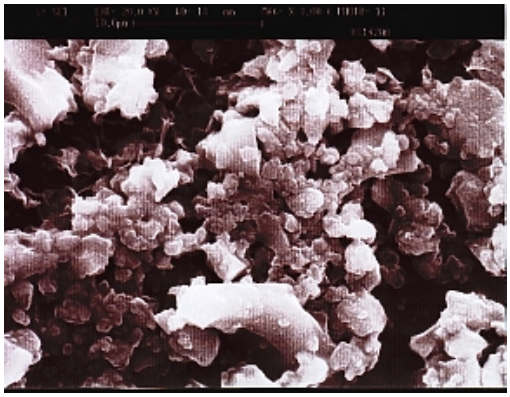


Fig. 4. Effect of DMF on the porous of the SiO_2-gels from TMOS and TEOS

Fig.5. shown morphologies of the aggregate formed. Matrice Si-O formed through agglomeration of its monomere silica nanoparticles (Φ=10-20 Å) to organize the secondary particles about 40-70 Å [8].



(a)



(b)

Fig. 5. The Micrograph of the SiO_2-gels from TMOS and TEOS in DMF (mag. 2000 times)

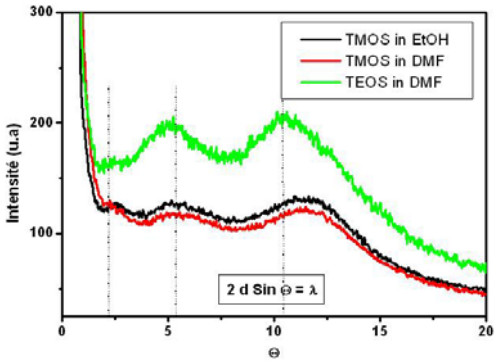


Fig. 6. Diffratogram patterns of the SiO_2-gels from TMOS and TEOS

X-ray diffractogram (Fig.6) shown that the gel agglomerate have the same structure as the lamellar structure of amorphous materials [8]. Thus, interactions between formamide in DMF and hydrolyzed monomers of alkoxysilane contribute to control the precipitation of silica nanoparticles to agglomeration gels [3, 4, 6].

4. Conclusions

The spectra data of NMR and XRD are enough to quantitative studies of molecular effect and physical chemistry fenomena, but for the qualitative studies need an other data's as micro polarization (MP), scanning micrograph (SEM), and N_2 adsorption-desorption isothermal.

The effect of formamide species from dimethylformamide solvent (DMF) on the gelation processes of TMOS) and TEOS were investigated by Polarization Microscope. The hydrolysis and polycondensation reactions can produce in mixture of alkoxysilane in variative farctionmole of DMF with ammonium fluoride catalysts. Both products showed the same textural properties. N_2 adsorption-desorption isotherms have indicated that at higher quantity DMF an increase in particle sizes and greater increase in the mean pore size. Micrographs have shown that sols are made of primary particles of about 10-20 Å in diameter. These primary structural units organize to form the secondary particles with diameter about 40-70 Å at the agglomeration solid.

Acknowledgements

The authors would like to thank Prof. Corriu for many valuable discussions measurements and Ahmad Mehdi for his helpful advice concerning the autoclave and Micromeritics.

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