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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; Lamellar 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$_3$H$_7$NO) on the gelation processes and organization structure of SiO$_2$-gels of alkoxysilane has been studied.

Tetramethyl octylsilicate or tetramethoxysilane (TMOS; C$_4$H$_9$O$_2$Si) of silica network and tetraethyl orthosilicate or tetraethoxysilane (TEOS; C$_8$H$_6$O$_2$Si) 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$_3$OH), ammonium fluoride (40%
NH$_4$F), 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 ($\rho$) and MWs
were used to calculate the concentrations of the
various chemicals: $\rho_{\text{TMOS}}=1.032$ kg/l,
$\rho_{\text{TEOS}}=0.93$ kg/l, $\rho_{\text{DMF}}=1.4305$ kg/l;
$\text{MW}_{\text{TMOS}}=152.22$ g/mol; $\text{MW}_{\text{TEOS}}=208.3$ g/mol;
$\text{MW}_{\text{DMF}}=73.10$ g/mol; $\rho_{\text{ethanol}}=0.78$ kg/l,
$\rho_{\text{methanol}}=0.79$ kg/l, g/mol;
$\text{MW}_{\text{ethanol}}=46.07$ g/mol;
$\text{MW}_{\text{water}}=18$ g/mol; $\rho_{\text{ammonia}}=0.89$ kg/l
(30% NH$_3$), $\text{MW}_{\text{ammonia}}=17$ g/mol; $\rho_{\text{NH}_4\text{F}}=1.11$ kg/l
(40% NH$_3$), $\text{MW}_{\text{ammonium fluoride}}=37.4$ 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
ammonium fluoride (NH$_4$F 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$_4$F, 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
ammonium fluoride 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$_2$O. 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$^1$, Q$^2$ 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 $Q^0$ on dried gels TEOS shown that there are effect of DMF solvent in the liquid phase reaction.

![Structure of TMOS and TEOS](image)

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

![29Si CP MAS NMR Spectra](image)

Fig. 2. $^{29}$Si CP MAS NMR Spectra for the SiO$_2$ dried gels formed in Etanol (a) and DMF (b).

Figure 2 shows a comparison of the time gelation of a reaction mixture containing 1.0 mol alkoxy silane (TMOS or TEOS) in fraction mole of DMF/EtOH. The effect 1% M [NH$_4$F] has very little on the disappearance of $Q^1$; however, $Q^1$ was rapidly hydrolyzed to $Q^0$, whereas $Q^2$ had chance to build of peak $Q^3$, 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 fraction mole 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].

![29Si CP MAS NMR Spectra](image)

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].

![Polarization Micrograph](image)

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.

![Effect of DMF](image)

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 ($\Phi=10-20$ Å) to organize the secondary particles about 40-70 Å [8].
4. Conclusions

The spectra data of NMR and XRD are enough to quantitative studies of molecular effect and physical chemistry phenomena, but for the qualitative studies need another data 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.

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References


