

Characterization of Hydrolyzed Products of Tetra Ethoxy Silane Prepared by Sol-Gel Method

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Abstract– In the present paper, the hydrolyzed products prepared by acid or base catalyzed hydrolysis of Tetra ethoxy silane (TEOS) were characterized using different Techniques such as Fourier Transform Infrared Spectroscopy (FTIR), X-ray diffraction (XRD), thermogravimetric analysis (TGA), and differential thermal analysis (DTA). FTIR spectroscopy revealed the existence of Si-OH and Si-O-Si bonds due to the formation of silanols reactive intermediate compounds in initial stage converted by condensation reaction to the gels as ultimate products. The results of (XRD) analysis showed that the hydrolyzed products had amorphous nature. Chemical reactions involved in Sol-Gel process have been emphasized by the results of thermal analysis as hydrolysis endothermic process followed by condensation exothermic process. Hydrolysis of TEOS in the presence of acid or base catalyst was studied. It was found that the gelation time for base catalyzed hydrolysis of TEOS is longer than the gelation time of acid catalyzed hydrolysis of TEOS in similar experimental conditions, because the rate of hydrolysis, or gelation increase as hydrogen ion concentration increases.

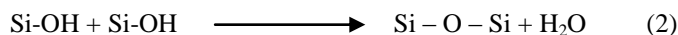
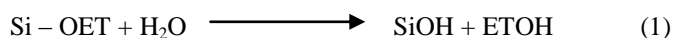
Keywords– Sol-Gel, Tetra Ethoxy Silane, Hydrolysis, FTIR Spectroscopy, Thermal Analysis and Silanols

I. INTRODUCTION

The Sol-Gel method received a new impetus when tetra methoxy silane and tetra ethoxy silane (TEOS) were employed as starting chemicals [1]. This method used

liquid alkoxide precursor such as tetra ethoxy silane to react with water in the presence of acid or base catalyst at room temperature to produce gel [2]. The stages of Sol-Gel process using tetra ethoxy silane precursor are presented in the following Fig. 1.

Sol-Gel process used tetra ethoxy silane as precursor can be described by three reactions:



Tetra ethoxy silane hydrolyzes in water to form silanol (Eq. 1). The silanol groups with elimination of water (Eq. 2) or silanol react with tetra ethoxy silane with elimination of ethanol (Eq. 3). Further hydrolysis and condensation reaction form a silicon oxide network. Despite metal alkoxide precursor is hardly understood [5]. Therefore, as a modest contribution to chemistry in the field of metal alkoxide precursor this work is presented. This work involve characterization of the obtained hydrolyzed products of TEOS prepared by Sol-Gel method using different techniques such as FTIR, XRD and thermal analysis. In addition to the study of chemical reaction parameters influence in Sol-Gel process.

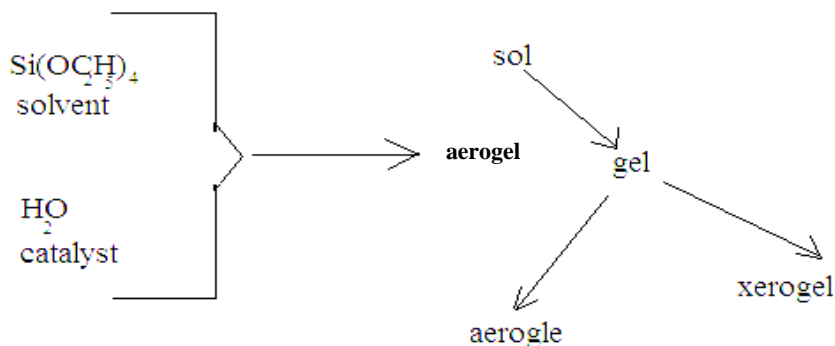


Fig. 1: stages of Sol-Gel process

II. EXPERIMENTAL

A) Chemicals

All chemical used were of analytical grade type.

B) Preparation of Gel by Acid or Base catalyzed Hydrolysis of TEOS

6ml of tetra ethoxy silane was placed in a test tube and 1 ml of hydrochloric acids was added. 1 ml of absolute ethanol used as solvent and drop wise of 1 ml of double distilled water. The mixture began to form gel. After 144 hrs. there was a finger of gel in the test tube at room temperature. After that test tube was wormed to take out finger of the gel and weighed. The gel was analyzed by FTIR, XRD and thermal analysis. For results see Table 1, Table 2 and Fig. 2 and Fig. 6 respectively.

C) Preparation of Gel by Base catalyzed Hydrolysis of Tetra ethoxy silane

6ml of tetra ethoxy silane was placed in a test tube and 1 ml of ammonium hydroxide was also added. 1 ml of absolute ethanol used as solvent and drop wise of 1 ml of double distilled water. The mixture began to form gel. After 216 hrs. there was a finger of gel in the test tube. After that test tube was wormed to take out finger of the gel and weighed it. The obtained gel was analyzed by IR, XRD. For results see Table 3 and Fig. 3 and Fig. 7, respectively.

D) Instrumentation

The obtained hydrolyzed products of TEOS were analyzed by FTIR spectroscopy. Infrared spectra were recorded on a 800-PC FTIR Schlimazel spectrophotometer using KBr pellets in the mid infrared region 4000- 400 cm^{-1} . Also infrared spectra were recorded on a4100- FTIR Jacso spectrophotometer using KBr pellets in region 4000-400 cm^{-1} . Hydrolyzed products of TEOS were also characterized by X-ray diffraction (XRD) analysis using AD₈ advanced X-ray form Bruker Analysis of hydrolyzed product of TEOS was carried out using shimadzu 50 thermal analyzer. About 10.65 mg of hydrolyzed product was used for analysis. Thermal analysis was carried out from $^{\circ}\text{C} - 600^{\circ}\text{C}$ at heating rate $10^{\circ}\text{C}/\text{min}$ under nitrogen flow of rate 20ml/min.

III. RESULTS AND DISCUSSION

Tow gels were prepared by Sol-Gel process using TEOS as precursor. This process includes the synthesis of gels by hydrolysis of tetra ethoxy silane in the presence of acid or base catalyst. The preparation of gels will be illustrated as the following:

A) Characterization of gel prepared by acid catalyzed hydrolysis of tetra ethoxy silane

Gel has been prepared by hydrochloric acid catalyzed hydrolysis of TEOS see section (2-B). The results of the experiment were summarized in Table 1. The final product was analyzed by FTIR, XRD, TGA & DTA. For results see Table 2 and Fig. 2 to Fig. 6.

Fig. 2 and Table 2 show the results of FTIR analysis for the prepared gel using acid catalyst. The FTIR absorption band near 3450 cm^{-1} is attributed to some adsorbed water. This band goes often accompanied by another at 1634 cm^{-1} which is attributed to O-H vibration of molecular water that is physically adsorbed in the network. Because the low intensity of 1634 cm^{-1} band, the 3433 cm^{-1} band would reflect the contribution of Silanol groups. The smaller amount of residual Si-OH, the larger degree of condensation. The most intense peak was observed at 1082 cm^{-1} due to the asymmetric stretching vibration of Si-O bond. Oxygen atoms play the role of bridges between each two silicon sites in this silicon – oxygen covalent bonds. On the other hand, the symmetric stretching vibration of Si-O-Si appears at 550 cm^{-1} . The low energy band at a round cm^{-1} is assigned to Si-O-Si stretching of the SiO_2 network defects.

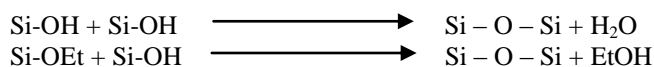
B) Characterization of gel prepared by acid catalyzed Hydrolysis of TEOS by Thermal Analysis

Thermal analysis was carried out for the gel prepared by hydrolysis of TEOS using HCl as catalyst, for the results see (Fig. 4 and Fig. 5). These figures show thermogravimetric and differential thermal analysis. Two major weight losses were observed in the thermal analysis curve. The first loss was attributed to the removal of ethanol as by product in hydrolysis and poly condensation steps of Sol-Gel reactions for tetra ethoxy silane. The resulted in the endothermic peak in the DTA curve, centered at the temperature 62°C . The second weight loss was observed as an exothermic peak in DTA curve centered at the temperature 106°C . This is due to a water desorption which occluded in the gel after the gelation point. At this stage of post gelation, water is obtained as by product of the reaction:

Hydrolysis



Condensation



Ethanol and water as byproducts of Sol- Gel reactions for tetra ethoxy silane have been confirmed by the results of thermal analysis as reported in literature [12], [13].

C) Characterization of Gel prepared by base catalyzed hydrolysis of TEOS using FTIR spectroscopy

Gel has been prepared by hydrolysis reaction between TEOS and water using, ammonium hydroxide as catalyst and absolute ethanol as solvent see section (II-B). The results of this experimental were presented in Table 3. The obtained gel product was analyzed by FTIR spectroscopy.

FTIR analysis of gel prepared by base catalyzed hydrolysis of TOES was shown in Fig. 4. The results of this analysis were found to be similar to the results of FTIR analysis of gel prepared by acid catalyzed of TEOS and water. The results

are in a good agreement compared with the literature values [6] indicating the formation of the gel.

D) Gelation time

In the current work the effect of the PH and the time for hydrolysis reaction of TEOS has been carried out in similar experimental conditions. Gelation time for Base catalyzed hydrolysis reaction of TEOS is longer than the gelation time of acid catalyzed of TEOS see Table 2 and Table 3. So that the acidic catalysis results in much quicker hydrolysis than the basic one at the same concentration of a photolytic catalyst, indicating that tetra ethoxy silane is stronger Lewis base than Lewis acid.

E) X-Ray Diffraction Analysis of the obtained gels

X-ray diffraction analysis of the prepared gels were carried out, results in (Fig. 6 and Fig. 7). It was found that the obtained gels were amorphous solids, because no crystalline phase was detected by conventional powder XRD. The XRD patterns of the prepared gels show wide peak at angles 2θ approximately 24° , characteristic of amorphous silica as reported in literature [14].

IV. CONCLUSION

Sol-Gel process involves the reaction of tetra ethoxy silane with water in the presences of acid or base catalysts were investigated. Acidic catalysis results in much quicker hydrolysis than the basic one at the same concentration of a protolytic catalyst indicating that tetra ethoxy silane is stronger Lewis base than Lewis acid. All hydrolyzed products of tetra ethoxy silane had amorphous structure as indicated by XRD analysis. FTIR spectroscopy showed that silanols were produced as primary products. These products were converted to the gels as final products. Thermal analysis confirmed that chemical reactions in Sol-Gel process included hydrolysis reaction as endothermic process followed by condensation reaction as exothermic process.

Table 1: Summary of gel prepared by acid catalyzed hydrolysis reaction of TEOS

Reactants, product & Gelation Time	Value
TEOS	6 ml
HCl	1 ml , PH=1
H ₂ O	1 ml
C ₂ H ₅ OH	1 ml
Gelation Time/hrs	144
Product weight/g	1.937

Table 2: Results of FTIR Characteristic bands for gel prepared by acid catalyzed hydrolysis of TEOS

Assignments	Frequency/cm ⁻¹		References
	Obtained	Literature	
O-H stretching	3433	3450 – 3400	[6], [7]
O-H deformation	1634	1653 – 1634	[11]
Si-O stretching	1082	1200 – 1000	[8], [9]
Si-O-Si stretching	795	800	[6], [7]
Si-O-Si bounding	467	467	[6], [7]

Table 3: summary of Gel prepared by base catalyzed hydrolysis reaction of TEOS

Reactants, product & Gelation Time	Value
TEOS	6 ml
NH ₄ OH	1 ml , PH=13
H ₂ O	1 ml
C ₂ H ₅ OH	1 ml
Gelation Time/hrs	216
Product weight/g	0.941

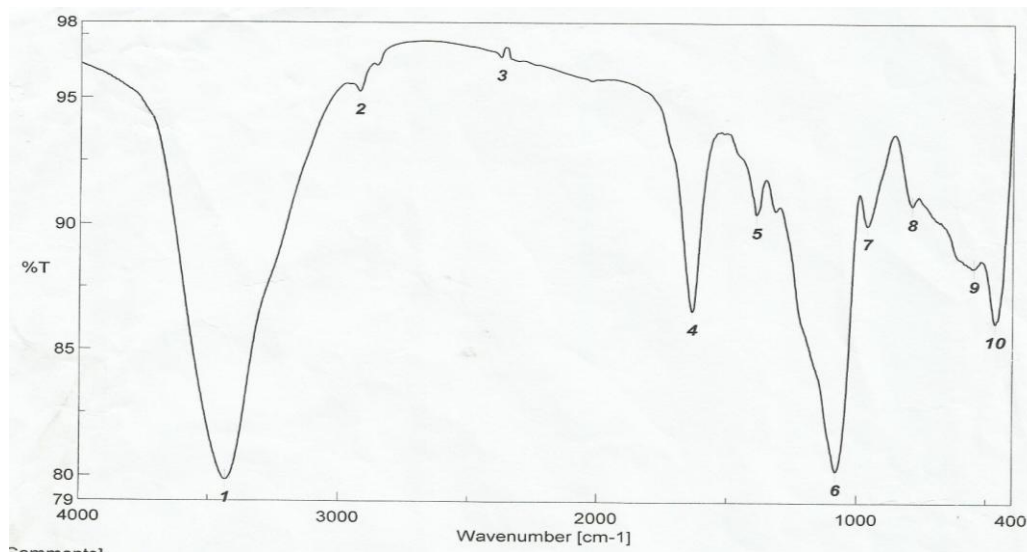


Fig. 2: Infrared spectra of gel prepared by Acid catalyzed hydrolysis TEOS

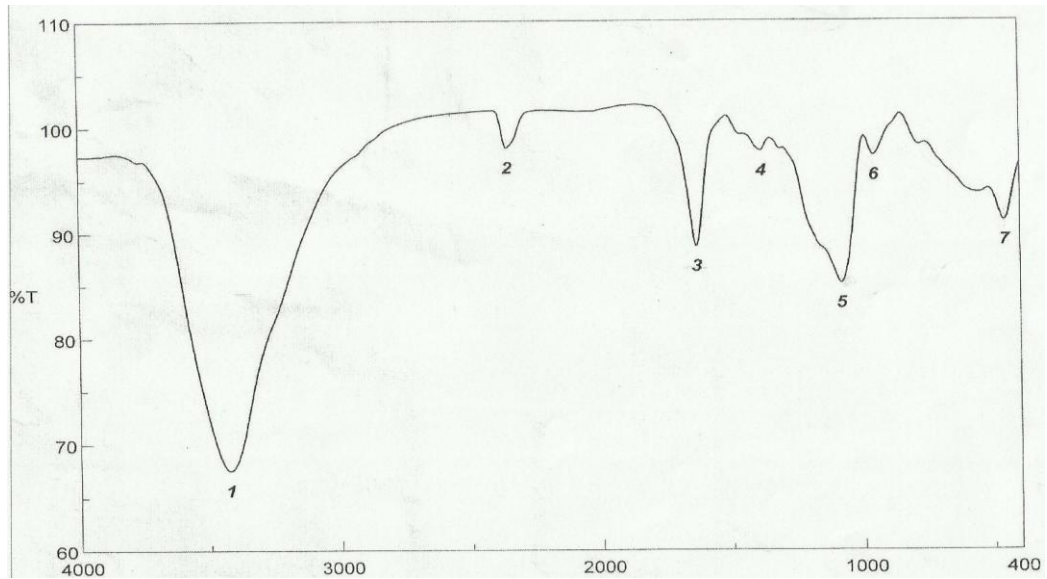


Fig. 3: Infrared spectra of gel prepared by Base catalyzed hydrolysis TEOS

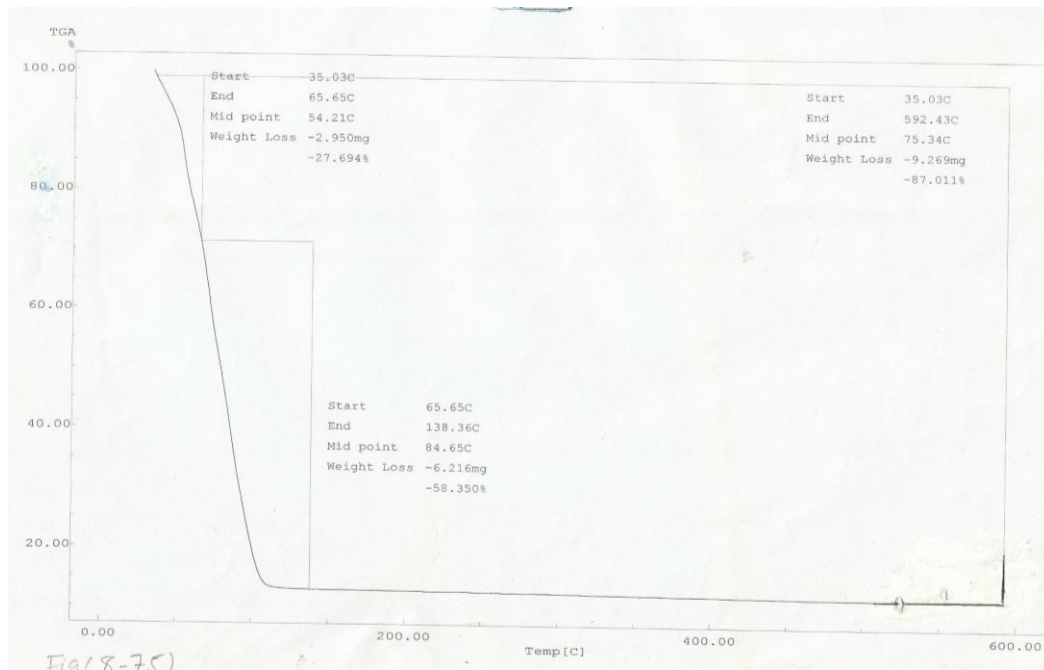


Fig. 4: Thermogravimetric analysis gel prepared Acid catalyzed Hydrolysis of TEOS in Temperature range 0 °C - 600 °C

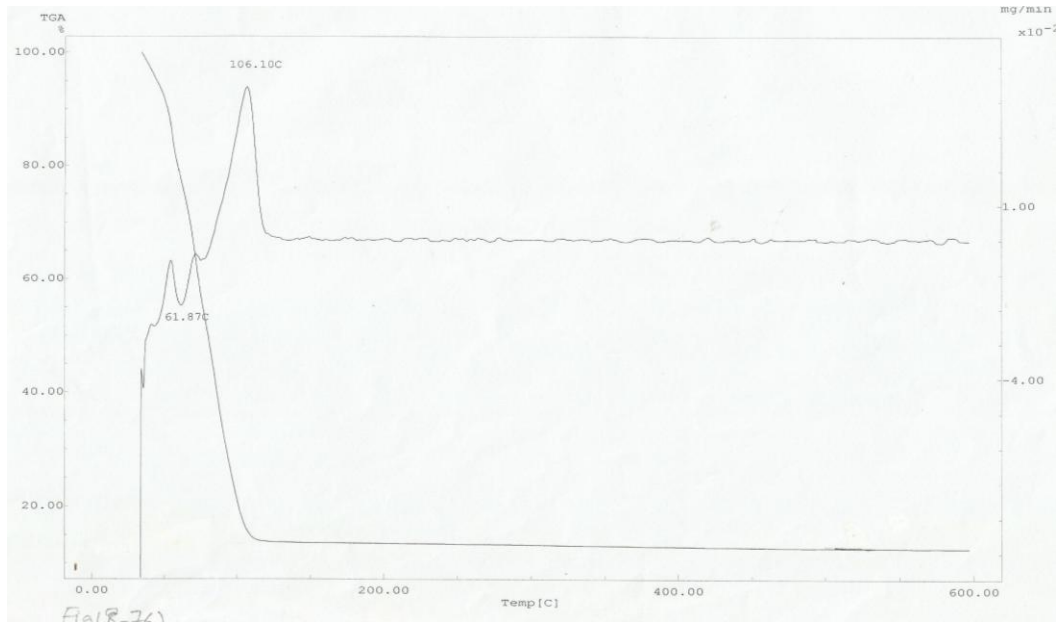


Fig. 5: Differential thermal analysis gel prepared Acid catalyzed Hydrolysis of TEOS in Temperature range 0 °C - 600 °C

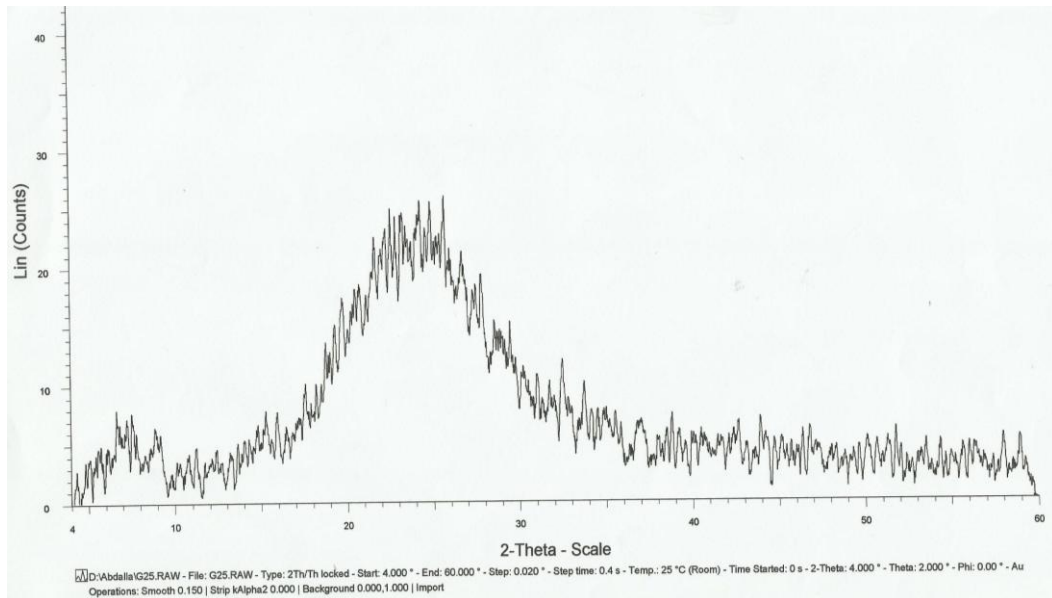


Fig. 6: X-ray diffraction pattern of the gel prepared by acid catalyzed hydrolysis of TEOS

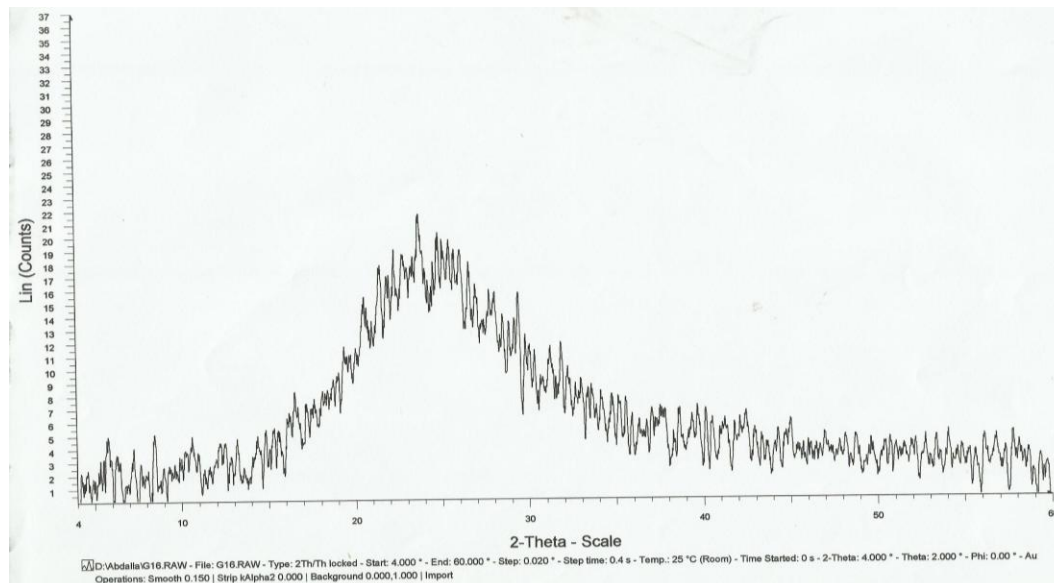


Fig. 7: X-ray diffraction pattern of the gel prepared by Base catalyzed hydrolysis of TEOS

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