



Mechanistic Investigation of Sol–Gel Reactions Using Alkoxysilane Precursor

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Authors' contributions

This work was carried out in collaboration between both authors. Author AHEY designed the study, performed the primary practical work, managed the literature searches and wrote the first draft of the manuscript. Author MSAE repeated some of the experiments, managed the analyses of the study and reviewed the draft of the manuscript. Both authors read and approved the final manuscript.

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ABSTRACT

The present study has been carried out to investigate the mechanisms of sol–gel reactions using TEOS as precursor in the presence of acid or base catalyst. The gels were prepared by hydrolysis of TEOS using hydrochloride acid or ammonium hydroxide catalyst. The obtained gels were also characterized by FTIR spectroscopy. The results of FTIR spectroscopy indicated the existence of silanol and siloxane bonds; due to the formation of hydrolyzed species as reactive intermediate compounds in initial stage converted by condensation reactions to gels as ultimate products. Accordingly, appropriate mechanisms have been proposed for sol – gel reaction using TEOS as precursor in the presence of acid or base catalyst. These mechanisms involve three-steps SN² mechanisms for base catalyzed hydrolysis reaction of TEOS and SN¹ mechanisms for acid catalyzed hydrolysis reaction of TEOS. Three mechanisms have been also proposed for condensation reaction as second stage in sol-gel process. These mechanisms include alcoxolation, oxolation and oltaion.

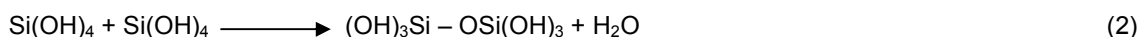
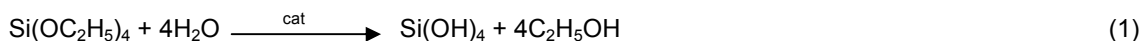
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Keywords: Sol-gel; TEOS; precursor; mechanism; FT-IR spectroscopy.

1. INTRODUCTION

Sol-gel precursors are mainly alkoxysilanes which can be obtained in a high degree of purity [1,2]. Tetraethoxysilane (TEOS) has been widely used as a cheaper and less toxic precursor; it has very poor reactivity in the sol-gel reaction [3]. So that sol-gel process involves the reaction

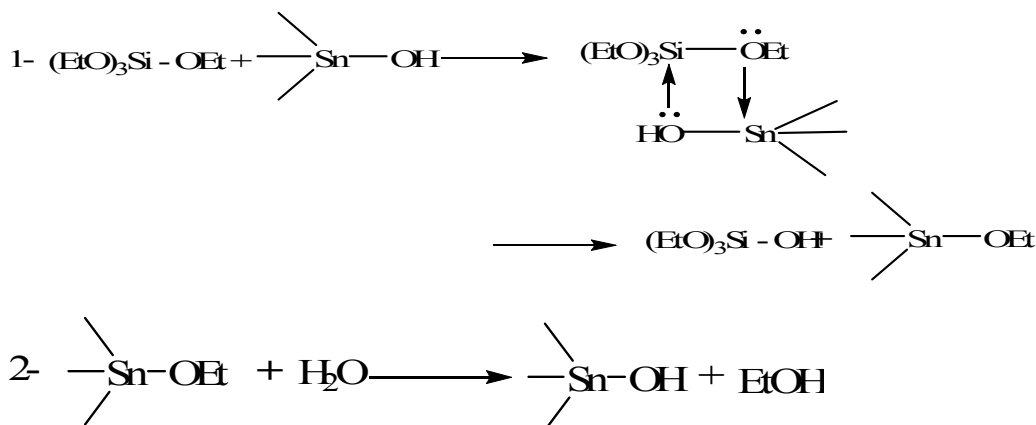
of liquid alkoxide precursor such as tetraethoxysilane (TEOS) with water in the presence of acid or base catalyst. In this process the first step is the hydrolysis of the precursor followed by the condensation of hydrolyzed species [4,5]. For example the hydrolysis and condensation reactions when using TEOS as precursor are the following [6]:



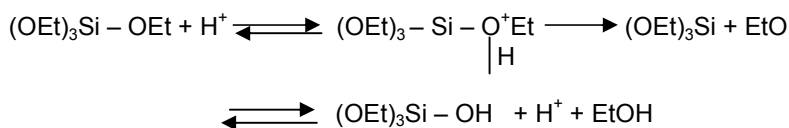
Tetraethoxysilane hydrolyze in water to form silanol (Eq. 1). The silanol groups with elimination of water (Eq. 2) or silanol react with tetraethoxysilane with elimination of ethanol (Eq. 3). Further hydrolysis and condensation form silicon oxide network [7].

The proposed mechanisms for hydrolysis reactions of tetraethoxysilane in different catalyst media and condensation of their hydrolyzed species are outlined in the following schemes:

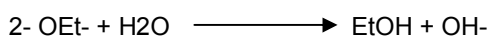
Scheme 1 organotin compounds (neutral catalyst) catalyzed hydrolysis of (TEOS) [8].



Scheme 2 Acid catalyzed hydrolysis of TEOS [7,8].



Scheme 3 Base catalyzed hydrolysis of TEOS [7,8].



Despite sol-gel is widely applied, the chemistry utilizing metal alkoxide precursor is hardly understood [9]. Moreover, the mechanisms of alkoxysilane $\text{Si}(\text{OR})_4$, hydrolysis and oligomerization in the initial stage of sol-gel processes are still not well understood [10]. Therefore, the aim of the present work is

a new attempt to investigate mechanisms of the reactions involved in this process using tetraethoxysilane as alkoxy silane precursor. The obtained gels are also characterized by FTIR spectroscopy to support the suggested mechanisms.

2. EXPERIMENTAL

A) Chemicals: All chemicals used were of analytical grade type.

B) Instrumentation: The obtained gels from TEOS were analyzed by FTIR spectroscopy, in a 800 – Pc FTIR Shimadzu spectrophotometer.

2.1 Synthesis of Gels by Acid or Base Catalyzed Hydrolysis of TEOS

2.2.1 Synthesis of gels by acid catalyzed hydrolysis of TEOS

(6 ml) of TEOS was placed in a test tube and (1 ml, pH = 1) of hydrochloric acid was added. (1 ml) of absolute ethanol and (1 ml) double distilled water added drop wise. After 48 hours a gel was formed. The gel was analyzed by FTIR spectroscopy.

2.2.2 Synthesis of Gels by base catalyzed hydrolysis of TEOS

(6 ml) of TEOS was placed in a test tube and (1 ml, pH = 1) of ammonium hydroxide was added. (1 ml) of absolute ethanol and (1 ml) double distilled water added drop wise. After 48 hours a gel was formed. The gel was analyzed by FTIR spectroscopy.

3. RESULTS AND DISCUSSION

3.1 FTIR Characterizations of the Prepared Hydrolyzed Gels of TEOS in Base or Acid

FTIR spectrum of the gel obtained was showed in (Fig. 1): peak at 3433 cm^{-1} was due to some

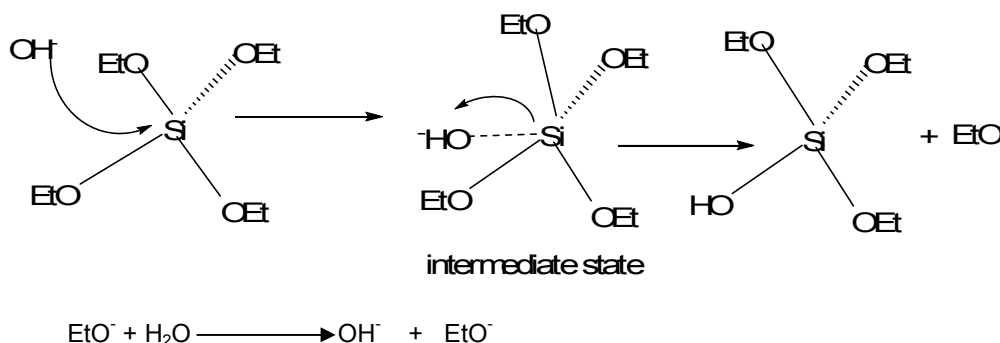
absorbed water, 1634 cm^{-1} (OH deformation vibration of molecular physically absorbed in the network), 1082 cm^{-1} (due to asymmetric stretching of Si – O bond); 795 and 467 cm^{-1} (due to Si – O – Si stretching vibration and deformation respectively). The above IR data clearly indicates the contribution of silanol groups.

FTIR spectrum of the gel obtained by base catalyzed hydrolysis of TEOS (Fig. 2) gave bands similar to those obtained in case of acid catalyzed hydrolysis of TEOS (Fig. 1).

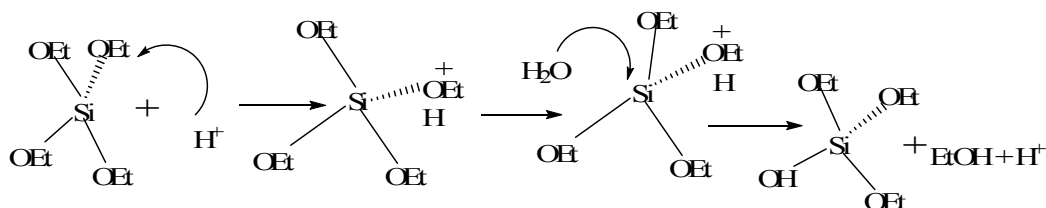
3.2 Proposed Mechanisms for Sol-gel Reactions Using TEOS as Precursor

Sol-gel technique is based on the hydrolysis of TEOS precursor and formation of colloidal sols and, after condensation, stable gel. The hydrolysis TEOS leads to formation reactive Si – O group. To understand the mechanisms of this reaction is need to look at (Si – OEt) bond. In this bond silicon atom has got 3d vacant orbitals and oxygen atom of the ethoxide group bears the lone pairs of electrons.

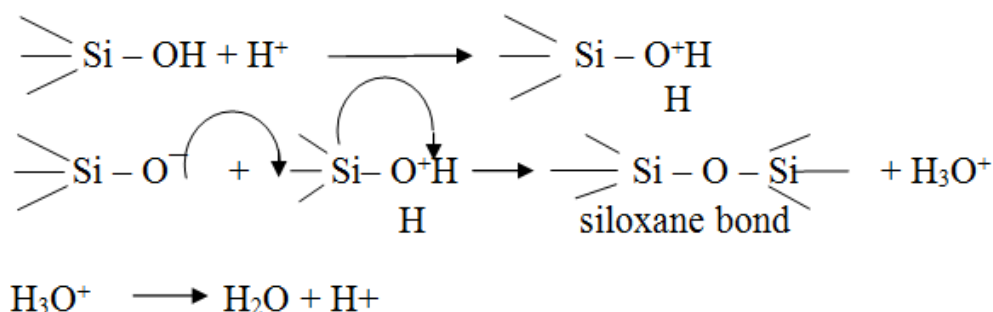
The bond offers for both nucleophilic and electrophilic attacks. Therefore, it has been suggested that hydrolysis of TEOS is either (OH⁻) attacks the silicon atom or the electrophile (H⁺) attacks the oxygen atom. Accordingly, three – step SN² mechanism is proposed for base – catalyzed reaction. The first step is a nucleophilic addition of hydroxide anion to the positively charged Si atom, this lead to a transition state, where the coordination number of Si has been increased by one. The second step involves a charge transfer within the intermediate state leading to release on ethoxide anion, which hydroxide catalyst. This SN² mechanism is elucidating as follows:



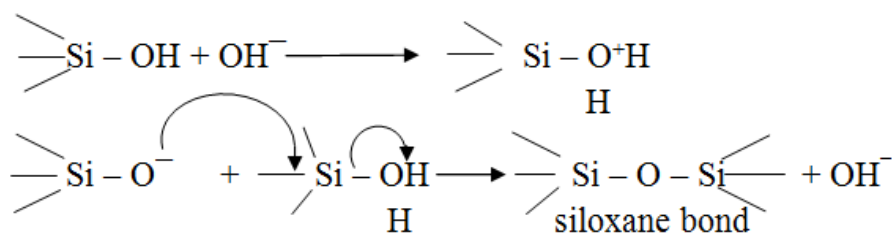
SN^1 – type mechanism is proposed for acid catalyzed reaction. This mechanism involves addition of acids at the first step to the protonation of an oxygen atom in the ethoxide ligand, leading to formation of the reactive cationic species. This step is rate determining, which results in an SN^1 type mechanism. The cation thus formed is attacked by a water molecule, which leads again to formation of a Si – OH bond, release of an ethanol molecular and regeneration of a proton catalyst. This mechanism is outline below:



The hydrolysis product followed by subsequent condensation to obtain gel. Condensation is a complex process depending on the experimental conditions; three competitive mechanisms have to consider: alcoxylation and olation. Alcoxylation is a reaction by which abridging oxo group is formed through elimination of an ethanol molecule. Oxolation follows the same mechanism as alcoxylation, but a water molecule is the leaving group. This mechanism under acidic and basic conditions can be elucidated respectively by the scheme 6 and scheme 7 below.



Scheme 6. Oxolation mechanism under Acidic condition



Scheme 7. Oxolation mechanism under basic condition

The formation of siloxane bonds have been supported by the results of FTIR analysis.

Olation can occur when full coordination of Si is not achieved. In this case bridging hydroxo group can be formed through elimination of a solvent

molecule. The latter can be H_2O or $EtOH$ depending on water concentration in the medium. All these reactions are catalyzed by proton, i. e., acidic medium, and are slowed in the presence of base.

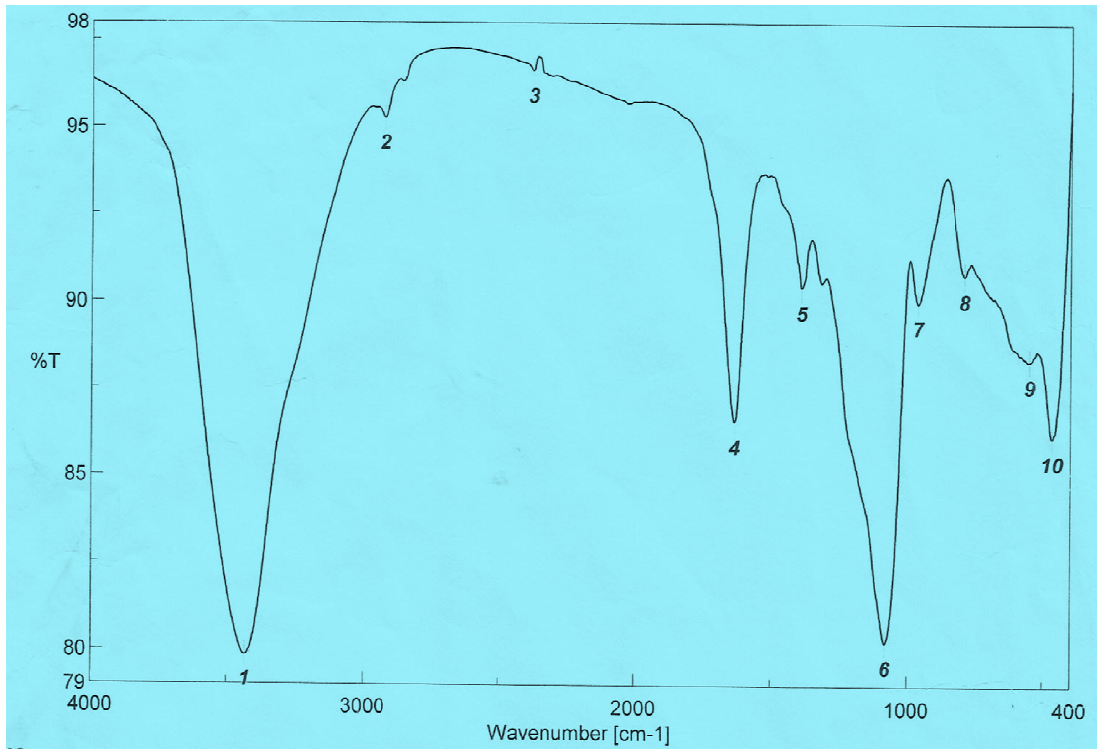


Fig. 1. IR spectrum of the gel obtained from the hydrolysis of TEOS using hydrochloric acid as catalyst

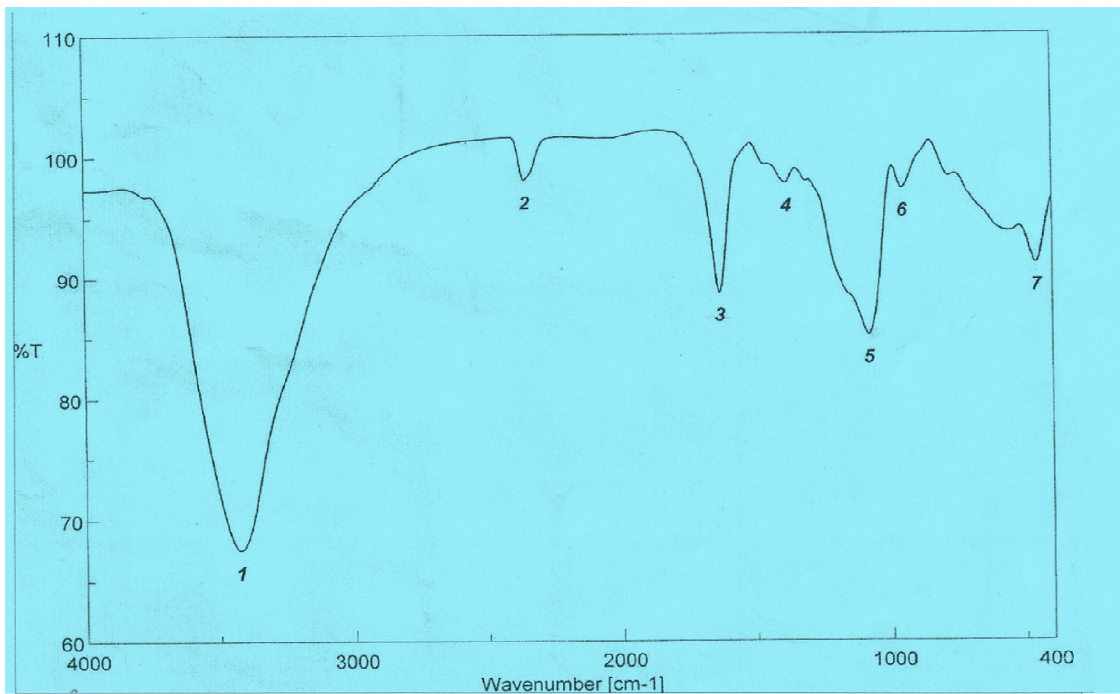


Fig. 2. IR spectrum of the gel obtained from the hydrolysis of TEOS using ammonium hydroxide as catalyst

Table 1. Results of FTIR analysis of the product obtained from the hydrolysis of TEOS using hydrochloric acid catalyst

Wave number , Cm ⁻¹	Chemical Bond	References
3433	O-H stretching	[3] , [11]
1634	O-H deformation	[12]
1082	Si-O stretching of silica network	[6] , [13]
795	Si-O-Si vibration mode	[3] , [11]
467	Si-O-Si deformation	[3] , [11]

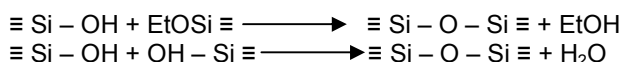
4. CONCLUSIONS

The gels were prepared in the present work using TEOS as precursor in the acid or base catalyst in order to investigate the mechanisms of sol-gel reactions. The sequence is believed to two step process for hydrolysis reaction of TEOS precursor in base or acid catalyst respectively.



- i. Empty 3d orbitals attracted (OH⁻)
- ii. Lone pairs of electrons attract (H⁺)

The hydrolysis of TEOS leads to formation of reactive Si – OH group. The hydrolyzed products followed by condensation reaction to obtain gel. The proposed subsequent condensation of the hydrolyzed products to produce gels include condensation of two OH – functionalities leads to formation of water and condensation of an OH – and OEt – group to formation of ethanol. Furthermore hetero – and homofunctional condensation process are described by the following equations:



Owing to cyclization, Cross – linking, and branching of siloxane chains, the primary products of hydrolytic polycondensation are oligomer and polymers containing the $\equiv \text{Si} - \text{O} - \text{Si} \equiv$, $\equiv \text{Si} - \text{OH}$, and $\equiv \text{Si} - \text{OEt}$ groups in various combinations and ratios in one molecule or macromolecule. Accordingly, three mechanisms have been suggested for condensation reaction of sol – gel process. These mechanisms are alcoxolation, oxolation and oltation.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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