

Synthesis of Silica Xerogels Obtained in Organic Catalyst via Sol Gel Route

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Abstract. Citric acid is an organic acid catalyst and content carbon that is templated into silica network. The mixture between these materials is gratefully useful to tailor pore size of silica-carbon mixtures in the form of silica-carbon sols which robust and good hydrostability properties. This fabricated materials is applied for coated membrane layers (thin film) coated onto membrane substrates for water desalination. This study was aimed to utilize sol gel process to synthesize the functionalization of organic catalyst in silica matrices. Silica xerogels was prepared from TEOS (Tetraethyl orthosilicate) with a two-step organic acid and base catalyst via sol gel method. The hydrolysis and condensation reactions were applied within 3 hours at 50 °C. IR spectra shows that.

Keywords: organic catalyst; silica xerogels; sol gel process; thin film

1. Introduction

The development of new synthetic methods and the functionalization of silica materials has become an important requirement in recent years. Mesoporous silica nanoparticles (MSNs) are chemically stable nanostructures due to their suitable porosity, surface area [1] and controllable morphology [2, 3]. The process of functionalization of this silica material becomes the basic knowledgeto understandthe mesoporous silica materials to be applied for water desalination as well as membrane technologies. This MSNs material will be used as the main material to manufacture the membrane layers (thin films/layers) during membranes fabrication applied for water desalination process. The acid catalyst used for this sol gel synthesis is by employing organic acid (in this case citric acid) which also enable to act as carbon source [1]. The benefit of using this organic acid is to functionalize the silica material with the carbon groups, therefore, the networks and surface properties of the silica-carbon structures will become much stronger than silica structures and also to increase hydrostability of silica materials. Thus, the aim of this study was to prepare and synthesize silica xerogels through the sol gel process in order to produce thin films of silica materials by using a sol gel process with a two-step organic acid-base catalysts which is very popular in the field of membrane technology. Considering the utilization of citric acid as an organic acid catalyst and carbon source, IR spectra has been conducted to investigate the functionalization of between silica and carbon groups in the silica matrices.

2. Methodology

2.1 Preparation of Silica Sols

Firstly, a two-step sol gel process employing organic acid and base as catalysts was applied. Tetraethyl orthosilicate (TEOS) was added drop-wise into ethanol (EtOH) solution and stirred for 5 min in ice bath condition at 0 °C to avoid partial hydrolysis followed by the addition of various diluted citric acid (0.0007;0.01;0.1 M citric acid). The sol mixture was refluxed for 1 hours at 50 °C with stirring to achieve a complete hydrolysis of the alkoxy groups. Ammonia solution (0.0003 M NH₃) diluted in ethanol was added drop wise into sol mixture to commence the condensation reaction and reflux was continued for another 2 hours to obtain the resultant sol. The composition total mol ratios for TEOS:Citric Acid:NH₃:EtOH:H₂O was 1:x:0.003:38:5.



2.2 Preparation of Xerogels

Silica-carbon sols was then placed in the petri dish and let it dry in the oven at temperature 60 °C for 24 hours. Then, silica-carbon xerogels was grounded into powder. Some of dried powder store at room temperature and some of them were calcined at 350 °C.

2.3 Characterization of Silica-Carbon Xerogels

FTIR (Fourier Transform Infra-Red) is used to evaluate and perform chemical properties of silica-carbon dried powder of xerogels calcined in air at 350 °C using RTP (Rapid Thermal Processing) method for 1 hour without applying ramping/cooling rates. FTIR spectra data were collected from FTIR type Bruker Alpha. Instrument type: alpha sample compartment RT-DLaTGS accessory: ATR platinum Diamond 1 Relf. The spectra were collected from a total of 30 scans ranging between wavelengths 500-4000 cm^{-1} .

3. Result and Discussion

a. Silica Sols Molar Ratios

Hydrolysis and condensation are the very important process to form silica oxide network from metal alkoxide precursor (TEOS). Employing citric acid as organic catalyst as well as carbon source to the silica matrices is an interesting method where usually carbon source is normally doped [4-12] into a liquid silica sols to form bonds of the Si–O–C network. Also, the type of catalysts (organic/citric acid, ammonia or both of them) determines the structure shape of silica networks [13].

The chemical composition of each molar ratio to form hydrolysis and condensation reactions can be seen in Table 1. In this composition, the molar ratio of citric acid was varied in order to investigate the influence of Si–O–C bonding through IR spectra (described in Fig.1). The other molar ratios followed our previous work [4, 14-16]. Acid catalyst promotes hydrolysis reaction to form microporous structures in silica matrices. In addition, base catalyst literally encourages condensation reaction to form mesoporous structures. These two type components of catalysts are very needed for membranes fabrication and the application during desalination process.

Acid catalyst is usually added into sol gel procedure to hydrolyse TEOS to form silanol (Si-O-H) groups. It is then continued by adding base catalyst to continue condensation reaction and configuratesiloxane (Si-O-Si) groups.

TABLE 1. MOLAR RATIO CO-HYDROLYSIS AND CONDENSATION OF THE BULK SILICA-CARBON XEROGELS

Sample	TEOS	EtOH [$\times 10^1$]	$\text{C}_6\text{H}_8\text{O}_7$ [$\times 10^{-4}$]	NH_3 [$\times 10^{-3}$]	H_2O
A	1	3.8	7	3	5
B	1	3.8	10	3	5
C	1	3.8	100	3	5

b. Material Characterization

Fig. 1 shows the IR spectra of dried silica-carbon xerogels with molar ratio of citric acid varied (0.0007; 0.001; and 0.1). A part of formation of Si–O–C bonding through the matrices, the addition of organic acid catalyst is to promote the hydrolysis reaction and end of chain condensation [13] to form a monolithic and microporous structure [16]. This structure is very appropriate to separate salt molecules which much larger than water molecules in desalination via pervaporation using silica-carbon membranes.

Although this microporous structure affect to permeate pass-through the membranes during separation process, however, it is very helpful to reject the salt ionsflow into mesoporous structure. It is reported that amorphous silica structures have a trimodal pore size distribution [16] consist small and large pores. That is why microporous structure is very important to control the percolative pathway of separating hydrated salt ions. The pathway between microporous and mesoporous structure (bottle neck formation)[16] link each other so that the water diffusion through the pores can be controlled.

IR spectra as seen in Fig. 1.(a) is for uncalcined xerogels and Fig. 1.(b) is for calcined xerogels at 350 °C using RTP method of calcination. From Fig.1 (a) is clearly shown that more concentration of citric acid added into sol gel process during hydrolysis and condensation reactions, more peaks found in the matrices. As can be seen at wavelength 703 cm^{-1} is C-H deformation and bending. Wavelength at 785 cm^{-1} is bending vibration of R=C-H and Si-O-Si. At 897 and 923 cm^{-1} are the vibration of Si=C-H and Si=C-H₂. Those all peaks are only found at xerogels which content 0.01 citric acid, while 0.001 and 0.0007 citric acid are only seen Si-O-Si peak at wavelength 802 cm^{-1} . At wavelength 940 cm^{-1} is related to Si-O-H (silanol groups) vibration. Continue to wavelength 1080 cm^{-1} , this peak is clearly shown for all samples. It is called asymmetric stretching vibration and a bending of Si-O-Si (siloxane) groups. It is due to the correlation and the main product of precursor used (TEOS). The interesting other peaks found are at wavelength 1145, 1180, 1372, 1400, 1445, 1718 and 1755 cm^{-1} , all of these peaks are related to stretching vibration of Si-CH₃. For last two peaks found at wavelengths 3311 and 3500 cm^{-1} are associated to H-bonded Si-O-H stretching vibrations and H-bonded water. Again those peaks are also found at citric acid 0.01. For xerogels samples content 0.001 and 0.0007 citric acid, the peaks mostly look similar concentration at similar wavelengths.

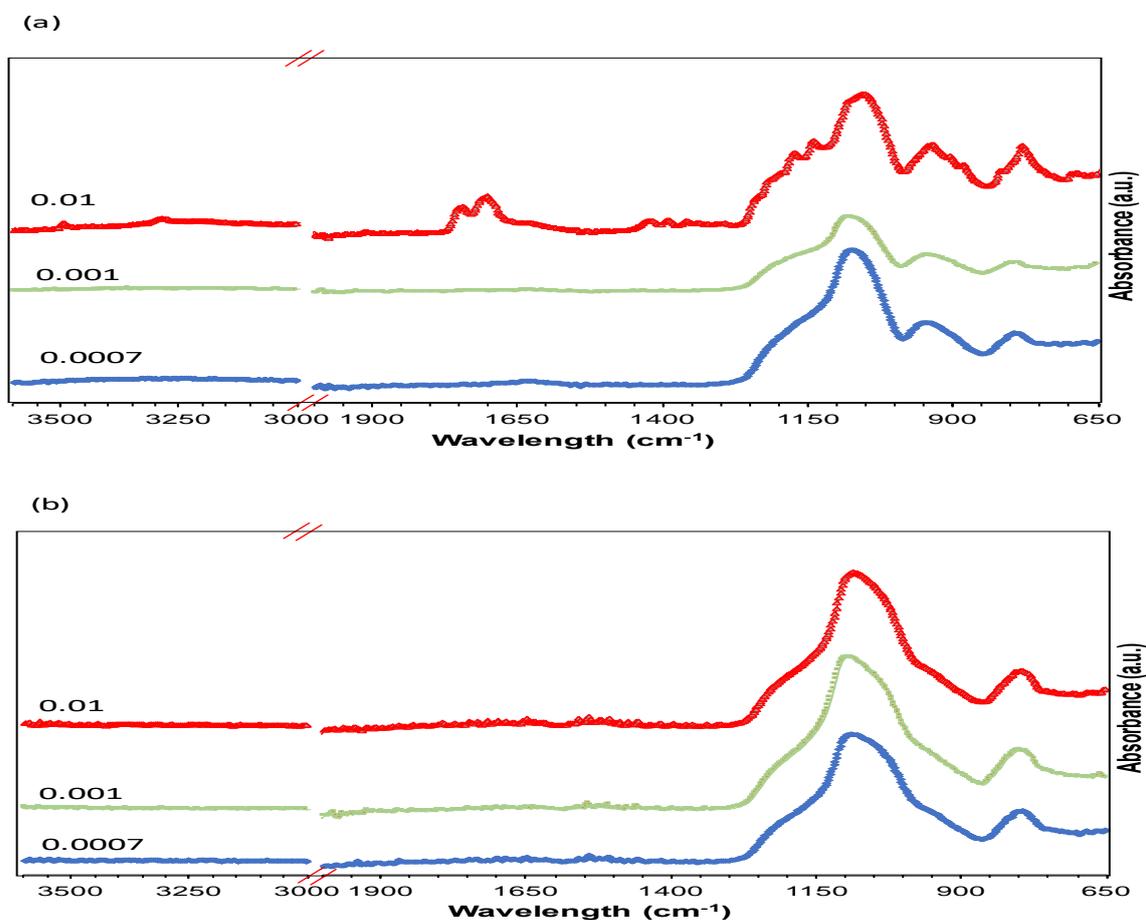


Fig. 1. IR spectra of silica-carbon xerogels with molar ratio 0.0007; 0.01 and 0.1 (a) uncalcined; (b) calcined at 350 °C

However, for the xerogel samples calcined at 350 °C (Fig. 1. (b).), all peaks related to vibration and stretching of carbon source were disappear. It is due to the calcination temperature was too high for dried xerogels at 350 °C, so that, the citric acid as a carbon source was easily to decompose at such temperature and only remain silanol as well siloxane the silica matrices.

4. Conclusion

The application of organic catalyst in the fabrication of silica sols through sol gel process is a prominent way to produce the combination between silica and carbon crosslinked together in the silica matrices. According to FTIR analysis, the higher concentration of citric acid as organic catalyst for uncalcined dried xerogels, the higher the crosslink happened between silica and carbon.

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