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Designing a mesoporous hybrid organo-silica thin film prepared from an organic catalyst

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Silica material has limited hydrostability when it is produced as a thin film. In order to mitigate this restriction a modification strategy is needed. This article provides details of mesoporous hybrid organo-silica thin films that were successfully fabricated from a combination of a dual silicate precursor of tetraethyl orthosilicate/triethoxy vinyl silane, using organic catalysts. The research investigated the effect of calcination temperatures (350°C and 600°C) on the materials, and compared the application of single (citric acid) and dual catalysts (citric acid and ammonia) during fabrication of the thin film.

In this study, hybrid organo-silica was synthesised using the sol-gel method at 50°C, and refluxed for 3 hours. The sol was calcined using the rapid thermal process (RTP) technique under conditions involving an inert atmosphere.

The calcined xerogels were characterised using thermal gravimetric analysis (TGA), Fourier transform infrared (FTIR) spectroscopy, and also Fityk curve-fitting and data analysis software, to obtain the best peak area for the silanols and siloxanes groups.

The results obtained show that hybrid organo-silica, using a single catalyst (citric acid), had an extremely high weight-loss profile of ~46% at 200°C. Deconvolution of hybrid organo-silica xerogel, using this single catalyst, exhibited a lower silanol/siloxane group area, compared with materials based on the dual catalyst (citric acid and ammonia).

According to Brunauer–Emmett–Teller (BET) characterisation, a thin film, prepared using the single catalyst at 600°C, produces

the highest surface area of 677.10 m²g⁻¹, however at 350°C it resulted in a pore diameter of 4.59 nm and pore volume of 0.73 cm³g⁻¹.

The research shows that a mesoporous hybrid organo-silica thin film, with a high surface-area, pore diameter and pore volume, can be successfully designed and fabricated by employing a single catalyst (citric acid), and this technique brings out hydrostatic properties and reduces the cost of the fabrication process used to produce the thin film.

Thin-film material type

The type of material used in a thin film determines its effectiveness^[1] in sea-water treatment applications.

A silica thin-film, attach to a membrane support, has the ability to be used in water desalination and gas separation processes^[2–13] and, compared with organic membranes,^[14] it is capable of withstanding high operating temperatures.

However, it has a shortage of silica pores. This leads to pores collapsing^[15] when the material is in contact with water for a long period – low membrane hydrostability.

This is because of the presence of hydrophilic silanol groups. Hence, a suitable material that can strengthen silica pores and increase hydrostability is needed.

Preventing pores from collapsing

The presence of carbon embedded in the silica sol will prevent membrane pores from collapsing.^[15] It increases the strength of the silica membrane matrix.

Carbon sources can be obtained through the addition of catalysts or precursors.^[16, 17]

Researchers Elma, Wang, Yacou and Diniz da Costa^[18] used a silica membrane with a P123 template and tetraethyl orthosilicate (TEOS) as a precursor to show the strength of a carbon-silica membrane. Triethoxy vinyl silane (TEVS) is a silica precursor that contains carbon and can be used to form Si–C bonds.

Yang, Elma, Wang, Motuzas and Diniz da Costa^[19] also reported that the combination of TEOS/TEVS/P123 with an acid–base catalyst (HNO₃ and NH₃) produces good performance in a desalination applications. Similar results were reported by Yang, Wang, Motuzas and Diniz da Costa,^[20] using TEVS/P123, with HNO₃ and NH₃ catalysts.

Basically, TEVS precursors contain vinyl groups as ligands bound to silica. TEVS tends to only form micropore structures on porous substrate interlayers.

A thin film made from TEOS has attracted the attention of researchers who have produced mesoporous materials.^[15, 21 & 22]

In addition, the RTP calcination technique has been applied by Wang, *et al.*^[23] This technique enables calcination to be performed with-

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out using a cooling rate at a high temperature of 1 hour/layer.

Pore size

Catalysts can affect the resulting pore size. Strong acid catalysts produce micropore pore-sizes, whereas a strong base results in macropore pore-sizes.^[24]

Previous research^[25] has used dual catalysts to produce mesoporous materials. However, the resulting membrane still has the disadvantage of low hydrostability. Therefore, to increase hydrostability, in this study we combined TEOS and TEVS, and focused on the calcination temperature effects and types of catalysts that have a high number carbon bonds.

Materials and methods

Chemicals and materials

Thin film was produced by employing the gel process, using the precursors TEOS and TEVS, and catalysts $C_6H_8O_7$ (citric acid) and NH_3 (ammonia).

The molar ratio TEOS : TEVS : EthOH : H_2O acid : base 0.9 : 0.1 : 38 : 5 : acid : base was used.

The investigation compared the catalysed effect for a single catalyst (0.0 N citric acid) and dual catalyst (0.001 N citric acid and 0.0003 N ammonia).

Preparation and characterisation of silica xerogel

In the first stage TEOS, TEVS and ethyl alcohol (EtOH) were mixed under specific operating conditions at 0°C. After stirring for 1 hour, the citric acid catalyst was then refluxed for 2 hours at 50°C.

In the following stage, the solution was placed in an oven for 24 hours, and a pestle and mortar was used to grind the processed material – producing what is called xerogel.

In the form of powder, the xerogel was then calcined for 1 hour using a furnace at 350°C and 600°C. The xerogel was characterised by FTIR spectroscopy, and the BET method and TGA tests.

Result and discussion

Characterisation using FTIR spectroscopy and BET

During this study, FTIR spectroscopy was used to determine the functional groups contained

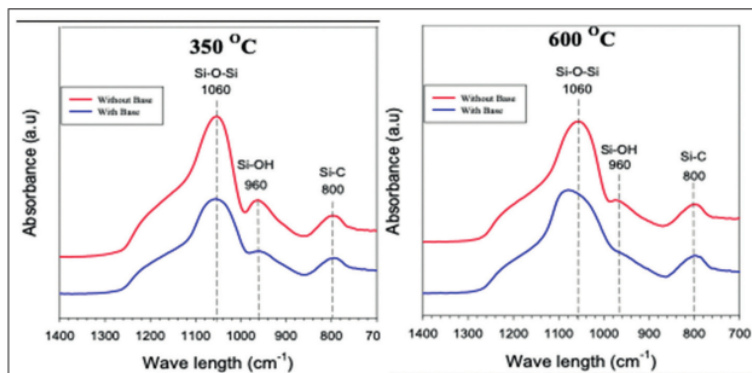


Figure 1. FTIR spectra of xerogel calcined at 350°C and 600°C.

in the mesoporous hybrid organo-silica xerogels (with the variation in calcined temperature and use of catalysts).

Three main functional groups of organo-silica materials were observed – namely silanol (Si–OH), siloxane (Si–O–Si) and carbon silica (Si–C) – for all samples.

Silanol is produced in the condensation process during precursors mixing with acid catalysts in reflux, whilst siloxane is produced in the condensation process when base catalysts^[15, 25–28] are added.

Acid–base catalysts are targeted at the production of mesoporous pore sizes. Acid catalysts produce micropore pore-sizes whereas base catalysts tend to produce macropores. A combination of acid–base catalysts was used to produce mesopores.

The results of the analysis done using FTIR spectroscopy are presented in Figure 1 (with temperatures of 350°C and 600°C). The silanol function group decreases with increasing temperature. This is because of the condensation process – where OH groups evaporate. As a result of this process, siloxane (Si–O–Si) and also silica–carbon (Si–C) bonds are increasingly formed.

The lowest silanol, associated with xerogel prepared with a base at 600°C, does not seem to be prominent. Whereas the highest peak of siloxane group is found in the sample using a single catalyst at 350°C.

The ratio that had the lowest silanol and also the highest carbon silica was investigated further.

Figure 2 shows the deconvolution of the peak area ratio of silanol (Si–OH)/siloxane (Si–O–Si) and silanol (Si–OH)/silica–carbon (Si–C). The optimum conditions were chosen from a sample which had the lowest ratio of Si–OH/Si–O–Si and Si–OH/Si–C, because of the large amount of siloxane and carbon. Silanol would be replaced by siloxane or a silica–carbon bridge, which is contained in the carbon precursor and catalyst.

The calcination temperature of 350°C for the single catalyst sample produced the lowest ratio of silanol/siloxane and silanol/carbon. This means that this sample offers the best characteristics. It was also evidenced by TGA (Figure 3).

Similar results also occurred in the study by Riani Ayu Lestari *et al.*,^[25] which resulted in the lowest silanol/siloxane ratio (–0.05) for the same type of single catalyst (citric acid) at 250°C.

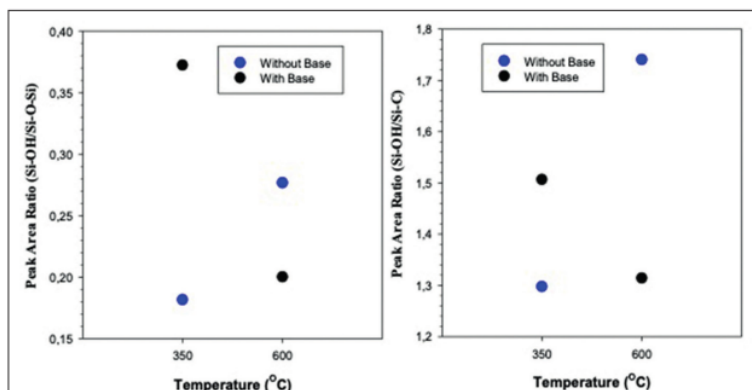
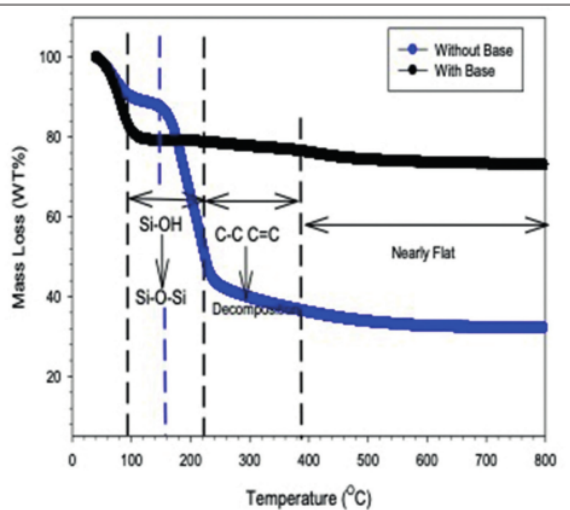


Figure 2. Deconvolution peak area, from silanol/siloxane and silanol/silica carbon.

Figure 3. Mass-loss curves of the xerogel single and dual catalyst.



However, too little silanol can produce large pores that are not suitable for use in desalination. Therefore, it is necessary to match the material type and suitable catalyst to the requirements of the application.

TGA characterisation revealed that the sample using a single catalyst can be applied at low temperatures < 95°C, whilst the base sample shows no difference in mass loss at high temperatures (300–400°C). This is reinforced by the results of the BET characterisation of both samples (Figure 4).

Referring to the graph, the process consists of three stages that describe the weight loss of the component mass.

In the first stage, the weight loss decreased by ~10%, for a sample using a single catalyst, which occurred at temperatures between 0°C–95°C. Meanwhile, weight loss in the base sample occurs at temperatures of 0–113°C, decreasing the weight loss by ~21%. This loss

happened because of water and ethanol evaporation in the materials.

Silica is a hydrophilic material that easily absorbs water molecules through hydrogen bonds; the –OH (Silanol) group.^[17, 29] Therefore, functional Si–OH is replaced by the formation of new bonds, Si–O–Si or Si–C. The Si–C bond has a low level of water adsorption on the carbon bond surface so that it increases membrane hydrostability.^[29]

Furthermore, the transition stage occurs at a temperature of 95–230°C, with a weight loss of ~46% for the use of the single catalyst, whereas a small weight loss of ~3% occurs at a temperature of 113–221°C for the base sample. The second stage also involves the process of forming siloxane or silica–carbon.

In the third stage, the silica–carbon decomposition sample, without a base, occurs at temperatures in excess of 230°C, with a weight loss of ~20%, whilst in the base samples there

is a greater weight loss of ~4%. The same thing happened in previous studies when carbon decomposes at temperatures over 450°C.

At a high temperature with a base it is better to use a single catalyst. This is because there is a smaller mass loss for the single catalyst and with the base the mass is 70%.

This shows that a material with a single citric acid addition will perform well at a low temperature compared with citric acid and ammonia.

BET characterisation

This analysis was applied in order to calculate the specific surface area, based on measurements of the nitrogen adsorption isotherm. Based on the results shown in Figure 4, the highest surface areas were found for samples using the single catalyst at low or high temperatures.

Surface area is related to the total reactive surface area as a pore structure that adsorbs small molecules. So the sample using the single catalyst is applicable in desalination processes.

This finding is in line with previous research done by Lestari *et al.*,^[25] which used a citric acid catalyst to produce the high surface area of 315 m²g⁻¹ for a TEOS membrane. This proves that using TEOS/TEVS will both increase Si–C bonds and the surface area.

Summary

In this study – using sol-gel methods and RTP techniques – mesoporous hybrid organo-silica thin films were successfully fabricated from the dual silicate precursor of TEOS and TEVS to produce materials with functional hydrostatic properties.

The resulting silica membrane has the following functional groups: Si–OH (silanol), 960 cm⁻¹; Si–O–Si (Siloxane), around 1060 cm⁻¹; and Si–C (carbon–silica), 800 cm⁻¹.

At 350°C a thin-film material using the single catalyst has the highest area of siloxane and silica–carbon. Based on TGA the use of the single catalyst produces very good results at low temperatures (around < 95°C).

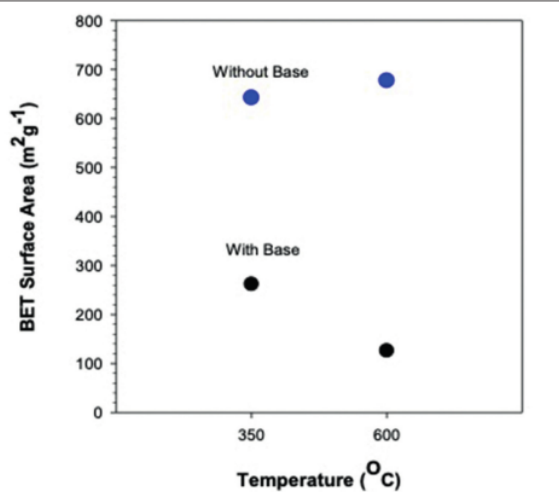
It can be seen that the highest surface area in the sample is produced using a single catalyst at both temperatures of 350°C and 600°C.

Mesoporous hybrid organo-silica prepared using the single catalyst (citric acid) has the largest pore diameter, 4.59 nm, and pore volume, 0.73 cm³g⁻¹, at 350°C. Also using the single catalyst, the largest surface area measured 642.39 m²g⁻¹ at 600°C.

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Figure 4. Surface properties of the single and dual catalyst.



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