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Riani Ayu Lestari, Muthia Elma, Erdina Lulu Atika Rampun, Anna Sumardi, Adhe Paramitha, Aptar Eka Lestari, Sadidan Rabiah, Zaini Lambri Assyaifi and Gesit Satriaji

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Functionalization of Si-C Using TEOS (Tetra Ethyl Ortho Silica) as Precursor and Organic Catalyst

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Abstract

Silica network was tailored configuring siloxane (Si-O-Si) and silanol (Si-OH) groups which are essential to produce porous-structured materials. As silanols are hydrophilic, react with water to form fouling. This research address to actualize strategy for synthesizing highly functionalized silica carbon (Si-C) using hybrid organic-inorganic structures as the primary method for improving hydro-stability by employing precursor TEOS and organic catalyst through a sol-gel process. Catalysis employs citric acid or citric acid-ammonia whereas carbon templated into silica network. The synthesis scheme involves: a) sol-gel process at 0°C and b) calcination. Silica sol dried into xerogels were prepared and calcined at 200°C and 250°C. Characterization of xerogels showed the infrared band areas of the organic groups to evaluate the thermal stability. For xerogel employed single (pH 5.5) and dual (pH 7.65) catalyst, infrared spectra showed mostly look similar Si-C area at similar wavelength. Silica xerogel is more effectively prepared from TEOS with one-step single acid catalyst including calcination.

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1 Introduction

Silica as inorganic material has best properties such as high chemical, thermal and mechanical stabilities [1]. The functionalization of silica material is important to know the mesoporous silica material applicable to desalination. TEOS (tetra ethyl ortho silicate) as hydrophobic inorganic material from metal alkoxide (precursor) is a skillfully utilized and easy controlled structure for membrane synthetic under the sol-gel process [2]. However, the limitation of using silica is low hydro-stability.

In order to increase hydro-stability and robustness of silica matrices against both physical and chemical resistances, many strategies of pure silica modification can be executed such as templated carbon silica, hybrid organic-inorganic silica structure [3], cobalt[4, 5], nickel [6-8], and iron [9]. Templated carbon modification was investigated in using Pluronics triblock copolymers [10] and surfactants for desalination application [11, 12]. For other method, hybrid organic-inorganic silica structure was investigated that silica-pectin as carbon templates promised excellent membrane due to its excellent performance indicated by 5 times water flux higher than using templeting carbon sourced from P123 triblock copolymer. Therefore, pectin as natural source of carbon and easy obtained from fruit peel or industries waste can

reduce one step process of templating and high production cost [13].

To reach efficiency cost in material and process, the importance of organic was utilized for catalyst as well as carbon source to form the silica network. Carbon addition from organic catalyst create robustness and change the structure of silica matrix [14, 15]. It is new potential strategy to solve the main problem in hydrostability by configuring Si-C on silica network. As reported by Elma and Setyawan [16] that success to obtain Si-O-C in silica network by employing citric acid as organic catalyst and carbon source [17]. But in this study the lower calcination temperatures are applied and compare the functionalization between acid catalyts and dual base acid catalyst. This research aims to synthesizing highly functionalized silica carbon (Si-C) using hybrid organicinorganic structures by employing precursor TEOS and organic catalyst through a sol-gel process. The functionalization using infrared spectra at 1400-700 cm⁻¹ of wavelength.

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2 Experimental

2.1 Variable and Materials

Silica sols was synthesized by using tetra ethyl ortho silicate (TEOS: Sigma-Aldrich), ethanol (EtOH: 70%) and water as solvent, also dilute citric acid (23.4 %, Merck) and ammonia (NH₃, Merck). Table 1 summarize each composition in molar ratio unit of materials to prepare two types of membrane.

FTIR analysis was delivered to understanding effect of experimental variables. Experiment was run as function of two types of catalyst (single citric acid catalyst and dual citric acid-base catalyst) and 3 thermal treatment condition (uncalcination; 200°C calcination and 250°C calcination).

2.2 Procedures

To reach characterization step for analyzing organic group in silica sol, there are many initial step to be executed. Pretreatment was followed by some material for preparation such as, precursor TEOS, ethanol solution, and acid or base catalyst. Sol-gel reaction consist of hydrolysis and condensation reaction. Sol-gel reaction was reacted precursor TEOS, ethanol, water, and catalyst to produced silica sol. For characterization silica sol should be transform into xerogel (dried sol) and grounded into powder to be applied as FTIR sample. Briefly, procedure of experiment can be showed in Fig. 1, and solgel process can be run in equipment installation in Fig 2.



Fig. 1. Flow Diagram of Experiment



Table 1. Silica sols molar ratio.

Types of membranes	Types of catalyst	TEOS	EtOH [x10 ¹]	C ₆ H ₈ O ₇ [x10 ⁻⁴]	NH3 [x10 ⁻³]	H ₂ O
A	Single acid catalyst (pH=5.5)	1	3.8	7	-	5
В	Dual acid-base catalyst (pH=7.6)	1	3.8	7	3	5

2.2.1 One-step sol gel process

This process employed citric acid as organic catalyst. Firstly, EtOH was added into reagent bottle followed by cooling process at 0°C and stirring at 250 rpm for 5 minutes. Then TEOS was dropped and resting. After resting for 5 minutes TEOS and EtOH mixture was dropped wise by $C_6H_8O_7$ to produce sol through one-step sol gel process.

2.2.2 Two-step sol gel process

According one-step sol gel process, this difference of procedure put on addition of base catalyst. Et-OH, TEOS and citric acid was mixed at 0°C for an hour. Then,

followed by addition of NH_3 and refluxed for 2 hours at 0°C and 250 rpm stirring.

2.2.3 Calcination

Silica sol was dried in oven at temperature controlled 60°C for 24 hours to obtain dried gel. Dried gel (xerogels) was subsequently grounded into fully homogeny powder and calcined in temperature controlled at varying temperature 200°C and 250°C for 1 h. Xerogels were characterized using FTIR at wavelength range 4000-600 1/cm.

2.3 Characterization Using FTIR

As one of indirect analysis methods, Fourier Transform Infrared (FTIR) provides information of functional group within the silica network[18, 19]. According to presence hypothesis of silanol, siloxane and Si-C bonds in matrix, Infrared spectra was carried out along with 1400-600cm⁻¹ wavelength. Some organic groups and silicone compound were summarized in Table 2.

Peak deconvulation wavelength for 1400-600cm⁻¹ was showed by FityK software based on Gaussian line shapes at least square and normalized peak against baselines[20] to understand proportional group in compound.

 Table 2. Group frequencies for organic and silicone-oxy

 compound[21]

Wave number	Organic group
(1/cm)	
1650	C=C stretch
1460	C-H methyl scissor
1375	C-H
1260	Si-C
1000-1100	Si-O-Si
990	C=C-H bend
940	Si-OH
< 800	Si-C

3 Result and Discussion

3.1 Silica carbon xerogels characterization

Xerogels were characterized to analyze functional group of siloxane (Si-O-Si), silanol (Si-OH) and silica carbon (Si-C) on the silica samples. Fourier Transform Infra-Red (FTIR) showed in Fig 3 was performed to analyze the functional group of silica xerogel and set as a function of catalyst type and calcination temperature. For asmuch as the aim of preparing this xerogel is to be used as thin film membrane coating, in order that it is so important to comprehend if there are 3 groups.

The spectra is at around 1060 cm⁻¹, 942 cm⁻¹ and 800 cm⁻¹ to siloxane, silanol, and silica-carbon groups, respectively [22]. The wavelength of ~1060 cm⁻¹ is called asymetric stretching vibration. Refer to Fig 3 employing single acid catalyst at 200°C calcined, 250 °C calcined and uncalcined there were 3 peaks indicating presence of siloxane (Si-O-Si), silanol (Si-OH), and silica-carbon (Si-C) at wave number around 1060 cm⁻¹,940 cm⁻¹, 780 cm⁻¹, respectively. As well as by employing only acid catalyst, by employing dual acid-base catalyst also were 3 peaks of compound at around 1062 cm⁻¹, 959 cm⁻¹, 790 cm⁻¹. This result show that xerogel peaks for single acid catalyst and dual acid-base catalyst using citric acid were similar. Higher calcination temperature also makes carbon dissapear due to decomposition, while silanol and siloxane are remain.

Increasing rate of sol-gel process by employing acid or base catalyst indirectly effected in formation of bonding, robustness and pore size of silica network. Silanol (Si-OH) is hydrophilic and damaged highly on silica network. Therefore, presence of organic compound sourced from organic catalyst effected to form silicacarbon (Si-C) bonds. Hybrid silica using precursor TEOS and organic catalyst for improving high hydro-stability and separating performance are critically reported by Elma (2012) [3].

3.2 Peak area ratio of carbon xerogels

Calcination as burning process is reaction decomposition to degrade carbonate gas or hydroxide content. Thus, powder after calcination has been in high purity. Calcination is run in high temperature depending on material properties.

Si-C formation and presence effected in both sol-gel reaction and calcination process, respectively. At high calcination temperature silica-carbon content carried out because of damaging. Consequently, due to network has leaving empty space, changing network structure and enlarging of pore size, robustness gradually decrease. Elma, *et al* (2019) reported that low calcination temperature are convenient for presence of silica-carbon in membrane network [22].

As addition analysis was carried out an overlapping of peak deconvolution to determine surface area of functionalize group compound in organosilica xerogels by Fityk software program as shown on Fig. 4. Employe of citric acid and based catalyst into organosilica sols were rendering to form silanol (Si-O) and siloxane (Si-O-Si) groups via hydrolysis and condensation reaction. According to fitting result as display on Fig.4 (dotted calcined 250 °C), deconvolution of surface area ratio of silanol:siloxane of single organo catalyst is showing better than dual organo catalyst of 0.1 a.u. is a bit than 0.5 a.u.. It means functionalize of siloxane group is dominate in organosilica xerogel which the significance of producing the organosilica structure become mesopore [23]. Comparing to previous study reported [24] by of relative ratio of Si-OH/Si-O-Si surface area in this work is quiet small 50% at same calcine temperature 250 °C. It is indicate both of result have similar structure.

The effect of calcination was investigated by deconvolution at a wavelength of 940/1080 cm⁻¹ (Si-OH/Si–O–Si) on Figure 4. It should be emphasized that silanol formation in the calcined xerogels (employs both single acid catalyst and dual acid-base catalyst) was reduced at 250°C. This means that once the calcination temperature increases the silanol concentration decreases. Rising of calcined temperature lead the minimize oH peak. In other hand, acid-acid at 250°C offers higher carbon content showed at wavelength of 800 cm⁻¹ (Si-C), which carbon in silica matrices may reduce the hydrophilic properties of silica network.

Deconvulation for Figure 4(d) showed that employing citric acid was leaded to decreasing of silanol/siloxane ratio as a function enhancing on calcination temperature. Equivalently, Figure 4d shows two interesting peak that is siloxane and silica carbon. Therefore, condensation process particularly produce high siloxane. Also, nucleophilic performance increases and partially substituted to form silica-carbon configuration in silica network.

Meanwhile, in Figure 4(c) the higher calcination temperature makes the lower silica-carbon effected in employing base catalyst to high siloxane formation. Increasing of catalyst concentration cannot effect steric factor for carbon substitution.





Fig. 4. The peak area ratio at 200oC calcined, 250oC calcined and uncalcined of silica carbon peak against siloxane peak (c) by employing dual citric-acid-ammonia catalyst at 790 cm⁻¹/1062 cm⁻¹ and silanol peak against siloxane peak at 959 cm⁻¹/1062 cm⁻¹ and (d) by employing single citric acid catalyst at 780 cm⁻¹/1060 cm⁻¹ and silanol peak against siloxane peak at 940 cm⁻¹/1060 cm⁻¹; as function of thermal treatment.

Fig. 3 FTIR spectra of the silica xerogels employed (a) dual citric acid-ammonia catalyst and (b) single citric acid catalyst.

Tabl	le 3.	Peak	area	using	Fityk	(curve-	fitting) softwar	¢
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Xerogel thermal				Area	(cm ²)			
treatment	Si-OH		Si-C	D-Si	Si-OH/Si-O-Si		Si-C (800)	
	Single	Dual	Single	Dual	Single	Dual	Single	Dual
Uncalcination	1.59	1.87	5.83	7.69	0.27	0.24	0.25	1.45
200°C calcination	1.22	2.54	4.70	11.64	0.26	0.22	0.33	1.06
250°C calcination	0.67	1.84	7.17	13.03	0.09	0.14	0.41	1.61

4 Conclusion

Silica sol xerogels were successfully fabricated using single acid catalyst (citric acid) and dual acid base catalyst (citric acid and ammonia) under low calcination process (200 and 250°C). Higher temperature makes carbon groups loss, while siloxanes and silanols are still remain. Based on FTIR, single acid catalyst using organic catalyst shows more efficient to produce mesoporous structure. It will minimize the use of base catalyst. Organic catalyst also enhancing hydrostability and robustness of silica network.

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1 Introduction

Silica as inorganic material has best properties such as high chemical, thermal and mechanical stabilities [1]. The functionalization of silica material is important to know the mesoporous silica material applicable to desalination. TEOS (tetra ethyl ortho silicate) as hydrophobic inorganic material from metal alkoxide (precursor) is a skillfully utilized and easy controlled structure for membrane synthetic under the sol-gel process [2]. However, the limitation of using silica is low hydro-stability.

In order to increase hydro-stability and robustness of silica matrices against both physical and chemical resistances, many strategies of pure silica modification can be executed such as templated carbon silica, hybrid organic-inorganic silica structure [3], cobalt[4, 5], nickel [6-8], and iron [9]. Templated carbon modification was investigated in using Pluronics triblock copolymers [10] and surfactants for desalination application [11, 12]. For other method, hybrid organic-inorganic silica structure was investigated that silica-pectin as carbon templates promised excellent membrane due to its excellent performance indicated by 5 times water flux higher than using templeting carbon sourced from P123 triblock copolymer. Therefore, pectin as natural source of carbon and easy obtained from fruit peel or industries waste can

reduce one step process of templating and high production cost [13].

To reach efficiency cost in material and process, the importance of organic was utilized for catalyst as well as carbon source to form the silica network. Carbon addition from organic catalyst create robustness and change the structure of silica matrix [14, 15]. It is new potential strategy to solve the main problem in hydrostability by configuring Si-C on silica network. As reported by Elma and Setyawan [16] that success to obtain Si-O-C in silica network by employing citric acid as organic catalyst and carbon source [17]. But in this study the lower calcination temperatures are applied and compare the functionalization between acid catalyts and dual base acid catalyst. This research aims to synthesizing highly functionalized silica carbon (Si-C) using hybrid organicinorganic structures by employing precursor TEOS and organic catalyst through a sol-gel process. The functionalization using infrared spectra at 1400-700 cm⁻¹ of wavelength.

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2 Experimental

2.1 Variable and Materials

Silica sols was synthesized by using tetra ethyl ortho silicate (TEOS: Sigma-Aldrich), ethanol (EtOH: 70%) and water as solvent, also dilute citric acid (23.4 %, Merck) and ammonia (NH₃, Merck). Table 1 summarize each composition in molar ratio unit of materials to prepare two types of membrane.

FTIR analysis was delivered to understanding effect of experimental variables. Experiment was run as function of two types of catalyst (single citric acid catalyst and dual citric acid-base catalyst) and 3 thermal treatment condition (uncalcination; 200°C calcination and 250°C calcination).

2.2 Procedures

To reach characterization step for analyzing organic group in silica sol, there are many initial step to be executed. Pretreatment was followed by some material for preparation such as, precursor TEOS, ethanol solution, and acid or base catalyst. Sol-gel reaction consist of hydrolysis and condensation reaction. Sol-gel reaction was reacted precursor TEOS, ethanol, water, and catalyst to produced silica sol. For characterization silica sol should be transform into xerogel (dried sol) and grounded into powder to be applied as FTIR sample. Briefly, procedure of experiment can be showed in Fig. 1, and solgel process can be run in equipment installation in Fig 2.



Calcination of xerogel

Characterization of xerogel

Fig. 1. Flow Diagram of Experiment



 Table 1. Silica sols molar ratio.

Types of membranes	Types of catalyst	TEOS	EtOH [x10 ¹]	C6H8O7 [x10 ⁻⁴]	NH3 [x10 ⁻³]	H ₂ O
А	Single acid catalyst (pH=5.5)	1	3.8	7	-	5
В	Dual acid-base catalyst (pH=7.6)	1	3.8	7	3	5

2.2.1 One-step sol gel process

This process employed citric acid as organic catalyst. Firstly, EtOH was added into reagent bottle followed by cooling process at 0°C and stirring at 250 rpm for 5 minutes. Then TEOS was dropped and resting. After resting for 5 minutes TEOS and EtOH mixture was dropped wise by $C_6H_8O_7$ to produce sol through one-step sol gel process.

2.2.2 Two-step sol gel process

According one-step sol gel process, this difference of procedure put on addition of base catalyst. Et-OH, TEOS and citric acid was mixed at 0°C for an hour. Then, followed by addition of NH_3 and refluxed for 2 hours at $0^{\circ}C$ and 250 rpm stirring.

2.2.3 Calcination

Silica sol was dried in oven at temperature controlled 60°C for 24 hours to obtain dried gel. Dried gel (xerogels) was subsequently grounded into fully homogeny powder and calcined in temperature controlled at varying temperature 200°C and 250°C for 1 h. Xerogels were characterized using FTIR at wavelength range 4000-600 1/cm.

2.3 Characterization Using FTIR

As one of indirect analysis methods, Fourier Transform Infrared (FTIR) provides information of functional group within the silica network[18, 19]. According to presence hypothesis of silanol, siloxane and Si-C bonds in matrix, Infrared spectra was carried out along with 1400-600cm⁻¹ wavelength. Some organic groups and silicone compound were summarized in Table 2.

Peak deconvulation wavelength for 1400-600cm⁻¹ was showed by FityK software based on Gaussian line shapes at least square and normalized peak against baselines[20] to understand proportional group in compound.

 Table 2. Group frequencies for organic and silicone-oxy

 compound[21]

Wave number (1/cm)	Organic group			
1650	C=C stretch			
1460	C-H methyl scissor			
1375	C-H			
1260	Si-C			
1000-1100	Si-O-Si			
990	C=C-H bend			
940	Si-OH			
< 800	Si-C			

3 Result and Discussion

3.1 Silica carbon xerogels characterization

Xerogels were characterized to analyze functional group of siloxane (Si-O-Si), silanol (Si-OH) and silica carbon (Si-C) on the silica samples. Fourier Transform Infra-Red (FTIR) showed in Fig 3 was performed to analyze the functional group of silica xerogel and set as a function of catalyst type and calcination temperature. Forasmuch as the aim of preparing this xerogel is to be used as thin film membrane coating, in order that it is so important to comprehend if there are 3 groups.

The spectra is at around 1060 cm⁻¹, 942 cm⁻¹ and 800 cm⁻¹ to siloxane, silanol, and silica-carbon groups, respectively [22]. The wavelength of ~1060 cm⁻¹ is called asymetric strething vibration. Refer to Fig 3 employing single acid catalyst at 200°C calcined, 250 °C calcined and uncalcined there were 3 peaks indicating presence of siloxane (Si-O-Si), silanol (Si-OH), and silica-carbon (Si-C) at wave number around 1060 cm⁻¹,940 cm⁻¹, 780 cm⁻¹, respectively. As well as by employing only acid catalyst, by employing dual acid-base catalyst also were 3 peaks of compound at around 1062 cm⁻¹, 959 cm⁻¹, 790 cm⁻¹. This result show that xerogel peaks for single acid catalyst and dual acid-base catalyst using citric acid were similar. Higher calcination temperature also makes carbon dissapear due to decomposition, while silanol and siloxane are remain.

Increasing rate of sol-gel process by employing acid or base catalyst indirectly effected in formation of bonding, robustness and pore size of silica network. Silanol (Si-OH) is hydrophilic and damaged highly on silica network. Therefore, presence of organic compound sourced from organic catalyst effected to form silicacarbon (Si-C) bonds. Hybrid silica using precursor TEOS and organic catalyst for improving high hydro-stability and separating performance are critically reported by Elma (2012) [3].

3.2 Peak area ratio of carbon xerogels

Calcination as burning process is reaction decomposition to degrade carbonate gas or hydroxide content. Thus, powder after calcination has been in high purity. Calcination is run in high temperature depending on material properties.

Si-C formation and presence effected in both sol-gel reaction and calcination process, respectively. At high calcination temperature silica-carbon content carried out because of damaging. Consequently, due to network has leaving empty space, changing network structure and enlarging of pore size, robustness gradually decrease. Elma, *et al* (2019) reported that low calcination temperature are convenient for presence of silica-carbon in membrane network [22].

As addition analysis was carried out an overlapping of peak deconvolution to determine surface area of functionalize group compound in organosilica xerogels by Fityk software program as shown on Fig. 4. Employe of citric acid and based catalyst into organosilica sols were rendering to form silanol (Si-O) and siloxane (Si-O-Si) groups via hydrolysis and condensation reaction. According to fitting result as display on Fig.4 (dotted calcined 250 °C), deconvolution of surface area ratio of silanol:siloxane of single organo catalyst is showing better than dual organo catalyst of 0.1 a.u. is a bit than 0.5 a.u.. It means functionalize of siloxane group is dominate in organosilica xerogel which the significance of producing the organosilica structure become mesopore [23]. Comparing to previous study reported [24] by of relative ratio of Si-OH/Si-O-Si surface area in this work is quiet small 50% at same calcine temperature 250 °C. It is indicate both of result have similar structure.

The effect of calcination was investigated by deconvolution at a wavelength of 940/1080 cm⁻¹ (Si-OH/Si–O–Si) on Figure 4. It should be emphasized that silanol formation in the calcined xerogels (employs both single acid catalyst and dual acid-base catalyst) was reduced at 250°C. This means that once the calcination temperature increases the silanol concentration decreases. Rising of calcined temperature lead the minimize oH peak. In other hand, aalcination at 250 °C offers higher carbon content showed at wavelength of 800 cm⁻¹ (Si-C), which carbon in silica matrices may reduce the hydrophilic properties of silica network.

Deconvulation for Figure 4(d) showed that employing citric acid was leaded to decreasing of silanol/siloxane ratio as a function enhancing on calcination temperature. Equivalently, Figure 4d shows two interesting peak that is siloxane and silica carbon. Therefore, condensation process particularly produce high siloxane. Also, nucleophilic performance increases and partially substituted to form silica-carbon configuration in silica network.

Meanwhile, in Figure 4(c) the higher calcination temperature makes the lower silica-carbon effected in employing base catalyst to high siloxane formation. Increasing of catalyst concentration cannot effect steric factor for carbon substitution.



Fig. 3 FTIR spectra of the silica xerogels employed (a) dual citric acid-ammonia catalyst and (b) single citric acid catalyst. Table 3. Peak area using Fityk (curve-fitting) software



Fig. 4. The peak area ratio at 200oC calcined, 250oC calcined and uncalcined of silica carbon peak against siloxane peak (c) by employing dual citric-acid-ammonia catalyst at 790 cm⁻¹/1062 cm⁻¹ and silanol peak against siloxane peak at 959 cm⁻¹/1062 cm⁻¹ and (d) by employing single citric acid catalyst at 780 cm⁻¹/1060 cm⁻¹ and silanol peak against siloxane peak at 940 cm⁻¹/1060 cm⁻¹; as function of thermal treatment.

Xerogel thermal				Area	(cm ²)			
treatment	Si-	OH	Si-O	D-Si	Si-OH/Si-O-Si		Si-C (800)	
	Single	Dual	Single	Dual	Single	Dual	Single	Dual
Uncalcination	1.59	1.87	5.83	7.69	0.27	0.24	0.25	1.45
200°C calcination	1.22	2.54	4.70	11.64	0.26	0.22	0.33	1.06
250°C calcination	0.67	1 84	717	13.03	0.09	0.14	0.41	1.61

4 Conclusion

Silica sol xerogels were successfully fabricated using single acid catalyst (citric acid) and dual acid base catalyst (citric acid and ammonia) under low calcination process (200 and 250°C). Higher temperature makes carbon groups loss, while siloxanes and silanols are still remain. Based on FTIR, single acid catalyst using organic catalyst shows more efficient to produce mesoporous structure. It will minimize the use of base catalyst. Organic catalyst also enhancing hydrostability and robustness of silica network.

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