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Preparation of C4-silica Gels from Waste Glass and Tributylamine

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Abstract

Waste glass materials coming from municipal and industrial processes have become a serious problem for the environment in the near future. Silica gels have been long attracting attention since it is widely used for many applications. It had also been studied by several fields because of its surface properties. In this study, semi-polar silica gels have been synthesized. C4-silica gels have been prepared by reaction between tributylamine (TBA) and silica gels produced from waste glass. The waste glass was powdered, soaked in NaOH, then heated at 400 ^oC to obtain sodium silicate. Silica gels were produced by neutralized the sodium silicate using HCl, dissolved in H_2O, and dried in an oven at 80 ^oC. Silica gels were solubilized in TBA, stirred, and dried in the oven to obtain C4-silica gels. Silica gels were characterized by X-ray Diffraction (XRD), while Infra Red (IR) and Scanning Electron Microscopy (SEM) analyses were conducted to obtained C4-silica gels. XRD analysis of silica gels showed that the highest peak intensity was observed at $2\theta = 22.655°$. The band at 1381.03 cm^{-1} in the IR spectrum was attributed to the nitro-oxygen bond (N-O). SEM images showed that the surface of C4-silica gels was smoother and more flat than the previous silica gels.

Keywords: C4-silica gels, sodium silicate, tributylamine, waste glass

1. Introduction

Waste glass is one of the big problems for the environment as an inorganic waste [1] In general, the sources of waste glass come from home appliances such as dishes, glasses, windows, and cabinet glasses, as well as from glass stores [2]. One of the efforts which can be carried out to decrease the number of waste glasses is to re-use them as one of the sources for making silica gels since the waste glass contains about 72.1% silicon dioxide (SiO_2) [3].

Silica gels could be modified to be a non-polar stationary phase by impregnating some non-polar organic compounds on the surface of silica gels [4,5]. Khosravan and Saljooghi had altered the surface of silica gels by applying 2-aminothiophenol to isolate an Mn^{2+} ion for column chromatography [6]. In gas chromatography, a mixture of alkane gases could also be separated by silica gels as a non-polar stationary phase which was modified with polyethylene glycol 2000 [7].

Generally, the non-polar silica gels were prepared by modification of the surface of silica gels with organic compounds that contain C8 or C18 [8]. On the other hand, information about the surface modification of silica gels with C4 is still limited. For example, aluminium plate of silica gels impregnated by tributyl phosphate could separate organic compounds from polar to semi-polar, such as a mixture of phenolics, amines, and a mixture of ions Cr^{3+}, Cr^{6+}, Mn^{2+}, and Fe^{3+}[9].

Moreover, Mohammad et. al., has impregnated paraffin oil, tributyl phosphate, tributylamine (TBA) and silicon oil on the surface of silica gels of Thin Layer Chromatography (TLC) for separation of pharmaceutical products. The results showed that TLCs modified by paraffin oil, tributyl phosphate, and TBA could separate gently a mixture of paracetamol, diclofenac sodium, ibuprofen, aspirin, and ascorbic acid, whereas poor separation was resulted by TLC modified by silicon oil [10].

This study reports the preparation of C4-silica gels from waste glass and TBA. Silica gels were produced by the sol-gel method toward sodium silicate produced from the powder of waste glass. Further, C4-silica gels were made by soaking silica gels in various concentrations of TBA at room temperature [9]. The optimum concentration of TBA was observed by IR spectra to characterize an N-O bond, whereas IR and SEM performed data of C4-silica gels.

2. Methodology

2.1. Preparation of sodium silicate solution

Waste glass (Figure 1a) was cleaned, dried, and powdered by sifter for 80-100 mesh. The glass powder (Figure 1b) was separated into three parts. 150 mL of 1.5M NaOH was added into each part (50 g) of dried glass powder and stirred in a beaker. Each solution was gradually dried in the oven, then subsequently each mixture was heated at 400 ^{o}C, 500 ^{o}C, and 600 ^{o}C, respectively in a furnace for 4 hours to obtain sodium silicate powder. Each was characterized by X-ray Fluorescence (XRF) Panalytical Minipal 4. A similar process was repeated only for 3M NaOH at 400 ^{o}C.

2.2. Preparation of silica gels

Sodium silicate powder was dissolved in hot H_2O (80-100°C) then filtered. Concentrated HCl (37%) was dropped stepwise into 100 mL of filtrate until pH 7 to produce hydrogel. The hydrogel was dried in the oven at 80 ^{o}C for 2-3 hours to obtain xerogel. Subsequently, powdered silica gels were yielded by washing the xerogel with H_2O, then dried in the oven at 80 ^{o}C. Finally, silica gels were characterized by IR and XRD. IR spectra were performed on a Shimadzu 8201 PC using KBr pellets, while the crystalline property of silica gels was recorded from an XRD Philips X'Pert diffractometer.

2.3. Preparation of C4-silica gels

Silica gels (10 g) were divided into five parts. Each part was dissolved in 200 mL of variant concentration of TBA solutions (0.0005M, 0.0001M, 0.001M, 0.01M, and 0.1M respectively) for 3 hours. During the reaction, each solution was stirred regularly, then filtered. Each filtrate was dried in an oven for 3 hours at 120 ^{o}C. C4-silica gels were characterized by FT-IR and SEM. Microscopes analyses of silica gels and C4-silica gels were performed on SEM Zeiss Evo MA 10.

3. Result and Discussion

XRF data (Table 1) revealed the composition of metal oxides in sodium silicate that was heated at various temperatures to get an optimum ratio between SiO_2 and Na_2O. The ratio between SiO_2 and Na_2O was 4.6:1 and 7.1:1 at 400 ^{o}C and 600 ^{o}C, respectively. The higher the temperature of the reaction, the more NaOH melted, and it reacted with SiO_2 to form sodium silicate [11]. Whereas, the ratio between SiO_2 and Na_2O at 500 ^{o}C could not be characterized since Na_2O was undetected.

a b

Figure 1. Waste glass (a) and glass powder (b)

Table 1. XRF data for metal oxides in sodium silicate

Metal oxides	Percentage (%)		
	400 ^{o}C	500 ^{o}C	600 ^{o}C
P_2O_5	2.30	3.00	2.50
K_2O	0.76	0.73	0.70
CaO	42.50	45.70	44.00
TiO_2	0.31	0.31	0.30
MnO	0.099	0.12	0.10
Fe_2O_3	2.33	2.91	2.06
CuO	0.32	0.38	0.30
Zr_2O	0.24	0.22	0.23
SiO_2	41.50	45.90	43.00
Na_2O	9.00	-	6.00
BaO	0.30	0.30	0.30
NiO	0.02	0.05	0.03
Cr_2O_3	0.15	0.24	0.17
SrO	-	0.14	0.13

According to Table 1, at 400 ^{o}C, SiO_2 and Na_2O displayed ratio of 4.6:1 respectively, closer to type I of Indonesian National Standard [12] for sodium silicate, which is 2.3:1.9 with 34-36% of SiO_2. Since the percentage of SiO_2 in the sample was still high (41.5 %), by increasing concentration of NaOH to 3M, the ratio between SiO_2 and Na_2O in sodium silicate at 400 ^{o}C could be increased to 2:1 with 38.3 % of SiO_2 (Table 2). These values were similar to type I of SNI for sodium silicate.

Table 2. XRF data for metal oxides in sodium silicate in 3M NaOH at 400 ^{o}C

Metal oxides	Percentage (%)
Phosphorus pentoxide (P_2O_5)	2.40
Potassium oxide (K_2O)	0.88
Calcium oxide (CaO)	36.10
Strontium dioxide (SrO_2)	0.10
Manganese oxide (MnO)	0.081
Iron (III) oxide (Fe_2O_3)	1.81
Copper (II) oxide (CuO)	0.40
Zirconium oxide (Zr_2O)	0.18
Silicon oxide (SiO_2)	38.30
Sodium oxide (Na_2O)	19.00
Titanium oxide (BaO)	0.32

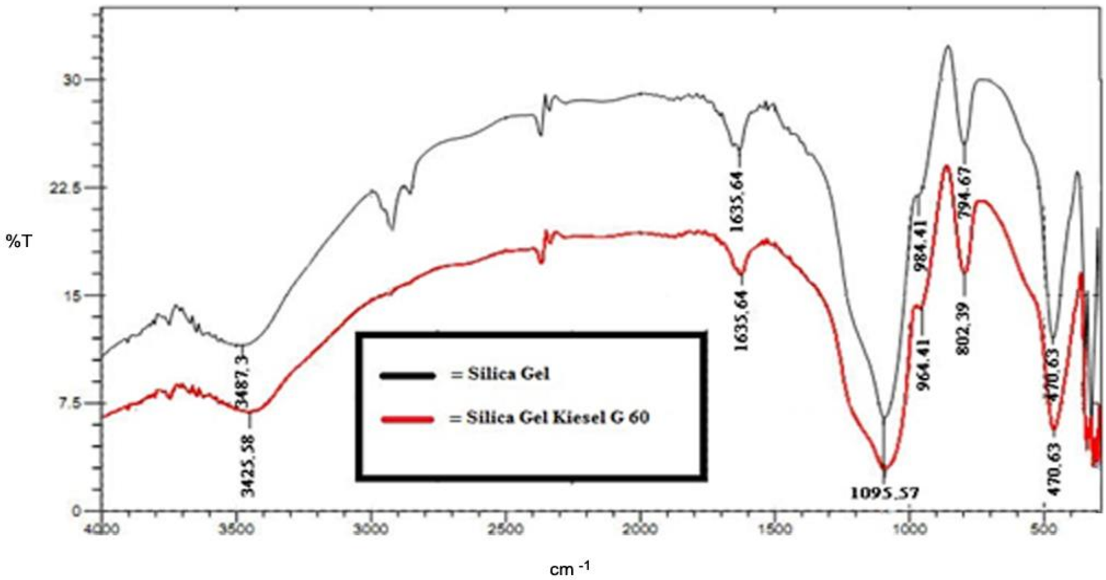


Figure 2. IR spectra comparison between silica gels and silica gels Kiesel G 60

Silica gels were obtained by making sol-gel toward sodium silicate. IR and XRD data revealed the characteristic of silica gels. IR spectrum showed a typical moiety at 3487.3 cm^{-1} attributes for a hydroxyl group. The broad peak for OH indicated the presence of an intramolecular hydrogen bond between oxygen and hydrogen among a group of Si-OH. Wavenumbers at 1635.64 cm^{-1} and 1095.57 cm^{-1} showed a bending vibration for OH in Si-OH and an asymmetric stretching vibration for Si-O in Si-O-Si, respectively. Further, a stretching vibration for Si-O in Si-OH and a symmetric stretching vibration for Si-O in Si-O-Si were revealed by wavenumbers at 984.41 cm^{-1} and 794.67 cm^{-1}, respectively [13]. New peaks at 2900 cm^{-1} – 2800 cm^{-1} are characteristic for C-H in CH_2 and CH_3 because organic chains of TBA were introduced [14]. On the basis of FT-IR analyses, the synthesis of silica gels from wasted glass has succeeded. IR spectra comparison between silica gels and silica gel Kiesel 60 can be seen in Figure 2. Additionally, XRD data for silica gels showed broadband with the highest intensity peak at $2\theta = 22.655^{o}$, which correspond to $d_{011} = 3.921$ Å (Figure 3). Abou Rida and Harb [13] mentioned that silica gels produced from sodium silicate had the highest peak at $2\theta = 21\text{-}22^{o}$ indicating this material is amorphous.

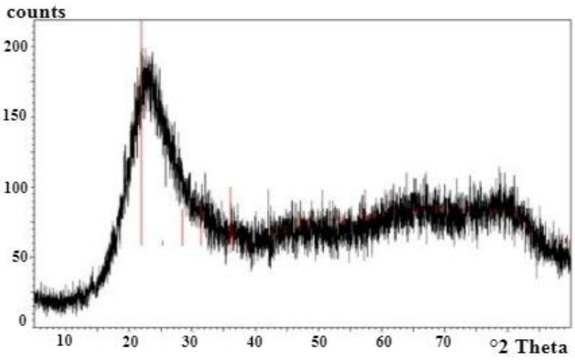
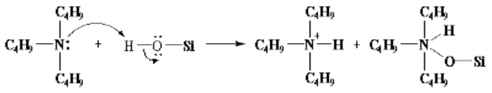


Figure 3. Diffractogram of silica gels

Figure 4 showed IR spectra comparison between silica gels and silica gels impregnated by TBA in various concentrations. All of the infrared spectra were similar, except for IR spectrum of silica gels impregnated by 0.001M TBA. The absorption peak at 1381.03 cm^{-1} indicated a characteristic moiety for the vibration of N-O.

Mohammad et al., stated that the optimum concentration of TBA to modify silica gels in thin layer chromatography (TLC) plate was 0.1 M. This difference is influenced by the size of particles of silica gels. Particles size of silica gels is bigger than silica gels on TLC, as a result, lower concentration was needed to substitute hydrogen atom in Si-OH by tributylamine.

Proposed reaction between silica gels and TBA is shown below:



$$C_4H_9-\overset{C_4H_9}{\underset{C_4H_9}{\ddot{N}}} + H-\ddot{O}-Si \longrightarrow C_4H_9-\overset{C_4H_9}{\underset{C_4H_9}{\overset{+}{N}}}-H + C_4H_9-\overset{C_4H_9}{\underset{C_4H_9}{N}}\genfrac{}{}{0pt}{}{H}{O-Si} \quad (1)$$

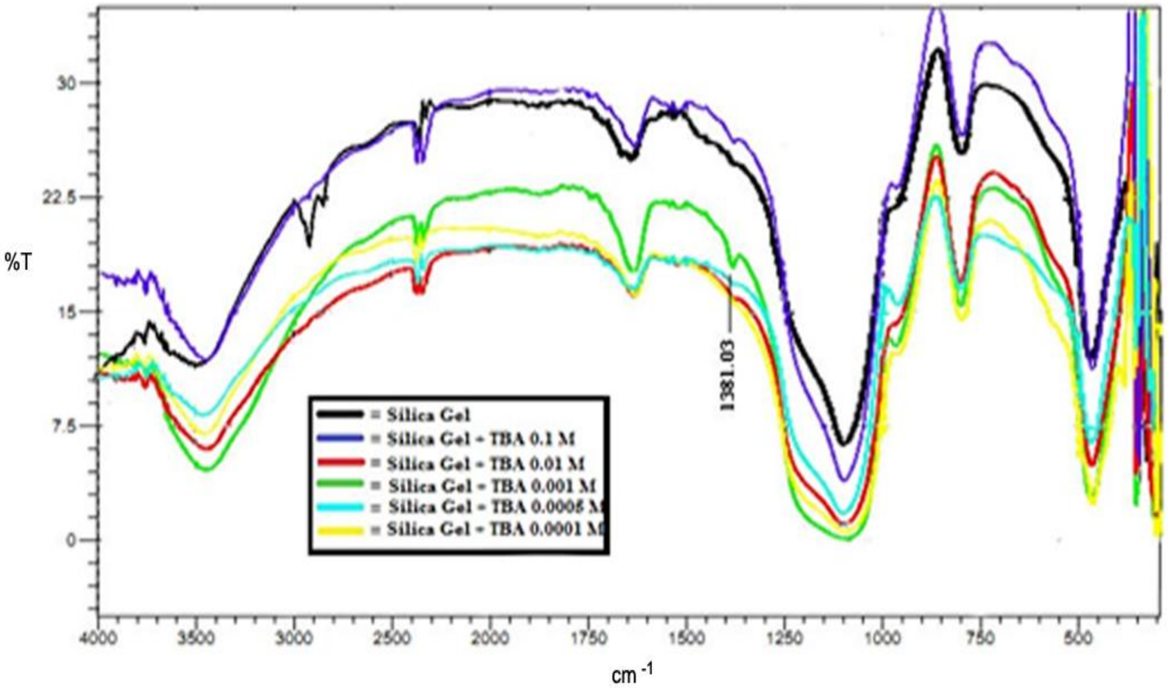
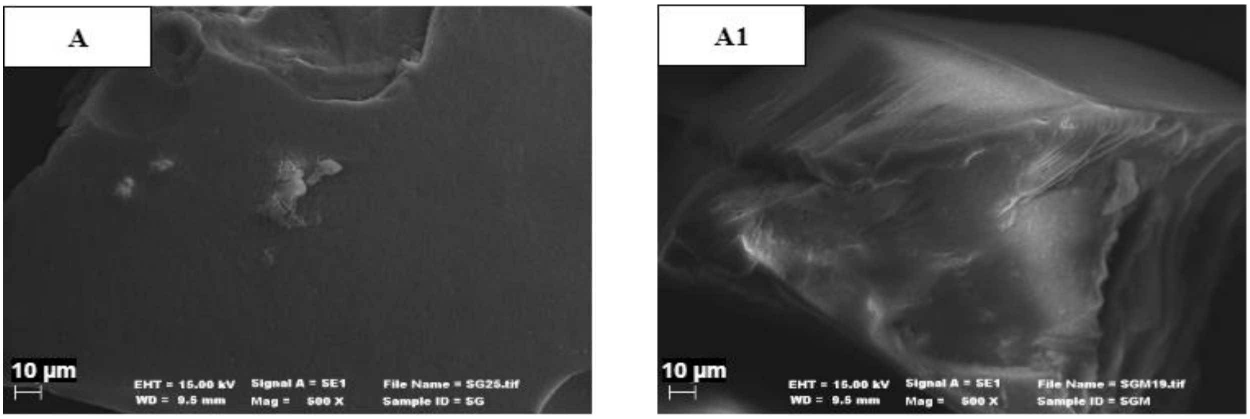
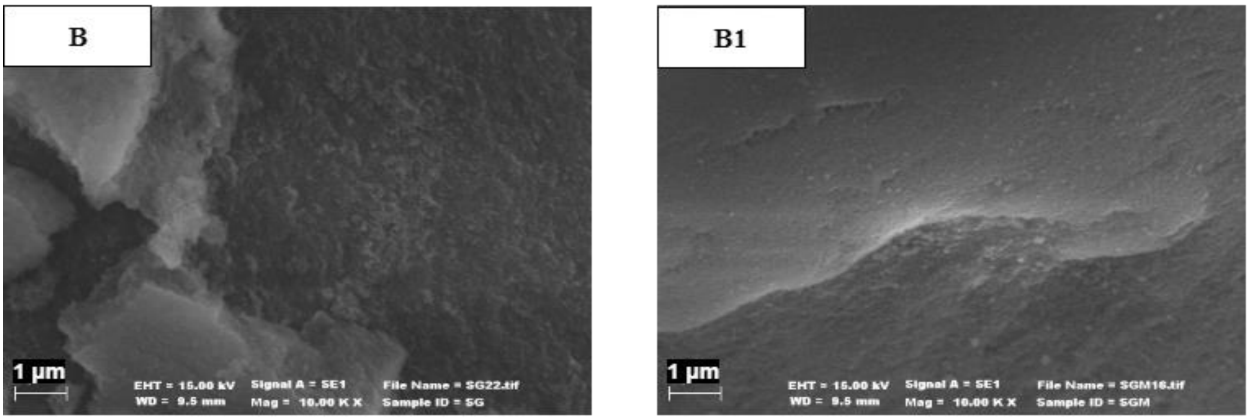


Figure 4. IR spectra of C4-silica gels in various concentrations of tributylamine



Magnification 500 X



Magnification 10,000 X

Figure 5. SEM photos of (A and B): Silica gels and (A1 and B1): C4-silica gels at magnifications of 500× and 10,000×

Furthermore, scanning electron microscopy (SEM) was conducted to study further morphology both on the surface of silica gels and C4-silica gels (Figure 5). The surface of silica gels was granular forms. In contrast, the surface on C4-silica gels was smoother and flatter, which indicated that TBA covered the silica gel surface and pore sizes of C4-silica gels were smaller than silica gels [15].

4. Conclusions

Preparation of C4-silica gels has succeeded by the reaction between TBA and silica gels produced from waste glass. IR spectrum of C4-silica gels revealed an N-O vibration at an absorption peak 1381.03 cm^{-1} that was obtained from 0.001M TBA. SEM data supported the existing of TBA on the surface of C4-silica gels, which were flat, smooth, and homogenous.

5. Acknowledgments

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