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Contributed Paper

Synthesis of Porous γ-A[illegible]sted by Resorcinol-Formaldehy[illegible]

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ABSTRACT

Porous alumina is always used as catalyst support in petrochemical field because the alumina has good thermal properties comparing with other ceramics. In this work, the synthesis of porous alumina by aluminium preformed sol and the controlling textural properties of alumina by using synthesized carbon template have also been studied. Firstly, aluminium acetylacetonate (A) has been dissolved with formaldehyde solution (F) to form aluminium preformed sol. Resorcinol-formaldehyde gel (RF-gel) has been also prepared by sol-gel processing as assisted-template to control morphology of alumina pore. The chemicals concentration to prepare the RF solution, aging time of both the preformed aluminium sol and the RF solution were fixed. After that, the RF solution was added into preformed aluminium sol. The sol-gel reaction was studied with the different aluminium acetylacetonate to formaldehyde (A/F) molar ratio and resorcinol (A/R) molar ratio. Finally, varying molar ratio of A/R and A/F changes textural properties of produced particles and obtains γ-phase alumina similarly. The highest surface area of synthesized alumina that can be reached is 221 m^2/g.

Keywords: γ-alumina, resorcinol-formaldehyde gel, mesoporous materials

1. INTRODUCTION

Porous ceramics are most widely used as catalyst supports because of their various excellent properties such as large surface area and high resistance to chemical agents and heat [1]. Specially, porous alumina is always used as catalytic supports in automotive and petrochemical industries. There are many methods to synthesis alumina especially precipitation method. Although, the precipitation method is easy to produce alumina and less time consuming with high surface area, there is the mainly disadvantage of alumina synthesis by this method. When synthesized alumina with precipitation and using alumimiun oxide-hydroxide precursor, the broad pore size distribution was occurred [2, 3]. Moreover, this method has more complicated steps when washing than sol-gel processing has.

The sol-gel processing is also used to produce porous ceramics. To synthesize alumina, the sol-gel processing often uses aluminium nitrate nonahydrate as precursors because of their low price. However, it is reactive substance which highly exothermic when react in alkali containing process. According to sol-gel processing, the surfactants are always used as template to produce high porous materials. Non-ionic surfactants like $EO_{20}PO_{70}EO_{20}$ could synthesize mesoporous alumina with high surface area when the triblock copolymer was used [4]. Resorcinol-formaldehyde gel can be also used as template because of their high porosities [5]. In addition, resorcinol-formaldehyde (RF) gel can be controllable in its porosity with varying some parameters such as substrate concentration, pH value, quantities of catalyst and aging condition [5].

In this work, porous alumina was synthesized by sol-gel process that used aluminium acetylacetonate (A) as precursor of the sol and resorcinol-formaldehyde gel (RF-gel) as template under the assumption that is production alumina with porous template. The difference ratio between aluminium alkoxide and formaldehyde (A/F) of the preformed sol and the aluminium alkoxide to resorcinol (A/R) ratio were studied in the effect on porosity.

2. MATERIALS AND METHODS

2.1 Chemicals

Aluminium acetylacetonate and resorcinol with purity 95% and 99% respectively were purchased from Sigma. Formaldehyde solution with 36.5-38.0 percent by weight and Sodium carbonate with purity 99% were purchased Ajax Fine Chemical. Ethanol absolute 99.9% was purchased VWR International S.A.S.

2.2 Preparation of Aluminium Formaldehyde Preformed Sol (AF sol)

Aluminium acetylacetonate (A) was dissolved by formaldehyde (F) solution at 60°C. The ratio of aluminium acetylacetonate to formaldehyde (A/F) was pepared, i.e., 0.013, 0.064, 0.097. Aluminium preformed sol was held for 3 days at room temperature.

2.3 Preparation of Resorcinol-Formaldehyde Gel (RF-gel)

Resorcinol (R) was dissolved by deionized water (W) while sodium carbonate (C) which used as catalyst was dissolved with concentration of 0.1 g in 10 ml water. After stirred the solution about 10 minutes, sodium carbonate solution was added into the solution and stirred 15 minutes. Finally, formaldehyde solution was added into the solution [6]. These above steps were run at room temperature with fixed concentration of all components and held for 21 hours.

2.4 Preparation of Alumina Particles

The aged preformed sol was added into the aged resorcinol-formaldehyde gel with stirring 10 minutes with investigating varied concentration of RF-gel that is molar ratio of A/R between 0.1 and 10. The sample was dried via conventional dry at 110°C overnight. The samples were also calcined at 800°C to remove carbon template obtained from resorcinol-formaldehyde gel and to obtain porous gamma alumina. The calcination was held with heating rate 5°C/min for 4 hours.

2.5 Characterizations

Functional groups of the aged gels were identified by Fourier transform infrared spectroscopy (FTIR). Morphology of the obtained products was observed by using a scanning electron microscope (SEM, JEOL JSM-6400). The phase of synthesized alumina was specified by x-ray diffraction pattern. The surface area, pore volume and pore size were measured by a BELSORP-mini nitrogen adsorption analyzer with Brunauer-Emmett-Teller (BET) method to specify the surface area of alumina and Barrett, Joyner and Halenda (BJH) method to analyze pore size distribution.

3. RESULTS AND DISCUSSION

3.1 Functional Group of The Gel

FTIR sprectra of RF-gel, AF sol and the mixed gel are shown in Figure 1. Wavenumber 1695,1605, 1217 and 982 cm^{-1} show the C=C and C-H vibration of aromatic ring of resorcinol. While the wavelength 1470 and 1100 cm^{-1} indicate methylene (-CH_2-) and methyl ether (-CH_2-O-CH_2-) bridge of RF-gel which occurred by cross-linking between resorcinol and formaldehyde gel respectively [7-9]. Obviously, there is an interesting peak occurs similarly between AF sol and the mixed gel in 1700 cm^{-1} which not shown in the pure RF-gel. The bands at wavenumber of 1700 cm^{-1} corresponding to -C=O- in functional group of ketone vibration was observed [9]. This functional group is shown in both of aluminium acetylacetonate and formaldehyde. Moreover, the 1700 cm^{-1} peak comparing between the mixed gel and AF sol are quite different. The result shows that aluminium acetylacetonate can react with formaldehyde when the both reactants are mixed together.

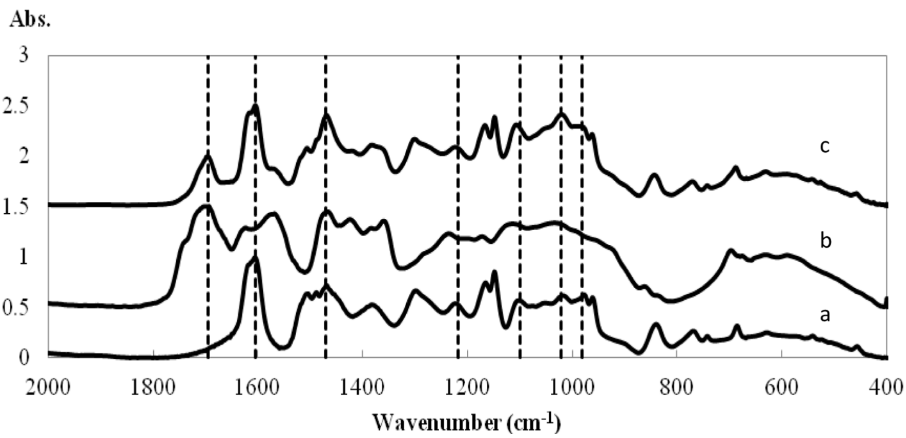

Figure 1. FTIR spectra of the synthesized samples (a) RF-gel, (b) AF sol and (c) the mixed gel.

3.2 Textural Properties

Table 1 shows the surface area of synthesized alumina and pore diameter which analyzed from Nitrogen adsorption desorption technique. Obviously, the molar ratio of A/R has an effect on surface of alumina. Increasing concentration of resorcinol-formaldehyde gel (decreasing A/R) increases BET surface area of alumina. This can be describes the aluminium preformed sol is made with higher porosity by cross-linking between RF-gel occurring. However, the amount of the gel has extremely an impact on the gelation time of the mixed gel. The high concentration of RF-gel makes the mixed gel to be solid rapidly. While formaldehyde concentrations affect the surface area of particles with no pattern. Nevertheless, formaldehyde concentration increases (decreasing A/F), average pore size diameter and pore volume of the particles also increase. This means formaldehyde concentration has a significant effect on textural properties of alumina particles.

Table 1. Textural properties of the synthesized alumina.

A/R	A/F	$S_{BET}(m^2/g)^a$	$d_p(nm)^b$	$V_p(cm^3/g)^b$
-	0.10	48	3.72	0.10
6.73	0.06	105	10.55	0.31
1.34	0.06	134	4.78	0.34
0.26	0.06	135	5.43	0.28
0.18	0.06	143	5.43	0.34
0.05	0.06	151	3.29	0.34
0.03	0.10	175	16.05	0.68
0.03	0.06	181	16.05	0.75
0.03	0.03	181	9.21	0.55
0.03	0.02	221	16.05	0.79
0.03	0.01	160	7.05	0.48

[a] The BET surface areas were calculated by using BET equation.
[b] The average pore diameters and pore volumes were calculated by using BJH equation.

Pore size distribution of alumina particle in Figure 2 and 3 shows that the range of pore diameter is between 2 to 55 nm. Both of the concentration of resorcinol-formaldehyde gel and the formaldehyde concentration in the AF sol have a significant effect on pore size distribution. According to varying A/R molar ratio (Figure 2), alumina that was synthesized with the high concentration of RF-gel obtained narrow pore size distribution with small pore diameter while the alumina with the low concentration of resorcinol reached broader pore size distribution. In addition, some low concentration of RF-gel including with A/R molar ratio 1.34 and 0.18 illustrate bimodal distribution. This effect explains the synthesized carbon template has high porosity that can control the porosity of the alumina particle. While increasing concentration of formaldehyde (Figure 3) in the preformed sol causes broad pore size distribution with bimodal and the average pore diameter is also reduced. This effect can be described by excess formaldehyde from AF sol reacted with RF-gel. The dilution effect (excess F) causes larger pore size of carbon structure that affects pore size of the alumina [5, 10].

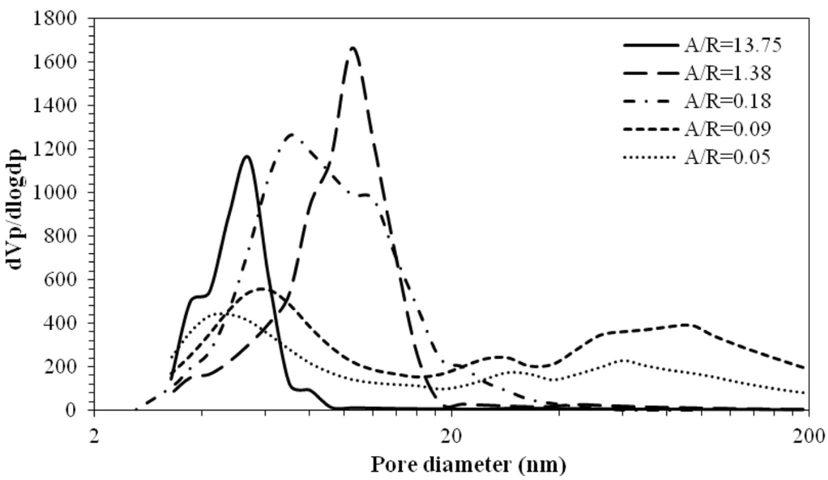

Figure 2. Pore size distribution of alumina particles with varying A/R molar ratio.

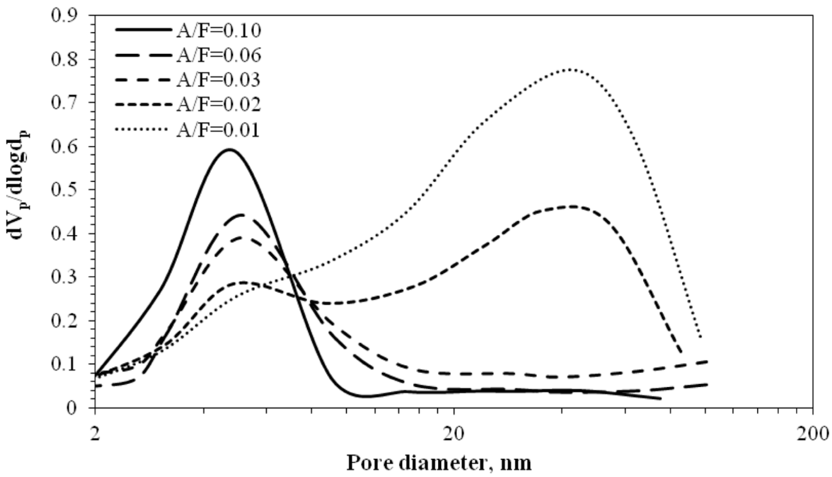

Figure 3. Pore size distribution of alumina particles with A/F molar ratio.

3.3 Morphology of Synthesized Alumina

Figure 4 presents some XRD patterns of synthesized alumina. All of the alumina products show diffraction peaks of γ-phase of alumina. The alumina can be produced by alumina preformed sol with sol-gel processing. The concentrations of formaldehyde in the preformed sol and resorcinol-formaldehyde gel have not an impact on phase transformation of alumina. This means the calcination temperature is the most important effect on alumina phase transformation.

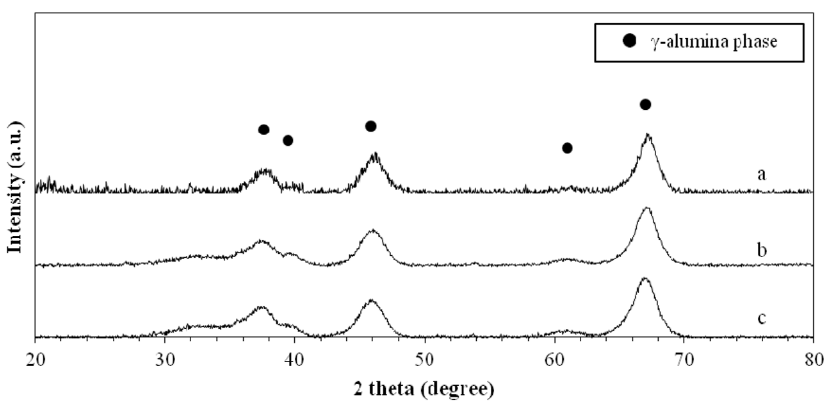

Figure 4. XRD patterns of some synthesized alumina with (a) A/F = 0.1 without RF-gel (b) A/F = 0.02, A/R = 0.18, (c) A/F = 0.06, A/R = 6.73.

Figure 5 confirms that concentration of formaldehyde in the AF sol has a significant effect on the products. The alumina cluster size decreases when A/F molar ratio decrease (Increasing formaldehyde concentration). The bimodal pore size distribution is indecated in the SEM images at A/F = 0.01 (as shown in Figure 5c1 and Figure 5c2). Bimodal pore size distribution consists of pores originate from the inter-particular void between alumina particles and the pore causes from RF-gel colloidal particles which are already removed after calcination. The results are explained previously by excess formaldehyde from AF sol reacted with RF-gel called 'dilution effect'.

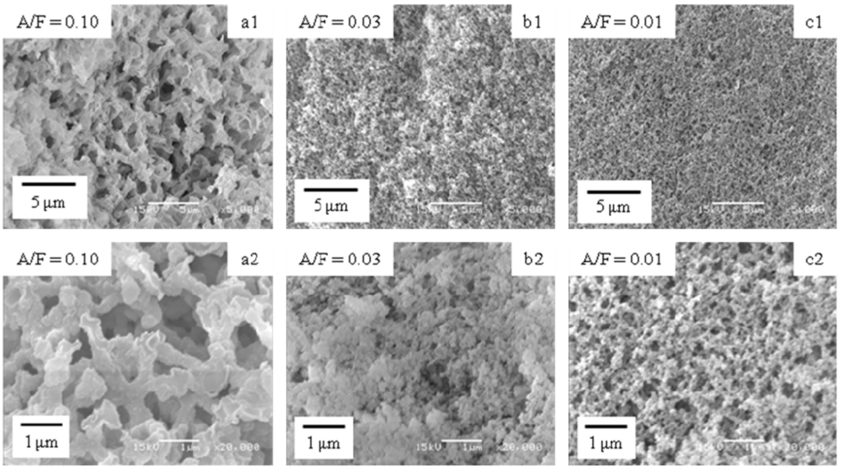

Figure 5. SEM images of synthesized alumina in different A/F molar ratio (a) 0.10, (b) 0.03 and (c) 0.01 with magnification (1) 5,000x and (2) 20,000x.

From section 3.2 and 3.3, concentration of chemicals which are formaldehyde and RF-gel significantly affect on textural properties of bulk alumina. These effects have an impact on colloidal particles structure of the mixed gel. The structures of colloidal particles which form from the mixed gel can be summarized as figure 6.

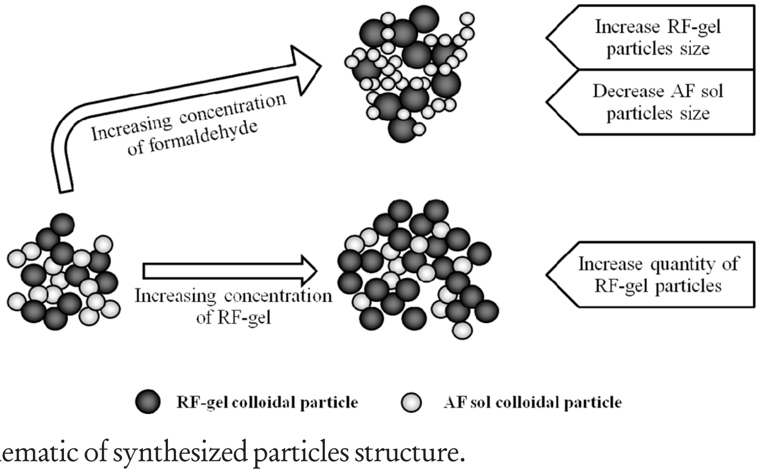

Figure 6. Schematic of synthesized particles structure.

4. Conclusions

Resorcinol-Formaldehyde gel can be used as template for the porous alumina synthesis with reached highest surface area of synthesized alumina 221 m^2/g. Although, the concentration of RF-gel has not an effect on phase transformation of alumina with calcination temperature 800°C, the concentration of RF-gel affects gelation time of the mixed gel and textural properties of synthesized alumina including surface area and pore size distribution.

Acknowledgements

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