

SYNTHESIS OF Na-Y NANOZEOLITE ON GLASSY CARBON BY SEEDING METHOD

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Abstract

Nanozeolite synthesis was carried out through seeding method, in which the seed was Y zeolite (member of faujasite, FAU, family) using tetraethyl ortho silicate (TEOS) as silica source, and aluminium isopropoxide $\text{Al}[(\text{CH}_3)_2\text{CHO}]_3$ as aluminum source, and tetramethylammoniumhydroxide (TMAOH) as template, under hydrothermal condition. The seeds then were grown on glassy carbon (GC) sheet, that prior being used was modified, using layer by layer (LbL) technique, with three layers of polyelectrolytes: Poly(diallyldimethylammoniumchloride), PDDA; Poly-4-sodiumstyrenesulfonate, PSS; and PDDA again. The seeded GC sheet then was immersed into colloidal suspension with molar composition as follow: $14\text{Na}_2\text{O} : \text{Al}_2\text{O}_3 : 10\text{SiO}_2 : 798\text{H}_2\text{O} : 3\text{Na}_2\text{SO}_4$ and the pH of the suspension was kept at 9,0 before was treated hydrothermally for 20 hours at 100 °C. The variation on number of seed layers on GC (1, 2 and 3 layers), observed by SEM, showed that homogenous structure and crystal size was obtained with 1 layer of seeds applied on the surface of glassy carbon. When more layers of seeds applied, the aggregation and intergrowth of zeolite crystals in the thin film of zeolite became more visible. XRD pattern of the as-prepared thin film zeolite indicates that the zeolite has nanoparticle structure. Furthermore, the pattern of glassy carbon predominated the XRD pattern and covered the pattern of Y-zeolite. On the other hand, XRD of as prepared bulk Y-zeolite shows structure of FAU framework.

Keywords: glassy carbon, FAU, nanozeolite, seeding method

1. Introduction

Zeolites are inorganic materials formed by three-dimensional aluminosilicate structure containing pores and cavities of molecular dimensions (ca. 3-15 Å) creating nanosize interconnected channels which can accommodate water or other guest molecules. This structure makes zeolites have unique properties that become versatile to be used for many applications such as sorbents, ion-exchangers and catalysts [1].

Along with extensive research in synthesis and application of nanomaterial, synthesis method of nanozeolite has been developed [2]. Several examples of structure of nanozeolites that have been prepared are FAU (NaY) [3-4], MFI (ZSM-5) [5-6], BEA (Zeolite Beta) [7] and LTA (Zeolite A) [8]. A crucial factor in preparing nanoparticle is how to avoid or minimize agglomeration of nanoparticles during and after synthesis [9]. In order to answer this problem, recent preparation of nanozeolite has been developed for application as a template to synthesize nanoparticles [10]. Zhang *et al.* [10] suggested that nanoparticles are grown inside zeolite pores, and the pores' walls behave as partition. Therefore, aggregation of nanoparticles could be minimized.

Synthesis of thin film NaY nanozeolite on pretreated glassy carbon (labelled as GC) through seeding method has been conducted. This research was based on the results reported by Zhang *et al.* [10] and Lassinati *et al.* [3]. They prepared thin film NaY nanozeolite on α -alumina, and synthesize faujasite (FAU) nanozeolite suspension as seeds. Synthesis of ZSM-5 nanocrystals on various types of porous carbon substrates for application as adsorbent and catalysis has been reported by Ozaki *et al.* [5].

In our work, instead of porous carbon substrate, glassy carbon was chosen as support because it is used as working electrode in other work [11]. In our previous work [12], nanozeolite was used to immobilized iron compounds and employed as arsenic detector in water phase. In that work, the as-synthesized zeolite was mordenite, and the research was focused on its application as electrode, but the properties of nanozeolite support was not yet thoroughly investigated. In this work, some characterizations on thin film of nanozeolite Y on glassy carbon as well as as prepared bulk nanozeolite are reported and discussed, especially the effect of seed concentration on crystallinity and size of the zeolite.

2. Experiment

Materials. Tetramethylammonium hydroxide pentahydrate, Glassy carbon Grade GC-20SS (Tokai Carbon Co. Ltd. Tokyo-Japan), TMAOH.5H₂O >99% (Sigma-Aldrich), Tetraethylortosilicate, TEOS 99% (Shintetsu), NaCl, Aluminium isopropoksida >98% (Sigma-Aldrich), NaOH (Merck), NH₄OH, H₂O₂ 30%, HCl, Poly(diallyldimethylammoniumchloride), PDDA (Aldrich), Poly-4-sodiumstyrenesulfonate, PSS (Florochem), Aquademin.

Synthesis of seed. FAU seeds were synthesized followed the procedure reported by Lassinati *et al.* [3] with some modification. The colloidal FAU zeolite crystals was prepared from homogeneous mixture with molar composition of: 2.46(TMA)₂O : 0.032Na₂O : Al₂O₃ : 3.40SiO₂ : 400 H₂O. The crystal seeds were prepared by dissolving 4.168 grams of Aluminum isopropoxide 98% in 10 mL aquademin and was stirred for 30 minutes, then 9.007 grams of TMAOH 99% was dissolved in 10 mL aquademin for 15 minutes. Both solutions then were poured slowly into polypropylene bottle containing 7.155 grams of mixture of tetraethoxysilane (TEOS>99%) and 10 mL aquademin, then was stirred for 30 minutes. Afterward, a mixture of 6.4 grams of 0.1 M NaOH solution and 41.819 mL aquademin were added slowly to the bottle with vigorous stirring for 60 minutes, and continued for 18 hours. During stirring, the pH solution was adjusted at 8-11 by adding drops of 6 M HCl solution. After that, the mixture was refluxed for 192 hours in waterbath at 100 °C, then cooled down to room temperature. Then, the mixture was centrifuged and the sediment was redispersed in 0.10 M ammonia solution for 24 hours. This process was repeated twice. Finally, the as-prepared sol was redispersed in aquademin, and the solid content and the pH of the sol were adjusted to 1.0% and 10.0, respectively (the latter by addition of a dilute ammonia solution). For characterization purpose, the sol was precipitated at room temperature, then dried at 100 °C for 18 hours. The crystals then were characterized with XRD, XRF and SEM.

Pretreating glassy carbon surface with layers of polymers and FAU seeds. Glassy carbon was cut about 1.0 cm x 1.0 cm, then polished using α -alumina slurry, and followed by silmutaneous ultrasonication in acidic solution (mixture of HCl, H₂O₂ dan H₂O) and basic solution (containing NH₄OH, H₂O₂ dan H₂O) for 20 minutes each. Then cleaned glassy carbon was labelled GC.

Prior to immobilization of nanozeolite on GC surface, GC was modified by polyelectrolytes using layer by layer method (LbL), by immersing GC in PDDA and PSS with order PDDA/PSS/PDDA [12]. The immersion time for each layer is 20 minutes, and after each

immersion GC was dried at room temperature. After coated by polyelectrolyte layers, GC was coated by FAU-seed using similar method with variation of 1, 2, and 3 seed layer(s).

Synthesis of Y-nanozeolite on GC surface. Coloidal solution with molar composition: 14Na₂O: Al₂O₃: 10SiO₂: 798H₂O: 3Na₂SO₄ was prepared by dissolving 6.732 grams of aluminum-sulfate-18-hydrate (Al₂(SO₄)₃ >99%) in 30 mL aquademin with vigorous stirring for 30 minutes. The solution then was poured into polypropylene bottle containing 29.001 grams of Nаметasilicate (Na₂SiO₃.9H₂O > 98%) that dissolved in 80 mL of 1.0 M NaOH solution, and stirred for 30 minutes slowly. Then 31.499 mL aquademin was added to this colloidal solution and stirred for 2 hours until the homogeneous solution was produced.

The nanozeolite immobilization process on pretreated GC surface was performed by immersed the GC into the colloidal solution prepared above for 20 hours at 100 °C under hydrothermal condition without stirring. After it was cooled down at room temperature, GC (glassy carbon) was washed with 0.1 M ammonia solution twice, then dried in the oven at 100 °C. The thin film nanozeolite on glassy carbon was characterized by SEM. In order to investigate the bulk of the synthesis solution, the bulk product was purified by sedimentation and redispersion in dilute ammonia solution. The purification step was repeated twice, and the dispersion was air dried at 100 °C. The white powder produced then was characterized by XRD and SEM.

3. Results and Discussion

Synthesis of seeds. XRD result displayed in Figure 1 indicates that the as-synthesized seeds have pattern similar to the pattern of NaY zeolite, based on peaks observed at $2\theta = 5.02$; $2\theta = 16.395$; $2\theta = 23.346$ and $2\theta = 31.04$, which is similar to the pattern reported by Holmberg *et al.* [4]. The huge lump in the range of 15–35 2-theta indicates that the seeds still have some amorphous silica. Characterization with XRF gives Si/Al ratio ≈ 1.78 , which is typical of Si/Al ratio from FAU-type of zeolite (<1-4) [13].

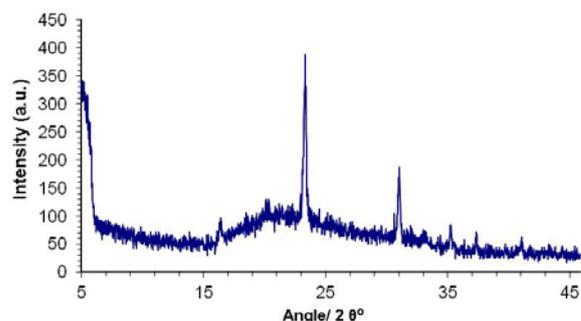


Figure 1. XRD Pattern of As-synthesis NaY Zeolite Seeds

Synthesis of NaY-nanozeolite on GC surface. Prior to immobilization of FAU-seeds on the GC surface, the surface was modified by polyelectrolyte layers using layer by layer (LbL) technique as illustrated by Figure 2.

This technique is required in order to provide positive surface of glassy carbon as a support of zeolite growth. Similar to carbon atoms in graphite, the carbon atoms in GC are networked in one plane with sp^2 orbital hybridization and the plane is connected to other planes (both upper and below) by sharing electron in p orbital [14]. As result, in the very top and the very bottom of carbon planes at GC, the partial charge is negative. Thus, bare GC surface is unlikely to accomodate zeolite seeds and need cationic substrate as charge reversing agent. Similar method was also reported by Valtchev *et al.* [15], in which cationic polymer was used for coating negatively charged polystyrene beads before preparation of nanozeolite thin films. In order to overcome this problem, GC surface was modified by PDDA polycation. Therefore the modified GC surface has positive formal charge and ready to accommodate the FAU-zeolite seeds, because zeolite framework by nature possesses negative formal charge [15]. Besides, the silanol groups (-Si-OH) on the surface of truncated zeolite creates hydrogen bonding with the quartener ammonium from PDDA, so that a strong interaction between zeolite and PDDA occurred. In order to avoid uneven coating of PDDA on the GC surface, after the first PDDA layer applied on the surface, PSS (polyanion electrolyte) then PDDA layer were placed, then the seeds were immobilized on the modified surface. The purpose of this immobilization is to control the growth of zeolite crystal based on the shape and amount of the seeds, as also reported by Lassinati [3].

Variation of seed layer thickness on modified glassy carbon is a focus in this work. Figure 3(a-b) shows SEM images of the as-synthesized NaY zeolite on glassy carbon with one layer of FAU seeds (the result is labelled zGC-1). It can be seen that the zeolite crystals covered most of the surface of modified GC. The crystals shape is cuboid and rather homogeneous for the imaged area. The size of the crystal is approximately

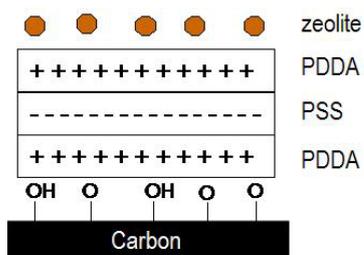


Figure 2. Illustration of Modification of Glassy Carbon (GC) Surface with Polyelectrolytes and Zeolite Seeds [12]

~660 nm. However, intergrowth of crystals occurred, so that some crystals aggregated into one larger shape.

Variation of the number of seed layer applied on the glassy carbon surface seems influencing the zeolite crystal growth. Figure 4(a-b) shows morphology of zeolite crystals on glassy carbon modified by 2 layers of FAU-seeds (labelled as zGC-2), while Figure 5(a-b) is taken from zGC-3, glassy carbon that modified by 3 layer of FAU seeds. In contrast to zGC-1, the zeolites in zGC-2 have larger size than that of zGC-1 (~800 nm). The crystals grew unevenly on zGC-2, and more intergrowth and aggregation of crystals were observed. This could be due to more amount of zeolite crystals grew on the same surface area of GC as in zGC-1, so that the crystals grew on top of each other (intergrowth). When three layers of FAU seeds were applied on the GC surface (zGC-3), severe intergrowth and agregation of zeolite crystals became more visible (Figure 5a), and the particle size is larger dan 1 μ m. Higher magnification on the surface (Figure 5b) shows that besides crystals

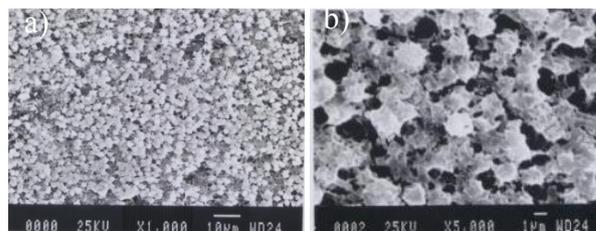


Figure 3. SEM Image of zGC-1: As-prepared NaY Zeolite Using 1 Layer FAU Seed on Modified Glassy Carbon

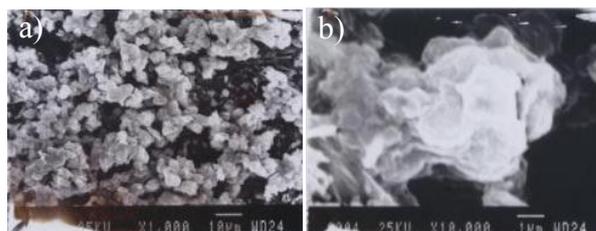


Figure 4. SEM Image of zGC-2: As-prepared NaY Zeolite Using 2 Layers of FAU Seed on Modified Glassy Carbon

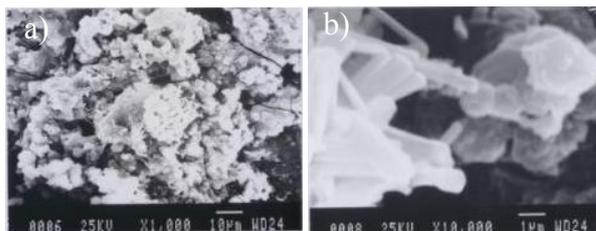


Figure 5. SEM Image of zGC-3: As-prepared NaY Zeolite Using 3 Layers of FAU Seed on Modified Glassy Carbon

with cuboid shape from NaY zeolite, crystals with perpendicular shape are also observed. This indicates that other zeolite type than NaY-zeolite was also produced.

XRD measurement on glassy carbon modified with zeolite thin film (Figure 6) show that the XRD patterns were predominated with peaks from glassy carbon while the patterns from zeolite thin films were not observed. The pattern glassy carbon is similar to patterns from graphite and turbostratic carbon [16], as well as carbon prepared from several aerosol gelation as reported by Dhaubhadel *et al.* [17]. This could be due to the film thickness was not adequate to produce useful x-ray diffraction data. Figure 7 displays the SEM images on cross section of zeolite thin films. It can be seen that the film thickness are 35 μm , 35 μm , and 59 μm for film prepared with 1, 2, and 3 layers of FAU seeds (zGC-1, zGC-2, and zGC-3), respectively.

From this work, it can be seen that adding the amount of seeds to the polyelectrolyte modified glassy carbon using LbL method seems do not result in zeolite growth

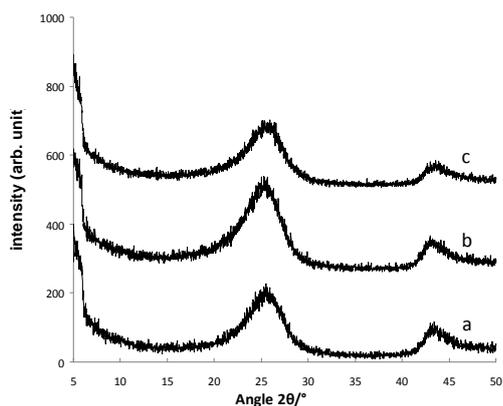


Figure 6. XRD Pattern of Zeolite Modified Glassy Carbon: a) zGC-1, b) zGC-2, and c) zGC-3

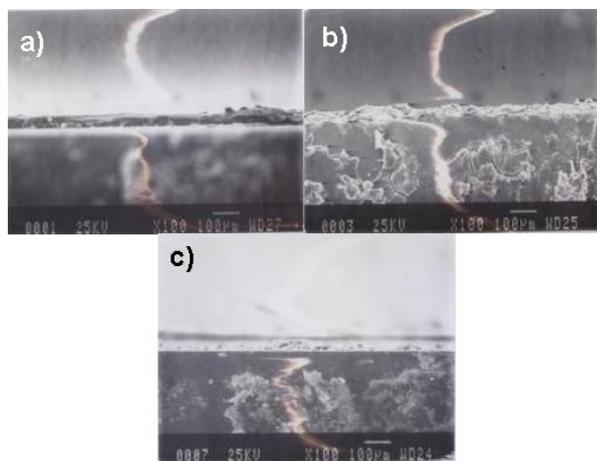


Figure 7. SEM Images: Zeolite Thickness of Zeolite on a) zGC-1, b) zGC-2, and c) zGC-3

in layer by layer assembly. Despite, the seeds were accumulative randomly on GC surface. This somehow is different from the results reported by Valtchev [15]. This could be influenced by difficulties in preparing well spread deposition of FAU seeds on the surface of polyelectrolyte modified glassy carbon.

4. Conclusion

In this research, Faujasite nanozeolite was synthesized through seeding method on polyelectrolyte modified glassy carbon. Optimum condition of this preparation is employing 1 layer of FAU seeds on polyelectrolyte modified glassy carbon under hydrothermal treatment for 20 hours at 100 °C and pH 9, that produced homogeneous structure and size of zeolite ~660 nm.

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