JOURNALOF

Ceramic Processing Research

Effect of interconnected molecular types on the packing rate of self-assembled monolayers of TMA-A zeolite nanocrystals on glass

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Well-shaped high quality TMA-A zeolite nanocrystals were synthesized in a mother solution with a composition of $Al(i-pro)_3$: 2.2 TEOS: 2.4 TMAOH: 0.3 NaOH: 200H₂O at 90 °C for 3 days using a hydrothermal method and self-assembled monolayers coated on glass substrates by different types of covalent linkages. The average size of the zeolites used was 60~100 nm with an average lattice constant of 24.61 Å. The self-assembled monolayers of zeolite oriented with faces parallel to the glass substrates showed only planes of the forms { $h \ 0 \ 0$ } with interconnected molecules. Scanning electron microscopy (SEM) and X-ray powder diffraction (XRD) were used to characterize the synthesized crystals and self-assembly monolayers of TMA-A zeolite with the surface-bound functional groups.

Key words : zeolite, molecular types, self-assembly, packing rate, packing density.

Introduction

High quality zeolite nanocrystals are ordered framework materials with regular cages and channels of subnanometre size of 3-8 Å. Their tailored structure, stability, and activity have led to a broad variety of applications such as a micro reactor for model reaction, chemical sensors, host-guest materials for nanoclusters, and templates for the fabrication of carbon nanotubes (CNTs) [1, 2]. Furthermore, stimulated by the great potential of zeolite monolayers, recently several novel covalent linkers have been devised with which they may be assembled on glass substrates. While efforts to investigate other novel covalent linkers should continue, simultaneously efforts should be also made to achieve spatial organizations of zeolite monolayers on various substrates. This has the potential to provide attractive monolayers of nanoporous crystals with more useful and versatile functional architectural types [3-5]. In general, self-assembly of building blocks in the form of highly-ordered thin films on glass with different covalent linkages is an effective way to organize building blocks into multi-functional entities, and this has been the focus of a major interest during the last several decades [6-8]. Futhermore, the well-defined organization of zeolite nanoparticles into nano- and microstructures has some advantages such as; tailoring of nanostructured materials, to have a surface high concentration, to predict the unique properties, to get a high surface area, and also to have durability of nano particle materials etc. [9, 10]. For this propose, we first synthesized a single phase of TMA-A zeolite nano crystals using a hydrothermal method and self-assembled monolayers coated on glass substrates with different interconnected covalent linkers.

Experimental Procedure

TMA-A zeolite nanocrystals of uniform particle sizes between 60-100 nm were synthesized using a hydrothermal method in a mother solution with a composition of Al(ipro)3 : 2.2 TEOS : 2.4 TMAOH : 0.3 NaOH : 200 H2O at 100 °C for 3 days. The reactant materials used were aluminum isopropoxide Al(i-pro)₃ (Aldrich, 98wt%), tetraethylorthosilicate (TEOS, Aldrich, 98wt%), tetramethylammonium hydroxide (TMAOH, Aldrich, 25wt% in water), and sodium hydroxide (NaOH, Aldrich, 99.99 wt%). The autoclave was removed at predetermined times from the dry oven to arrest the reactions. The crystallized samples were collected and separated by centrifugation. The products were repeatedly dispersed in distilled water using ultra sonication and centrifugation as outlined above to remove the remaining mother solution until the pH of the dispersion was close to 7-8. (3-aminopropyl) triethoxysilane (APS, 99%), 4-diisocyanatobutane (DIC-4, 97%), (3-choropropy) triethoxysilane (CPS, 97%), and fullence (95%) from Aldrich were used as covalent linkages for the self assembly monolayers between the zeolite and glass substrates. These functional groups were distilled and kept in a Schlenk storage flask under argon. The samples were obtained by drying at 80 °C for 4 h. The zeolite nonocrystals and self-assembled monolayers with

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glass surface via different covalent linkages were characterized by XRD (Model RAD-2B, Rigaku Co.) with CuK α radiation and scanning electron microscopy (SEM, XL-30, FEG).

Surface treatment of cover glass for the tethering functional groups.

Cover glasses $(18 \times 18 \text{ mm}^2)$ were purchased from Marienfeld and treated in a piranha solution (H₂SO₄: 30% H₂O₂ = 3:1) at 95-100 °C for 1h to remove organic residues on the surface. The acid-treated glasses were washed with distilled water and dried at 120 °C for 30 minutes before undergoing tethering steps with (3aminopropyl) triethoxysilane (APS, 99%), 4-diisocyanatobutane (DIC-4, 97%), (3-choropropy) triethoxysilane (CPS, 97%), and Fullence (95%) as novel molecular binders. For this purpose, we prepared a glass incubation chamber consisting of a flat-bottomed cylinder (diameter = 20 cm, height = 20 cm) and a top lid (height = 3 cm) attached with a greaseless stopcock. The chamber was evacuated to 0.133 µPa for 30 minutes at room temperature. The chamber was subsequently transferred into an oven whose temperature was maintained at 100 °C and kept there for 15 minutes. After being cooled to room temperature, the glass plates with tethering covalent groups were removed from the chamber and washed with copious amounts of ethanol and finally with distilled water. The water-washed glass plates were dried by blowing them using a soft stream of N₂ gas. The dried glass plates were kept for 30 minutes in an oven at 110 °C.

Tethering APS groups to the TMA-A zeolite surface

To prepare the APS-tethered TMA-A zeolite, toluene (50 ml) was introduced into a Schlenk flask containing TMA-A zeolite nanocrystals under N_2 gas, and the mixture was sonicated for 10 minutes in an ultrasonic cleaner to evenly disperse zeolite particles in the toluene. APS (0.5 ml) was injected into the toluene slurry under the counter flow of N_2 gas, and the heterogeneous mixture was refluxed at 100 °C for 1 h under N_2 gas. After cooling to room temperature, the APS-tethered zeolite crystals were collected by rapid filtration in an atmosphere over filter paper. The filter papers were wetted with toluene prior to filtration. The collected powders were successively washed with fresh toluene (100 ml) and ethanol (100 ml). The collected powders were dried at 110 °C for 30 minutes in an dry oven.

Reaction of APS-coated zeolites with APS - fullerene - APS tethered glass

To prepare the glass plates assembled with zeolite monolayers with APS-fullerene-APS as the linkers between the zeolite and glass, dry toluene (50 ml) was introduced into a Schlenk flask containing TMA-A zeolite crystals tethered by APS under N_2 gas and the heterogeneous mixture was sonicated for 10 minutes in an ultrasonic cleaner to disperse the zeolite particles evenly in the

toluene. However, the APS groups on the glass can not directly connected with OH groups of zeolite crystals in toluene according to Fig. 2(a). We then anchored fullerene groups between the surface of APS-tethered zeolite crystals and APS-tethered glass as shown Fig. 3(a), since APS groups of on the surface of zeolite and on the APS-tethered glass can be bound together through the interconnected fullerene molecular linkages as shown in Fig. 3(b).

Reaction of zeolites with DIC-4 and CPS-tethered glass

To prepare the glass plates assembled with zeolite monolayers with DIC-4 and CPS as the linkers, firstly dry toluene (50 ml) was introduced into a Schlenk flask containing TMA-A zeolite crystals under N2 gas and the mixture was refluxed under N2 gas for DIC-4 at 110 °C for 2 h and for CPS at 110 °C/3 h, respectively. The heterogeneous mixture was sonicated also for 10 minutes in an ultrasonic cleaner to well disperse the zeolite particles evenly in the toluence. Secondly, the DIC-4 and CPS tethered glass plates were introduced into a Schlenk flask containing the well-dispersed zeolite crystals in the toluene solution and then sonicated for 10 minutes in an ultrasonic cleaner to assemble the monolayer coatings. DIC-4 and CPS groups bound to the glass surface directly react with surface hydroxyl groups of zeolite crystals according to Fig. 4(a) and Fig. 5(a), respectively. The assembled zeolite powders on the glass were successively washed with fresh toulence (100 ml) and ethanol (100 ml) and dried at 120 °C for 30 minutes in an dry oven.

Results and Discussion

The crystal morphology of the TMA-A zeolite shows that a cube is comprised of well-controlled crystals between 60 and 100 nm in size in a configuration with six planes, as shown in Fig. 1. The cube {001} is composed of six perfect square faces with 90° angles. The XRD results of this morphology showed only the TMA-A zeolite phase, $2\theta = 7^{\circ}$ (200), 10° (220), and 24° (600), single phase which has an average lattice constant of 24.61 Å with a



Fig. 1. XRD-pattern of TMA-A zeolite synthesized by a hydrothermal method and SEM image of TMA-A zeolite nanocrystals.

Effect of interconnected molecular types on the packing rate of self-assembled monolayers of TMA-A zeolite nanocrystals on glass

SiO₂/Al₂O₃ molar ratio of 1.6~2.0, as determined by XRD and XRF, respectively. In general, the framework of TMA-A zeolite crystals can be described in terms of two types of polyhedra ; one is a simple cubic arrangement of eight tetrahedra, the D4R; the other is a truncated octahedron of 24 tetrahedra or cages as previously described for the sodalite-type minerals. The cages are interconnected in a simple cubic structure by sharing windows of 4 Å diameter. The center distance between two neighboring supercages is 12.389 Å [11].

Typical scanning electron microscope (SEM) images of the TMA-A zeolite monolayers assembled on the glass plates with APS, APS-fullerene-APS, DIC-4, and CPS as the linker are shown in Fig. 2(b), 3(b), 4(b), and 5(b), respectively. All of the TMA-A zeolite crystals assembled on the glass plates by four different type linkages are oriented with a face parallel to the glass surface and appeared similar in SEM images in terms of their orientation, coverage, and close packing characteristics with increasing reaction time. SEM images of monolayers prepared by APS for 7 h and APS-fullerene-APS for 9h revealed the presence of large empty spots within them as shown in Fig. 2(b) and 3(b), respectively. In contrast, most of the zeolite crystals in the monolayer prepared by DIC-4 for 3 h and CPS for 1 h were very tightly closely-packed as shown in Fig. 4(b) and 5(b). Accordingly, the XRD patterns of the TMA-A zeolite-bound glass plates by CPS group showed only five $(h \ 0 \ 0)$ lines at



Fig. 2. APS group mounted on the top of the glass substrates via siloxane linkages (a) and assembly of a monolayer of TMA-A zeolite as a function of the reaction time (b).



305

Fig. 3. APS-fullerene-APS group mounted on the top of the glass substrates via siloxane linkages (a) and assembly of a monolayer of TMA-A zeolite as a function of the reaction time (b).



Fig. 4. DIC-4 group mounted on the top of the glass substrates via covalent linkages (a) and assembly of a monolayer of TMA-A zeolite by DIC-4 as a function of the reaction time (b).



Fig. 5. (3-Choropropyl) trimethoxysilane (CPS) group mounted on the top of the glass substrates via silane linkages (a) and assembly of a monolayer of TMA-A zeolite by CPS as a function of the reaction time.

(200), (600), (800), (1000) and (1200) as shown in Fig. 6.

As there are no established methods at this point for measuring the packing rate between the zeolite crystals and substrates, the packing rates were measured directly via the coating area of zeolite on the glass substrates as a function of the reaction time. To obtain monolayer assembly of the nanocrystals on glass substrates typically required a reaction time for achieving close to 100% degree of close packing of the substrate surface with crystals. Fig. 7 shows the plots of the packing rate as a function of the reaction time. The packing rate as a function of the reaction time. The packing rate with APS reached about 60% during the initial 3 h and then slowly increased to 95% for APS and 60% for APS-fullerene during the next 6 h but it took only 2 h for the degree of close packing to reach 100% with CPS and 60% with DIC-4, respectively.

In general, the binding strength of TMA-A crystals to glass substrates, which is expressed by the surviving amount of crystals after sonication of TMA-A zeolite attched glass plates in toluene for 60 minutes with respect to the initially attched amount, varied in accordance with the variation of the degree of coverage. The progressive loss of zeolite crystals from the glass plates as the sonication time increased was monitored by directly weighing the plates on a micro-balance. For each type of linkage, five samples were run separately, and the average weight loss was plotted against the sonication time. Fig. 8 shows three distinct profiles of weight loss that resulted from the three different glass-bound zeolite monolayers.



Fig. 6. X-ray patterns of assembled-monolayer zeolite using CPS as the linkager.



Fig. 7. The profiles of the packing rate of the monolayers of zeolite crystals assembled on glass plates by four different types of linkages as a function of the reaction time.



Fig. 8. The profiles of the sonication-induced weight loss of the monolayers of zeolite crystals assembled on glass plates by four different types of linkages.

For zeolite monolayers assembled with a direct APS linkage, nearly 75% of the zeolite crystals fell off the glass plates during the initial 5 minutes sonication.

In strong contrast, only 10% and 5% losses were observed from the monolayers assembled with DIC-4 and CPS, respectively. It is interesting to note that, even for the direct CPS linkage, approximately 85% of the zeolite crystals endured the initial 20 minutes of sonication and approximately 75% survived after 60 minutes of sonication. The corresponding amount of survival zeolite crystals after 60 minutes of sonication were approximately 70% and 65% for DIC-4 and APS-fullerene-APS as the linkers, respectively.

The detachment of the zeolite crystals started from the outermost edges and particularly from the four corners of the glass plates that were in contact with the round vials. Such a phenomenon appears to arise due to transmission of stronger vibrations from the vials to the glass plates through the corners. The zeolite-free, empty area progressively expanded toward the center of the glass plates.

Conclusions

All of the TMA-A zeolite crystals assembled on the glass plate by four different type linkages were oriented with a face parallel to the glass surface and appeared similar from the SEM images in terms of their orientation, coverage, and close packing characteristics with increasing reaction time. The XRD patterns of the TMA-A zeolite-bound glass plates by CPS group showed only five ($h \ 0 \ 0$) lines at (200), (600), (800), (1000) and (1200). The CPS and DIC-4-tethering zeolite crystals showed a tendency to pack closely to reach 100% for CPS and 70% for DIC-4 during the initial 2 h. The amount of survival zeolite crystals assembled on the glass after 60 minutes of sonication were approximately 70% with DIC-4 and 65% with APS-fullerene-APS as the linkers, respectively.

Acknowledgement

This research was supported by a grant from the 2009 Fundamental R&D Program of Hanseo University, the Korea-Romania Foundation for International Cooperation of Science & Technology(KICOS) through a grant provided by the Korean Ministry of Education, Science & Technology(MEST), and a grant from the Fundamental R&D Program for Core Technology of Materials funded by the Ministry of Knowledge Economy, Republic of Korea.

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