

Orientation-controlled self-assembled monolayers of zeolite nanocrystals on glass with 4-diisocyanates as covalent linkers

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High-quality TMA-A zeolite nanocrystals were synthesized using a hydrothermal method from a $\text{Al}(\text{i-pro})_3 : 2.2 \text{ TEOS} : 2.4 \text{ TMAOH} : 0.3 \text{ NaOH} : 200\text{H}_2\text{O}$ composition. The average size of the zeolite crystal used was 60-130 nm with a lattice constant of 12.389 Å. The well-oriented self-assembled monolayers of zeolite with a face parallel to the glass surface treated with the 4-diisocyanates (DIC-4) showed only planes of the form of $\{h\ 0\ 0\}$ by covalent linkages. High resolution transmission electron microscopy (HRTEM), scanning electron microscopy (SEM), X-ray powder diffraction (XRD), and dynamic light scattering (DLS) were used to characterize the self-assembled monolayers of synthesized zeolite crystals.

Key words: Zeolite, Nanocrystals, Self-assembly, Covalent linkage, Orientation, 4-diisocyanate.

Introduction

The synthesis of perfect crystalline zeolite nanocrystals and the organization of these crystals into uniformly orientated monolayers on glass is just a beginning towards nanostructured materials. In a next step, these nanoparticle building blocks need to be arranged into well-defined ensembles and superstructures to give novel and unique properties that are not found in the individual components [1, 2]. One of the most important key factors to the success in the application of zeolite as an advanced material is for the organization of its nanocrystals in a uniform orientation by the use of a self-assembly processes. The organization is determined by the interactions among the primary building blocks, and there is no doubt that adequately tailored surface properties are the fundamental parameter in the design of novel nanobuilding blocks [3, 4].

In general, the well-defined organization of zeolite nanoparticles into nano- and mesostructures has some advantages such as; tailoring for nanostructured materials, giving a surface high concentration, being able to predict the unique properties, to get a high surface area, and also to have durability of nano particle materials etc. [5-7]. Well-shaped high quality zeolite crystals are ordered framework materials with regular cages and channels of sub-nano sizes of 3-8 Å. Their tailored structure, stability, and activity have led to a broad variety of applications such as a micro reactor for a model reaction, chemical sensors, bio-membranes, host-guest materials for nanoclusters, and templates for the fabrication of

carbon nanotubes (CNTs) [8, 9]. Furthermore, stimulated by the great potential of zeolite monolayers recently several novel covalent linkers have been devised with which to assemble them on glass substrates. While efforts to explore other novel covalent linkers should continue, simultaneous efforts should also be made to achieve the spatial organization of the zeolite monolayers on various substrates. This has the potential to provide the attractive monolayers of microporous crystals with more useful and versatile functional architectural types [10-13].

For this propose, we first synthesized a single phase of TMA-A zeolite nanocrystals using a hydrothermal method and a self-assembly monolayer coated onto glass substrates with the 4-diisocyanates (DIC-4) as covalent linkers.

Experimental Procedure

TMA-A zeolite nanocrystals of uniform particle sizes between 60-130 nm were synthesized using a hydrothermal method in a mother solution with a composition of $\text{Al}(\text{i-pro})_3 : 2.2 \text{ TEOS} : 2.4 \text{ TMAOH} : 0.3 \text{ NaOH} : 200\text{H}_2\text{O}$ at 100 °C for three days. The reactant materials used were aluminum isopropoxide $\text{Al}(\text{i-pro})_3$ (Aldrich, 98 wt%), tetraethylorthosilicate (TEOS, Aldrich, 98 wt%), tetramethylammonium hydroxide (TMAOH, Aldrich, 25 wt% in water), and sodium hydroxide (NaOH, Aldrich, 99.99wt%). The autoclave was removed at predetermined times from the 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. 4-disocyanates (DIC-4, 97%, Aldrich) was used as novel molecular binders for the self assembly

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monolayers between zeolite and glass substrates. This organic was distilled and kept in a Schlenk storage flask under argon. The samples were obtained by drying at 80 °C for 4 h. The synthesized crystals, and monolayer coated samples were characterized by XRD (Model RAD-2B, Rigaku Co.) with CuK α radiation, high-resolution transmission electron microscopy (HRTEM, Tecnai G2, STEM), and dynamic light scattering (DLS).

Surface treatment of cover glass

Cover glasses (18 × 18 mm²) were purchased from Marienfeld and treated in a piranha solution (H₂SO₄ : 30% H₂O₂ = 3 : 1) at 95–100 °C for 1 h 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 4-diisocyanates (DIC-4) as novel molecular binders. For tethering DIC-4 groups to the glass surface, DIC-4 (0.5 ml) was injected into the toluene slurry using a hypodermic syringe with acid under a counter flow of N₂ gas and the mixture was refluxed for 1 h under N₂ gas at 110 °C/3 h. 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 133.3 μ Pa 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 DIC-4 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.

Assembly of TMA-A zeolite monolayer

The zeolites were washed with copious amount of water

until the wash solution was neutral. Centrifugation was necessary to separate the fine powders of zeolite from the aqueous slurry. The collected powders were successively washed with fresh toluene (100 ml) and ethanol (100 ml), and dried for 30 minutes in an oven at 120 °C before assembly on the glass. To prepare the glass plates assembled with the zeolite monolayer with DIC-4 as the linkers, firstly dry toluene (50 ml) was introduced into a Schlenk flask containing TMA-A zeolite crystals under N₂ gas and the heterogeneous mixture was sonicated for 10 minutes in an ultrasonic cleaner to well disperse the zeolite particles evenly in the toluence. Secondly, the DIC-4 tethered glass plates were introduced into a Schlenk flask containing well-dispersed zeolite powders in a toluene solution and then sonicated for 10 minutes in an ultrasonic cleaner to assembly monolayer coatings. DIC-4 groups bound to the glass surface readily react with surface hydroxyl groups of zeolite crystals according to Fig. 1.

Subsequently tethered DIC-4 groups on the glass with dispersed zeolite crystals in the toluene solution led to easy assembled monolayers of zeolite crystals. The assembled zeolite powders on the glass were successively washed with fresh toluence (100 ml) and ethanol (100 ml) and dried for 30 minutes in an oven at 120 °C.

Results and Discussion

The morphology of TMA-A zeolite crystals from a TEM images shows that they are comprised of well-controlled nanocrystals about 60–130 nm in size in a configuration having six planes, as shown in Fig. 2(a). The images show both high crystallinity and perfect crystal morphology. The particle size distribution can be estimated from the low-magnification image and is further characterized by DLS as shown in Fig. 2(b). The DLS measurement of TMA-A zeolite shows two different maxima at 100 °C and 60 nm in the size distribution, which is in agreement

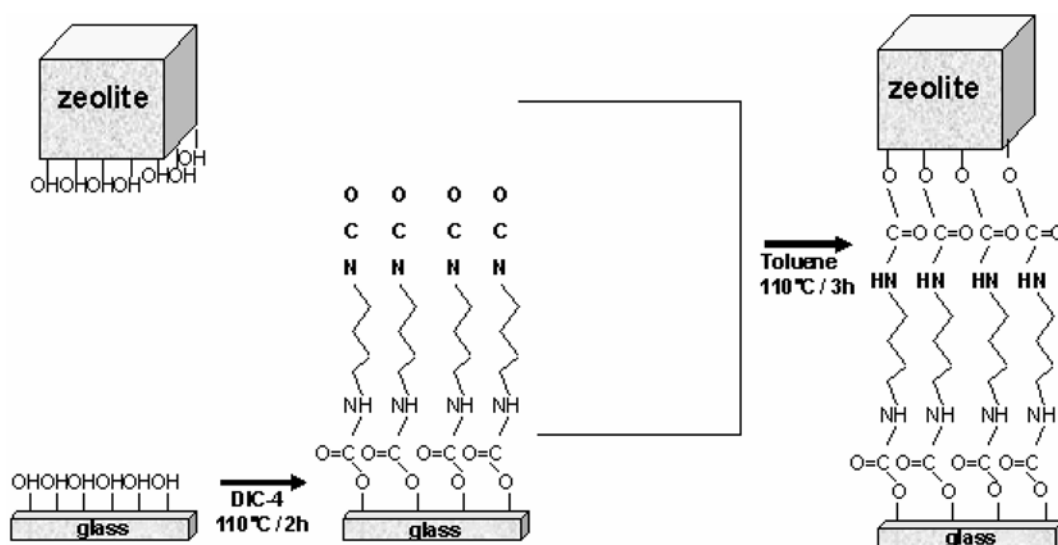


Fig. 1. Diisocyanates (DIC-4) group mounted on the top of the glass substrates via silane linkages.

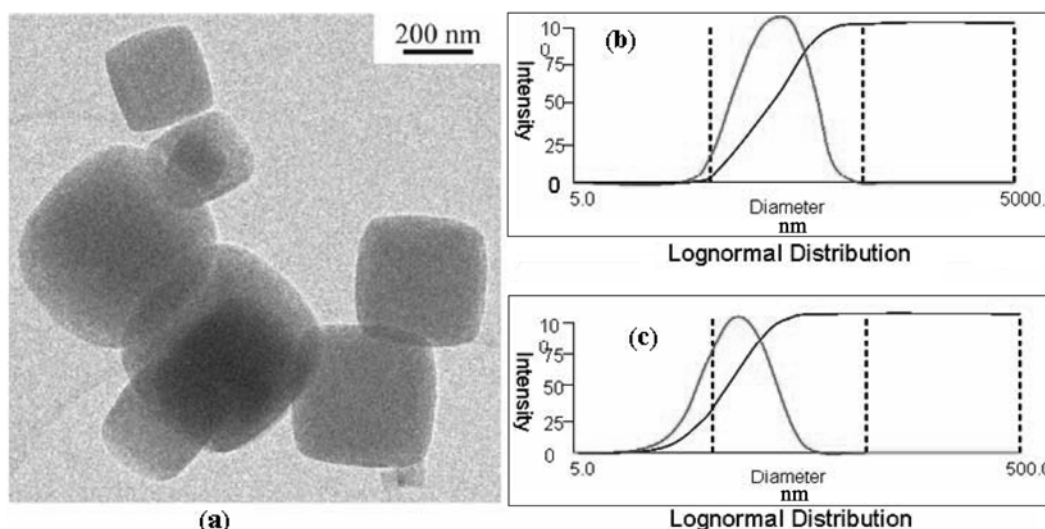


Fig. 2. TEM image of TMA-A zeolite nanocrystals (a), particle size distribution of TMA-A zeolite nanocrystals collected by centrifugation with a relative centrifugal speed (rpm) of 3,000 (b), and 5,000 (c), respectively from DLS measurements.

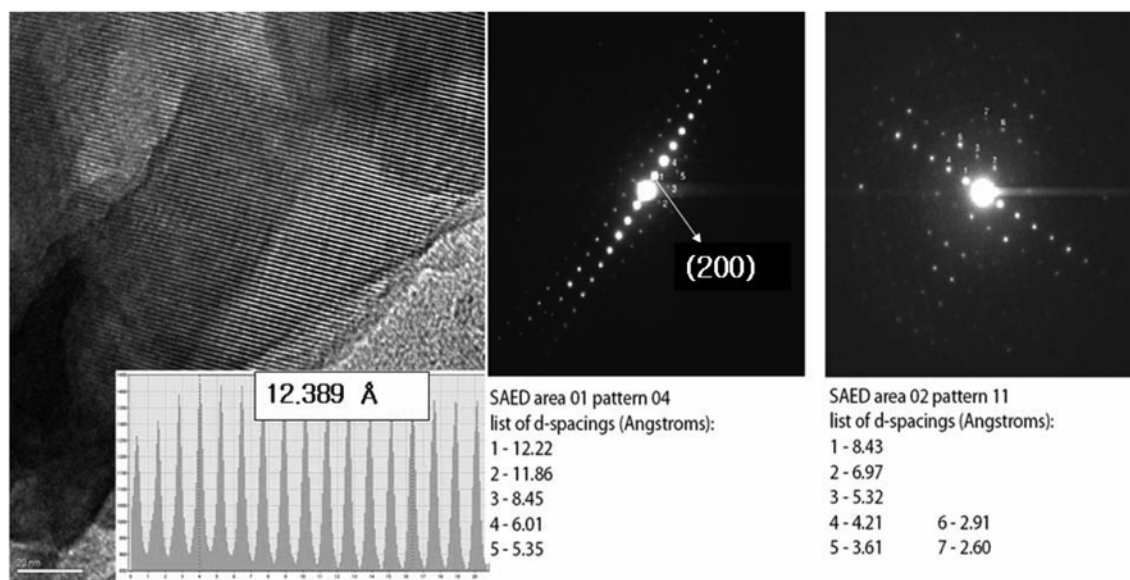


Fig. 3. HRTEM image of a zeolite particles (a) and d-spacing patterns (b).

with the TEM observation as shown in Fig. 2(b). This bimodal size distribution potentially reflects different nucleation process [12, 13]. The resulting crystals of 130 nm and 60 nm sizes were collected and separated by centrifugation with a relative centrifugal speed (rpm) of 3,000 and 5,000, respectively.

Fig. 3 shows an HRTEM image of a nanocrystal of the TMA-A zeolite. The image shows a high degree of structural order and a perfect crystal morphology. It is clear from the low-magnification image that the crystals with an experimental lattice constant of 12.389 Å which have a typical round cubic form with a difference in edge size of approximately 60 or 130 nm as shown in Fig. 2(a) and (b), respectively. In general, the framework of TMA-A zeolite can be described in terms of two types of polyhedra; one has a simple cubic arrangement of eight tetrahedra

and is termed D4R, and the other is a truncated octahedron of 24 tetrahedra or cages as previously described for the sodalite-type (β -cage) minerals. The TMA-A zeolite is generated by placing the cubic D4R units in the center of the edges of a cube [14]. These well-shaped zeolite crystals are excellent host materials having the ordered framework structure with regular supercages (α -cage) and channels of sub-nano size (4Å) for the encapsulation of (1-10 nm) particles [5, 6].

Typical scanning electron microscope (SEM) images of the TMA-A zeolite monolayers assembled on glass plates with DIC-4 as the linker are shown in Fig. 4. All of the TMA-A zeolite crystals are oriented with a face parallel to the glass surface. Accordingly, the XRD patterns of the TMA-A zeolite-bound glass plates showed only five ($h\ 0\ 0$) lines at (200), (600), (800), (1000) and (1200)

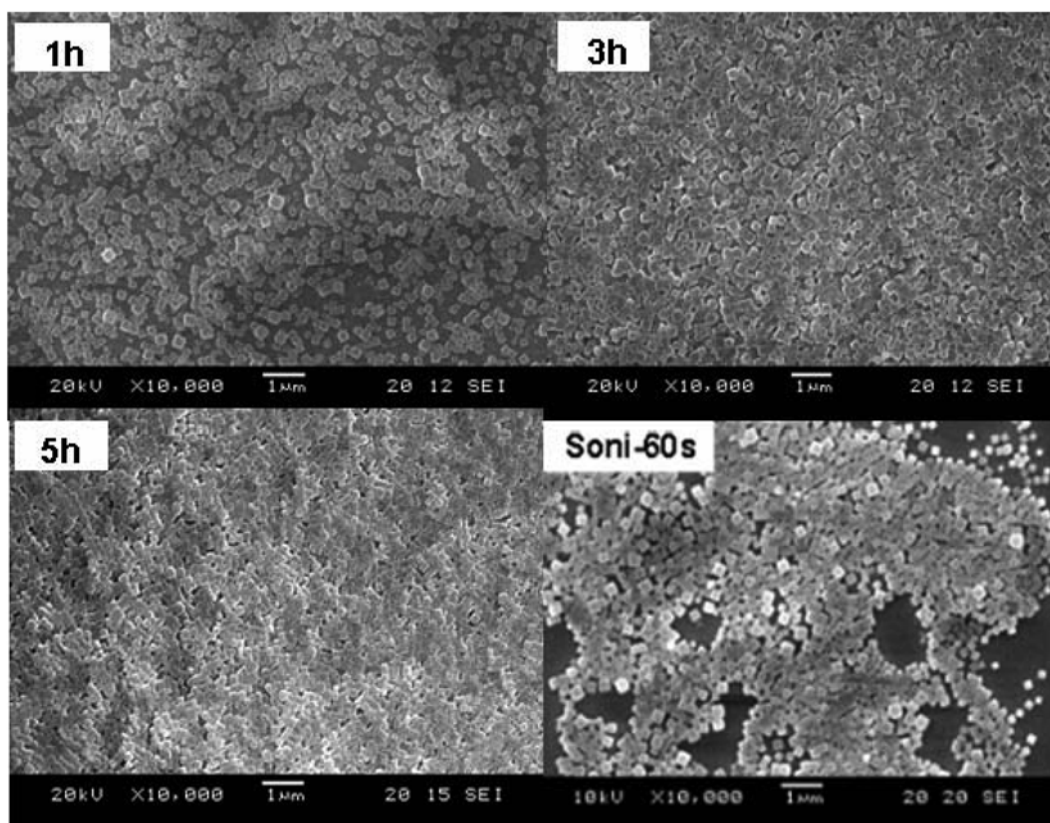


Fig. 4. SEM images of assembled monolayers of TMA-A Zeolite by DIC-4 as a function of reaction time and after sonication for 1 minute.

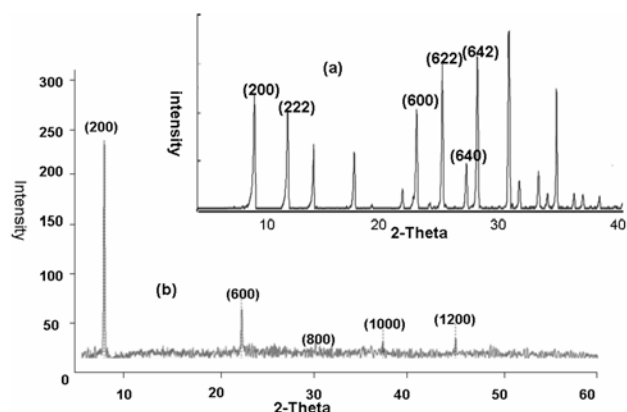


Fig. 5. X-ray patterns of TMA-A zeolite synthesized by a hydrothermal method (a) and well-oriented self assembled monolayer of zeolite with DIC-4 as covalent linkage (b).

as shown in Fig. 5(b). As there are no established methods at this point for measuring the packing degree and the strength of the binding between the zeolite crystals and substrates, the packing degree was measured directly via the coating area of zeolite on the glass substrates as a function of the reaction time. As shown in Fig. 4, the zeolite crystals coated on the glass plates with DIC-4 linkage was survived approximately 70% after 1 minutes of sonication. An ultrasonic cleaning bath was used as a qualitative device to compare the strengths of the bindings. Interestingly, the DIC-4 tethered zeolite crystals showed a

tendency to pack closely despite the fact that the surface-lining groups are incapable of hydrogen bonding [11].

The diffraction patterns of $(h\ 0\ 0)$ planes with $h = 2, 4, 6, 8, 10,$ and 12 are likely to arise from the twined crystals protruding from the parent TMA-A zeolite crystals with the a -axis perpendicular to a - c plane of the parent crystals. The appearance of the $(h\ 0\ 0)$ diffraction patterns from the monolayers, was not apparent from the synthesized zeolite powders as shown in Fig. 5(a).

Interestingly, the glass substrates modified with the DIC-4 monolayer have been shown to give rise to highly-oriented crystals of TMA-A zeolite with a family of $\{200\}$ planes. This phenomenon of close packing between the assembled TMA-A zeolite crystals is attributed to the surface migration of the weakly bound crystals [7]. These well-oriented nanoporous zeolite films will be useful for display devices for the next generation to provide ideal media for the organization of semiconductor quantum dots necessary to develop novel optoelectronic and magnetic materials.

Conclusions

The crystal morphology of TMA-A zeolite shows that a cube is comprised of well-controlled single phase nano-crystals between 60 and 130 nm in size in a configuration having six square planes and an average lattice constant of 12.389 Å. All of the TMA-A zeolite crystals are well

oriented with a face parallel to the glass surface. Accordingly, the XRD patterns of a monolayer of TMA-A zeolite bound glass plate showed only five (*h* 0 0) lines with (200), (600), (800), (1000) and (1200).

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