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Orientation-Controlled Monolayer Assembly of Zeolite Crystals on Glass Using Terephthaldicarboxaldehyde as a Covalent Linker

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Abstract—Glass plates and pseudo hexagonal prismatic ZSM-5 crystals tethered with 3-aminopropylsilyl (APS) groups, respectively, were prepared by treating them with 3-aminopropyltriethoxysilane. Subsequent treatment of the APS-tethering glass plates with terephthaldicarboxaldehyde led to facile assembly of benzaldehyde (BA) units over the glass plates via imine (–CH=N–) linkages. When the BA-tethering glass plates and the APS-tethering zeolite crystals were allowed to contact in boiling toluene, the ZSM-5 crystals strongly adhered onto the glass plates in the form of closely packed monolayers with perfect one-dimensional orientation. © 2000 Elsevier Science Ltd. All rights reserved.

Introduction

Assembly of small molecules in the form of thin films on various substrates or organization of small molecules into highly ordered arrays of molecules on various supports has been the focus of intense interest during the last three decades as the ability to do so has many implications in material science and in the development of new electronic and opto-electronic devices.[1,2] Scrutiny of the general trend reveals that the sizes of building blocks (molecules) have gradually increased from relatively small molecules to very large ones. Extrapolation of the above trend predicts that they will soon reach several micrometers. Under such circumstances, various systems of molecules such as micrometer-sized crystals and living cells rather than single molecules will more routinely be employed as the basic building blocks.[3]

In an effort to explore '*the chemistry of large building blocks*', we recently demonstrated that zeolite crystals can be readily assembled in the form of highly oriented monolayers over glass and mica via several different types of covalent linkages between each zeolite crystal and the substrate.[4] The use of zeolite crystals as the prototypical well-defined inorganic crystals has many advantages in various respects. First, they have a great potential to be used as organizing media for semiconductor quantum dots for their future application as the novel opto-electronic materials.[5] Second, they can effectively serve as well-defined nanoreactors ideal for exploration of novel photo- and the related fine chemistry under the highly confined and organized environments.[6] Furthermore, the assembled monolayers of zeolite crystals can readily be developed into hosts for sensors and membranes for size-selective separations.[7] In this regard, continuous efforts should be made to explore various other novel methodologies for effective assembly of zeolite crystals. In particular, development of various novel covalent linkers is important in the respects that the strength of the crystal-substrate binding, the orientation of the crystals, the degree of intercrystalline packing between the crystals, and the future application of the surface-bound crystals for various purposes will sensitively depend on the nature of the interconnecting 'molecular linkers'. Herein we introduce a novel method to assemble zeolite crystals over the glass substrate using terephthaldicarboxaldehyde (TPDA) as the covalent linker between the terminal amino groups independently tethered to zeolite and glass substrate.

Results and Discussion

Pseudo hexagonal prismatic ZSM-5 crystals (average size of $\sim 2.0\times 1.5\times 0.8$ μm) were synthesized according to the well-known procedure.[8] The tetrapropylammonium ion used for a template for zeolite synthesis was not removed prior to assembly. The dried zeolites were treated with 3-aminopropyltriethoxysilane (APTES) in boiling toluene for 1 h (Scheme 1, step A). The presence of 3-aminopropylsilyl (APS) groups over the zeolite surfaces was confirmed by ninhydrin (pale yellow) which is known to transform into Ruhemann's Purple (diketohydrindylidenediketohydrindamine) in the presence of amines.[9] Thus, when ninhydrin was refluxed with the APTES-treated ZSM-5 crystals in ethanol, the solution turned purple and the UV–Vis

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Keywords: monolayer assembly; ZSM-5; terephthaldicarboxaldehyde; 3-aminopropyltriethoxysilane.

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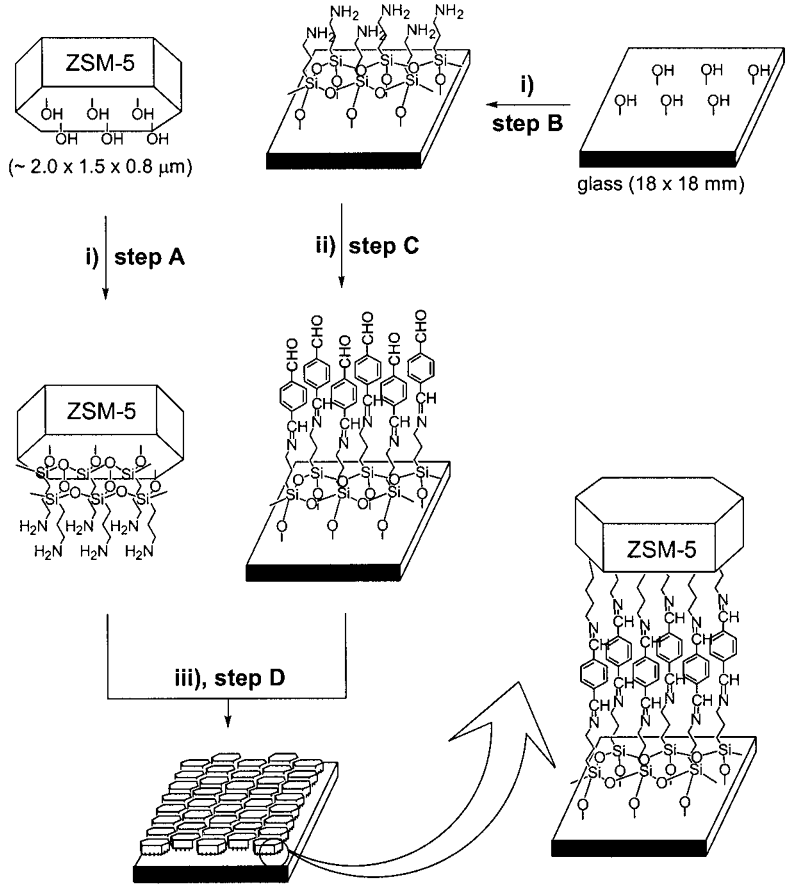

Scheme 1. (i) APTES, $PhCH_3$, 110°C, 1 h; (ii) TPDA, AcOH, $PhCH_3$, 110°C, 3 h; (iii) $PhCH_3$, 110°C, 4 h.

spectrum of the supernatant solution revealed the characteristic bands of Ruhemann's Purple at 405 and 570 nm.[9]

The APS-tethering glass plates (18×18 mm) were prepared (Scheme 1, step B) and characterized similarly. Subsequent treatment of the APS-tethering glass plates with TPDA led to facile assembly of benzaldehyde BA units over the APS groups via imine (–CH=N–) formation between one of the two formyl groups of TPDA and the terminal amino unit of the APS group. Typically, the toluene solution of TPDA was refluxed for 3 h in the presence of APS-tethering glass plates (Scheme 1, step C). The presence of BA units over the glass plate was confirmed spectrophotometrically. A fused silica plate (optical grade) was used for this purpose since it is optically transparent even in the UV region. Thus, as shown by the solid curve (a) in Fig. 1, the TPDA-treated APS-tethering fused silica plate revealed an absorption band with the maximum (λ_{max}) at 276 nm. This spectrum is distinctively different from that of TPDA which has two well resolved bands at 261 and 300 nm with a shoulder band at 270 nm as shown in the inset. The new absorption band of the fused silica plate more resembles that of 4-(*t*-butyliminomethyl)-benzaldehyde[10] (λ_{max}=271 nm) represented by the dashed curve (b) in Fig. 1 in the respect that the 300-nm band is nearly absent. It is also important to note that the fused silica plate covered with only APS units does not show any absorption in the spectral range (c). Accordingly, the 276-nm band is attributed to the absorption of the 4-(propyliminomethyl)-benzaldehyde moieties tethered onto the surface of the silica plate via siloxane bridges. To suppress the possible consecutive reaction of TPDA with two surface-bound APS groups we used large excess of TPDA during the reaction with the APS-covered glass plates.

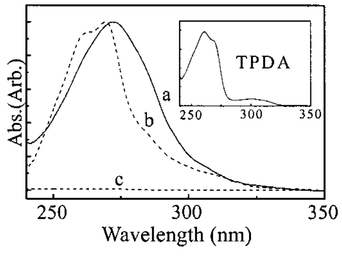

Figure 1. UV–Vis spectra of the APS-tethering fused silica plate treated with TPDA (a), 4-(*t*-butyliminomethyl)-benzaldehyde in chloroform (b), and APS-tethering fused silica plate (c). The inset shows the spectrum of TPDA in chloroform.

The glass plates remained transparent even after assembling monolayers of BA units on the surfaces. However, they turned opaque when allowed to contact with the APS-covered ZSM-5 crystals in boiling toluene (Scheme 1, step D). The scanning electron microscope (SEM) images of the opaque glass plates taken after sonication for 1 min in toluene revealed that the ZSM-5 crystals bind to the surface in the form of a monolayer as typically shown in Fig. 2A. The degree of close packing (or coverage) was nearly the

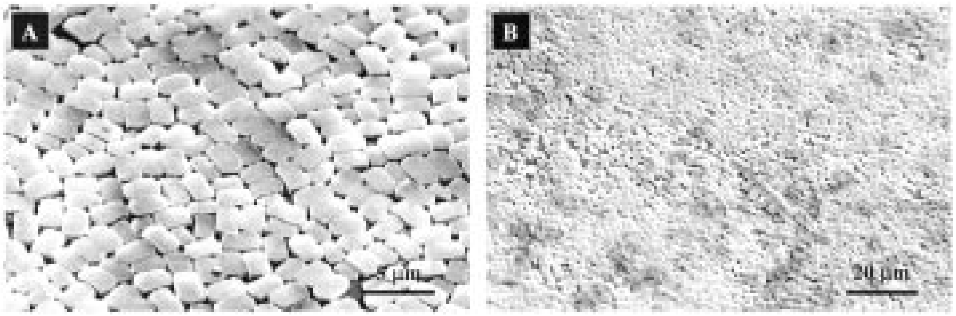

Figure 2. SEM images showing the monolayer of ZSM-5 crystals bound to a glass plate at two different magnifications.

same over the entire glass plates as can be seen at a lower magnification (Fig. 2B). Most of the crystals remained 'glued' onto the glass substrate even after prolonged sonication for 10 min. In strong contrast, omission of either the step A or C in Scheme 1 led only to assembly of very weakly bound (physisorbed) ZSM-5 crystals that readily fell off even after brief (<5 s) sonication. Based on the above two sets of contrasting results, we conclude that a new imine (–CH=N–) linkage is readily formed between the glass-bound BA unit and the terminal amino unit of the APS groups tethered to ZSM-5. Furthermore, from the very strong binding of the zeolite crystals onto the glass substrates, it can be inferred that the number of covalent linkage or 'molecular glue' between each crystal and the glass substrate is high enough to endure the weight of the crystal even under the severely vibrating conditions.

Scrutiny of the SEM images further revealed that all of the ZSM-5 crystals tend to pack very closely over the glass plates. We attribute such a remarkable tendency to a large number of hydrogen bonding that prevails between the zeolite-bound terminal amino groups. The SEM images further revealed that all the ZSM-5 crystals assemble over the surface with each b axis normal to the surface of the glass plate. Consistent with the SEM images, the X-ray diffraction pattern of the glass-bound zeolite crystals revealed only the specific reflections that correspond to (0 2 0), (0 4 0), (0 6 0), (0 8 0), and (0 10 0) planes at 2θ=8.9, 17.8, 26.8, 36.0, and 45.5°, respectively, as typically shown in Fig. 3.

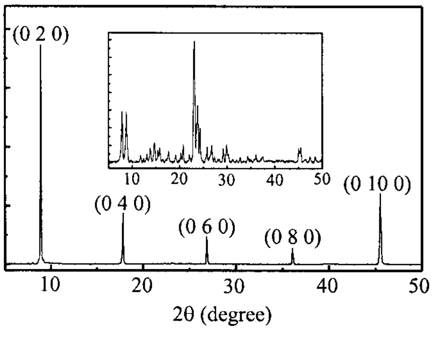

Figure 3. X-Ray diffraction pattern of a ZSM-5 monolayer assembled over a glass substrate showing the unidirectional alignment of the crystals. The corresponding pattern of the randomly oriented powders is shown in the inset for comparison.

Conclusion

This paper demonstrates a novel method to assemble one-dimensionally oriented monolayers of zeolite (ZSM-5) crystals over the glass substrates via a large number of diimine covalent linkages. We believe the methodology introduced in this paper will serve as an experimental basis for the conceptual development of '*the chemistry of crystal assembly*' necessary to understand the natural biomineralization and to develop the ceramic material science.

Experimental

Materials

Pseudo hexagonal prismatic ZSM-5 crystals (average size of ~2.0×1.5×0.8 μm) were synthesized according to the well-known procedure.[8] The zeolites were washed with copious amounts of water until the wash was neutral. The template ion (tetrapropylammonium) used for zeolite synthesis was not removed prior to assembly. Cover glasses (18×18 mm) were purchased from Marienfeld and dipped into an acid bath consists of piranha solution (H_2SO_4: 30% H_2O_2=3:1) at 95–100°C for 1 h to remove organic residues on the surface. The acid-treated glasses were washed with copious amounts of distilled deionized water. The washed glasses were dried at 120°C for 10 min before proceeding to the following steps for tethering APS groups. APTES from Aldrich was distilled and kept in a Schlenk storage flask under high purity argon. Ninhydrin (1,2,3-triketohydrindene, Aldrich) and TPDA were used as received. Toluene was treated with sulfuric acid at room temperature until the acid layer remained colorless. The acid treated toluene was washed with distilled deionized water, and dried with $CaCl_2$ prior to distillation over sodium under argon. The purified solvents were kept in Schlenk storage flasks under an argon atmosphere.

Preparation of APS-tethering glass plates

About eight to ten pieces of thin glass plate (18×18 mm) were treated with 10 mL APTES solution (2 mM) in toluene at 110°C for 1 h under argon. After cooling down to room temperature, the APS-tethering glass plates were washed with freshly distilled toluene and subsequently with ethanol. The washed glass substrates were dried with a gentle stream of high purity nitrogen and were kept in an oven at 120°C for 30 min.

Preparation of APS-tethering ZSM-5 crystals

ZSM-5 (50 mg) was introduced into a round-bottomed flask containing 10 ml of dry toluene under an argon atmosphere. Into the toluene slurry of zeolite, 0.1 ml of APTES was added under the argon flow. The mixture was refluxed for 1 h under an argon atmosphere. After cooling down to room temperature, the APS-tethering ZSM-5 powders were collected by rapid filtration. The filtered zeolites were then washed with freshly distilled toluene and ethanol. The collected powders were placed in an oven at 120°C for 30 min prior to assembly over the glass plates.

Preparation of BA-tethering glass plates

Typically, 10 μl of acetic acid and 20 ml of the toluene solution of TPDA (100 mM) were introduced into a round-bottomed flask containing a single APS-tethering glass plate. After refluxing for 3 h, the BA-tethering glass plate was removed from the flask and then washed with a series of solvents in the order of toluene, chloroform, and ethanol. The washed glass substrate was dried using a gentle stream of high purity nitrogen. The glass plate was kept in an oven at 120°C for 30 min prior to assembly of APS-covered ZSM-5.

Assembly of ZSM-5 monolayer on glass plate

Freshly prepared APS-tethering ZSM-5 (20 mg) and an APS-tethering glass plate were introduced into a round-bottomed Schlenk flask containing 20 ml of toluene. The mixture was refluxed for 4 h under an argon atmosphere. The zeolite-coated glass plate was removed from the flask and sonicated in toluene for 1 min to remove physisorbed zeolite crystals.

Instrumentation

The scanning electron microscope (SEM) images of zeolites and the zeolite-coated plates were obtained from a FE-SEM (Hitachi S-4300) at an acceleration voltage of 10 kV after deposition of the samples with platinum/palladium alloy (in the ratio of 8 to 2) with a thickness of about 15 nm. The X-ray diffraction patterns were obtained from a Rigaku diffractometer (D/MAX-1C) with the monochromated beam of CuKα. The UV–Vis spectra of the samples were recorded on a Shimadzu UV-3101PC. The diffuse reflectance UV–Vis spectra of solid samples were obtained using an integrating sphere. Sonication of the samples was carried out using an ultrasound-cleaning bath operated at 28 KHz.

Acknowledgements

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10. 4-(*t*-Butyliminomethyl)-benzaldehyde was prepared from *t*-butylamine and TPDA in ethanol in the presence of catalytic amounts of acetic acid. ^{1}H NMR ($CDCl_3$/TMS): δ (ppm)=10.05 (s, 1H), 8.34 (s, 1H), 8.06 (s, 2H), 7.92 (s, 2H), 1.32 (s, 9H).