POLYAMINES AS STRONG COVALENT LINKERS FOR THE ASSEMBLY OF MONO AND DOUBLE LAYERS OF ZEOLITE CRYSTALS ON GLASS

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SUMMARY

Two types of glass plates tethered with 3-(2,3-epoxypropoxy)propyl (EP) and 3-chloropropyl (CP) groups, respectively, were prepared and they were subsequently treated with polyamines such as polyethylenimine and a dendritic polyamine to induce multiple covalent linkages between the polyamines and the surface-bound EP or CP groups. Subsequent reaction of the polyamine-tethering substrates and the independently prepared EP- or CP-tethering zeolite-A or ZSM-5 crystals led to assembly of the monolayers of corresponding zeolite crystals on the substrates through covalent linkages with perfect one-dimensional orientation and close packing. Introduction of polyamines led to a remarkable increase in the strength of the binding between the zeolite crystals and glass compared to those made by direct linkages between the surface-bound AP, EP, CP, and hydroxyl groups. Such a result is proposed to arise from the ability of the large polyamine linkers to position in such a way between the two uneven surfaces as depicted in Figure 1 (C and D), that results in the large increase in the number of covalent linkage between the multiple amine groups and the surface-bound EP or CP groups. Such a remarkable increase in the binding between zeolite crystals and glass substrates allowed us successful assembly of second layers of zeolite crystals on top of the first layers.

INTRODUCTION

In compliance with the trend of modern chemistry evolving away from the manipulation of sets of individual molecules toward the description and manipulation of systems of molecules [1], the sizes of building blocks subjected to be assembled on supports have been expected to increase from nanometer to micrometer scales. Indeed, we have recently demonstrated facile monolayer assembly of zeolite crystals with the sizes of several hundred nanometers to micrometers on glass and mica by use of covalent linkers [2-7]. This opens a new conceptual chemistry of crystal assembly on supports and the resulting supported zeolite monolayers can be widely applied as thin-film catalysts, molecular sieves, hosts for chemical sensors [8-15], organizing media for quantum dots and nonlinear optical molecules.
[16,17], and arrays of well-defined nanoreactors for exploration of novel chemistries under highly confined and organized environments [18].

Unlike small molecules, a very large number of interconnecting chemical linkages is required to maintain adhesion between the micrometer-sized crystals and solid supports. Indeed, over 600,000 interconnecting linkages are estimated to be possible between a cubic zeolite-A crystal with the size of $1 \times 1 \times 1 \ \mu m^3$ and a solid support provided that both surfaces are atomically flat. However, the actual number of interconnecting covalent linkage is expected to be much less considering the microscopic unevenness of both surfaces [19], especially if each surface-anchored component for interconnection is shorter than the peak-to-valley depths on each uneven surface as depicted in Figure 1A and B. Presumably due to this, most of the zeolite crystals bound to glass plates by direct linkages between EP and AP, CP and AP, and surface hydroxyl groups (OH) and CP tethered to zeolite crystals and glass plates, respectively, have shown the tendencies to fell off the glass plates after a few minutes of sonication.

In fact, the weakly bound zeolite monolayers can be more strongly bound to the glass substrates by subsequent thermal treatment at 450 °C under flowing oxygen, presumably due to development of direct siloxane linkages between the two contacting surfaces. Although the thermal treatment is highly useful for application of the oriented thin films for various purposes, it is not applicable for thermally unstable substrates. Furthermore, it removes the specific functions of the interconnecting molecular linkers, which may be necessary for exploring fine chemistries such as interfacial electron and energy transfer in the future, by

Figure 1. Schematic illustrations depicting the limited number of linkage between the surface hydroxyl groups of zeolite crystals and the glass-bound CP groups (A) and the zeolite-bound EP or CP groups and the glass-bound AP groups (B) due to the unevenness of the surfaces. The positioning of DPA (C) and PEI (D), respectively, between the two uneven CP- or EP-tethering surfaces is proposed to yield large increase in the number of the corresponding covalent linkages. A denotes the corresponding terminal amino groups and X denotes either CP or EP groups.
employing the zeolite-linker-substrate composite materials as model systems [18]. Therefore, it is necessary to provide a general guideline about the molecular linkers to increase the strength of binding between zeolite crystals and substrates for wider applications. As a possible means, we recently reported a preliminary account about increasing the strength of binding between zeolite crystals and glass substrates by use of the polymeric linkers such as polyethylenimine and dendritic polyamine as the flexible, multiple point linkers. We now report a more thorough description about the use of the polymeric linkers to induce stronger binding between zeolite crystals and glass supports and the successful assembly of double layers of zeolite crystals on glass supports by use of polyethylenimine as the strong linkers.

**EXPERIMENTAL**

Zeolite-A and ZSM-5 with two different sizes, respectively, were synthesized according to the literature procedures [20]. The corresponding sizes are zeolite-A; $0.5 \times 0.5 \times 0.5$ and $1.7 \times 1.7 \times 1.7 \ \mu m^3$ and ZSM-5; $\sim 2.0 \times 1.2 \times 0.5$ and $2.5 \times 1.5 \times 0.7 \ \mu m^3$, respectively. [3-(2,3-epoxypropoxy)propyl]trimethoxysilane (EP-TMS), 3-chloropropyltrimethoxysilane (CP-TMS), 3-aminopropyltriethoxysilane (AP-TES), polyethylenimine (PEI, average MW = 25 000), dendritic polyamine (DPA, generation 4 Starburst PAMAM dendrimer, with 64 surface primary amino groups, $M_n = 14 215$) were purchased from Aldrich. Toluene was distilled over sodium under argon.

To prepare EP- or CP-tethering glass plates, 10 pieces of glass plates ($18 \times 18 \ \text{mm}^2$) supported on a Teflon mount were immersed into a toluene solution (20 mL) of EP-TMS or CP-TMS (0.1 M) and the toluene solution was refluxed under argon for 3 h. The glass plates tethered additionally with DPA were prepared by allowing the EP- or CP-tethering glass plates to react with DPA in boiling methanol for 2 h under argon. For the attachment of PEI, toluene was used instead of methanol. The physisorbed, unanchored DPA was removed from the glass plates by repeated washing with hot ethanol and water. The glass plates tethered with PEI were prepared similarly. Independently, the zeolite-A and ZSM-5 crystals tethered with EP- and CP groups, respectively, were prepared by treating them with EP-TMS and CP-TMS (0.1 M), respectively, in boiling toluene (20 mL) for 2 h under argon. The EP- or CP-tethering zeolite crystals (0.03 g) and two AP-tethering glass plates were introduced into toluene (20 mL) and then the heterogeneous mixture was refluxed for 3 h under argon. Similarly, the glass plates covalently attached with monolayers of zeolite crystals through the EP-DPA-EP, EP-PEI-EP, CP-DPA-CP, and CP-PEI-CP linkages were prepared by refluxing each toluene mixture of EP- or CP-tethering zeolite crystals and the corresponding DPA- or
PEI-tethering glass plates. The glass plates attached with the monolayers of zeolite crystals through direct linkages between the surface hydroxyl groups of the plain zeolite crystals and the CP-tethering glass plates were also similarly prepared by employing the plain, untreated zeolite crystals and CP-tethering glass plates.

The opaque glass plates coated with the monolayers of zeolite crystals were sonicated in toluene for 1 min to remove physisorbed zeolite particles over the chemically bound first layers. The glass plates attached with double layers of zeolite crystals were prepared by further treating the glass plates covered with the monolayers of appropriate zeolite crystals with PEI followed treatment of the glass plates with CP-tethering zeolite crystals. Samples were analyzed by X-ray powder diffractometry (Rigaku, D/MAX-1C) and scanning electron microscopy (FE-SEM, Hitachi S-4300). The linkage-dependent strengths of the binding between zeolite crystals and glass plates were compared by monitoring the progressive loss of zeolite crystals from the glass plates with increasing the length of sonication in toluene. Sonication of the samples was carried out using an ultrasonic cleaning bath. After each period of sonication, the weight of each glass plate was measured on a microbalance (Mettler MT5). The details about the procedure can be found from our previous communication [7].

RESULTS AND DISCUSSION

A typical scanning electron microscope (SEM) image of the zeolite-A monolayer assembled on a glass plate with EP-PEI-EP as the linker is shown in Figure 2A. All of the zeolite crystals also oriented with a face parallel to the glass surface. Interestingly, the EP-tethering zeolite crystals showed the tendency to closely pack despite the surface-lining groups are incapable of hydrogen bonding [2-4]. The corresponding SEM images of the monolayers prepared by the direct AP-EP and EP-DPA-EP linkages looked similar to that of Figure 2A in terms of orientation, coverage, and close packing [2].

Figure 3A shows three distinct profiles of weight loss resulted from the three different glass-bound zeolite monolayers. In the case of zeolite monolayers assembled by direct AP-EP linkage, close to 80% of zeolite crystals fell off the glass plates during the initial 5-min sonication. In strong contrast, only 17 and 7% losses were observed from the monolayers assembled with DPA and PEI, respectively, as the linkers. It is interesting to note that, even for the direct AP-EP linkage, about 10% of zeolite crystals endured initial 20 min of sonication and about 4% survived even 1-h sonication. The corresponding amounts of zeolite crystals that survived 1-h sonication were about 50 and 75% for DPA and PEI, respectively, as the linkers. This result thus clearly establishes that the strength of binding between zeolite
crystals and the substrates increases dramatically by employing polyamines as the linkers. Such a result is proposed to arise from the ability of the large polyamine linkers to position in such a way as depicted in Figure 1 (C and D) to result in the large increase in the number of covalent linkage between the multiple amine groups and the surface-bound EP groups between the two uneven surfaces. Similar results were obtained from the employment of CP groups rather than EP groups on both surfaces as compared in Figure 3B. Thus it is proposed that the increase in the bond strength as a result of employing polymeric linkers as the multiple linkers is a general phenomenon. The results in Figure 3 further show that the inexpensive PEI gives rise to stronger binding than DPA.

Interestingly, the sonication-induced detachment of zeolite crystals started from the outermost edges and particularly from the four corners of the glass plates that were contacting with the round vials. Such a phenomenon seems to arise due to transmission of stronger vibrations from the vials to the glass plates through the contacting corners. As a result, the zeolite-free, empty area progressively expanded toward the center of the glass plates. More interestingly, most of the zeolite monolayers that survived 1-h sonication retained the original degree of coverage and close packing as typically shown in Figure 2B.

The use of PEI also enabled facile assembly of zeolite-A monolayers on the curved surfaces of glass fibers as typically shown in Figure 2C. Even on such curved surfaces, the tendency of zeolite-A crystals to align and closely pack prevailed. Most of the zeolite crystals endured sonication in toluene for 30 min as shown in Figure 2D, despite the fiber surfaces are curved. This contrasted with the ready detachment of the monolayers assembled on glass fibers assembled via direct AP-EP linkages even after a few minutes of sonication.
The use of PEI also enabled assembly of the second layers on top of the first layers of zeolite crystals. In fact, we have tried to assemble the second layers of zeolite crystals on top of the first layers using relatively short linkers such as AP, CP, EP, fullerene, and terephthaldicarboxaldehyde. However, none of our previous attempts resulted in satisfactory results. The most common phenomenon we have observed from our previous trials is that the first layers are readily detached from the glass substrates rather than the second layers are attached on top of the first layers. As a result, we often observed the decrease in the coverage of the first layers accompanied by attachment of new zeolite crystals onto the glass plates by replacement of the previously attached zeolite crystals. This phenomenon was attributed to the weakness of the binding between the zeolite crystals and the glass substrates. The large increase in the degree of unevenness of the surface of the first layers due to the non-uniform sizes of zeolite crystals forming the first layers has also been proposed to play important roles in the previous failures.

However, by use of CP-PEI-CP as a prototypical strong linkage, we could achieve assembly of double layers on glass substrates as typically shown in Figure 4 (B and C). Thus, Figure 4A shows a typical monolayer of ZSM-5 crystals assembled on a glass plate though CP-PEI-CP linkages. The subsequent treatment of the ZSM-5 crystals with PEI followed by introduction of large zeolite-A crystals tethered with CP groups led to ready assembly of a new layer of large zeolite-A crystals on top of the first ZSM-5 layer as shown in Figure 4B.

**Figure 3.** The profiles of weight loss from the monolayers of zeolite-A crystals assembled on glass plates by three (A) and four (B) different types of linkers (as indicated).
Figure 4C shows the glass plate attached with larger ZSM-5 crystals in the first layer and smaller ZSM-5 crystals in the second layer through CP-PEI-CP linkages. The panels of D, E, and F in Figure 4 further show the corresponding cross sections of the glass plates. The X-ray diffraction pattern of the glass plate attached with ZSM-5 in the first layer and zeolite-A in the second layer (Figure 4B) shown in Figure 5A clearly demonstrates that the glass plate consists of two different types of zeolite and both of them are perfectly aligned.

We were also able to assemble the third layers on top of the second layers of zeolite-A and ZSM-5. However, the degree of coverage and close packing is inferior to those of the second layers.

Figure 5. X-ray diffraction pattern of sample B in Figure 4 (A) and the corresponding patterns of glass plates assembled with a monolayer of zeolite-A (B) and ZSM-5 (C), respectively.
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REFERENCES