9308 *J. Am. Chem. Soc.* **2000,** *122,* 9308−9309

Polyamines as Strong Molecular Linkers for Monolayer Assembly of Zeolite Crystals on Flat and Curved Glass

Alexander Kulak, Yong Soo Park, Yun-Jo Lee,
Yu Sung Chun, Kwang Ha, and Kyung Byung Yoon*

Center for Microcrystal Assembly, Department of Chemistry
Sogang University, Seoul 121-742, Korea

Received April 17, 2000

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 a few nanometers even 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.[2,3] 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,[4−11] organizing media for quantum dots and nonlinear optical molecules,[12,13] and arrays of well-defined nanoreactors for exploration of novel chemistries under highly confined and organized environments.[14]

Unlike small molecules, a very large number of interconnecting linkages is required for the micrometer-sized crystals and the solid supports to maintain adhesion. Indeed, over 600 000 interconnecting linkages are estimated to be possible between a one micrometer-sized cubic zeolite-A crystal and a support provided both surfaces are atomically flat. Considering the microscopic unevenness of both surfaces,[15] however, the actual number of interconnecting covalent linkage is expected to decrease significantly 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. Presumably due to this, the zeolite-A crystals bound to glass plates by direct linkage between 3-(2,3-epoxypropoxy)propyl (EP) groups tethered to zeolite-A and 3-aminopropyl (AP) groups tethered to glass readily fell off the glass plates after sonication for a few minutes.[2]

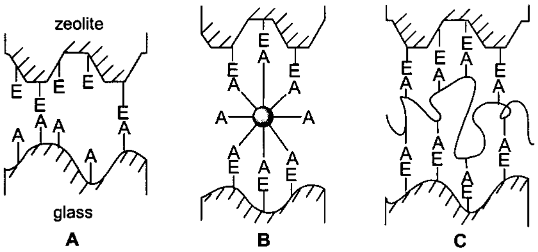

Figure 1. Schematic illustrations depicting the limited number of linkage between the zeolite-bound epoxy groups and the glass-bound amino groups due to the unevenness of the surfaces (A) and the proposed positioning of DPA (B) and PEI (C), respectively, between the two uneven epoxy-tethering surfaces to result in the large increase in the number of the β-amino alcohol linkage. E and A denote the corresponding epoxy and amino groups, respectively.

In fact, the weakly bound zeolite-A monolayers can be more strongly bound to the glass substrates by subsequent calcination at 450 °C, presumably due to formation of direct siloxane linkages between the two contacting surfaces. This, however, is not applicable for thermally unstable substrates. It also removes the specific functions of the interconnecting molecular linkers which may be useful for exploring fine chemistries such as interfacial electron and energy transfer using the zeolite−linker−substrate composite materials.[14] Therefore, it is necessary to provide a general guideline to increase the strength of the binding between zeolite crystals and substrates for wider applications. As a possible means, we anticipated that insertion of polyamines as molecular linkers between the two EP-tethering zeolite and glass surfaces would lead to a significant increase in the number of β-amino alcohol linkage, which eventually leads to stronger binding between the two solids.

As a test, we chose two different polyamines, namely, dendritic polyamine (DPA, generation 4 Starburst PAMAM dendrimer, with 64 surface primary amino groups, $M_n = 14\,215$, Aldrich) and polyethylenimine (PEI, average MW = 25 000, Aldrich) as the molecular linkers. For comparison, we first prepared 10 glass plates (18×18 mm^2) assembled with zeolite-A monolayers on the surfaces by direct linkage between the zeolite-bound EP groups and the glass-bound AP groups (Figure 1A). For this, 10 AP-tethering glass plates were introduced into 25 mL of toluene dispersed with 30 mg of EP-tethering zeolite. The temperature was slowly increased until toluene began to boil, and then it was allowed to reflux for 2 h under argon. The EP-tethering cubic zeolite-A crystals with the nearly uniform size of $\sim$0.5 μm were prepared by treating with [3-(2,3-epoxypropoxy)propyl]trimethoxysilane (Merck) in boiling toluene for 2 h under argon. AP-tethering glass plates were similarly prepared using 3-aminopropyltriethoxysilane (Aldrich).

To prepare the glass plates assembled with zeolite monolayers with DPA as the linkers, 10 EP-tethering glass plates were first allowed to react with DPA in boiling toluene for 2 h under argon. The physisorbed, unanchored DPA was removed from the glass plates by repeated washing with ethanol and water. The DPA-tethering glass plates were then washed with ethanol and subsequently with toluene before the reaction with the EP-tethering zeolite-A crystals in boiling toluene under argon. The third set of 10 samples with PEI as the linkers was similarly prepared by replacing DPA with PEI.

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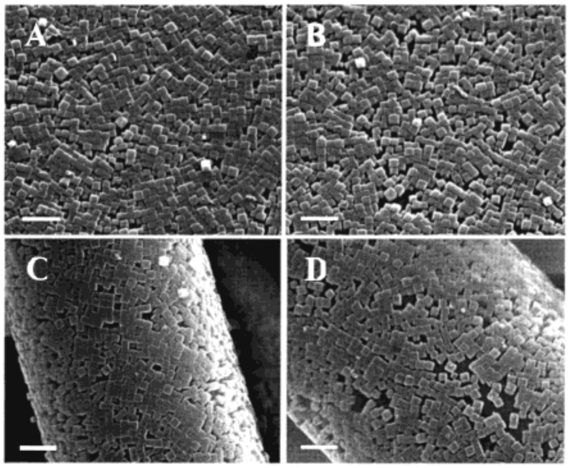

Figure 2. Typical scanning electron microscope images showing the monolayers of zeolite-A crystals assembled using PEI as the covalent linker on glass plates after sonication for 1 min (A) and 1 h (B) and glass fibers after sonication for 1 (C) and 30 min (D) in toluene. Each scale bar represents 2 μm.

A typical scanning electron microscope (SEM) image of the zeolite-A monolayer assembled on a glass plate with PEI as the linker is shown in Figure 2A. All of the zeolite crystals oriented with a face parallel to the glass surface. Accordingly, the XRD patterns of the zeolite-A-bound glass plates showed only six (h 0 0) lines with $h = 2$, 4, 6, 8, 10, and 12. Interestingly, the EP-tethering zeolite crystals showed the tendency to closely pack despite the surface-lining groups are incapable of hydrogen bonding.[2,3,5] 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.[16]

Since there are no established methods at this stage to measure the strengths of the binding between zeolite crystals and substrates, we used an ultrasonic cleaning bath as a qualitative device to compare the strengths of the binding.[17] The progressive loss of zeolite crystals from the glass plates with increasing sonication time was monitored by directly weighing the plates on a microbalance. For each type of linkage, five samples were run separately, and the average weight loss was plotted against sonication time.

Figure 3 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 survived amounts of zeolite crystals after 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 (B,C) to result in the large increase in the number of β-amino alcohol linkage between the multiple amine groups and the surface-bound EP groups despite the fact that the surfaces are uneven. Figure 3 further reveals that the inexpensive PEI gives rise to stronger binding than DPA.

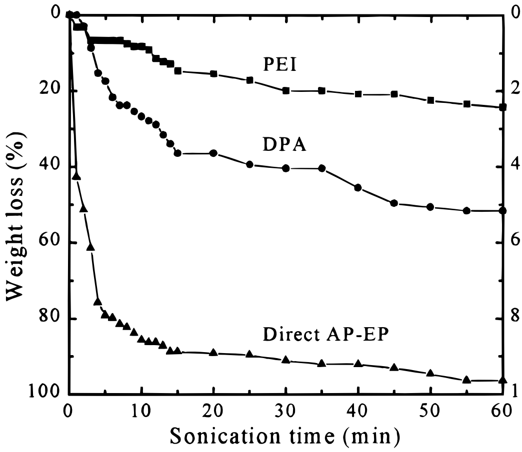

Figure 3. The profiles of weight loss from the monolayers of zeolite-A crystals assembled on glass plates by three different linkers (as indicated).

Interestingly, the 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 corners. 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.

Overall, this report demonstrates a way to increase the strength of binding between zeolite crystals and the substrates, which allows assembly of strongly bound zeolite monolayers even on curved glass surfaces (fibers). This method may be especially useful to fabricate optical fibers coated with zeolite crystals in high coverage for the photochemical application recently introduced by Raftery et al.[18]

Acknowledgment. We thank the Ministry of Science and Technology of the Korean Government for supporting this work through the Creative Research Initiatives Program.

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[16] The glass plates covered with zeolite-A crystals were first sonicated in toluene for 30 s to remove physisorbed zeolite crystals over the covalently bound monolayers.

[17] Typically, a zeolite-binding glass plate was placed in a vial (i.d. = 2.4 cm) filled with 10 mL of toluene. The vial was then placed in an ultrasonic cleaning bath (22 × 12 × 11 cm^3) filled with 1.5 L of water, 3 cm above one of the two ultrasound generators (28 kHz, 95 W each) mounted under the bath. A rack was built into the bath to place vials always in the same position. The water inside the bath was circulated through an external heat exchanger to keep the temperature constant (∼25 °C). After each period of sonication, the glass plate was removed from the vial and dried in an oven (120 °C) for 3 min, and the weight was measured on a microbalance. For each run, fresh toluene was charged into the vial. The initial sonication period was 1 min, and after 15 runs the interval was increased to 5 min. After sonication for 1 h (accumulated), the remaining zeolite crystals were completely removed from the glass plate by rubbing on a soft cloth, and the weight of the zeolite-free glass plate was measured. The total weight of pure zeolite crystals bound to the glass plate was deduced from the initial weight of the zeolite-binding glass plate that was measured after sonication for 30 s to remove physisorbed crystals. Since each glass plate binds about 250 μg of zeolite crystals, a microbalance is sensitive enough to detect the loss of zeolite crystals.

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