

Marked Increase in the Binding Strength between the Substrate and the Covalently Attached Monolayers of Zeolite Microcrystals by Lateral Molecular Cross-Linking between the Neighboring Microcrystals

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Acquiring the ability to organize micrometer-sized building blocks with well-defined molecular linkages is of great importance for the expansion of the sizes of chemists' building blocks from subnano- and nano- to micrometers. With this background in mind, we have explored the methods for organizing zeolite microcrystals into closely packed mono- and multilayers on various substrates by inducing a large number of chemical linkages between the organic functional groups tethered to both surfaces.¹⁻⁷ However, due to the relatively small surface area-to-mass ratios of the microcrystals, the binding strengths between the microcrystals and the substrates were rather weak, as judged by easy removal of them from the substrates even with mild sonication.¹⁻³ One way to increase the binding strengths we found was to increase the number of covalent linkages by employing flexible polymeric linkers.⁴ In such cases where glass plates were substrates, calcination of the resulting composites at high temperatures (~500 °C) was another way to induce strong binding between the zeolite microcrystals and the substrates, presumably due to the development of direct Si-O-Si linkages between the two contacting solid surfaces. However, to offer larger versatility to the molecularly assembled mono- and multilayers of microcrystals during their future applications, and to gain insights into the effect of bonding on the binding strength, we have kept searching for novel methods for increasing the binding strengths without burning off the interlinking organic molecular linkers.

Knowing the fact that cross-linking between the molecules self-assembled on substrates gives rise to a dramatic increase in the binding strengths between the monolayers and the substrates,^{8,9} we have wondered whether such a principle can also be applied to the stronger attachment of microcrystals to the substrates. As a test case, we assembled closely packed monolayers of cubic zeolite-A microcrystals ($1.7 \times 1.7 \times 1.7 \mu\text{m}^3$) on glass through imine (-CH=N-) or urethane (-HN-CO-NH-) linkages, by reacting the zeolite-A crystals tethering aminopropyl (AP) groups (AP-Z) and the glass plates tethering benzaldehyde or *n*-butylisocyanate groups, which were prepared by treating AP-tethering glass plates (AP-G) with a large excess of terephthalaldehyde (TPDA) or 1,4-diisocyanatobutane (DICB) in toluene, respectively, according to the previously reported procedures.^{3,6} Figure 1A shows the schematic illustration of the mode of linkage between AP-Z and AP-G via TPDA or DICB through imine or urethane bonding. Figure 2A shows a typical optical microscope image of the AP-Z monolayers assembled on glass by imine linkages. Similar monolayers were obtained by urethane linkages.

Since the five faces that were not making contact with the substrate were still covered with AP groups, we further treated the closely packed AP-Z monolayers with TPDA or DICB in toluene (see Supporting Information for details) with the hypothesis that it would lead to lateral cross-linking between the closely packed neighboring crystals via imine or urethane linkages as schematically

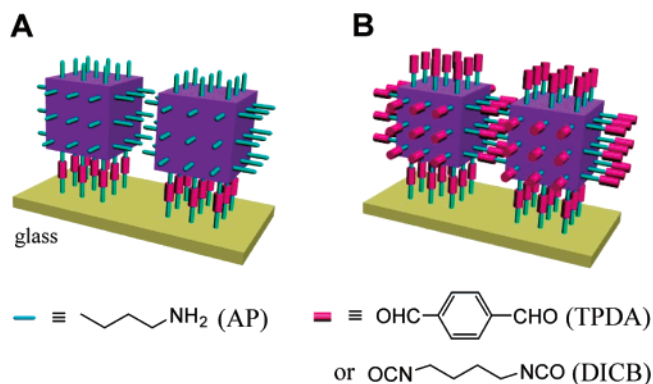


Figure 1. Schematic representations of the modes of linkages between the substrate and the zeolite microcrystals and between the closely packed neighboring microcrystals before (A) and after (B) cross-linking.

shown in Figure 1B. A typical optical microscope image of the cross-linked monolayer (with imine linkages) is shown in Figure 2B. As noticed, the optical microscope images did not show any noticeable difference between the two monolayers whether they were cross-linked or not. Nevertheless, we compared the sonication-induced detachment profiles of zeolite crystals from the two sets of glass plates attached with cross-linked and non-cross-linked monolayers, respectively, both by monitoring the same spots with an optical microscope and by measuring the weight loss of the glass plates on a microbalance.

Thus, as typically shown in Figure 2, investigation of the centers of the glass plates with an optical microscope revealed that the non-cross-linked zeolite microcrystals fell off the glass plates much more readily than the cross-linked microcrystals. For instance while the detached amount of non-cross-linked zeolite microcrystals was 27% after sonication for 5 min, that of the cross-linked zeolite microcrystals was only 1% (compare panels C and D in Figure 2) under the identical condition, which corresponds to as much as 27-times stronger adhesion. Similar trends maintained over longer periods of sonication. Thus, while the detached amount of non-cross-linked zeolite microcrystals was 89% after sonication for 10 min, that of the cross-linked zeolite microcrystals was only 4% even after sonication for 30 min (compare panels E and F in Figure 2).

Figure 3 demonstrates the marked difference in the average detached amounts of zeolite microcrystals observed from five sets of glass plates monitored by measuring weight loss on a microbalance. Thus, while more than 70% of non-cross-linked zeolite microcrystals fell off the glass plates after 30 min, that of the cross-linked zeolite microcrystals was less than 10%. This shows that the cross-linking leads to a 7-fold increase (by average) in binding strength between the monolayers and the substrates in the particular

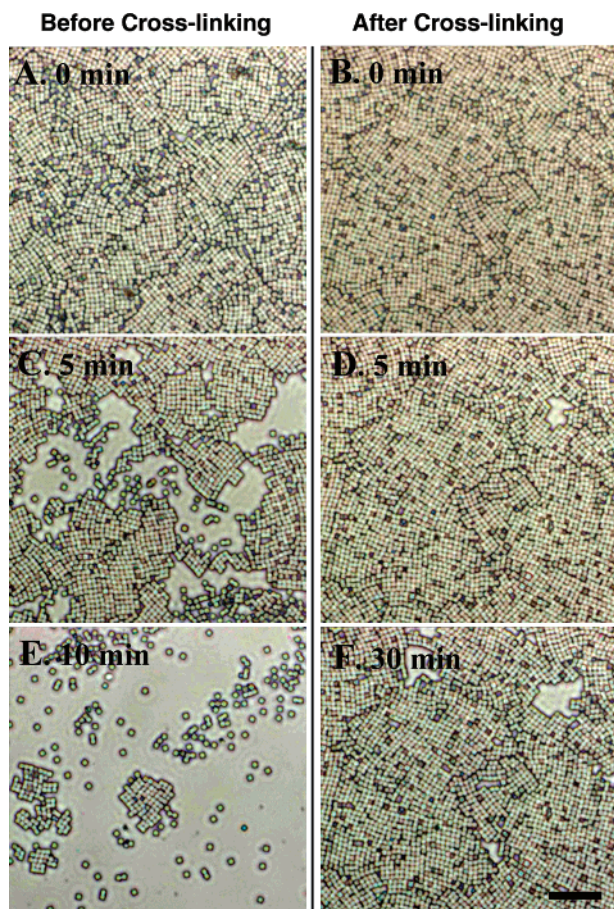


Figure 2. Optical microscope images showing the non-cross-linked (left) and cross-linked (right) monolayers of AP-Z microcrystals assembled on glass plates according to the schemes shown in Figure 1, and after sonication in toluene for the period indicated in each panel. The little squares indicate cubic zeolite-A crystals ($1.7 \times 1.7 \times 1.7 \mu\text{m}^3$), and the scale bars represent $15 \mu\text{m}$.

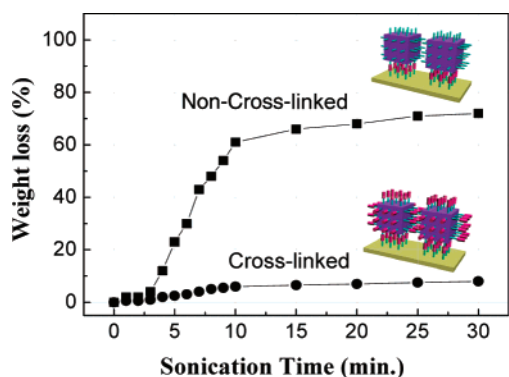


Figure 3. Average weight-loss profiles of AP-Z crystals from the five monolayers assembled on glass plates with imine linkages before and after imine cross-linking with respect to sonication time (as indicated).

system investigated in this report. Similar results were obtained from DICB cross-linking.

Coupled with the spectroscopic evidence (see Supporting Information), the above results demonstrate that the additional treatment of the closely packed monolayers of AP-Z microcrystals with TPDA

or DICB leads to lateral molecular cross-linking between the microcrystals, and it gives rise to a marked increase in the binding strengths between the monolayers of zeolite microcrystals and the glass substrate despite the fact that there was no further increase in the number of linkages between the microcrystals and the underlying glass substrate. This result clearly indicates that the phenomenon of cross-linking-induced marked increase in the binding strength between the substrate and the monolayers of building blocks works not only for small molecules but also for microcrystals with much higher mass-to-surface area ratios. We envisioned that such an effect will be more prominent with decreasing the size of building blocks due to the decrease in mass-to-surface area ratio. Indeed, a 38-fold increase (by average) in binding strength was observed upon lateral cross-linking between the zeolite crystals when their sizes were reduced to 300 nm (see Supporting Information). It is therefore expected that such an effect will be even more pronounced for nanoparticles. We believe that the insight gained from this work will not only help provide better opportunities for zeolites to be used as advanced materials¹⁰ but also serve as a guideline for the stronger attachment of nano- as well as microbuilding blocks onto substrates which is necessary for fabrication of the nanobuilding blocks into useful devices, such as two- and three-dimensional semiconductor quantum dot arrays on substrates.¹¹

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

Supporting Information Available: Experimental details for the synthesis of cubic zeolite-A, for the monolayer assembly of AP-Z on AP-G, and for cross-linking of the AP-Z microcrystals; verification of each step; experimental results obtained from 300 nm zeolite crystals (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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JA038605T