

## Effect of Mode of Binding Linkage on Monolayer Assembly of Zeolite

Jin Seok Lee

*Department of Chemistry, Sookmyung Women's University, Seoul 140-742, Korea. \*E-mail: jinslee@sookmyung.ac.kr*  
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During the monolayer assembly of zeolite microcrystals using sonication with stacking (SS) method, the factors that govern the degree of close packing (DCP) between the microcrystals, the rate of attachment ( $r_A$ ) of microcrystals onto the substrate, the degree of coverage (DOC), and the binding strength (BS) between each crystal and the substrate were investigated for each mode of binding linkage (MBL). The tested MBLs were covalent linkage (CL), ionic linkage (IL), and polyelectrolyte-mediated ionic linkage (p-IL). Unlike the monolayers of zeolite crystals assembled on glass with a covalent linkage, the strong BS, very high DOC, and very high DCP do not decrease during monolayer assembly on glass through ionic linkages. This results indicate that the surface migration of crystals undergo linkage-nondestructively when crystals were attached to the substrates through ionic linkages.

**Key Words :** Zeolite, Monolayer assembly, Sonication, Binding linkage, Surface migration

### Introduction

The bottom-up approach for fabricating nano-structured materials, which could lead to highly integrated functional entities, has played an important roles in utilizing building blocks to advanced materials.<sup>1,2</sup> Using several building blocks with different shape and size, we can design and fabricate multi-functional heterogeneous system on various substrates, and this has been the focus of interests during the last several decades.<sup>1-9</sup> The organization of building blocks have been intensively explored, and a number of assembly methods have been demonstrated to achieve ordered arrays on various substrates.

From the efforts to organize micro building blocks in the form of closely packed monolayers on various substrates, a number of attempts have been reported to improve the degree of close packing (DCP) between the microcrystals, the rate of attachment ( $r_A$ ) of microcrystals onto the substrate, the degree of coverage (DOC), and the binding strength (BS) between each crystal and the substrate using large numbers of interconnecting molecular linkages.<sup>10-19</sup> Recently, we discovered that sonication-induced strong agitation of the microcrystals and the interposition of a functional-group-tethering glass plate between two bare glass plates leads to very high DOC and DCP of the microcrystals on substrates within very short periods of time ( $< 2$  min) during the monolayer assembly of microcrystals on substrates through covalent linkages.<sup>20,21</sup> This method was named as 'sonication with stacking' (SS). Furthermore, under the SS mode, we found an interesting phenomenon that BS, DOC, and DCP gradually decrease with increasing the reaction time, despite of DOC reaches  $\sim 100\%$  with a quite fast  $r_A$ . Conclusively, we ascribed the progressive decrease in DOC to the progressive weakening of BS between the crystals and glass substrate under the sonication conditions as a result of the diminution of the numbers of func-

tional groups on the surfaces of the crystals and glass substrates upon repeatedly undergoing of the cycle of bond-formation and bond-breakage during the courses of surface migration and replacement of the attached crystals with those in the solution.<sup>20,21</sup>

As a means to settle the above critical limitation for applications, we try to change covalent linkages with ionic linkages during the monolayer assembly of microcrystals on glass using SS mode.<sup>22</sup> For this purpose, we adopted the previously established methods of forming ionic linkages between the surface-bound full-fledged ionic centers or ionic linkages mediated by alternating layer of oppositely charged polyelectrolytes.<sup>14</sup> Here, we report that indeed, the mode of binding linkage (MBL) sensitively affects to  $r_A$ , rate of the surface migration ( $r_{SM}$ ), DCP, DOC-t profile, and BS-t profile. Furthermore, we have discovered that DOC and BS are governed with not only the mode of reaction promotion (MRP) but also the MBL undergoing of the cycle of bond-formation and bond-breakage during the courses of surface migration and replacement of the attached crystals with those in the solution.

### Experimental Section

**Materials.** 3-Aminopropyltrimethoxysilane (AP-TMS, Aldrich) was distilled and kept in a Schlenk storage flask under argon. 3-Chloropropyltrimethoxysilane (CP-TMS, Aldrich) and 3-Cyanopropyltrichlorosilane (CNP-TCS, Merck) were used as received. For simplicity, 3-aminopropyl, 3-Chloropropyl, and 3-Cyanopropyl are denoted as AP, CP, and CNP, respectively. Poly(sodium 4-styrenesulfonate) ( $\text{Na}^+\text{PSS}^-$ ,  $M_w$  70,000, Aldrich) and poly(diallyldimethylammonium chloride) ( $\text{PDDA}^+\text{Cl}^-$ , 20 wt % in water,  $\sim M_w$  100,000-200,000, Aldrich) was used as received. Cover glasses ( $18 \times 18 \text{ mm}^2$ ) were purchased from Marienfeld and treated in a piranha solution ( $\text{H}_2\text{SO}_4$ : 30%  $\text{H}_2\text{O}_2 = 3:1$ ) at 95-

100 °C for 1 h to remove organic residues on the surface. The acid-treated glasses were washed with distilled deionized water and dried at 120 °C for 30 min prior to treatment with AP-TMS or CP-TMS. Optical grade fused silica plates were purchased from CVI Laser Co. and the surfaces of them were similarly cleaned with piranha solution prior to treatment with CNP-TCS. All the organic solvents were purified according to the well-known literature procedures prior to use.

**Mode of Binding Linkage.** The types of linkage used in this report were (a) the covalent linkage achieved by reaction between bare silicalite crystals (Z) and chloropropyl-tethering glass (CP-G) plates, (b) the direct ionic linkage achieved by reaction between sodium butyrate-tethering silicalite (Z) crystals and trimethylpropylammonium iodide-tethering glass ( $G^+$ ) plates, and (c) poly(sodium 4-styrenesulfonate) ( $Na^+PSS^-$ ) and poly(diallyldimethylammonium chloride) ( $PDDA^+Cl^-$ )-mediated ionic bonding between Z and  $G^+$ , respectively. Preparation of CP-G, Z, and  $G^+$  was carried out according to the procedures described in previous report.<sup>14</sup> The size of each glass plate was  $1.8 \times 1.8 \text{ cm}^2$ . The average size of Z was  $1.3 \times 0.6 \times 1.8 \text{ }\mu\text{m}^3$ .

**Assembly of  $Z^-$  on  $G^+$  (or  $PDDA^+/PSS^-/G^+$ ) using the SS Mode.** The MRPs tested in this report were sonication with stacking between the glass plates (SS mode).<sup>20,21</sup> Comb-shaped Teflon supports were used as such without attaching underlying supporting legs so that the glass plates inserted into the gaps can have direct contacts with the bottom of the round-bottomed flasks (50 mL). Typically, a comb-shaped Teflon support was placed at the bottom of a round-bottomed flask charged with 40 mL of toluene and 50 mg of  $Z^-$ . For the test of the effect of SS mode, a  $G^+$  (or  $PDDA^+/PSS^-/G^+$ ) plate was interposed between two clean bare glass (BG) plates, and three sets of BG/ $G^+$  (or  $PDDA^+/PSS^-/G^+$ )/BG stack were inserted, stack by stack, into each gap of the comb-shaped Teflon support. Sonication of the glass reactors was carried out using an ultrasonic bath with the dimension of  $22 \times 12 \times 11 \text{ cm}^3$  equipped with two ultrasound generators (28 kHz, 95 W each) attached to the bath from the bottom. After reaction, the  $Z^-$ -attached  $G^+$  (or  $PDDA^+/PSS^-/G^+$ ) plates were mildly sonicated for 30 s in toluene to remove the microcrystals that were physically or very weakly adhered to the glass plates and to the silicalite monolayers that were chemically attached to the glass plates using the ultrasonic bath equipped with two 50-W ultrasound generators before conducting the measurements of the attached amounts ( $W_A$ s) onto  $G^+$  (or  $PDDA^+/PSS^-/G^+$ ) plates on a microbalance, the analyses of the glass plates with scanning electron microscopy (SEM), and the sonication-induced silicalite detachment test. DOC was deduced from each  $W_A$  based on eq. (1),

$$DOC = (W_A / W_{A,\max}) \times 100 \quad (1)$$

where,  $W_{A,\max}$  represents the maximum obtainable  $W_A$  on a glass plate used in our study (on both sides of  $1.8 \times 1.8 \text{ cm}^2$ ). As for the  $W_{A,\max}$ , the average  $W_A$  obtained from  $Z^-/G^+$  (or  $Z^-/PDDA^+/PSS^-/G^+$ ) plates prepared by carrying out the

attachment reaction under the condition of SS was used since the silicalite monolayers obtained under the above condition were nearly perfect in many respects such as DCP, coverage, negligible amounts of microcrystals on the monolayers.

**Comparison of the Linkage-Dependent BS between Silicalite Crystals and Glass Plates.** The linkage-dependent BS between silicalite crystals ( $Z$  or  $Z^-$ ) and glass plates ( $CP-G$ ,  $G^+$ , or  $PDDA^+/PSS^-/G^+$ ) were compared by monitoring the progressive DOC-t profile, and BS-t profile. The details about the procedure can be found from our previous report.<sup>20,21</sup>

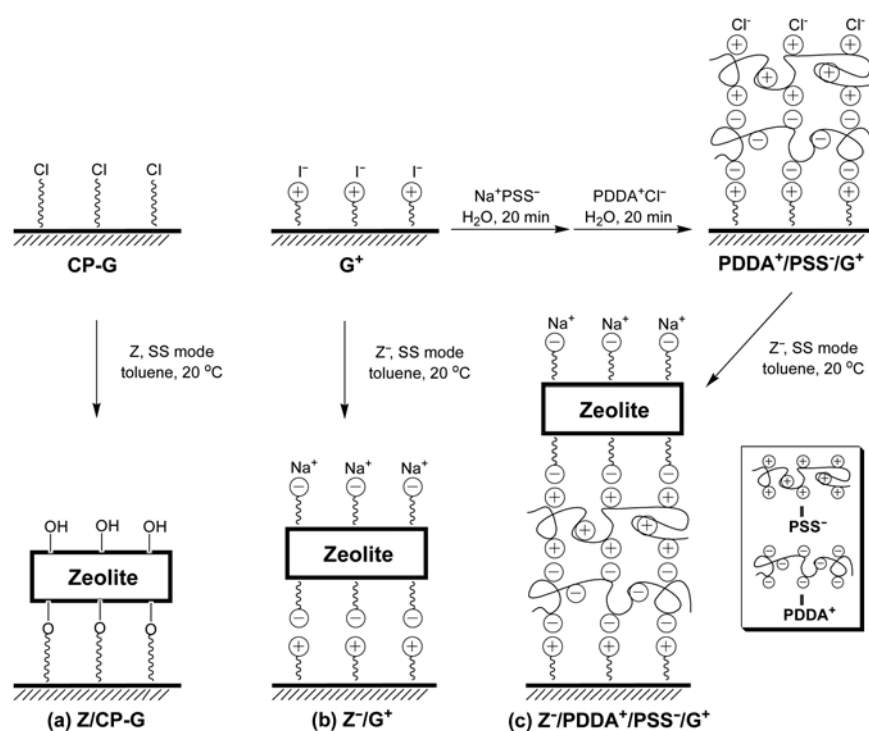
**Sonication-Induced Detachment Test.** Into an independent ultrasonic cleaning bath equipped with two 100 W ultrasound generators was added 2.5 L of water. Into a vial (i.d. = 2.4 cm, length = 5.4 cm) were added a Z-G ( $Z/CP-G$ ,  $Z/G^+$  or  $Z/PDDA^+/PSS^-/G^+$ ) plate and 10 mL of fresh toluene. With the help of a clamp and a clamp holder placed outside the bath, the vial was placed in the center of the water pool, 9 cm above from the bottom of the bath. The water inside the bath was maintained at  $\sim 20^\circ\text{C}$  using an immersion cooler. After 30 min of sonication, the substrate was removed from the vial, dried in an oven ( $120^\circ\text{C}$ ) for 3 min, and its weight was measured on a microbalance. Fresh toluene was charged into the vial after each weighing. The total weight of pure silicalite crystals bound to the substrate was deduced from the initial weight of the Z-G plate that was measured after removal of physisorbed crystals by mild sonication for 30 s. The  $W_A$ s from three Z-G plates were averaged for each data point.

**Instrumentation.** The SEM images of silicalite crystals and the Z-G plates were obtained from a FE-SEM (Hitachi S-4300) at an acceleration voltage of 10 to 20 kV. The SS method were tested using an ultrasound cleaning bath equipped with two 95-W ultrasound generators operated at 28 kHz (Saehan Ultrasonic SH-2100). The weights of the glass plates were measured on a Mettler microbalance (MT5).

## Results and Discussions

**Basic Concept for the Linkage-Dependent Promotion Test.** In the previously study,<sup>20,21</sup> we have investigated the effects of MRP on the progress of the monolayer assembly of zeolite microcrystals on glass through large numbers of molecular covalent linkages between zeolite microcrystals and glass plates and the characteristic properties of the assembled monolayers. Again, by charged amount ( $A_C$ ) of zeolite microcrystals into account, we have discussed how DOC and BS are governed with the MRP undergoing of the cycle of bond-formation and bond-breakage during the courses of surface migration and replacement of the attached crystals with those in the solution.

However, we now have fixed several factor, such as MRP (SS mode), charged amount ( $A_C$ ) of zeolite microcrystals ( $A_C = 50 \text{ mg}$ ) and reaction temperature ( $20^\circ\text{C}$ ), for the investigation of the only linkage-dependent attachment and detachment profile. As illustrated in Figure 1, the tested



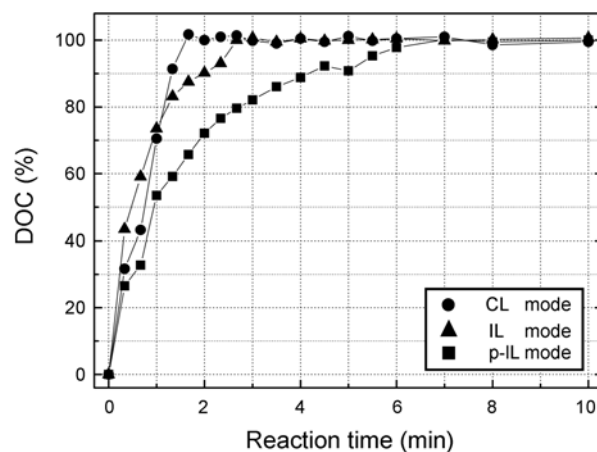
**Figure 1.** Schematic illustration of the three different types of mode of binding linkage, (a) covalent linkage, (b) ionic linkage and (c) ionic linkage mediated by alternating layer of oppositely charged polyelectrolytes, during the monolayer assembly of zeolite on glass tested in this work.

MBL between the zeolite microcrystals and the glass substrates is covalent linkage (CL), ionic linkage (IL) and ionic linkage mediated by alternating layer of oppositely charged polyelectrolytes (p-IL). For the attachment in the mode of IL and p-IL, we prepared to the negatively charged zeolite microcrystal (Z<sup>-</sup>) and the positively charged glass substrates (G<sup>+</sup>) on the each surface.<sup>14</sup> In particular, for the p-IL mode, we have also adopted PSS<sup>-</sup> and PDDA<sup>+</sup> as the negatively charged polyelectrolyte and the positively charged polyelectrolyte, respectively, and layered on the G<sup>+</sup> in the order, PSS<sup>-</sup>, PDDA<sup>+</sup> (denoted as PDDA<sup>+</sup>/PSS<sup>-</sup>/G<sup>+</sup>) as typically shown Figure 1(c).

**Comparison of the MBL-Dependent DOC-t Profile During 10 min.** In the sonication induced condition (SS mode) for the monolayer assembly of zeolite microcrystals, regardless of Z or Z<sup>-</sup>, the purplish scattered light was detected from the entire solution with a uniform intensity immediately after the sonication begins, indicating that the microcrystals were homogeneously dispersed into the solution. On the temperature kept constant at 20 °C, the DOC-t profile obtained under the each MBL condition shows that DOC increases with time, except for the different slope as the MBL. The DOCs were 100, 90, and 72% after 2 min, and rose to 101, 100, and 91% after 5 min from the conditions of CL, IL, and p-IL, respectively, as shown in Figure 2. Conclusively, above phenomenon clearly shows that DOC increases with time and that DOC reaches plateaus, the state of a fully covered zeolite-attached glass (Z-G) plates, at 1.7, 3, and 7 min in the mode of CL, IL, and p-IL, respectively. The SEM analyses of the Z-G plates removed

from the solution after 2 min and 5 min, respectively, revealed that the attached crystals were assembled over the entire glass plates with different DOC, which were increasing as shifting the mode from CL to IL, and to p-IL, respectively (not shown).

Comparison of the DOC-t profile in Figure 2 revealed that the  $\tau_{AS}$  observed from the mode of CL, IL, and p-IL, respectively, were very different from each other despite the fact that the MRPs were same. Based on the fact that the microcrystals were homogeneously dispersed into the solution in the SS mode, the above difference in the DOC-t



**Figure 2.** The DOC-t profiles for the attachment of zeolite microcrystals onto glass substrates during the period of 10 min obtained under the mode of CL (filled circle), IL (filled triangle), and p-IL (filled square), respectively.

profile is primarily ascribed to the difference in the MBL.

In the previously study,<sup>20-22</sup> we have shown that the attachment of the zeolite microcrystals starts from the bottom and then propagate to the top with time through repeatedly undergoing the cycle of bond-formation and bond-breakage. Therefore, we demonstrated that the initially intruded microcrystals are pushed up by the subsequently intruding crystals, leading to higher DCPs from the beginning. Despite of the fact that DOC reaches the fully covered Z-G plates after 100 sec (1.7 min) in the mode of CL, the DOCs were 88, and 66% in the mode IL, and p-IL, respectively. Again, when the DOC reaches the fully covered Z-G plates after 180 sec (3 min) in the mode of IL, the DOC was 82% in the mode p-IL. In the case of p-IL, more long time, 420 sec (7 min), needed for the fully covered Z-G plates. Conclusively, the above phenomenon clearly shows that the mode-shifting from CL to IL, and to p-IL leads to a decrease in the initial  $r_A$  which was deduced from DOC-t profile.

We attribute the above decrease in  $r_A$  to the decrease in  $r_{SM}$  under the mode-shifting from CL to IL, and to p-IL, caused by the followings; the number of linkage in the mode IL is larger than that in the mode CL, despite of the assumption that the nature of linkage (whether it is ionic or covalent linkage) does not greatly affect the binding strengths. This is conceivable in the sense that ionic bonding is nondirectional or omnidirectional and can also tolerate slight variation in the distance between the positive and negative centers while covalent linkages require stringent angles and distances for the approaching functional groups for successful formation of linkages.<sup>14,22</sup> Besides, due to both the zeolite microcrystals and a glass surface were uneven, the polyelectrolytes intercalated in a mode of p-IL are much more favorable for the attachment with larger numbers of bonding than the simply charged center in IL. Accordingly, even if the Z-Gs prepared from each mode look like the same, the number of linkage is increasing in the order, CL < IL < p-IL, and BS is expected to increase under the mode-shifting from CL to IL, to p-IL. However, as an above observation of attachment process with time, regardless of the kind of a MBL, the initially bonded linkages should be broken for the fully covered Z-G plates, which DOC is ~100%. Therefore, the fact of that a both the number of linkages and the binding strength between zeolite microcrystals and glass plates are increasing in the order, CL < IL < p-IL, is critically caused by the decrease in  $r_{SM}$  under the mode-shifting from CL to IL, and to p-IL, since the surface migration of the microcrystals attached on the substrate is promoted by the process of bond breakage between the microcrystals and the substrates.

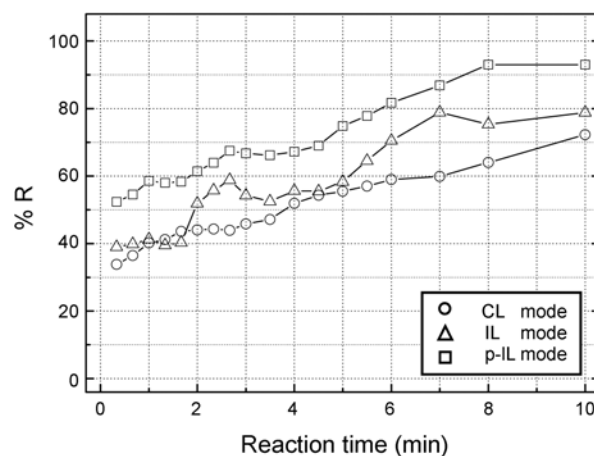
To sum up the above descriptions for a  $r_A$  and a  $r_{SM}$  during 10 min, we concluded that the  $r_A$  are governed with MBL dependent- $r_{SM}$  under the same condition of MRP (SS condition) and  $A_C$  during the monolayer assembly of microcrystals on the glass substrates. This is also quite reasonable since the increase in the binding strength that result from the increase of the number of linkages between zeolite microcrystals and glass plates caused by the MBL-shifting from CL to IL, and to p-IL, will prevent the microcrystals attached

on the glass from migrating on the glass surface through the process of bond breakage between the microcrystals and the substrates.

**Comparison of the MBL-Dependent BS-t Profile During 10 min.** From the details of the characteristics of each DOC-t profile, we ascribed the progressive increase in time required for ~100% in DOC to the progressive strengthening of BS between the crystals and glass substrate under the mode-shifting from CL to IL, and to p-IL, deduced from the fact that the number of linkage is increase in the order, CL < IL < p-IL, upon repeatedly undergoing of the cycle of bond-formation and bond-breakage during the monolayer assembly of zeolite microcrystals on the glass. As a means to seek the supporting evidence for the above we designed the methods for obtaining the BS-t profile under the condition of each MBL.

For the above, three Z-G plates were freshly prepared after certain periods of reaction time under the condition of each MBL, which is CL, IL and p-IL, with  $A_C = 50$  mg, and the average residual amount of zeolite crystals was deduced from each set of three Z-Gs after independently sonicating each in fresh toluene for 30 min under the sonication-induced detachment test condition (see Experimental Section). Since the initial DOCs of the Z-Gs before the detachment test were all different depending on the reaction period and MBL, the percentages of the survived, residual amounts (%R) were obtained with respect to each initial DOC. The profiles of %R with respect to time (%R-t profiles) in the mode of CL, IL and p-IL, respectively, are shown in Figure 3. Since, %R is related to BS, a %R-t profile can also be regarded as a BS-t profile.

Under the mode of CL, IL and p-IL, %Rs progressively increased to 72, 79 and 93%, respectively, during the reaction period of 10 min. Thus, except for the difference in the slope and initial %R, all of %R-t profiles increase with a similar tendency. The above results show that a BS progressively increases with time under the mode of CL, IL and p-IL during 10 min, indicating that the number of molecular linkages between the crystals and glass plates progressively



**Figure 3.** The %R-t profiles for the Z-G plates produced under the mode of CL (empty circle), IL (empty triangle), and p-IL (empty square), respectively, for the period of 10 min.

increases during 10 min.

Interestingly, comparison of DOC-t profiles and %R-t profiles in Figure 2 and 3, respectively, also revealed that they progressively increase with a symmetrical relationship. Based on the characteristics of MBL in the above description, this is primarily ascribed to the increase of the number of molecular linkages between the crystals and glass plates in the order,  $CL < IL < p-IL$ . Thus, the increase in the number of molecular linkages lead to the decrease of  $r_A$  in the DOC-t profile as well as the increase of %BS (%R) in the %BS-t (%R-t) profile as the mode-shifting from CL to IL, and to p-IL. Conclusively, we now proposed that MBL sensitively governs the reaction profile of the monolayer assembly of microcrystals on glass with a symmetry in the relationship of DOC-t and %BS-t (%R-t) profiles.

**Comparison of the MBL-Dependent DOC-t and BS-t Profile During 6 h.** During the initial 10 min, DOC reached plateaus, the state of a fully covered Z-G plates, at 1.7, 3 and 7 min for MBL = CL, IL, and p-IL mode, respectively (Figure 2). Monitoring the DOC-t profile over a longer period of time (6 h) revealed that the MBL dependent-DOC-t profiles are classified into fore regimes as shown in Figure 4(a)-(c). The initial 1.7, 3 and 7 min regions in which DOC increases very rapidly and reaches the maximum under the mode CL, IL, and p-IL, respectively, are classified as Regimes I<sub>CL</sub>, I<sub>IL</sub>, and I<sub>p-IL</sub>, respectively. After reaching the maximum, DOC stays nearly constant for 10, 10 and 30 min under the mode CL, IL and p-IL, respectively. These regions are classified as Regimes II<sub>CL</sub>, II<sub>IL</sub> and II<sub>p-IL</sub>, respectively. The following regions in which DOC slowly decreases are classified as Regimes III<sub>CL</sub>, III<sub>IL</sub> and III<sub>p-IL</sub>, respectively. In particular, Scrutiny of the Regimes III, except for the CL mode, further revealed that a DOC equilibrates 83 and 87% after ~2.5 and ~3 h in the mode of IL and p-IL, respectively, which was classified as Regimes IV<sub>IL</sub> and IV<sub>p-IL</sub>, respectively.

Based on the fact that the attached microcrystals on the glass plate are continuously and rapidly replaced by those dispersed in solution under the sonication condition,<sup>21</sup> the above phenomenon was interpreted as the gap between  $r_A$  and the detachment rate ( $r_D$ ) of zeolite microcrystals from the glass plate. Under the Regimes I,  $r_A$  mostly govern the DOC-t profile regardless of the MBL, but, after reaching the maximum (~100%) in DOC,  $r_A$  and  $r_D$  are the same for the desired time which is dependent on the MBL (Regimes II). The  $r_D$  then starts exceeding  $r_A$  in the reaction profile of the monolayer assembly of microcrystals on glass, which was classified as Regimes III. Again, under the mode of IL and p-IL, the decreasing DOC-t profile equilibrates at the desired point, indicating that  $r_A$  and  $r_D$  are the same at the desired DOC which is dependent on the MBL, which was classified as Regimes IV.

Under the Regimes II, we now proposed that the retention time at the maximum in DOC is relate to the BS between the crystals and glass plates and finely results in increase as the mode-shifting from CL to IL, to p-IL. This is quite reasonable from the sense that the number of molecular linkage

increase in the order,  $CL < IL < p-IL$ , indicating that the breakage of molecular linkages is more difficult as the mode-shifting from CL to IL, to p-IL.

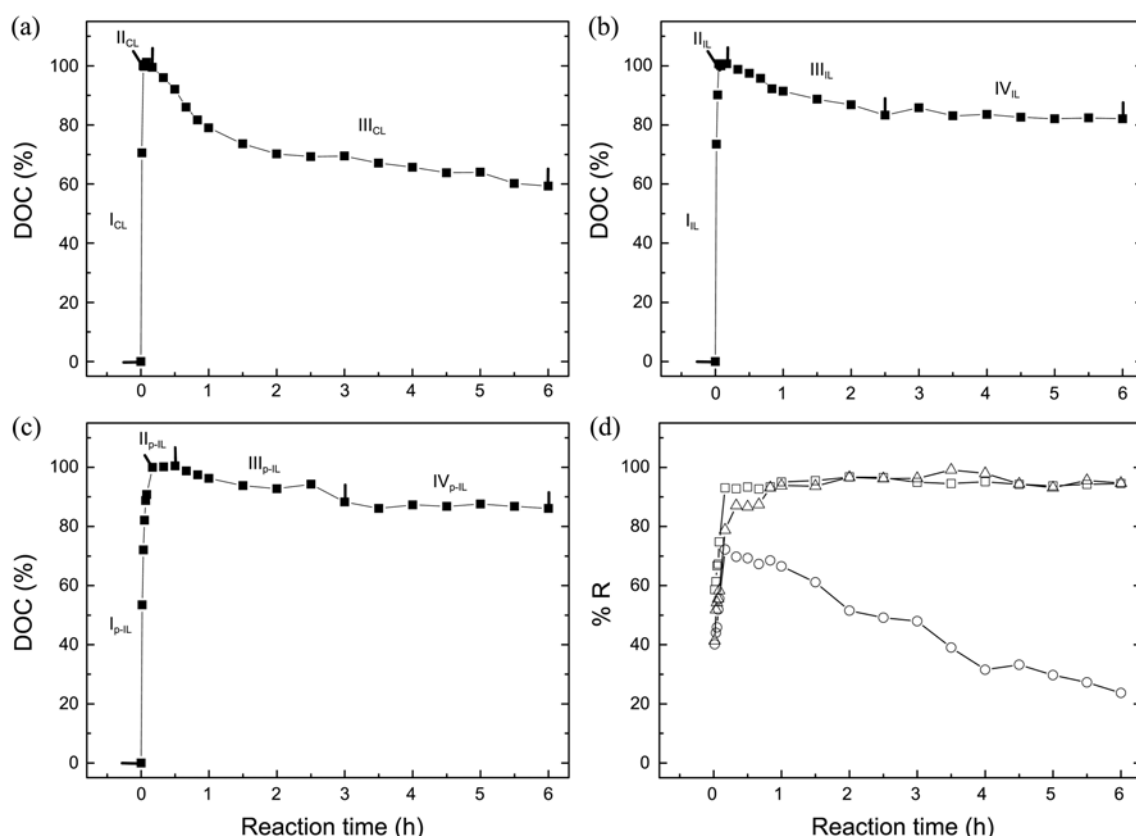
The fact that DOC decreases in Regimes III and the degree of decrease in DOC is dependent on the MBL is very intriguing. Based on our previous finding that the microcrystals in the solution tended to aggregate with their (0 1 0) faces contacting each other,<sup>20,21</sup> the fact that a  $r_A$  decrease as time is quite reasonable. Again, under the mode-shifting from CL to IL, to p-IL, the fact that  $r_D$  decrease is also understood from the sense that the number of molecular linkage increase as time under the sonication process. Accordingly, we proposed that above phenomenon that DOC decreases in Regimes III is explained with decreasing  $r_A$ , and the fact that degree of decrease in DOC is high in the order,  $p-IL < IL < CL$ , is also explained with increasing  $r_D$  in the order,  $p-IL < IL < CL$ .

The above phenomenon that decreasing DOC curve reaches an equilibrium-DOC in Regimes IV<sub>IL</sub> and IV<sub>p-IL</sub>, is highly impressive. For a reasonable understanding, supporting evidence and more detailed discussion are described in the later part.

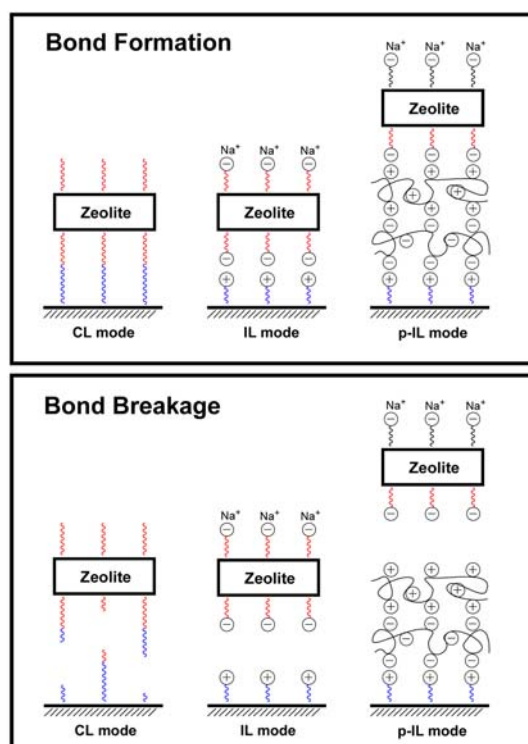
From our previous research on the covalent bonding as a molecular linkages,<sup>20,21</sup> when we let the attachment reactions continue up to 6 h on monitoring the DOC-t profile under the conditions of SS, we concluded that the progressive decrease in DOC results from the progressive weakening of BS between the crystals and glass substrate under the sonication conditions as a result of the diminution of the numbers of functional groups on the surfaces of zeolite crystal and CP-G (OH and CP, respectively) upon repeatedly undergoing of the cycle of bond-formation and bond-breakage during the courses of surface migration and replacement of the attached crystals with those in the solution. Therefore, as a means to check whether above critical problem indeed cause the decrease of DOC with time in the case of MBL-dependent monolayer assembly, we investigated the BS-t profile for each MBL for a long period time (6 h).

Under the CL mode, %R rapidly increased from 34 to 72% during the initial reaction period from 20 s to 10 min (Figure 4(d)). After 10 min, however, it decreased gradually to 24% during the course of 6 h. Based on the fact that %R gradually started decreasing after 10 min, the phenomenon that DOC started decreasing is quite reasonable. Coupled with the phenomenon that both DOC and %R, hence BS simultaneously increase by the initial 10 min (Figure 3), the phenomenon of the simultaneous decreases of both DOC and BS after 10 min strongly suggests that the progressive decrease of DOC in the DOC-t profile under the CL mode occurs due to the progressive decrease in BS, or due to the progressive diminution of the number of molecular linkages between zeolite microcrystals and glass.

The %R-t profiles obtained under the mode of IL and p-IL were basically similar to each other with respect to their shape, except that the former was slower than the latter in an ascending rate, albeit small. In contrast to the case of CL mode, they progressively increased with time, and then the



**Figure 4.** The regimes classified into each DOC-t profile for the period of 6 h obtained under the mode of (a) CL (filled circle), (b) IL (filled triangle) and (c) p-IL (filled square), respectively. And, (d) the %R-t profiles for the Z-G plates produced under the conditions of CL (empty circle), IL (empty triangle), and p-IL (empty square), respectively, for the period of 6 h.



**Figure 5.** Schematic illustration of the proposed cycles of bond-formation and bond-breakage during the progress of the mono-layer assembly of zeolite microcrystals on glass with the three different types of bonding, CL, IL, and p-IL.

%Rs were equilibrated at ~97% during the reaction period of 6 h. In particular, both of the %R-t profiles in IL and p-IL mode were generally shifted up by ~25% with respect to that obtained under the mode of CL, indicate that the average BS of the microcrystals in the Z-G plates prepared with the ionic bonding such as IL or p-IL is stronger by ~25% than that in the Z-G plates prepared with the covalent bonding (Figure 4(d)). Based on the fact that diminution of the number of molecular linkages between zeolite microcrystals and glass as a result of repeatedly undergoing the cycles of bond formation and bond breakage under the strong sonication condition interferes with the preparation of Z-G plate, above descriptions for the %R-t profiles obtained under the mode of IL and p-IL is very interesting. This demonstrated that diminution of the number of molecular linkages between solids don't occur under the IL and p-IL mode (Figure 5). Furthermore, based on the fact that the surface of zeolite microcrystals and glass is uneven, %R-t profile obtained under the mode of p-IL reach the equilibrium plateau more faster than that under the IL mode, since the Z-G plate prepared by p-IL mode can be prepared with highly number of linkages than one by IL.

## Conclusion

Overall, this research reports the difference in the nature of surface migrations, linkage-destructive and linkage-non-

destructive, during monolayer assembly of zeolite microcrystals on glass with covalent and ionic linkages, respectively. Since the ionic bonding is nondirectional and can more tolerate slight variation in the both of distance and angle between zeolite microcrystals and glass plates, the number of linkage in the mode of ionic linkages is larger than that of the covalent linkages and leads to the increase in BS between zeolite microcrystals and glass plates. Unlike the monolayers of zeolite crystals assembled on glass with a covalent linkage, very high DOC and very high DCP of the monolayers on glass do not decrease even after the use of ionic linkages for the monolayer assembly of zeolite microcrystals on glass plates. And, the polyelectrolytes intercalated in a mode of p-IL are much more effective to attach with strong BS between uneven zeolite microcrystals and uneven glass plates. Therefore, we conclude from the above results that DOC and BS are governed with not only the mode of reaction promotion (MRP) but also the mode of binding linkage (MBL), which affects to  $r_A$ ,  $r_{SM}$ , and DCP, undergoing of the cycle of bond-formation and bond-breakage during the monolayer assembly of zeolite microcrystal on glass substrates. We suggest that the use of ionic linkage and SS method is an ideal combination for the preparation of zeolite crystal monolayers on glass plates with very large areas.<sup>23-26</sup>

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