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# Diisocyanates as novel molecular binders for monolayer assembly of zeolite crystals on glass†

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**Isocyanate groups readily form urethane linkages with surface hydroxy groups on glass and zeolites and this phenomenon was utilized in the assembly of monolayers of zeolite microcrystals on glass by employing diisocyanates as novel molecular binders.**

The ability to organize micrometer-sized building blocks with well-defined molecular binders is one of the essential elements for the advancement of materials science.[1–4] Accordingly, we have recently been interested in developing methods to assemble highly oriented mono- and multilayers of zeolite microcrystals on glass and other substrates through well-defined covalent and ionic linkages.[5] For this, organic functional groups have usually been attached onto the solid surfaces followed by subsequent chemical coupling or ionic interaction between the surface-bound functional groups.[5] The attachment of organic functional groups onto solid surfaces has so far been carried out by reaction between the reactive silyl groups such as $-SiX_3$, $-SiX_2R$ and $-SiXR_2$ (X = methoxy, ethoxy or chloride, R = methyl or ethyl) tethered to the organic functional groups and the hydroxy groups on the surfaces. Although the use of silyl compounds has been shown to be highly effective, continuing efforts should be directed towards diversification of the types of molecular binders to take full advantage of a wide variety of other types of molecular binders and to gain insights into the relationship between the types of molecular binders and the binding strengths between the microcrystals and the substrates. As a step to this, we have tested the feasibility of employing diisocyanates (DICs) as a new type of molecular binder between the zeolite crystals and glass substrates. We now report that DICs are highly effective alternatives to the traditional silyl compounds, and the use of flexible macromolecular binders coated with DIC leads to a dramatic increase in the binding strength between the glass substrates and zeolite crystals.

The prototypical DICs that have been employed in this communication are 1,4-diisocyanatobutane (DIC-4), 1,6-diisocyanatohexane (DIC-6), tolylene 2,4-diisocyanate-terminated poly(1,4-butanediol) ($M_n$ = *ca.* 900, DIC-T), and isophorone diisocyanate-terminated poly(1,4-butanediol) ($M_n$ = *ca.* 1550, DIC-I). We first tested DIC-4 as the molecular binder for the monolayer assembly of zeolite-A (size = $\sim 0.5 \times 0.5 \times 0.5$ μm) or ZSM-5 (size = $2.5 \times 1.5 \times 0.7$ μm) crystals according to the scheme shown in Fig. 1 (See ESI† for detailed procedures). Scanning electron microscopy (SEM) images of the glass plates revealed that the zeolite crystals indeed readily self-assemble in the form of monolayers on both sides of the entire glass plates ($18 \times 18$ mm) as typically shown in Fig. 2. The SEM images also show that the crystals have a strong tendency to closely pack. Other DICs also gave similar results.

The above results therefore unambiguously demonstrate that isocyanate groups readily form urethane linkages with the surface hydroxy groups of zeolite and glass plate, and hence that DICs can serve as highly efficient molecular binders for the monolayer assembly of zeolite crystals despite the fact that both of the two isocyanate groups could possibly react with two glass surface hydroxy groups. The above results also indicate that substantial amounts of DICs, if not all, readily self-assemble vertically on the glass surface to allow subsequent attachment of monolayers of zeolite crystals on the glass plates according to the scheme shown in Fig. 1.

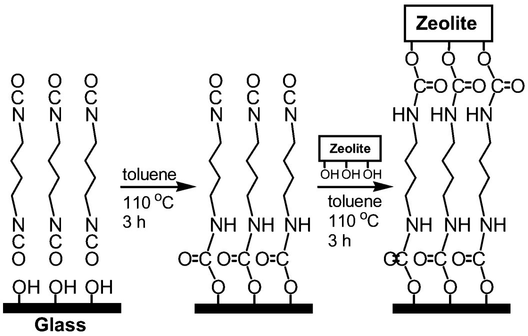

**Fig. 1** Schematic representation of the procedure to assemble monolayers of zeolite crystals on glass substrates using DIC-4 as the molecular binder.

The above results also open a novel pathway to attach various organic and inorganic functional groups onto hydroxy-bearing solid surfaces through urethane linkages by employing various isocyanate compounds. From the viewpoint that isocyanate-bearing compounds can be easily derived from a wide variety of compounds such as alkyl halides,[6] alkyl amides,[7] acyl azides,[8] and amines,[9] while reactive silyl group-bearing compounds can

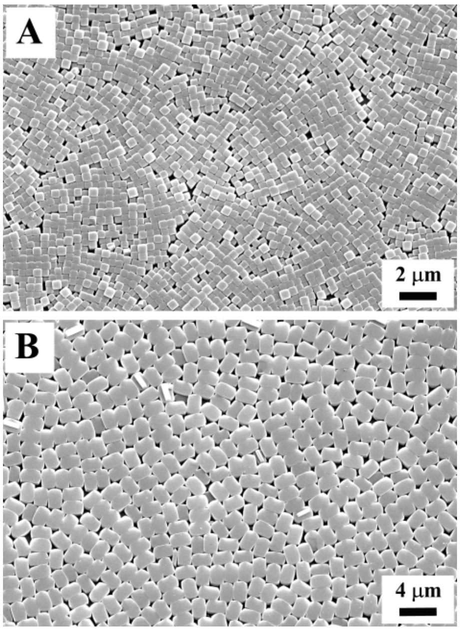

**Fig. 2** Scanning electron microscopy (SEM) images showing the monolayers of zeolite-A (A) and ZSM-5 (B) crystals assembled by employing DIC-4 as the molecular binder.

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† Electronic supplementary information (ESI) available: experimental details. See http://www.rsc.org/suppdata/cc/b2/b205046c/

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be produced only from olefins, the '*urethane pathway*' is expected to offer a higher degree of structural and functional variety to the compounds intended to be attached onto the solid surfaces than the '*siloxyl pathway*'. DICs also offer advantages over the silyl compounds in that zeolite crystals do not require independent surface-functionalization with organic compounds for the monolayer assembly of zeolite crystals on glass plates, and the number of available DICs is higher than that of silyl compounds since a wide variety of DICs has been developed for production of polyurethane foams.

To gain insights into the relationship between the binding strength and the type of DIC employed in this report, we also carried out sonication-induced detachment tests[10] of the zeolite-A crystals bound to the glass plates by the four different DICs. For comparison, we independently prepared glass plates covered with zeolite-A monolayers assembled *via* the previously reported[5a] coupling between 3-aminopropyl (AP) and 3-(2,3-epoxypropoxy)propyl (EP) groups that were tethered to the surfaces of zeolite crystals and glass plates, respectively, through siloxyl linkages. The detachment tests revealed that the binding strengths between the zeolite crystals and glass plates are in the order of DIC-4 > DIC-6 > DIC-T > DIC-I ≅ AP/EP, as shown in Fig. 3. This result indicates that DICs offer higher or at least the same strengths with those of siloxyl-based linkages.

We attribute the above increase to the increase in the number of inter-surface molecular binders as a result of the decrease in the required number of surface hydroxy groups for binding of the molecular binder from three (maximum) to one upon changing the type of the surface-anchoring group from trialkoxysilyl to isocyanate. As a corollary, the increase in the binding strength with DIC-4 as the molecular binder with respect to that with AP/EP suggests that most of the compound vertically self-assembles on the glass plates upon contact. Interestingly, we found a negative relationship between the binding strength and the length of the spacer between the two terminal isocyanate groups, *i.e.*, while the binding strengths increase in the order DIC-4 > DIC-6 > DIC-T > DIC-I, the spacer length increases in the order DIC-4 < DIC-6 < DIC-T < DIC-I. We propose that such a negative relationship arises from the progressive increase in the ease of the DICs to fold into a U-shape, allowing both ends of some of the DICs to be connected to the glass surface, which eventually leads to the decrease in the net number of inter-surface linkages. Consistent with the above proposal, 4,4′-oxybis(phenyl isocyanate), an intrinsically bent DIC, resulted in much weaker binding than the above four DICs. Thus, we conclude that the DICs that tend to vertically assemble on glass plates are most promising as molecular binders. We also tested the readily available 1,4-phenylene diisocyanate (PDIC) as another DIC candidate. However, PDIC was ineffective due to its very poor solubility in toluene (< 1 mg/100 mL).

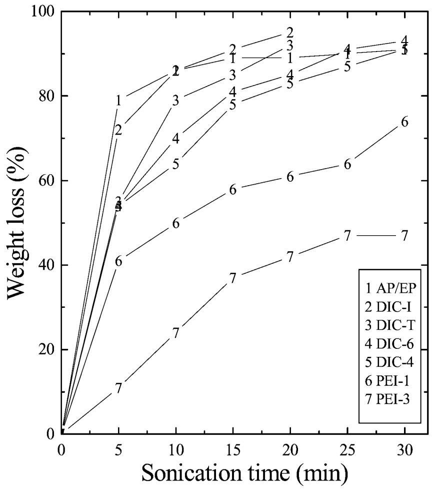

**Fig. 3** Profiles of the sonication-induced weight loss of the monolayers of zeolite-A crystals assembled on glass plates by seven different types of urethane linkage (as indicated).

As an extension to the use of DICs as the molecular binders, we also assembled zeolite monolayers on glass plates coated with DIC-4, polyethylenimine (PEI, $M_n$ = *ca*. 25000), and DIC-4 [G/DIC-4/PEI/DIC-4] by layer-by-layer treatment, and on glass plates similarly coated with four layers of DIC-4 and three intervening layers of PEI [G/(DIC-4/PEI)$_3$/DIC-4] designated as PEI-1, and PEI-3, respectively. Interestingly, as shown in Fig. 3, the employment of PEI led to a marked increase in the binding strength of zeolite crystals to the glass plates with increasing number of PEI layers, consistent with our previous results.[5e] Again, we attribute the marked increase to the ability of the polyamines to position themselves to fit between the two uneven surfaces of zeolites[11] and glass plates to result in significant increases in the number of linkages between the solid surfaces.

Although the average binding strengths between the zeolite monolayers and glass plates varies markedly depending on the nature of linkage, they all become very strong and nearly permanent when calcined at 450 °C for 3 h, presumably due to development of direct siloxyl linkages between the two solid surfaces.

In summary, isocyanate groups readily form urethane linkages with hydroxy groups on glass and zeolites, and DICs form a new class of convenient molecular binders for the monolayer assembly of zeolite microcrystals or other functional groups on glass plates.

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11 The AFM study of zeolite surfaces has revealed that the depth from the highest to the lowest points of zeolite surfaces easily exceed a few nm, which is longer than the lengths of DIC-4 and DIC-6 (see: J. R. Agger, N. Pervaiz, A. K. Cheetham and M. W. Anderson, *J. Am. Chem. Soc.*, 1998, **120**, 10754).