Photochemical Pattern Transfer and Patterning of Continuous Zeolite Films on Glass by Direct Dipping in Synthesis Gel**

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Ceaseless exploration of new applications of zeolites and related porous materials is indispensable for the continual development of the science and technology of zeolites. A new breakthrough in their applications can possibly be achieved by seeking utilization of the porous materials for combinatorial catalysts and as low-dielectric packing materials for integrated circuits. One of the key steps in realizing such applications is to develop reliable methods to pattern them as thin films on various supports. However, despite the availability of a large number of methods to prepare thin films on various supports,[1–12] the methods to pattern them are rare since they have begun receiving attention only recently. Ozin and co-workers first reported a way to selectively deposit mesoporous silica on patterned, alkanethiol-covered regions of gold by carefully positioning the substrate between the air and synthesis gel interface.[13] Stucky and co-workers demonstrated the preparation of patterned, hierarchically ordered mesoporous silica films on silicon supports through direct heating of the patterned, micromolded precursor gel.[14] By replacing the precursor gel with nanocrystalline microporous silica (silicalite) in the above micromolding/heating method, Yan, Zhao, and co-workers were able to prepare patterned microporous and micro-macroporous silica films.[15] As a result of our interest in the assembly of covalently bound monolayers of zeolite crystals on mica and glass substrates,[12] we also developed a versatile method to pattern monolayers of oriented and covalently bound zeolite crystals.[16]

In all of the above-mentioned methods, however, microcontact printing, also known as poly(dimethylsiloxane) (PDMS) stamping, has been adopted as the only way to transfer patterns. Alternative photochemical approaches have not been explored, although, in principle, they have many intrinsic advantages over PDMS stamping, e.g., higher resolution, reproducibility, reliability, and processability.[17] Furthermore, zeolite film patterning by direct dipping of the supports patterned with surface-protecting organic functional groups into the synthesis gel has not been explored, although it is likely to be the most practical and simplest method to pattern continuous zeolite films on supports. We now report that photochemical degradation of various organic functional groups tethered to glass plates is a highly versatile and effective way of preparing glass plates patterned with organic functional groups and that direct dipping of the patterned glass plates into the synthesis gel readily leads to glass plates patterned with continuous zeolite films.

First, we prepared glass plates with tethered 3-iodopropyl (IP) groups via siloxane linkages (see Experimental section), with the intention of transferring the pattern through photochemical decomposition of IP groups. The glass plates with tethered IP groups were then exposed to UV light generated by a high-pressure Hg lamp with a photomask on top of each glass plate as depicted in Scheme 1 (left). As a test, we employed grids as convenient photomasks. We also adopted our previously reported zeolite film patterning method[19] as a test procedure to check the validity of our photochemical pattern transfer. Thus, after exposure to UV light for 1 h, the IP-tethered glass plates were allowed to come into contact with plain ZSM-5 crystals in boiling toluene for 3 h. The scanning electron microscopy (SEM) image of the glass plates, after sonication for 2 min, revealed that the ZSM-5 crystals are attached only on the masked regions, as shown in Figure 1A (left). The image of the zeolite film at a higher magnification (×10) clearly reveals that the film consists of a monolayer of ZSM-5 crystals.

Upon switching from plain ZSM-5 crystals to those with tethered 3-chloropropyl (or any 3-halopropyl) groups, only the unmasked spots became covered with the monolayers of ZSM-5 crystals (Fig. 1B). Thus, these results verify that the above photochemical approach is an excellent procedure for transferring patterns for patterning glass plates with covalently assembled monolayers of zeolite crystals on glass as...
illustrated in Scheme 1 (paths I and II). The zeolite crystals become very tightly attached to the glass surface by calcination at 500°C.

We propose that such a facile patterning arises from the generation of either carbon- or silicon-based hydroxyl groups from the photodecomposition of IP groups in the atmosphere (Scheme 1, left). The vulnerability of iodoalkyl compounds to UV light and the established fact that the zeolite crystals with tethered 3-halopropyl groups on the surface assemble monolayers only on the surfaces of substrates covered with hydroxyl groups support the above proposal. The related, facile, UV-induced generation of silicon- and carbon-based hydroxyl groups from surface-bound phenyl and aminopropyl groups via siloxane linkages further supports the validity of the scheme in the left part of Scheme 1. Interestingly, it took longer periods of UV exposure to achieve a similar degree of patterning of ZSM-5 monolayers for less photosensitive functional groups such as 3-bromopropyl (>2 h) and 3-chloropropyl (>4 h) tethered to the glass plates. The difference in the rate suggests that the carbon–halogen bond cleavage serves as the initial step for the complete photochemical decomposition of the 3-halopropyl compounds.

We also explored patterning of continuous ZSM-5 films by direct dipping of the glass plates patterned with organic functional groups into the synthesis gel. We found that vividly patterned square ZSM-5 films (~70 μm), after the shape of the grid, are readily achieved by direct dipping of glass plates patterned with n-propyl (PR) groups into the synthesis gel (180°C, 3 h), as shown in Figure 2A. SEM images of the patterned films at higher magnifications revealed that the films are indeed continuous films of intergrown ZSM-5 crystals; a typical example is shown in Figure 2B. Therefore the “direct dipping” method differs from the “covalent assembly” method in that it produces patterned continuous films of intergrown crystals while the latter leads to patterned monolayers of highly oriented, closely packed, discrete crystals (Fig. 1A).

The patterned continuous zeolite films remain intact even after 10 min sonication in water, indicating that they bind to the glass plates very tightly. This result further elucidates the marvelous fact that the monolayers of PR, OD, and AP groups are highly effective for protecting the glass plates from the attack of a strong base even at 180°C.

3-Halopropyl groups, although they are effective for patterning covalently bound monolayers of ZSM-5, are less effective for the direct dipping method since they lead to blurring of the patterns. The blurring seems to arise from the vulnerability of the functional (3-halo) groups to strong bases in the synthesis gel, especially at high temperature (180°C). This explains why the basic AP groups efficiently protect the glass plates.

Interestingly, for AP groups to be used as inert protectors for clear patterning, the AP groups should be tethered to the glass plates via two alkoxy linkers, i.e., by use of (3-aminopropyl)diethoxymethylsilane (AP-DES). The use of the closely related three-alkoxy analog, i.e., (3-aminopropyl)triethoxysilane (AP-TES), only results in blurred patterns. This difference seems to arise from the tendency of AP-TES to result in multilayers of AP groups with inhomogeneous thickness on the glass plates via multiple siloxane linkages, whereas AP-DES gives only a monolayer, as pointed out recently.
The blurring is therefore likely to occur due to inhomogeneous photoinduced decomposition of the multilayers with inhomogeneous thickness during the given period (1 h) of irradiation.

Another interesting point to note is that the irradiation period of 1 h is long enough to achieve a very clear pattern of continuous zeolite film on the glass plates using PR, OD, and AP as the protecting groups, although the same period of irradiation is not sufficient to completely decompose the inert groups, as indirectly judged by an only slight decrease in the water contact angle of the glass plates with tethered PR (from 82° to 78°) after irradiation for 1 h. This contrasts with path II, which requires very clean HO-covered glass surfaces. This indicates that even partial photo decomposition of the inert functional groups is enough for clear patterning of the continuous thin films by direct dipping. In this respect, it can be said that photoinduced patterning is best suited for the direct dipping method.

Overall, this communication demonstrates that photo decomposition of organic functional groups tethered on glass substrates is a convenient, highly reproducible, reliable, and versatile approach to transferring patterns for patterning of zeolite films. This report also introduces a highly practical “direct dipping” method for patterning continuous zeolite films on glass plates.

**Experimental**

ZSM-5 crystals with average size 1.6 μm × 1.2 μm × 0.6 μm were synthesised with the molar ratio tetraethyl orthosilicate (TEOS)/tetrapropylammonium hydroxide (TPAOH)/NaAlO$_2$/H$_2$O = 0.8 : 0.1 : (0–0.08) : 50, where the composition of NaAlO$_2$ was 31–35% Na$_2$O and 34–39% Al$_2$O$_3$. TEOS was first introduced into TPAOH solution, followed by addition of sodium aluminate solution. The final clear gel was stirred for 2 h and transferred into an autoclave. The synthesis was carried out at 180°C for 24 h under constant stirring with a magnetic stirrer. The obtained ZSM-5 crystals were thoroughly washed with copious amounts of water and dried at 120°C for 3 h prior to use.

(3-Iodopropyl)trimethoxysilane (IP-TMS, Fluka), (3-bromopropyl)trichlorosilane (BP-TCS, Aldrich), (3-chloropropyl)trimethoxysilane (CP-TMS, Aldrich), (o-propyl)trimethoxysilane (PR-TMS, Aldrich), octadecytrimethoxysilane (OD-TMS, Aldrich), AP-TES (Aldrich), and AP-DES (Fluka) were used so that the water jacket did not absorb the 254 nm wavelength beam with the highest intensity in the UV region. No cutoff filters were used. The glass plates were placed 1 cm away from the water jacket, where the beam can homogeneously cover the glass plates. Irradiation continued for a given period of time.

A Teflon plate supporting two glass plates photopatterned with 3-halopropyl groups was introduced into a reaction flask containing a toluene slurry of dried plain ZSM-5 (30 mL, 20 mg). The mixture was refluxed for 3 h to induce covalent linkages between the surface hydroxyl groups of ZSM-5 crystals and the glass-bound 3-halopropyl groups. Independently, CP-tethered ZSM-5 crystals were prepared by refluxing (1 h) the toluene (30 mL) slurry of ZSM-5 crystals (100 mg) and CP-TMS (0.1 mL) contained in a small round-bottomed Schlenk flask under argon. The resulting glass plates patterned with covalently bound ZSM-5 crystals were sonicated in toluene for 2 min to remove physisorbed zeolite crystals over the covalently patterned monolayers of zeolite crystals.

The primary growth of continuous ZSM-5 or silicalite-1 film over the patterned glass plates was carried out by immersing several glass plates patterned with PR, OD, or AP groups into the aforementioned synthesis gel used for preparing the corresponding crystals. The autoclave was placed for 3 h in an oven at 180°C or for 12 h at 120°C. The resulting patterns were analyzed by a field emission scanning electron microscope (Hitachi S-4300).

Received: November 20, 2000