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Zeolite Coatings on Three-Dimensional Objects via Laser Ablation

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We have recently shown that pulsed laser deposition (PLD)[1] can be used to generate thin films of zeolite molecular sieves.[2−7] In some cases highly oriented zeolite films may be prepared.[6,7] The application of such zeolite films as membranes for catalysis or separations might require a nonplanar configuration. However, there are relatively few examples of three-dimensional objects that have been coated with zeolite films. Zeolite Beta has been grown onto macroporous alumina spheres with a 4% loading by immersing the support in a synthesis mixture.[8] Similarly, metal and ceramic monoliths were also coated with zeolite Beta, Mordenite, and ZSM-5 by this technique.[8] Zeolite films prepared by direct deposition of crystals from solution often suffer from defects and poor adhesion. Additionally, controlling film thickness and orientation are a challenge. In contrast, zeolite films derived from PLD are generally well-adhered and continuous, with reasonable control over thickness. Coating large nonplanar surfaces by PLD can be achieved by manipulating the object in the plume or by directing the plume.[1] However, small three-dimensional (3-D) objects (smaller than a few millimeters) would be difficult to mount and evenly coat by PLD. Therefore, we have developed a simple method for moving small nonplanar substrate surfaces within the plume generated by striking target materials with an excimer laser beam.

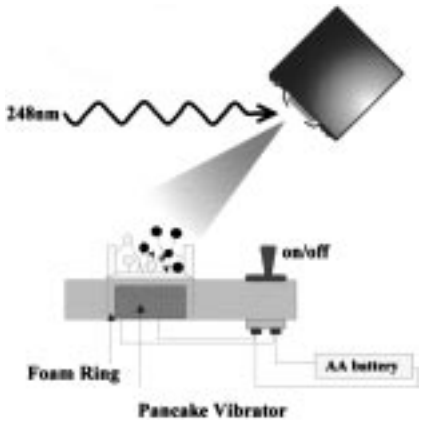

Figure 1. Apparatus for coating three-dimensional objects by laser ablation.

In this paper we report a technique for coating small three-dimensional objects with molecular sieves using pulsed laser deposition and a novel vibrating substrate holder. The molecular sieve used in this study is the all-silica zeolite UTD-1. The structure of UTD-1 involves a one-dimensional channel system having pores defined

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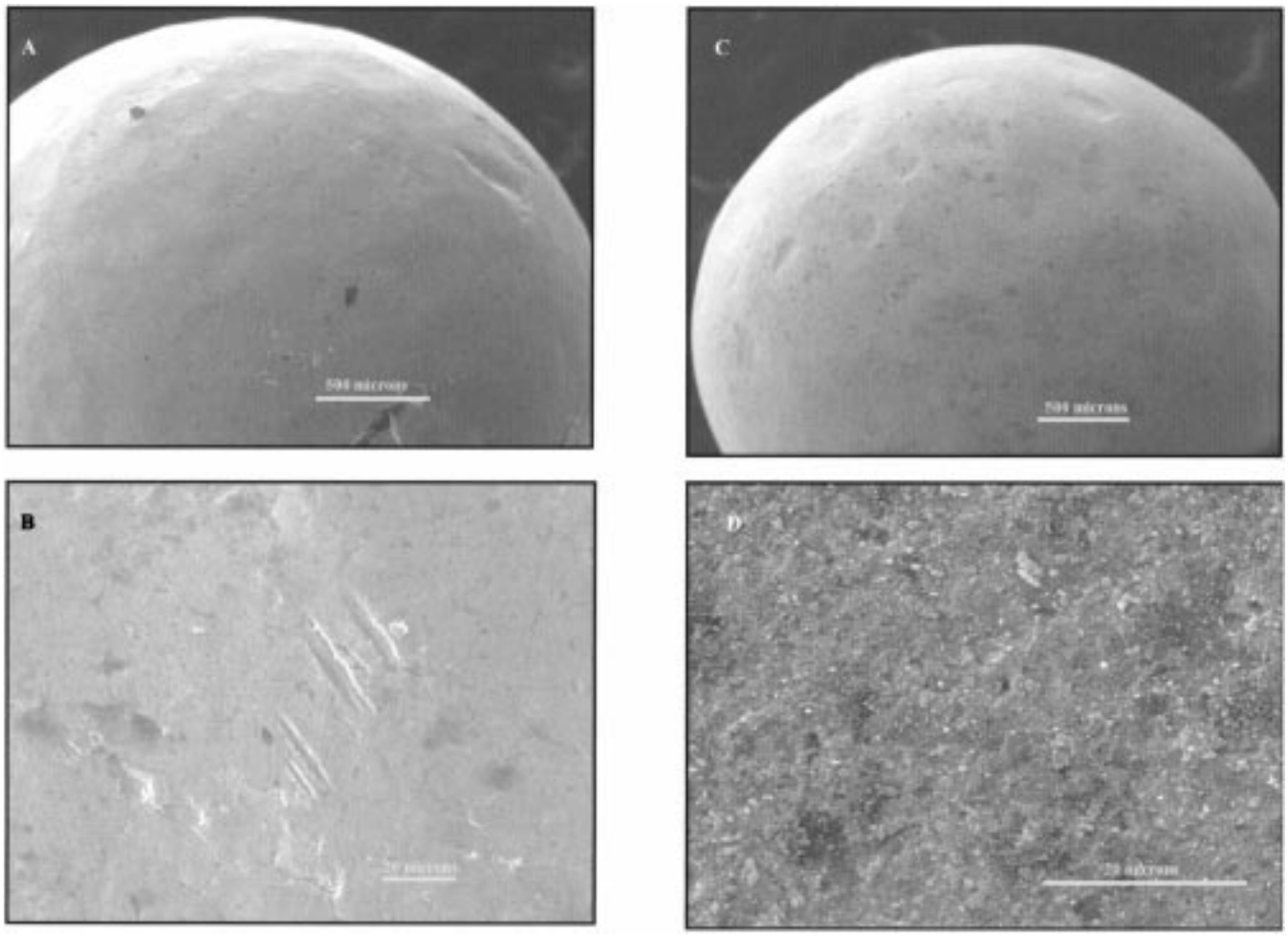

Figure 2. Scanning electron micrographs of (A) metal ball substrate and (B) surface close-up before coating; (C) PLD UTD-1 on a metal ball, and (D) a close-up view of the surface.

by 14 silicon atoms with dimensions of 10 × 7.5 Å.[9−13] Oriented membranes of UTD-1 have shown promise in gas separations[14] and catalytic oxidations. The UTD-1 target material was prepared as previously reported using bis(pentamethylcyclopentadienyl)cobalt(III) hydroxide, Cp^*_2CoOH, as the structure-directing agent.[11,12] A 2.5 cm pressed pellet of as-synthesized UTD-1 was mounted in a controlled atmosphere chamber and irradiated using a pulsed 248 nm laser beam under conditions previously reported.[6,7] The substrates used in this study were spherical, zinc-galvanized, coated stainless steel buck shot pellets (Winchester) measuring 0.5 mm in diameter. To evenly coat these 3-D objects, a special apparatus was designed to elevate the metal balls into the UTD-1 plume. Figure 1 shows a representation of this apparatus which consists of a glass dish (∼2.5 cm diameter and ∼1 cm deep) attached to a 8.25 × 3.2 cm steel plate. This plate sits directly on top of a pancake vibrator that is insulated by a foam ring. The single speed vibrator is controlled by an on/off switch attached to the steel plate and is powered by a AA battery. The vibrator apparatus is mounted on a 15 × 7.5 cm steel pipe (not shown), approximately ∼2.5 cm from the target, which maintains the substrate holder in a horizontal position. The directional nature of the laser-generated plume allows substrates to vibrate in the plume and become evenly coated. We have examined objects that range in size from 75 μm to 1 mm and they can all be effectively coated with this setup. Typical experimental conditions are as follows: laser power, 70−156 mJ/pulse; repetition rate, 10 Hz; substrate temperature, 25−60 °C; and a background pressure of 150 mTorr, which results in a deposition rate of ∼70 nm/min.

Parts A and B of Figure 2 show scanning electron micrographs of the metal spheres at different magnifications, which reveal a fairly smooth surface. After pulsed laser deposition of UTD-1 for 13 min, a uniform coating 0.9 μm thick is obtained on the balls vibrating in the plume, as shown in Figure 2C,D. This PLD film is mostly amorphous to X-rays, which is the same as for flat substrates. Therefore, the PLD UTD-1 films were hydrothermally treated by placing the metal balls in a Teflon-lined Parr reactor containing a UTD-1 synthesis gel mixture having a molar ratio of 1:0.05:0.1:60 SiO_2:Na_2O:$Cp^*_2Co^+$:H_2O. The reactor was heated at 175 °C

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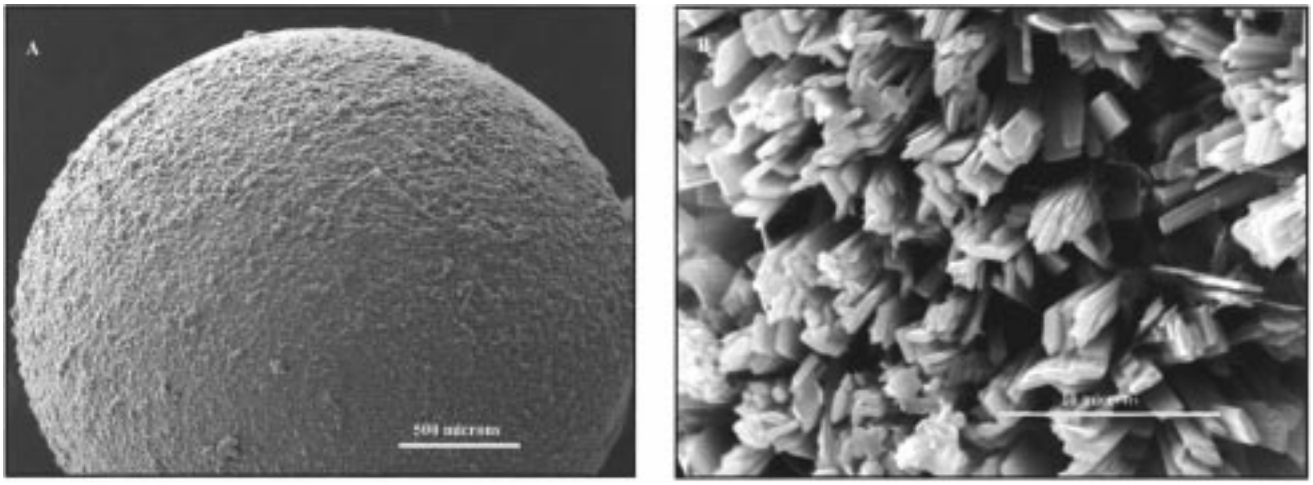

Figure 3. Scanning electron micrograph of (A) PLD UTD-1 on the metal bead after hydrothermal treatment and (B) a close-up view of the surface.

for 72 h under static conditions. The reorganized UTD-1-coated beads were isolated, washed with deionized water, and dried at room temperature. The resulting three-dimensional substrates were evenly covered with a film ~14 μm thick of highly crystalline UTD-1, as shown by the SEM images in Figure 3A,B. It would appear that the UTD-1 crystals, which have a planklike morphology, radiate up from the laser-deposited surface. This is the preferred orientation, because the one-dimensional zeolite channels run in parallel along the length of the planks (*b*-axis), which appear to be normal to the surfaces of the spheres. XRD analysis of these films confirms the phase identity of UTD-1, but the X-ray pattern (not shown) does not reflect the preferred orientation, because of the curvature of the surface. The mechanism for achieving the preferred orientation is under investigation, but the tightly packed UTD-1 fragments in the PLD layer coupled with preferential growth in the *b*-direction clearly lead to films with pores perpendicular to the substrate surface. The well-adhered film achieved by PLD in a heated oxygen atmosphere probably reflects some bonding through an oxide layer at the substrate/zeolite interface. This would appear to be the first example of a 3-D object coated with an oriented zeolite film derived from pulsed laser ablation. It should be noted that the PLD film is required for formation of the well-adhered, continuous, oriented UTD-1 coating. If blank metal spheres are placed in the same synthesis gel described above, then only loosely bound and scattered clusters of randomly oriented UTD-1 crystals deposit on the metal surface. There is no evidence yet that thermal or chemical pretreatment of the bead surface alters these results. This suggests that the seeded[15] or other synthesis methods[16] are not likely to produce continuous oriented UTD-1 coatings on spherical surfaces. The PLD method is distinctly different in that the initial coating is composed of zeolite fragments that act as nuclei where, upon reorganization under conditions that might not form a zeolite in the bulk, a highly crystalline and oriented film is obtained.

Although nonplanar objects such as the inside of tubes have been coated by laser ablation,[1] our vibrator assembly is convenient for preparing zeolite films on the outer surface of small 3-D objects. By way of example, we have prepared the first oriented UTD-1 films on a 3-D metal surface. This technique has been extended to other metal, glass, and ceramic particulate substrates as well as zeolite crystals as substrates.[17] We anticipate many applications for these zeolite-coated objects in areas such as separations and catalysis, where one could envision columns packed with zeolite-coated beads. Additionally, new types of reactivity might be realized from zeolites or other catalysts coated with a different zeolite layer, especially if preferred orientation can be achieved.

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