272g Fabrication of Zeolite Films Using Layer-by-Layer Depositions

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High quality zeolite films have been successfully synthesized in the last decade using hydrothermal crystallization based methods such as in situ[1] and seeded growth.[2] However, the hydrothermal process is usually very corrosive, time-consuming and costly. Here we report an alternative way to fabricate zeolite films using Layer-by-Layer depositions. In this method, thin plate-like zeolite tiles are self-assembled on substrate surface in a preferential orientation. The deposition conditions are optimized to achieve that each layer is almost a close-packed monolayer. Intercrystalline gaps are closed by overlapping between layers. Since the thickness of each zeolite tiles is very thin, so the overall thickness of the film after several depositions can be still kept in sub-micrometer range. Therefore, a thin, compact and oriented zeolite film can be achieved using this Layer-by-Layer deposition method. The zeolite we chose to demonstrate this idea is MCM-22. The precursor of zeolite MCM-22, namely MCM-22(P), is a layered aluminosilicate.[3] Layers in the as-synthesized MCM-22(P) are weakly linked together with organic structure directing agents, Hexamethyuleneimine (HMI), along the [001] direction. Two-dimensional 12MR, i.e. defined by twelve interconnected SiO4 tetrahedra, channels are running in-plane of the MCM-22(P) layers. However, the limiting apertures for transport perpendicular to the layers (along [001] direction) are 6MR's. Thus, molecules like water and O2 cannot penetrate along the c-axis. Upon calcination, MCM-22(P) condenses to MCM-22. On the other hand, layers in MCM-22(P) can be delaminated.[4] After calcination, it forms another material called ITQ-2. Either the MCM-22(P) or MCM-22 particles we synthesized have plate-like shapes with thickness of about 50 nanometers and diameter of about 1 micrometer. The thinnest dimension is along the c-axis. Delaminated layers in ITQ-2 were even thinner. These particles were deposited on substrate surfaces using methods as described in literature.[2,5,6] In these methods, the first layer of zeolite particles are covalently bonded to the substrate surface, while other physically adsorbed top layers are removed by sonication. With these methods we have successfully prepared thin, compact and highly c-oriented MCM-22 films on aluminum alloy Al-2024-T3 surfaces for corrosion protection. The film fabrication procedure, characterization results by XRD, SEM, TEM, etc., and their corrosion performance will be presented.

Citations [1] Yan, Y. S.; Davis, M. E.; Gavalas, G. R. Preparation of Zeolite ZSM-5 Membranes by In-situ Crystallization on Porous a-Al2O3. Ind. Eng. Chem. Res. 1995, 34, 1652-1661. [2] Lai, Z. P.; Bonilla, G.; Diaz, I.; Nery, J. G.; Sujaoti, K.; Amat, M. A.; Kokkoli, E.; Terasaki, O.; Thompson, R. W.; Tsapatsis, M.; Vlachos, D. G. Microstructural Optimization of a Zeolite Membrane for Organic Vapor Separation. Science 2003, 300, 456-460. [3] Leonowicz, M. E.; Lawton, J. A.; Lawton, S. L.; Rubin, M. K. MCM-22 - A Molecular Sieve with 2 Independent Multidimensional Channel Systems. Science 1994, 264, 1910-1913. [4] Corma, A.; Fornes, V.; Pergher, S. B.; Maesen, T. L. M.; Buglass, J. G. Delaminated Zeolite Precursors as Selective Acidic Catalysts. Nature 1998, 396, 353-356. [5] Ha, K.; Lee, Y. J.; Lee, H. J.; Yoon, K. B. Facile Assembly of Zeolite Monolayers on Glass, Silica, Alumina, and Other Zeolites Using 3-Halopropylsilyl Reagents as Covalent Linkers. Adv. Mater. 2000, 12, 1114-1117. [6] Lee, J. S.; Ha, K.; Lee, Y. J.; Yoon, K. B. Ultrasound-aided Remarkably Fast Assembly of Monolayers of Zeolite Crystals on Glass with a Very High Degree of Lateral Close Packing. Adv. Mater. 2005, 17, 837-841.