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An overview of highly porous oxide films with tunable thickness prepared by molecular layer deposition

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ABSTRACT

This paper is a short review about the principle, preparation, and applications of ultra-thin oxide films prepared by molecular layer deposition (MLD). Porous oxide films, with well-defined porous structures and precisely controlled thicknesses down to several angstroms, can be prepared from dense organic/inorganic hybrid polymer films grown by MLD. The organic constituents in the film can be removed either by calcination at elevated temperatures or mild water etching at room temperature. Because of the layer-by-layer growth process for MLD, the deposited polymer films have regular structures and the removal of organic components from MLD polymer films produces uniform interconnected highly porous structures with a high surface area. For example, porous aluminum oxide films prepared by such a method have both micropores and mesopores with a BET surface area as high as 1250 m^2/g. Examples of the versatility of the technique for fabrication of novel functional materials for various applications are discussed, including thermally stable, highly selective metal nanoparticle catalysts, defect-free inorganic membranes for gas separation, and photocatalytic layers prepared from titanium alkoxide MLD films.

Introduction

Porous thin films/coatings have wide applications in separations [1], corrosion protective coatings [2], drug delivery [3,4], and catalyst encapsulation for controlling reaction selectivity and maintaining catalytic activity [5]. Porous films are generally prepared by template-directed synthesis. In order to create porous structures, organic templates must be removed gently by calcination at high temperature. Inorganic films/coatings with few defects, such as zeolite membranes and mesoporous films, have been prepared by hydrothermal synthesis [6] and sol–gel methods [7]. While these films/coatings have well defined uniform porous structures, it is difficult to control their thickness with the precision of angstroms. Many techniques, such as the chemical vapor deposition method (CVD) and the Langmuir–Blodgett method have been developed for fabricating polymeric thin films. However, these methods cannot control the order and location of molecular compounds on substrate surfaces. Also, they cannot precisely control the film thickness, especially when it falls within the range of nanometers, which may inhibit the desired functionality of the coatings. Atomic layer deposition (ALD) has the capability of growing films with precise atomic layer control [8,9]. Molecular layer deposition (MLD) [10–13] is similar to ALD and is also based on sequential, self-limiting surface reactions. In this process, molecules are stacked on substrates one by one in order of preference. The MLD technique offers the same advantages for polymer film deposition as ALD does for ceramic films [10,14–16]. In addition, MLD can deposit hybrid polymer films using suitable precursors [17], such as trimethylaluminum (TMA) and ethylene glycol (EG) for aluminum alkoxide (alucone) hybrid polymer. This vapor-phase method, which operates at reduced pressure and does not require solvents or catalysts, is a useful and promising technique for the fabrication of functional ultra-thin polymeric layers. Porous metal oxide films with well-defined porous structures and precisely controlled thicknesses down to several angstroms can be prepared from dense organic/inorganic hybrid polymer films grown by MLD.

There has been increased interest in fine particles in a variety of fields for different applications [18–20]. As new systems are studied, there have been increasing numbers of new applications with the ability to modify the surface of particles with thin porous films, which can add new surface functionalities and keep the bulk properties of the particles largely the same. For example, porous nanocoatings on fine capsules can modify drug release characteristics and provide physical and chemical protection for the drugs [3,4]. MLD is an ideal technique for depositing conformal films on particle substrate surfaces with precise thickness control. CVD

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processes cannot be adequately performed on submicron-sized particles due to the tendency of these particles to aggregate. In this review, ultra-thin porous metal oxide films coated on particles by MLD, and applications of such porous films will be discussed.

MLD thin film coating on particles

MLD growth has been demonstrated for a variety of pure organic polymers, such as polyimide [10], polyamide [21–23], polyimide–polyamide [24], polyurea [25,26], and polythiourea [27], as well as hybrid organic–inorganic polymer films, such as alucone [16,28,29], zinc alkoxide (zincone) [15,30], titanium alkoxide (titanicone) [31], and zirconium alkoxide (zircone) [32]. Many challenges are encountered during MLD with large quantities of fine particles. First, the native cohesive properties of the nanoparticles will form agglomerates that are several times larger than the primary particles [33,34]. Therefore, the particles need to be fluidized or agitated to perform the MLD surface reactions in reasonable times and to prevent the particles from being aggregated by the MLD polymer film. Second, it is difficult to deliver the low vapor pressure, bulky organic monomer precursors to the reaction chamber and to subsequently remove the relatively sticky bifunctional monomers from the primary nanoparticle surfaces. Sufficient reactant flux can be obtained by preheating the organic precursors; however, they tend to decompose more at lower temperatures than typical ALD precursors do. Third, polymer films fabricated by MLD have more of a tendency to stick than those ceramic films fabricated by ALD, which may increase particle aggregation during the MLD coating process.

Fluidized bed reactors (Fig. 1) are inherently scalable and provide for intimate contact between solids and gases [33–38]. They have been demonstrated to provide for the ALD coating of primary fine particles, including nanoparticles [39,40]. Further, *in situ* mass spectrometry [40] has shown that virtually 100% of chemical precursors (essentially no waste) can be used for many ALD reactions, thereby, providing a low cost and highly efficient process to functionalize fine particle surfaces. As shown in Fig. 2, alucone MLD can

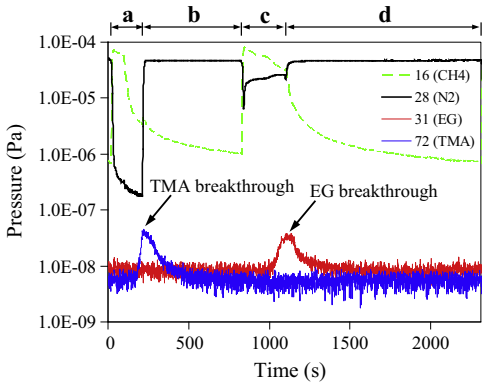

Fig. 2. *In situ* mass spectrometry results during one complete alucone MLD cycle: (a) TMA dose, (b) N_2 purge, (c) EG dose, and (d) N_2 purge. There were 10 s of evacuation between the N_2 purge and the precursor dose. Reprinted with permission from Ref. [41].

be carried out with minimal waste of unreacted precursors [41]. Here, alucone MLD is used as an example to demonstrate this powerful technique. The proposed AB MLD half-reactions between TMA (precursor A) and EG (precursor B) are listed as follows:

$$\text{A}: \ \text{S-OH}^* + \text{Al(CH}_3)_3 \rightarrow \text{S-OAl(CH}_3)_2^* + \text{CH}_4 \quad (1)$$

$$\text{B}: \ \text{S-AlCH}_3^* + \text{OHCH}_2\text{CH}_2\text{OH} \rightarrow \text{S-AlOCH}_2\text{CH}_2\text{OH}^* + \text{CH}_4 \quad (2)$$

where the asterisks indicate the surface species. The expected reaction product is CH_4. The *in situ* mass spectrometry results of alucone MLD on silica particles at 100 °C, shown in Fig. 2 [41], indicate that the chemistry of TMA and EG MLD was self-limiting, which is similar to ALD chemistry. When TMA was dosed into the reactor, there was an instantaneous increase in the CH_4 byproduct. It is clear that all TMA entering the reactor was completely utilized until the time at which the TMA signal increased. This is called the "breakthrough" time. Evidence that supports complete surface conversion

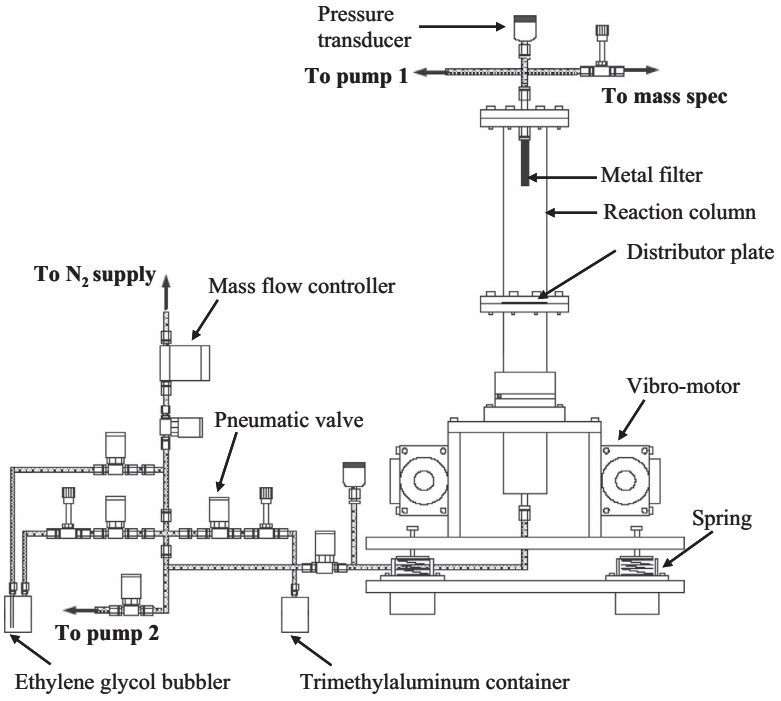

Fig. 1. Schematic of the MLD fluidized bed reactor. Reprinted with permission from Ref. [41].