4th International Symposium on
Energy Challenges & Mechanics
- working on small scales

11-13 August 2015
Aberdeen, Scotland, UK

Atomic Layer Deposition of Zinc Glutarate Thin Films

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Accepted for publication on 28th March 2015

The depleting crude oil reservoirs have made the search for renewable carbon based raw materials an important topic. Using CO_2 as a precursor in polycarbonate synthesis is very attractive environmentally and economically. However, the copolymerization reaction of CO_2 with epoxides requires a catalyst with high activity to overcome the high thermodynamic barrier. Current industrial systems rely mostly on zinc-dicarboxylate systems, including zinc glutarate (ZnGA), making them one of the most studied catalyst groups. It is known that despite the intrinsic porosity of ZnGA, catalytic activity is restricted to the outer surface. Thus, one approach to increase the catalytic activity has been the use of high surface area substrates for ZnGA.

Atomic layer deposition (ALD) is an advanced thin film deposition method. It relies on saturative surface reactions of gaseous precursors supplied alternately onto the substrate and separated by inert gas purging. This enables self-limiting film growth leading to good control over film thickness, perfect step coverage and large area uniformity even on complicated 3D substrates. Originally ALD research concentrated mainly on inorganic materials but in recent years the deposition of organic polymers has gained attention. Combining inorganic and organic ALD is an easy way for depositing inorganic-organic hybrid materials. Thus, ALD could provide a convenient way for coating high surface area substrates with ZnGA to be used as CO_2 copolymerization catalysts. Furthermore, ZnGA coated monolithic catalysts would be more straightforward to reuse.

In this work we have studied the feasibility of depositing ZnGA thin films by ALD. Zinc acetate and glutaric acid were used as the precursors. The films deposited at 200 °C were crystalline as-deposited. GIXRD revealed a structure matching closely to bulk ZnGA. Characteristic features of ZnGA were also seen in FTIR spectra. Finally, to assess the catalytic activity of the films, steel mesh was used as the substrate. The ZnGA coated mesh was used as the catalyst in the copolymerization of propylene oxide with CO_2. Despite the relatively low surface area of the substrate, the catalytic activity of the material was verified.

Keywords: ALD; zinc glutarate; catalysis; carbon dioxide