

OXIDATIVE DECOMPOSITION OF CELLULOSIC MATERIALS

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INTRODUCTION

There are several ways in the literature to break down cellulose for future fuel and chemical production, such as acid breakdown using mineral acids, enzymatic hydrolysis, pyrolysis, and reductive hydrolysis by precious metals under high pressure. The disadvantages of these processes include large waste production, high energy input and low product selectivity. In this project, our interest is to oxidatively break the glycosidic (C-O-C) bond connecting the two glucose moieties in cellulose using specific probe molecules that can be reacted in the gas phase. The goal is to minimize the breakage of non-glycosidic bonds including the C-C and C-OH bonds as well as the C-O-C bond contained in the glucose ring. The probe molecules which mimic some of the characteristic of the glycosidic bond in cellulose have sufficiently high vapor pressures to allow investigating their reactivity in the gas phase. The specific focus of this project is to investigate the selectivity and reactivity of supported metal clusters with sub-nanometer dimensions in the conducted reactions.

EXPERIMENTAL

The catalytic membrane samples were synthesized by Atomic Layer Deposition (ALD) method beginning with nanostructured templates consisting of anodic aluminum oxide (AAO) membranes having an integral aluminum metal ring around the perimeter. These AAO membranes are then coated using ALD to have a series of functional layers. The first layer consists of 1 nm Al₂O₃. This layer serves to cover the aluminum oxalate impurities that remain in the walls of the AAO pores following the anodization. Next, a layer of 2 nm ZnO is applied to render the membranes electrically conducting. This conductivity is extremely helpful for the catalysts prepared by Cluster Deposition (CD), because it allows the catalyst coverage to be quantified in situ by recording integrating current of the cluster beam ions. Finally, the catalyst support layer is deposited by ALD for vanadia, cobalt oxide, Pd, or Pt, and the catalyst loading was controlled by the number of ALD cycles performed. Catalysts made by CD method were produced by depositing a narrow distribution of cobalt cluster sizes on by alumina pre-coated AAO membranes.

In catalytic testing, 1-methoxy-2-methyl-2-propanol (MMP) was chosen as a model compound. The reactions were

conducted in a gas mixture of 4%MMP-2%O₂-4%H₂O-He at 1 atmosphere. Gas composition was analyzed by an on-line GC with a TCD detector. At each temperature the reaction was held for 1h and the condensed liquid products (ice bath) were analyzed by GC-MS.

RESULTS

We have conducted catalytic testing over several samples prepared by ALD technique and size-selected CD technique on AAO membranes for the oxidative decomposition of MMP. The support effect (Al₂O₃, ZnO), metal effect (Pd, Pt, VOx, Co) and preparation effect (ALD and CD) were investigated for this reaction.

Three major products were identified by GC-MS in the condensed liquid phase after reactions. C-O-C bond breakage is involved in all three proposed reaction pathways. Selectivity patterns over these products vary depending on the nature of the catalysts.

In addition to well defined size of the nanocatalysts, cluster deposition possesses another advantage, namely the precise control of the location of the catalytic particles at the entrance or at the exit of the nanochannels of the membrane. The latter enables straightforward studies of the effect of the contact times on catalytic performance and tuning selectivity.

Both ZnO and Al₂O₃ supports are not active in the formation of either 1,2-butanediol or 3-hydroxy-2-butanone. Overall, ZnO is a better support than Al₂O₃ for 2, 3-butanedione formation. Even though Pt and V have significant activity in the reaction, gas product analysis shows that Pt facilitates the combustion reaction in higher extent. Reaction conditions have to be modified for Pt to minimize the deep oxidation reaction.

Among Pd, V, Co, and Pt metals, Pd is not active for all three reaction pathways up to 300°C on both alumina and zinc oxide supports.

Different from monolayer Co₃O₄ prepared by ALD, small Co clusters produced from CD favor the production of acetone and 1,2-butanediol but inhibit 2,3-butanedione totally. Furthermore, at high reactivity, product selectivity is changed by placing the Co₁₇₋₃₂ clusters at exit or entrance of the Al₂O₃/ZnO/AAO membrane, indicating the effects of re-adsorption versus single touches as far as catalyst selectivity concerns.

ACKNOWLEDGMENTS

This work was supported by the U.S. Department of Energy's Laboratory Directed Research and Development (LDRD) program.