

## Oxidative Decomposition of Cellulosic Materials

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### Introduction

Renewable biofuel and chemical production from degradation of biomass such as cellulose is one of the alternative energy supplies<sup>1-3</sup>. Cellulose is composed of hundreds to thousands of glucose monomer units, linked together by beta-1, 4- glycosidic bonds. There are several ways in the literature to break down cellulose for future fuel and chemical production, such as acid hydrolysis using mineral acids<sup>4, 5</sup>, enzymatic hydrolysis<sup>6-8</sup>, gasification<sup>9</sup>, and reductive hydrolysis by precious metals under high pressure<sup>3</sup>. The disadvantages of these processes include large waste acid production, high energy input and low product selectivity. Our interest is to oxidatively break the glycosidic (C-O-C) bond connecting the two glucose moieties using specific probe molecules that can be reacted in gas phase. In our work, the probe molecule is 1-methoxy-2-methyl-2-propanol, which mimics the characteristic of the glycosidic bond in cellulose and has sufficiently high vapor pressures to allow conducting reactions in 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.

### Materials and Methods

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 were then coated using ALD to have a series of functional layers. The catalyst support layer was deposited by ALD for V<sub>2</sub>O<sub>5</sub>, Co<sub>3</sub>O<sub>4</sub>, Pd, or Pt, and the catalyst loading was controlled by the number of ALD cycles performed. Catalysts made by cluster deposition (CD) method were produced by depositing a narrow distribution of cobalt cluster sizes on 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%O<sub>2</sub>-4%H<sub>2</sub>O-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 and Discussion

Catalytic experiments were conducted over several samples prepared by ALD and CD technique on AAO membranes for the oxidative decomposition of MMP. The support effect (Al<sub>2</sub>O<sub>3</sub>, ZnO), metal effect (Pd, Pt, VOx, Co) and preparation effect (ALD and CD) were investigated. Product identification by GC-MS confirmed that C-O-C bond breakage was seen

in reactions over these catalysts. Pt catalyst ranked as the most active in the MMP decomposition but half of the oxygen was used to do the combustion reaction. Table 1 lists the most selective catalysts in this work for each of the five products we saw in the reactions. In addition to well defined size of the nanocatalysts, cluster deposition technique 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. This enables straightforward studies of the effect of the contact times on catalytic performance and tuning selectivity. As seen in Table 1, product distribution is changed by placing the Co clusters at exit or entrance of the Al<sub>2</sub>O<sub>3</sub>/ZnO/AAO membrane, indicating the effects of re-adsorption versus single touches as far as catalyst selectivity concerns.

**Table 1. Product distribution in oxidative decomposition of MMP.**

Catalyst	Production rate ( x 10 <sup>-8</sup> mol/s)				
	Acetone	Methanol	2,3-Butanedione	1,2-Butanediol	3-hydroxy-2-butanone
300°C					
4 cycles VOx/ZnO (ALD)	0	0	10	3.7	2.5
2 cycles Pt/ZnO (ALD)	36	14	0	12	7.2
Co/Al <sub>2</sub> O <sub>3</sub> (CD) (gas exit)	4.4	4.9	2.9	13	40
Co/Al <sub>2</sub> O <sub>3</sub> (CD) (gas entrance)	31	18	0	5.2	14
1cycle Co <sub>3</sub> O <sub>4</sub> /Al <sub>2</sub> O <sub>3</sub> (ALD)	6.3	3.3	6.3	1.8	11

Reaction condition: 4%MMP-2%O<sub>2</sub>-4%H<sub>2</sub>O-He; total flow rate: 30ml/min.

ALD-prepared cobalt sample has very different catalytic activity from the CD-prepared sample, which is correlated with their structure/composition. These results as well as characterization data from SEM, EXAFS, and ICP will be discussed in the presentation.

### Significance

This is the first work to investigate C-O-C bond breakage in an oxidizing gas condition by heterogeneous catalysis.

### References

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