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Conversion of Ethanol to 1,3-Butadiene

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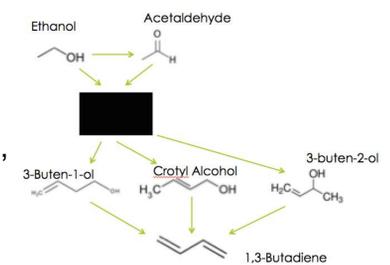
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Introduction

Since its discovery in the 19th century, synthetic rubber has gradually overtaken natural rubber and became one of the most popular polymers in the world. Presently, steam cracking of petroleum naphtha remains the most popular and cost-efficient manufacturing process of its precursor, 1,3-butadiene. Alternative methods are actively being researched due to the unsustainability of the oil industry.

Gaseous ethanol, acetaldehyde, or a combination were reacted over a catalyst under TPSR conditions. The gas product was fed into a mass spec to track the production of 1,3-butadiene, the reactants leading up to 1,3-butadiene at various temperatures, and the various side products. Deuterated reactant experiments are able to theoretically track hydrogens in the molecules to allow easier deciphering of the reaction mechanism. DRIFTS was done under similar conditions in attempt to determine the reaction mechanism. DFT was also used to simulate the catalyst surface.

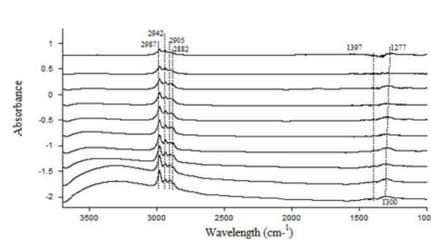
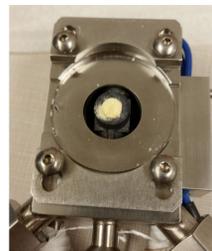
Mechanism



Methods

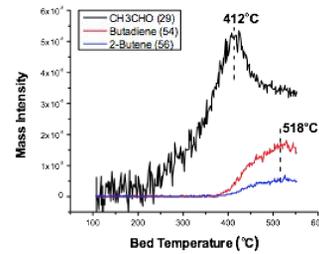
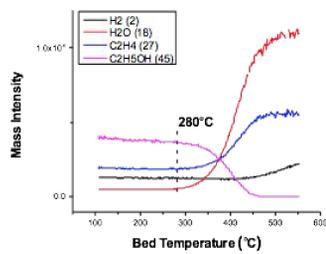
In-Situ DRIFTS

Catalyst was loaded into the reaction chamber and pretreated at 500°C for 1 hr. Then the reactant is adsorbed onto the surface of the catalyst and the temperature was ramped by 10°C/min until 450°C either under continuous flow of reactants or under a stream of nitrogen. SiO₂ with 3% and 10% ZrO were used as the catalysts and ethanol and acetaldehyde were used as reactants. IR Spectra were taken every minute. Key spectra were plotted against each other.



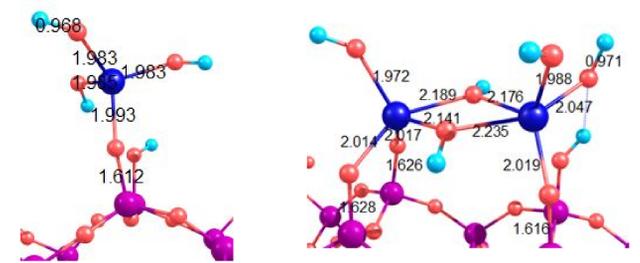
TPSR

Temperature Programmed Surface Reactor (TPSR) ramps up the temperature by 10°C/min up to 550°C to track the production and consumption of molecules at certain temperatures. Reactive gas (ethanol, acetaldehyde, or both) is flowed over the catalyst. The catalysts used are 3ZrSiO₂, 10ZrSiO₂, and 5Zn10ZrSiO₂. Deuterated ethanol and acetaldehyde were also reacted to track the deuterium in order to see what the key reactants are.

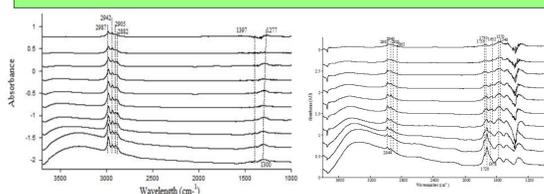


DFT

DFT was done to simulate the surface geometry of the zirconia cluster on the silica surface. Gas phase zirconia were simulated to determine the coordination of adsorbed Zr atoms and cluster size. Physisorbed states and adsorbed states were simulated to determine the cluster orientation and its optimal bonding scheme of the cluster onto the surface.

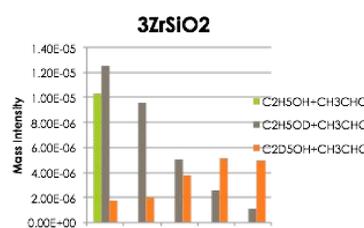
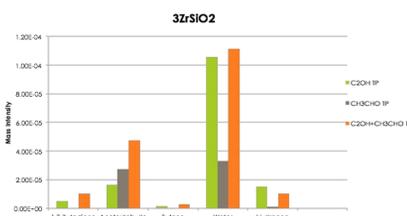


Results



No reaction from surface or gas phase ethanol or acetaldehyde alone. The only peaks seen on the surface when only ethanol was reacted are peaks due to surface carbonates. A small amount of acetaldehyde seems to have combined into 2-butenal.

□ C₂D₅OH+CH₃CHO produces high amounts of C₄H₃D₃. C₄H₃D₃ has 1:1 ratio of H:D → the D came from ethanol and the H came from CH₃CHO.



Extremely low yield of 1,3-butadiene for CH₃CHO shows that Ethanol and Acetaldehyde are needed for 1,3-BD.

The most stable arrangements of the single and dimer ZrO cluster are determined by DFT. Bond angles and bond lengths are also found and tabulated

ZrO _n H _m *	Energy (eV)	Coordination	Bond Length (Å)
ZrO ₄ H ₄ *	-15232.85	0	Zr-O-Zr 112-114
ZrO ₃ H ₃ *	-14893.47	10.45	Zr-OH 1.95-2.05
Zr ₂ O ₈ H ₈ *	-16547.65	0.00	Zr-OZr 2.10-2.25
Zr ₂ O ₆ H ₆ *	-15882.45	7.32	Zr-OSi 1.95-2.05
Zr ₂ O ₅ H ₅ *	-15553.73	7.10	ZrO-Si 1.60-1.62
Zr ₂ O ₄ H ₄ *	-15220.50	11.39	Zr=O 1.80-1.82

Conclusions and Future Work

TPSR data shows that with a 10% ZrO impregnated SiO₂ catalyst and under the presence of acetaldehyde, the conversion occurs at a much lower temperature and yields the most butadiene. DRIFTS data shows that the reaction occurs in neither only the gas phase nor the catalyst surface, and that the reaction only proceeds when the reactants exist at both locations. Finally, DFT data shows that singular and dimer ZrO sites exist on the catalyst surface in 4 and 5 fold coordination to facilitate the reaction. Future research will use DRIFTS to study the steady state conversion of ethanol at temperatures and conditions previously determined by TPSR. DFT will be used to simulate the reaction mechanisms to compare with DRIFTS data and to calculate the reaction's energy barriers.

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Gao, Xingtao, PhD, JL G. Fierro, PhD, and Israel E. Wachs, PhD. "Structural Characteristics and Catalytic Properties Of Highly Dispersed ZrO₂/SiO₂ and V₂O₅/ZrO₂/SiO₂ Catalysts." *Langmuir* 15 (1999): 3169-178. Web. 7 Aug. 2015.



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