Reaction of Ethylene with Nucleophiles on Titania

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Introduction

Ethylene adds to a nucleophile resulting in its chain growth. This possibility is exploited in producing higher alcohols from ethanol. This is of particular importance since higher alcohols (such as 1-butanol) results in higher yields of gasoline compared to when either methanol or ethanol were reacted over H^+/ZSM-5 [1]. Since ethanol can be produced from syngas on Rhodium based catalysts [2,3], a bi-functional rhodium and titania catalyst could produce butanol directly from syngas combined with ethylene. It is quite novel that polycrystalline Titania, a base catalyst with a few Lewis acid sites should be able to, both dehydrate ethanol and also catalyze nucleophilic addition of ethylene to ethanol resulting in 1-butanol. But there is evidence in the literature that ethanol can be produced by a vapor phase hydration of ethylene over a tungsta monolayer promoted on Titania [4].

Materials and Methods

Ethanol (Fisher brand) was used on poly crystalline Titania (Fisher brand) as a nucleophile. Some of the initial reactions are performed in 425 ml batch reactor (Parr Inst.) and further reactions are performed in a ½" diameter flow reactor. The reactions in the flow reactor are performed with packed bed configuration of catalyst. The reactions are performed both in the presence of and the absence of ethylene (Nexair). The characterization of the catalyst surface area (multipoint BET with N_2 adsorption) and pore volume distribution were performed by Micromeritics, Inc (Norcross, GA). Gas Chromatography with Flame Ionization Detector (GC_FID) (Agilent) was used for sample analysis.

Results and Discussion

When ethanol was reacted on Titania at 350^{o}C in a batch reactor in inert atmosphere of He, butanol, 1-methyl propanol formation were observed (see Fig 1). Also, some ethyl ether, 1,1 diethoxyethane and ethyl acetate were also formed. But conversion of ethanol was quite low, <5%. This led to further reactions of ethanol on Titania in a flow reactor at different temperatures and pressures. Since we propose that ethanol would dehydrate to ethylene due to Lewis acid sites of Titania and that ethylene would combine with ethanol to form butanol, reactions are performed with ethanol on Titania in the presence of pressurized ethylene. This part of the project is in progress. We believe that this mechanism can be extended to other nucleophiles such as acetone as well. The results on poly crystalline titania will be compared with supported titania catalysts.

Significance

Production of higher alcohols from ethanol would be a significant step in making gasoline from bio-renewable energy sources. Bio-ethanol could be treated on Titania to give higher alcohols which when passed on microporous zeolite such as H^+/ZSM-5, would result in gasoline range hydrocarbon. Also, syngas combined with ethylene could be passed on Rhodium –Titania or Molybdenum-Titania catalytic systems where Rh based catalyst [2,3] and Mo based catalyst [5] would assist in forming ethanol while Titania could use the ethylene in the feed flow to convert ethanol to butanol and other higher alcohols.

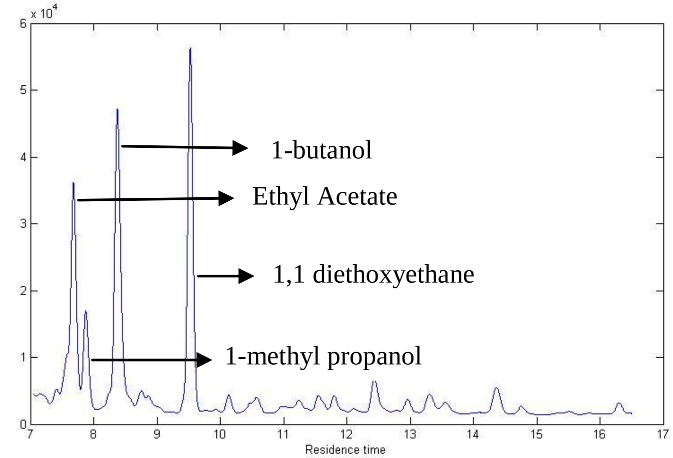

Figure 1. GC-FID Chromatogram of ethanol reaction on Titania in batch reactor. The signal strength is show on the y axis and Residence time on the X Axis. The peaks are labeled. Butanol and 1-methyl propanol can be observed. Unreacted ethanol is not shown. (Conditions of the reaction are 350 ^{o}C, Pressure =1atm, Catalyst = Titania (8-10 mesh) of 1 g. Ethanol=20 g)

References

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