Tailoring Active Sites Towards High Selectivity for Paired-Electrochemical Biomass Upgrade over Medium/High-Entropy Sulfide Aerogels

Bezawit Z. Desalegn, and Jeong Gil Seo*
Hanyang University, Department of Chemical Engineering, 04763, Seoul, South Korea.
Hanyang University, Clean-Energy Research Institute, 04763, Seoul, South Korea.
** jgseo@hanyang.ac.kr*

Significance and Relevance

Multi-element [Medium (MES) and High-entropy (HES)] sulfide aerogels were successfully synthesized for the first time via a simple sol-gel method followed by supercritical drying and solid-gas phase sulfurization at a relatively low temperature. With successive addition of each metal a change in specific surface area, acidic/basic sites and adsorption orientation of substrates/intermediates was observed with significant implications to performance descriptors for electrochemical furfural upgrade. A direct relationship between the nature and number of acidic/basic sites is discovered for both selectivity (100%) and yield (85%) towards furoic acid, moving from mono-metallic to high-entropy systems.

Preferred and 2nd choice for the topic: Preferred: *Catalysis to electrify the chemical production/**2nd choice**: Green chemistry and biomass transformation, renewable resources conversion.*
Preferred presentation: *Oral preferred or Short Oral*

Introduction and Motivations

Severe environmental problems due to expedited technological advancements along with the gradual depletion of fossil fuel resources have initiated a surge in the utilization of renewable and abundant lignocellulosic biomass to produce sustainable, valuable, functional, and fine chemicals.[1] Furanic derivatives are substrates of prime interest as they represent a synthetic platform for numerous value-added compounds. Drop-in biofuels can be produced by reduction [hydrogenation/hydrodeoxygenation], while partial oxidation can yield various fine chemicals.[2] However, the conventional thermocatalytic process for the generation of platform chemicals requires extremely harsh reaction conditions, including high pressure, high temperature, and the use of external oxidants and reductants, which fueled the need for the development of greener conversion technologies. In this regard, electrochemical biomass upgrade, benefiting from room temperature/pressure operations with in-situ generated oxidations/reductants along with the advantage of controlling selectivity via voltage/electrolyte adjustments is gaining increased attention. However, due to the co-existence of various unsaturated functional groups in biomass feedstocks, selective transformation is a highly challenging task[3] that requires the design of task oriented, densely packed and synergistic active sites. Accordingly, in this work an array of MES/HES aerogels with unique inherent properties were synthesized and utilized as highly active electrodes for the paired electrochemical furfural upgrade.

Materials and Methods

The medium and high-entropy sulfide aerogels were synthesized via a two-step method. Specifically, wet gels with different metal combinations were prepared via a sol-gel method followed by CO_2 supercritical drying to obtain the high-entropy oxide aerogels, which were subjected to solid-gas sulfurization with elemental sulfur to obtain the final high-entropy sulfide aerogels. Electrochemical oxidation and reduction reactions were conducted in an H-type electrochemical cell separated by an anion exchange membrane, with graphite rod as the counter electrode, saturated Ag/AgCl as the reference electrode and the as-prepared aerogels drop-casted on nickel foam as working electrodes. 50mM furfural dissolved in 1M KOH was used as the anolyte and catholyte for anodic and cathodic reactions, respectively. The conversion, selectivity, yield and FE% were calculated by quantifying the products using high performance liquid chromatography (HPLC).

Results and Discussion

A progressive increase in conversion, selectivity, yield and FE% was observed with successive addition of metals. The mono-metallic sulfide aerogels (FeS_2 AG and NiS_2 AG) exhibited higher conversion for furfural with negligible selectivity towards the target product while the bimetallic sulfide [$FeNiS_y$ AG] showed the highest conversion along with increased furfuryl alcohol conversion. Interestingly, the incorporation of Cu to the bimetallic sulfide aerogel resulted in a significant improvement in selectivity, more specifically for electrodes where Cu replaced Fe ($Fe_{1.5}Ni_{2.5}CuS_y$ AG). Consecutively, the addition of Co ($Fe_2Co_1Ni_5Cu_2S_y$ AG [MES-Co]) to the trimetallic sulfide resulted in the highest selectivity of 98% towards furoic acid while maintaining conversion. Lastly, the incorporation of Zn to the MES-co ($Fe_2Co_1Ni_4Zn_1Cu_2S_y$ AG [HES-Zn])resulted in a 100% selectivity and the highest FA yield of 85%. It is believed that with successive addition of elements/metals the adsorption orientation of furfural was modified from a parallel to tilted and finally to a vertical configuration which favors the selective activation of the C=O bond and the formation of carboxylic acid by the nucleophilic attack of C=O with OH^- (**Figure 1**).

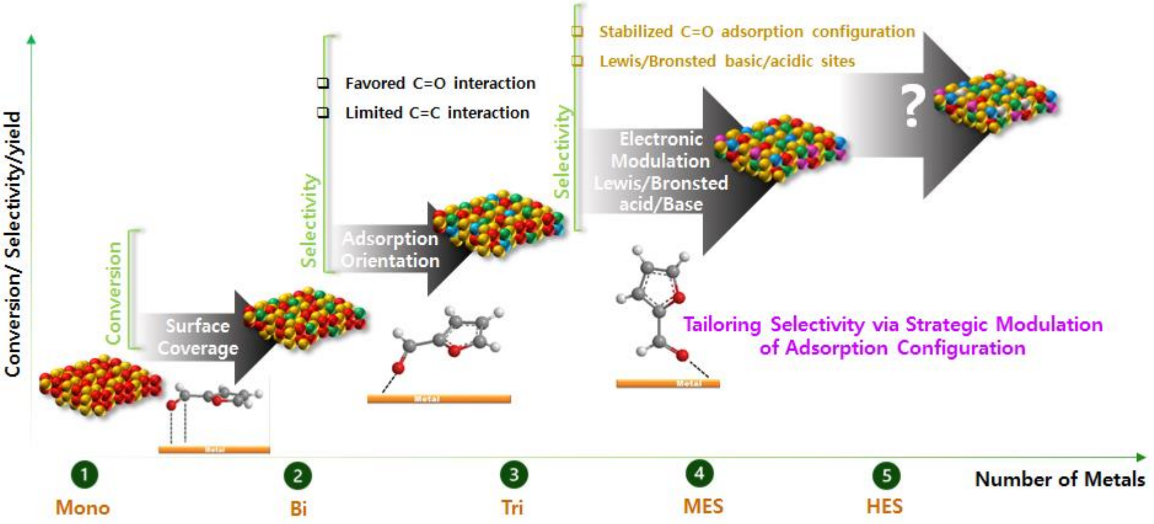

Figure 1 Schematic illustration of the effect of addition of metals on the adsorption orientation and performance descriptors of furfural towards furoic acid.

The presence of multi-component, adjacent and synergistic active sites is believed to bring forth systematic modifications in surface coverage, adsorption orientation, electronic modulation, and Lewis's acid-base pairs leading to improved conversion, selectivity and yield.

References

1. H. Wu, J. Song, H. Liu, Z. Xie, C. Xie, Y. Hu, X. Huang, M. Hua and B. Han, *Chem. Sci.*, 2019, **10**, 4692-4698.
2. B. You, X. Liu, N. Jiang and Y. Sun, *J. Am. Chem. Soc.*, 2016, 138, 13639–13646.
3. S. Liu, R. Tu, K. Liang, Y. Sun, X. Fan, J. Hu, H. Yang and X. Xu, *Fuel Process. Technol.*, 2023, **252**,107976.

Acknowledgements

This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korean government (MSIT) (No. 2022R1I1A1A01064469).