

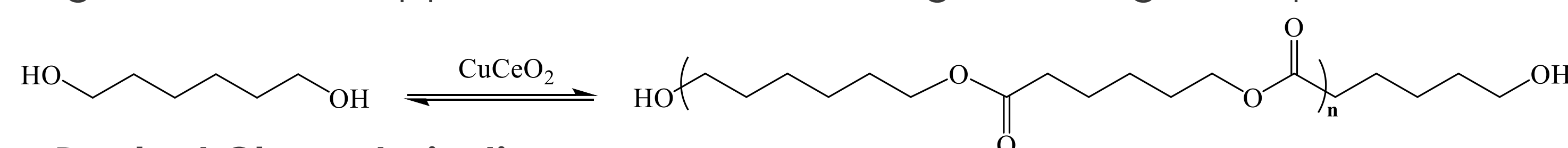
Direct Synthesis of Polyester from Biomass Derived 1,6-hexanediol using a Copper-Ceria Catalyst

Anitha Shankara Linge Gowda^{1,2}, Swarom Kanitkar^{1,2}, Daniel Haynes¹

¹US Department of Energy, National Energy Technology Laboratory, Morgantown WV; ²NETL Support Contractor, Morgantown WV.

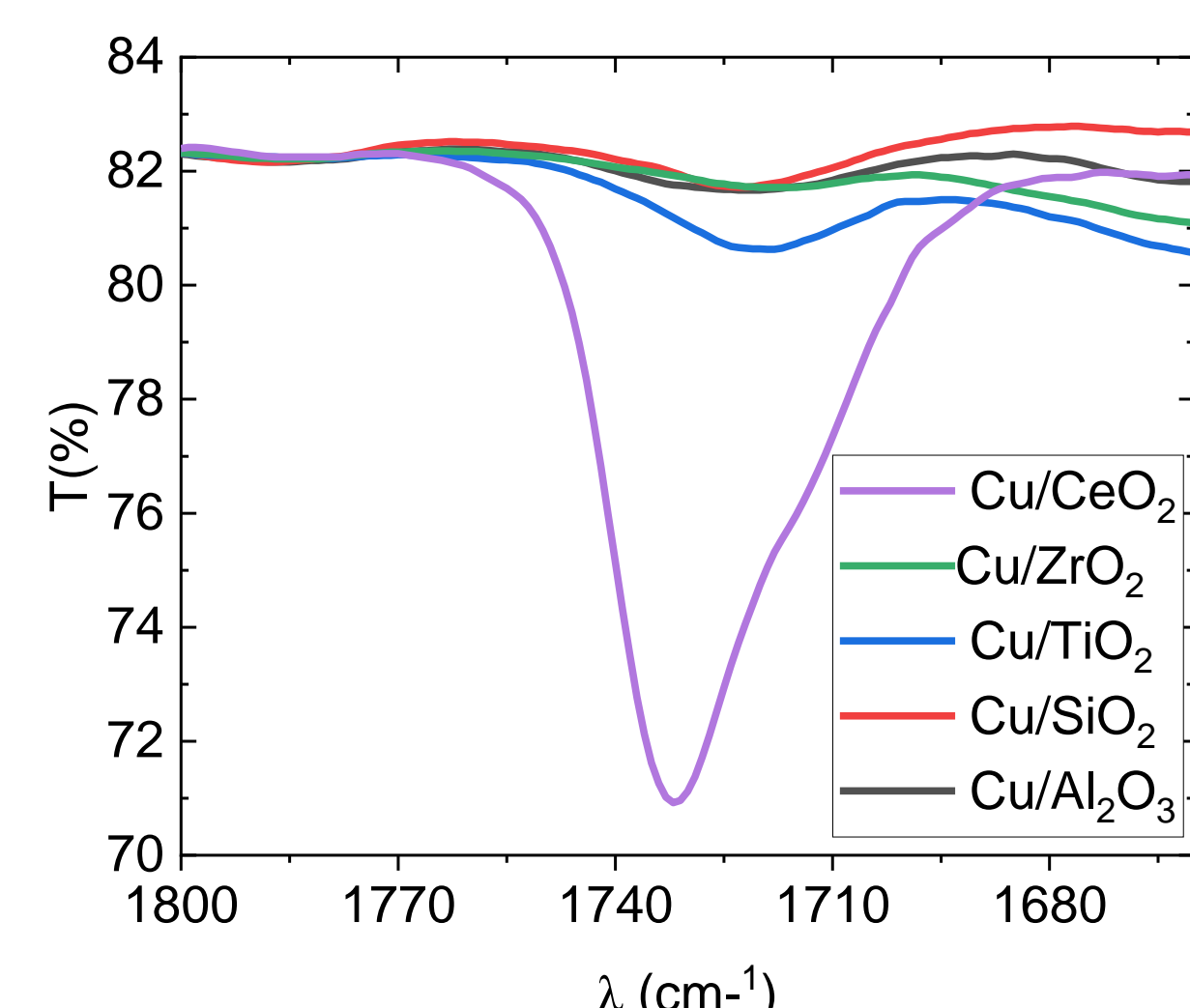
Introduction

The current production of polyester polymers involve a reaction between a carboxylic acid and diol. However, synthesis of carboxylic acid itself is a energy intense process. Although these methods are well-established, there are benefits to simplifying polyester synthesis to a one-step process to minimize resource utilization, reduce energy consumption, and improve process efficiencies. Despite these advantages, a single step process has yet to be reported. However, our research discovered a direct route to polyesters from 1,6-hexanediol (HDO) using a heterogeneous CuCeO₂ catalyst in a semi-batch reactor system used by Gu et al. to make polycarbonates using a CeO₂ catalyst.² This study seeks to provide insights into the reaction mechanism of the direct polyester synthesis reaction by characterizing and evaluating different Cu supported materials, Cu weight loadings, and process conditions.



Polyester Product Characterization

- IR peak around 1735 cm⁻¹ confirmed the presence of the carbonyl group.
- C¹³ NMR analysis showed a peak at 174 ppm confirming carbonyl ester peak.
- The LCMS analysis confirm the repeating units of polyester with the mass of 114 m/z.



Cu on different supports

- CuCeO₂ showed higher performance compared to other catalyst.
- No direct correlation with oxygen vacancy content with reactivity.
- Balance between surface acidity and Cu dispersion are the key factors for polyester formation.
- Interfacial metal sites near acid sites and the oxygen vacancies from the support are likely the active sites enabling OH oxidation to aldehyde and carboxylic acid for polymer formation.

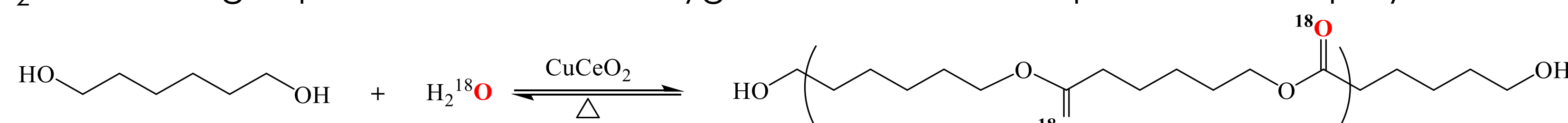
Effect of Cu loading on CeO₂

- Low (<5wt%) Cu loadings leads to more low oxidation state Cu (Cu(I) and/or Cu(0)).
- Increasing Cu loading leads to more Cu(II) and stronger Lewis acidity.
- Pure CuO has a highly defective surface with both CuO and Cu(I)/Cu⁰.
- Performance data suggests that Lewis acid sites (Cu(II) and Cu(I)) and Cu(0) are needed for polyester formation.

Catalyst (Fresh)	% Total Ce		% Total Cu		Atomic concentration (%)			
	Ce(+3)	Ce(+4)	Cu(0/+1)	Cu(+2)	C	O	Ce	Cu
CuO	-	-	40.3	59.71	16.4	43.8	-	39.8
50%Cu/CeO ₂	30	70	39.4	60.6	20.7	46.2	13.30	19.8
25%Cu/CeO ₂	39.7	60.3	26.2	73.8	24.5	45.6	14.50	15.4
16%Cu/CeO ₂	24.3	75.7	35.9	64.1	14.8	51.8	13.50	19.9
10%Cu/CeO ₂	24.0	76.0	47.8	52.2	18.0	57.7	15.90	8.4
5%Cu/CeO ₂	24.8	75.2	100	0	28.2	51.4	16.30	4.1
2.5%Cu/CeO ₂	27.5	72.5	100	0	17.0	61.3	19.8	1.9
CeO ₂	32.8	67.2	-	-	23.1	56.2	20.70	-

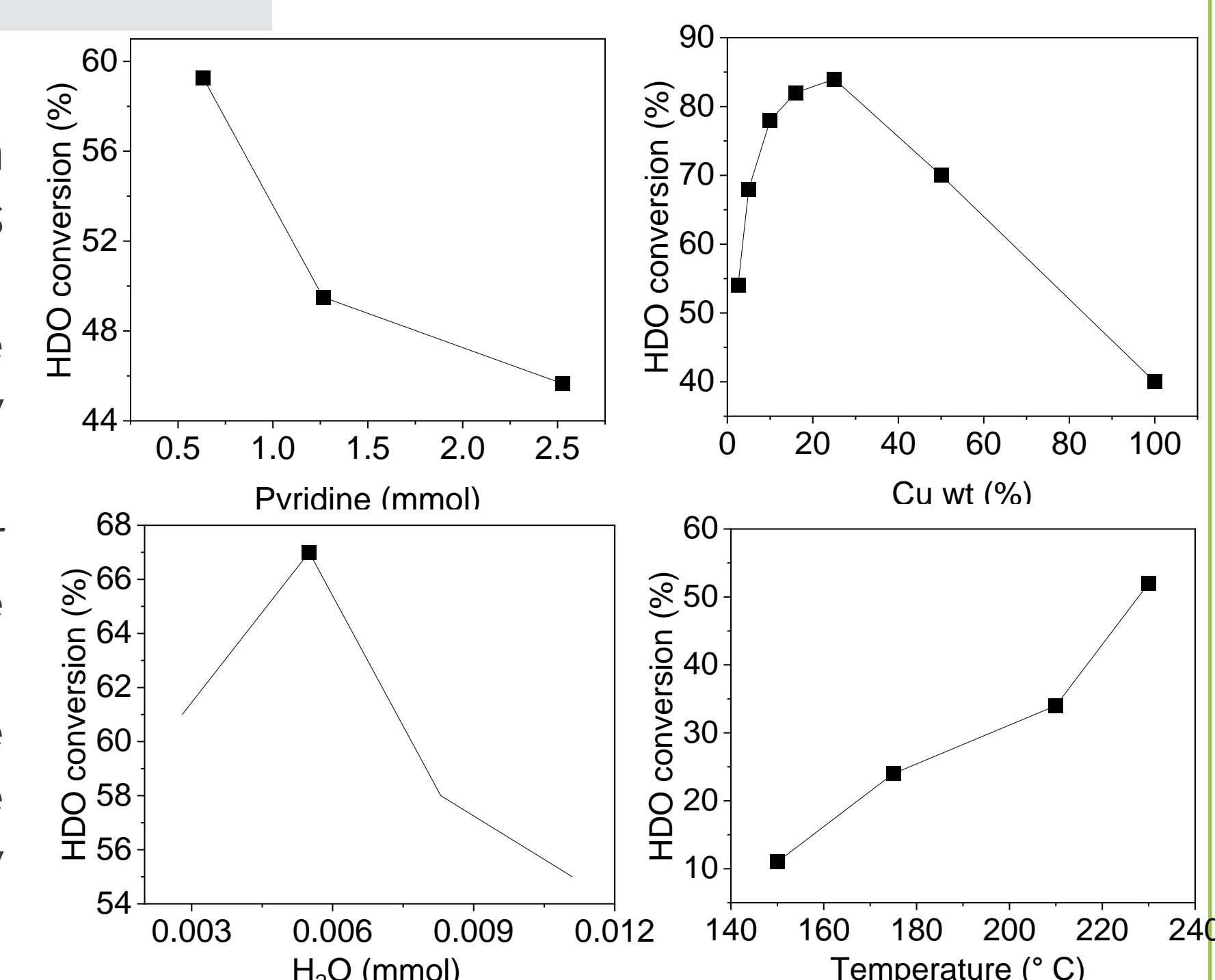
Role of water

- Small levels of water present in the reactant mixture are key to polyester formation.
- No reaction was observed in the presence of a dehydrating agent.
- The initial water level was between 1400-2500 ppm, and increased water levels inhibited the formation of the polyester synthesis.
- H₂¹⁸O labeling experiments showed oxygen from water was present in the polyester.



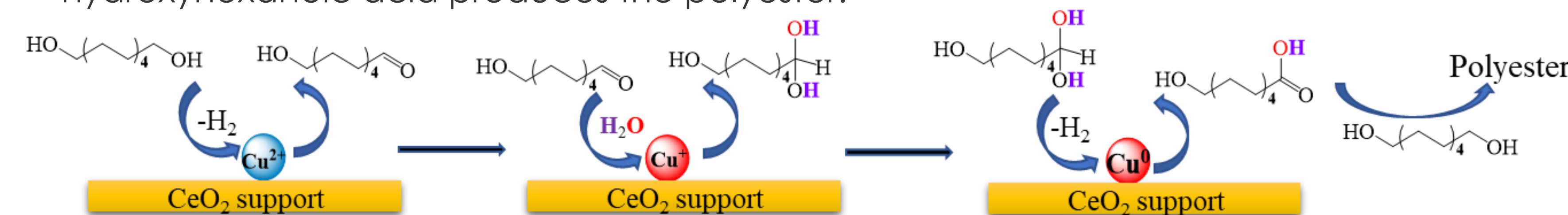
Effect of reaction parameters

- Increase in pyridine concentration shows an inhibition of the reaction rate, indicating Lewis acid sites are the active sites for the reaction.
- The reaction rate increased with temperature which suggests the reaction is catalyzed by acid site transesterification.⁶
- A volcano curve is observed for water concentration indicating an inhibition of rate with higher water levels.
- Diol conversion also exhibits a volcano curve with metal loading due to the increased surface coverage with Cu metal-Lewis acid-vacancy sites.



Possible reaction mechanism

- Cu^{1+/2+} in proximity to defect sites mediate the conversion of HDO to 6- hydroxyhexanal.
- HDO dissociatively adsorbs on to Lewis Ce⁴⁺ and Cu acid sites, Cu metal near oxygen vacancies activates water dissociation and insertion of the OH group into the locally adsorbed 6- hydroxyhexanal species to form 6-hydroxyhexanoic acid.⁵
- HDO heterolytically dissociated on Lewis acid (Cu^{1+/2+} or Ce⁴⁺) transesterifies with 6- hydroxyhexanoic acid produces the polyester.

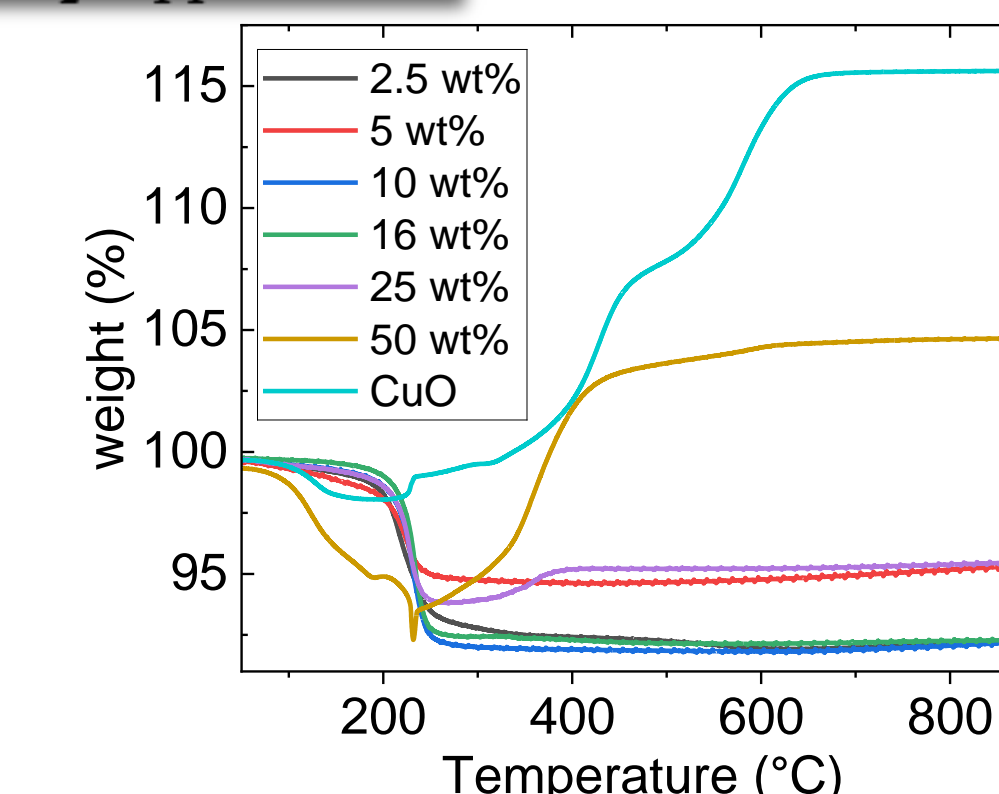


Catalyst Deactivation

- Agglomeration was the main reason for loss or reactivity at higher Cu weight loadings.
- The deposition of the polymer on the catalyst surface may also block the active site on the catalyst.
- TGA analysis showed significant carbon deposition on the catalyst.

Conclusions

- CuCeO₂ is an efficient catalyst for direct diol conversion to polyester, and the interplay between oxygen vacancies, Cu metal, and Lewis acid sites enables the reaction.
- H₂O labelling experiment showed that oxygen of the carbonyl group is derived from water.
- The reaction likely proceeds through an aldehyde and carboxylic acid intermediate.
- The agglomeration and the polymer deposition are likely the main pathways for catalyst deactivation.



Disclaimer

This project was funded by the United States Department of Energy, National Energy Technology Laboratory, in part, through a site support contract. Neither the United States Government nor any agency thereof, nor any of their employees, nor the support contractor, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

References

- Challa, P.; Enumula, S. S.; K, S. R.; Kondeboina, M.; Burri, D. R.; Rao Kamaraju, S. R. *Ind. Eng. Chem. Res.*, **2020**, 59, 17720– 17728.
- Gu, Y.; Tamura, M.; Nakagawa, Y.; Nakao, K.; Suzuki, K.; Tomishige, K. *Green Chem.*, **2021**, 23, 5786-5796.
- Li, G.; Wang, B.; Resasco, D. E. *ACS Catal.* **2020**, 10, 5373– 5382.
- Hunsicker, D. M.; Dauphinais, B. C.; Mc Ilrath, S. P.; Robertson, N. J. *Macromol. Rapid Commun.* **2012**, 33 (3), 232– 236.
- Lei, L.-j.; Fan, W.; Hou, F.-x.; Wang, Y.-q.; Sun, C.; Zhang, Y. J. *Fuel Chem. Technol.* **2023**, 51 (7), 1007–1017.
- Zhang, Z.; Meng, P.; Luo, H.; Pei, Z.; Liu, X. *Catalysts*, **2024**, 14, 731