DEPARTMENT OF INORGANIC CHEMISTRY

Spectroscopic insights into an industrial Cu/ZnO-Al_2O_3 catalyst for CO_2-to-Methanol production at different pressure regimes

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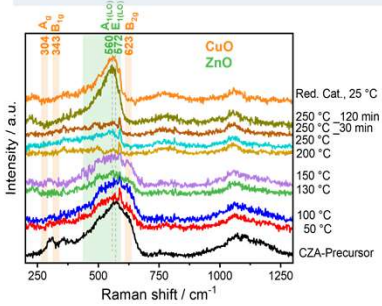
INTRODUCTION

The Cu/ZnO-Al_2O_3 (CZA) catalyst is the industrial choice for methanol synthesis from $CO/CO_2/H_2$ feed. It holds great potential for (pure) carbon dioxide valorization.[1] It is a highly dynamic catalyst, whose structure adjusts to the chemical potential of the reaction feed.[2] However, the structure under reaction conditions, the active sites and the reaction interemediates remain elusive.

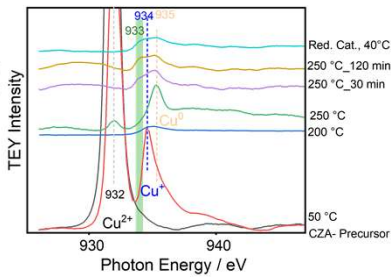
In this work, we apply Raman spectroscopy, near ambient pressure x-ray photoelectron spectroscopy (NAP-XPS) and near edge x-ray absorption fine structure (NEXAFS) to obtain insights on the reduced (activated) catalyst and its evolution under operando conditions.

Raman is particularly suitable to identify polymorphisms in ZnO, probe and elucidate defects, while NAP-XPS and NEXAFS reveal information on the oxidation states, and ZnO_x wetting (at 1 mbar and 1 bar, respectively).

REDUCTIVE TREATMENT

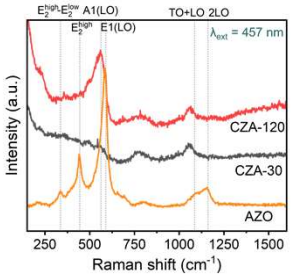


❖ZnO restructuring and formation of ***defects*** (at 250 °C)



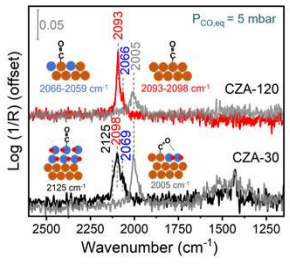
❖Cu L-edge at 250 °C: new Cu species (defects or insertion into ZnO)

REDUCED CATALYSTS AND COMPARISON WITH AZO

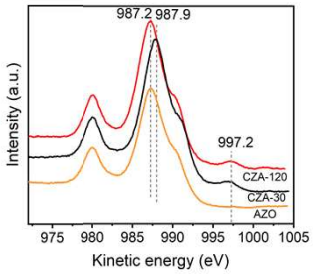


❖No long range order: only defects-related modes are visible in CZA

❖ Multicomponent (broad band) 560 cm^{-1} in CZA: possibly Zn interstitial and oxygen vacancies



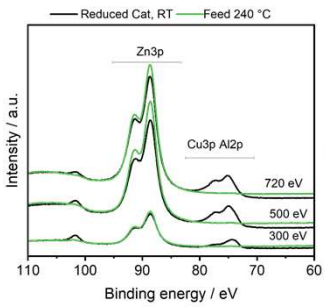
❖2093-2098 cm^{-1}: metallic Cu
❖2066-2069 cm^{-1}: CuZn surface alloy
❖2125 cm^{-1}: graphitic ZnO
❖2005 cm^{-1} (upon evacuation): Cu/ZnO



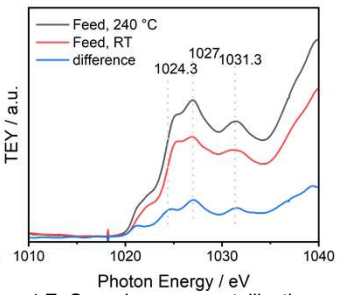
❖ CZA-30: shift from CZA-120 and AZO

❖CuZn (surface) alloys: 997.2 eV feature[3]

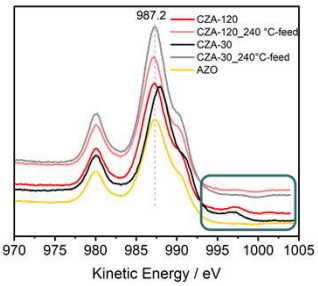
UNDER REACTION Feed: H_2/CO_2 3/1



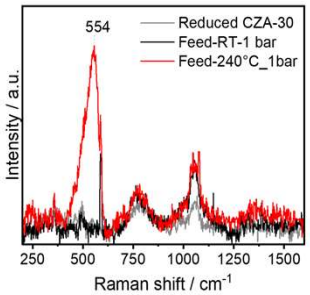
❖Total coverage of Cu by ZnO_x



❖ZnO_x undergoes crystallization under reaction condition[4]

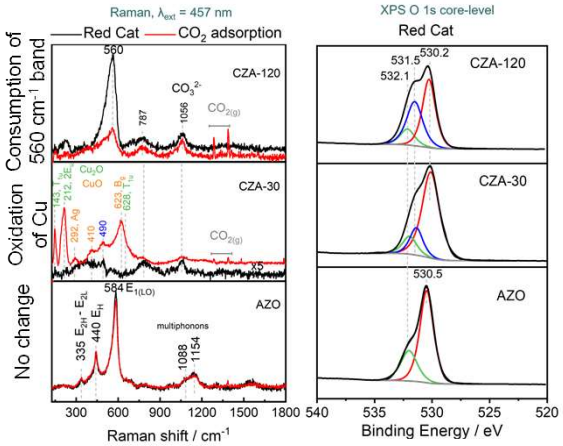


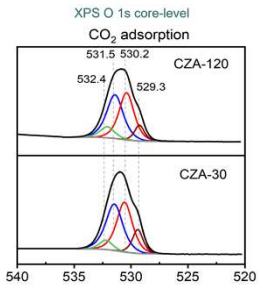
❖Consumption of CuZn surface alloys



❖Metastability of CZA-30 converting to CZA-120

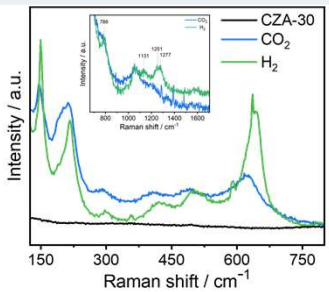
CO_2 INTERACTION WITH THE ACTIVATED CATALYSTS AT 25 °C



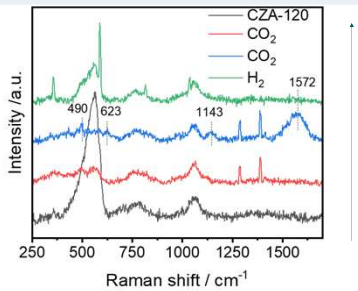


❖Lattice O (ZnO)
❖Defective O (ZnO)
❖O from $Cu(OH)_2$
❖529.3 eV: Cu^{2+}

REDOX REACTION WITH HYDROGEN AT 25 °C



❖Slow re-reduction to Cu
❖Likely generation of *formyl* species



❖Hydrogenation of formate (ν_{as}(COO),1572 cm^{-1}) and methoxy (ν(CO), 1143 cm^{-1}) species
❖Partial restoring of defects

CONCLUSIONS AND OUTLOOK

❖Raman spectroscopy reveals that longer reductive treatments lead to the formation of ZnO-defects in CZA. These defects are different to those in the Cu-free catalyst (AZO).
❖Differences in the activated states and their redox behaviour with CO_2 and H_2 are revealed by NAP-XPS and Raman spectroscopy.
❖ Such differences disappear under reaction condition (240 °C, feed H_2/CO_2 3/1).
❖Total coverage of Cu by ZnO_x is revealed by NAP-XPS (at 1 mbar).
❖Raman measurements at 30 bar are currently being performed.

REFERENCES AND ACKNOWLEDGMENTS

1. Beck, A.; *et al.*, Chem. Rev. 2024, 124, 4543−4678, 2. Jiang, X.; *et al.*, Chemical Reviews 2020, 120, 7984-8034. 3. Jensen S. *et al.*, Nature Comm, 2024, 15, 3865, 4. Cho D-Y *et al.*, Appl. Phys. Lett., 2009 95, 261903.

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