

Insights into the Mechanism of Tandem Alkene Hydroformylation over a Nanostructured Catalyst with Multiple Interfaces

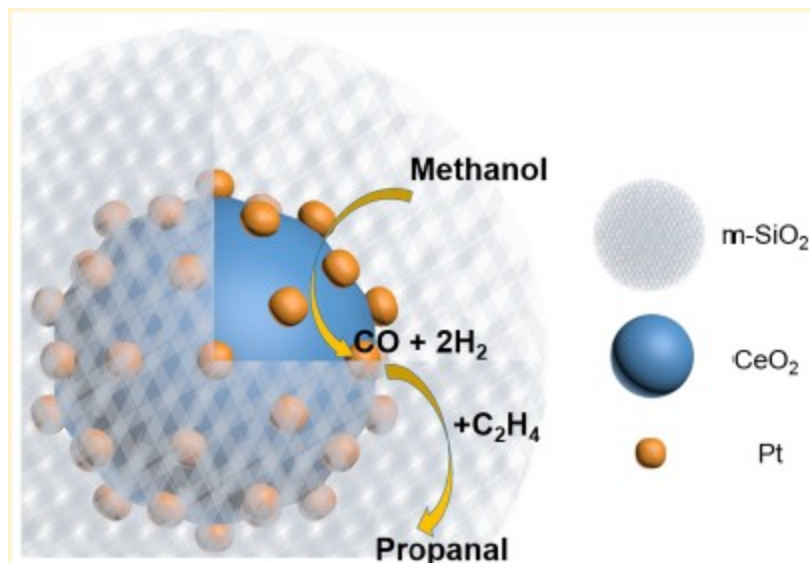
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INTRODUCTION:

- ❖ The catalytic activity of nanocrystalline catalysts used to have single-interface length scale, where the atomic arrangements on the catalytic interface are tuned to alter the activity.
 - ❖ Recently tandem catalysis was demonstrated wherein two metal oxide interfaces catalyzed sequential chemical conversions with high product selectivity.
 - ❖ Specifically this tandem catalyst design takes advantage of the synergy between different chemical conversion on multiple interfaces to get desirable product distributions.
- In this paper...**
- They have made a model system for tandem catalysis for ethylene hydroformylation reaction which undergoes two chemical conversions.
 - Here by using this approach they have overcome the low selectivity for aldehyde formation.
 - They have synthesized three-dimensional $\text{CeO}_2\text{-Pt}@ \text{mSiO}_2$ which shows greater stability compared to the drop-casted bilayer $\text{CeO}_2\text{-Pt-SiO}_2$ catalyst.
 - Tandem hydroformylation reactions carried out by this 3D catalyst show greatly enhanced propanal selectivity compared to the single step ethylene hydroformylation with CO and H_2 .

SYNTHESIS AND CHARACTERIZATIONS:

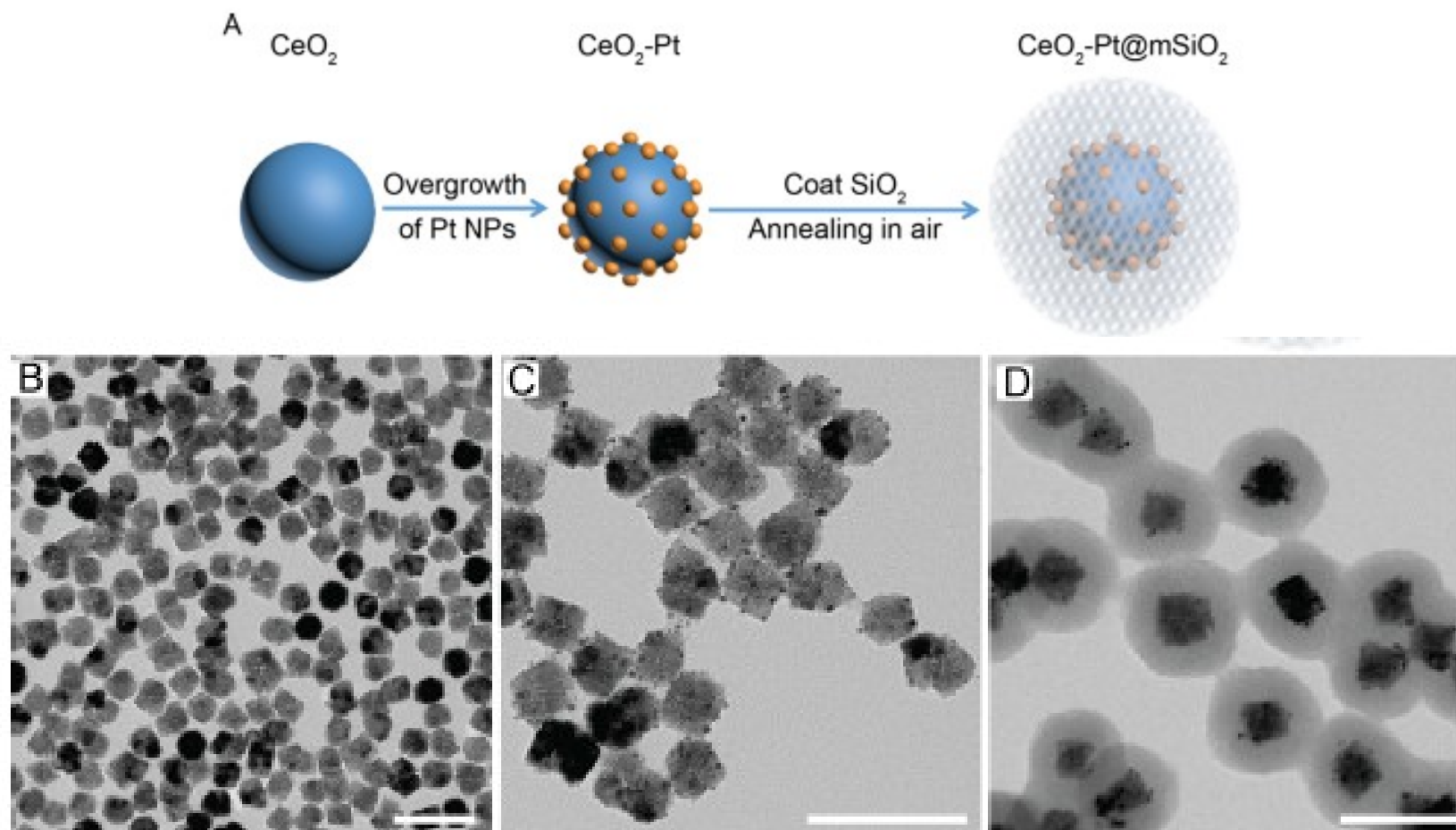


Figure 1. Synthesis and characterization of the 3D nanocrystal tandem catalyst $\text{CeO}_2\text{-Pt@mSiO}_2$. (A) Synthesis of the tandem catalyst. (B) TEM image of well-dispersed CeO_2 nanoparticles. (C) TEM image of $\text{CeO}_2\text{-Pt}$ nanoparticles synthesized the overgrowth of Pt. (D) TEM image³ of core-shell $\text{CeO}_2\text{-Pt@mSiO}_2$ nanoparticles. Scale bar: 100 nm.

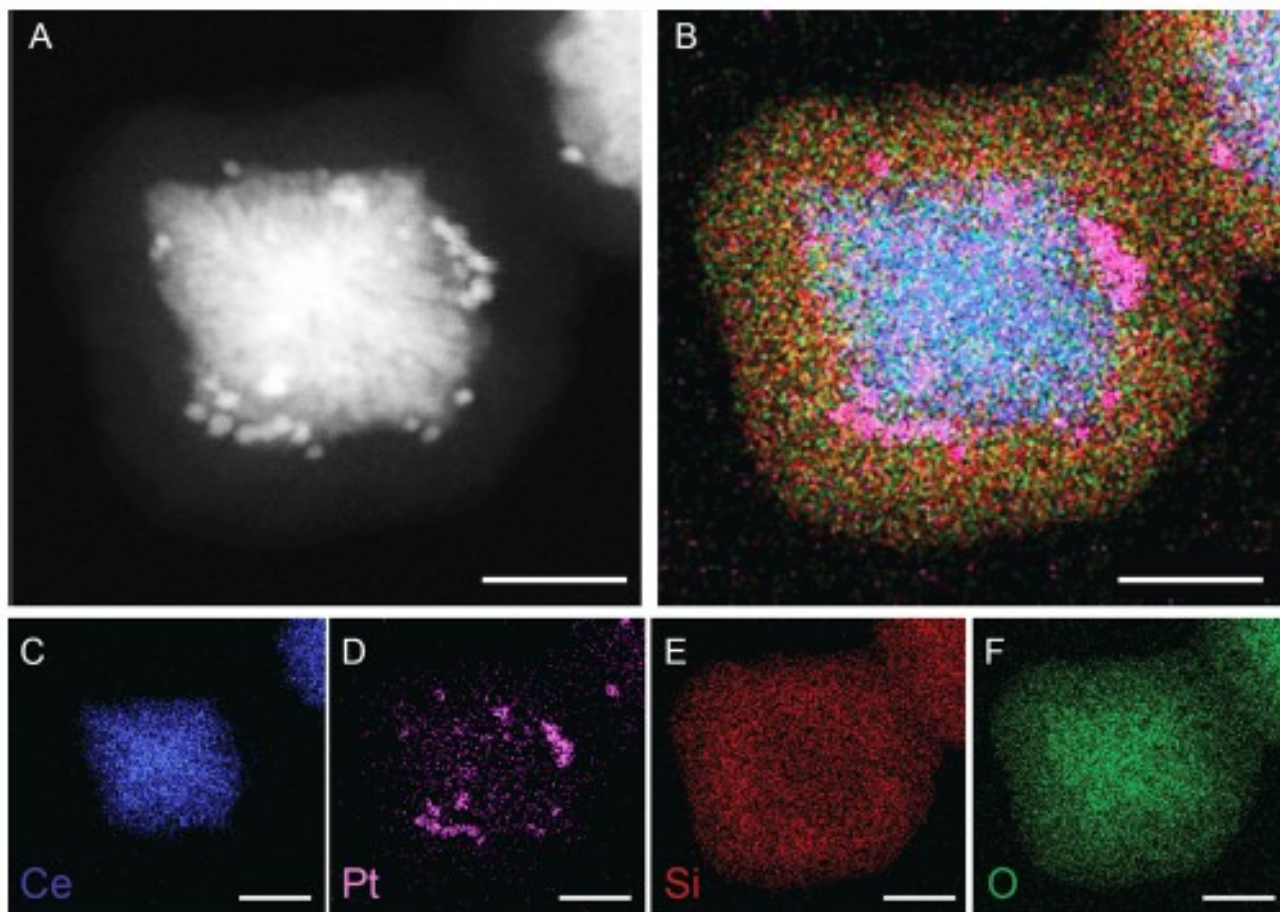


Figure 2. (A) Imaging of $\text{CeO}_2\text{-Pt@mSiO}_2$ via high-angle annular dark-field scanning transmission electron microscopy. (B) Elemental mapping of $\text{CeO}_2\text{-Pt@mSiO}_2$ with energy dispersive X-ray spectroscopy (EDS). Corresponding EDS elemental mapping for (C) Ce, (D) Pt, (E) Si, and (F) O, respectively. Scale bar: 30 nm.

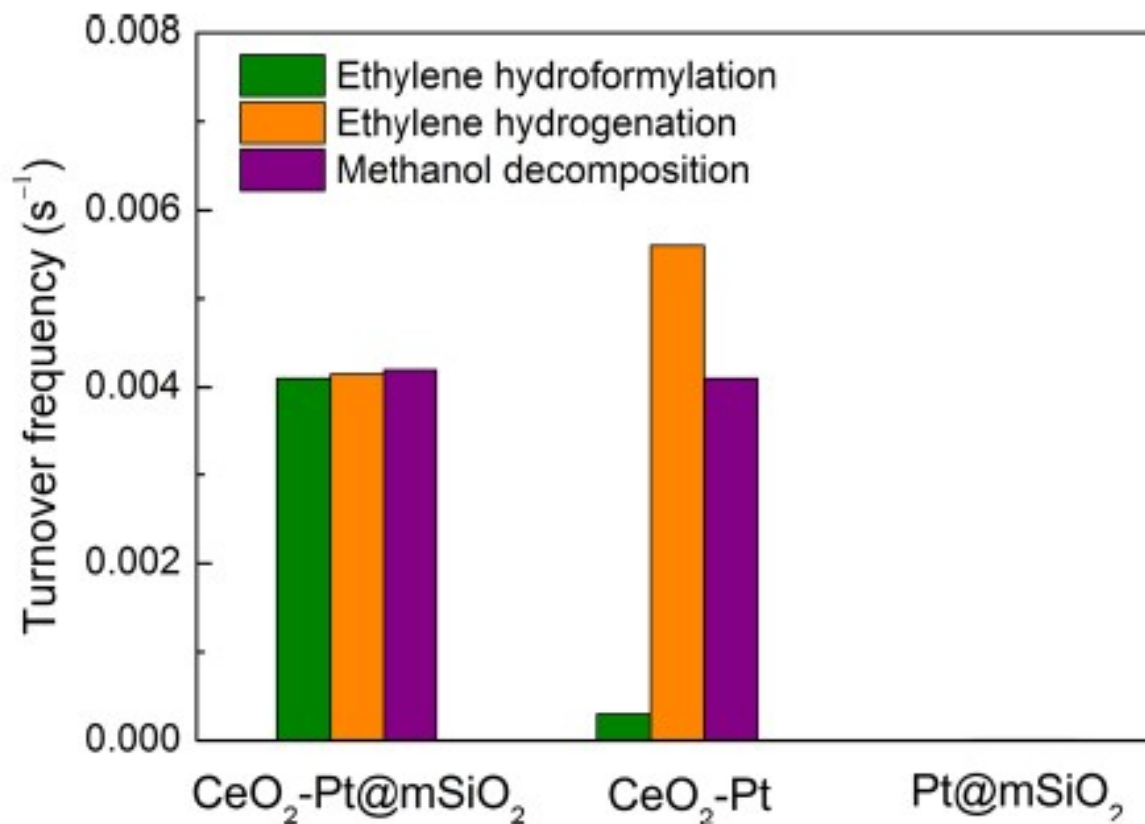
alytic performances:

Figure 3. Ethylene hydroformylation with methanol carried out at 150 °C over CeO₂-Pt@mSiO₂ and single interface catalysts CeO₂-Pt and Pt@mSiO₂. Methanol, ethylene, and helium partial pressures were 35, 7.5, and 727.5 Torr, respectively.

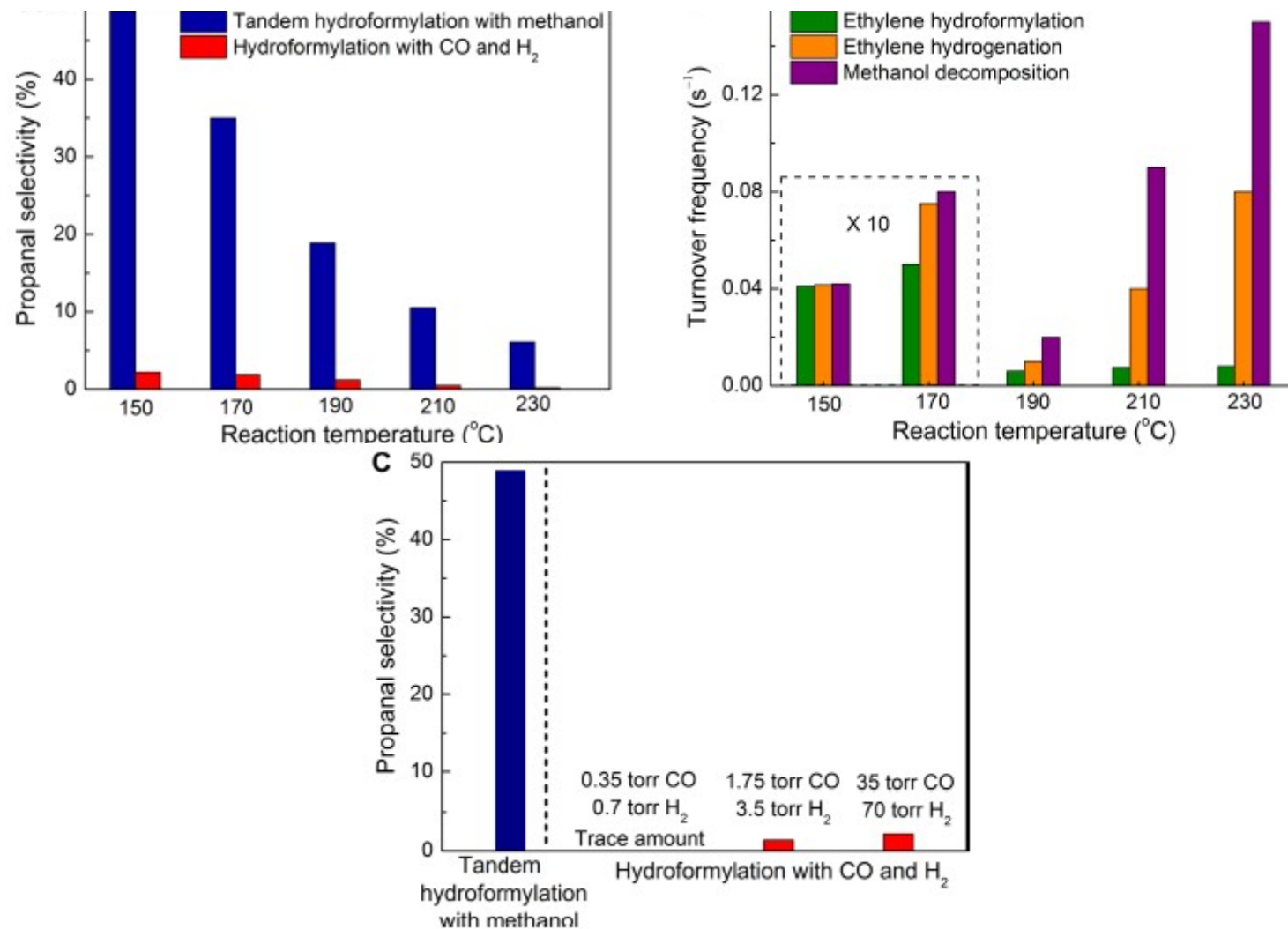


Figure 4. Catalytic performance of CeO₂-Pt@mSiO₂ for the hydroformylation of ethylene with methanol at an ethylene pressure of 7.5 Torr. (A) Comparison of tandem hydroformylation of ethylene with methanol and single-step hydroformylation with CO and H₂. (B) The influence of temperature on tandem hydroformylation of ethylene. (C) Catalytic performance of single-step hydroformylation under a deficiency of CO and

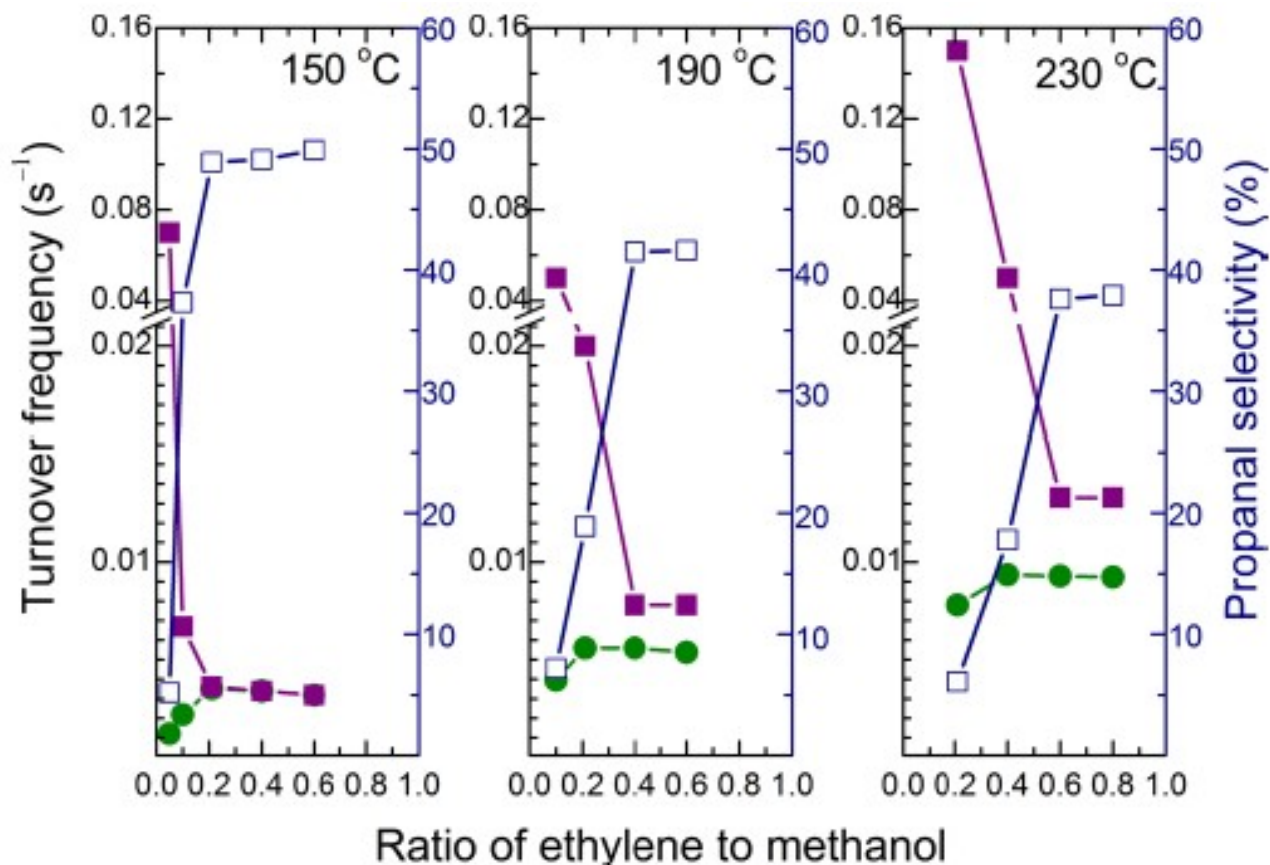
Effect of ethylene on methanol decomposition:

Figure 5. Inhibiting effect of ethylene on methanol decomposition over the CeO₂-Pt@mSiO₂ catalyst: changes in methanol decomposition rate (purple ■), ethylene hydroformylation rate (green ●), and propanal selectivity (blue □). Methanol partial pressure was 35 Torr, and the reaction temperature was 150 °C.

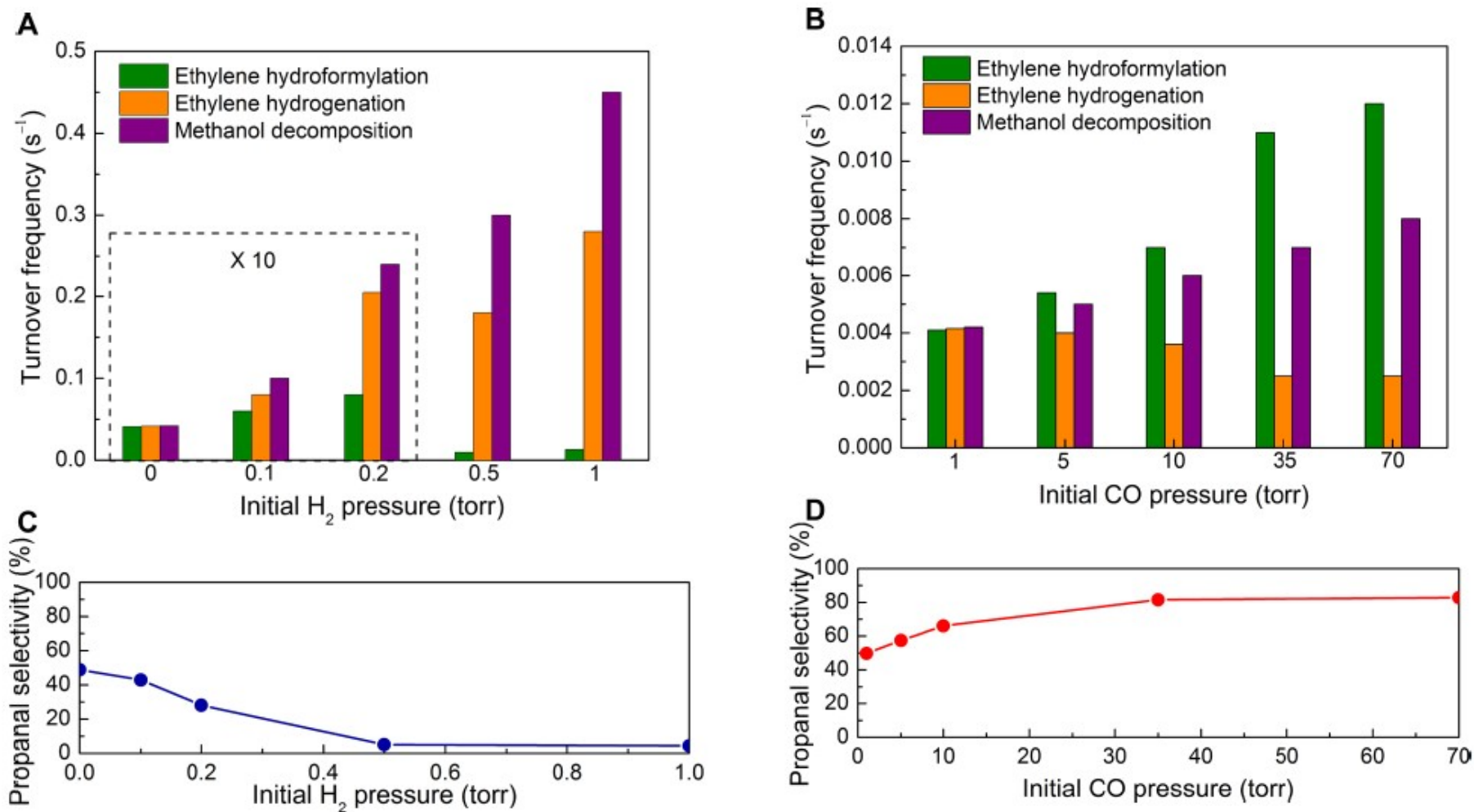


Figure 6. (Top) The effect of cofeeding H₂ or CO on the tandem hydroformylation of ethylene. (A) Cofeeding with H₂ and (B) cofeeding with CO. (Bottom) Propanal selectivity of tandem hydroformylation. (C) Cofeeding with H₂ and (D) cofeeding with CO.

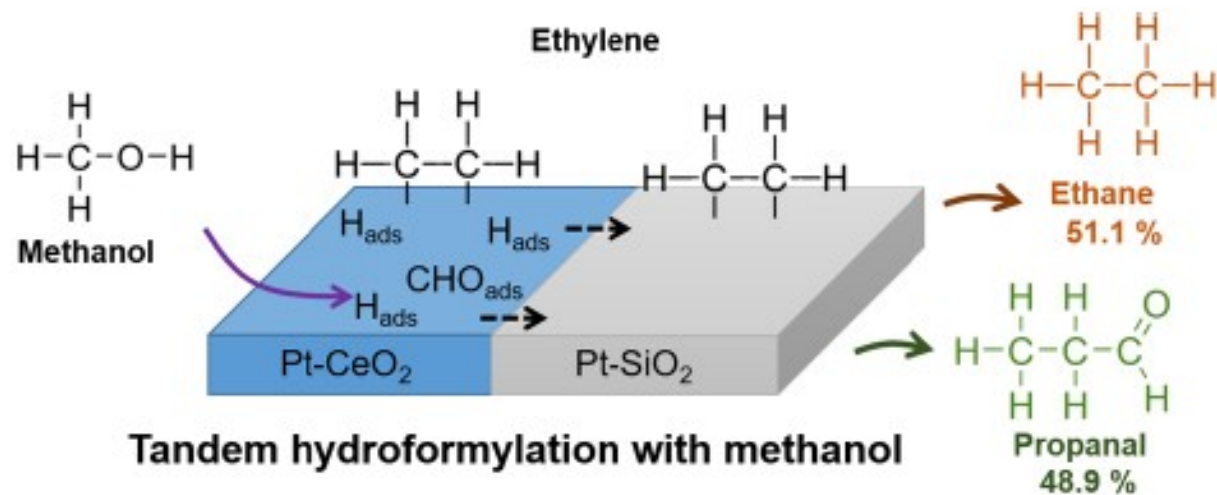


Figure 7. Proposed reaction pathway for the tandem ethylene hydroformylation

CONCLUSIONS:

- A stable 3D tandem catalyst $\text{CeO}_2\text{-Pt@mSiO}_2$ with well defined catalytic interfaces was developed, and its catalytic performance was studied in tandem alkene hydroformylation with methanol.
- Importantly, the tandem ethylene hydroformylation exhibited greatly enhanced propanal selectivity compared to the single-step ethylene hydroformylation with CO and H_2 .
- This effective production of propanal results from synergy between the two sequential chemical conversions facilitated by $\text{CeO}_2\text{-Pt@mSiO}_2$ and the altered reaction pathway, compared to the single-step reaction.

FUTURE DIRECTIONS.....

Instead of coating with SiO_2 , if we can take some other semiconductor oxide e.g, TiO_2 then it can be acts as a photocatalyst also.

THANK
YOU...