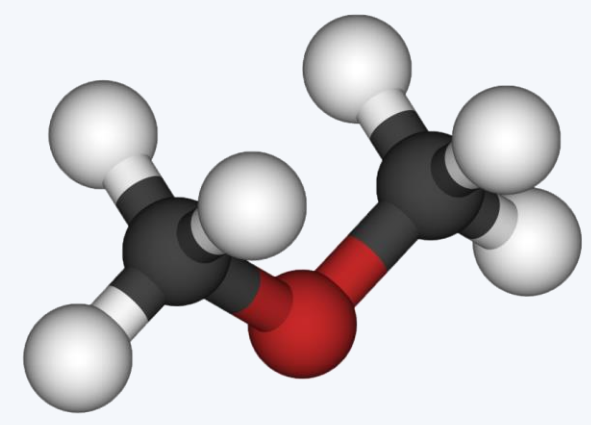


Direct synthesis of dimethyl ether from syngas on bifunctional catalysts based on Cu-ZnO(Al) and supported $H_3PW_{12}O_{40}$: Effect of heteropolyacid loading on catalytic activity



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Why dimethyl ether (DME)?

- ♦ Important chemical **INTERMEDIATE** for production of widely used chemicals (diethyl sulphate, methyl acetate, olefins..)
- ♦ Direct & **ULTRA CLEAN-FUEL ALTERNATIVE** for diesel engines

INDUSTRIAL Production

DME is industrially produced from methanol dehydration in **TWO STEPS** process

- (1) Methanol formation from syngas: $CO/CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$
- (2) Dehydration of methanol to DME: $2CH_3OH \rightarrow CH_3OCH_3 + H_2O$

LIMITATION → Strong **thermodynamic restriction** of methanol step (low gas conversion per pass 15-40 %)

ALTERNATIVE Production

DIRECT SYNTHESIS of DME from SYNGAS (STD)!

Both reaction coupled in a single reactor ↑ conversion (up to 90 %)

Bifunctional reference: **Cu-ZnO(Al) (CZA) – Zeolite (HZSM-5)**

.. but.. Bifunctional catalyst **DEACTIVATES**

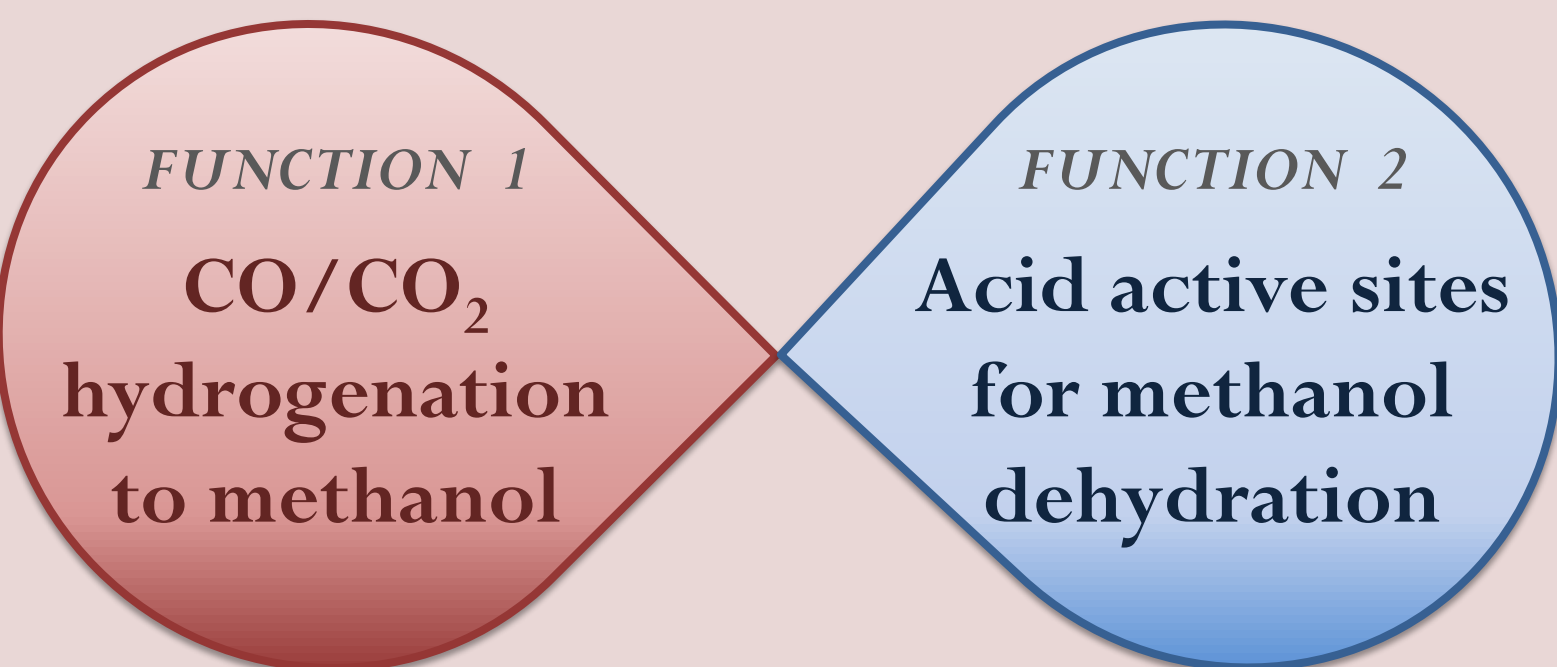
- ✗ by water (copper oxidation or sintering)
- ✗ by strong interactions CZA-zeolite (Cu migration and H^+ exchange)
- ✗ by coke deposition



..CHALLENGE

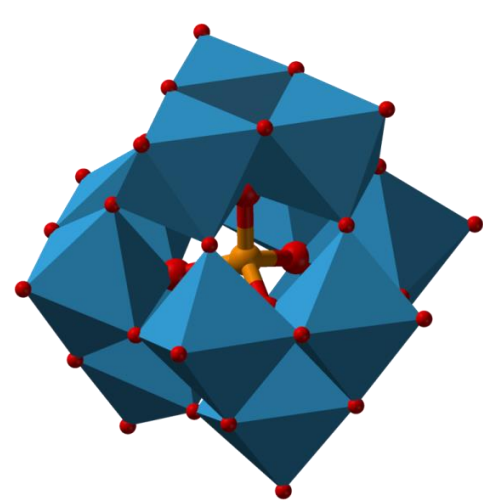
The effectiveness of current catalysts for direct synthesis is still limited, so..

Development of highly efficient **BIFUNCTIONAL CATALYSTS**



OBJECTIVE of this WORK

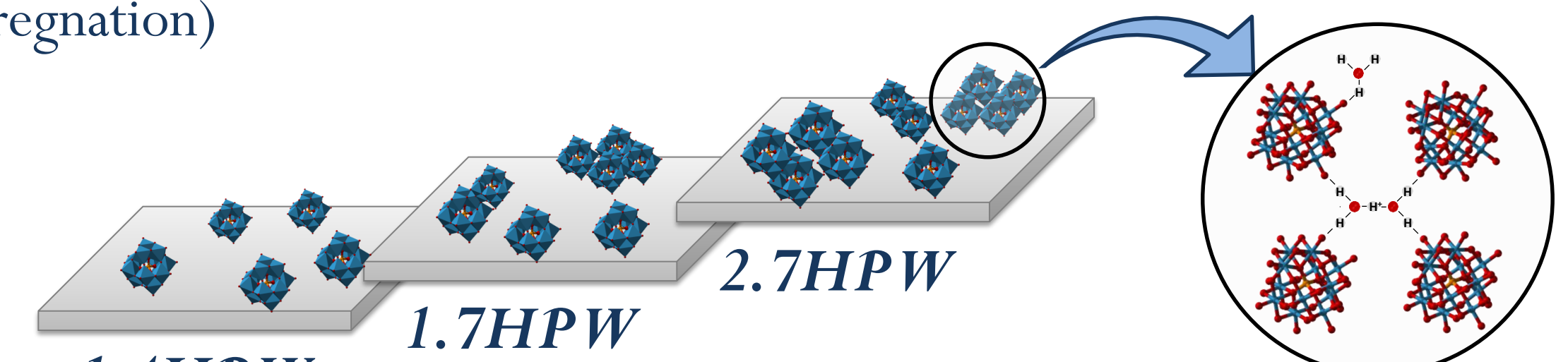
- ✓ Development of bifunctional catalysts for STD (simple mixing, mass ratio 2:1)
- ✓ Optimized Cu catalysts (by co-precipitation) combined with highly promising **heteropolyacids ($H_3PW_{12}O_{40}$, HPW)!**



- ♦ HPW limitation: *low surface area*
- ♦ **SUPPORTED on TiO_2** to get larger specific area (**HPW loading**: "X" theoretical monolayers)

Methodology

- ✓ Study of **different HPW LOADING on TiO_2** as support (by incipient wetness impregnation)

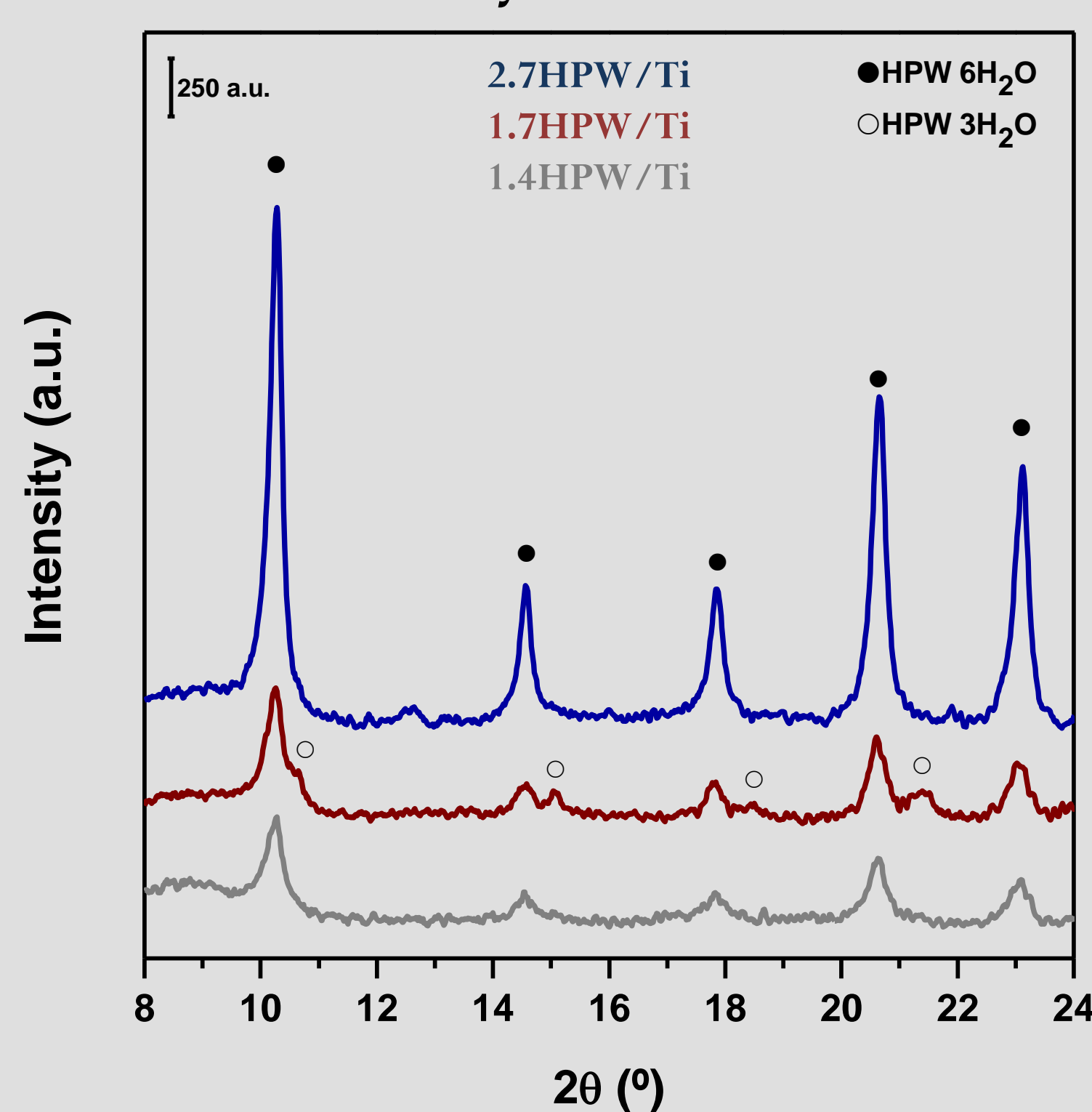


Crystallization water

- ✓ **Characterization** at different catalysts stages: XRD, Raman, DRIFTS, N_2 isotherms, H_2 -TPR, N_2O chemisorption and NH_3 -TPD
- ✓ **Activity of the bifunctional catalysts** was tested for STD at 30 bar and 250 °C

RESULTS & DISCUSSION

X-Ray Diffraction



- ✦ HPW- TiO_2 interaction depends on HPW loading, that affects..

HPW Dispersion
 Structure / Water content
 Acidic properties

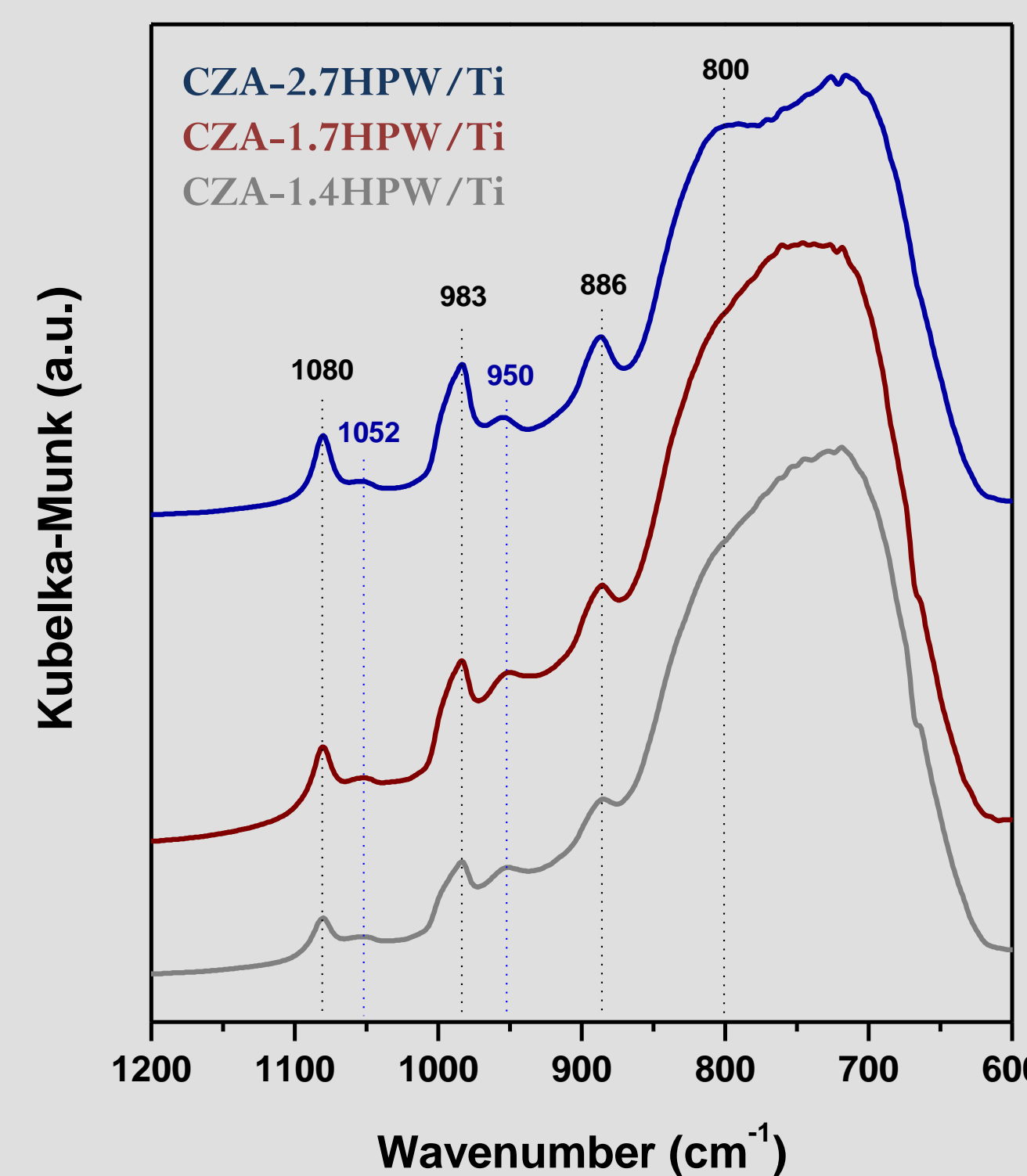
- ✦ HPW loading (HPW/ TiO_2):
 1.4 (≈ monolayer) → strong interaction HPW-support
 >1.7 monolayers → 3D HPW crystals (acidity ≈ bulk HPW)

N_2O -chemisorption & NH_3 -TPD

- ✦ Physical mixing of HPW/ TiO_2 with CZA modifies characteristics of both catalysts:
 ↓ Cu surface area
 ≈ Moderate acid sites

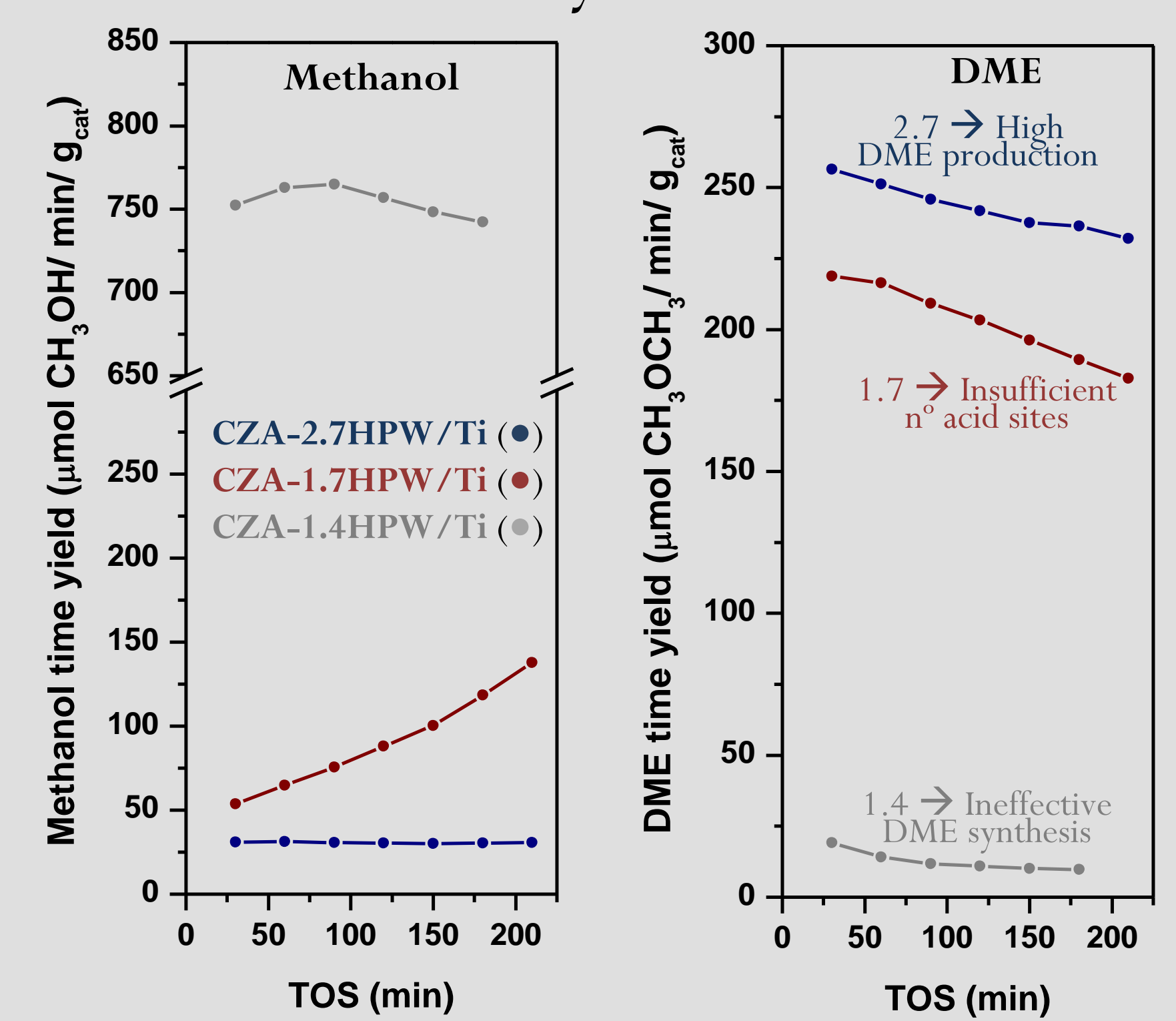
	Cu area (m^2/g_{cat})	NH_3 (desorb./ g_{HPW})
CZA-1.4HPW/Ti	28.6	1.0
CZA-1.7HPW/Ti	35.5	-
CZA-2.7HPW/Ti	39.1	1.0
CZA	43.4	-

DRIFTS



- ✦ HPW structure modifications by exchange Cu^{2+}/Zn^{2+} from CZA with H^+ of HPW

Activity Performance



- ✦ Catalytic activity depends on HPW loading:
 >1.4 monolayers → activity for STD
 2.7 monolayers → higher activity than CZA-HZSM5
- ✦ ↓ **Total conversion** – ↑HPW → H_2O inhibitory effect (and some Cu sintering)
 ↑ **DME Selectivity** – ↑HPW → 3D HPW formation (pseudo-liquid behavior) and n° acid sites
- ✦ ↓ **DME (TOS)** → deactivation of both active sites (by H_2O and/or cationic exchange)

CONCLUSIONS

There is a strong influence of the HPW loading on TiO_2 on the structure and acidity of HPW that affects the activity of bifunctional catalysts prepared by its physical mixing with Cu/ZnO. The differences in activity and stability are related with the different interaction of HPW with the support that affects its dispersion, structure and degree of hydration. There is a loading threshold that must be exceeded to achieve activity for DME production since HPW loading close to monolayer on TiO_2 results in strong interaction of HPW units with the support decreasing its acidity for DME production. The hybridization of HPW/ TiO_2 with CZA implies modifications in both functions by cation exchange which need to be carefully analyzed.

References

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