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FTIR Study of Methanol Decomposition on Cu & Au Catalysts Supported on ZnO & on TiO_2

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☺ H_2 - fuelled engine

But... using H_2 for vehicle applications :

- STORAGE
- SAFETY
- REFUELING

H_2 on-board production from a liquid fuel

methanol

Reactions of interest:

✓ **decomposition**

$$CH_3OH \longrightarrow 2H_2 + CO \qquad \Delta H > 0$$

✓ **steam reforming**

$$CH_3OH + H_2O \longrightarrow 3H_2 + CO_2 \qquad \Delta H > 0$$

✓ **partial oxidation**

$$CH_3OH + 1/2\ O_2 \longrightarrow 2H_2 + CO_2 \qquad \Delta H < 0$$

✓ **combined or autothermal reforming**

$$CH_3OH + (1-2a)H_2O + aO_2 \rightarrow CO_2 + (3-2a)H_2 \qquad 0 < a < 0.5$$

✓ **Cu catalysts: rapid deactivation, Au catalysts: very active in CO oxidation, WGSR**

F. Boccuzzi, A. Chiorino, M. Manzoli, P. Lu, T. Akita, S. Ichikawa, M. Haruta, J. Catal., 2001, **202**, 256.

F. Boccuzzi, A. Chiorino, M. Manzoli, D. Andreeva, T. Tabakova, *J. Catal.*, 1999, **188**, 176.

Materials:

✓ **Cu/ZnO & Au/ZnO**
(co-precipitation method)

Cu ≈ 8-10 at. %
Au ≈ 5 at. %

✓ **Cu/TiO_2 & Au/TiO_2**
(deposition-precipitation method)

Interaction with 2 mixtures at increasing temperature

pure CH_3OH & $CH_3OH–H_2O–O_2$ (1:1:0.2 ratio)

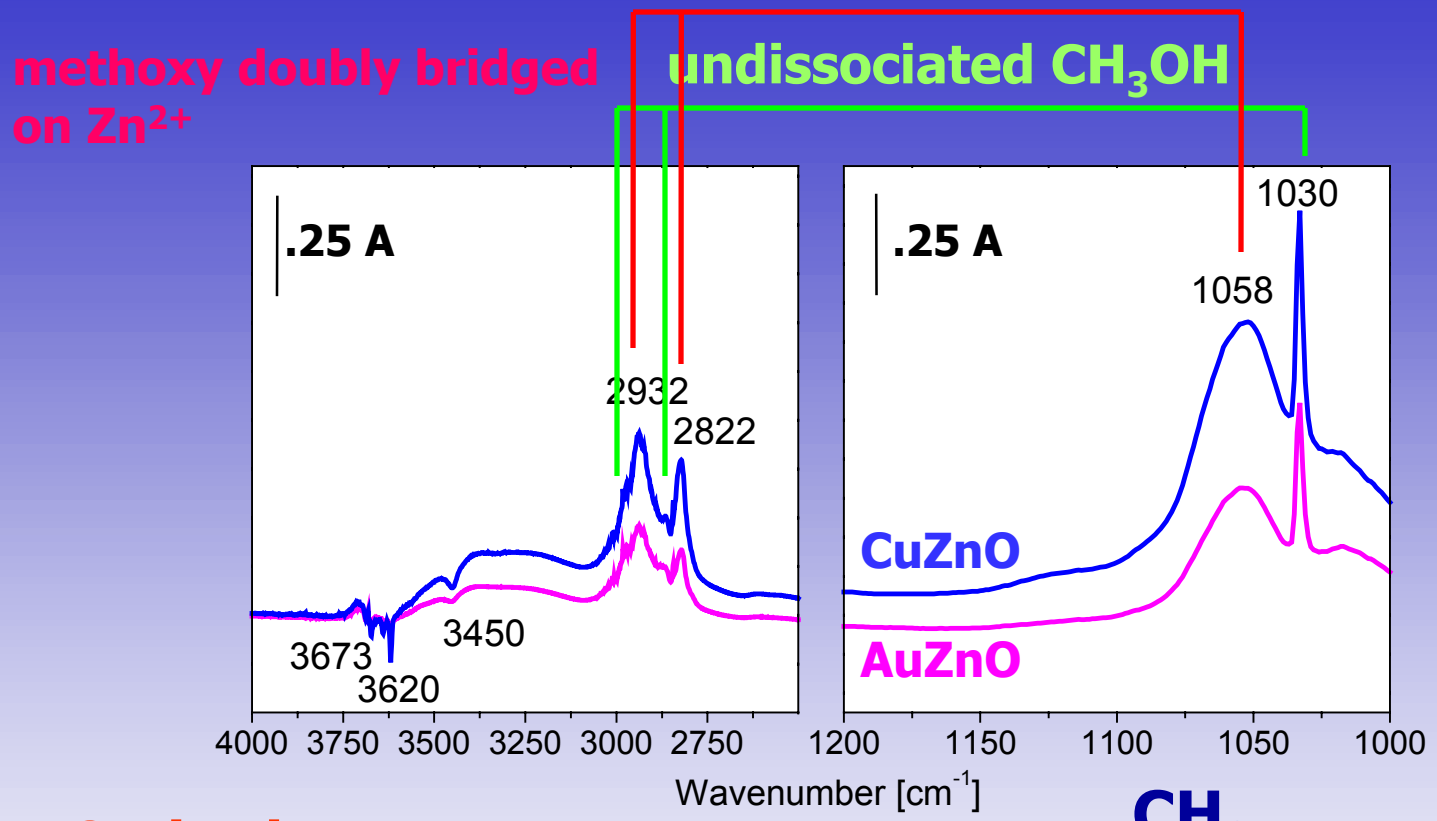
FTIR Spectroscopy + Mass Spectrometry

in situ spectra in controlled atmospheres & temperatures

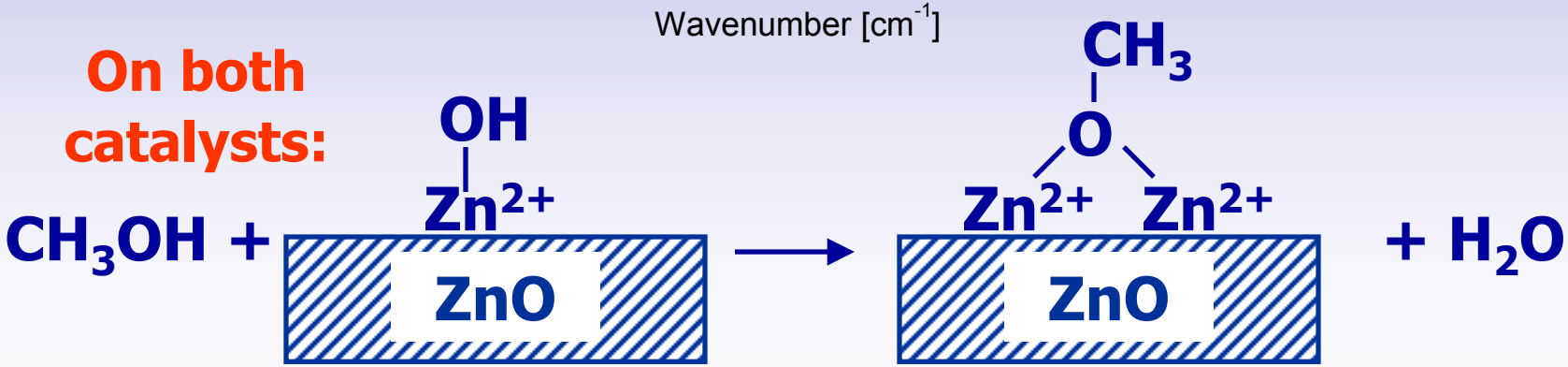
Aims of the study:

- ✓ Produce H_2
- ✓ Clean-up of H_2 fuel from CO
- ✓ Identify surface & gas phase species
- ✓ Understand the reaction mechanism on both Cu and Au catalysts

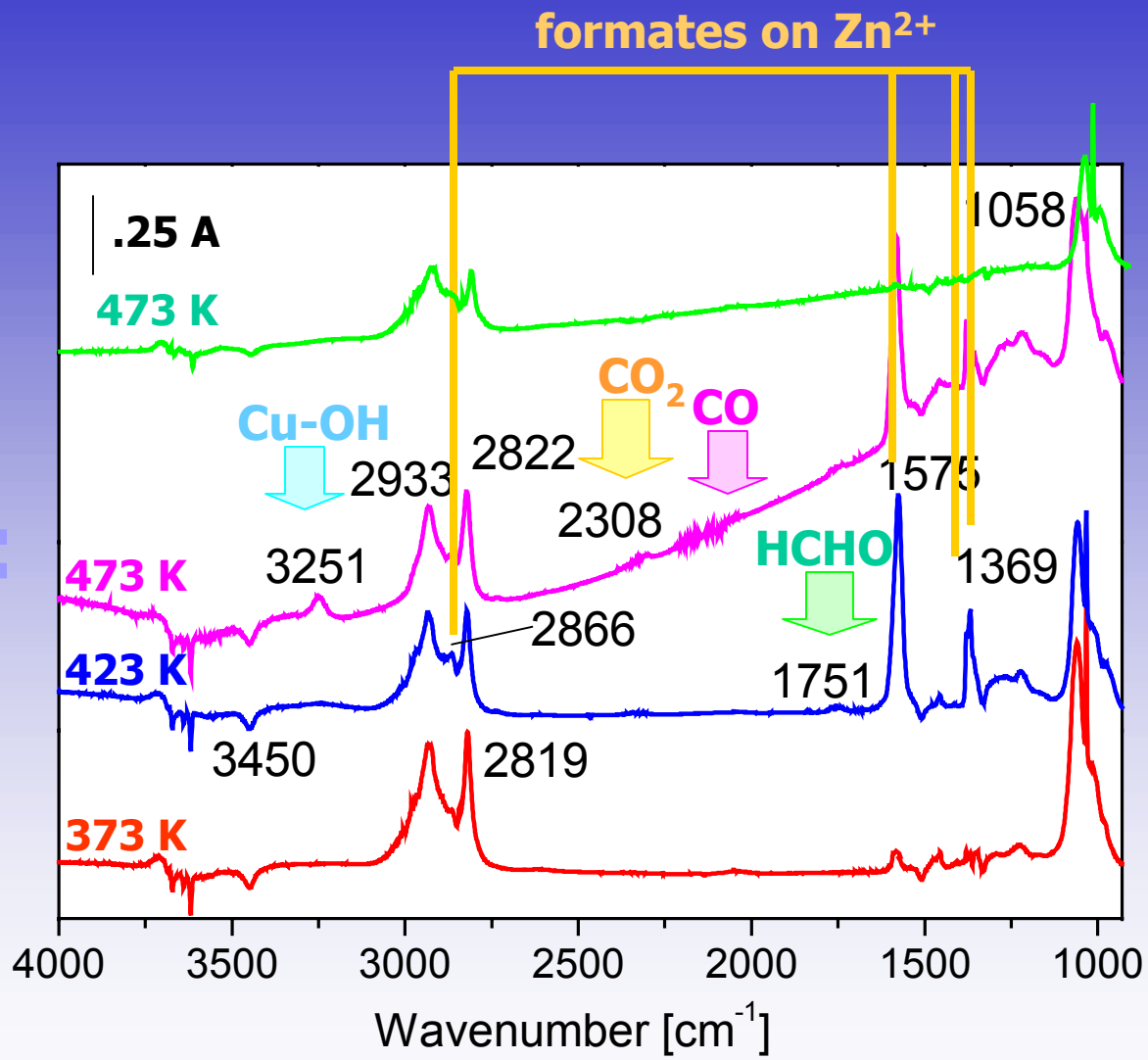
✓ CH_3OH interaction at r.t.:



On both catalysts:



✓ CH_3OH interaction at increasing temperature:

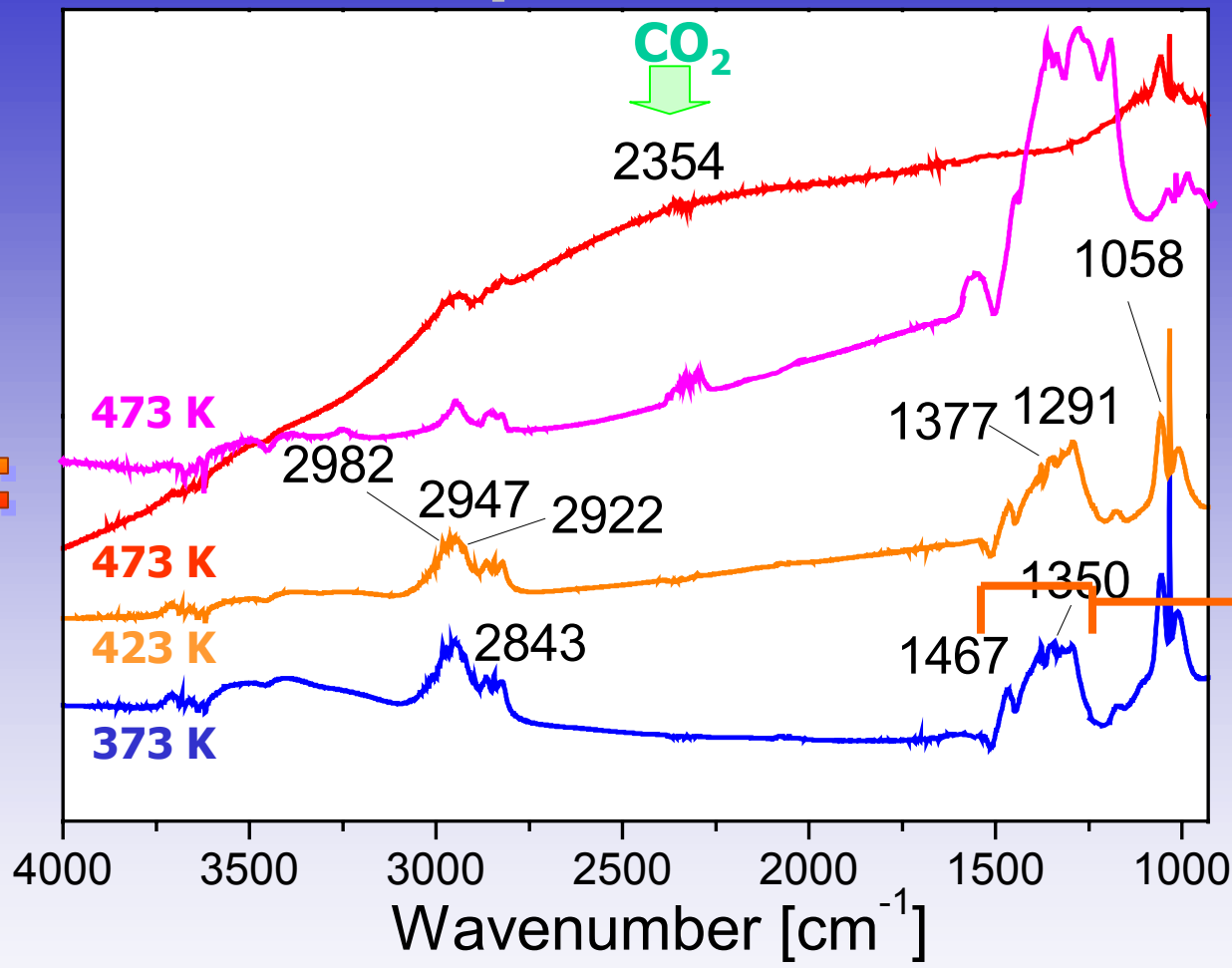


✓ QMS: CO & CO_2. H_2 starting from 423 K

✓ CH_3OH-H_2O-O_2 interaction at increasing temperature:

Cu/ZnO

Au/ZnO:



already at r.t., absent in CH_3OH

✓band related to methoxy species less intense

About Cu & Au on the same support:

Different thermal evolution & stability of the species:

✓ **Au/ZnO**

(both CH_3OH & MIXTURE: bands completely depleted at 473 K)

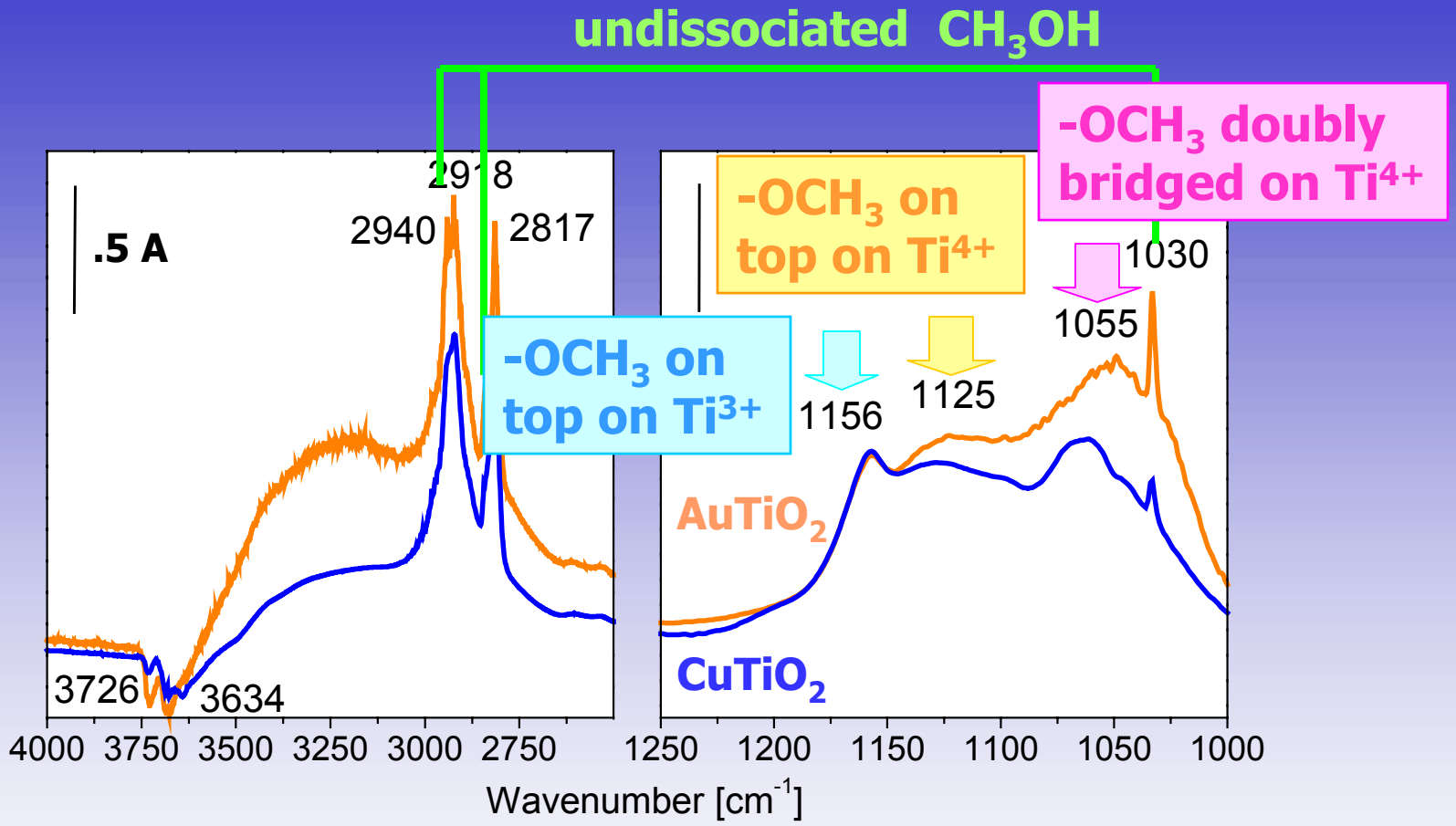
✓ **Cu/ZnO**

(at 473 K CH_3OH: formates, MIXTURE: strong bands)

✓ **O_2 is probably adsorbed in atomic form on small Cu and Au particles at the interface with ZnO**

✓ **Highly basic oxygen sites extract H atoms from $-OCH_3$ species inducing the formation of carbon–containing species $C_xO_yH_z$**

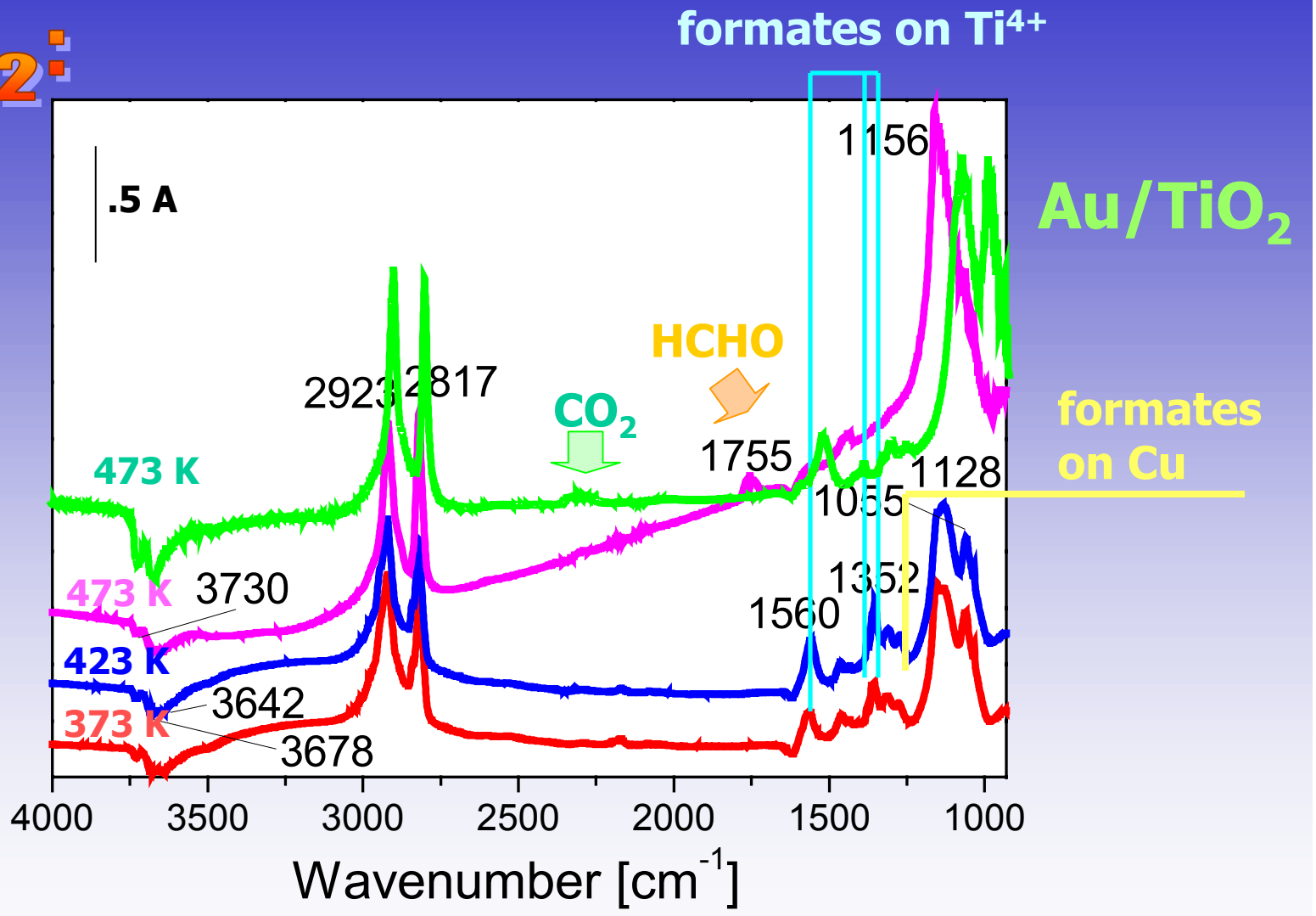
✓ CH_3OH interaction at r.t.:



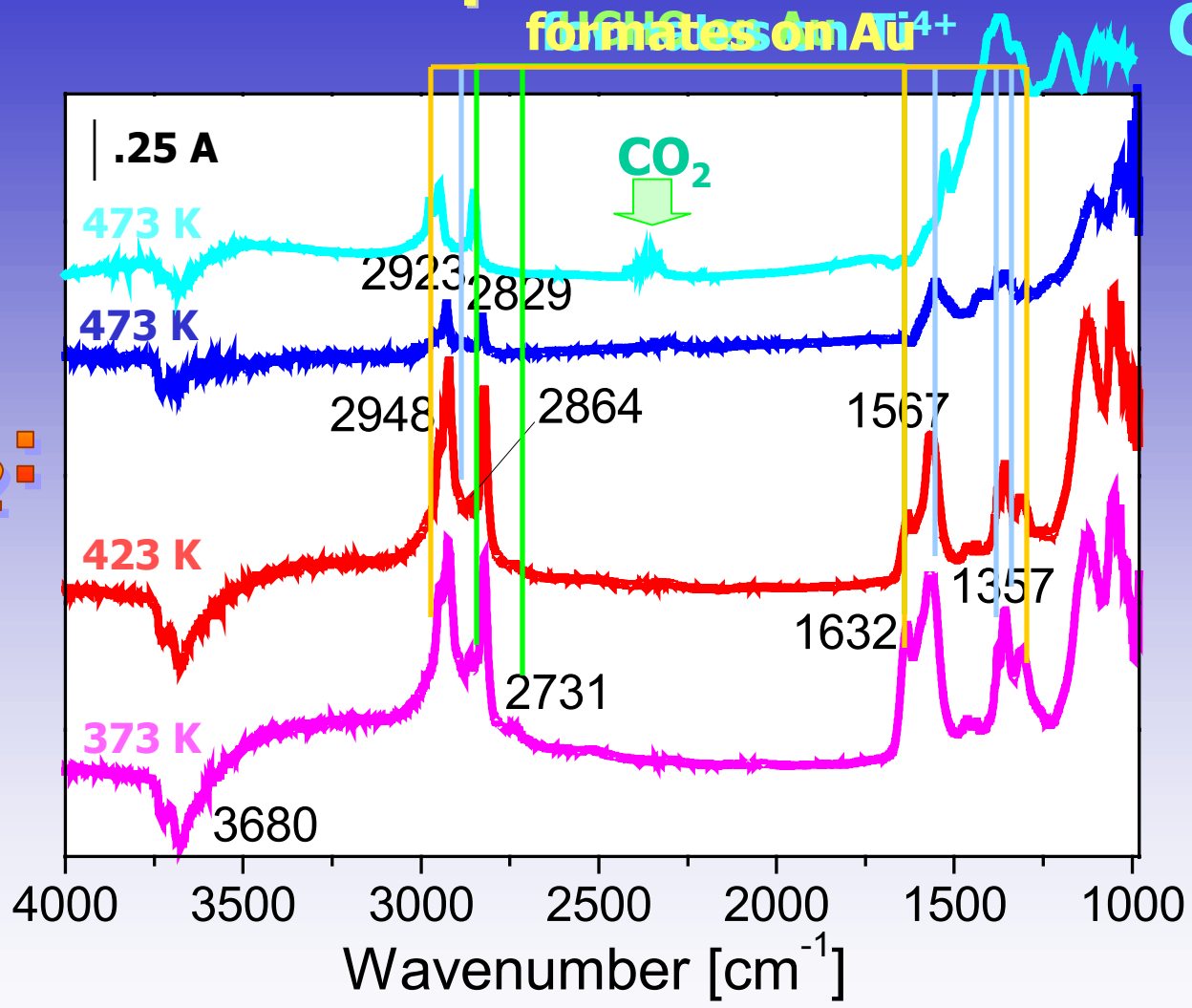
✓ On TiO_2: differently coordinated methoxy species

✓CH_3OH interaction at increasing temperature:

Cu/TiO_2:

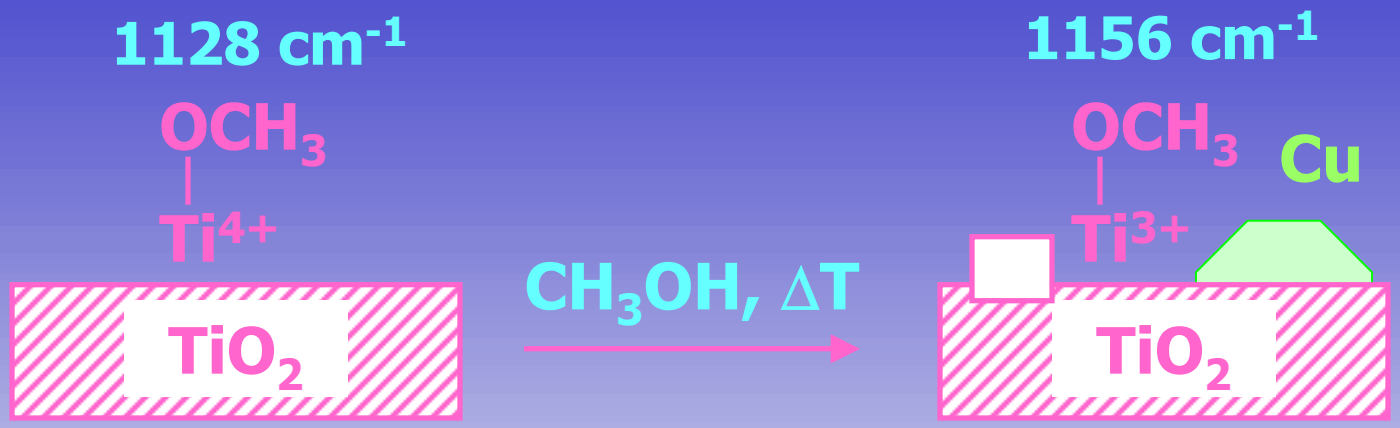


✓ CH_3OH-H_2O-O_2 interaction at increasing temperature:



F. Boccuzzi, A. Chiorino, M. Manzoli, *J. Power Sources*, 118 (2003) 304.

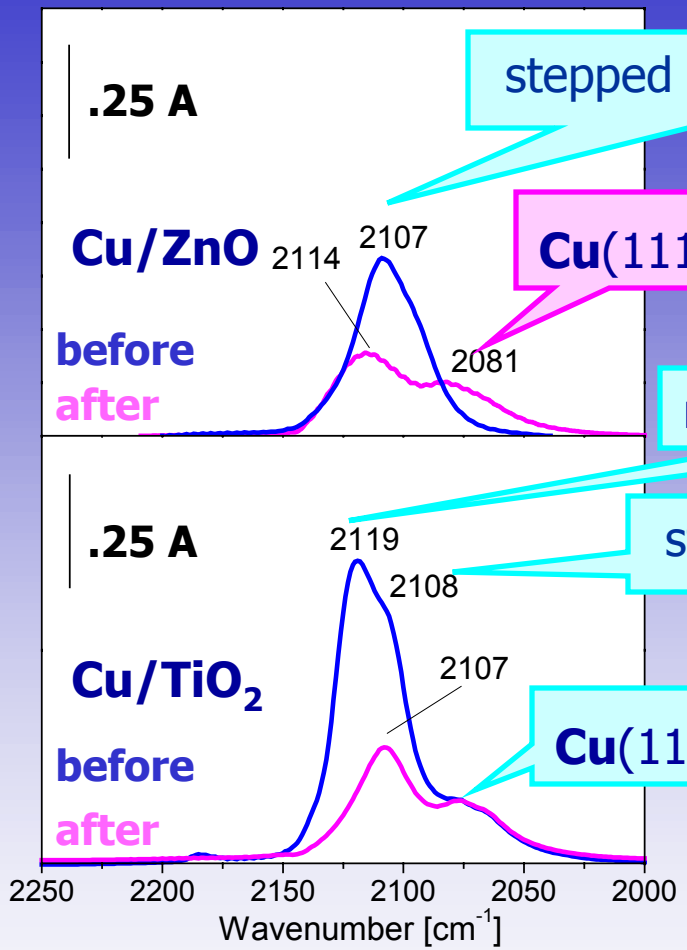
About Cu & Au both supported on TiO_2:



Mixture:

✓ O_2 enhances the formation of reaction intermediates on Au/TiO_2 (formates on both metal & support)

CO adsorption at r.t. on Cu catalysts before & after CH_3OH decomposition reactions



stepped **Cu⁰** surfaces

Cu(111)

blue shift of the 2107 cm^{-1} band

not fully reduced **Cu**

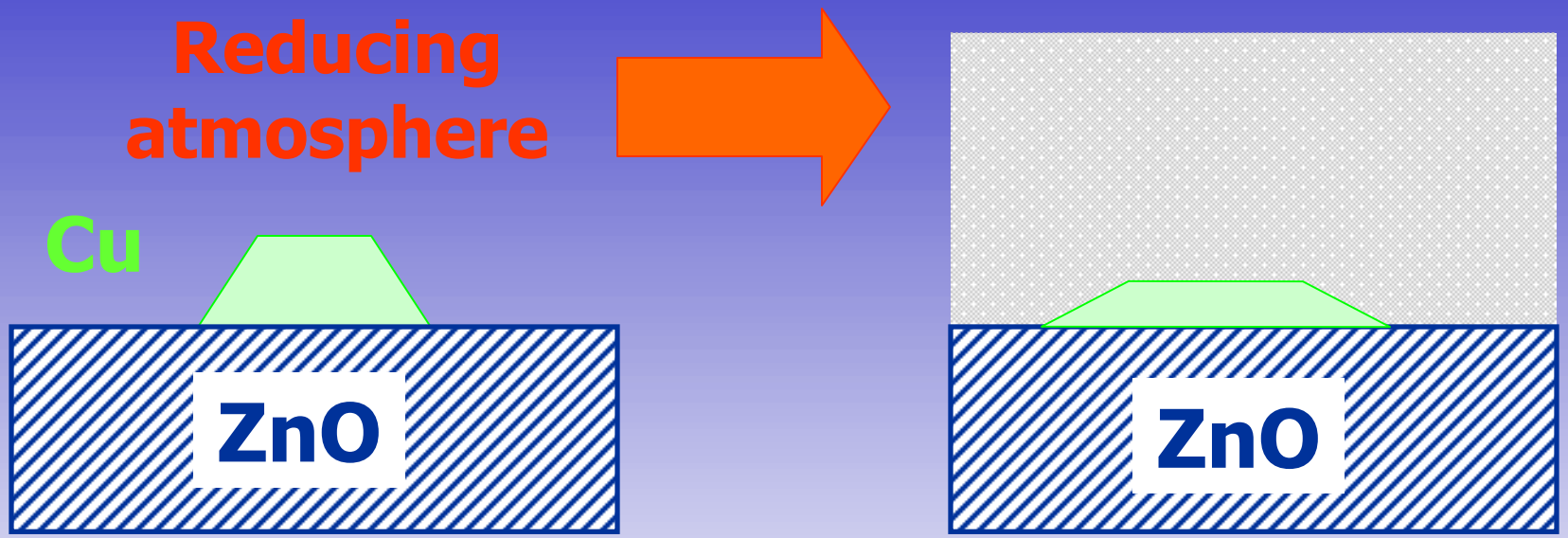
stepped **Cu⁰** surfaces

Cu(111)

Cu sites: reduced, either agglomerated into larger particles or covered by residual species

✓ **A fraction of the surface metallic area (more uncoordinated & reactive sites) is no more able to adsorb CO**

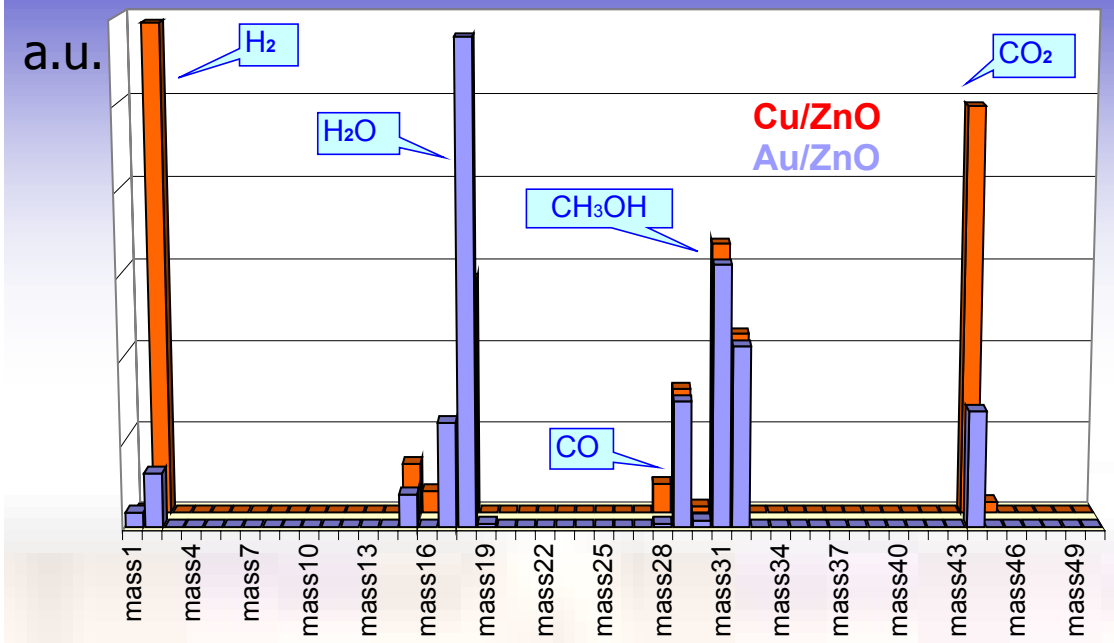
✓ **blue shift of the band at 2107 cm^{-1}**



spectroscopic evidences of an evolution towards a flatter morphology*

* P.L. Hansen, J.B. Wagner, S. Helveg, J.R Rostrup-Nielsen, B.S. Clausen, H. Topsøe, *Science*, 295 (2002) 2053.

Mass Spectrometry results



✓ high H_2 & CO_2 amounts on Cu/ZnO

✓ very low CO amount on Au/ZnO

Final remarks

✓ Surface species, reaction intermediates & gaseous products in different relative amounts (depending on the nature of the metal & of the support) have been evidenced