FTIR Study of Methanol Decomposition on Cu & Au Catalysts Supported on ZnO & on TiO$_2$

Maela Manzoli, Anna Chiorino, Flora Boccuzzi and Salvatore Coluccia

XXI Congresso della Società Chimica Italiana
Torino, 22-27 Giugno 2003
But... using H₂ for vehicle applications:

- H₂ on-board production from a liquid fuel
- methanol

H₂ - fuelled engine

STORAGE
SAFETY
REFUELING

sulfur pollutants
unburned hydrocarbons
CO
NOx
CO₂
particulate
Reactions of interest:

✓ decomposition

\[ CH_3OH \rightarrow 2H_2 + CO \quad \Delta H > 0 \]

✓ steam reforming

\[ CH_3OH + H_2O \rightarrow 3H_2 + CO_2 \quad \Delta H > 0 \]

✓ partial oxidation

\[ CH_3OH + \frac{1}{2} O_2 \rightarrow 2H_2 + CO_2 \quad \Delta H < 0 \]

✓ combined or autothermal reforming

\[ CH_3OH + (1-2a)H_2O + aO_2 \rightarrow CO_2 + (3-2a)H_2 \quad 0 < a < 0.5 \]

XXI Congresso della Società Chimica Italiana

Torino, 22-27 Giugno 2003


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


Materials:

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

✓ Cu/TiO₂ & Au/TiO₂  
(deposition-precipitation method)

Interaction with 2 mixtures at increasing temperature

pure CH₃OH & CH₃OH–H₂O–O₂ (1:1:0.2 ratio)
in situ spectra in controlled atmospheres & temperatures

Aims of the study:

- Produce H₂
- Clean-up of H₂ fuel from CO
- Identify surface & gas phase species
- Understand the reaction mechanism on both Cu and Au catalysts
**CH₃OH interaction at r.t.:**

- Methoxy doubly bridged on Zn<sup>2+</sup> on CuZnO and AuZnO.
- Undissociated CH₃OH.

**On both catalysts:**

\[
\text{CH}_3\text{OH} + \text{Zn}^{2+} \rightarrow \text{CH}_3\text{OZnO} + \text{H}_2\text{O}
\]
CH₃OH interaction at increasing temperature:

QMS: CO & CO₂. H₂ starting from 423 K

XXI Congresso della Società Chimica Italiana
Torino, 22-27 Giugno 2003
CH$_3$OH-H$_2$O-O$_2$ interaction at increasing temperature:

Cu/ZnO

Au/ZnO:

Band related to methoxy species less intense

XXI Congresso della Società Chimica Italiana
Torino, 22-27 Giugno 2003
About Cu & Au on the same support:

Different thermal evolution & stability of the species:

✅ Au/ZnO
(both CH₃OH & MIXTURE: bands completely depleted at 473 K)

✅ Cu/ZnO
(at 473 K CH₃OH: formates, MIXTURE: strong bands)

✅ O₂ 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 –OCH₃ species inducing the formation of carbon–containing species CₓOᵧHᵣ
**CH₃OH interaction at r.t.:**

- undissociated CH₃OH
  - -OCH₃ on top on Ti³⁺
  - -OCH₃ doubly bridged on Ti⁴⁺

**On TiO₂:** differently coordinated methoxy species

XXI Congresso della Società Chimica Italiana
Torino, 22-27 Giugno 2003
CH$_3$OH interaction at increasing temperature:

Cu/TiO$_2$:

formates on Ti$^{4+}$

Au/TiO$_2$

formates on Cu

Wavenumber [cm$^{-1}$]

4000 3500 3000 2500 2000 1500 1000

3730

1156

1755

1560

1055

1128

3678

2817

1128

2923

2817

3642

3678

373 K

473 K

423 K

1352

XXI Congresso della Società Chimica Italiana

Torino, 22-27 Giugno 2003
\[ \text{CH}_3\text{OH}-\text{H}_2\text{O}-\text{O}_2 \] interaction at increasing temperature:

- Au/TiO_2:
  - 373 K: 3680
  - 423 K: 2948, 2864, 2731, 1632, 1357
  - 473 K: 2923, 2829

- Cu/TiO_2:

About Cu & Au both supported on TiO₂:

1128 cm⁻¹
OCH₃
↓
Ti⁴⁺

1156 cm⁻¹
OCH₃
↓
Ti³⁺

Mixture:

✓ O₂ enhances the formation of reaction intermediates on Au/TiO₂ (formates on both metal & support)
CO adsorption at r.t. on Cu catalysts before & after CH₃OH decomposition reactions

- Stepped Cu⁰ surfaces
- Blue shift of the 2107 cm⁻¹ band
- Not fully reduced Cu
- Stepped Cu⁰ surfaces

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

XXI Congresso della Società Chimica Italiana
Torino, 22-27 Giugno 2003
✓ blue shift of the band at 2107 cm\(^{-1}\)

Reducing atmosphere

spectroscopic evidences of an evolution towards a flatter morphology*


XXI Congresso della Società Chimica Italiana
Torino, 22-27 Giugno 2003
Surface species, reaction intermediates & gaseous products in different relative amounts (depending on the nature of the metal & of the support) have been evidenced.

- High $\text{H}_2$ & $\text{CO}_2$ amounts on Cu/ZnO
- Very low CO amount on Au/ZnO

Mass Spectrometry results