

Formaldehyde Adsorption on Rutile TiO₂(110) Surface Probed by IR Spectroscopy

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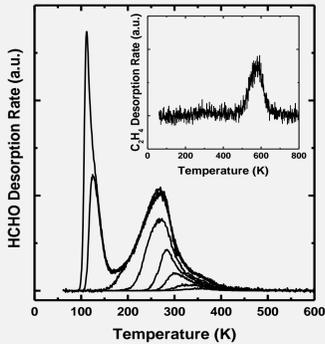
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Introduction

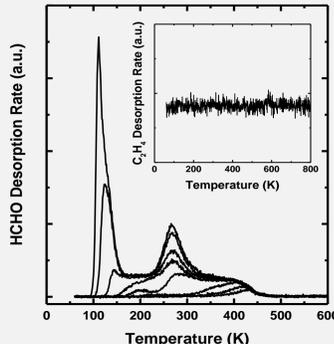
Titanium dioxide (TiO₂) is one of the most important metal oxides used in catalysis and photocatalysis. Understanding the surface chemistry of formaldehyde (CH₂O) on this material is of particular interest because CH₂O is a key species (reagent, intermediate, or product) in numerous catalytic and photocatalytic reactions such as methanol synthesis, methanol oxidation and hydrocarbon production. Here, we present a thorough surface science study on the interaction of formaldehyde (CH₂O) with the rutile TiO₂(110) surface using a novel ultra-high vacuum infrared reflection-absorption spectroscopy (UHV-IRRAS) apparatus.

TPD: CH₂O adsorption on TiO₂(110) at 80 K

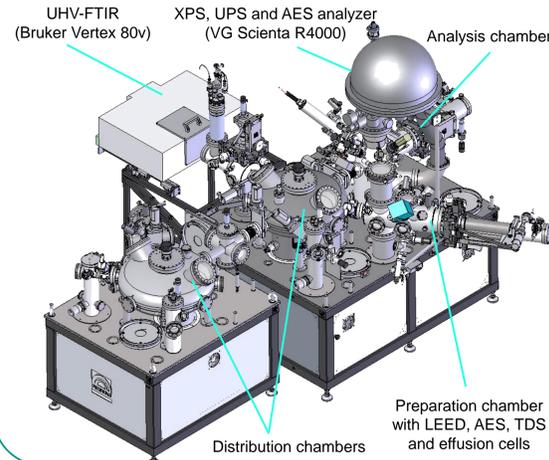
CH₂O on reduced TiO₂(110)



CH₂O on oxidized TiO₂(110)



UHV-IRRAS apparatus



Strategy to overcome challenge of low reflectivity:

- Attach spectrometer directly to UHV chamber.
- Do not introduce any additional optical element.
- Minimize mechanical vibrations, - crucial for time-resolved experiments.

Additional features of "THEO":

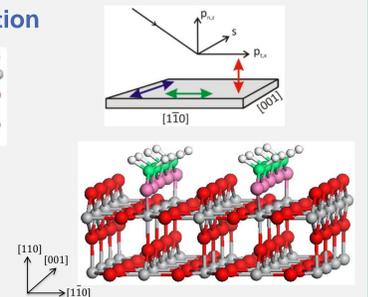
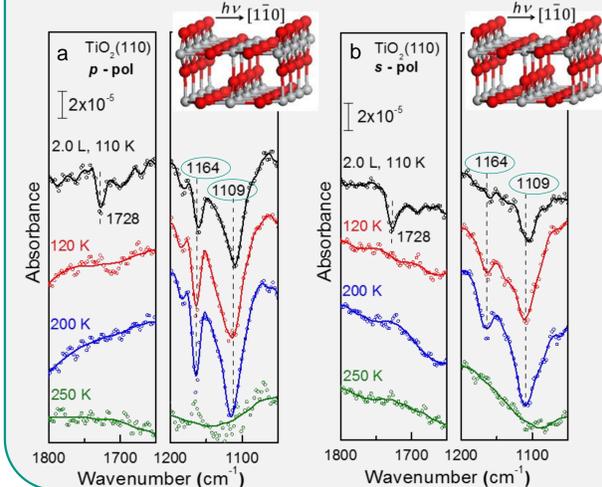
- Allows transmission measurements on powder samples.
- Cooling to 100 K (LN₂) or 60 K (LHe);
- Heating up to 1200 K.
- Equipped for XPS, UPS, AES, LEIS, and LEED.

IRRAS- Measurements:

- Pressure: $\leq 8 \times 10^{-11}$ mbar
- Reflection mode
- Grazing Incidence (80°)
- p- and s-polarized light

Paraformaldehyde

p- and s-polarized light incident along [1-10] direction

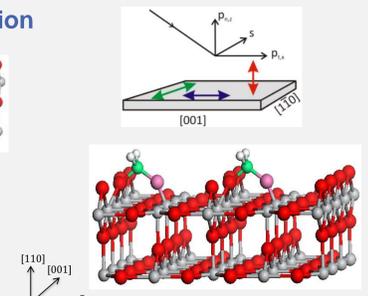
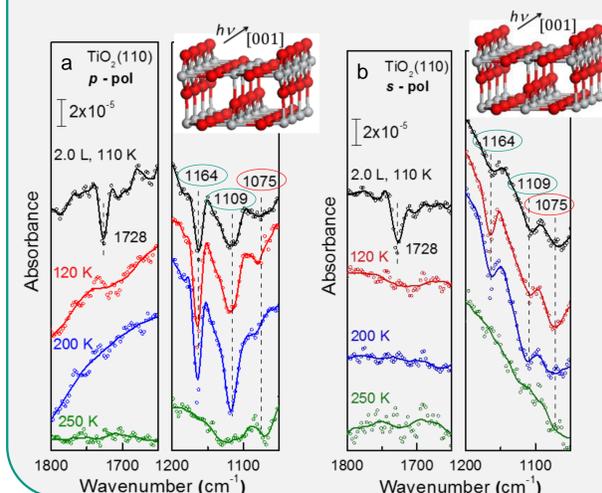


- Paraformaldehyde (POM) is formed via coupling reactions of CH₂O monomers at Ti_{5c} sites.
- The POM chain is oriented primarily along the [001] direction in a slightly disordered configuration.

$\nu(\text{C-O})$: 1164, 1109 cm⁻¹ (exp.)
1158, 1120 cm⁻¹ (DFT)

Dioxymethylene

p- and s-polarized light incident along [001] direction



- Dioxymethylene (DOM) was detected as minority species formed via reaction of Ti_{5c}-bound CH₂O monomers with surface O-atoms.

$\nu(\text{C-O})$: 1075 cm⁻¹ (exp.)
1077, 818 cm⁻¹ (DFT)

Conclusions

- CH₂O adsorption at 65 K leads to the formation of multilayer CH₂O, which desorbs completely upon heating to 120 K.
- The CH₂O monomer was identified after submonolayer adsorption at 45-60 K, in which CH₂O is bound to the surface Ti_{5c} sites via σ -donation in a tilted geometry.
- Upon heating, the CH₂O monomers polymerize to form paraformaldehyde (POM) chains, oriented primarily along the Ti_{5c} rows ([001] direction).
- Dioxymethylene was detected as minority species formed via reaction of Ti_{5c}-bound CH₂O monomers with surface O-atoms.

References:

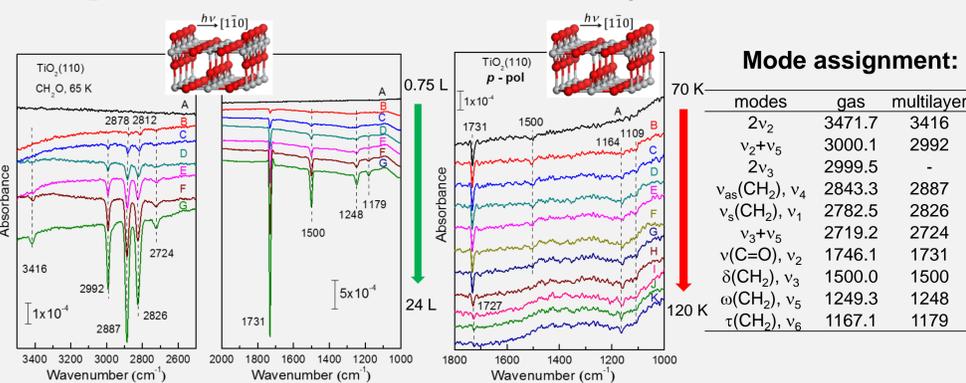
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CH₂O adsorption on TiO₂(110) : Multilayers

CH₂O adsorption at 65 K IRRAS thermal desorption data



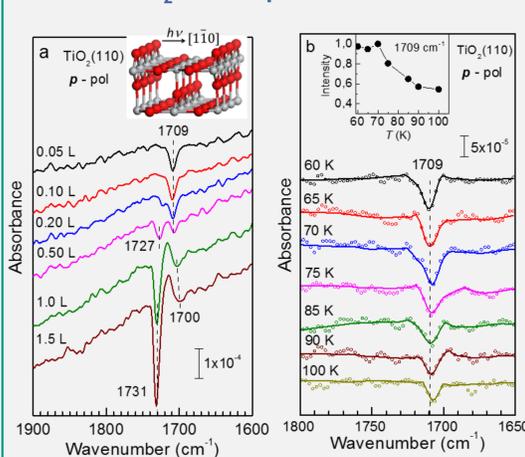
Mode assignment:

| modes | gas | multilayer |
|--|--------|------------|
| 2v ₂ | 3471.7 | 3416 |
| v ₂ +v ₅ | 3000.1 | 2992 |
| 2v ₃ | 2999.5 | - |
| v _{as} (CH ₂), v ₄ | 2843.3 | 2887 |
| v _s (CH ₂), v ₁ | 2782.5 | 2826 |
| v ₃ +v ₅ | 2719.2 | 2724 |
| v(C=O), v ₂ | 1746.1 | 1731 |
| δ(CH ₂), v ₃ | 1500.0 | 1500 |
| ω(CH ₂), v ₅ | 1249.3 | 1248 |
| τ(CH ₂), v ₆ | 1167.1 | 1179 |

- Intermolecular interaction: dipole-dipole attractions between polar carbonyl groups
- Fermi resonance: v₂ + v₅ combination mode and v₄ mode, same symmetry (B₁)

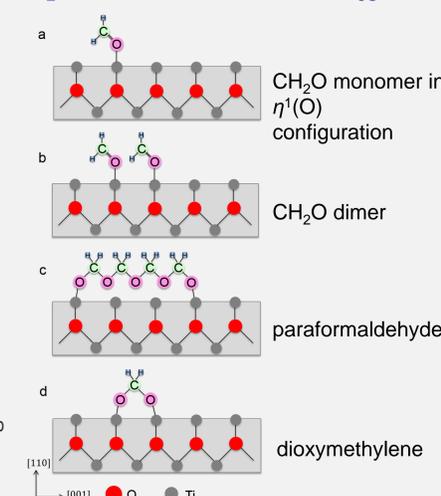
CH₂O adsorption on TiO₂(110) : Monomers

CH₂O adsorption at 65 K

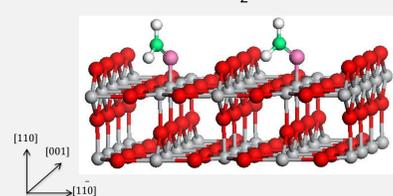


*v₂ = 1727 cm⁻¹: O_{2c}-bound CH₂O at the second-layer

CH₂O polymerization at the Ti_{5c} rows

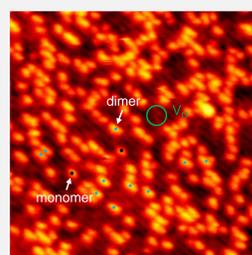


Isolated CH₂O monomer



$\nu(\text{C=O})$: 1709 cm⁻¹ (exp.)
1695 cm⁻¹ (DFT)

STM



0.07 ML CH₂O at 45 K
77 % isolated monomers at Ti_{5c} sites
23 % dimers at Ti_{5c} sites