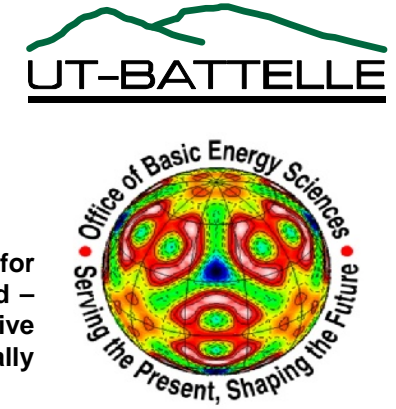


On the Active Au Species for Low Temperature CO Oxidation on Au/SiO₂



FWP KCC053 Fundamentals of Heterogeneous Catalysis on Surfaces and Nanostructures

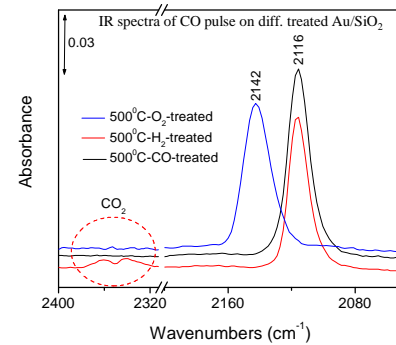
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Synopsis: Revealing the nature of catalytically active Au species in low temperature CO oxidation on supported Au catalysts is essential for understanding the reaction mechanism as well as improving the synthesis and activation routes. In this study, *operando* diffuse reflectance infrared – mass spectrometry (DRIFTS-QMS) was employed to investigate room temperature CO oxidation on differently pretreated (oxidative or reductive treatment) Au/SiO₂ catalysts. It was found that the active Au species in room temperature CO oxidation on a functioning Au/SiO₂ catalyst is essentially metallic Au located at the interface between Au nanoparticles and SiO₂ support while cationic Au species alone is not active.

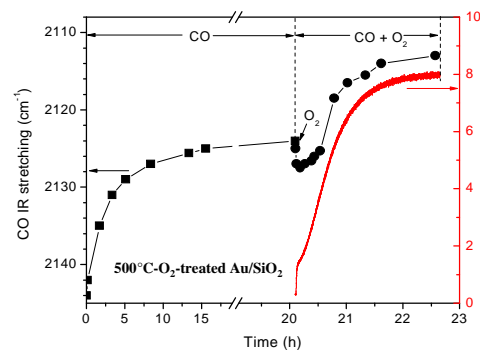
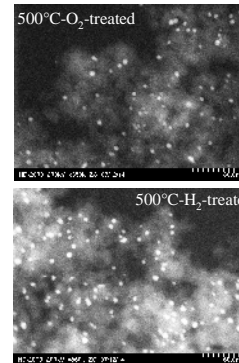
Introduction

- Why CO oxidation? Scientifically: a probe reaction for Au nanocatalysis; Practically: selective removal of CO impurities in H₂ feed for fuel cell
- Why Au/SiO₂? Scientifically: SiO₂ is inert, supposedly to simplify the complexity of Au-support interaction, better understanding of reaction mechanism. Practically: SiO₂ has high surface area, thermal stability, mechanical strength and non-reducible characteristics → industry interest
- Gold supported on silica with small particle size (≤ 6nm) was recently recognized also very active for low T CO oxidation. No spectroscopic characterization work has been reported on this system yet → aiming to gain insights into the **nature** and **role** of Au species in CO oxidation.
- Experimental: a 4% wt Au/SiO₂ (prepared via deposition-precipitation method using Au(ethylenediamene)₂Cl₃ precursor) was differently pretreated at 500°C (O₂-calcination, H₂ or CO reduction) before subject to room temperature CO oxidation (CO:O₂ = 1:4, space velocity 11250 ml.g⁻¹ h⁻¹) in a DRIFT cell. The process was monitored by both *in situ* IR (surface species) and online QMS (activity).

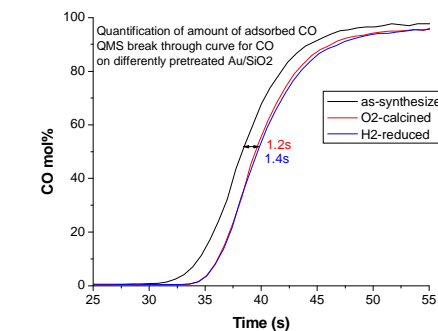
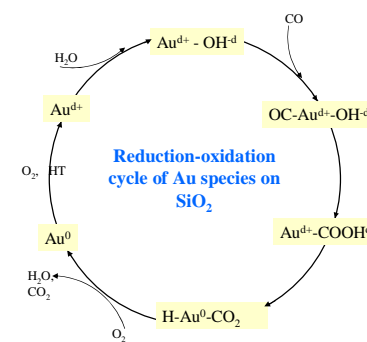
Nature of Au Species



- O₂-treated: 2142 cm⁻¹ → CO on **cationic Au** (Au^{d+}, 0<d<1), partial oxidation of surface Au sites upon high temperature O₂-treatment despite of thermodynamic instability of cationic Au at high temperature.
- H₂/CO-treated: 2116 cm⁻¹ → CO on **metallic Au** (Au⁰), H₂ and CO completely reduced Au sites. H₂ reduction generates some surface hydroxyls reactive to CO at room temperature.
- Au particles (~ 5nm) **thermally very stable** on SiO₂



Left figure shows CO band shift vs time without and with the presence of oxygen. CO can only partially reduce cationic Au at room temperature. Surprisingly, **O₂ promotes the reduction!** Combining other IR results including isotopic labeling (¹⁸O₂), the O₂-assisted reduction is proposed to proceed via a **COOH intermediate**. The reduction-reoxidation cycle is illustrated in the **right** scheme.



With the flow rate, the catalyst amount, and assuming hemispheric shape of the Au particles, CO/Au ration can be obtained :

	O ₂ -treated	H ₂ -treated
CO-Au/Total Au (%)	1.7	2
CO-Au/Surface Au (%)	8.5	10

- There is **very small percentage of Au atoms that can adsorb CO** on Au/SiO₂ → precautions when using bulk technique to access the nature of active sites, i.e., XANES for the oxidation state of active Au sites.
- It is reasonable to assume that the sites for CO adsorption locate at **perimeter / cus sites**.

Catalytic Role of Different Au Species

Left figure:

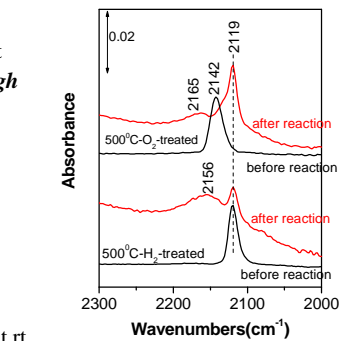
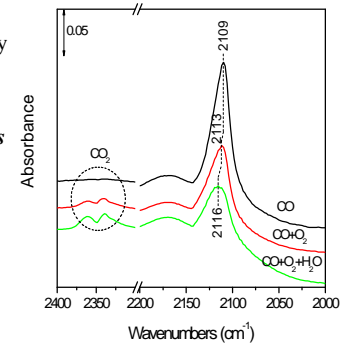
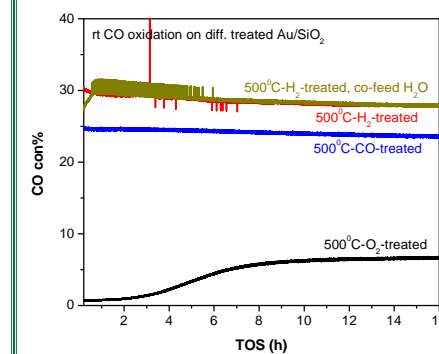
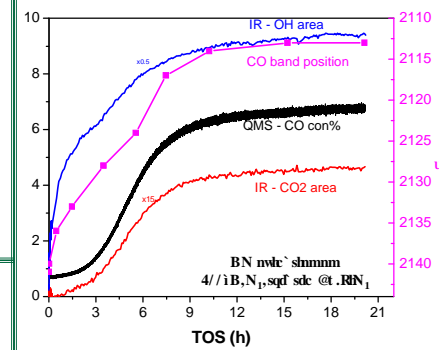
- The CO band red shift parallels to CO oxidation activity → **metallic Au plays major role** in rt CO oxidation, **cationic Au alone is not active**.
- OH band area parallels to other plots → **OH/water helps the reduction and activity**, confirmed by co-feeding water
- Red shift upon coadsorption of CO and O₂ due to formation of **O₂-Au-CO** species --- indicator for O₂ activation.
- Co-feeding H₂O further blue shift CO --- **H₂O may help to activate O₂** on Au surface.

Right figure:

- Red shift upon coadsorption of CO and O₂ due to formation of **O₂-Au-CO** species --- indicator for O₂ activation.
- Co-feeding H₂O further blue shift CO --- **H₂O may help to activate O₂** on Au surface.
- Metallic Au species are essential for CO oxidation, but they are different **depending on activation history**. **High temp reduction generates more active Au sites** --- stronger Au-support interaction (formation of Au-Si bonding?).
- Highest activity on H₂-treated Au/SiO₂ is due to both **metallic Au and surface hydroxyls** generated during reduction.

Right figure:

Although CO/O₂ can reduce cationic Au to metallic Au at rt, **some metallic Au being reoxidized during CO oxidation** --- may contribute to **catalyst deactivation**



Summary

Nature of Au species:

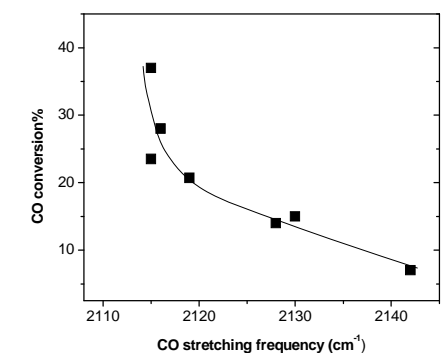
- O₂-treated Au/SiO₂: cationic; reduced to metallic by CO with the help of O₂ via a COOH intermediate
- H₂/CO-treated Au/SiO₂: metallic; but some being oxidized during rt CO oxidation.
- Both cases: very small percentage (< 2%) of Au atoms can adsorb CO and thus being active for CO oxidation, probably locate at interfacial sites.

Role of different Au species:

- Cationic Au alone is not active while metallic Au is essential for rt CO oxidation. Activity parallels the reduction extent of Au species (Left figure).
- Metallic Au with strong interaction with support is more active.
- Surface hydroxyls/water enhance the reduction of Au species as well as help to activate O₂ and thus promote CO oxidation activity.

Implications:

- Activation: Reduction in hydrogen is the best route
- Catalysis: CO absorbing sites are not necessarily catalytically active sites for CO oxidation (i.e., both cationic and metallic Au can absorb CO), metallic Au is essential as it is also able to activate O₂.



Correlation between CO oxidation activity and CO band position (representing reduction extent of Au)