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Nano Structured Interface between Gold Nanoparticles and Oxide and the Role in CO oxidation

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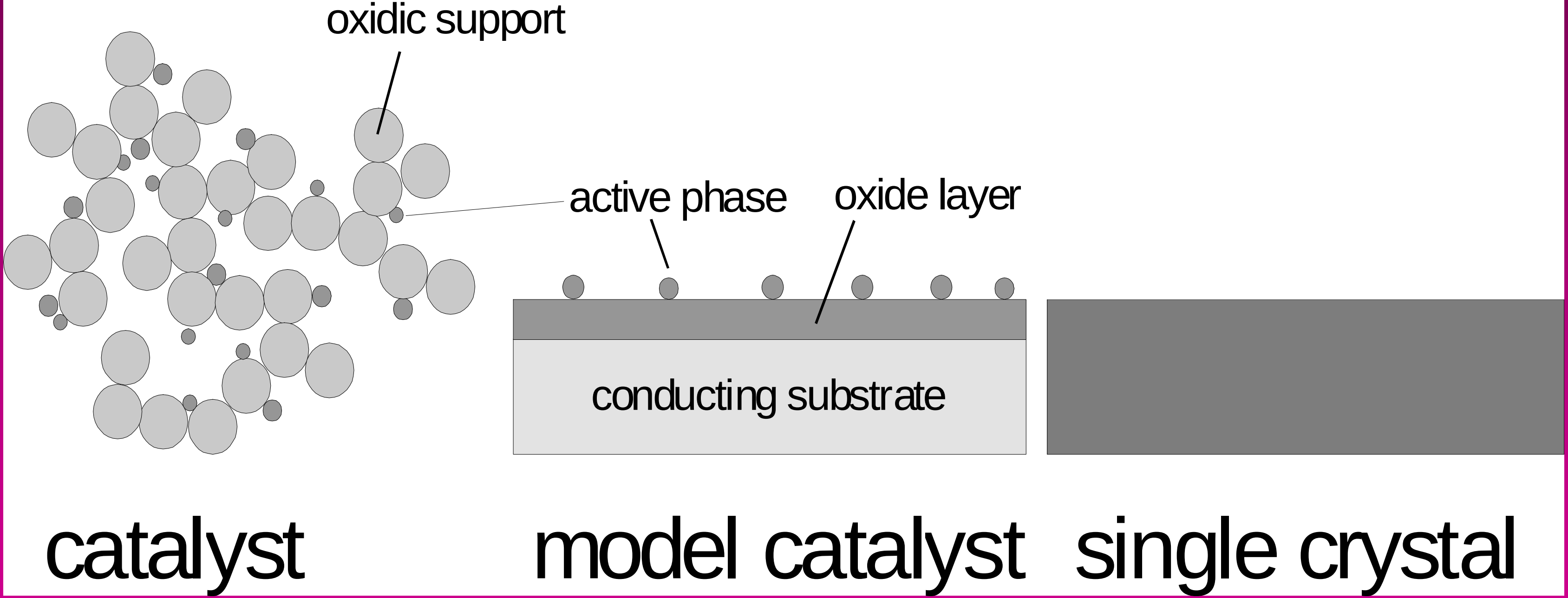
BACKGROUND

- Unique electronic and chemical properties are known to develop in solid when its dimensions reach the nanoscale.
- Changes including discrete electronic structures, modified physical structures and altered chemical reactivity, manifest themselves as new physical and chemical properties not observed in ‘bulk’ form of the material.

Why to Use Model Catalysts ?



Long range ordering:

single crystals

Short range ordering :

nanoscale metal particles

How to fabricate model nanoparticles ?

Using pulsed laser deposition on a Si(100) single crystal

(„bottom up" approach)

Partial destroying thin films by e.g. implantation

(„top down" approach)

MAIN GOAL

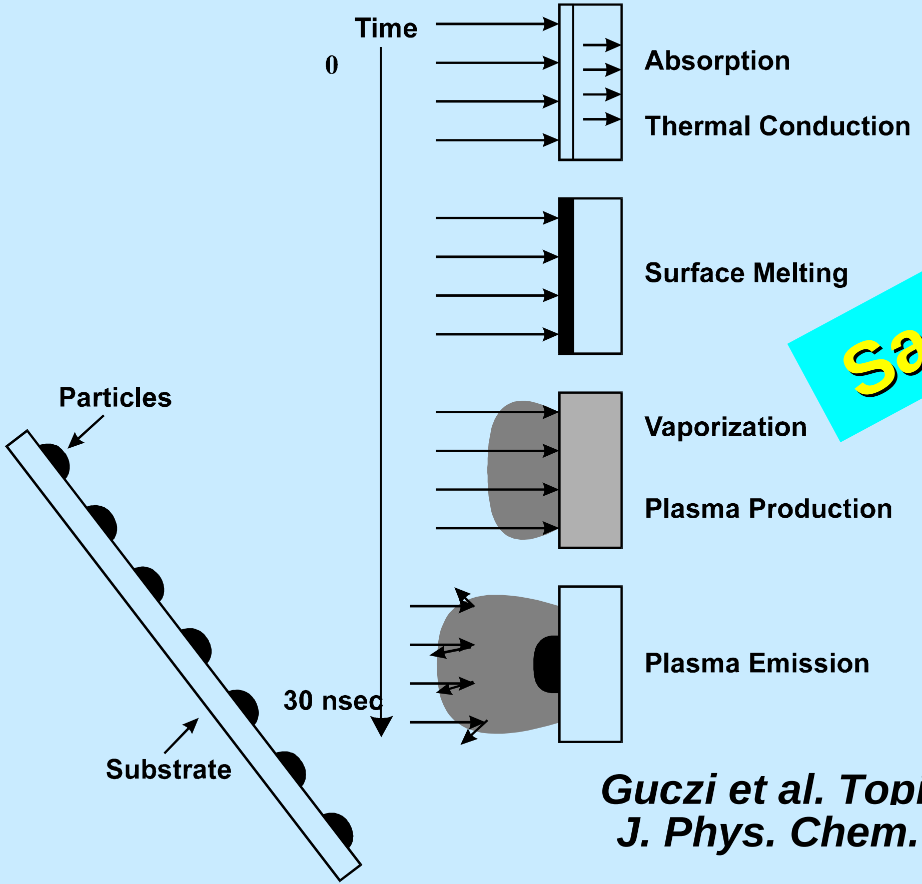
Nanosized gold particles interfaced with Fe_2O_3 is highly active catalyst for CO oxidation.

The present work is aimed at modeling the Au/FeO_x interface to find out whether

- ❖***FeO_x/SiO_2/Si(100) substrate promotes Au nano-particles through the Au/FeO_x interface, or***
- ❖***the burried interface also affects iron oxide by Au particles.***
- ❖***the electron structure, morphology and CO oxidation are investigated***

Pulsed Laser Deposition (PLD)

Interaction of High Power Laser with Target

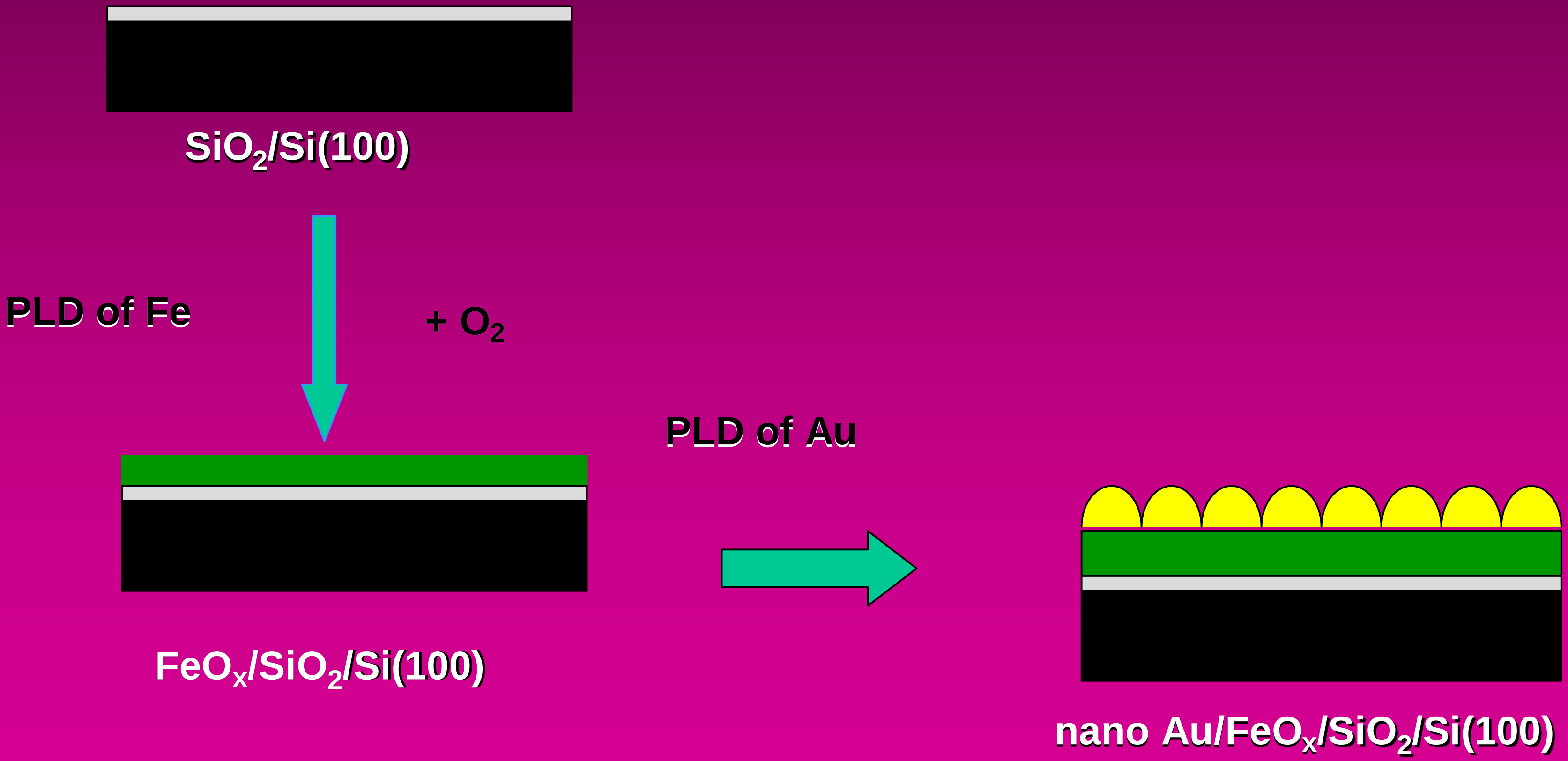


Sample preparation

Guczi et al. Topics in Catal., **29** (2004) 129
J. Phys. Chem. B., **101** (1997) 9973

Sample preparation (I)

J. Phys. Chem. B, 104 (2000) 3183



$SiO_2/Si(100)$

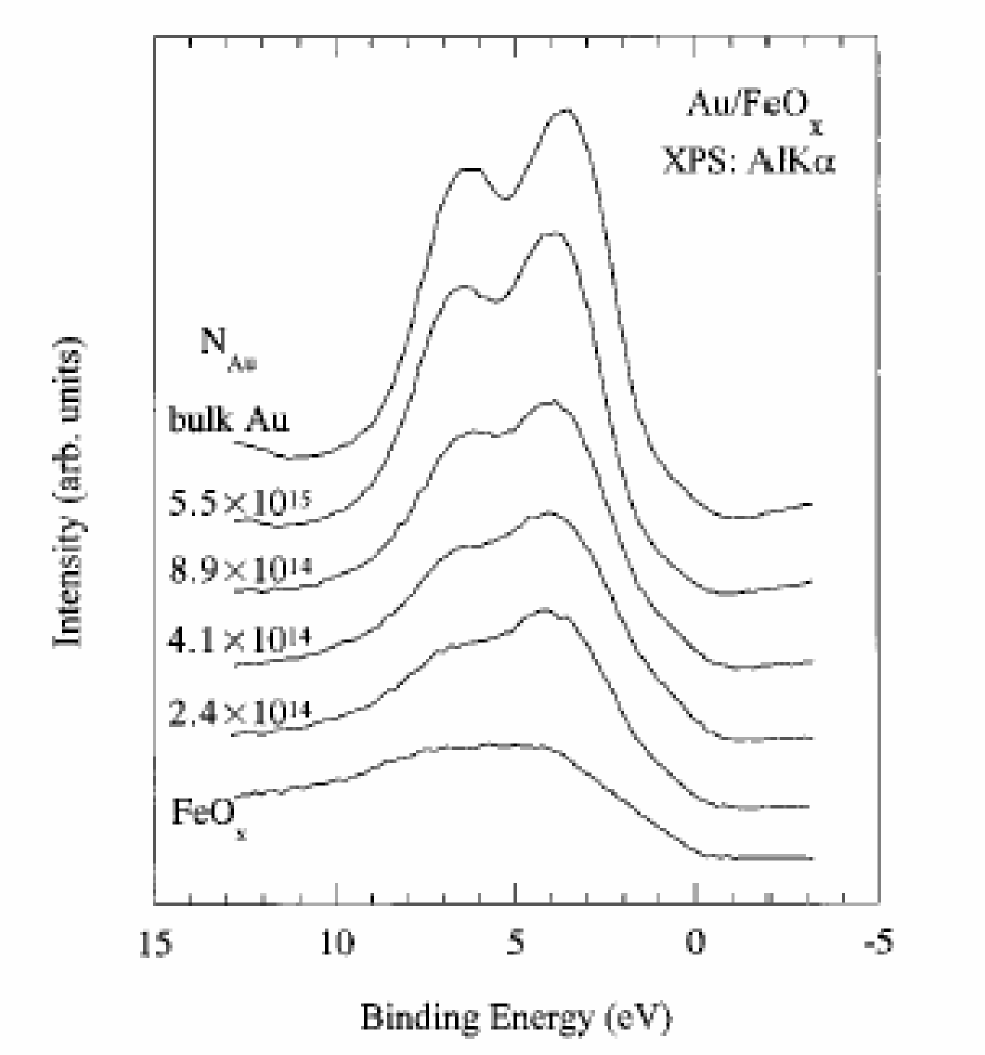
PLD of Fe

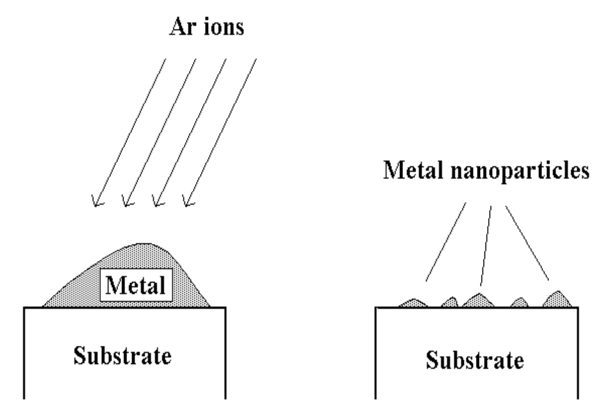
+ O_2

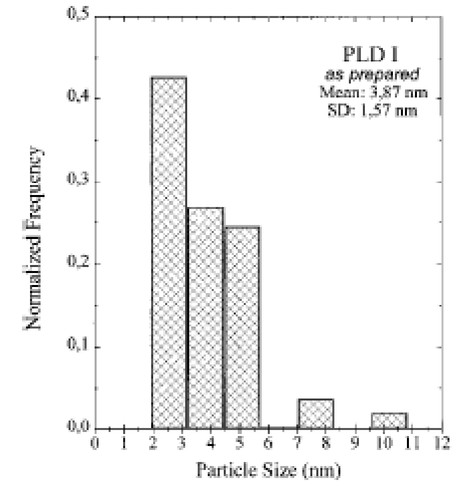
PLD of Au

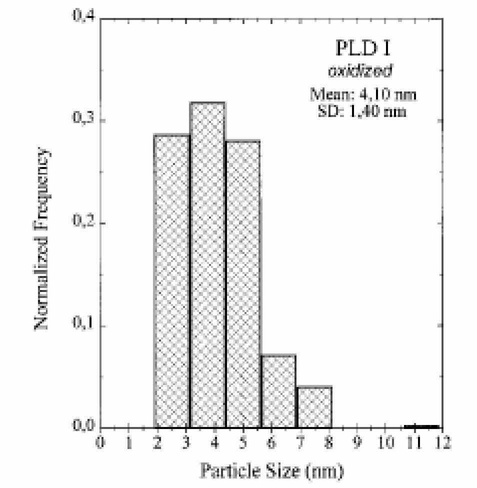
$FeO_x/SiO_2/Si(100)$

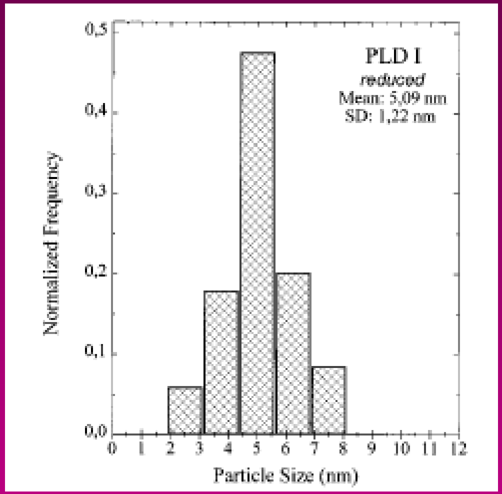
nano $Au/FeO_x/SiO_2/Si(100)$


Au/FeO$_x$
XPS: AlKα
N$_{Au}$
bulk Au
5.5×10^{15}
8.9×10^{14}
4.1×10^{14}
2.4×10^{14}
FeO$_x$
Intensity (arb. units)
15
10
5
0
-5
Binding Energy (eV)


Ar ions
Metal
Substrate
Metal nanoparticles
Substrate







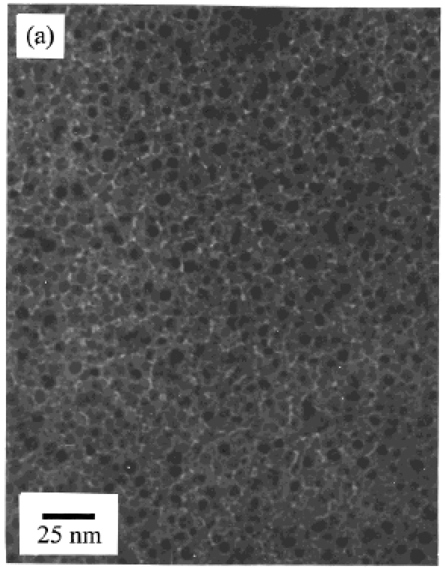
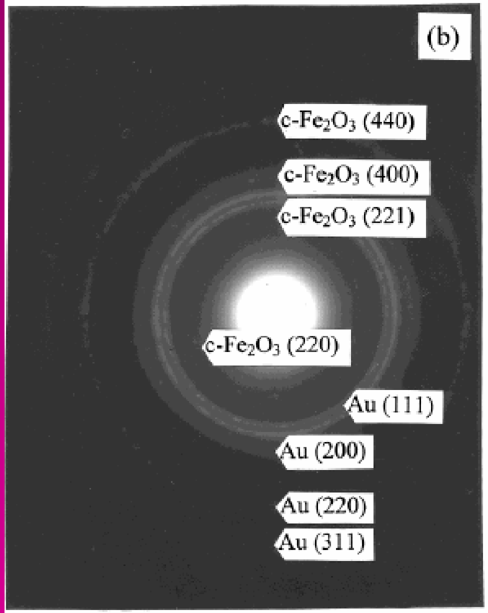


Figure 9. (a) Plan-view TEM micrograph of the reduced PLD I sample



(b) electron diffraction pattern for the reduced PLD I sample.

Composition and core level characteristics of PLD sample

Binding Energy (eV)	Possible chemical state	Au surface conc. (at/cm^2)
Au 4$f_{7/2}$: 84.0	Au^0	$(4.0\pm0.5)\times10^{15}$
Fe 2$p_{3/2}$: 710.9	Fe^{3+}	
O 1s: 529.9	Fe-O	
O 1s: 531.5	-OH	
O 1s: 533.1	water	

Catalytic activity of PLD in CO oxidation at 523 K

Treatment	Activity of PDL(I) μmol CO_2/mg_{Au}/ min
As prepared	13.7
Oxidized	35.2
Reduced in H_2	2.2

Oxidation converts FeO(OH) species on the surface at the gold/iron oxide interface (perimeter) FeO according to the following equations:

$$4\,FeO(OH) \rightarrow 4\,FeO + \square + 2\,H_2O_{(g)} + O_{2\,(g)} \qquad (1)$$

$$Fe^{2+} + \square + O_{2\,(g)} \leftrightarrow Fe^{3+} + O_{2\,(s)}^{-} \qquad (2)$$

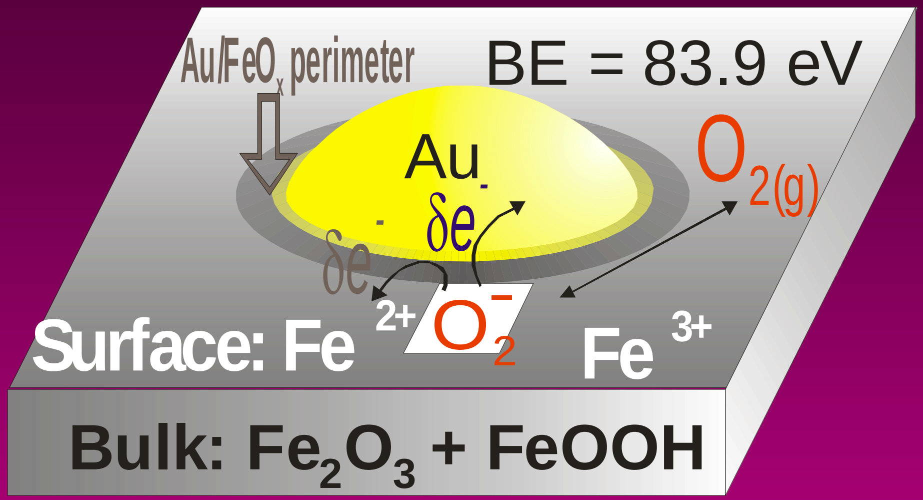
where □ means an oxygen vacancy on the surface.

- **Reaction (1) does not require oxidative atmosphere to remove water.**
- **Reaction (2) occurs in the vicinity of the gold particles. Reactions (1) and (2) take place along the perimeter of the gold/iron oxide interface: XPS results show that FeO species are created when after the oxidation the gold particles is partially covered by support species.**
- **$O_{2\,(s)}^-$ species formed interact with iron ions formed in the vicinity of the gold particles**

$$O_2^- + Au^{\delta+} \rightarrow O_2 + Au \qquad (3)$$

Evidences

- **Heating *in He in place of O_2* the Au/FeO(OH) shows no phase transition, only some water desorption. No change in activity is found although Au – ☐ vacancy pairs are generated.**
- ***If the support (FeO(OH)) alone is treated in O_2* there is no changes neither in the Fe 2p B.E., nor in the catalytic activity.**



This effect is a consequence of the interface created during the treatment along the Au/Fe$_2$O$_3$ perimeter.

Catal Letter, 67, (2000) 117

Conclusion on Au nanoparticles deposited onto $Fe_2O_3/SiO_2/Si(100)$ by PLD

- **The reactivity of the samples in the CO oxidation decreases in the sequence of**

  $Au/FeO_x/SiO_2/Si(100)>FeO_x/SiO_2/Si(100)>$

  $>Au/SiO_2/Si(100)>Si(100)$.

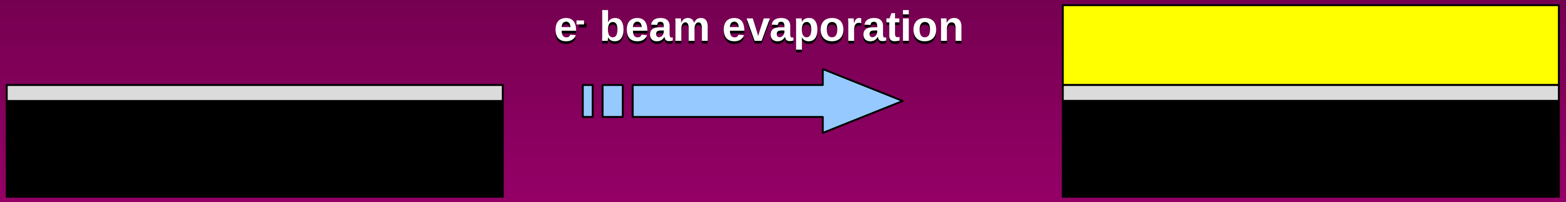
- **It was established that in developing the catalytic activity the *gold is metallic* and the *support is amorphous* with Fe 2p B.E. of 710.8 eV B.E;**
- **reaction occurs at Au/FeOx interface along the perimeter of gold particles.**

J. Phys. Chem. B., 104 (2000) 3183

Effect of gold particle size alone ?

10 nm thick film was treated using *implantation by Ar+ ions at 40 keV energy and 10^{15} atom/cm^2 dose (incident angle is 90 degree).*

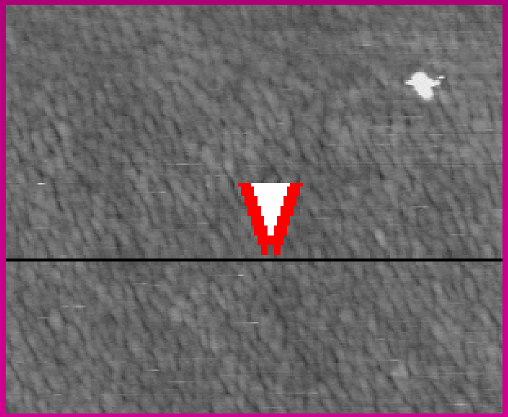
80 nm thick film was used as reference

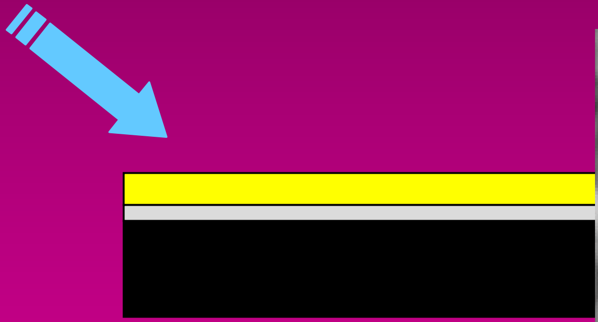


e- beam evaporation

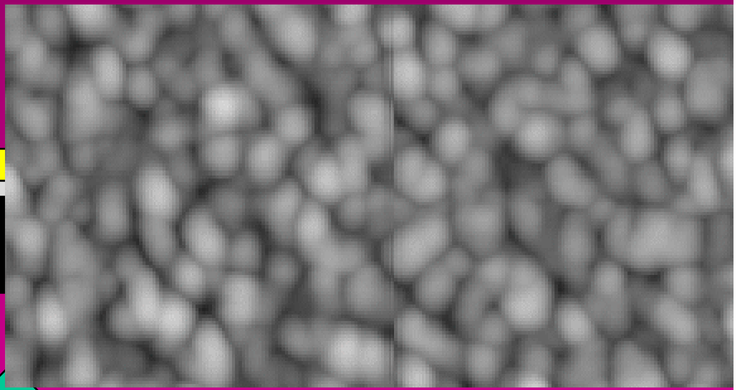
$SiO_2/Si(100)$

e- beam evaporation





10nm $Au/SiO_2/Si(100)$

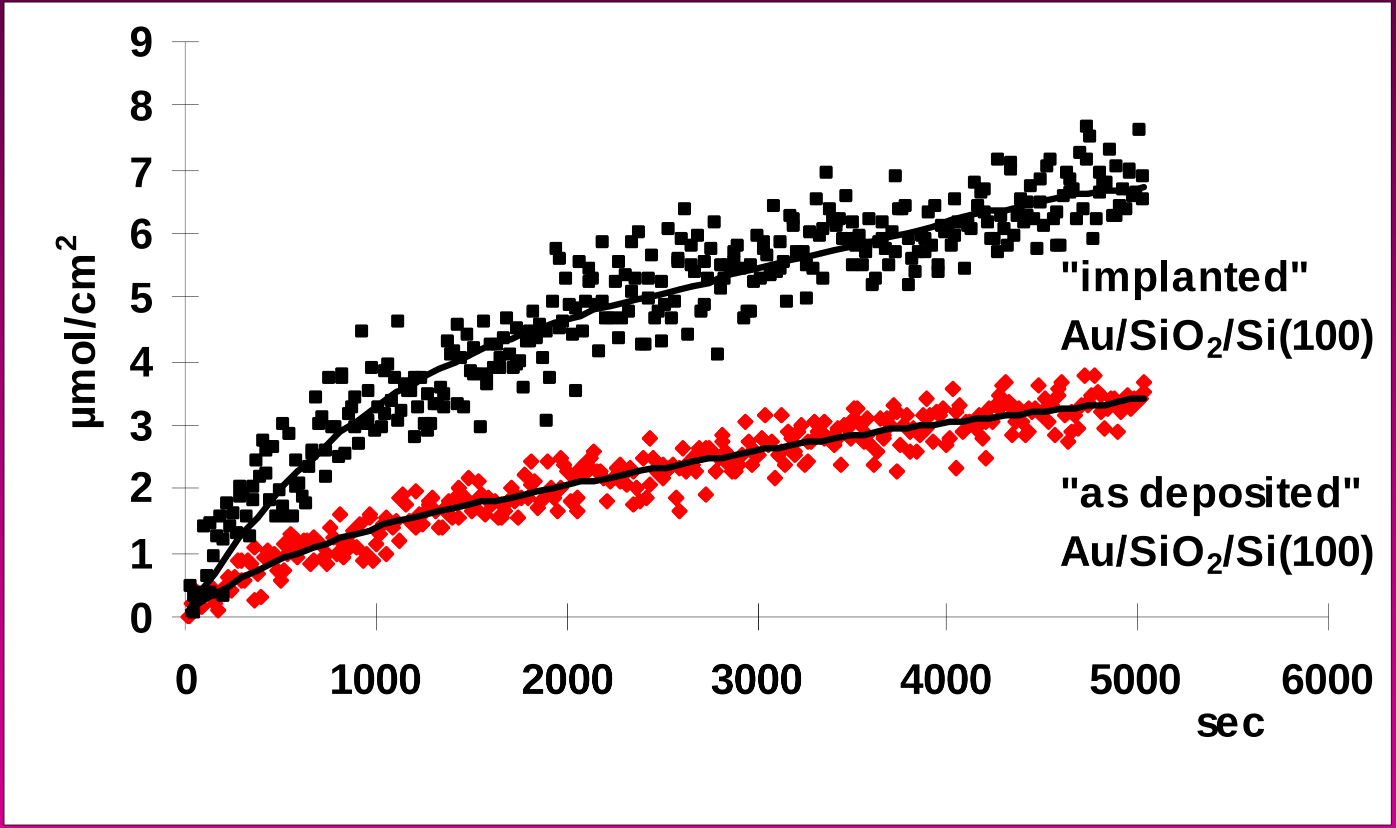


Implantation by Ar ions

nano $Au/SiO_2/Si(100)$

J. Am. Chem. Soc., **125**, 4332 (2003)

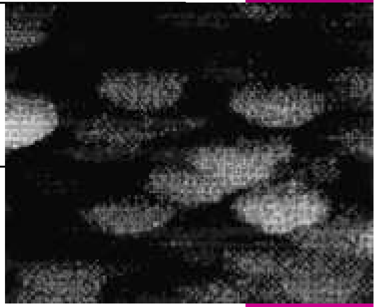
CO oxidation as test reaction over 10 nm Au film and Au nanoparticles on SiO_2/Si(100)

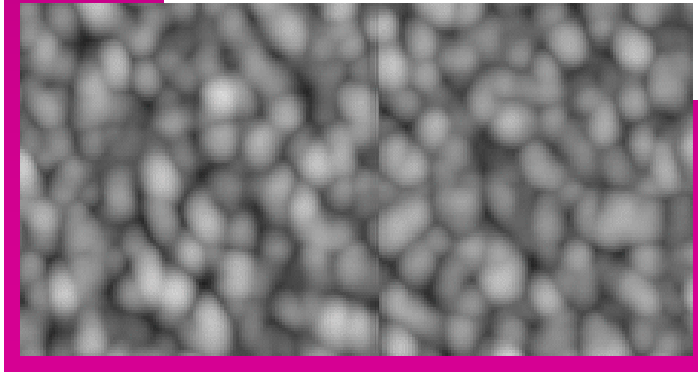


Rate of CO oxidation on Au/SiO_2/Si(100) substrate: small Au nano paticles are more active.

CO oxidation (initial rates)

Sample	CO/O_2 : 10/20 Torr T = 803 K	Initial reaction rate $\mu mol.s^{-1}.cm^{-2}$
$SiO_2/Si(100)$		$4.7x10^{-4}$
$Au/SiO_2/Si(100)$ (implanted)		$1.5x10^{-3}$
$Au/SiO_2/Si(100)$ (implanted) 2nd reaction		$2.0x10^{-4}$
Fe_2O_3 deposited on $Au/SiO_2/Si(100)$ sample after 2nd reaction		$9.5x10^{-2}$
Fe_2O_3 deposited on $SiO_2/Si(100)$		$2.3x10^{-2}$



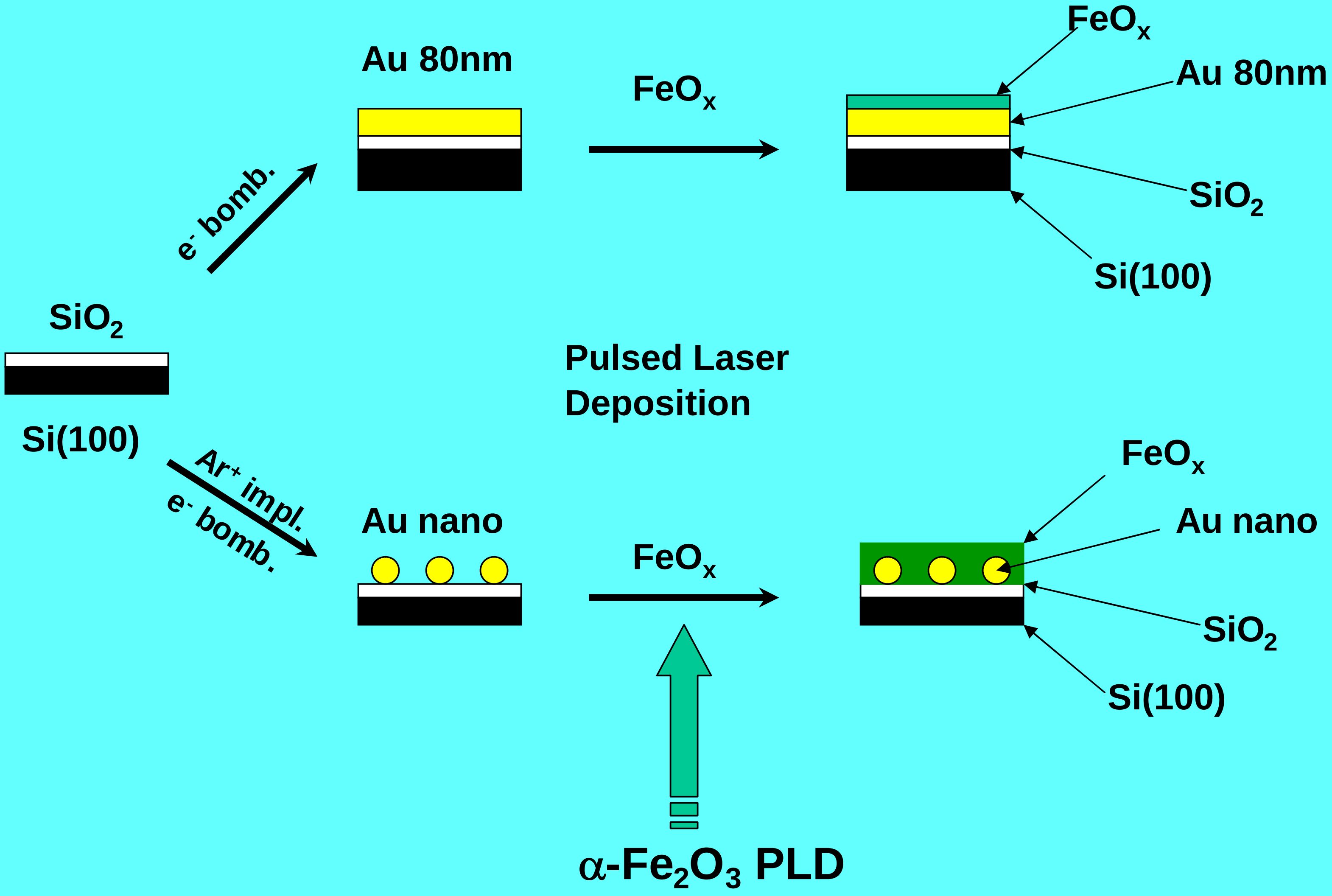


J. Am. Chem. Soc., **125**, 4332 (2003)

Decoration of gold nanoparticles by Fe_2O_3/Au interface creates active sites with enhanced catalytic activity.

Model experiments is required to compare the effect of “direct” Au/Fe_2O_3 and “inverse” Fe_2O_3/Au interface.

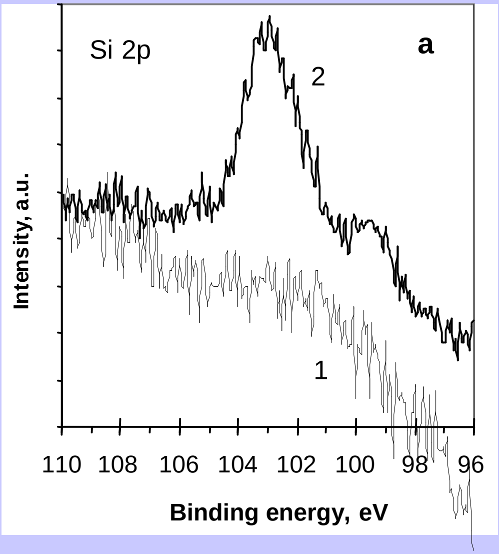
Modelling „inverse" Fe_2O_3/Au system

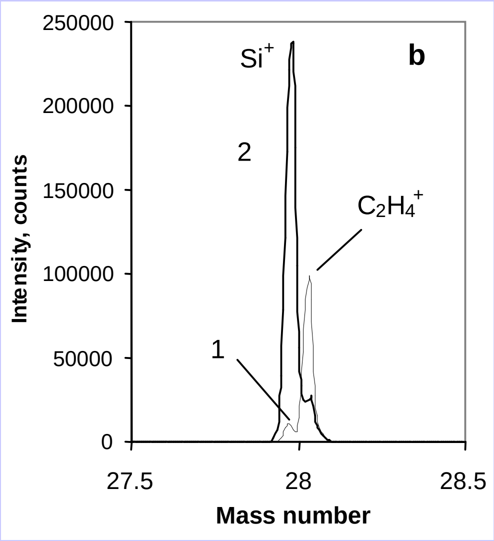


Structure of gold particles and film

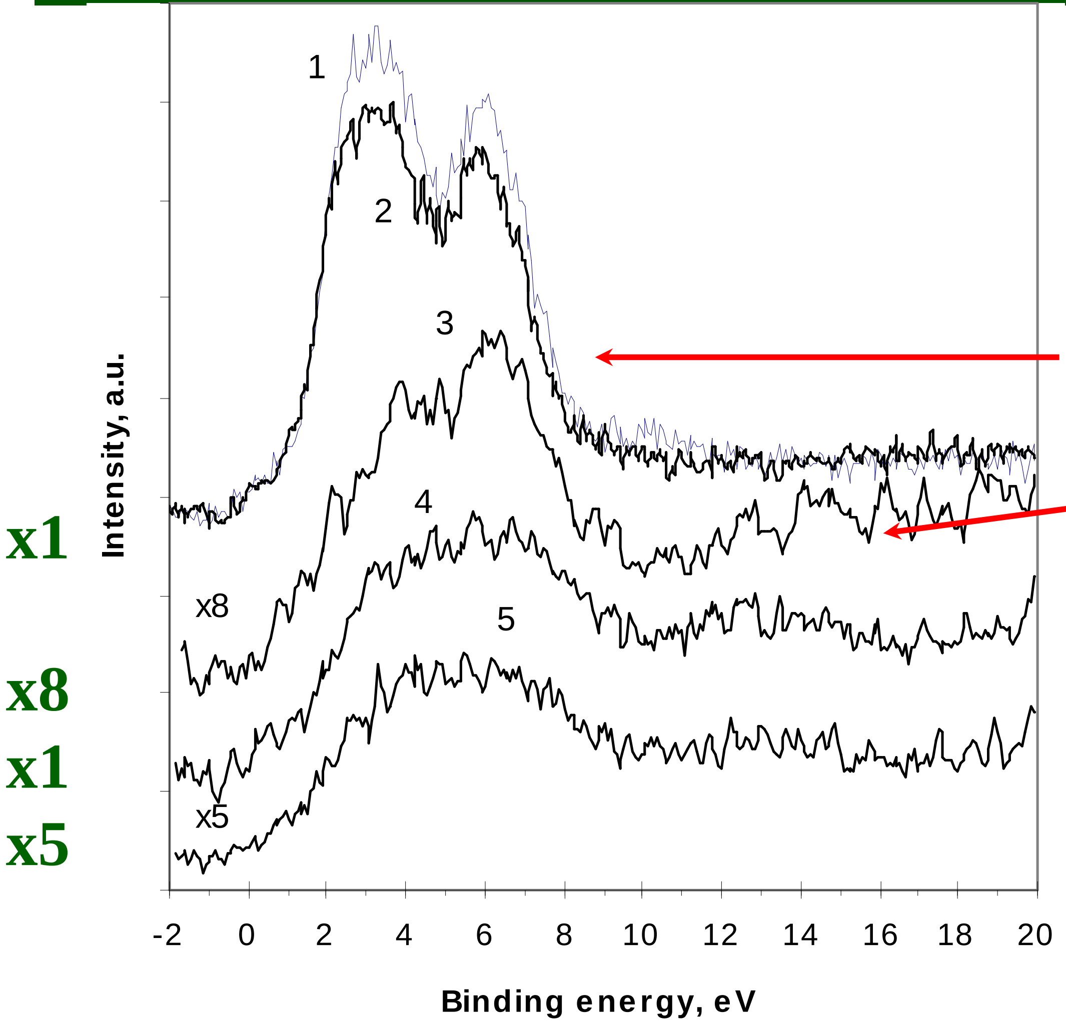
Si 2p XPS

Si ToF SIMS





Valence band spectra of gold



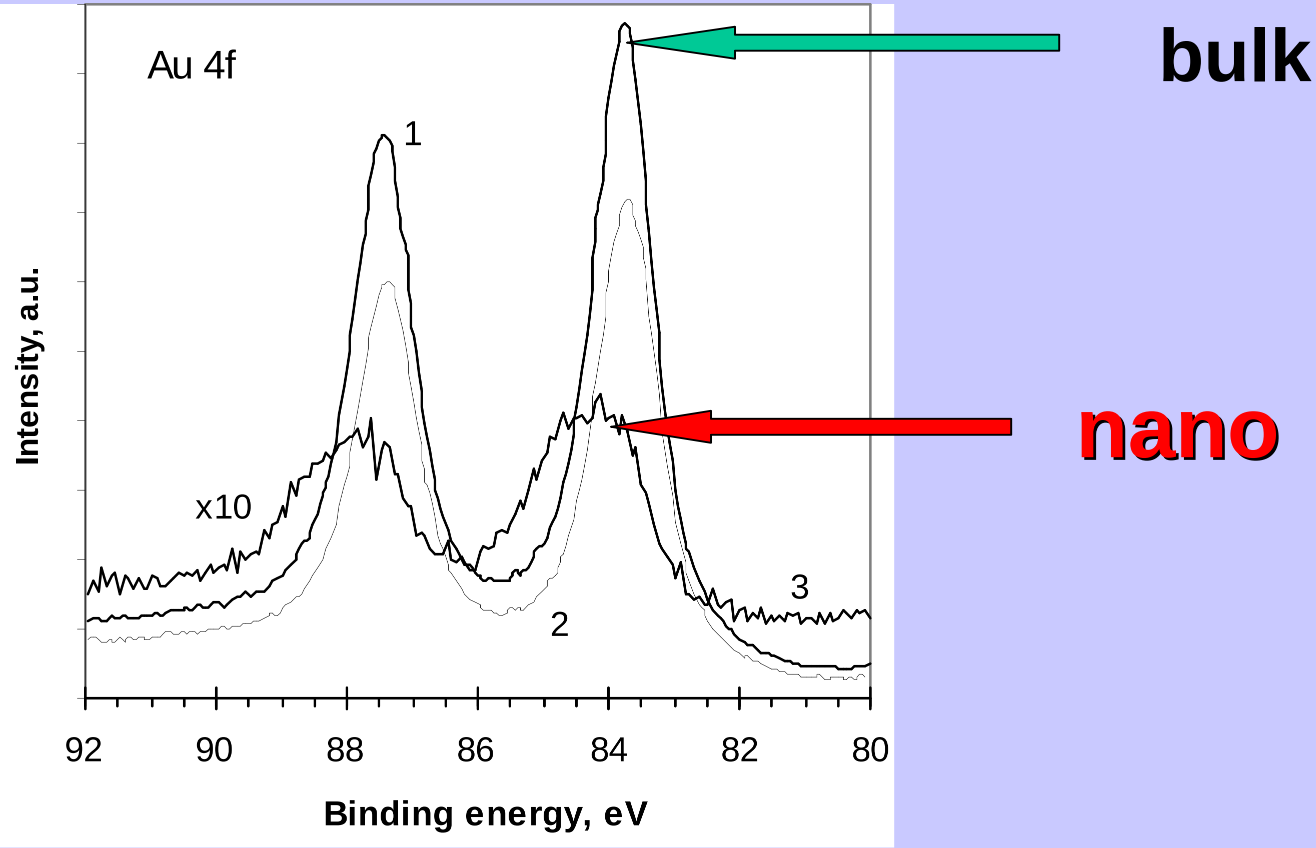
XPS

80 nm Au/SiO_2/Si(100) is used as a reference.

nano Au/SiO_2/Si(100)

Bulk or nanoparticles ?

Au 4f core level B.E.



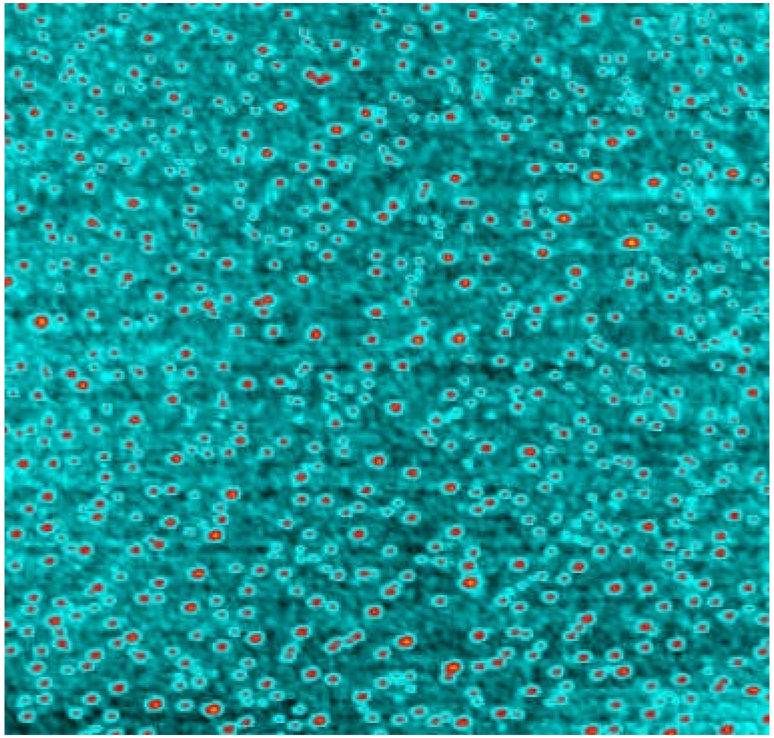
Structure of iron oxide layer

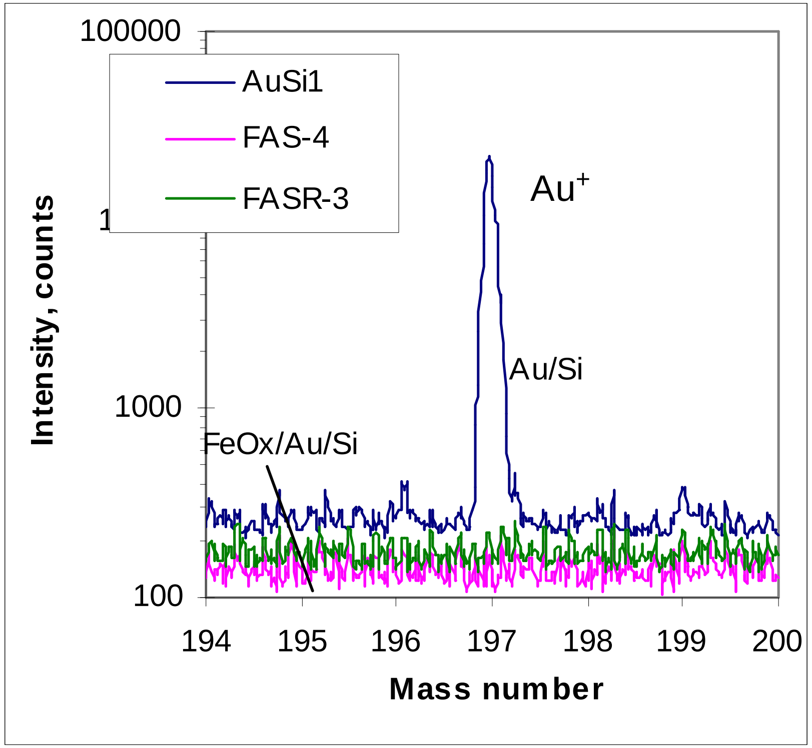
$FeO_x/Au/SiO_2/Si(100)$

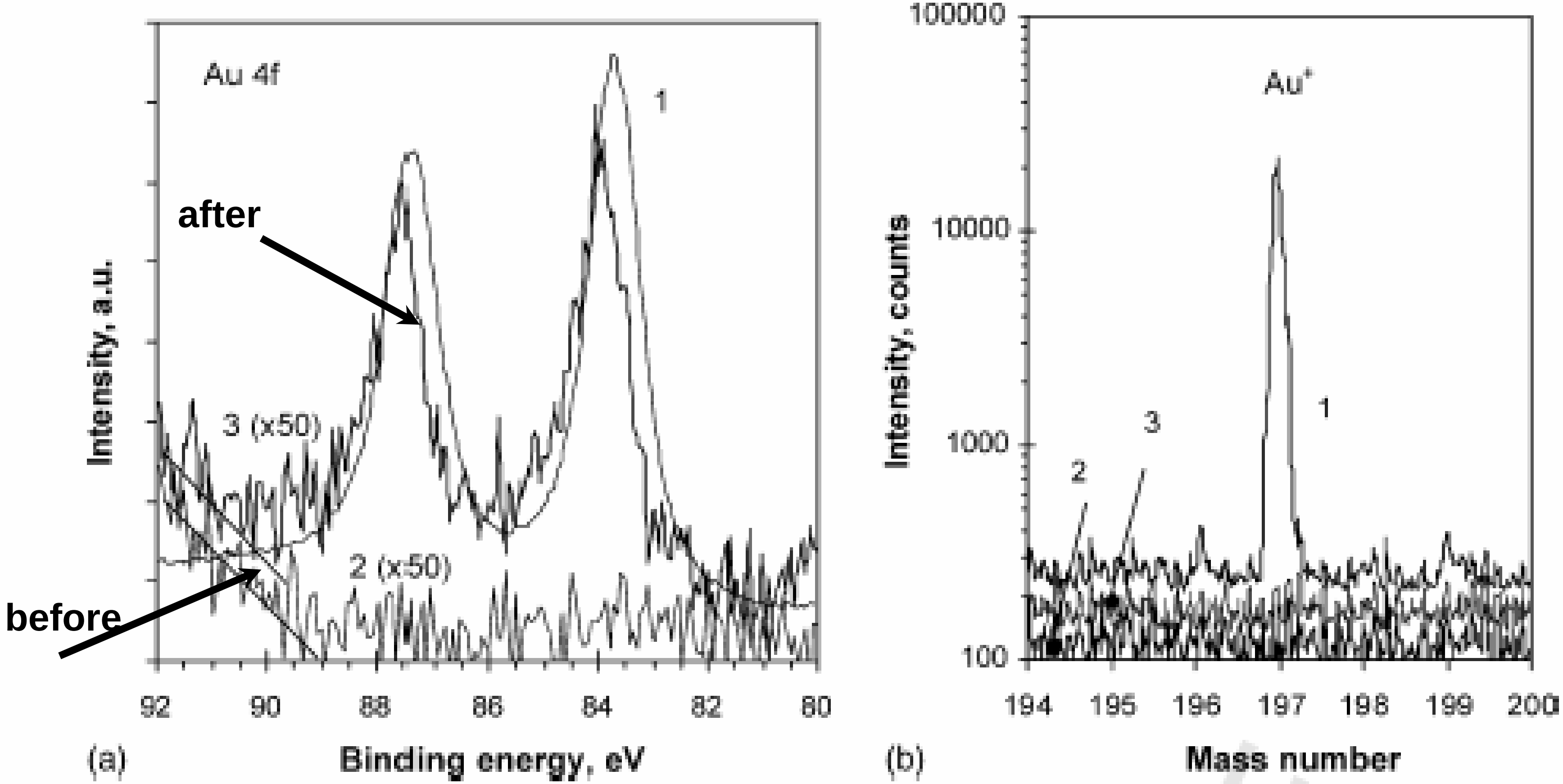
AFM

Au nanoparticles/SiO_2/Si(100)

SIMS

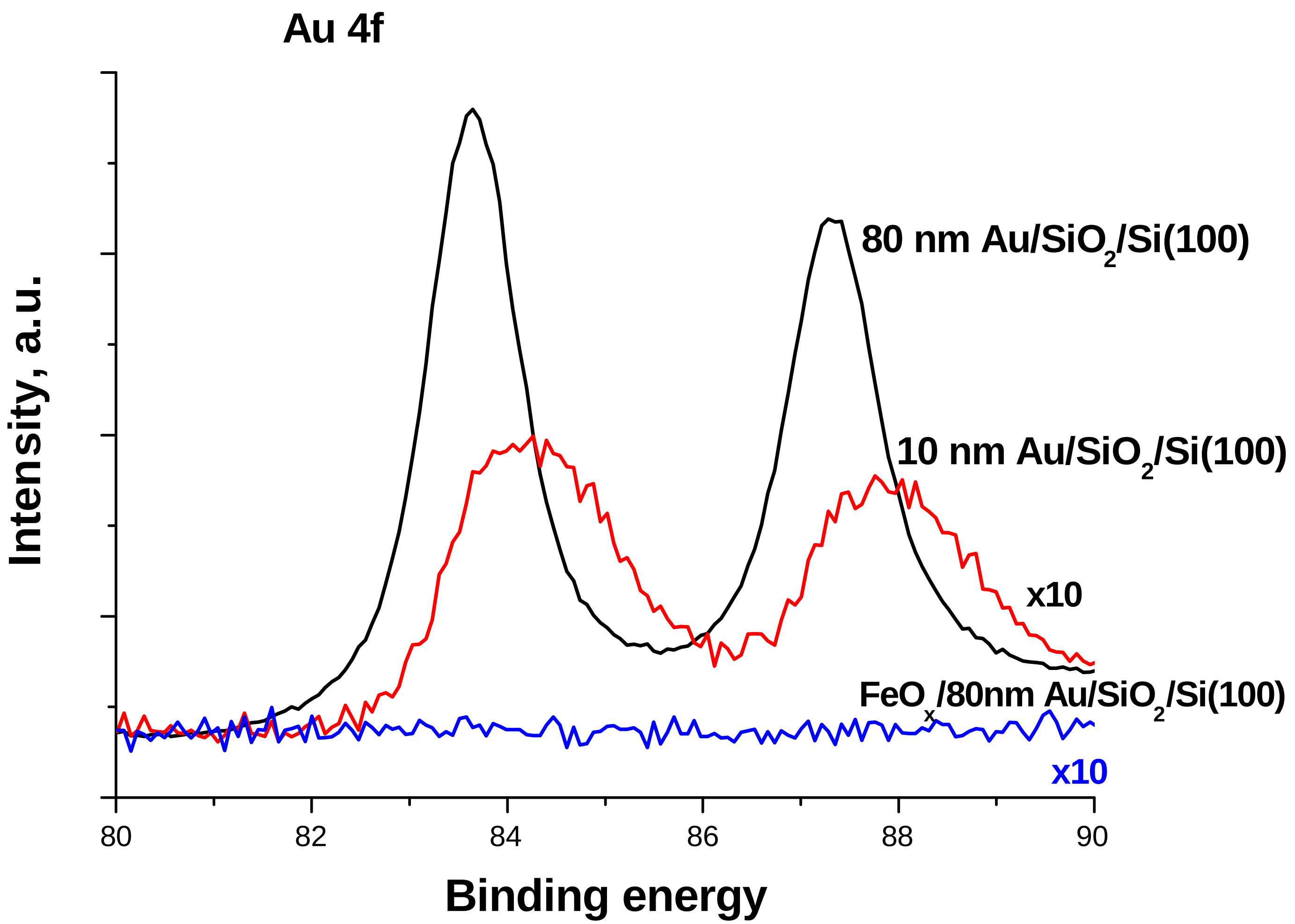




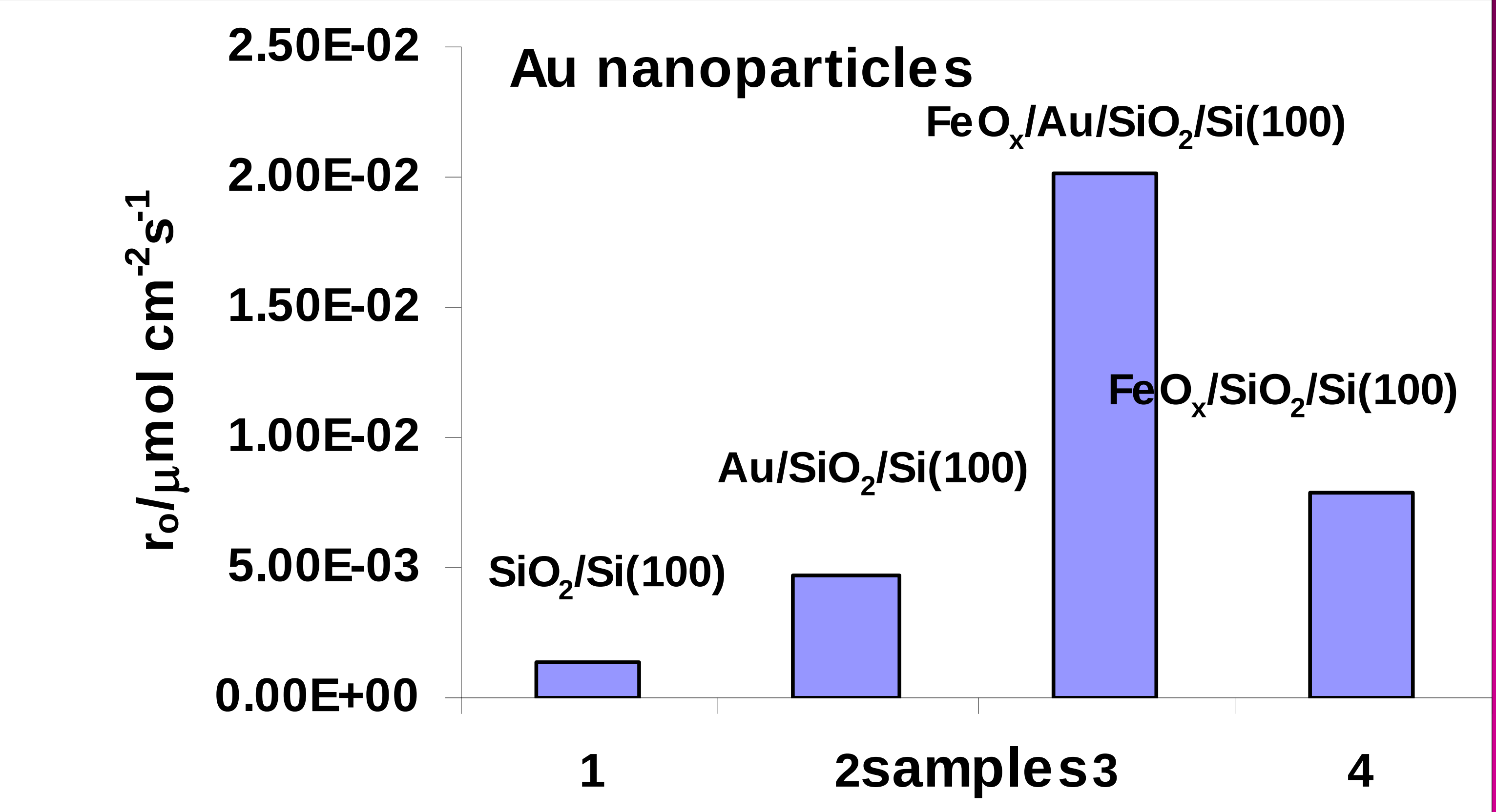


after

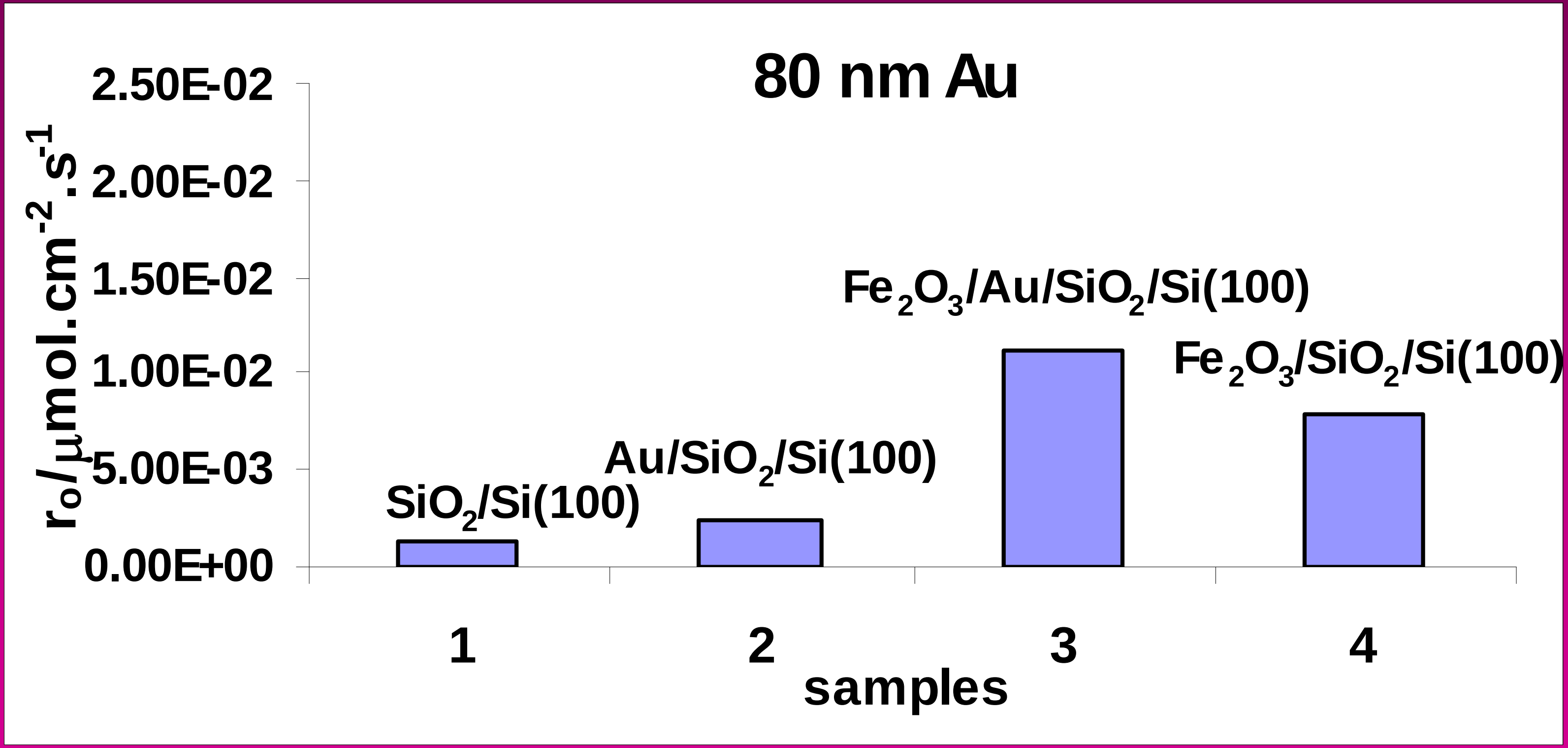
before


Au 4f
Intensity, a.u.
80 nm Au/SiO$_2$/Si(100)
10 nm Au/SiO$_2$/Si(100)
x10
FeO$_x$/80nm Au/SiO$_2$/Si(100)
x10
80
82
84
86
88
90
Binding energy

CO oxidation over FeO_x covered Au nanoparticles on deposited on $SiO_2/Si(100)$

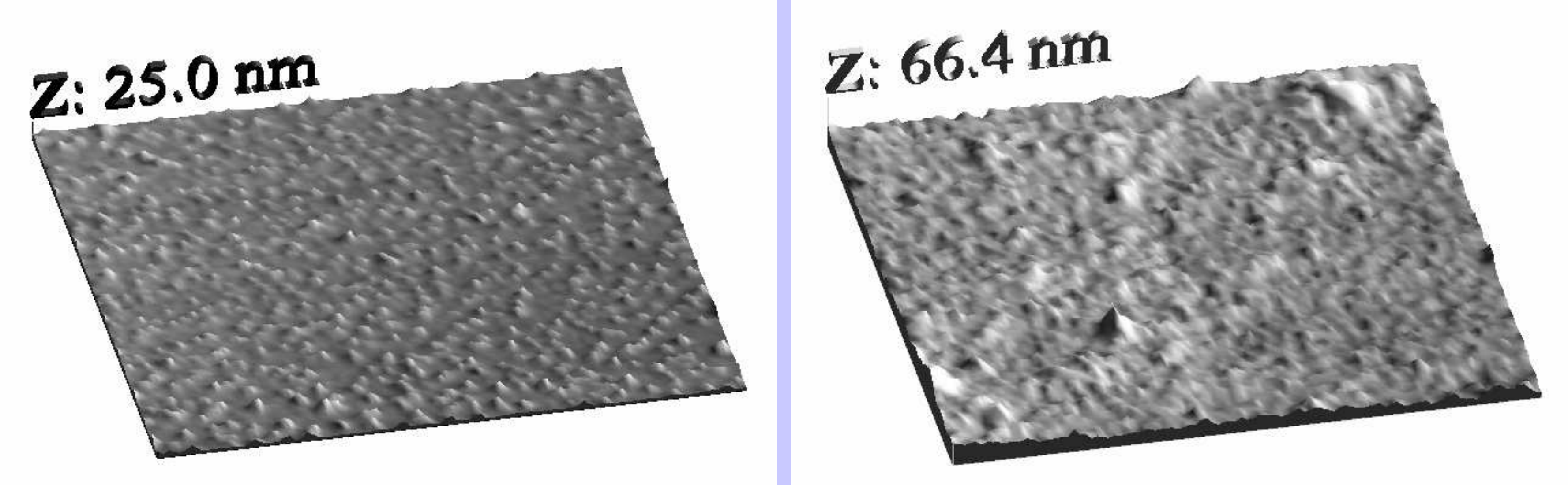


CO oxidation over FeO_x covered 80 nm thick Au film on deposited on SiO_2/Si(100)



Effect of temperature used in CO oxidation on the surface

AFM after 5 min reaction

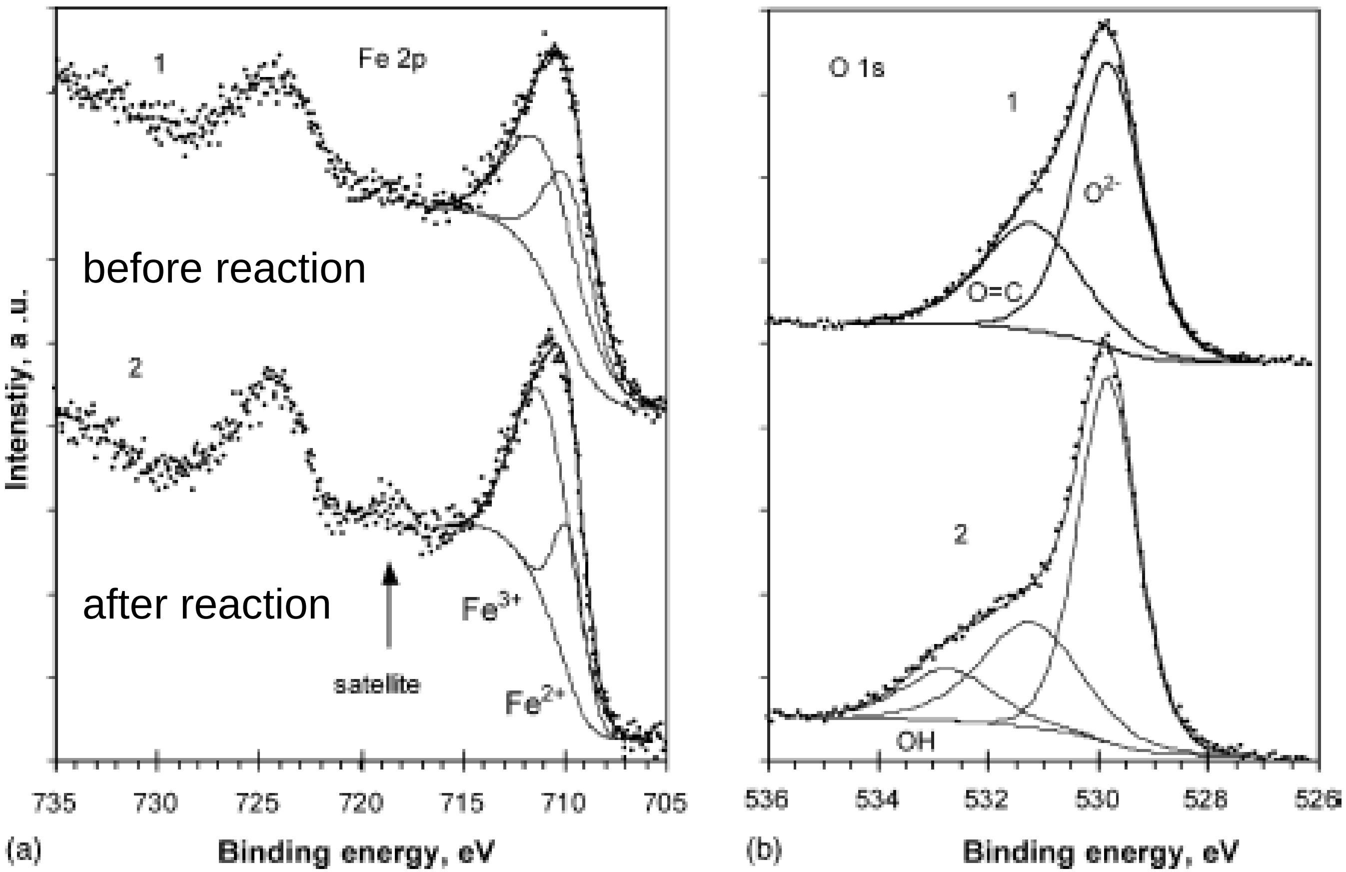


before reaction

after reaction

After heating up in reaction the FeO_x surface is roughening.

XPS on FeO$_x$/Au/SiO$_2$/Si(100) sample



Fe_2O_3 (Fe^{3+}), FeOOH (Fe^{3+}), FeO (Fe^{2+}),

Sites in the CO oxidation are located on the iron oxide itself promoted by Au underneath.

Similar effects were observed in the CO oxidation on Pt(111)/CeO_2. If the CeO_2 coverage is around 1.3–10 ML (no exposed Pt), the activity is higher than on Pt(1 1 1) or CeO_2 alone. The authors concluded that the reaction occurred at the surface of the thin oxide film whose properties were radically altered by the presence of the underlying fully encapsulated Pt.

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C. Hardacre, et al., J. Phys. Chem. 98 (1994) 10901

Presence of oxide overlayer clearly confirms the absence of an Au/FeO$_x$ interface exposed to the surface.

The FeO$_x$ deposited on Au nanoparticles is more active than that on 80 nm Au layer, we advance the hypothesis of the occurrence of a strong electronic „coupling through" effect at the FeO$_x$/Au nanoparticle interface *due to the size reduction*.

Morphology of gold (nano vs layer) affects the chemical composition and the structure of the iron oxide, consequently, its reativity.

This is analogous of V_2O_5 deposited on Au(111) or Au foil (Somorjai). Under vacuum conditions oxygen was found to desorb and after hydrogen treatment some oxygen was removed as H_2O resulting in surface segregation of bulk oxygen.

Similarly, when iron oxide is deposited on Pt(111) and Pt(100) the chemical reactivity is strongly influenced by the substrate orientation.

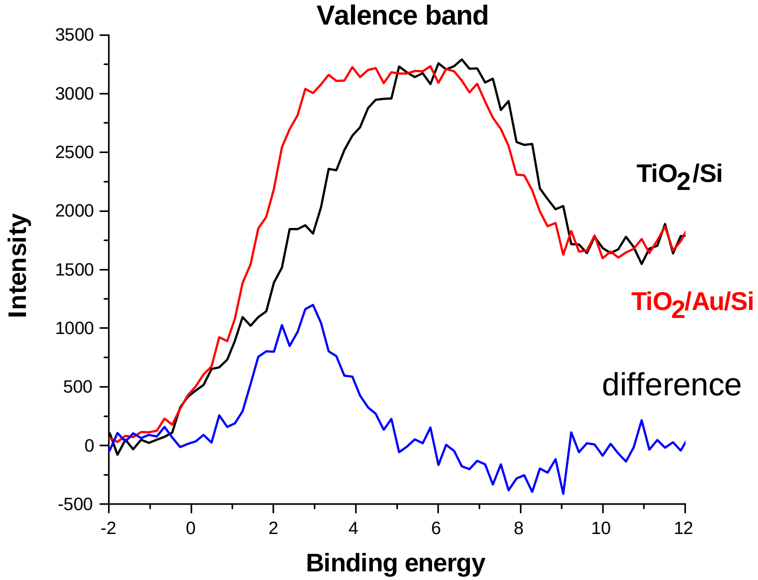
We can conclude that

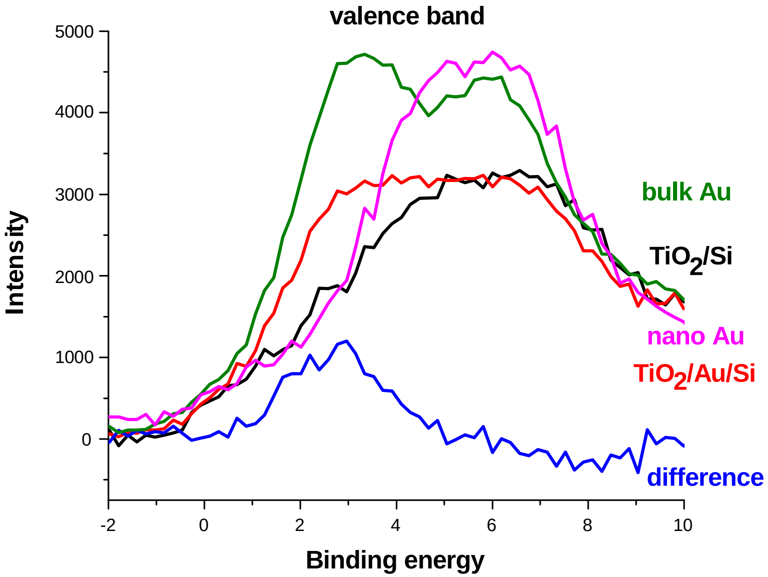
- When an “inverse” Au/Fe_2O_3 is fabricated by Fe_2O_3 deposition onto either Au/SiO_2/Si(100) nano-particles or 80 nm reference sample, the catalytic activity in the CO oxidation is enhanced compared to both Au/SiO_2/Si(100) and Fe_2O_3/SiO_2/Si(100).
- Increasing the thickness of iron oxide vanishes the effect of gold on the active surface.
- The activity enhancement is larger for nano-type Au/Fe_2O_3 than for bulk-type Au/Fe_2O_3 co-operation. The gold effect can be indirect, because Au is not exposed to the surface and it modifies the catalytically working Fe_2O_3

Acknowledgments

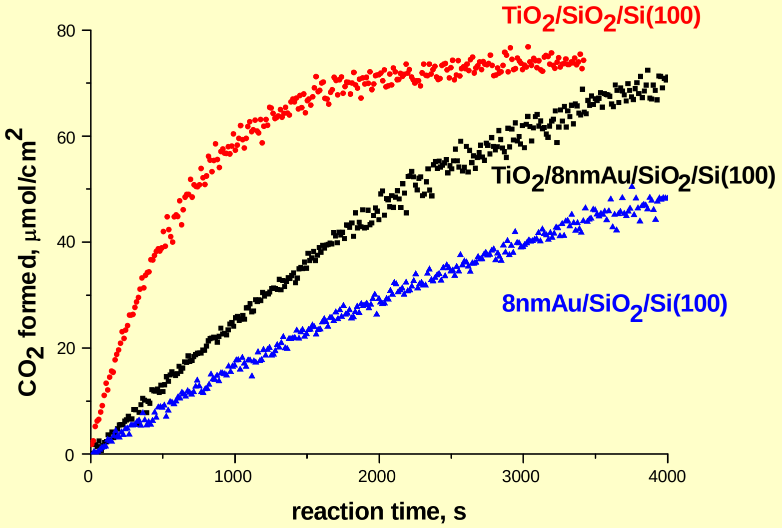
The support from COST D15/005/99 and National Science and Research Fund (grant # 34920 and 30427) are acknowledged.

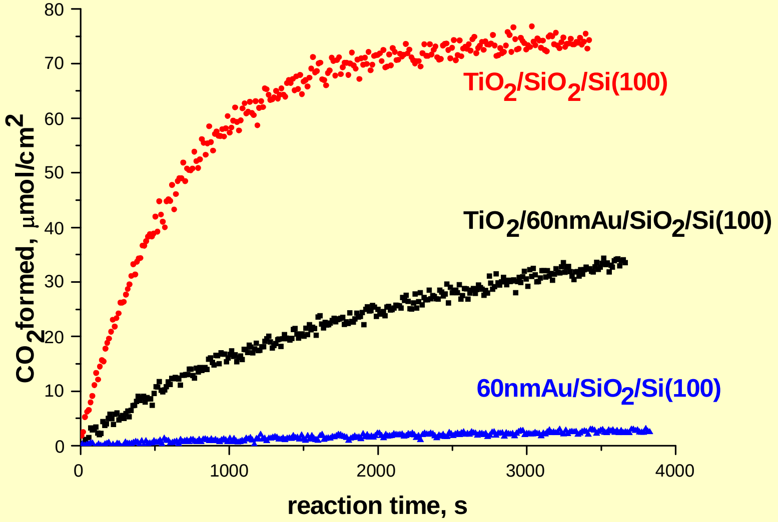
Effect of gold on TiO_2 valence band

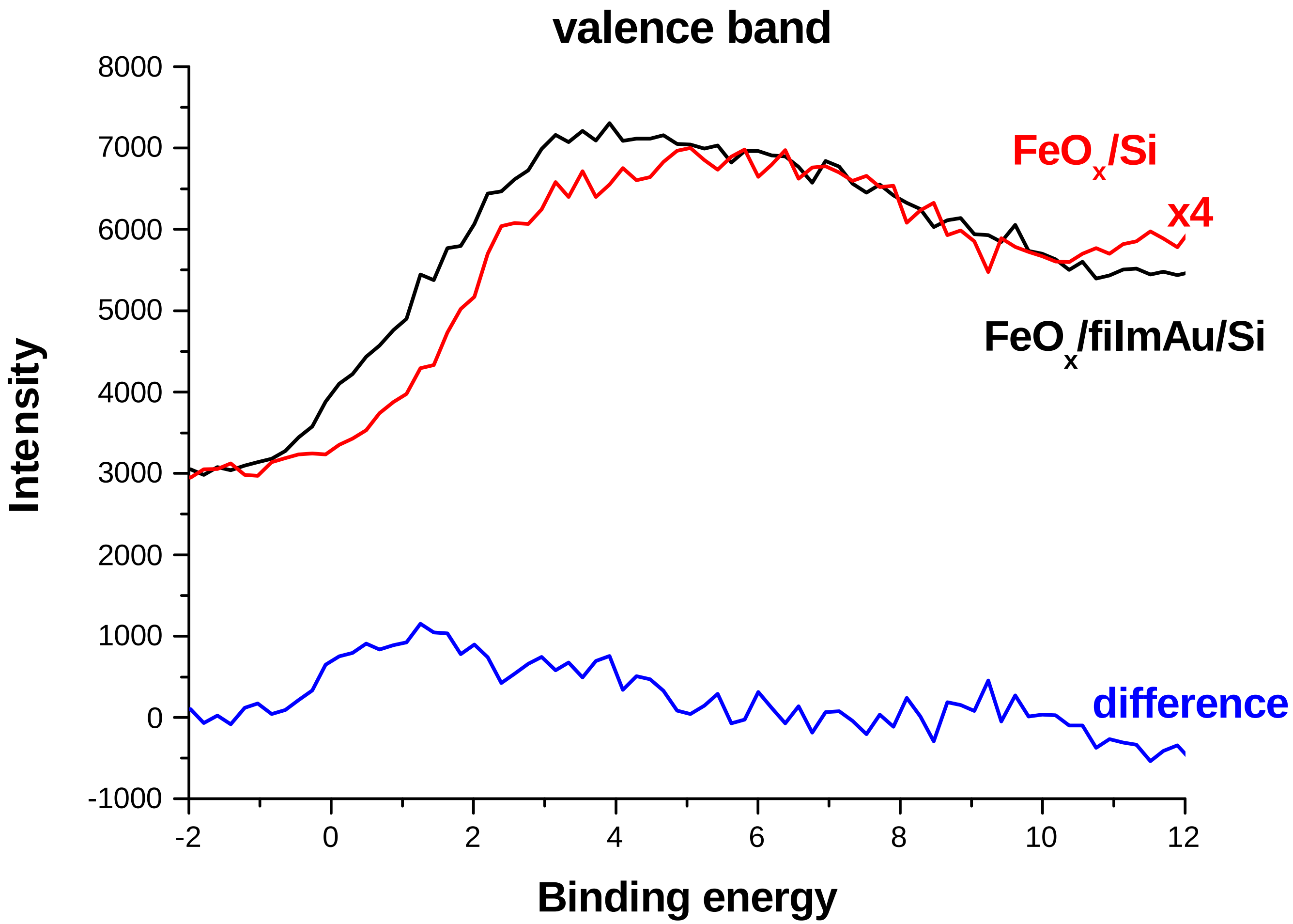




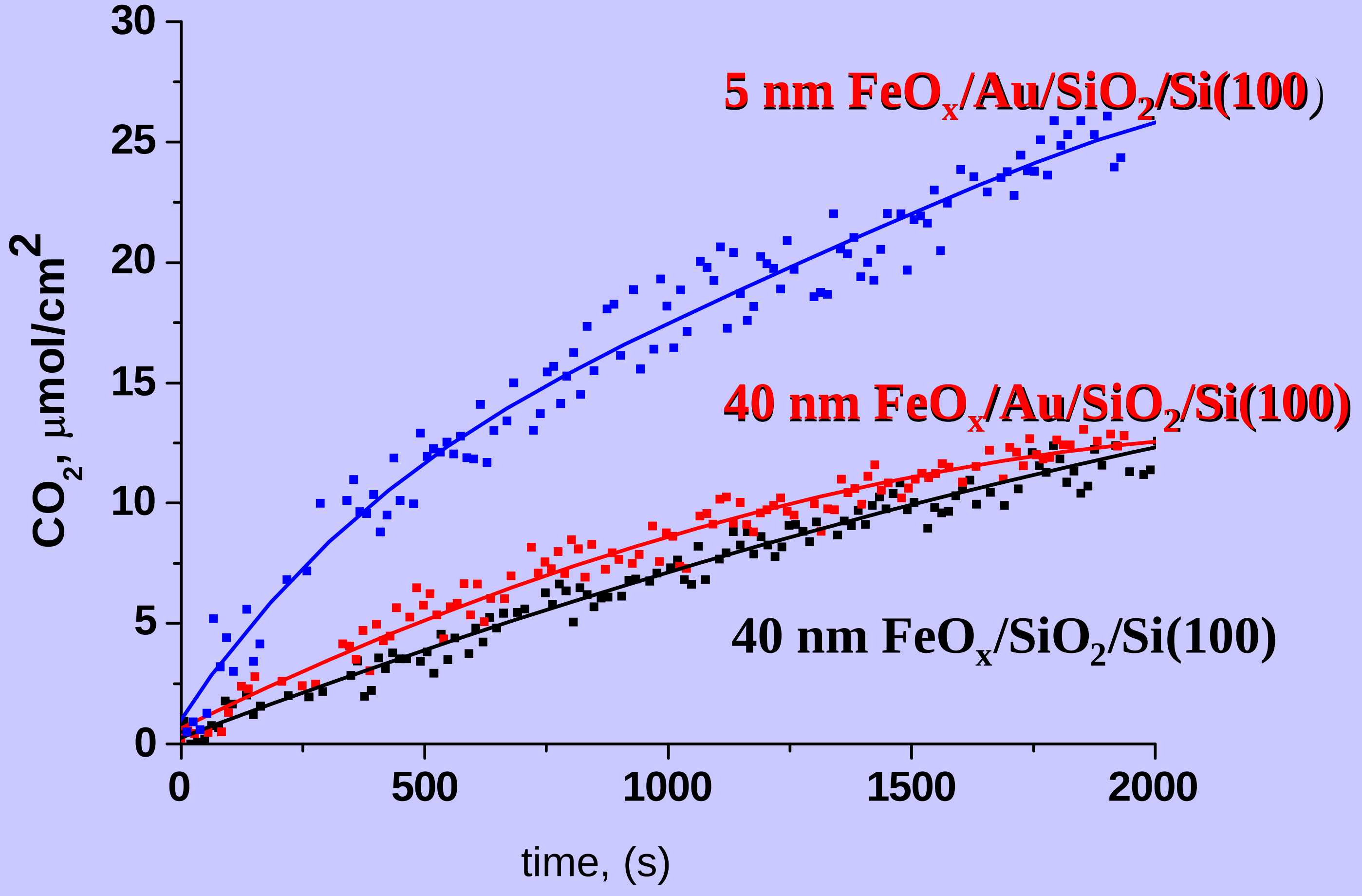
Effect of gold on activity of TiO_2



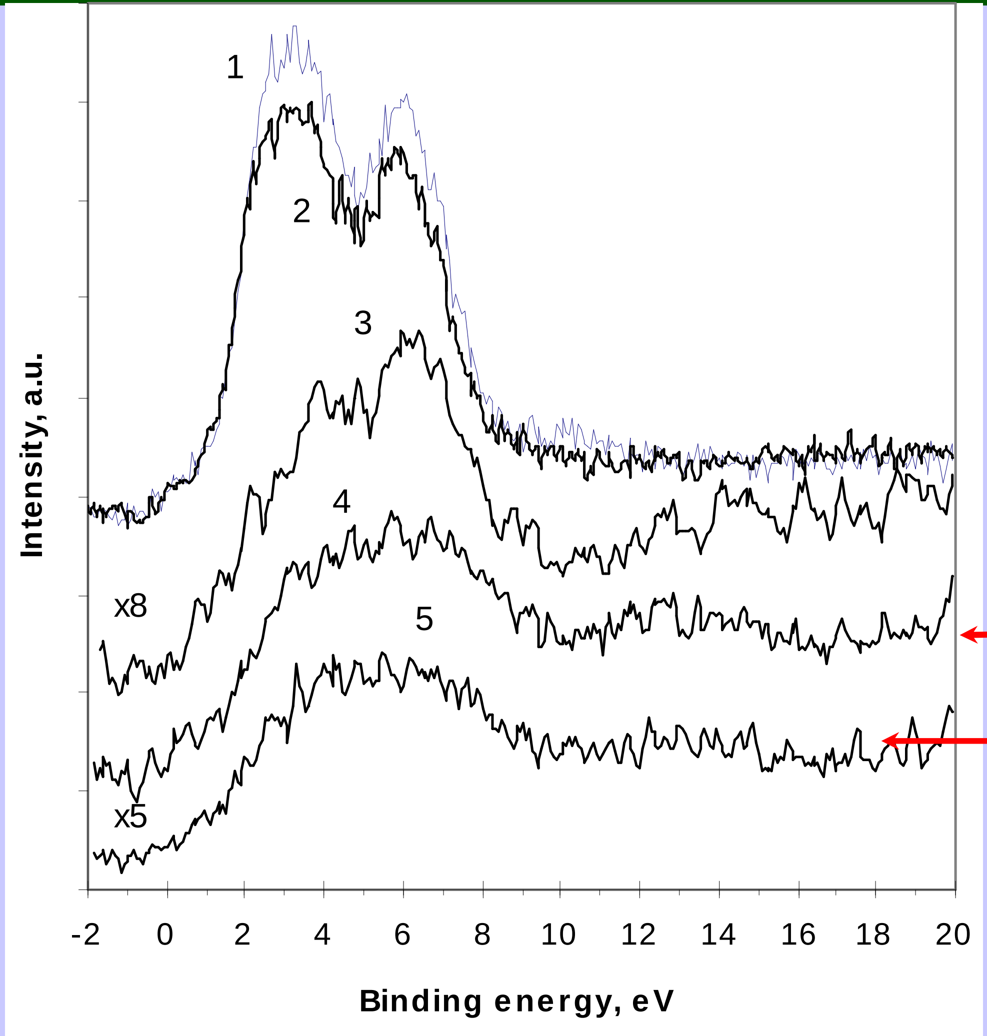



valence band
Intensity
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-2
0
2
4
6
8
10
12
Binding energy
FeO$_x$/Si
x4
FeO$_x$/filmAu/Si
difference

$FeO_x/Au/SiO_2/Si(100)$
Effect of thickness on rate



Valence band spectra of FeO_x covered gold ?



x1

x8

x1

x5

XPS

FeO_x/film Au/SiO_2/Si(100)

FeO_x/nano Au/SiO_2/Si(100

Experiments carried out on TiO_2/Au model systems built on a Pt foil shows a fundamental difference between both samples in terms of preparation. TiO_2 film was prepared under in situ conditions by evaporating Ti in oxygen atmosphere, whereas in the present case stoichiometric Fe_2O_3 was sputtered onto the gold film or nano-particles. Nevertheless, they showed that Au is visible after evaporation (AES) and O_2 activation occurs on Au nanoparticles.

Z.M. Liu, M.A. Vannice, Catal. Lett. 43 (1997) 51

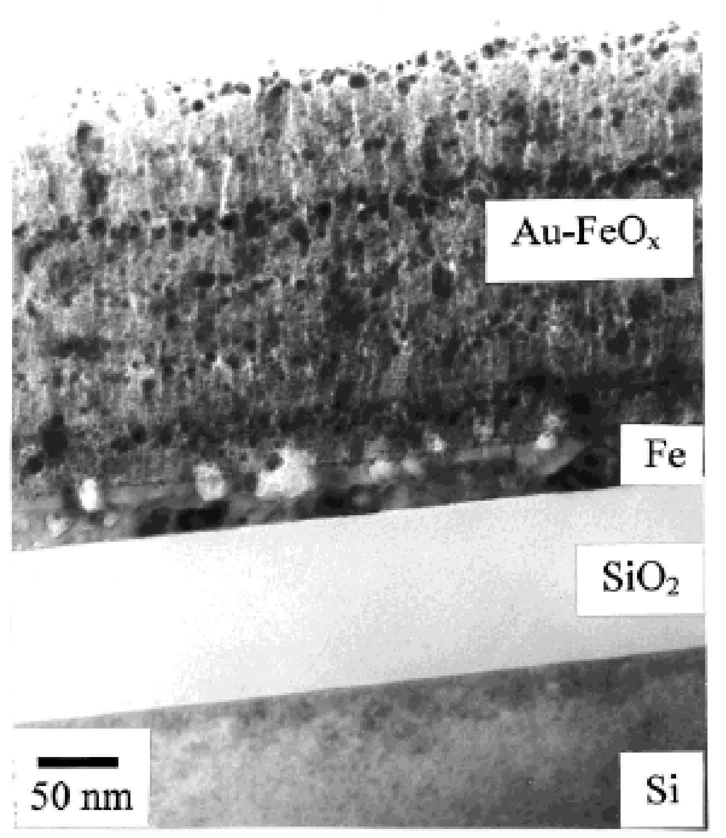
Freund and coworkers prepared gold particles with a mean diameter of 3 nm deposited on Al_2O_3, FeO and Fe_3O_4 model supports and found these particles to adsorb CO quite strongly and more or less independent of the support. Furthermore, the role of the oxide support was ascribed to oxygen activation and stabilisation of very small gold particles

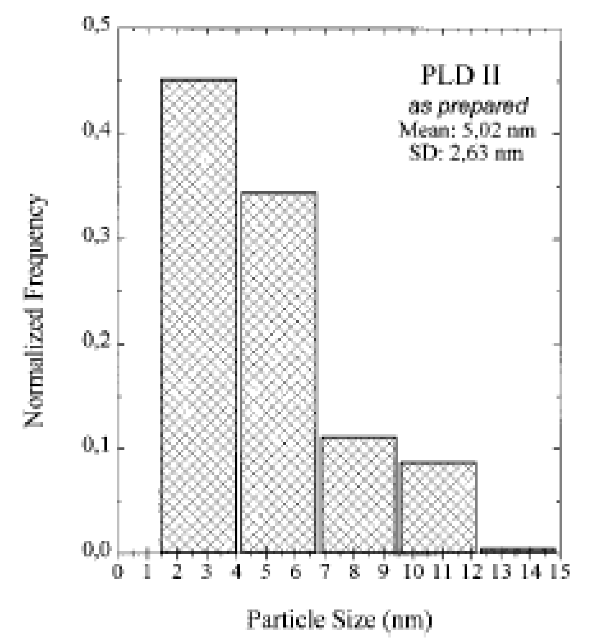
Shaikhutdinov et al., Catal. Lett., 86 (2003) 211.

Why is the large difference in activity among the Au/Fe_2O_3 CP, PLD created Au/FeO_x/SiO_2/Si(100) & FeO_x/Au/SiO_2/Si(100) samples ?

It is believed that amorphicity of the iron oxide is one of the reasons causing such differences. This decreases in sequence of

CP > Fe in O_2 evaporation > α-Fe_2O_3 evaporation


Au-FeO$_x$
Fe
SiO$_2$
50 nm
Si


PLD II
as prepared
Mean: 5,02 nm
SD: 2,63 nm
Normalized Frequency
0,0
0,1
0,2
0,3
0,4
0,5
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15
Particle Size (nm)