

**Modification of gold/transition metal oxide interface:  
studies on the relationship between structure and  
catalytic properties**

Ph.D. Thesis

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# 1. Introduction

The nanosize materials have increasing importance as they are widely used in different areas, like semiconductor and electronic industry, the environmental protection (e.g. sensors, catalysts) etc. The heterogeneous catalysts are basically nanosize materials but the specific electron, morphological and catalytic properties and the controlled preparation of the nanoparticles still contain several unsolved problems. Besides the improvement of known catalytic systems, the catalytic research should be expanded towards new catalytic materials. The gold was regarded earlier as catalytically inactive metal, however, in nanoscale it results in outstanding activity when deposited on a reducible metal oxide. The nanosize of gold and the Au/support interface have key importance in the exceptional catalytic behaviour.

However, the details of the modification of gold nanoparticles by external effects (structure of the interface, addition of second metal) and the synergism between Au and metal oxide is not well understood yet. In the presented work model studies were performed to answer the following questions.

- (i) How does the particle size and morphology of gold and the Au/iron oxide interface modify the electron structure and CO oxidation catalytic activity of gold?
- (ii) What kind of interactions co-operate in the synergism at the Au/metal oxide perimeter. Do the components modify each other's own catalytic properties? Namely, does affect and how affect Au the activity of iron oxide itself?
- (iii) Could the metal oxide component in the active Au/metal oxide perimeter be substituted by palladium, which is also a very good oxidising catalyst as the so called active metal oxide themselves are? How does this interface interaction work if we modify the gold by Pd?

Au/iron oxide and Au, AuPd/titania interfaces were studied by model systems prepared by physical methods on SiO<sub>2</sub>/Si(100) support, and by high surface area oxide supported Au, Pd nanoparticles prepared by chemical methods, respectively.

The model study on Au/iron oxide system is the continuation of the earlier research pursued in our laboratory using both high surface area powder and model systems. The investigation of Au-Pd co-operation in CO oxidation, which had no antecedents in our laboratory, was started by high surface area powder catalysts, since the catalytic properties can be studied better by these systems. The Au-Pd co-operation was studied in alloyed particles on two different supports. SiO<sub>2</sub> can be regarded as an inert support, on which the exclusive effect of Au-Pd interaction can be studied, TiO<sub>2</sub> is an active partner of Au, in AuPd/TiO<sub>2</sub> samples the co-operation of three active component can be investigated.

## 2. Experimental

Model catalysts were prepared by evaporation of gold onto native SiO<sub>2</sub> covered Si(100) wafers producing gold film of 10 and 80 nm thickness. The 10 nm Au/SiO<sub>2</sub>/Si(100) sample was implanted by Ar<sup>+</sup> ions (40 keV, 10<sup>15</sup> atom/cm<sup>2</sup>) for 30 minutes creating nanosize gold particles on the support surface. FeO<sub>x</sub>/Au/SiO<sub>2</sub>/Si(100) were prepared by pulse laser deposition (PLD) of Fe<sub>2</sub>O<sub>3</sub> on the surface of 80 nm Au film and Au nanoparticles supported on SiO<sub>2</sub>/Si(100).

AuPd/SiO<sub>2</sub> samples and the monometallic analogous were prepared by ethanol reduction of the HAuCl<sub>4</sub> and PdCl<sub>2</sub> precursors in the presence of PVP as stabilizer and high surface area SiO<sub>2</sub> powder as support at 363 K in N<sub>2</sub> atmosphere. The TiO<sub>2</sub> supported AuPd, Au and Pd nanoparticles were produced

by adsorption of appropriate metal hydrosols prepared from the same precursors by tannic acid-sodium citrate reduction and stabilization.

The electron properties of the model systems were characterised by UV-photoelectron spectroscopy (UPS), the oxidation state and surface composition the samples were studied by X-ray photoelectron-spectroscopy (XPS). The surface morphology of the model samples supported on  $\text{SiO}_2/\text{Si}(100)$  were determined by atomic force microscopy (AFM). The composition of the outermost atomic layer of the surface in the model samples was measured by secondary ion mass spectroscopy (ToF-SIMS). The metal particle sizes were measured by transmission electron microscopy (TEM). The crystalline phases in  $\text{AuPd}/\text{SiO}_2$  and  $\text{AuPd}/\text{TiO}_2$  samples were characterised X-ray powder diffraction (XRD). The Pd surface was estimated by CO-chemisorption measurements. X-ray fluorescence (XRF) was used to determine the metal content of the powder systems. Temperature programmed oxidation (TPO) measurements gave information on the amount and the nature of organic contamination originating from the preparation conditions.

The catalytic activity of the samples was tested in CO oxidation. The  $\text{SiO}_2/\text{Si}(100)$  supported samples were measured in an all-glass circulation reactor connected to a quadrupole mass spectrometer using 9 mbar CO + 18 mbar  $\text{O}_2$  + 153 mbar He reactant mixture at 803 K. The  $\text{AuPd}/\text{SiO}_2$  és  $\text{AuPd}/\text{TiO}_2$  powder samples were measured in 3 different catalytic aparatuses: (i) in Palermo/Italy and (ii és iii) in Budapest/Hungary.  $\text{AuPd}/\text{SiO}_2$  samples were tested in apparatus (i), in a pulse flow system equipped with QMS, in 4500 ppm CO + 5000 ppm  $\text{O}_2$ /He reactant mixture and in apparatus (ii), in a static circulation reactor with QMS analysis, in 9 mbar  $\text{O}_2$  + 9 mbar CO + 162 mbar He reaction mixture. The  $\text{AuPd}/\text{TiO}_2$  samples were measured in apparatus (iii), in a plug flow reactor with GC analysis, in 0,55 % CO + 9,1 %  $\text{O}_2$ /He.

### 3. New scientific results

#### 1. Au/SiO<sub>2</sub>/Si(100) model system

- 1.1. The formation of Au nanoparticles by Ar<sup>+</sup> ion implantation of the 10 nm Au film/SiO<sub>2</sub>/Si(100) sample was established. The nanoparticle character was proved by the rearrangement of the Au 5d valence band, namely the decrease of the bands at 2-3 eV and at 6-7 eV, and by the 1 eV shifts of the Au 4f core level binding energies to the higher values.
- 1.2. It was shown that the catalytic activity of the Au nanoparticles/SiO<sub>2</sub>/Si(100) sample in CO oxidation is significantly higher than that of the 80 nm Au film/SiO<sub>2</sub>/Si(100) having Au with bulk character and higher surface area. Activity of the SiO<sub>2</sub>/Si(100) support is more than one order of magnitude lower than that of gold containing samples.
- 1.3. The activity decrease of Au nanoparticle containing samples in the repeated reaction was explained by the agglomeration of gold particles demonstrated by AFM and TEM measurements, accompanied by the reformation of the characteristic bulk XPS spectrum of gold.
- 1.4. The XPS spectra confirmed that the gold retains its nanoparticle or bulk character after the PLD deposition of 5-10 nm thick FeO<sub>x</sub> overlayer onto Au/SiO<sub>2</sub>/Si(100) samples.
- 1.5. ToF-SIMS and XPS studies revealed that in FeO<sub>x</sub>/Au/SiO<sub>2</sub>/Si(100) samples the FeO<sub>x</sub> overlayer is continuous, fully covers the Au/SiO<sub>2</sub>/Si(100) surface and it is composed of Fe<sub>2</sub>O<sub>3</sub> (Fe<sup>3+</sup>) and FeO (Fe<sup>2+</sup>).
- 1.6. An increased activity of the 5-10 nm FeO<sub>x</sub>/Au/SiO<sub>2</sub>/Si(100) as compared to the corresponding FeO<sub>x</sub>/SiO<sub>2</sub>/Si(100) was demonstrated, which is

regarded as the promotion effect of gold not exposed to the gas phase, on the contacting iron oxide.

- 1.7. The promoting effect of Au depends on the Au particle size, in the case of nanoparticles it is significantly higher than in the case of the bulk type Au film.
- 1.8. The migration of Au into the FeO<sub>x</sub> overlayer during the catalytic reaction test was detected by XPS and SIMS, but Au did not reach the surface.
- 1.9. The promoting effect of Au depends on the thickness of the iron oxide: it could not be observed on the surface of a 40 nm thick FeO<sub>x</sub> overlayer.

## **2. Bimetallic AuPd/SiO<sub>2</sub> and AuPd/TiO<sub>2</sub> systems**

- 2.1. We produced SiO<sub>2</sub> and TiO<sub>2</sub> supported bimetallic AuPd and monometallic Au and Pd particles of similar size (6-13 nm in diameter) using a novel preparation method to clarify the cooperation of the two metals in alloyed phase.
- 2.2. The increased resistance of Pd in the bimetallic particles toward the oxidation was shown, Pd retained its metallic state during calcination in air at 673 K.
- 2.3. The activity of Au/SiO<sub>2</sub> was significantly lower than that of Pd/SiO<sub>2</sub>. The alloying of Pd with gold decreased the activity of Pd related to one surface Pd atom. This was attributed to the modified oxidation properties of Pd and the decreased number of the active sites containing more neighbouring Pd atoms, which could cause the reduced oxygen activation ability of palladium.
- 2.4. The activity of Au/TiO<sub>2</sub> and Pd/TiO<sub>2</sub> was similar. The alloying of Au and Pd showed slight synergism. The different effect compared to the SiO<sub>2</sub> supported AuPd system was explained by the O<sub>2</sub> activating ability of the metal/TiO<sub>2</sub> perimeter.

## Publications connected to the thesis

- 6

Au/SiO<sub>2</sub>/Si(100): Promoting effect of Au on the catalytic activity of iron oxide in CO oxidation,

*Applied Catalysis A. General*, **291**, (2005) 116

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- L. Guzzi, Z. Pászti, **K. Frey**, A. Beck, G. Pető and Cs. S. Daróczi:  
Modelling gold/iron oxide interface system,  
*Topics in Catalysis* in press

## Presentations and posters connected to the thesis

- **K. Frey**, D. Horváth, Zs. Koppány, A. Beck, A. M. Venezia and L. Guzzi:  
SiO<sub>2</sub> supported Au-Pd Nanoparticles: Structure and Catalytic Activity in CO Oxidation  
*6th Pannon Conference on Catalysis, September 2002, Ötztal, Austria*
- **K. Frey**, D. Horváth, Zs. Koppány, A. Beck, L. F. Liotta, G. Pantaleo, A. M. Venezia and L. Guzzi: SiO<sub>2</sub> Supported Au-Pd Nanoparticles: Structure and Catalytic Activity in CO Oxidation  
*EFCATS School, September 26-29, 2002, Tihany, Hungary*
- **K. Frey**, A. Beck, A. Horváth, Zs. Koppány, G. Stefler, D. Bazin and L. Guzzi: AuPd/TiO<sub>2</sub> bimetallic nanoparticles: XRD, TEM, in situ EXAFS studies and catalytic activity in CO oxidation,  
*EUROPACAT6, Innsbruck, 2003, August 31-September 5*
- **Frey Krisztina**: Catalytic activity of SiO<sub>2</sub> and TiO<sub>2</sub> supported AuPd bimetallic nanoparticles in CO oxidation  
*VII. Ph.D. Chemical School, Tahi 2004, Apryl 27-28.*



- **K. Frey**, A. Beck, A. Horváth, Zs. Koppány, G. Stefler, D. Bazin and L. Guzzi: AuPd/TiO<sub>2</sub> bimetallic nanoparticles: XRD, TEM, in situ EXAFS studies and catalytic activity in CO oxidation, *EUROPACAT6, Innsbruck, 2003, August 31-September 5*
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*VII. Doktori Kémiai Iskola, Tahi 2004, április 27-28.*
- **Frey Krisztina**: SiO<sub>2</sub> és TiO<sub>2</sub> hordozós AuPd kétfémes nanorészecskék katalitikus vizsgálata a CO oxidációban  
*MTA KK IKI, Tudományos Tanácsülés 2004. május 10.*
- **Frey Krisztina**, Guzzi László, Pető Gábor, Beck Andrea: Arany nanorészecskék határfelületi szerkezetének modellezése: elektronszerkezet és aktivitás  
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- **Frey Krisztina**: Módosított Au nanorészecskék: szerkezet és katalitikus tulajdonságok közötti összefüggés vizsgálata  
*Felületkémiai és Nanoszerkezeti Munkabizottsági ülés 2004. június 8.*
- **Frey Krisztina**: Modelling interfacial structure of gold nanoparticles: electron properties and activity  
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- **K. Frey**, A. Beck, A. Horváth, Zs. Koppány, Gy. Stefler, D. Bazin, L. Liotta, A.M. Venezia and L. Guzzi: Catalytic activity of SiO<sub>2</sub> and TiO<sub>2</sub> supported AuPd bimetallic nanoparticles in CO oxidation  
*Third International Taylor Conference, Belfast, 2004, 5<sup>th</sup> – 8<sup>th</sup> september*

structure and catalytic properties

*Meeting of the Hungarian Catalysis Group, Szeged, 2004.*

- **K. Frey**, G. Pető, A. Beck, L. Guczi: Au/SiO<sub>2</sub>/Si(100) and Fe<sub>2</sub>O<sub>3</sub>/Au/SiO<sub>2</sub>/Si(100) model nanosystems: size effect on electron structure and catalytic activity in CO oxidation  
*COST D15, Interfacial Chemistry and Catalysis, Maribor, 2005, 2nd – 5th February*
- **Krisztina Frey**, Gábor Pető, Andrea Beck, László Guczi: Iron oxide overlayer on Au layer and Au nanoparticles supported by SiO<sub>2</sub>/Si(100): Promoting effect of Au on the catalytic activity of iron oxide  
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- **Krisztina Frey**, Gábor Pető, Andrea Beck, László Guczi, Csaba Daróczi, Norbert Kruse, Sergey Chenakin: Iron oxide overlayer on Au layer and Au nanoparticles supported by SiO<sub>2</sub>/Si(100): Promoting effect of Au on the catalytic activity of iron oxide  
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- **Krisztina Frey**, Gábor Pető, Andrea Beck, László Guczi, Csaba Daróczi, Norbert Kruse, Sergey Chenakin: Iron oxide overlayer on Au layer and Au nanoparticles supported by SiO<sub>2</sub>/Si(100): Promoting effect of Au on the catalytic activity of iron oxide  
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## Publications not connected to the thesis

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