

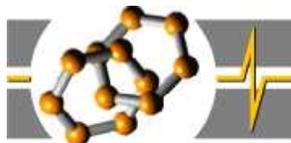
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Preparation and modification of supported gold catalysts used in CO oxidation

PhD thesis

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Introduction and Aims

Due to the pioneering work of Hutchings¹ and Haruta² in the middle of 80's in the last century, the research of the supported gold nanoparticles became the most vibrant field of heterogeneous catalysis.

Supported gold catalysts have been found active in different kind of oxidation and hydrogenation reactions (for example, epoxidation of propene, oxidation of glucose to gluconic acid, oxidation of cyclohexane to cyclohexanol and cyclohexanone, CO oxidation, hydrogenation of vegetable oils, etc.), water-gas shift reaction and hydrogen peroxide production, vinyl acetate synthesis³.

Among of the above mentioned reactions, the oxidation of carbon monoxide is the most intensively studied reaction of gold catalysts due to its practical importance. Catalysts are applied in gas masks and indoor air quality controlling systems to sense and avoid breathing the poisonous gas. The presence of CO is also undesirable in many other applications for example in hydrogen fuel cells and in CO₂ lasers.

Owing to the intensive research of carbon monoxide oxidation on supported gold catalysts, it was evidenced that the catalytic activity of these catalysts strongly depends on both the size of the gold nanoparticles and the nature of the support material. In this respect 'active' (easily reducible supports) and 'inactive' (inert, stable oxides) were distinguished. The reducible oxides (Fe₂O₃, TiO₂, MnO₂, SnO₂) may responsible for both the chemisorption and activation of oxygen in the close vicinity of gold nanoparticles on which the CO adsorbs. In the case of inert oxides (Al₂O₃, SiO₂, MgO), the proper choice of the preparation method is crucial for the formation of gold nanoparticles and hence for the high catalytic activity.

In spite of the tremendous efforts, several questions remained unsolved. For instance, it is not clear that the ionic or metallic nanoparticles are active, the nature of the support effect is not well understood, and the role of surface OH-groups is not unambiguous.

The fundamental goal of my work was the preparation and modification of gold catalysts supported on different inert oxides (Al₂O₃ and SiO₂), and their examination in CO oxidation. The main objective was the investigation of the effect of different kind of preparation, pretreatments procedures and of the presence of a reducible oxide (tin oxide) on the properties of supported gold catalysts. In this respect the particle size, electronic state and

¹ G.J. Hutchings, *J. Catal.* 96 (1985) 292-295.

² M. Haruta, T. Kobayashi, H. Sano, N. Yamada, *Chem. Lett.* (1987) 405-408.

³ BP Chemicals, European Patent Application EP 0654301, 1994.

the catalytic activity of gold nanoparticles supported on alumina and silica were investigated. Further aim was also to describe the structure of the active sites by using *in situ* techniques such as Mössbauer and FTIR spectroscopy.

Experimental methods

In the first step, the modification of supports used was investigated. Method of surface organometallic chemistry was applied using the surface reaction between the tetraethyltin and surface hydroxyl groups of the supports (Al_2O_3 and SiO_2). In the second step the decomposition of the surface organotin moieties in oxygen or hydrogen was performed. The gold was deposited onto these materials by different preparation methods: in the case of alumina, direct anionic exchange and deposition-precipitation with urea were applied, while in the case of silica, a new method was developed in our laboratory, i.e., the deposition-precipitation of gold by ammonia solution was applied.

The activity of the catalysts was tested in CO oxidation. XPS and Mössbauer spectroscopy was applied for studying the pretreatment induced changes in the oxidation state of gold and tin oxide nanoparticles. The nature of the active sites was investigated by *in situ* Mössbauer spectroscopy and *in situ* infrared spectroscopy. The size of the gold nanoparticles was studied by x-ray diffraction and transmission electron microscopy.

New scientific results

Preparation of the supported gold catalysts.

- It was found, that the deposition-precipitation with urea is more suitable method for the preparation of alumina supported gold catalysts than the direct anionic exchange, because higher gold content with good reproducibility can be achieved.
- A new method was developed for the preparation of Au/SiO₂ catalysts. The key step of this preparation route is the electrostatic interaction between the positively charged gold precursor and the negatively charged silica surface. The positively charged complexes were formed by addition of ammonia solution into the solution of H₂AuCl₄.
- It has been stated that the mechanism of deposition-precipitation with urea is different on alumina and silica. In the case of alumina, first, the gold-chloro-hydroxo complexes are adsorbed on the surface of silica and serve as coordination sites for the gold-urea complexes. In the case of silica, the adsorption of gold-chloro-hydroxo

complexes doesn't take place due to the electrostatic repulsion between the silica surface and the gold complexes. Therefore the precursor-support interaction is rather weak and it leads to the increase of the gold particle size during activation of the catalyst.

Formation of SnO₂ nanoparticles on the support

- The application of surface organometallic chemistry, namely the reaction between the surface OH-groups and the tetraethyltin leads to the formation of nano-sized tin oxide particles on the large surface area supports. It was found that the alumina was more active in the above mentioned surface reaction than the silica, that can be explained by the presence of different amount and type of surface OH-groups on the two different supports.
- It was shown by Mössbauer spectroscopy that the 80 % of supported tin(IV) oxide reduced to tin(II) oxide at 350 °C in flowing hydrogen atmosphere. In the presence of gold, the formation of atomic tin was observed after the high temperature reduction.

The nature of gold-tin interaction

- The hydrogen pretreatment of the catalysts leads to the formation of gold-tin interaction. It was found that the character of Au-Sn interaction depended on the tin content: in the case of low tin content alloy formation was observed, while at high tin content, the tin was enriched on the surface of the gold nanoparticles.
- After the tin anchoring, the decomposition of the grafted organotin complexes in hydrogen lead to the formation of tin species in low valence state on the silica surface. It was found that during deposition of gold by surface reduction onto this support, the particle size of the metal can be controlled by the pH of the gold precursor solution. At pH=8 smaller gold particles were formed than at pH=3.
- It was shown that high temperature oxygen treatment or the addition of the (CO + O₂) reaction mixture at room temperature to the prereduced Au-Sn catalysts lead to the oxidation of AuSn alloy and a tin rich Au-SnO_x metal-support interface formed.
- It was evidenced by XPS and FTIR spectroscopy measurements that gold nanoparticles with partial negative surface charge had formed after pretreatment in hydrogen at 350 °C, however positive charge was observed on gold particles after

treatment in oxygen. This fact was explained by both the effect of the pretreatment and the change of the oxidation state of tin in the close vicinity of gold particles.

Effect of gold-tin interaction and of the pretreatments on the activity in CO oxidation.

- The presence of tin increases the catalytic activity of supported gold catalysts due to its oxygen activation ability and it changes the average surface charge of gold nanoparticles. The activity of tin containing catalysts is much higher after pretreatment in hydrogen than after pretreatment in oxygen when tin exists on the surface as SnO₂.
- The activity decrease of Au/Al₂O₃ and Au/SiO₂ catalysts after pretreatment in oxygen can be explained by the increase of gold particle size or changes in the morphology of the particles. The presence of tin stabilizes the size of gold particles.
- The *in situ* FTIR measurements revealed that the surface OH-groups of the silica in the close vicinity of gold nanoparticles have significant role in the CO oxidation reaction. The results refer to the OH-groups assisted dissociative adsorption of oxygen on gold nanoparticles. In the case of tin containing catalysts the oxygen can be activated not only by the OH groups surrounding gold, but also by the presence of tin oxide vacancies at the perimeter of supported gold nanoparticles.

Thesis

1. A new method was developed the preparation of Au/SiO₂ catalysts. By using this method, formation of gold nanoparticles with 5 nm average size became possible. The key step of this preparation route is the electrostatic interaction between the positively charged gold precursor and the negatively charged silica surface. The positively charged complexes were formed by addition of ammonia solution into the solution of HAuCl₄. The catalysts showed high activity in CO oxidation [1].
2. It was shown that the modification of non-reducible oxides by tetraethyltin resulted in the formation of highly dispersed tin oxide phase on the surface of support oxides (SiO₂, Al₂O₃). Large amount of this SnO₂ can be reduced to SnO at elevated temperatures leading to formation of SnO_x mixed oxide. The tin modified non-reducible oxides are suitable for the preparation of supported gold catalysts with high activity [2,4].

3. It was found that the presence of gold facilitates the reduction of tin oxide. It was pointed out that in the case of low tin content AuSn alloy was formed, while higher tin content resulted in enrichment of tin on the surface of gold nanoparticles [2, 3, 4].
4. It was shown that the gold nanoparticles can be deposited from HAuCl_4 solution onto the $\text{SnO}_x/\text{SiO}_2$ supports by surface reduction. The size of the gold nanoparticles can be controlled by the pH of the gold solution and the tin content of the support [5].
5. The existence of Au- SnO_x interaction and its promoting effect on the activity of catalysts was evidenced. Based on the experimental results the promoting effect of tin oxide has threefold role on the catalytic activity: (i) due to its reducibility it can change the average charge density of gold particles which might have a crucial role in the activation of O_2 ; (ii) provides unique adsorption sites for O_2 at the metal-support interface, and (iii) in reduced form the tin oxide-layer has an ability to stabilize small gold nanoclusters [2].

Application possibilities

As it was mentioned before, the application of catalysts developed for the oxidation of CO has great practical importance.

Gold nanoparticles supported on non-reducible or low IEP oxides might have outstanding role in the preparation and development of new gas mask, electrodes and gas sensors. The application of the catalytic systems presented in this work may be important in the future fuel cell systems as cathode, because recently it was demonstrated that Au- SnO_x systems showed significant catalytic activity in the four electron reduction of oxygen.

The size control of the gold nanoparticles important not only in the catalysis but also in many other application fields. For instance, preparation of gold nanolayer on silica nanospheres may be applied as contrast enhancers in biomedical imaging and potential thermal therapeutic agent for cancer treatment. These materials also can be useful in SERS applications.

PUBLICATIONS

1. Modified preparation method for highly active Au/SiO₂ catalyts used in CO oxidation

Ferenc Somodi, Irina Borbáth, Mihály Hegedűs, András Tompos, István E. Sajó, Ágnes Szegedi, Sergio Rojas, Jose Luis Garcia Fierro, József L. Margitfalvi
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2. Promoting effect of tin oxides on alumina supported gold catalyts used in CO oxidation

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S. García-Rodríguez, F. Somodi, I. Borbáth, J.L. Margitfalvi, M.A. Peña¹, J.L.G. Fierro, S. Rojas

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CONFERENCE TALKS

„Új CO oxidációs eredmények arany katalizátorokon”

[New results in oxidation of CO on supported gold catalysts]

Somodi Ferenc, Margitfalvi József

Nanokémiai és Katalízis Intézet Szeminárium, MTA Kémiai Kutatóközpont, Budapest

Seminars of the Institute of Nanochemistry and Catalysis, Chemical Research Center, Hungarian Academy of Sciences, Budapest , 30 June 2009

Application of controlled surface reactions for the preparation of highly active tin modified Pt/C catalysts for electrooxidation of ethanol

S. García-Rodríguez, F. Somodi, I. Borbáth, J.L. Margitfalvi, M.A. Peña¹, J.L.G. Fierro, S. Rojas

21st North American Catalysis Society Meeting, San Francisco, 7-12 June 2009

„Hordozós arany katalizátorok előállítása, módosítása és vizsgálata CO oxidációjában”

[Preparation and modification of supported gold catalysts used in CO oxidation]

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Kutatóközponti Tudományos Napok, MTA Kémiai Kutatóközpont, Budapest

Annual Scientific Meeting of the Chemical Research Center of the Hungarian Academy of Sciences, Budapest, 3-5 December 2008

„Szilícium-dioxid hordozós arany katalizátorok előállítása és vizsgálata”

[Preparation and investigation of silica supported gold catalysts]

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Molecular design of new type of supported catalysts modified by Sn and Ge prepared via tin anchoring technique

Irina Borbáth, József L. Margitfalvi, Ferenc Somodi, Sándor Göbölös, Mihály Hegedűs, Irene M. J. Vilella, Sergio R. de Miguel, Osvaldo A. Scelza

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[Promoting effect of tin oxide on silica supported gold catalysts]

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Peculiarities of supported gold catalysts. The role of nano-environment in the activity of supported gold catalysts.

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Application of the in situ Mössbauer spectroscopy for the study of Au/SnO_x-Al₂O₃ catalysts used in CO oxidation

F. Somodi, I. Borbáth, J.L. Margitfalvi, S. Stichleutner, K. Lázár

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Peculiarities of supported gold catalysts. The role of nano-environment of gold

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Preparation of Au nanoparticles on the surface of silica particles using HAuCl_4 precursor solution

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Modification of supported Au catalyst used for low temperature CO oxidation

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