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**Modification of Au/Al<sub>2</sub>O<sub>3</sub> catalysts, and testing their catalytic activities in CO oxidation**

**Ph.D. Thesis**

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## 1. Introduction

The oxidation of CO is a very important heterogeneous catalytic reaction. Due to its simplicity it is often investigated as a model reaction. The CO is a by-product in many chemical processes, it can be removed by catalytic oxidation.

The interest for supported gold catalysts has been extended from the eighties, due to Haruta's pioneering works. Earlier it was generally accepted that gold is a catalytically inactive metal. Haruta proved that gold stabilized in nanosize on various supports shows high catalytic activity in oxidation reactions.

Supported gold catalysts show high activity in CO oxidation even at low temperature (-70 °C). According to the literature data the stabilization of gold nano-particles in the size of 2-5 nm is responsible for high activity in CO oxidation, but the role of support in the activity control is not elucidated yet enough. Some of the authors consider that the catalytic activity depends only on the gold particle size, the nano-environment of gold has no effect on the activity in CO oxidation. One of the aims of my work is to demonstrate that this statement is not always valid.

At the Department of Organic Catalysis at the Institute of Surface Chemistry and Catalysis of Chemical Research Center MgO supported gold catalysts and their modified variants has been investigated. It was demonstrated that these catalysts have high activity in CO oxidation. The Al<sub>2</sub>O<sub>3</sub> supported gold catalysts are less active, but they are more stable in continuous operation. In the literature there are only few articles regarding to the surface modification of Al<sub>2</sub>O<sub>3</sub> and its effect on the oxidation activity. Therefore, I have studied the promoting effect of MgO, MnO<sub>x</sub>, CoO<sub>x</sub> and FeO<sub>x</sub> as modifiers on the activity of Al<sub>2</sub>O<sub>3</sub> supported gold catalysts in CO

oxidation. In addition, spinels – the mixed oxides of these metals with alumina – were also used as support materials.

The objectives of my work are as follows:

1. The study of the role of gold nano-environment on supported gold catalysts by investigating the relationship between the catalytic activity and introduction of different amounts and types of modifiers.
2. The alteration of the nano-environment was done by the modification of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support by MgO, MnO<sub>x</sub>, CoO<sub>x</sub> and FeO<sub>x</sub>, and by the preparation of mixed oxides of these metals with alumina. In this respect the amount of both the modifiers and gold were systematically altered. In addition various experimental parameters, such as preparation condition and cooling atmosphere after pretreatment, influencing the catalytic activity were also investigated.
3. Stabilization of gold nano-particles on different supports with the aim to obtain highly active gold catalysts.
4. Characterization of prepared gold catalysts in CO oxidation in both temperature-programmed and isotherm conditions, detailed study of the effect of modifiers, comparison of modifiers deposited onto the surface of alumina and stabilized in the bulk (spinel)
5. Characterization of prepared catalysts in catalytic oxidation of CO in the presence of hydrogen (PROX) under isotherm condition, comparison the behaviour of preferential and non-preferential oxidation.
6. Study of the long-term stability of catalysts in time on stream experiments.
7. Study of the influence of cooling atmosphere after reduction on the catalytic activity in CO oxidation.

8. Investigation of bulk and surface properties of the catalysts with BET and XRD methods. The study of CO chemisorption by IR method in the presence and absence of oxygen. The investigation of parameters influencing the adsorption: the quality of the support, the amount of modifier and gold.
9. Interpretation of the high activity of supported gold catalysts in CO oxidation. Elucidation of the nature of catalytically active sites in various modified gold catalysts.

## 2. Experimental methods

The alteration of gold nano-environment was done by the modification of the support in two ways:

- modification of  $\text{Al}_2\text{O}_3$  support with  $\text{MgO}$ ,  $\text{MnO}_x$ ,  $\text{CoO}_x$  and  $\text{FeO}_x$ ;
- preparation of spinel type supports containing Al and Mg, Mn, Co, Fe, respectively.

The  $\gamma\text{-Al}_2\text{O}_3$  support was prepared by precipitation of aluminum nitrate. The prepared support was modified by adsorption with the chosen metal nitrates. The spinel type support was prepared by coprecipitation of the required metal nitrates, followed by reduction. The gold was loaded onto the support by impregnation or deposition-precipitation.  $\text{HAuCl}_4 \times 3 \text{H}_2\text{O}$  was used as gold precursor.

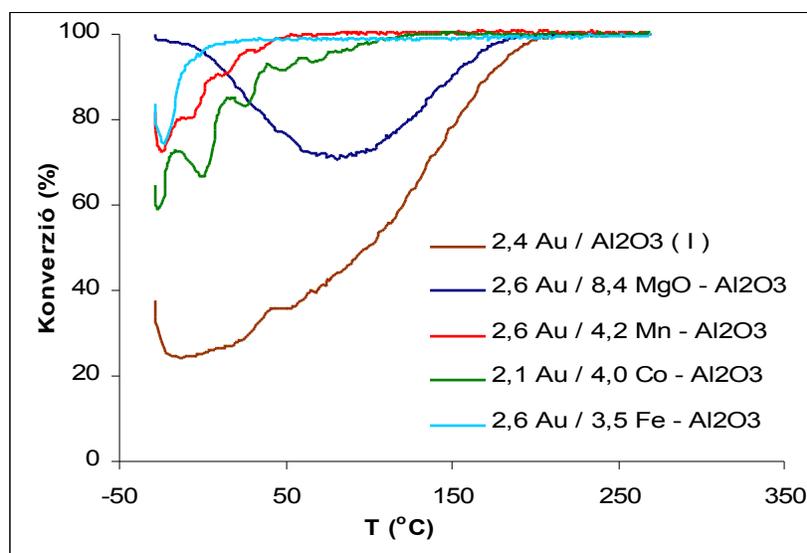
The structure of the prepared  $\text{Al}_2\text{O}_3$  and spinel type supports was investigated by XRD, their surface area was measured by BET methods. The metal content of catalysts was determined by ICP. Some catalysts were characterized by TPD, XRD, TEM, FTIR and DRIFT methods.

The catalytic activity was investigated in temperature programmed CO oxidation in one-channel (-30 – +270 °C) and 16-channel (30 – 300 °C)

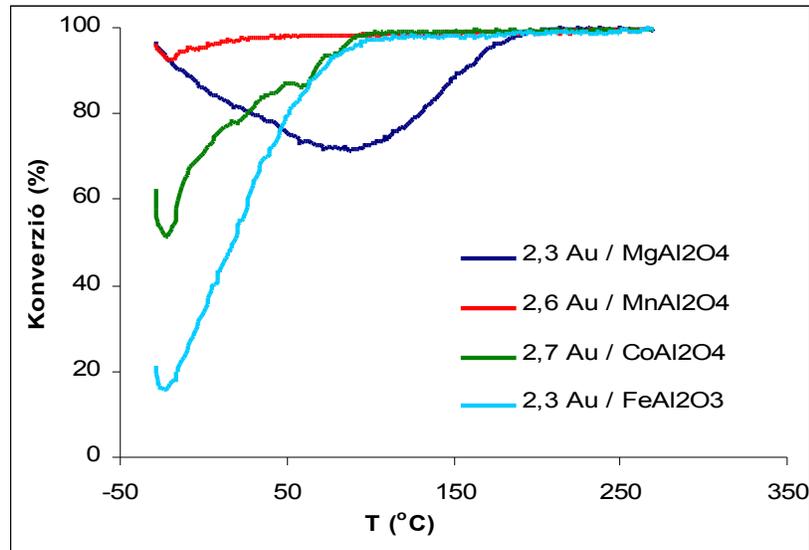
reactors. Further investigations were done in the 16-channel reactor under isotherm condition both in the presence and absence of hydrogen and the long-term stability of catalysts was also investigated in the presence of hydrogen.

### 3. Results

By XRD and BET measurements it was evidenced that high surface area  $\text{MgAl}_2\text{O}_4$ ,  $\text{MnAl}_2\text{O}_4$ ,  $\text{CoAl}_2\text{O}_4$  and  $\text{FeAl}_2\text{O}_4$  spinel were prepared, without oxide impurities. By application of different modifiers considerable amount of  $\text{Al}_2\text{O}_3$  and spinel type supported gold catalysts were prepared and tested in CO oxidation. Upon using temperature-programmed CO oxidation technique it was found that the alteration of nano-environment of gold changes significantly the catalytic activity of supported gold catalysts. The activity of modified supported gold catalysts in CO oxidation was higher than that of the parent  $\text{Au}/\text{Al}_2\text{O}_3$ . The effects of modifiers are shown in **Figures 1. and 2.**



**Figure 1.** The effect of metal oxide modifiers on the CO conversion over  $\text{Al}_2\text{O}_3$  supported gold catalysts.



**Figure 2.** The effect of support on the CO conversion over spinel supported catalysts.

Upon increasing the amount of modifier the activity passed through a maximum, i.e., at high concentration of modifier the catalytic activity decreased. This fact indicated that there is an optimum in the Au/modifier ratio. At high concentration of modifier it can cover the surface of gold nano-particles reducing in this way the number of active centers (as shown in the **Scheme 1**). On the other hand at high modifier concentration spontaneous reduction of gold can take place resulting in the growth of the nano-particles.

At a given gold content and temperature Mg, Mn and Co spinel supported gold catalysts showed higher activity in TPO measurements than the impregnated ones. This observation indicated that the modification in the bulk has more beneficial effect than the modification of the surface. Bulk modifiers resulted in higher activity because in this case the modifier exists in the form of a continuous surface layer and it is bonded into the lattice. This form of modifier is not capable to cover the surface of Au nano-particles. On the other hand it is suggested that the interaction between the

spinel type support and gold is stronger than that of between the metal-oxide type modifier stabilized on the alumina surface and gold.

In temperature-programmed CO oxidation (TPO) it was found that the heating of the catalyst to 300 °C in the presence of CO + O<sub>2</sub> mixture resulted in deactivation in the case of Mg, Mn and Fe modifiers. The deactivation led to the decrease of activity in the cooling part of TPO measurements. This can be attributed to the change of the structure of gold nano-particles during heating in the oxidative atmosphere, reducing the coordinately unsaturated surface atoms (the edges and corners). Moreover, the activity decrease can also be attributed to the formation of surface carbonates at high temperature. In the case of MgO modified catalysts the gold particles at high temperature can migrate from the MgO islands (as shown in **Scheme 1.**). At low temperature the newly formed active sites are less active than the parent ones, it might be the reason for the loss of the U type pattern in the cooling part of the TPO measurements. However, the deactivation is reversible, as after subsequent reduction at 350 °C in hydrogen the activity is restored completely.

We have mentioned for the first time in the literature that the cooling atmosphere after hydrogen pretreatment alters the catalytic activity. It was observed that both alumina and magnesia modified supported gold catalysts show higher activity after cooling in hydrogen. The manganese modified samples resulted in higher activity after cooling in helium. In the case of iron modified catalysts at low temperature the He atmosphere, while at high temperature region the H<sub>2</sub> cooling atmosphere resulted in higher activity. The Co modified catalysts in the heating cycle show higher activity after cooling in H<sub>2</sub> atmosphere, while in the cooling cycle resulted in higher activity after cooling in He atmosphere.

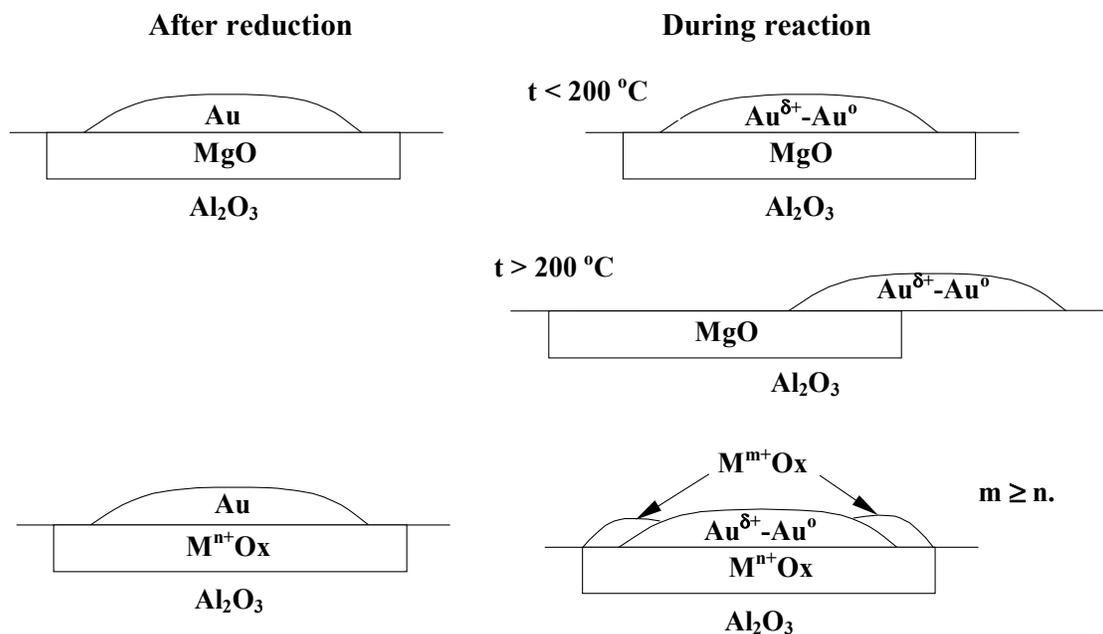
The reduction in H<sub>2</sub> at 350 °C changes the surface structure of gold nano-particles, changing the ratio of edges and corners. This ratio could be further modified during cooling the sample in H<sub>2</sub> atmosphere. Probably these phenomena play role in the alteration of the activity of catalysts cooled in different atmosphere.

The particle size distribution based on TEM measurements show that the gold particles deposited on different type of supports has been stabilized in nano-size. 80 % of the particles are under 2 nm.

The gold particle size in Au/MgO-Al<sub>2</sub>O<sub>3</sub>, Au/MnO<sub>x</sub>-Al<sub>2</sub>O<sub>3</sub> and Au/MnAl<sub>2</sub>O<sub>4</sub> catalysts is slightly larger than in Au/Al<sub>2</sub>O<sub>3</sub> catalyst. Despite the activity of modified catalysts is higher than that of Al<sub>2</sub>O<sub>3</sub> supported ones. This means that in case of these modifiers the nano-environment of gold plays more important role in the catalytic activity than the size of nano-particles.

Infrared spectroscopic measurements showed that the CO adsorption band depends on the gold content of the catalyst. In the presence of O<sub>2</sub> the band shifts towards higher wave numbers and a broad band with a shoulder appears. The high frequency part of this band can be assigned to the *in situ* formed Au particle with partial positive charge. This phenomenon occurred over each sample. Furthermore, after cooling the catalysts in H<sub>2</sub> the CO adsorption bands shifted towards the lower wave numbers compared to the samples cooled in He. This suggested that the CO adsorption is stronger in the former case. In addition, the formation of negative charge on the gold nano-particle can be suggested. On catalysts cooled in H<sub>2</sub> atmosphere – due to the spillover of hydrogen – the coverage of the surface OH groups increased as it has been evidenced by the OH region in the IR spectra.

Regarding to our proposal two types of active sites can be involved in CO activation: **a)**  $\text{Au}^{\delta+} - \text{Au}^0$ ; **b)**  $\text{M}^{n+} - \text{Au}^0$ . At low temperature over  $\text{Al}_2\text{O}_3$  and magnesia modified supports the “**a**” type active sites, while at higher temperature and in the case of redox type modifiers the “**b**” type active sites are responsible for CO activation, as can be seen in the **Scheme 1**.



**Scheme 1.** Suggested active centres formed and involved in CO activation.

The effect of the presence of hydrogen was also investigated in kinetic measurements over  $\text{Au}/\text{Al}_2\text{O}_3$  catalysts. It was found that in the presence of hydrogen the rate of the CO conversion substantially increased, while the reaction order regarding to the CO increased only slightly.

Time on stream measurements were performed over selected catalysts in CO oxidation in the presence of hydrogen. These results indicate the good stability both in conversion and selectivity.

My results unambiguously show that the gold nano-particles stabilized on the support and their nano-environment is responsible for the high catalytic activity.

## **Thesis**

1. High surface area  $\text{MgAl}_2\text{O}_4$ ,  $\text{MnAl}_2\text{O}_4$ ,  $\text{CoAl}_2\text{O}_4$  and  $\text{FeAl}_2\text{O}_4$  spinel were prepared, without oxide impurities.
2. It was found that the alteration of gold nano-environment changes the catalytic activity of  $\text{Au}/\text{Al}_2\text{O}_3$  catalysts. All modified catalysts showed higher activity than the parent  $\text{Au}/\text{Al}_2\text{O}_3$ .
3. It was found that at high modifier concentration the catalytic activity of modified catalysts decreases, i.e. an optimum Au/modifier ratio is needed to obtain maximum activity.
4. In TPO experiments it was found that in the case of using Mg, Mn and Co spinel type supports the activity of Au/spinel type samples is higher than that of the impregnated ones at a given gold content and temperature. This means, that the modifier in the bulk has more beneficial effect than the modifier created at the surface of alumina.
5. In temperature-programmed CO oxidation (TPO) it was found that over catalyst modified by  $\text{MgO}$ ,  $\text{MnO}_x$  and  $\text{FeO}_x$  after heating up to  $300\text{ }^\circ\text{C}$  a deactivation occurred in the cooling cycle of TPO measurements. However, the deactivation is reversible, as after subsequent reduction at  $350\text{ }^\circ\text{C}$  in hydrogen the activity is restored.
6. We have described for the first time in the literature that the cooling atmosphere after hydrogen pretreatment alters the catalytic activity.
7. The particle size distribution based on TEM measurements show that the gold particles deposited on different type of supports has been stabilized in nano-size.
8. Based on TEM and TPO measurements we have demonstrated that the nano-environment of gold plays more important role in the catalytic activity than the size of nano-particles.

9. Based on infrared spectroscopic measurements it was found that the CO adsorption band depends on the gold content of the catalyst. In the presence of O<sub>2</sub> the band shifts towards higher wave numbers and a broad band with a shoulder appears. The higher frequency part of the shoulder can be assigned to the *in situ* formed Au particle with partial positive charge.
10. Furthermore we have shown that the CO adsorption is stronger when the catalysts were cooled in H<sub>2</sub> compared to the samples cooled in He. This finding can be attributed to the appearance of the negative charge on the gold nano-particle.
11. According to our proposal two types of active sites are involved in CO activation: **a)** Au<sup>δ+</sup> - Au<sup>0</sup>; **b)** M<sup>n+</sup> - Au<sup>0</sup>. At low temperature over Al<sub>2</sub>O<sub>3</sub> and magnesia modified supports “**a**” type active sites, while at higher temperature and in case of redox type modifiers the “**b**” type active sites are responsible for CO activation.
12. Based on time on stream measurements it was found that the prepared catalysts have high stability both in conversion and selectivity.
13. The results unambiguously show that both the stabilization of nano-sized gold particles on the support and their proper nano-environment is responsible for the high catalytic activity in CO oxidation.

#### **4. Application possibilities**

Carbon monoxide is formed as by-product in various technological processes, for example in partial and total burning of hydrocarbons, in reforming processes of alcohols, at coke production, in carbon dioxide lasers. As an environmental pollution source the exposure of CO by vehicles has to be mentioned. The CO formed as by-product can be eliminated by catalytic oxidation. Another application of low temperature CO oxidation is air cleaning. Various air-conditioning devices and gas helmets contain gold catalysts. The applicability of gold catalysts in gas helmets is greatly enhanced by the fact that the activity of supported gold catalysts increase in the presence of moisture. Catalysts prepared in this study could be suitable for the use in gas helmets.

In the future, fuel cells will receive great importance in electrically operated environment-friendly automobiles. In these cars mainly hydrogen will be used as fuel. Hydrogen is obtained by steam reforming of hydrocarbons and methanol. After reforming hydrogen always contains CO that is a poison for the Pt based fuel cell catalysts. The CO content can be lowered only to 0.5-1 % by water-gas reaction. The desired 10 ppm level can be obtained by selective catalytic oxidation of the CO in the presence of hydrogen. This requirement can be obtained by catalysts prepared in this study after suitable modification.

## 5. Publications

1. E.Gy. Szabó, M. Hegedűs, Á. Szegedi, I. Sajó and J.L. Margitfalvi, **CO oxidation over Au/Al<sub>2</sub>O<sub>3</sub> catalysts modified by MgO**, *React. Kinet. Catal. Lett.* 86 (2005) 339.
2. E.Gy. Szabó, A. Tompos, M. Hegedűs, Á. Szegedi, J.L. Margitfalvi, **The influence of cooling atmosphere after reduction on the catalytic properties of Au/Al<sub>2</sub>O<sub>3</sub> and Au/MgO catalysts in CO oxidation**, *Appl. Catal. A: General*, 320 (2007) 114.
3. E.Gy. Szabó, M. Hegedűs, J.L. Margitfalvi, **The role of the nano-environment of supported gold catalysts in the activity control. Modification of Au/Al<sub>2</sub>O<sub>3</sub> catalyst by redox-type metal oxides.**, *React. Kinet. Catal. Lett.*, accepted for publication.
4. E.Gy. Szabó, M. Hegedűs, Á. Szegedi, A.K. Datye, J.L. Margitfalvi, **Preparation, characterization and activity of Au/Al<sub>2</sub>O<sub>3</sub> catalysts modified by MgO**, *Catal. Commun.*, submitted for publication.

## Other publications

5. A. Tompos, M. Hegedűs, J.L. Margitfalvi, E.Gy. Szabó, L. Végvári, **Multicomponent Au/MgO catalysts designed for selective oxidation of carbon monoxide. Application of a combinatorial approach.**, *Appl. Catal. A: General*, under publication, (2007), doi:10.1016/j.apcata.2007.10.022

## Oral presentations, Posters

1. Szabó Gy.E., Hegedűs M., Margitfalvi J., **Stabilization of Au nanoclusters over Al<sub>2</sub>O<sub>3</sub> modified by metal oxides**, *VI. Hungarian Materials Science Conference*, 14-16 October 2007, Siófok, (*oral presentation*).
2. Szabó Gy.E., Tompos A., Hegedűs M., Szegedi Á., Margitfalvi J., **The influence of cooling atmosphere on the catalytic properties of Au/Al<sub>2</sub>O<sub>3</sub> and Au/MgO catalysts in CO oxidation**, *Chemical Research Center, HAS, Scientific Days*, 23-24 May 2007, Budapest, (*oral presentation*).
3. Szabó Gy.E., Tompos A. és Margitfalvi J., **The influence of cooling atmosphere on the catalytic activities of Au/Al<sub>2</sub>O<sub>3</sub> catalysts in CO oxidation**, *Chemical Research Center, HAS, X. Ph.D. School on Chemistry*, 7-9 May 2007, Mátraháza, (*oral presentation*).
4. Szabó Gy. E., **Modification of Au/Al<sub>2</sub>O<sub>3</sub> catalysts and investigation of the activity in CO oxidation**, *Catalyst Committee Meeting*, 15 May 2007, Budapest, (*oral presentation*).
5. E. Gy. Szabó, A. Tompos and J.L. Margitfalvi, **Testing supported gold catalysts by high-throughput experimental technique**, *4<sup>th</sup> EFCATS School on Catalysis*, 20-24 September 2006, Sanktpetersburg, Russia, (*oral presentation*).
6. E.Gy. Szabó, A. Tompos, J.L. Margitfalvi, **Comparison of different supported gold catalysts in CO oxidation in the presence or absence of hydrogen**. *8<sup>th</sup> Pannonian International Symposium on Catalysis*, 4-7 July 2006, Szeged, (*poster*).
7. J. L. Margitfalvi, M. Hegedűs, E.Gy. Szabó, A. Tompos, **The role of the nano-environment of supported gold nano-clusters in the activity**

**control**, 7<sup>th</sup> *European Congress on Catalysis*, 28 August – 1 September 2005, Sofia, Bulgaria, (*poster*).

8. Szabó E., **The influence of nano-environment on the activity of supported gold catalysts**, *Chemical Research Center, HAS, VIII. Ph.D. School on Chemistry*, 5-6 May 2005, Tahi, (*oral presentation*).
9. Szabó E., **The influence of nano-environment on the activity of supported gold catalysts**, *Technical University of Budapest, Chemical Engineering Department, 2-nd Scientific Conference for Ph.D. students*, 2004 nov. 24, Budapest, (*oral presentation*).
10. Szabó E., Margitfalvi J., Hegedűs M., Göbölös S., Tompos A., **Low temperature CO oxidation over supported gold catalysts** *Chemical Research Center, HAS, Scientific Days*, 2-3 June 2004, Budapest, (*oral presentation*).
11. Szabó E., **Low temperature CO oxidation over supported gold catalysts**, *Chemical Research Center, HAS, VII. Ph.D. School on Chemistry*, 2004 ápr. 27-28, Tahi, (*oral presentation*).
12. Szabó E., **Low temperature CO oxidation over MgO-Al<sub>2</sub>O<sub>3</sub> and Mg-Al spinel supported Au catalysts**, *Chemical Research Center, HAS, VI. Ph.D. School on Chemistry*, 29-30 April 2003, Tahi, (*oral presentation*).

#### **International conferences, where my results were presented**

13. J.L. Margitfalvi, M. Hegedűs, E. Szabó, A. Tompos, F. Somodi, Á. Szegedi, **Modification of supported Au catalysts used for low temperature CO oxidation**, *Fifth Tokyo Conference on Advanced Catalytic Science and Technology*, 23-28 July 2006, Tokyo, Japan, (*poster*).

14. J.L. Margitfalvi, M. Hegedűs, E. Szabó, Á. Szegedi, O. Geszti, **Activity control of supported gold catalysts by altering the nano-environment of gold nanoclusters.** *5<sup>th</sup> World Congress on Oxidation Catalysis*, 25-30 September 2005, Sapporo, Japan, (*poster*).
15. J.L. Margitfalvi, M. Hegedűs, E. Szabó, F. Somodi and A. Tompos, **The importance of the nano-environment of supported gold catalysts in the activity control,** *North American Catalysis Society, 19<sup>th</sup> North American Meeting*, 22-27 May 2005, Philadelphia, Pennsylvania, (*oral presentation*).