



BUDAPEST UNIVERSITY OF TECHNOLOGY AND ECONOMICS
FACULTY OF CHEMICAL AND BIOENGINEERING
OLÁH GYÖRGY DOCTORAL SCHOOL

SYNTHESIS AND STUDY OF GOLD CATALYSTS
IN CO OXIDATION AND SELECTIVE OXIDATION OF GLUCOSE

Thesis

Author: Tímea Benkó
Supervisor: Prof. Zoltán Schay, D.Sc.
Consultants: Andrea Vargáné Beck, C.Sc.
Anita Nagyné Horváth, Ph.D.



Department of Surface Chemistry and Catalysis
Centre for Energy Research
Hungarian Academy of Sciences

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1. Introduction

Catalytic reactions play important roles in our life. Catalysis contributes to sustainable development through decreasing the energy consumption of the processes and eliminating or at least dramatically decreasing pollution from chemical and refining processes. The development of selective, highly active catalysts working under mild conditions meets the requirements of green chemistry. Application of nanoparticles and nanostructures in catalytic materials may generate improved unique properties.

Gold – the most stable among all metals – was thought to be inactive in catalysis until Haruta's discovery of the catalytic power of gold in carbon monoxide oxidation when its size is in the nanometer range. Later high activity of gold nanoparticles was demonstrated in various oxygen-transfer and hydrogenation reactions. Gold catalysts have many advantages compared to platinum group metals; it is resistant to oxidative atmosphere, moreover gold has greater price stability. The performance of a gold based catalyst is sensitively affected by many different structural properties that must be understood and well controlled. As a result of research and development nowadays supported gold nanoparticles are already used in the catalytic converter of vehicles, respiratory protectors, in fuel cells operating in electric vehicles and in chemical processes.

In my work I focused on comparison of supported gold catalysts in two different type oxidation reactions; in CO oxidation and selective glucose oxidation to gluconic acid to understand better the nature of the active sites and on reaction specific modifications to develop more efficient catalysts for the two reactions.

2. Literature background

It is widely accepted that the activity of gold catalysts in CO oxidation reaction depends on the particle size, the oxidation state of Au, the type and structure of oxide support, the interaction between gold particle and the support.¹ The activity of gold catalyst increases exponentially with the reducing size of the nanoparticles below 5 nm. The optimum size for gold particles is 2–3 nm.² The chemical nature of the support plays important role determining the activity. Oxide supports are divided into two groups according to their reducibility. Generally, the reducible oxides CeO₂, TiO₂, Fe₂O₃ etc. are considered to be “active supports” since they provide good activity for Au, while the irreducible ceramic oxides SiO₂, Al₂O₃ can be regarded as inactive or much less active supports;³ showing moderate activity if the Au particles are small enough. However many exceptions can be found due to the different preparation method which results different metal-support interactions.

Selective oxidation processes represent a large class of organic reactions where the development of clean and efficient “green” processes can have a significant positive economic and environmental impact. Catalytic oxidation of reducing sugars, like D–glucose, D–lactose and D–maltose over gold give products of greater value. The oxidation product of D–glucose is gluconic acid (or its salts). The annual gluconic acid production is about 60 000 tonnes, that is made by fermentation.⁴ Utilization of selective heterogeneous catalysts allows the use of mild reaction conditions and molecular oxygen or air as oxidizing agent and avoids problems with the control of by-products and disposal of waste water, which are environmentally advantageous.

First, Biella et al. published⁵ the highly efficient utilization of gold catalyst in the reaction. In contrast with the Pt and Pd based catalysts (exhibiting high activity but low selectivity), using gold catalysts gluconate was obtained with 100% selectivity moreover self-poisoning and metal leaching were also avoided.⁶ Comotti et al.⁷ reported that the support is of

¹ G.C. Bond, C. Louis, D.T. Thompson, *Catalysis by Gold*; Imperial College Press: London, 2006.

² G.C. Bond, D.T. Thompson, *Catal. Rev. Sci. Eng.* 41 (1999) 319-388.

³ R. Grisel, K.J. Westrate, A. Gluhoi, B.E. Nieuwenhuys, *Gold Bull.* 35 (2002) 39-45.

⁴ S. Biella, L. Prati, M. Rossi, *J. Catal.* 206 (2002) 242-247.

⁵ S. Biella, G.L. Castiglioni, C. Fumagalli, L. Prati, M. Rossi, *Catal. Today* 72 (2002) 43.

⁶ Y. Önal, S. Schimpf, P. Claus, *J. Catal.* 223 (2004) 122–133.

⁷ M. Comotti, C. Della Pina, R. Matarrese, M. Rossi, *Angew. Chem. Int. Ed.* 43 (2004) 5812-5815.

limited importance in the origin of the catalyst activity in the oxidation of glucose. However the gold - support interaction was declared to be essential for the formation of a stable catalyst system. On the contrary other authors⁸ reported different catalytic activity using different type of carbon supports with the same Au particle size indicating a specific metal - support interaction. Ishida et al.⁹ observed that gold particle size influences the catalytic effect more significantly than the nature of the support comparing carbon and different metal oxide supports such as Al₂O₃, ZrO₂, TiO₂, CeO₂. So the results published on glucose oxidation by gold catalysts are not consistent and many unclear questions have emerged.

The catalytic performance of gold can be modified by its combination with a second (third) metal. Numerous publication reports on activity enhancement of AuPd systems in different processes¹⁰. Other less intensively investigated bimetallic compositions of Au with other metals (as Pt, Ag, Cu, Ni, Co, Rh, Ir, Ru) also presented superior catalytic properties to that of either component separately, mostly in oxidation reactions.¹

In our laboratory Au sols for heterogeneous catalytic purposes have been studied and applied for more than 10 years.¹¹ Gold supported on mixed oxide supports such as TiO₂-SiO₂ and TiO₂-SBA15 or CeO₂-SBA15 was prepared with special regard to ensure intimate contact of the active oxide and Au on a high surface area amorphous and mesoporous SiO₂. A unique approach, the so-called localized oxide promotion of gold, has been established and developed producing Au/SiO₂ catalysts that contain TiO₂ moieties on Au particles due to the post-modification of preformed Au particles.¹² The aims of the present work are significantly determined by and based on the preceding activity of the laboratory and naturally on the results published in the literature of the field. The results and deductions gained for the gold catalysts in CO oxidation as a model of total oxidation reactions is to be investigated how show up or alter in a partial oxidation, in the other large class of oxidation reactions, using glucose as a model organic substrates. The other issues relate to two of the most important modification

⁸ A. Stephen, K. Hashmi Chem. Rev. 107 (2007) 3180-3211.

⁹ T. Ishida, N. Kinoshita, H. Okatsu, T. Akita, T. Takei, M. Haruta, Angew. Chem. Int. Ed. 47 (2008) 9265-9268.

¹⁰ D.J. Enache, J.K. Edwards, P. Landon, B. Solsona-Espriu, A.F. Carely, A.A. Herzing, M. Watanabe, C.J. Kiely, D.W. Knight, G.J. Hutchings, Science 311 (2006) 362.

¹¹ A. Beck, A. Horváth, Gy. Stefler, M. S. Scurrill, L. Guzzi, Top. Catal. 52 (2009) 912-919.

¹² Horváth, A.; Beck, A.; Sárkány, A.; Stefler, Gy.; Varga, Zs.; Geszti, O.; Tóth, L.; Guzzi, L. J. Phys. Chem. B 110 (2006) 15417-15425.

possibilities of gold catalysts, as active oxide promotion and interaction with another metal in bimetallic particles. After the investigation of TiO_2 promotion, modification with CeO_2 was chosen as another active co-operator of gold typically in total oxidation reactions, which was studied primarily in the form of CeO_2 supported Au systems earlier. On the other side Ag as second metal in supported Au-based bimetallic system was decided to investigate, because of the well-known own activity of Ag in oxidation reactions and oxygen activation and on the other hand the promising results on AuAg cooperation in selective oxidation reaction reported in literature on unsupported bimetallic AuAg colloids.

3. Experimental

Preparation of the catalysts

Colloid adsorption method was used for the preparation of all the samples. In the first step the metal sol was prepared by reduction of metal-precursor in the presence of reducing agent and stabilizing agent. Then metal colloids were adsorbed on the support surface with the consideration of the surface charge of the support and the colloid. Next filtering, washing and drying were carried out. Oxidation and (in several cases) reduction treatment were applied to remove the organic residues from the surface. For modification by oxide promoter the precursor was introduced either in the Au sol before adsorption on the support or in the dried Au/SiO₂. In the case of modification by a second metal bimetallic colloids were applied for the catalysts preparation.

Characterization techniques

The following methods were selected for the structural characterization of the catalysts: ICP-MS, XRF and PGAA techniques were used to determine the metal and CeO₂ content of the catalysts; TEM and XRD measurements to calculate the particle sizes; HRTEM, EELS and SAED techniques to discover the structure of the metal – oxide interface; UV-visible spectroscopy to observe the surface plasmon resonance of the metal nanoparticles; X-ray photoelectron spectroscopy to determine the surface concentrations and the oxidation states.

Catalytic investigations

The CO oxidation was measured in a quartz plug flow reactor of 4 mm inside diameter at atmospheric pressure connected to a quadrupole mass spectrometer (QMS). Temperature programmed reaction was performed. The activity of the catalysts was described by the temperature required for 50% CO conversion.

Oxidation of glucose was carried out at 35°C, in a thermostated, magnetically stirred batch reactor, bubbling oxygen at atmospheric pressure through the liquid phase. Analysis of the reaction mixture samples withdrawn at different reaction times was performed by HPLC. The initial reaction rates were determined and compared.

4. Results

First, unmodified gold catalysts of two different gold particle sizes supported on reducible (TiO_2 , CeO_2) and irreducible (SiO_2) oxides were prepared and their catalytic behaviors were compared in CO and glucose oxidation. A correlation was found between the temperature required for 50% CO conversion and the glucose oxidation initial reaction rate, the activity order of the catalysts was reverse in the two reactions (Figure 1). This result revealed that the known support and size effect in CO oxidation is not valid for glucose oxidation. In the latter reaction weak metal – support interaction is favored, the silica supported catalysts showed higher activity than the ceria or titania supported ones. The higher activity of the larger gold particles found in glucose oxidation is explained by the different surface geometry needs for the larger glucose molecule compared to CO.

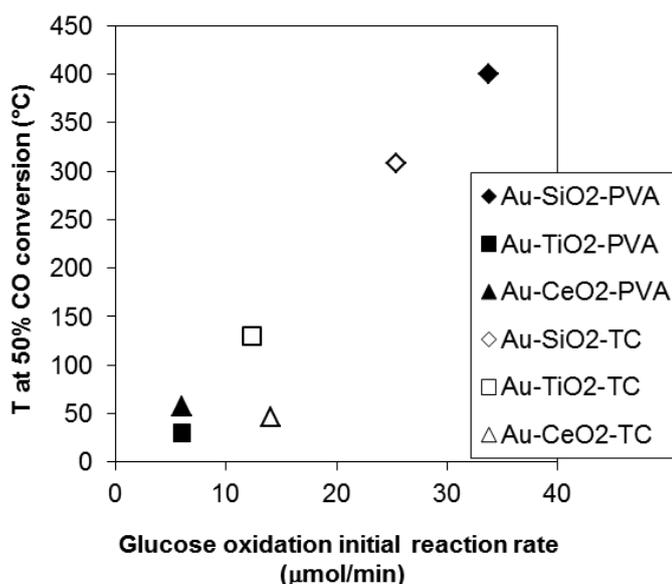


Figure 1. Comparison of activities in CO oxidation and glucose oxidation. The higher the T of 50 % CO conversion the lower the activity is.

In CO oxidation further development of the most active Au/ CeO_2 catalysts was carried out. For this purpose Au/ SiO_2 catalysts modified by different amount of CeO_2 in a special way were prepared, when nanosize Au was decorated with CeO_2 patches. High resolution transmission electron microscopy (HRTEM) measurements revealed thin, nanosize

CeO₂ moieties over gold already at extremely low 0.04wt% CeO₂ loading, which decreased the temperature of 50% CO conversion by 280°C compared to Au/SiO₂ parent catalyst. 0.16wt% CeO₂ was enough to approach the activity of the Au/CeO₂ reference sample. At 0.6wt% CeO₂ content the catalyst greatly exceeded the activity of the pure Au/CeO₂ used as reference. Further increase of the CeO₂ content above 0.6wt% did not change the activity significantly. HRTEM proved that up to this concentration ceria is attached preferentially onto gold surface (Figure 2) and further increase in Ce-loading caused CeO₂ spread over the support surface as well (Figure 3). Strong interaction of Ce species with stabilizer ligands surrounding Au is suggested as the reason for CeO₂ localization on gold.

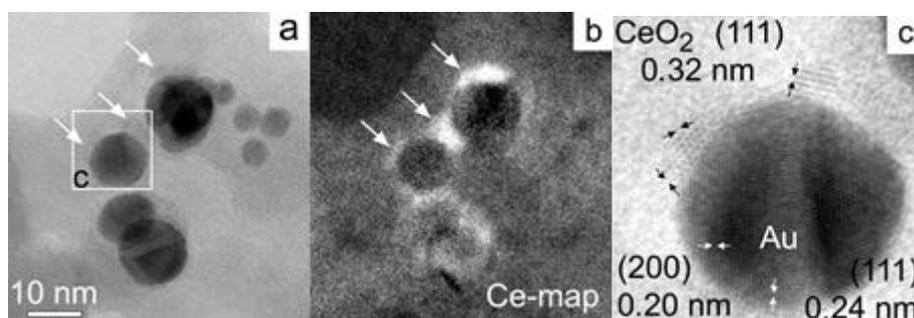


Figure 2. Unfiltered micrograph (a) and EELS Ce map (b) of sample Au/CeO₂/SiO₂ 4 with 0.04 wt% CeO₂. The bright contrast in the Ce map (b) marks regions that contain Ce. The enlarged image (c) shows CeO₂ particles (0.32nm lattice spacing) on the Au crystal (from the center of (a)). Practically no CeO₂ was found apart from Au.

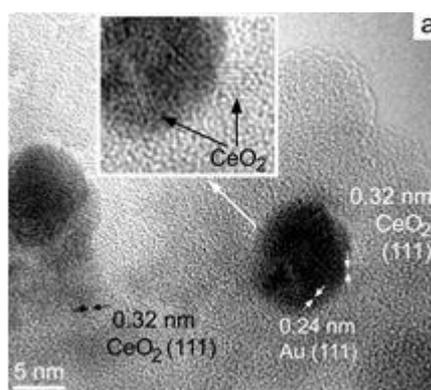


Figure 3. HRTEM of Au/CeO₂/SiO₂ with 7.4 wt% CeO₂. The 0.32 nm period lattice fringes represent CeO₂ crystals both attached to the Au particles and located, in large patches, on the SiO₂.

For the further development of the most active Au/SiO₂ catalysts in selective glucose oxidation the addition of silver to Au nanoparticles was

decided. AgAu bimetallic colloids were reported to show increased activity in glucose oxidation but supported AgAu nanoparticles were firstly applied in this work.

SiO₂ supported AgAu bimetallic catalysts were prepared by sol adsorption method with 10/90, 20/80, 33/67 and 50/50 Ag/Au molar ratios. UV-visible spectroscopy and HRTEM proved that the reduction of HAuCl₄ in Ag sol resulted in alloyed AgAu colloid particles and their alloyed structure remained after calcination and reduction treatment. The AuAg bimetallic effect and its dependence on the Ag/Au molar ratio were studied in glucose oxidation. Synergistic activity increase was observed compared to the Au/SiO₂ reference sample in case of the bimetallic samples up to Ag/Au=33/67 molar ratio (Figure 4). Maximum activity was reached at Ag/Au=20/80. Reduction pretreatment of the calcined catalysts slightly affected their activity; however the activity order of the samples remained the same. A reaction mechanism was proposed for glucose oxidation over our silica supported silver–gold catalysts, which is consistent with our experimental results and based on previous studies for alcohol and glucose oxidation on gold catalysts reported in the literature. The higher activity of the bimetallic samples is suggested to be caused by the improved O₂ activating ability provided by Ag sites. The further increase of Ag loading above the optimal concentration may dilute or cover the Au to such an extent that the number of gold ensembles necessary for glucose activation decreases deteriorating the activity.

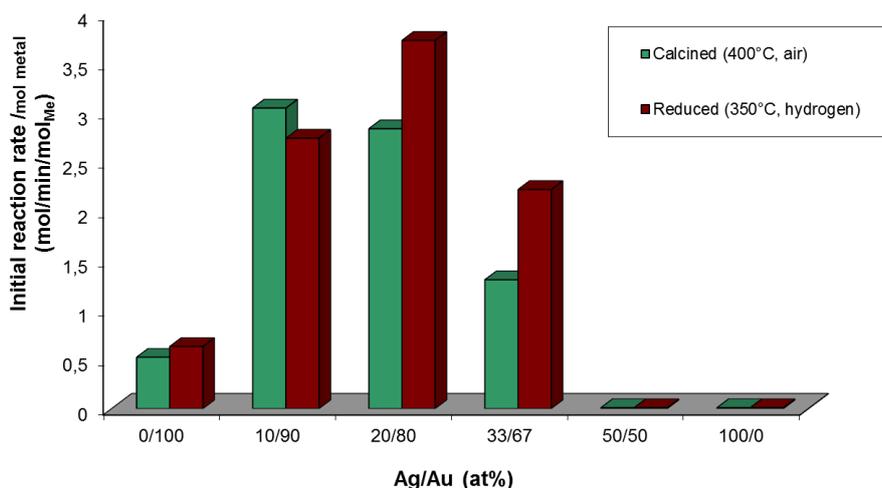


Figure 4. Catalytic activities of the AgAu/SiO₂ samples in glucose oxidation; T=35°C, pH 9.5, c_{glucose} =0.1M.

Characterization of the parent monometallic Ag sol by HRTEM and Selected Area Electron Diffraction (SAED) showed the coexistence of the commonly known face centered cubic crystal phase of Ag nanospheres with the rarely observed hexagonal $4H$ -Ag structure in about the same concentration (Figure 5). This hexagonal polytype of Ag has been observed, to date, only in nanocrystalline and continuous films or nanorods; in nanospherical form it was reported, to the best of my knowledge, for the first time.

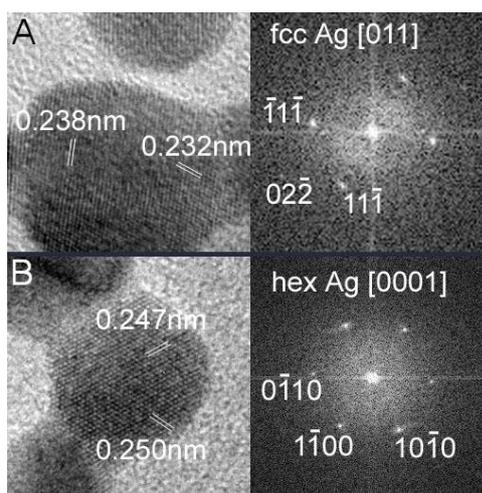


Figure 5. HRTEM image of the Ag sol. The particles marked with A and B with corresponding FFT patterns represent fcc and hexagonal Ag phases, respectively.

5. Thesis

1.) Inverse correlation has been found between the activities of supported gold catalysts in CO oxidation and in selective glucose oxidation applying two different size-ranges of reducible oxide (CeO_2 and TiO_2) and non-reducible oxide (SiO_2) supported gold nanoparticles. The type of the support and the Au particle size both affects the activity of the catalysts in glucose oxidation: the larger-size, non-reducible SiO_2 supported samples showed higher activity, in contrast with the known support and particle size effect of gold catalysts in CO oxidation. [3,4]

2.) CeO_2 decoration on SiO_2 supported Au catalysts derived from Au colloid provided higher CO oxidation activity at already 0.6wt% CeO_2 content compared to the CeO_2 supported Au catalyst, which is caused by the thin, nanosize CeO_2 in contact with gold forming higher activity perimeter than bulk CeO_2 with Au. [2]

3.) The activity of the CeO_2 decorated SiO_2 supported Au catalysts did not change above 0.6wt% CeO_2 content. Up to 0.6wt% concentration CeO_2 is attached dominantly onto the gold surface and further increases in Ce-loading caused CeO_2 spread over the support surface as well. Strong interaction of limited amount of Ce species with stabilizer ligands around Au nanoparticles is suggested as the reason for CeO_2 localization preferentially on gold up to a given CeO_2 loading. [2]

4.) AgAu alloy nanoparticles were proved to be formed during the reduction of HAuCl_4 by sodium borohydride in Ag sol at different Ag/Au molar ratios. The alloy structure of the AgAu nanoparticles was retained after adsorption on SiO_2 support and subsequent oxidation and reduction treatments. [1]

5.) SiO_2 supported bimetallic AgAu nanoparticles of different Ag/Au molar ratios were applied for the first time in selective glucose oxidation. The catalysts showed synergetic activity increase up to Ag/Au =33/67 molar ratio compared to the monometallic SiO_2 supported Au and Ag catalysts. The activity of the catalysts was similar after oxidation and reduction pretreatments. [1]

6.) The nanospherical form of hexagonal $4H$ -Ag crystal structure was described for the first time. Reduction of AgNO_3 with sodium-borohydride

in the presence of polyvinylalcohol results in silver sol with face centered cubic and hexagonal $4H$ crystal structured Ag nanoparticles in about the same amount. [1]

6. Possible applications

Gold nanoparticles decorated by CeO_2 are promising materials for sensor applications (detection of CO and other organic gases) due to their high activity and stability in room temperature CO oxidation reaction. The bimetallic silica supported AuAg nanoparticles can be promising selective glucose oxidation catalysts after improving the catalyst stability. For the fabrication of nanospherical $4H$ -Ag crystals the preparation method applied in this PhD research work is promising. This metastable structure may have advantageous unique plasmonic properties compared to that of the stable fcc Ag.

7. Publications

Related to the Thesis

[1] **T. Benkó**, A. Beck, K. Frey, D.F. Srankó, O. Geszti, G. Sáfrán, B. Maróti, Z. Schay, *Bimetallic Ag-Au/SiO₂ catalysts: Formation, structure and synergistic activity in glucose oxidation*, Applied Catalysis A: General, 479 (2014) 103-111

IF: 3.410 (2013) C:0

[2] A. Horváth, A. Beck, G. Stefler, **T. Benkó**, G. Sáfrán, Z. Varga, J. Gubicza, L. Guzzi, *Silica-Supported Au Nanoparticles Decorated by CeO₂: Formation, Morphology, and CO Oxidation Activity*, Journal of Physical Chemistry C, 115 (42), (2011) 20388-20398

IF: 4.805, C: 7

[3] L. Guzzi, A. Beck, **T. Benkó**, Z. Pászti, *Gold Catalysis: Particle Size or Promoting Oxide Morphology?*, MRS Online Proceedings Library, 1351 (2011) mrrs11-1351-ff13-02, doi: 10.1557/opl.2011.1168

[4] **T. Benkó**, A. Beck, O. Geszti, R. Katona, A. Tungler, K. Frey, L. Guzzi, Z. Schay, *Selective oxidation of glucose versus CO oxidation over supported gold catalysts*, Applied Catalysis A: General, 388 (2010) 31

IF: 3.383; C: 9

Other publications

[5] A. Beck, G. Magesh, B. Kuppan, Z. Schay, O. Geszti, **T. Benkó**, R. P. Viswanath, P. Selvam, B. Viswanathan, L. Guzzi, *Specific role of polymorphs of supporting titania in catalytic CO oxidation on gold*, Catalysis Today, 164(1), (2011) 325-331

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[6] E. Nieddu, L. Mazzucco, P. Gentile, **T. Benkó**, V. Balbo, R. Mandrile, G. Ciardelli, *Preparation and biodegradation of clay composites of PLA*, Reactive and Functional Polymers, 69 (6), (2009) 371-379

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Oral presentations

Hordozós arany-ezüst katalizátorok előállítása és aktivitása glükóz szelektív oxidációjában, **T. Benkó**, A. Beck, K. Frey, G. Sáfrán, D.F. Srankó, Z. Schay,

Tavaszi Szél Konferencia, Debrecen, 21-23 March 2014.

Glükóz szelektív oxidációja hordozós arany katalizátorokon, **T. Benkó**, A. Beck, K. Frey, G. Sáfrán, D.F. Srankó, Z. Schay, XXXVI. Kémiai Előadói Napok, Szeged, 28-30 October 2013.

Research in the Institute of Isotopes, HAS, **T. Benkó**, K. Frey, Regional Training Course on Nanomaterials and Radiation: Synthesis, Characterization, Applications, University of Reims Champagne Ardenne, Reims, France, 30 November 2009.

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Liquid phase oxidation of glucose over gold catalysts, **T. Benkó**, A. Beck, A. Tungler, L. Guzzi, Z. Schay, COST CHEMISRTY D36/003/06 Working Group Meeting, Palermo, 15-16 May 2009.

Posters

Silica-supported bimetallic Ag-Au nanoparticles: Formation, structure and high activity in glucose oxidation, **T. Benkó**, K. Frey, A. Beck, O. Geszti, L. Guzzi, Z. Schay, 11th European Congress on Catalysis – EuropaCat-XI, Lyon, France, 1-6 September 2013.

SiO₂ supported Ag-Au alloy nanoparticles with high catalytic activity in selective oxidation of glucose, K. Frey, **T. Benkó**, O. Geszti, L. Guzzi, Z. Schay,

Proc. of Final workshop of the COST D36 Action. pp. 39-40., Fuengirola, Spain, 18-20 May 2011.

Supported gold catalysts in selective glucose oxidation and CO oxidation, **T. Benkó**, K. Frey, A. Beck, A. Horváth, L. Gucci, Z. Schay, EFACTS School, Anakara, Turkey, 13-19 September 2010.

Supported gold catalysts in selective oxidation of D-glucose, **T. Benkó**, K. Frey, A. Beck, L. Gucci, A. Tungler, Z. Schay, 10th Pannonian Symposium, Kraków, Poland, 29 August – 2 September 2010.

Selective oxidation of D-glucose versus CO oxidation over supported gold catalysts, **T. Benkó**, A. Beck, A. Horváth, L. Gucci, Z. Schay, The Sixth Tokyo Conference on Advanced Catalytic Science and Technology, Sapporo, Japan, 18-23 July 2010.

Glükóz szelektív oxidációja arany katalizátorokon – hordozó hatás vizsgálata,

T. Benkó, A. Beck, A. Tungler, L. Gucci, Z. Schay, Oláh György Doktori Iskola VII. Konferenciája, 4 February 2010.

Selective d-glucose oxidation over gold catalysts – support effect, **T. Benkó**, A. Beck, L. Gucci, A. Tungler, Z. Schay, COST Chemistry D36 3rd Workshop, Benahavis, Spain, 21-23 October 2009.

Propene total oxidation over gold catalysts: Influence of TiO₂ and CeO₂ decoration on Au / mesoporous SBA-15, **T. Benkó**, A. M. Venezia, L. F. Liotta, G. Pantaleo, A. Beck, L. Gucci, Z. Schay, CLEAR Summer School, Porto Carras, Greece, 24-30 May 2009.

