

“BABES – BOLYAI” UNIVERSITY
CLUJ NAPOCA
FACULTY OF CHEMISTRY AND CHEMICAL ENGINEERING

**Supported metal catalysts studies using H/D isotopic
exchange**

– Ph.D. Thesis Abstract –

Ph. D. Student

Mihaiela Diana Lazăr

Jury:

President: **Conf. Dr. Cornelia Majdik**–Dean of the Faculty
of Chemistry and Chemical Engineering Cluj Napoca

Scientific Advisor: **CS I Dr. Damian Axente** – INCDTIM Cluj
Napoca

Reviewers: **Prof. Dr. Liana Mureşan** –Faculty of Chemistry
and Chemical Engineering Cluj Napoca

Conf. Dr. Eng. Rodica Zăvoianu – Faculty of
Chemistry, Bucureşti University

CS I Dr. Eng. Valer Almăşan – INCDTIM Cluj
Napoca

Cluj Napoca

2010

Ph. D. THESIS OUTLINE

Introduction.....	3
Chapter 1	
The catalytic properties of dispersed gold in reactions involving hydrogen. Hydrogen spillover. Adsorption and reaction of H ₂ and O ₂ on bulk gold.....	5
1.1 The catalytic activity of supported gold nanoparticles.....	6
1.2 The activity of gold supported catalysts in reactions involving hydrogen.....	12
1.3 Adsorption and reaction of H ₂ and O ₂ on bulk gold surface.....	15
1.4 Isocyanide adsorption on bulk gold surface.....	17
1.5 Hydrogen spillover phenomenon	18
Chapter 2	
Supported gold catalysts active for H/D isotopic exchange reactions.....	24
2.1 Preparation of nanostructured gold catalysts supported on oxides.....	25
2.2 Characterization of supported gold catalysts	30
2.3 Nanostructured gold catalysts active for H ₂ /D ₂ O isotopic exchange reaction	41
2.4 H ₂ +D ₂ isotopic exchange reaction. Hydrogen spillover	46
2.5 Quantification of spiltover hydrogen using H/D isotopic exchange method...	57
Chapter 3	
Bulk gold – a catalyst for isocyanide and amine reactions in the presence of oxygen...	69
3.1 Adsorption and stability of isocyanide on gold surface.....	70
3.2 Reactions of isocyanide and primary amines catalyzed by bulk gold	80
3.3 Reactions of isocyanide and secondary amines catalyzed by bulk gold.....	95
3.4 Dehydrogenation and coupling of primary amines catalyzed by non nanostructured gold and Au/Al ₂ O ₃	102
Conclusions	110
References.....	114

Keywords: gold catalysts, hydrogen chemisorption on gold, H/D isotopic exchange, isocyanide monolayer, carbodiimide, substituted urea, imines

INTRODUCTION

Gold, the mankind most valued metal, own its value to some very special physico – chemical properties: does not oxidize, it is not attacked by acids and alkalies, does not react with common pollution agents or with usual organic and inorganic substances from environment. The gold surface can not chemisorb molecules such as: hydrogen, oxygen, carbon oxides, nitrogen oxides, hydrocarbons, which are the most common reagents in industrial catalytic processes. This is due to its electronic structure, with complete 5d orbital. If the gold is split in very small parts, with particle size smaller than 5 – 7 nm, uniform distributed on a proper support, it shows amazing catalytic properties. It is very active for carbon monoxide oxidation at temperatures below 0°C, nitrogen oxides reduction, water gas – shift, or organic molecules hydrogenation.

The objective of this paper is to study the possibilities of nanostructure and bulk gold to activate small molecules containing unpolar covalent bonds, such as H₂ and O₂.

The thesis is structured on three chapters. First chapter is a bibliography study presented the last results in thesis area. Chapters 2 and 3 present my own results regarding gold catalysts. At the end there are the conclusions and the references.

CHAPTER 1

The catalytic properties of dispersed gold in reactions involving hydrogen. Hydrogen spillover. Adsorption and reaction of H₂ and O₂ on bulk gold

The explanations of particular catalytic activity of gold nanoparticles take into consideration 4 main factors: (i) particle size effect; (ii) preparation method; (iii) support and/or promoters effect; (iv) the nature of active sites [1], [2].

The activity of gold supported catalysts for hydrogen involving reactions is inferior to that of nickel or platinum based catalysts, mainly to reduce capacity of gold catalysts to chemisorb hydrogen. Nevertheless these type of catalysts are important for hydrogenations also, due to their very good selectivity in partial hydrogenations. From this point of view they are superiors to nickel or platinum. In this chapter, were presented the results reported by now, on hydrogen chemisorption experiments, H/D isotopic exchange study and main results in partial hydrogenation.

Bulk gold is not able to chemisorb by dissociation molecular hydrogen at any catalytically interesting temperature. The oxygen chemisorption experiments leads to the same conclusions: that O₂ is not chemisorbed on bulk gold in any detectable amounts at temperatures around room temperature [3], [4].

The only molecules for which we have proof that are chemisorbed and form stable monolayers on bulk gold are the ones with active functional groups, like SH, CN, NC, N=N, S-S, etc.

CHAPTER 2

Supported gold catalysts active for H/D isotopic exchange reactions

The objective of this chapter is to study the processes which involve hydrogen on the surface of nanostructured gold catalysts. The chosen method is H/D isotopic exchange in two systems: (i) $H_2 + D_2O$ and (ii) $H_2 + D_2$. The first one is a usual test reaction used in supported metal catalysts study, in which hydrogen is chemisorbed only on metal surface and water on oxide surface. There is the advantage on having only hydrogen on the metal. The advantage of using the second reaction is the existence of only the interest species on the catalysts surfaces. The usage of hydrogen isotopes makes possible the observation of hydrogen surface processes

2.1 Preparation of nanostructured gold catalysts supported on oxides

The nanostructured supported gold catalysts were prepared by deposition – precipitation method (DP) using urea [82]. This preparation method is very appropriate for obtaining gold catalysts with small nanoparticles and good catalytic properties. It is also, reproducible. The method consist in gold deposition on the support by precipitating from $H[AuCl_4]$ solution with OH ions generated in the system by slowly decomposition of urea in water, at $80^\circ C$. The prepared catalysts are: Au/Al_2O_3 , Au/TiO_2 , Au/ZrO_2 , Au/CeO_2 , Au/Cr_2O_3 , Au/SiO_2 . For silica supported gold catalysts two other methods were used: the wet impregnation, $Au/SiO_2(IMP)$ and the deposition of gold onto a support obtained by sol – gel method [86]. All catalysts were calcined in air at $300^\circ C$

2.2 Characterization of supported gold catalysts

After preparation, the catalysts were characterized by determination of: gold nanoparticle size, local structure of gold nanoparticles, total surface area, metal surface area, gold concentration.

2.2.1 The determination of gold nanoparticle size

Due to the direct dependence between the gold nanoparticle size and their catalytic properties, the correct evaluation of this property is one of the major task of the gold catalysts characterization. We used the X Ray diffraction method (XRD), which beside the crystallite size offer a serie of other information regarding nanoparticles structure. The XRD measurements were made on a X Ray diffractometer with Bragg – Bretano geometry, with incident wavelength 1,5406 Å and NaI detector. The probe was scanned with a 2θ angle between 20° and 80° . The resulting spectra were processed using the Fourier transforms method [89]. The resulted parameters: crystallite size (d_{ef}), microstraines (MS) and the fault probability (SFP) are presented in Table 2.1.

The crystallite sizes are very different for different catalysts supports [92]. For gold supported on Al_2O_3 , CeO_2 and TiO_2 the crystallite size are smaller then 4 nm. For Au/ZrO_2 and Au/Cr_2O_3 the particles are 2 -3 times bigger. For Au/SiO_2 catalysts, the particles sizes are approximately the same, around 12 nm, no matter of the preparation method.

Table 2.1. The XRD results for gold supported catalysts [92].

No.	Catalyst	Line	d_{ef} (nm)	d_m (nm)	MS x 10^{-5}	SFP (%)
1	Au/SiO ₂ (DP)	(111)	18,1	14	1,12	0,72
		(200)	15,0		1,51	0,96
		(220)	11,0		1,10	1,32
2	Au/SiO ₂ (IMP)	(111)	19,2	12	1,44	1,28
		(200)	7,4		1,74	1,70
		(220)	11,1		1,10	1,32
3	Au/SiO ₂ (SG)	(111)	19,6	13	-	-
		(200)	13,6		-	-
		(220)	13,1		-	-
4	Au/ZrO ₂	(111)	21,2	7,5	0,06	0,12
		(200)	14,2		0,82	0,54
5	Au/Cr ₂ O ₃	(200)	15,2	8,4	0,10	0,35
6	Au/TiO ₂	(111)	3,8	4	8,10	5,73
7	Au/CeO ₂	(111)	3,2	3,5	11,29	5,92
8	Au/Al ₂ O ₃	(113)	2,7	3,2	12,10	5,97

d_{ef} – crystallite size; d_m – medium crystallite size; MS microstraines; SFP – fault probability

For Au/SiO₂ and Au/ZrO₂ the size of the crystallite corresponding to different planes are very different. This means that the gold particles have an irregular form. The microstrain parameter of the lattice can also be correlated with the crystallite size in the following way: the value of the crystallite size increases when the microstrain value decreases. For Au/CeO₂ and Au/TiO₂ catalysts, with similar crystallite size, the difference in MS is due to the different nature of the support.

2.2.2 The determination of local structure of gold crystallites using X Ray Absorption Spectroscopy

When the energy of an incident X Ray photon hitting the surface exceeds the binding energy of the surface atoms, the photon is absorbed and a photoelectron is emitted. The outgoing electron is scattered by all atoms near the absorbing atom and by analyzing the resulted flux, the disorder of the metal network can be elucidated. Due to the fast attenuation of electron wave, the resulted information is about the atoms situated in vicinity of the scattering atom. The resulted structural information are: the average number of atoms in first coordination shell (N₁), the average number of atoms in second coordination shell (N₂) and the interatomic distance.

The results are presented in Figure 2.1.

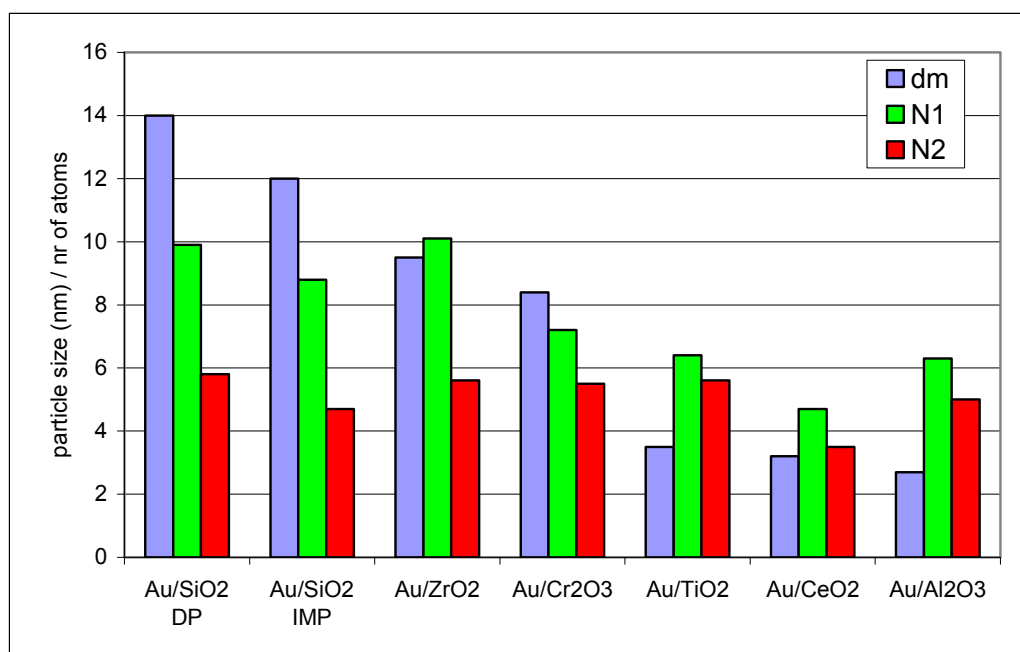


Figure 2.1. The structural properties of supported gold catalysts.

The number of atoms in the first coordination shell is smaller than in standard gold network (where $N_1 = 12$, $N_2 = 6$) with 2 up to 7 atoms, proving a strong deformation of metallic lattice [92]. The value of interatomic distance is close to the standard value. This means that the remaining atoms of the first coordination shell are still in their position, so the metallic network is still there. The rest of the gold atoms (which should have been in the first coordination shell) are out of their places. For the second coordination shell the average number of atoms is close to the standard value, and there is a certain difference between the calculated interatomic distance and the standard value.

Our XAS and XRD results confirm the metallic structure of gold in nanoparticles with minimum 2.5 nm diameter, and are not in agreement with the hypothesis of the presence of amorphous ionic gold in such nanoparticles.

2.2.3 Determination of gold concentration in gold supported catalysts

The prepared gold catalysts had a target gold concentration of 5% wt. The precipitation process (which can take place outside the support, also) and the washing techniques used in preparation process, can lead to metal lost, so it is important to determine the gold content of the final catalysts. The following method was used: the gold is dissolved from the support in aqua regia, and the resulting solution is analyzed by Atomic Absorption Spectroscopy (AAS).

The results are presented in Table 2.2.

Table 2.2. The gold content of supported gold catalysts.

Cat.	Au/SiO ₂ (DP)	Au/SiO ₂ (IMP)	Au/SiO ₂ (SG)	Au/ZrO ₂	Au/Cr ₂ O ₃	Au/TiO ₂	Au/CeO ₂	Au/Al ₂ O ₃
C _{Au} (%)	3,3	1,2	3,05	3,8	3,7	3,3	3,6	3,7

The metal lost during preparation procedure using deposition – precipitation with urea, are relative constant, around 30% from the calculated value. The low gold content obtained for Au/SiO₂ (IMP), is explained by the segregation of gold from the support in calcination step.

2.2.4 Determination of the total and metal surface area

In heterogeneous catalysis, the catalytic processes appear on the catalyst surfaces: metallic or oxidic ones, so the determination of surface area is an important step in catalysts characterization. The method used for total surface area determination is BET method. We used the nitrogen adsorption at liquid nitrogen temperature, in a Sorptomatic 1990 apparatus. For gold supported catalysts, the determination of metallic surface area using hydrogen chemisorption is not appropriate, because the poor adsorption of hydrogen molecule on gold at room temperature. The gold area was estimated from particle size and gold concentration data, using the formula 2.1

$$S_{Au} = (50.000 \times C_{Au}) / (\rho \times d_m) \quad (2.1)$$

S_{Au} – gold surface area; C_{Au} – gold content (%); ρ – gold density (19,3 g/cm³) și d_m – average particle size (Å). The gold area is obtained m²/g of catalyst. The results are presented in Table 2.4.

Table 2.4. Surface area and porosity for gold supported catalysts..

Cat.	Au/SiO ₂ (DP)	Au/SiO ₂ (IMP)	Au/SiO ₂ (SG)	Au/ZrO ₂	Au/Cr ₂ O ₃	Au/TiO ₂	Au/CeO ₂	Au/Al ₂ O ₃
S_{sup} (m ² /g)	316	316	920	175	45	47	72	158
S_{cat} (m ² /g)	209	261	192	162	41	44	67	133
S_{Au} (m ² /g)	0,61	0,25	0,59	1,31	1,14	2,14	2,66	2,99
V_p (cm ³ /g)	0.39	0.42	0.40	0.8	0.08	0.09	0.12	0.90
R_m (Å)	42	45	40	20	120	134	72	21

S_{sup} – support surface area; S_{cat} – total surface area; S_{Au} – gold surface area; V_p – total pores volume; R_m – average pore radius.

For all catalysts, except the silica supported ones, the total surface area is slight smaller than the oxide support area. For silica support the total surface area decrease very much during catalysts preparation. This can be explained by pores filling with metal particles (these catalysts have small pores and big gold particles) or by thermal treatment during the preparation. For silica xerogel the highly porous structure is destroyed during catalysts preparation.

The pores sizes are smaller for the catalysts with bigger surface area.

2.3. Nanostructured gold catalysts active in H₂/D₂O isotopic exchange reaction

The Au/oxide nanostructured catalysts proved to be very active in hydrogenation reactions, which involve in a compulsory way dissociative adsorption and activation of H₂ molecule. Our goal was to study the influence of the metallic nanoparticle size, of the preparation method, and of the support nature on the catalytic activity of gold catalysts in hydrogen involving reactions. For this, a reaction test is used, namely the isotopic exchange reaction between hydrogen and heavy water:



It is a common reaction, used to evaluate the catalytic activity in reactions where hydrogen is involved, catalyst comparison and assessment of the factors that influence this catalytic activity.

The experiments were performed in an experimental set up composed from a saturator, a catalytic reactor, and a gas-chromatograph. The saturator contains D₂O, and it is kept at the reaction temperature. Hydrogen is bubbled through the saturator; depending on the temperature hydrogen is loaded with D₂O vapor in requested molar ratio and afterwards is led in the catalytic reactor. The catalyst is placed inside the reactor. The temperature of the reactor can be controlled, so that experiments can be performed in isothermal conditions as well as following a temperature controlled scheme.

The outlet gasses obtained in the reaction are analyzed by gas-chromatograph equipped with classic column (activated coal) and thermo conductivity detector TCD. HD is the reaction product and its intensity is measured. The experimental conditions used in the first trial series are:

- reaction temperature 200°C (a) or raising with 3°C/min, to 300°C (b)
- saturator temperature 45°C;
- mass of catalyst 0,2 g;
- gas flow 12,5 ml/min;
- reagents ratio 1:1.

The results are expressed in: (a) hydrogen conversion – C – defined as the percent of hydrogen transformed in HD and presented in Figure 2.2; and (b) the half conversion temperature – $T_{50\%}$ – the temperature at which conversion is 50%.

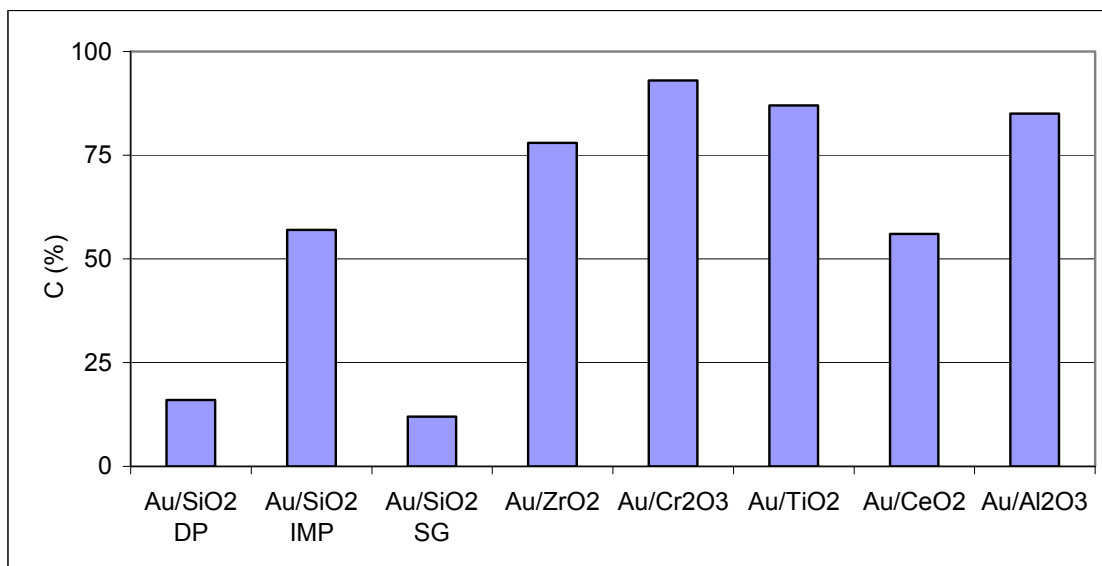


Figure 2.2. Hydrogen conversion to HD in the reaction of H₂ and D₂O catalyzed by Au/oxide.

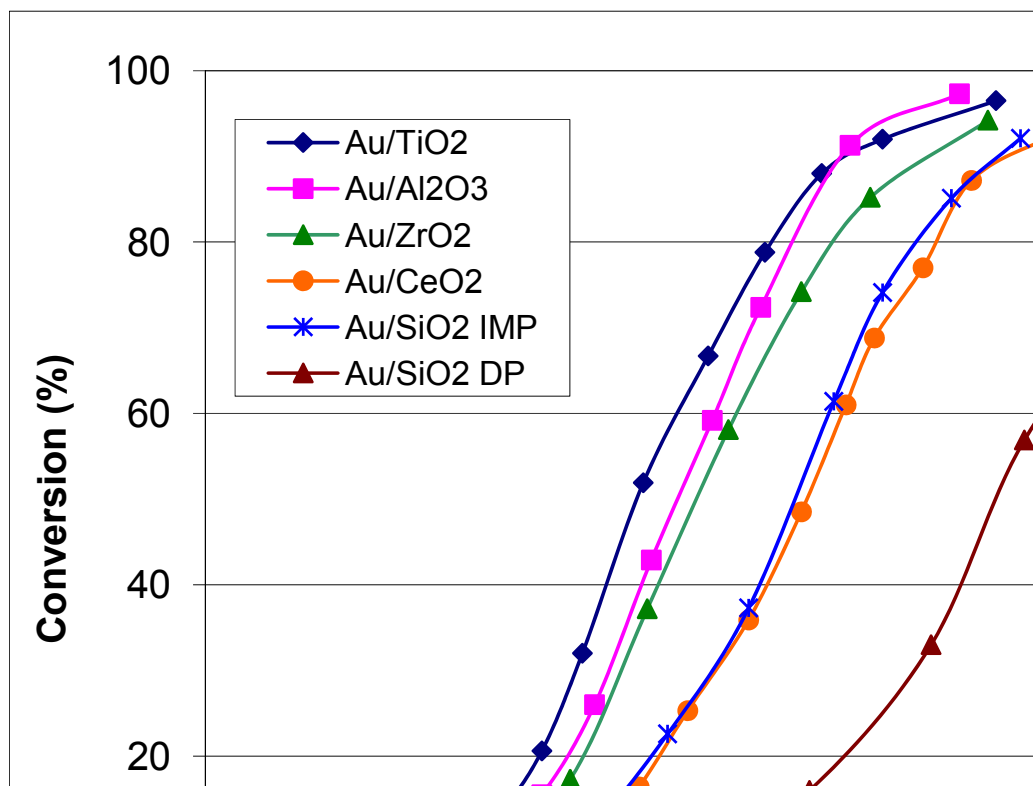


Figure 2.3. Hydrogen conversion versus temperature in the exchange reaction H₂ - D₂O.

The catalysts are divided in three groups regarding their catalytic activity [98]:

In the first group are the active ones: Au/TiO₂, Au/Al₂O₃ and Au/ZrO₂, in the second group are Au/CeO₂ and Au/SiO₂ (IMP) with a similar behavior and in the last group is Au/SiO₂ (DP). The influence of the preparation method can be seen for gold deposited on silica. The catalyst obtained through deposition – precipitation method has the lowest catalytic activity regardless of the support is classical oxide or xerogel obtained through sol-gel method. The ones obtained by impregnation present a good catalytic activity if we take into account that the nature of the support is the same and that the gold particle size are almost similar. The answer to this problem is tight to the structure of the gold nanoparticles. Crystallite shape for the catalyst obtained through IMP is more irregular (Table 2.1) than of the one obtained through DP. This means that the crystallite has more active sites represented by edges, steps or peaks suitable for hydrogen adsorption and activation. Another factor that could influence the good activity of Au/SiO₂ (IMP) is low gold concentration on the support which leads to a better dispersion of the metal.

Au/ZrO₂ presents also a good conversion; although the size of its nano particles are twice as big as the nano particles of Au/TiO₂ and Au/Al₂O₃, the catalytic activity of Au/ZrO₂ is similar to the above mentioned catalysts. It was proposed that the good catalytic activity is due to the contribution of the support, namely zirconium oxide. A similar behavior has been observed in Ni/oxide catalysts tested in isotopic exchange reaction H₂-D₂O where Ni/ZrO₂ has the best catalytic activity [99]. The influence of the support can be also seen for Au/CeO₂ which has a poor hydrogen conversion compared to Au/TiO₂ and Au/Al₂O₃ although they have similar concentration of gold on the support and similar dimension and structure of the nanoparticles.

2.4 H₂+D₂ isotopic exchange reaction. Hydrogen spillover from metal to support

The above presented results (chapter 2.3) indicated that H₂ molecule is chemisorbed and activated on the surface of gold nanoparticles dispersed on oxide support. A direct proof of this phenomenon can be obtained studying the catalyzed

H/D isotopic exchange in $H_2 - D_2$ system. The main advantage of using this reaction consist in the existence on the catalysts surface, of only one chemical species – hydrogen – which is proved to don't chemisorb on the oxides. The complex processes which take place at the interaction of hydrogen molecule with the surface of supported metal catalysts imply: hydrogen chemisorption on the metal surface, molecule dissociation and generation of active species H^* and the spillover of these species to support surface. There is a dynamic equilibrium between the spillover and the reverse spillover. On the oxide surface the activated hydrogen species arrived from support, are in dynamic equilibrium with the hydrogen atoms bond by oxide surface as OH groups.

The objective of this chapter is to study the capacity of gold nanoparticles supported on oxides to chemisorb H_2 using the H/D isotopic exchange between the isotopic hydrogen species existed on the oxide surface as OH groups and the other hydrogen isotope present in gaseous phase.

The experimental protocol consists in [101], [106]:

- catalyst activation in hydrogen, at 300°C , for 2h. During this step all catalyst surface is covered with hydrogen in different forms: chemisorbed on the metal and bond by oxide as OH groups;
- Argon gas is passed through the catalyst at the reaction temperature; the effluent gases are analyzed using a quadrupole mass spectrometer (QMS). During this step the hydrogen is desorbed from the metal surface, remaining only on the oxide. The metal surface is clean when the H_2 concentration in the effluent gases is zero.
- an Ar + D_2 mixture is introduced in the catalytic reactor; in same time the QMS analyze the effluent gasses, searching for 2, 3 and 4 masses (correspond to H_2 , HD and D_2).

This experimental technique monitories the system evolution from point zero to the steady state. A given catalyst presents catalytic activity for the H/D isotopic exchange reaction, when the resulted QMS spectrum contains mass 3, corresponding to reaction product HD.

Figure 2.4 presents the experimental mass spectrum for Au/Al₂O₃ at 250°C.

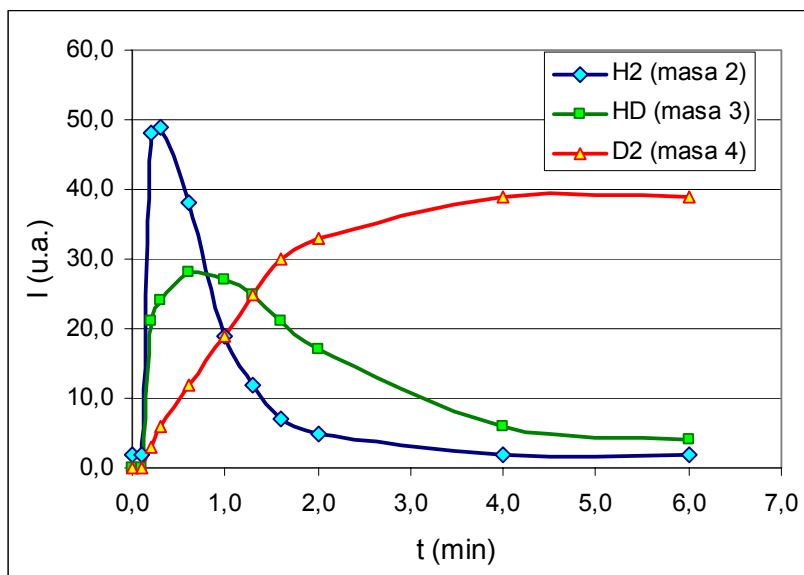


Figure 2.4 The evolution of 2, 3, 4 masses versus time in the H/D isotopic exchange reaction of gaseous D₂ and H from support, for Au/Al₂O₃ catalyst at 250°C. On OY axis is QMS signal intensity

The reaction is:



The hydrogen proceeded from support leaves the system as H₂ and HD, being replaced by deuterium. At the end of the experiment all the surface is covered by deuterium.

Using a special developed software it was determined the volume of spillover hydrogen as being the volume of hydrogen isotope dislocated from 1 m² of support in the above presented experiments – V_{sp}. At a given temperature V_{sp} depend on support nature; the higher values were obtained for Au/Al₂O₃ and the lower for Au/SiO₂ (IMP). For some catalysts Au/Al₂O₃, Au/ZrO₂ and Au/SiO₂ (IMP), V_{sp} is not dependent on temperature. For the rest of the studied catalysts it decreased with increasing temperature.

The results presented in this chapter are a direct proof of H₂ dissociative chemisorption on nanostructured gold. The process is activated, an activation temperature was identified, which is the lower temperature required for hydrogen chemisorption to take place.

CHAPTER 3

Bulk gold – a catalyst for isocyanide and amine reactions in the presence of oxygen

In chapter II it was proofed, using H/D isotopic exchange, that nanostructured gold with particle size smaller than 15nm, has the capacity to dissociative chemisorb hydrogen. This is impossible in the case of solid gold, which cannot chemisorb and activate stable molecules with non polar covalent bond e.g. H₂ or O₂. So it has been said that solid gold is not catalytic active. The research presented in this chapter will demonstrate that this affirmation is not entirely truth. We started in searching possibilities to influence the bulk gold surface in order to imply it in catalytic reactions involving simple molecules. Seeing that we did not found any possibility for H₂ we choose to work with O₂. We will demonstrate that the presence in the reaction system of molecules containing functional groups with lone electrons (e.g. isocyanides) which can be donated to gold, can influence the surface long enough to catalyze a reaction which implies the activation of O₂ molecule. The goals of this chapter are:

- (i) the study of the isocyanides adsorption and reaction process on the bulk gold surface
- (ii) the mechanism by which the bulk gold surface gets involved in heterogeneous catalytic reaction

3.1 Alkyl isocyanides adsorption and stability on gold

Isocyanides can adsorb on gold surface through donation of the lone pair of electrons from carbon to gold. The most frequent method used to study the adsorption and stability of the isocyanides on gold surface is IR spectroscopy. The NC group has an absorption band at around 2200 cm⁻¹, a zone in the IR spectrum where no other peaks from other bonds of isocyanides molecule can be found [65]. The adsorption studies made on gold were performed using two types of substrates: gold films deposited on glass and gold powder. The three studied isocyanides (n-

butyl isocyanides *n-BuNC*, 1,1,3,3-tetramethyl *n*-butyl isocyanides *TMBC* and cyclohexyl isocyanides *CyNC*) form on the gold surface a monolayer through self assembly of the isocyanides molecules from hexane solution. The self assembled monolayer is stable against desorption in the non polar solvent (hexane), as it was shown by monitoring the NC peak intensity with the help of IR spectroscopy. The monolayer is removed from the surface with polar solvents in approximately 4-5 h. The addition of a small quantity of amine in hexane leads to the removal of all isocyanides from the surface of gold film in very short time (few seconds). The used amines were: *n*-butyl amine (*n*-BuNH₂), *n*-dodecyl amine (*n*-DoNH₂), cyclohexyl amine (*Cy*NH₂), benzyl amine (*Bz*NH₂).

The speed of the NC peak disappearance from IR spectra depends on the amine basicity and on the carbon chain structure of the isocyanide molecule. We assumed that isocyanide is removed from gold due to the reaction with amines from solution, according to Figure 3.1.

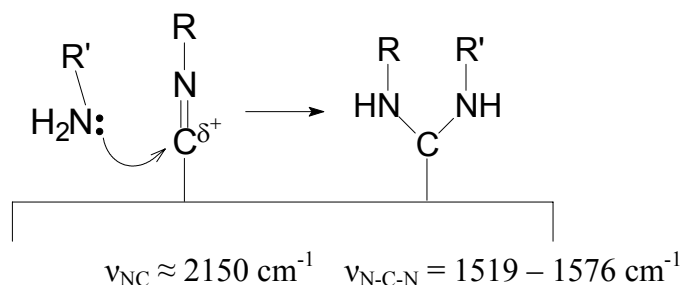


Figure 3.1. The nucleophilic attack of amine molecule on the adsorbed isocyanide on gold surface.

Follow this reaction the intermediate which could be formed is a diaminocarbene bond by the surface. The performed IR studies, could not lead to identify this product on the gold surface, which means that this is rapidly desorbed in the form of a reaction product.

3.2 Reactions of isocyanide and primary amines catalyzed by bulk gold

The identification of the reaction product was made working with gold powder, *n*-BuNC and *n*-BuNH₂. 1 g of gold powder with isocyanide monolayer on its surface is putted in a test tube and 1 ml *n*-butyl amine solution 5 mM in hexane (*n*-

BuNH₂) is added. The test tube is closed and stir for 10 minutes. Samples of hexane solution were analyzed by GC-MS in order to identify the desorbed isocyanide and/or a possible reaction product. The resulted GC spectrum contains the pick due to desorbed *n*-BuNC and a supplementary one, which was identified to correspond to *N,N'*-dibutylcarbodiimide, having the formula *n*-Bu–N=C=N–*n*-Bu (Figure 3.2).

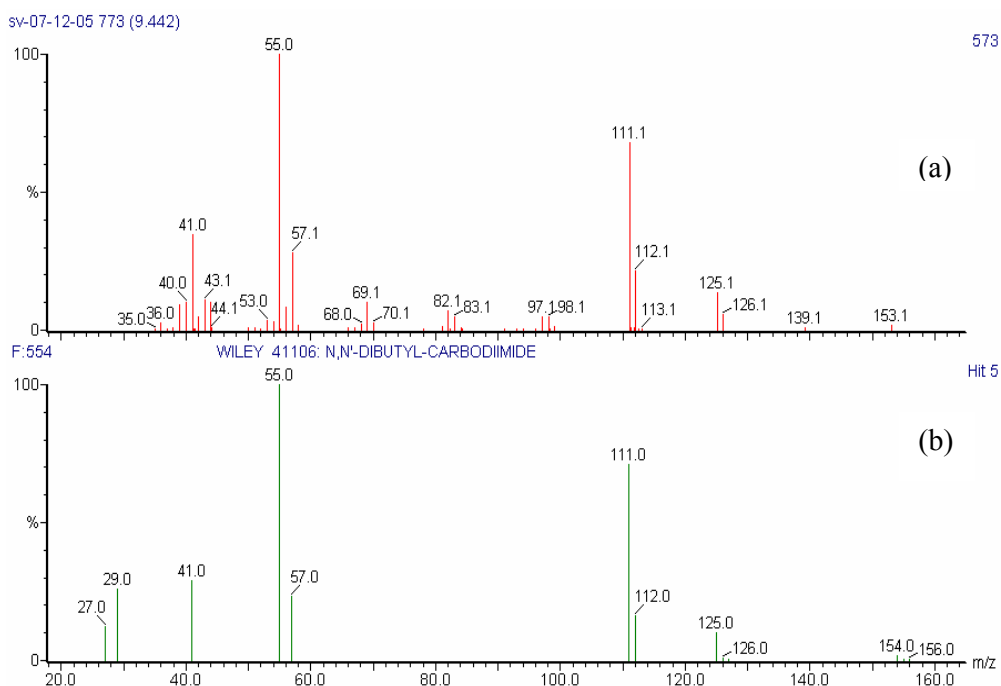
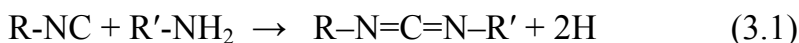


Figure 3.2. (a) MS spectrum for the reaction product of *n*-BuNC and *n*-BuNH₂ catalyzed by bulk gold; (b) MS spectrum of *N,N'*-dibutylcarbodiimide from Wiley data base.

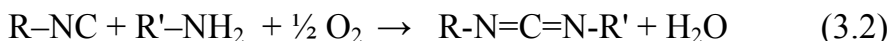
Similar experiments were made in order to identify the reaction product, using different amines and different isocyanides. The resulting product was in all cases the corresponding carbodiimide.

Following the product identification, the reaction of isocyanides and amines can be written:



In order to establish in which form hydrogen leaves the system, several attempts were made to identify H₂ in reaction gases, with no success. The lack of H₂ in the reaction flask suggests that hydrogen atoms could have combined with oxygen from solvent to form water. To confirm this hypothesis a series of experiments were

done in argon atmosphere. Careful measures were taken to avoid the oxygen presence in solvent and reaction flask. The GC-MS analysis revealed that the reaction does not take place in the absence of oxygen. Taking into consideration all the presented results, the reaction of isocyanides, amines and oxygen catalyzed by bulk gold is as follow [110]:



The attempts to identify water by GC gave inconclusive results, due probably to the low concentrations.

To establish if the bulk gold act as a catalyst for the reaction, or the pre-adsorption of isocyanide is required, a mixture of 0,5 mM *n*-BuNC, 5mM *n*-BuNH₂ and 0,1 g *n*-decane (as internal standard for GC analysis) in hexane was prepared. 1 g of gold powder was added and the mixture was stir in air, at room temperature. Periodically small samples were analyzed by GC, revealing the presence of reaction product *n*Bu-N=C=N-*n*Bu (*N,N'*-dibutylcarbodiimide). Its concentration increase in time and the concentration of isocyanide decrease. Except the main product, the reaction mixture contains small quantities of *N,N'*- dibutyl urea.

Table 3.1. The conversion of isocyanide and the yield of carbodiimide in reaction of *n*-BuNC, *n*-BuNH₂ and O₂ catalyzed by bulk gold.

Exp nr.	<i>n</i> -BuNC (mmol)	T (°C)	C (%)	η (%)	t _{1/2} (h)
1	1.6x10 ⁻³	20	97	42	72
2	17x10 ⁻³	20	98	47	120
3	1.6x10 ⁻³	60	100	70	5
4	17x10 ⁻³	60	100	73	40

The reaction rate is small at room temperature; conversion of 95% is reached after 7 days. Increasing the reaction temperature, the rate is drastically improved. Table 3.1 contains data for isocyanide conversion C(%), carbodiimide yield η(%) and half time of isocyanide concentration t_{1/2}(h), at both studied temperatures: room temperature and 60°C.

The kinetic studies reveal that the reaction is first order on the amine concentration.

The proposed mechanism for the reaction of alkyl isocyanides, primary amines and oxygen, catalyzed by bulk gold is presented in Figure 3.2. The mechanism is based on the following experimental and kinetic data:

- isocyanides adsorb stable on the gold surface;
- we didn't obtain any experimental proofs of the adsorption of amine to the gold surface; this suggest the existence of a Elley Rideal catalytic mechanism in which only the isocyanide is adsorbed on the catalyst surface;
- the reaction does not take place in the absence of oxygen, so at least one of the mechanism steps imply the reaction with molecular oxygen;
- the reaction rate in air and pure oxygen is the same; the mechanism step which involve oxygen is not rate determining taking place, most probable, after the rate determining step;
- the rate determining step is the amine attack on the adsorbed isocyanide; this affirmation is sustained by the mechanism type and by the reaction order on the amine concentration

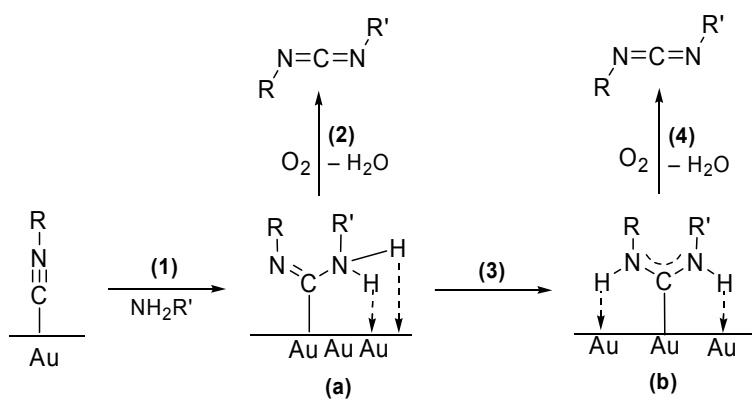


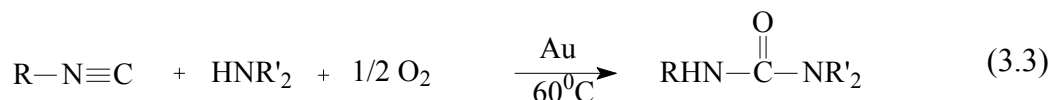
Figure 3.2. The proposed mechanism for the reaction of alkyl isocyanides, primary amines and oxygen, catalyzed by bulk gold.

3.3 Reactions of isocyanide and secondary amines catalyzed by bulk gold

Secondary amines, $RR'NH$, with only one hydrogen atom in the amino group, cannot participate in the reaction with isocyanides as described in 3.2. The aim of the present chapter is the study of the gold catalyzed reaction of isocyanides and secondary amines and the determination of reaction products and mechanism. From among isocyanides *n*-butyl isocyanide (*n*-BuNC) was tested with di-*n*-propyl amine

((*n*-Pr)₂NH), piperidine ((CH₂)₅NH), and morpholine (O(CH₂CH₂)₂NH). The gold powder is the same as that used in experiments presented in chapter 3.2. The identification of reaction products by GC-MS, and their quantification by GC was accomplished by means of the same apparatus used for the reactions of isocyanides with primary amines. The working procedure is similar to that previously presented.

MS spectra were recorded in order to identify the reaction product. The analyzed product presents a molecular ion at M = 200, but comparison of the spectrum with the spectra in the data bases didn't lead to a certain identification of the molecular structure. MS analysis in the module with precise atomic masses leads to a molecular formula of C₁₁H₂₄N₂O. To our surprise, O is present in the molecule, despite our expectations regarding the structure of the product, that is R-N=CH-N(R₂) formamide structure, if the carbodiimide structure isn't possible in this case anymore. The structural formula corresponding to the afore mentioned molecular formula, as well as to the structure of the reactants is given by *n*-Bu-NH-C(O)-N(*n*-Pr)₂, that is urea substituted at both N atoms. Additional confirmation of this structure was achieved by proving the presence of C=O group in the molecule by means of IR spectroscopy. The obtained spectrum shows an absorption band at 1676 cm⁻¹ corresponding to C=O group in urea [128]. All these results lead to the conclusion that the equation of the reaction between isocyanides, secondary amines, and oxygen catalyzed by gold is given by:



The dependence of isocyanide conversion as a function of amine basicity, amine concentration, and oxygen concentration in the reaction medium was studied. The greater the basicity of the amine the greater the isocyanide conversion and reaction product yield. Isocyanide conversion is directly dependent on the amine concentration. The reaction doesn't take place in the absence of oxygen. Unlike the isocyanide reaction with primary amines, a certain dependence of the reaction rate

with the oxygen concentration can be observed, but a direct relationship between them cannot be established.

The reaction mechanism presented in Figure 3.3 was formulated taking into account all the aforementioned experimental data [127]. This mechanism is similar to that proposed for the reaction of isocyanides with primary amines. The first reactions steps, i.e. isocyanides absorption, nucleophilic attack of the amine from the solution upon the adsorbed isocyanide group and formation of the adsorbed reaction intermediate are common for the two situations. In this case, the carbenic structure of the reaction intermediate is directly suggested by the formula of the reaction product.

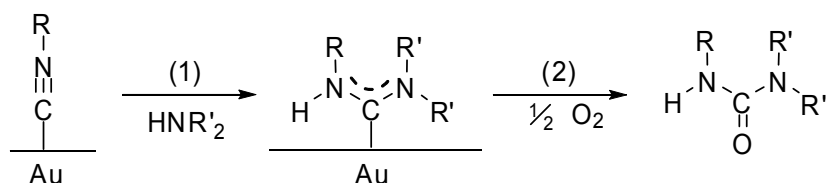


Figure 3.3. The proposed mechanism of the isocyanide reaction with secondary amines.

The reaction of the intermediate with oxygen, which takes place in the second stage, is possible only if the oxygen molecule is activated in the vicinity of the reaction intermediate. The reaction of carbene with oxygen has a greater reaction rate compared to that corresponding to the reaction of the amine from solution with the adsorbed isocyanide; this is proven by the low influence of oxygen concentration on the global reaction rate. However, the reaction rate depends on the amine concentration and basicity, as well as on the structure of the adsorbed isocyanide, which leads to the assumption the nucleophilic attack of the amine is the rate determining step of the process.

3.4. Dehydrogenation and coupling of primary amines catalyzed by bulk gold and Au/Al₂O₃

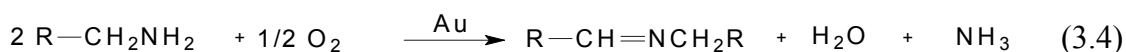
During the experiments regarding the kinetic study of secondary amines – isocyanides reaction catalyzed by metallic gold, the appearance of a secondary reaction product was observed, for which the concentration increases with time

(chapter 3.2). Further research led to the conclusion that this secondary reaction product is an imine, which results as a product from the dehydrogenation reaction of the secondary amine on the gold surface [130]. The object of this chapter is the study of primary amines reaction on the metallic gold surface, and the influence of gold deposition on an oxide support upon catalytic activity.

Au/Al₂O₃ catalyst with 5 wt% Au was prepared by incipient wetness impregnation method, also called wetting. In this way, a uniform dispersion of the impregnated metal is obtained on the support surface. The sample is kept at room temperature overnight for ageing, is dried at 100°C in an oven for 1 h, followed by calcination in air and reduction in hydrogen. Both calcination and reduction take place at 300°C (heating rate of 3°C/min) for 1 h. The catalyst thus obtained is washed with warm water for several times in order to remove the Cl⁻ ions, is filtered, dried at 100°C and calcinated at 700°C for 68 h [136]. Calcination was performed in order to obtain gold particles as large as possible, dispersed on the alumina support. The catalyst thus prepared has a medium particle dimension between 50 and 100 nm.

The experimental procedure for the study of amine dehydrogenation is similar to that described in the previous chapter. The amine solution is stirred for 24 h together with 1 g of gold powder or 100 mg Au/Al₂O₃ catalyst, followed by GC-MS analysis of the prepared solution.

The obtained results show that primary amines are involved in a dehydrogenation reaction, as well as in a coupling one, resulting in a symmetric imine.



Use of gold supported catalyst led to a significant increase of reaction yield in all cases. This phenomenon is explained by two factors: surface area of active metal and the influence of the support. Gold dispersion on the support resulted in metallic ‘islands’ with a larger surface area than their thickness, meaning that for the same gold quantity the obtained surface is larger. Unlike these, in the gold powder, the majority of the metal is to be found inside the particles, being thus inaccessible for

the reactants. A second factor to influence the catalytic activity is the support onto which is dispersed the metal. The boundary between metal and support represents a special zone of the catalyst, active for the majority of reactions catalyzed by metal/support materials. Migration of species adsorbed on metal and their interaction with the support influences the catalytic activity as well. Although quantification of the aforementioned factors isn't possible, their combined action leads to significant increase of the catalytic activity of supported gold compared to metallic gold (experimental observation). Results obtained by a different research group and recently published [138] are in good agreement with our data. Using Au/TiO₂ with three different particle sizes (3 nm, 6 nm, and 25 nm) and Au/C with large surface area (1100 m²/g) they obtain the same reaction products with similar yields. The reaction depends on the support nature and on the particle size.

CONCLUSION

The main final observations and conclusions of this thesis are:

1. 8 nanostructured gold catalysts supported on oxides were prepared, using 3 preparation methods: impregnation, deposition – precipitation and deposition – precipitation of gold on a silica support obtained by sol – gel method. The as prepared catalysts are: Au/SiO₂ (DP), Au/SiO₂ (IMP), Au/SiO₂ (SG), Au/ZrO₂, Au/Cr₂O₃, Au/TiO₂, Au/CeO₂, Au/Al₂O₃. All gold catalysts were characterized for determination of: gold nanoparticle size, local structure of metal network, gold concentration on the support, total surface area and metal surface area. It was established that *the preparation method* (big particles were obtained by impregnation and small particles by deposition – precipitation) and *the support* (for Au/Cr₂O₃ the particle size are more than twice bigger than for Au/TiO₂, Au/CeO₂ or Au/Al₂O₃ though the preparation conditions were the same) influence the size of prepared gold nanoparticles. In our gold catalysts the gold is in metallic state, but the network is profoundly affected by deformation. Approximately half of the atoms are out of their places, and the microstrain and fault probability are big.

2. The gold catalysts present catalytic activity for H/D isotopic exchange in both studied reactions: H₂ + D₂O, and H₂ + D₂. The catalytic activity depends on the preparation method and support nature, and does not depend directly on the particle size, for nanoparticles smaller than 15 nm. Two types of active sites were found on the gold surface: First types are more active working at lower temperatures, and the other types are less active requiring bigger temperatures.

3. It was developed and applied an original model to study the hydrogen spillover from gold to oxide, based on isotopic exchange reaction H₂ + D₂. The obtained results represent a direct proof of the dissociative chemisorption of hydrogen molecule on gold nanoparticles surface. By applying the H₂ + D₂ isotopic exchange

reaction, the mathematical model and the software developed by us, it was calculated the volume of hydrogen desorbed from the catalysts support, which in our work conditions represent the volume of spillover hydrogen. This volume depends on the temperature, catalysts support and preparation method.

4. Two forms of bulk gold were prepared: deposited film obtained by physical evaporation (300 nm thickness) and gold powder obtained by precipitation having the average size of 1 μm . In this form the gold is not active for the adsorption of non-polar molecules like H_2 and O_2 .

5. The primary and secondary amines react in oxygen presence with isocyanides adsorbed on gold. It was proved that the reaction is catalyzed by bulk gold, and the reaction product is the corresponding carbodiimide for primary amines, and N-N-substituted urea for the secondary amines. The infrared studies couldn't identify an adsorbed amine on the gold surface, so the only possibility remains the nucleophilic attack of amine from solution to the adsorbed carbon atom from NC group. A reaction mechanism was proposed which imply the activation of the gold surface in the vicinity of the adsorbed intermediate, to make it capable to bond the hydrogen atoms from carbene intermediate and to activate the oxygen molecule to react with them and to form water. For the reaction of isocyanides and secondary amines, the reaction product contains oxygen, proving the implication of O_2 molecule in reaction mechanism catalyzed by bulk gold.

SELECTED REFERENCES

- [10] G.C. Bond, D.T. Thompson, "Catalysis by Gold", *Cat. Rev. – Sci. Eng.*, 41 (1999) 319
- [13] G.C. Bond, C. Louis, D.T. Thompson, "Catalysis by Gold", Imperial College Press, 2006
- [52] A. G. Sault, R. J. Madix, C. T. "Campbell, Adsorption of oxygen and hydrogen on Au(110)", *Surf. Sci.*, 169 (1986) 347
- [53] P. Claus, "Heterogeneously catalyzed hydrogenation using gold catalysts", *Appl. Catal. A*, 291 (2005) 222
- [82] J.W. Geus, "Preparation of Catalysts III", G. Poncelet, P. Grange, and P.A. Jacobs, Eds., Elsevier, Amsterdam, 1983, p. 1
- [65] M. Lazăr, R.J. Angelici, "Isocyanide Binding Modes on Metal Surfaces and in Metal Complexes", în *Modern Surface Organometallic Chemistry*; Basset, J.-M.; Psaro, R.; Roberto, D.; Ugo, R., Eds.; Wiley-VCH Verlag: Weinheim, 2009, p 513
- [99] P. Mărginean, A. Olariu, "Metal/oxide support effects in the H₂-H₂O deuterium exchange reaction catalyzed by nickel", *J. Catal.*, 95 (1985) 1
- [128] Handbook of Organic Structural Analysis, Yasuhide Yukawa Editor, W.A. Benjamin Inc., New York, 1965
- [130] B. Zhu, R.J. Angelici, „Non nanogold catalyzed aerobic oxidation of secondary amines to imines“, *Chem. Commun.*, 21 (2007) 2157
- [138] A. Grirrane, A. Corma, H. Garcia, "Highly active and selective gold catalysts for the aerobic oxidative condensation of benzylamines to imines and one-pot, two-step synthesis of secondary benzylamines", *J. Catal.*, 264 (2009) 138

PUBLISHED PAPERS

- [86] **M. Lazăr**, C. Savii, V. Almășan, N. Aldea, P. Mărginean, “Ni/SiO₂ catalysts obtained by sol-gel methods”, *Annals of West University of Timișoara, Series chemistry*, 12 (2003) 1345
- [89] N. Aldea, B. Barz, P. Mărginean, T.D. Silipaș, **M. Lazăr**, C. Ducu, X. Yaning, H. Tiandou, Liu Tao, Z. Wu, Florica Aldea, “The measurement of the metal nanoparticle size”, *Studia Universitatis Babes-Bolyai, Physica*, 2 (2005) 123
- [92] **M. Lazăr**, V. Almășan, S. Pinteă, B. Barz, C. Ducu, V. Malinovski, X. Yaning, N. Aldea, “Preparation and Structural Characterization by XRD and XAS of the Supported Gold Catalysts”, *J. Optoelectron. Adv. M.*, 10 (2008) 2244
- [98] **M. Lazăr**, C. Ducu, V. Almășan, N. Aldea, B. Barz, P. Mărginean, C. Sutan, V. Malinovski, “Nanostructured gold supported catalysts: relation between structure and hydrogen catalytic activity”, *Rom. Journ. Phys.*, 51 (2006) 299
- [101] V. Almășan, T. Gaeumann, **M. Lazăr**, P. Mărginean, N. Aldea, “Hydrogen spillover effect over the oxide surface in supported nickel catalysts”, *Studies in Surface Science and Catalysis*, 109 (1997) 547
- [106] V. Almășan, **M. Lazăr**, P. Mărginean, “H/D isotopic exchange between oxide surface and spillover hydrogen on nickel supported catalysts”, *Studies in Surface Science and Catalysis*, 122 (1999) 435
- [110] **M. Lazăr**, R.J. Angelici, “Gold Metal-Catalyzed Reactions of Isocyanides with Primary Amines and Oxygen: Analogies with Reactions of Isocyanides in Transition Metal Complexes”, *J. Am. Chem. Soc.* 128 (2006) 10613
- [125] R.J. Angelici, **M. Lazăr**, “Isocyanide Ligands Adsorbed on Metal Surfaces: Applications in Catalysis, Nanochemistry and Molecular Electronics”, *Inorg. Chem.* 47 (2008) 9155
- [127] **M. Lazăr**, B. Zhu, R.J. Angelici, “Non-nanogold Catalysis of Reactions of Isocyanides, Secondary Amines, and Oxygen to Give Ureas”, *J. Phys. Chem.C*, 111 (2007) 4074
- [136] B. Zhu, **M. Lazăr**, B. G. Trewyn, R.J. Angelici, “Aerobic oxidation of amines to Imines catalyzed by bulk gold powder and by alumina-supported gold”, *J.Catal.*, 260 (2008) 1