FACULTY OF CHEMISTRY

UNIVERSITY OF LATVIA

Kristīne Edolfa

DEVELOPMENT AND INVESTIGATION OF COBALT CATALYSTS FOR 2,3-DIHYDROFURAN SYNTHESIS FROM 1,4-BUTANEDIOL

Abstract of the dissertation

RIGA

2006

This work was carried out in the Faculty of Chemistry, University of Latvia, during 2003-2006.

Referies of the dissertation:

Dr. Habil. Chem., Prof. **G. Duburs** (Latvian Institute of Organic Synthesis)

Dr. Chem., Prof. **V. Kokars** (Riga Technical University)

Dr. Chem., Asoc. Prof. **A. Prikšāne** (University of Latvia)

Scientific supervisers:

Dr. Habil. Chem., Leading researcher **Ludmila Leite**

Dr. Habil. Chem., Prof. **Andris Zicmanis**

Scientific consultant:

Dr. Chem. **Vladislavs Stonkus**

Dissertation in chemistry will be publicly examined in the University of Latvia, Faculty of Chemistry (48, Kr. Valdemara Str.) on February 28, 2007.

The complete dissertation is available at the Library of the University of Latvia, 4, Kalpaka Boulv., at the Latvian Academic Library, 10, Rupniecibas Str., and at the Library of Latvian Institute of Organic Syntheses, 21, Aizkraukles Str.

INTRODUCTION

Dihydrofurans, including 2,3-dihydrofuran, are used to obtain products of the fine organic synthesis and biologically active substances. Constant interest is caused by the research of 1,4-butanediol transformation reactions under the conditions of heterogeneous catalysis. The processes of alkanol dehydrogenation and dehydration, which can be considered important processes of fundamental chemistry, are surely in the focus of the specialists in catalysis nowadays. The number of corresponding publications shows that the theme of these investigations is on the top. The studies concerning the synthesis of cobalt catalysts and their mechanism of action are undoubtedly important because they are widely involved in the fine organic synthesis and in the production of large-tonnage products. The surface structure of catalysts, as well as the nature of the surface active centers, have been experimentally and theoretically studied. Unfortunately, the investigations of such kind are mainly dedicated to the catalytic transformations of simple alcohols – ethanol and butanol.

The results of the dissertation extend the knowledge on the mechanism of alkanol dehydrogenation reaction on metals and their oxides. Hence, it can be considered that the work presented for the defense possesses both practical and theoretical significance.

The catalysts described in the literature for the synthesis of 2,3-dihydrofuran are characterized by low yields of 2,3-dihydrofuran or low specific activity, as well as they are prepared by complicated, environment-unfriendly methods.

The investigations of this reaction were started in the Latvian Institute of Organic Synthesis many years ago by the initiative of the Pharmaceutical Company "Grindeks", because this reaction is one of the steps to produce the medicine Ftorafur.

Before our researches, there was certain confusion about the surface structure of the Co-kaolin catalyst and the role of metal and oxide active centres in alkanol dehydrogenation reaction, as well as the nature of optimal dehydrating component and its activation possibilities. Moreover, the possibilities to modify the Co-kaolin catalyst, as well as to decrease of the temperature reduction of the catalyst, have not been investigated.

The Objective of the present study is to synthesize and investigate a new active and selective bifunctional cobalt catalyst for synthesis of 2,3-dihydrofuran with lower optimum of the reduction temperature, using ecologically safe methods (mechanochemistry and treatment by ultrasound) for preparation and activation of catalysts.

The work actuality

Up to the present time, the Chemical Pharmaceutical Company "Grindeks" performed 2,3-dihydrofuran synthesis for Ftorafur production on the basis of the cobalt catalyst used for the butanol synthesis. The catalytic activity and selectivity of this catalyst was low. The problems mentioned above appeared after Latvia had resumed its independence, when the Russia's embargo policy in the export of materials has made it impossible to buy this catalyst. In order to fulfill the Agreement on Ftorafur export, there was a need to develop our own catalyst. Therefore, a new catalyst was made, its suitability for 2,3-dihydrofuran synthesis was studied, and a lot of improvements of the catalyst and the catalytic process were carried out. Simultaneously with the studies, "Grindeks" approbated the obtained results.

The work novelty
1. A new active Co-kaolin catalyst for synthesis of 2,3-dihydrofuran from 1,4-butanediol was developed.
2. A new effective ecologically safe method for the preparation of the catalyst for synthesis of 2,3-dihydrofuran was developed, that would be applicable by "Grindeks" for the synthesis of the medicinal substance.
3. Were found a cheap and suitable novel dehydrating component for Co catalyst, and their activation conditions.
4. The effect of the promotion of Co-kaolin catalyst with gold, copper and palladium on 1,4-butanediol conversions into 2,3-dihydrofuran was established.
5. A possibility was found to increase the catalyst activity, selectivity and specific activity upon its treatment with ultra-sound.
6. On base of the quantum chemistry calculations the new information was obtained about of mechanism catalytic transformation of 1,4-butanediol

Practical importance of the work

New catalysts for synthesis of 2,3-dihydrofuran from 1,4-butanediol were developed, that differ from described ones by high activity, selectivity and lower temperature of reduction. So, used of Co-kaolin catalyst modified with ortho-phosphoric acid led to a 2,3-dihydrofuran with 80-84% yield, decrease of the temperature reaction from 480 to 240°C and to increase of the catalyst specific activity at 1.4-1.6 times. Mechanochemical method was used for prepare of the catalyst, and gives a possibility to accelerate the process for the catalyst synthesis 20 times and to make it ecologically safe. Dependence of the catalyst activity and selectivity on the catalyst reduction level was detected, and the process of the catalyst activation was optimized. Were shows that both modified and non-modified Co-kaolin catalyst optimum reduction degree was achieved when 75-80% of Co_3O_4 were reduced to metallic cobalt and the rest 20-25% - to CoO. It was detected that in the case of Co-Pd catalyst its reduction process can be accomplished in the same reactor, where the catalytic reaction proceeds, thus considerably improving and simplifying the transformation process of 1,4-butanediol in to 2,3-dihydrofuran.

Active centers of catalysts, the structure of phases, surface morphology, as well as the reduction ability, were studied together with the physico-chemists from Russian, Bulgarian, Polish and Romanian research institutes. The work was performed within the frames of cooperation projects. The reaction mechanism was investigated by quantum chemical calculations with supervision of Dr. Chem. M. Fleisher.

Results of the work

CREATION OF COBALT CATALYST FOR 2,3-DIHYDROFURAN SYNTHESIS FROM 1,4-BUTANEDIOL USING NON-TRADITIONAL METHODS

The conversion of 1,4-butanediol (1,4-BD) into 2,3-dihydrofuran (2,3-DHF) in the presence of Co catalyst occurs through several reaction stages, such as those shown in Scheme 1:
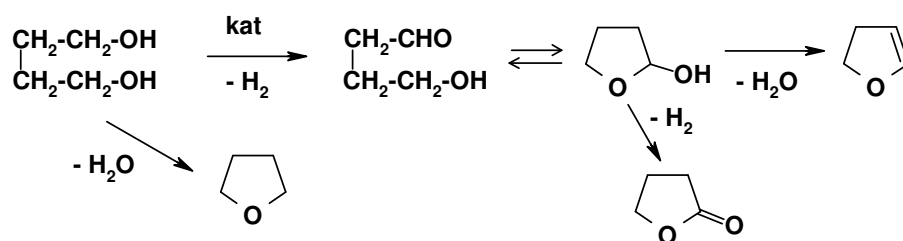
Scheme 1. Conversions of 1,4-butanediol in the presence of Co catalysts.

The Scheme 1 includes of the dehydrogenation and dehydration steps, and it means that this reaction needs bifunctional catalysts. For the preparation of catalysts, cobalt compounds (Co_3O_4, $Co(NO_3)_2$) and aluminosilicates (kaolin, kaolinite, montmorillonite) with different arrangement of the tetrahedral and octahedral sheets in lattice layers or SiO_2 were used.

1. DESIGN OPTIMIZATION OF THE NEW Co CATALYST PREPARED USING MECHANOCHEMICAL METHOD FOR 2,3-DIHYDROFURAN SYNTHESIS

The effect of the thermal and acidic treatment of aluminosilicates on the activity of cobalt catalysts in 1,4-BD transformation was studied. Calcination was carried out in the range of 110-870°C. The thermal activation of the clay resulted in the increase of 2,3-DHF yields. The maximum yields (68-69%) were reached in the presence of catalyst containing the clay calcined at 750°C. Surface area of clay decreases from 15-24 m^2/g to 0.7-3.6 m^2/g during the thermal pre-treatment.

Kaolin with a BET surface area of 22.7 m^2/g and an average particle size of 570 nm was chosen as a component of Co catalyst due to its dehydration activity, availability and low price.

Acid treatment of kaolin was performed by impregnation with HCl, H$_3$BO$_3$ and H$_3$PO$_4$. The best results were reached after impregnation with 10 wt.% of H$_3$PO$_4$.

According to the quantum chemical calculations (literature data), the favourable influence of the thermal and acidic pre-treatment of the kaolin is supposedly related to the formation of surface clusters involving acidic-basic pair (the bicentric active surface cluster) which may be active in dehydration and dehydrogenation reactions.

Co-kaolin catalysts containing 10-50 wt.% of cobalt were prepared by mehanochemical method, namely, by mixing of well-powdered appropriate amount of the individual oxide Co$_3$O$_4$ and kaolin in an agate mortar and then grinding in a vibrator (number of rotations per minute 1420, excentre 9 mm) for 15 min. Before the catalytic test each sample was reduced in hydrogen flow *ex situ.*

The maximum yields of 2,3-DHF (84%) and specific activity (5.3 g×g$_{kat}^{-1}$×h^{-1}) were reached using catalysts with 20-50 wt.% of cobalt (Table 1, entries 1-4).

The temperatures of the preliminary catalyst reduction were chosen based on TPR measurements. It was established that the optimal reduction temperature depends on cobalt amount in the catalyst, the lesser cobalt content need higher temperature. When the cobalt level was diminished from 40 to 20%, the optimum reduction temperature was increased from 470 up to 510°C.

In the presence of Co$_3$O$_4$ without kaolin, 1,4-BD converts into 2,3-DHF and THF also, albeit the yield of 2,3-DHF and specific activity were significantly lower (correspondingly 15% and 2 g×g$_{kat}^{-1}$×h^{-1}). Special experiments show that 1,4-BD gives THF with 70% yield in the presence of kaolin.

2. PROMOTION OF COBALT-KAOLIN CATALYST BY TRANSITION METALS

The promotion of Co-kaolin catalyst with gold, copper and palladium to improve the catalytic properties and to decrease the optimum of the reduction temperature of catalyst has been studied.

Table 1

Catalytic activity in the conversion of 1,4-butanediol into 2,3-dihydrofuran and tetrahydrofuran of Co-, Co-Au, Co-Cu and Co-Pd-based catalysts prepared by mechanochemistry

Entry	Content, wt.%		Reduction temperature, °C	2,3-DHF	
	Co	Promotor		Yield, %	Specific activity in relation to 2,3-DHF, $g \times g_{kat}^{-1} \times h^{-1}$
Co-kaolin					
1.	20	-	510	84	5.3
2.	50	-	470	60	3.4
3.		-	480	82	5.3
4.		-	490	78	5.2
Co-Au-kaolin					
5.	40	4 (Au)	300	60	3.8
6.			330	66	4.3
7.			350	50	3.2
Co,Cu-kaolin					
8.	34	8 (Cu)	355	74	6.7
9[1].	34	8 (Cu)	320	81	6.8
Co,Pd-SiO$_2$					
10[2].	40	0.46 (Pd)	232	70	6.5
11[2].	40		240	72	7.1
12[2].	40		255	64	8.6
13[2].	40	0.9 (Pd)	250	71	6.6

[1] Sample was treated by mechanochemistry and ultrasound; [2]*SiO_2 was pretreated for 3 h at 200ºC.*

2.1. Promotion of Co-kaolin catalyst with gold

Gold was considered to be extremely chemically inactive for a long time. Due to the success in heterogeneous catalysis, this assessment has fundamentally changed. Gold has not been previously utilized in synthesis of 2,3-DHF.

The catalysts were prepared by co-precipitation of $HAuCl_4 \cdot 3H_2O$ and $Co(NO_3)_2 \cdot 6 H_2O$ with a solution of sodium carbonate. The samples were dried at 120^oC or were calcined in the air at 400^oC for 2 h. A mechanical mixture of the precursors and the kaolin was made in the next step of the catalysts preparation. The Co loading was 40 wt.%. The amount of Au in Au–Co samples was 4 wt.%.

TPR data show that the Au-promotion effect provides the formation of new phases with considerably lower reduction temperature (Table 1, entries 5-7).

It was established by XRD analysis (diffractometer URD-6) that the reduction of Co-kaolin at 340^oC occurs via CoO formation. After the treatment of the catalyst sample in H_2 at 470^oC, the reduction to metallic cobalt phase with hexagonal (Co^{hex}) and cubic (Co^{cub}) structure takes place. In the XRD pattern of Co-Au–kaolin sample reduced at 340^oC there are lines of metallic Co^{hex} and Au^0. It can be seen in the diffractograms that, after the reduction of Co-Au-kaolin sample at 650^oC, the amount of metallic Co sharply grows and the Co structure is cubic. Taking into account the XRD results and the higher activity of gold-promoted catalyst in relation of 2,3-DHF formation than that of non-promoted one, it might be suggested that the selectivity of the reaction studied is connected with the structure of the metallic cobalt phase. Co^{hex} is more favourable for 2,3-DHF formation than Co^{cub} (Table 2).

Table 2.

Catalytic properties of the different phases of the metallic Co- and Co-Au-kaolin catalysts for the conversion of 1,4-butanediol into 2,3-dihydrofuran

Catalyst	Catalyst reduction temperature, °C	Phase	Yield, %		Specific activity in relation to 2,3-DHF formation, $g \times g_{cat}^{-1} \times h^{-1}$
			2,3-DHF	THF	
Co-Au-kaolin	300	Co^{hex}	60	10	3.8
Co-Au-kaolin	330	Co^{hex}	66	11	4.3
Co-kaolin	470	$Co^{hex}+Co^{cub}$	57	11	3.7
Co-Au-kaolin[*]	650	Co^{cub}	20	10	1.3

[*]Conversion of 1,4-BD is 82%, selectivity to 2,3-DHF 30%

To explain the interesting experimental fact, i.e. the presence of the maximum in the yield of 2,3-DHF which depends on the reduction temperature of Co and Co–Au catalysts, XPS analysis (spectrometer VG Scientific ESCALAB-210) was applied for

the study of a corresponding oxidation state of surface cobalt. The spectra show that the reduction of cobalt at optimum temperature is not complete because a part of Co^{2+} species still is visible on the surface. The reduction degree of the cobalt of on the surface Co-kaolin catalyst is approximately 82%, and of Co-Au-kaolin - aproximately 77%. It may mean that an optimum ratio of metallic cobalt/cobalt in ionic state exists for the reaction studied.

To clarify the influence of Co^{2+} ion on 1,4-BD transformations, quantum chemical calculations *ab initio* were used. On the basis of bond order analysis, it was found that in the presence of Co^{2+} the bonds O–H and C–H (breaking in the 1,4-BD dehydrogenation) are weaker (smaller bond order) than in the isolated molecule, and in this way they are activated for 4-hydroxybutanal formation. The bond order of C–O bond also decreases in the presence of Co^{2+}, meaning that the dehydration process is also possible. The second O–H, C–O and C–H bonds in the 1,4-BD molecule have unchanged bond order, meaning that a further dehydrogenation of 4-hydroxybutanal is highly improbable. On the basis of our experimental and theoretical studies, as well as on the literature data on catalytic dehydrogenation of alcohols, it can be proposed that both metallic and ionic cobalt particles take part in the dehydrogenation reaction stage. The cooperative behaviour of Co^{2+} and Co^0 surface sites is an essential requirement for the 1,4-BD dehydrogenation to 4-hydroxybutanal.

2.2. Promotion of cobalt catalyst with copper

The promoting effect of copper and the influence of the precursor reduction temperature on the yield and specific activity of cobalt catalysts in synthesis of 2,3-DHF, have been studied. Co-kaolin, Cu-kaolin and Co-Cu-kaolin (2.7-18 wt.% of Cu) catalysts were prepared by mechanochemical treatment of Co_3O_4, Cu_2O and kaolin solids followed by reduction in a hydrogen flow. The promotion with copper leads to the catalyst reduction at significantly lower temperatures in comparison to that of the non-promoted catalysts (Table 1, entries 8-9). The maximum decrease in the reduction temperature attained due to the addition of copper was ~100ºC.

The results shown in Table 1 are in an agreement with our previous data on Co and gold-promoted Co catalysts in the same reaction - there is an optimum in the Co^0/Co^{2+} ratio and, respectively, an optimum in the reduction temperature is observed as well. The optimum composition of Co-Cu-kaolin catalyst corresponds to 34 wt.% of cobalt loading and 8 wt.% of copper loading. The ultrasonical treatment (Bardelin

RK514 BH, 225/450W, 35 kHz) for 2 h causes an additional increase in the specific activity to 6.8 $g \times g_{cat}^{-1} \times h^{-1}$ and decrease in the optimum reduction temperature to 320-350°C.

According to the XRD data, a spinel of Co_3O_4 and Cu_2O phases was registered in the initial Co, Cu-kaolin sample. Besides, due to the strong interaction between these oxides during of the mechanochemical and ultrasonic treatment, a $CuCoO_2$ phase was also formed. After the reduction of the catalyst sample in H_2 at 350°C, both metallic cobalt phases with defectively packaged hexagonal structure and metallic copper, as well as the CoO phase, can be seen.

The increased specific activity of copper-containing catalysts could be related to the lowering of the reduction temperature, which leads to a hexagonal metallic cobalt phase formation. The latter is favourable for synthesis of 2,3-DHF. The advantage of mechanochemical preparation of Co, Cu-kaolin catalyst is that the method prevents the penetration of cobalt ions into the support (according to TPR), thus the whole amount of cobalt loaded is available for the catalyst performance.

The geometric structure of the surface of Co, Cu-kaolin catalysts prepared by mechanical and ultrasonic treatment was tested by the transmission electron microscopy (HRTEM).

2.3. Promotion of cobalt catalyst with palladium

Mechanochemical method was applied to prepare Co, Pd-SiO$_2$ catalysts with 0.09-1.9 wt.% of Pd. Optimum content of Pd is 0.46 or 0.9 wt.% (the yield of 2,3-DHF 70-72%, specific activity 6.6-8.6 $g \times g_{kat}^{-1} \times h^{-1}$) (Tab. 1, entries 10, 11, 13). In the presence of Pd, optimum reduction temperature of catalyst decreases to 230-250°C. It means that the catalyst can be reduced in the reaction flask *in situ*. According to TPR method, the reduction degree of surface cobalt at such temperature is approximately 80% (it was determined by Dr. G.Kadinov, Institute of Catalysis, Bulgarian Academy of Science), and is very close to the value of that one which was found for Co-Au catalyst by XPS method.

Quantum chemical calculations suggest that both acidic and basic species of SiO$_2$ may be also involved in the rate-determining step - dehydrogenation of 1,4-BD into 4-hydroxybutanal intermediate.

CONCLUSIONS

1. New bifunctional cobalt-containing catalysts for highly selective and productive synthesis of 2,3-dihydrofuran from 1,4-butanediol have been created.

2. The promoting effect of gold, copper and palladium on the activity and reductivity of Co-kaolin catalyst has been studied. It has been defined that supported Co-Cu catalyst is the most selective catalyst for 2,3-dihydrofuran synthesis. The promotion of cobalt catalyst with palladium is favourable for 2,3-dihydrofuran synthesis, concerning both the specific activity and catalyst reductivity (the reduction temperature decreases from 480 down to 240°C).

3. It has been determined with X-ray photoelectron spectroscopy that the cobalt catalysts reach the maximum activity and selectivity if, after the precursor reduction, the catalyst contains approximately 75-80% of metallic and 20-25% of ionic cobalt.

4. The yield of 2,3-dihydrofuran depends on the crystalline structure of metallic cobalt. The hexagonal cobalt is more favorable for synthesis of 2,3-dihydrofuran in comparison to cubic cobalt phase, which is formed at the temperature above 400°C.

5. The clay (kaolin, kaolinite, montmorillonite) and silica gel are good dehydrating components for the Co catalyst. The procedures of their thermal and chemical activation have been elaborated.

6. Quantum chemical calculations suggest that in the presence of Co^{2+} ions, the initial step of the 1,4-butanediol transformation into 2,3-dihydrofuran may be the cleavage of O-H bond to form alkoxide species. Both acidic and basic centres of the catalyst surface are involved in the catalytic process.

7. Simple mechanochemical, ecologically safe waste-free method for the preparation of the cobalt catalyst has been developed for effective synthesis of 2,3-dihydrofuran from 1,4-butanediol.

PAPERS

1. *Edolfa K.* Modification of cobalt catalyst for 2,3-dihydrofuran synthesis. Latv. Ķīm. Žurn., 2002, 1, 107.

2. *Leite L., Stonkus V., Edolfa K., Lukevics E., Fleišers M., Rašmane Dz.* Nesēja termiskās aktivācijas ietekme uz kobalta katalizatora aktivitāti 1,4-butāndiola pārvēršanā par 2,3-dihidrofurānu. Latv. Ķīm. Žurn., 2003, 2, 181.

3. *Leite L., Stonkus V., Edolfa K., Ilieva L., Andreeva D., Plyasova L., Sobczak J.W. Ionescu S., Munteanu G.* Active phases of supported cobalt catalysts for 2,3-dihydrofuran synthesis. J. Mol. Catalysis, 2004, **215,** 1-2, 95.

4. *Edolfa K.* Influence of Copper on the Conversion of 1,4-butanediol over Cobalt-Kaolin Catalyst. Latv. Ķīm. Žurn., 2006, 1, 64.

5. *Leite L., Stonkus V., Edolfa K., Ilieva L., Nedyalkova R., Zicmanis A.* Novel preparation route for active Co-Cu catalysts designed for 2,3-dihydrofuran synthesis. Bulg. Chem. Commun., 2006, **38,** 2, 140.

6. *Leite L., Stonkus V., Edolfa K., Ilieva L., Plyasova L., Zaikovskii V.* Copper-promoted cobalt catalysts for 2,3-dihydrofuran synthesis. Appl. Catal., 2006, **311**, 86.

Abstracts of International conferences:

1. *Edolfa K.* Modification of cobalt catalyst for 2,3-dihydrofuran synthesis. Paula Valdena 2. simpozijs, Rīga, Latvijas Organiskās sintēzes institūts, 1-2 Oktobris, 2001.

2. *Edolfa K., Stonkus V., Leite L., Lukevics E.* Influence of the Support Thermal and Acidic Treatment on the Catalytic Properties of Cobalt-Clay System. In: Third Youth School-conf. on Organic Synthesis in the New Century (YSCOS-3), Saint-Peterburg, 24-27 June, 2002, Book of Abstracts: 223c, 2002, 344.

3. *Stonkus V., Edolfa K., Leite L., Lukevics E., Ruplis A., Plyasova L., Khassin A.* Effect of high temperature treatment of support on the cobalt catalyst activity in 2,3-dihydrofuran synthesis. In: The 15th International Congress of Chemical and Process Engineering, Praha, Czech Republic, 25-29 August, 2002, Book of Abstracts: P1.47, 2002, 177.

4. *Leite L., Stonkus V., Fleisher M., Edolfa K., Rozovskii A., Slavinska V., Lukevics E.* Catalytic synthesis of dihydrofurans by cyclodehydration of alkanols over

modified cobalt catalysts. In: The 6th International Symposium on Catalysis Applied to Fine Chemicals, Delft University of Technology, The Netherlands, April 6-10, 2003, Book of Abstracts: P101, 2003, 101.

5. *Leite L., Stonkus V., Edolfa K., Ilieva L., Zicmanis A., Ionescu S., Munteanu G. Plyasova L., Zaikovskii V.* 1,4-Butanediol Reactivity in the Presence of Cobalt- and Copper-based Catalysts. In: The 3rd International conference BALTICUM ORGANICUM SYNTHETICUM (BOS 2004), Riga, June 27 – July 1, 2004, Program & Abstracts: PO46, 2004, 98.

6. *Edolfa K., Stonkus V., Leite L., Ilieva L., Zicmanis A.* Environment Friendly Preparation Method of Co-Cu-kaolin Catalyst Used for 2,3-Dihydrofuran Synthesis. In: International Conference "Integrative Approaches towards Sustainability", Baltic sea of region sharing knowledge internally, across Europe and worldwide, Jurmala, Latvia, 11-14 May, 2005, Book of Abstracts: B16, 2005, 61.

7. *Leite L., Stonkus V., Edolfa K., Ilieva L., Zicmanis A., Plyasova L., Zaikovskii V.* Development of Cobalt Based Catalysts for 2,3-Dihydrofuran Synthesis. In: Seventh European Congress on Catalysis, Sofia, Bulgaria, 28 August – 1 September, 2005, Book of Abstracts: P8-27, 2005, 252.

8. *Edolfa K.* Influence of Copper on the Conversion of 1,4-Butanediol over Cobalt- kaolin Catalyst. Paula Valdena 4. simpozijs, Rīga, Latvijas Organiskās sintēzes institūts, 15-16 Septembris, 2005.

9. *Leite L., Stonkus V., Edolfa K., Fleisher M., Shopska M., Shtereva I., Spasov L., Kadinov G., Sobczak J.W.* Promoting Effect of Palladium in Co-Pd-SiO$_2$ Catalysts for 2,3-Dihydrofuran Synthesis. In: The 7th CAFC The Seventh International Symposium on Catalysis Applied to Fine Chemicals, BINGEN/ MAINZ, GERMANY, 23-27 October, 2005, Book of Abstracts, 2005, 136.

10. *Edolfa K., Stonkus V., Fleisher M., Leite L., Zicmanis A., Kadinov G.* Activity of Co-Pd/SiO$_2$ Catalysts in 1,4-Butanediol Transformation reactions. In: The 46th International Scientific Conference of Riga Technical University, Riga, October 11-14, 2005.

11. *Stonkus V., Edolfa K., Leite L., Zicmanis A., Ilieva L., Nedyalkova R., Plyasova L.* An Improved Catalytic Synthesis of 2,3-dihydrofuran. In: The 4th Eurasian Meeting on Heterocyclic Chemestry, Thessaloniki, Greece, 27-31 August, 2006, Book of Abstracts: 2-PO92, 2006, 268.

12. *Stonkus V., Edolfa K., Leite L., Zicmanis A., Ilieva L., Nedyalkova R., Plyasova L.* Mechanochemically Prepared Co-Catalyst for 2,3-dihydrofuran Synthesis. In: XXII European Colloquium on Heterocyclic Chemistry, Bari, Italy, 2-6 September, 2006, Book of Abstracts: PO74, 2006, 160.

Abstracts of national conferences:

1. *Stonkus V., Leite L., Ļebedevs A., Edolfa K., Fleišers M., Mekšs P., Lukevics E.* Aktīvu kobalta katalizatoru izstrāde 2,3-dihidrofurāna sintēzei. II PASAULES LATVIEŠU ZINĀTNIEKU KONGRESS, Latviešu Biedrības nams, 14-15. augusts, 2001, 296.

2. *Edolfa K., Leite L., Zicmanis A.* Kobalta katalizatora pētījumi 2,3-dihidrofurāna iegūšanai no 1,4-butāndiola. Latvijas Universitātes 63. konference, Latvijas Universitāte, 4. februāris, 2005.

3. *Edolfa K.* Kobalta katalizatora radīšana 2,3-dihidrofurāna sintēzei no 1,4-butāndiola. Akadēmiķa Alfrēda Ieviņa piemiņas lasījumi, Latvijas Zinātņu Akadēmija, 13. decembris, 2005.