

Experimental investigation of ethylene hydroformylation to propanol on Rh and Co based catalysts

N. Navidi, ¹J. W. Thybaut, G. B. Marin

Laboratory for Chemical Technology, Ghent University, Krijgslaan 281 – S5, 9000 Ghent Belgium; tel. +3292645572, e-mail: Nima.Navidi@UGent.be; ¹tel. +3292644519, e-mail: Joris.Thybaut@UGent.be; tel. +3292645517, e-mail: Guy.Marin@UGent.be.

Abstract

Hydroformylation, or oxo synthesis, is an important process for the production of aldehydes from alkenes. Alkene and aldehyde hydrogenation are undesired parallel and consecutive reactions. Whereas present-day industrial process configurations typically operate in a homogenous mode, the development of a heterogeneous hydroformylation catalyst is aimed at to avoid the well-known drawbacks of homogenous catalysis such as catalyst recuperation and corrosiveness. Kinetic measurements have been performed in a high-throughput kinetic test set up. Temperatures varied from 448 to 498 K, with the total pressure ranging from 1 to 3 MPa. A gaseous feed containing CO, C₂H₄ and H₂ was used with space times varying from 5.4 kg_{cat}-s/mol_{C₂H₄,in} to 149 kg_{cat}-s/mol_{C₂H₄,in}. Three catalysts have been investigated, i.e., 5%Rh/Al₂O₃, 1%Co/Al₂O₃ and 0.5%Co-0.5%Rh/Al₂O₃. The main products observed were ethane, propanal and propanol. The Rh catalyst showed the highest hydroformylation and hydrogenation site time conversions in the investigated range of operating conditions. Moreover it was found that on all investigated catalysts, a temperature increase has a more pronounced effect on hydrogenation than on hydroformylation.

Keywords: Heterogeneous catalysts; Ethylene hydroformylation; Fischer-Tropsch; High-throughput experiments; Rhodium/Cobalt catalysts

1. Introduction

The ever increasing crude oil price has led to the exploration of alternative feeds such as natural gas, and correspondingly new processes for the production of hydrocarbons. Hydroformylation, or oxo synthesis, that was discovered by the German scientist Otto Roelen in 1938, is an important process for production of aldehydes from alkenes. Hydroformylation catalysts are also active in double bond hydrogenation converting the reactant alkene into the corresponding alkane as well as the product aldehydes into alcohols [1]. Typical

hydroformylation products are in the carbon number range from 3 to 19. The reactant alkene is selected based on the desired product aldehyde.

Aldehydes are useful intermediates in the production of valuable products such as alcohols, carboxylic acids, amines, diols, etc. Recently, hydroformylation is also widely applied in fine chemicals in the production of drugs, vitamins, herbicides and perfumes [2, 3].

The name 'hydroformylation' becomes clear when looking at the nature of the products that are formed. The reaction entails the addition of a formyl group (CHO) and a hydrogen atom to a carbon – carbon double bond. Depending on the catalyst used, the aldehyde can be further hydrogenated to the corresponding alcohol. The hydroformylation of ethylene that is shown in Figure 1, in particular is a spontaneous, exothermic reaction ($\Delta H^\circ = -129.0 \text{ kJ mol}^{-1}$, $\Delta G^\circ = -56.9 \text{ kJ mol}^{-1}$) [4]. Due to high energy barriers, the reaction rate remains low, however.

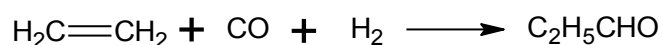


Figure 1- Ethylene hydroformylation to prapanal

In principle, all the transition metals capable of forming carbonyls, such as Rh, Co, Ir, Ru,.. are potential hydroformylation catalysts. The order of activity from the most to the least active metal, is as follows: Rh > Co > Ir, Ru > Os > Pt > Pd > Fe > Ni [5].

Commercially, homogeneous Co or Rh complexes are typically applied at temperatures ranging from as low as 360 K up to 573 K [6,7]. The homogeneous character of industrial process configurations leads to inherent operational problems such as difficulties in catalyst separation from products, expensive metal losses and corrosivity of catalytic solutions. The successful implementation of an active and stable heterogeneous hydroformylation catalyst would allow avoiding these drawbacks. Although the research into heterogeneously catalysed hydroformylation is in an early stage, a wide range of research activities has been performed on experimental heterogeneous hydroformylation with various reactants, catalysts and operation conditions [8-17].

The present work concentrates on heterogeneous ethylene hydroformylation on a series of Rh and Co based catalysts. Gas phase experimentation was performed in a high-throughput kinetics setup to compare the Rh and Co catalysts and to investigate the effect of the operation conditions on the main and by product formation rates on these catalysts. The results of this study provide key insight into the corresponding reaction mechanism that may be exploited in further catalyst design.

2. Procedures

Gas phase hydroformylation measurements have been performed in a high-throughput kinetic test set up. The setup consisted of eight reactors in parallel and each individual reactor had three feed lines for gases and one feed line for a liquid with corresponding mass flow controllers. The reactor temperature and pressure were controlled per reactor pair. A reactor tube was made of AISI 316 cold worked steel with 890mm height and 11mm internal diameter.

The reactors are capable of operating up to 600°C and 15 MPa, i.e., far beyond the operating range as required for hydroformylation. A three-zone reactor temperature control was established, the catalyst being situated at the bottom of the second zone and the top of third zone.

Between 1 and 10 g of 5%Rh/Al₂O₃, 1%Co/Al₂O₃ and 0.5%Rh-0.5%Co/Al₂O₃ was pelletized. The fraction with a diameter between 0.3 and 0.5mm was retained and mixed with an identical mass of dilution material prior to loading into the reactor tubes of the high-throughput set up. Considering the investigated operating conditions in the literature and some preliminary experiments that were conducted in the lab, the following operating conditions were selected. Temperatures varied from 448 to 498 K, with the total pressure ranging from 1 to 3 MPa. A gaseous feed containing CO, C₂H₄ and H₂ was used with space times that varied from 5.4 kg_{cat.}.s/mol_{C₂H₄,in} to 149 kg_{cat.}.s/mol_{C₂H₄,in}.

Online effluent analysis was performed with a four channel Agilent 3000 micro gas chromatograph equipped with thermal conductivity detectors (TCDs). Argon as an internal standard has been added to the reactants stream in order to verify the mass balances. The conversions and product molar flow rates were calculated using calibration factors as reported by Diets [18]. In order to compare the performance of the mentioned catalysts under identical experimental conditions the conversions were reported versus the site time. At first, for calculating the site time, space time (kg_{cat.}.s/mol_i) was divided by standard atomic weight of metal catalyst to be converted to (mol_{cat. atoms}.s/mol_i) thereafter, this value was multiplied by the fraction of exposed metal atoms to calculate the numbers of accessible moles. The fraction exposed was calculated employing the relation between the particle size and dispersion [19]. In order to estimate the particle sizes, Transmission Electron Microscopy (TEM) method was used.

TEM specimens were prepared by applying simple immersion of a carbon-support film on a nickel grid into the catalyst powder followed by careful shaking

off the excess powder. A microscope JEOL JEM2200FS-Cs-corrected, operated at 200 kV and equipped with Schottky-type FEG, EDX JEOL JED-2300D and JEOL in-column omega filter, was used.

It was verified by using the proper correlations, that at the selected operating conditions so-called intrinsic kinetics are measured, i.e., the observations are not affected by mass or heat transfer limitations [20].

3. Results and discussion

3.1 catalyst comparison

The measured particle sizes and corresponding fractions exposed of the mentioned catalysts are reported in Table 1.

Table 1- Fraction of exposed metal, accessible metal atoms and site time conversions per catalyst

Catalyst	Particle size (nm) TEM	Fraction of exposed metal (%)	Accessible metal atoms (mol/g _{cat.})	CO site time conversion (mol _{CO, converted} /mol _{cat. atoms} /s)*	C ₂ H ₄ site time conversion (mol _{C₂H₄, converted} /mol _{cat. atoms} /s)*
5%Rh/Al ₂ O ₃	2	51.11	2.4757×10 ⁻⁴	0.01356	0.04071
1%Co/Al ₂ O ₃	11	12.38	0.2098×10 ⁻⁴	0.00359	0.01486
0.5%Rh- 0.5%Co/Al ₂ O ₃	4.3 for Co 35 for Rh	28.10 for Co 3.81 for Rh	0.2575×10 ⁻⁴	0.00746	0.02626

* at 473 K, 2.0 MPa and equimolar C₂H₄/CO/H₂ gas phase composition

Based on the TEM results, the 5%Rh catalyst as it is depicted in Figure 2 has well dispersed particles with a small size (2nm) resulting a high fraction of exposed metal. On the contrary, in the 1%Rh-Co catalyst rhodium was observed in big particles or clusters (20-50nm).

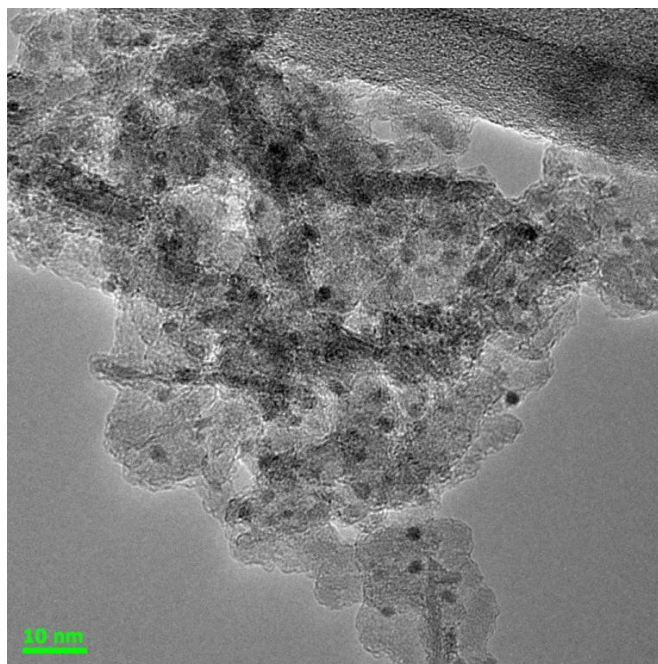


Figure 2- TEM image of 5%Rh/Al₂O₃ catalyst

Figures 3 and 4 show the observed CO and C₂H₄ conversion as a function of the site time at 473 K and 2 MPa. An equimolar feed composition containing CO, C₂H₄ and H₂ was used with space times that were varied 5.4 kg_{cat.}.s/mol_{C₂H₄,in} to 149 kg_{cat.}.s/mol_{C₂H₄,in}

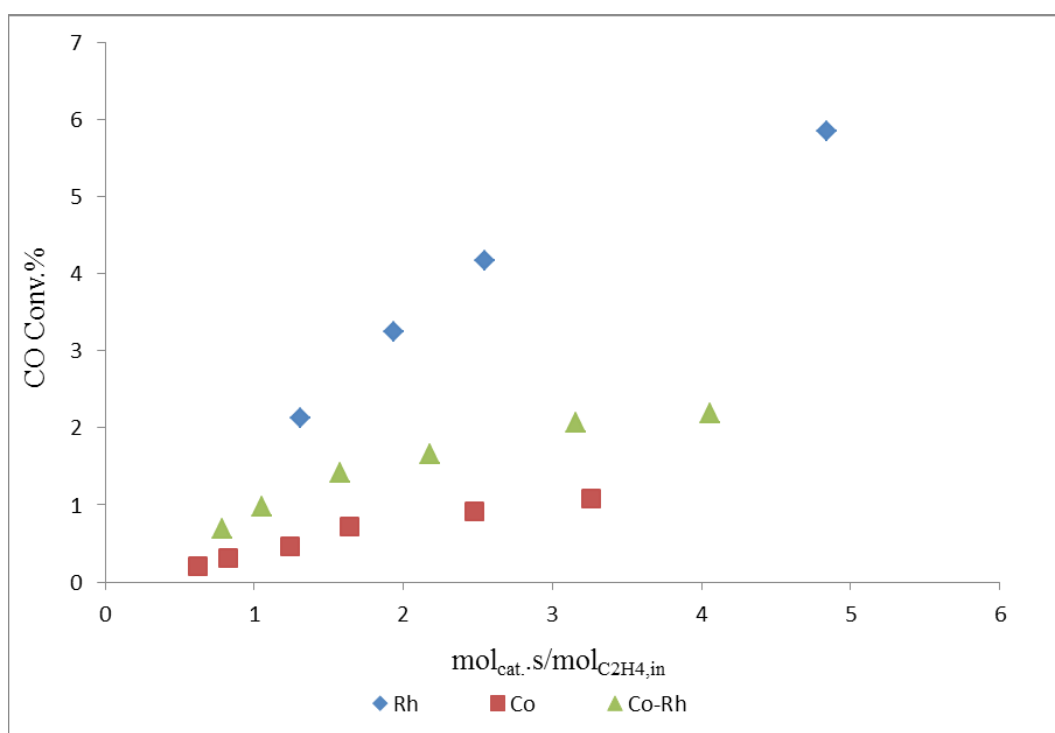


Figure 3- CO conversion versus molar site time. Temperature 473K; Pressure (C₂H₄:CO:H₂:Ar=30:30:30:10), 2 MPa

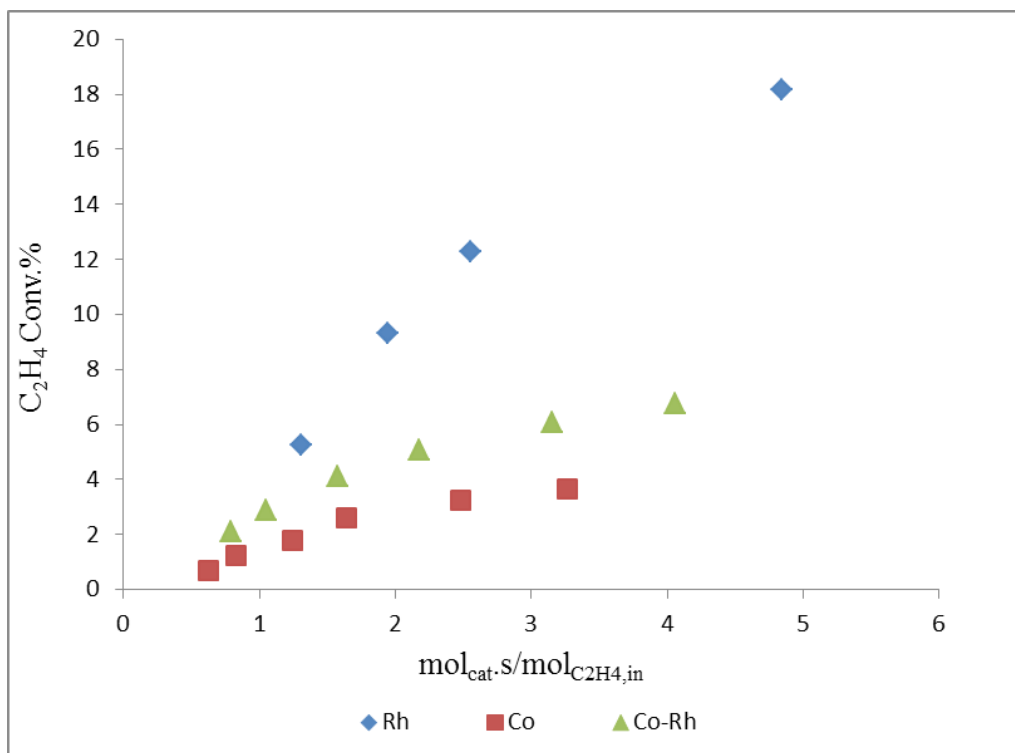


Figure 4- C₂H₄ conversion versus molar site time. Temperature 473K; Pressure (C₂H₄:CO:H₂:Ar=30:30:30:10), 2 MPa

The accessible number of metal atoms and site time conversions are also reported in Table 1. As it can be seen in these figures and the table, the Rh catalyst shows the highest site time conversions at the investigated operating conditions.

Based on the site time conversions obtained in monometallic catalysts and the knowledge of the fractions exposed on the bimetallic catalyst, see Table 1, an expected site time conversion on this bimetallic catalyst amounting to 0.00429 mol_{CO, converted} /mol_{cat. atoms} /s was calculated, which is lower than the experimentally observed site time conversion. Considering the size of Rh clusters in Rh-Co catalyst, this metal cannot show considerable activity in the hydroformylation reaction, so the reason that bimetallic catalyst shows slightly higher activity than pure cobalt catalyst can be explained by the fine Co particles in the Rh-Co catalyst that enhances the activity of this catalyst. It has been already reported in the literature [8, 14] that small metal particles exhibit higher hydroformylation activity than large metal clusters.

3.2 Temperature effect

In order to investigate the temperature effect on hydroformylation, a series of experiments were carried out on two of the mentioned catalysts, i.e., 5%Rh/Al₂O₃ and 1%Co/Al₂O₃.

A temperature increase leads to a more pronounced increase of the C₂H₄ site time conversion than of the CO site time conversion on both tested catalysts. As a result, as it is depicted in Figure 5, the apparent activation energy for ethane formation exceeds that for propanal formation.

The above observations correspond with an increasing selectivity towards ethane with the temperature, which is confirmed by the literature [9, 12]. It was observed by Balakos et. al., that in heterogeneous ethylene hydroformylation on 4%Rh/SiO₂ with increasing the temperature from 483 K to 573 K the hydroformylation selectivity, defined as TOF_{propanal}/TOF_{C₂H₆}, decreased from 0.136 to 0.039 [9].

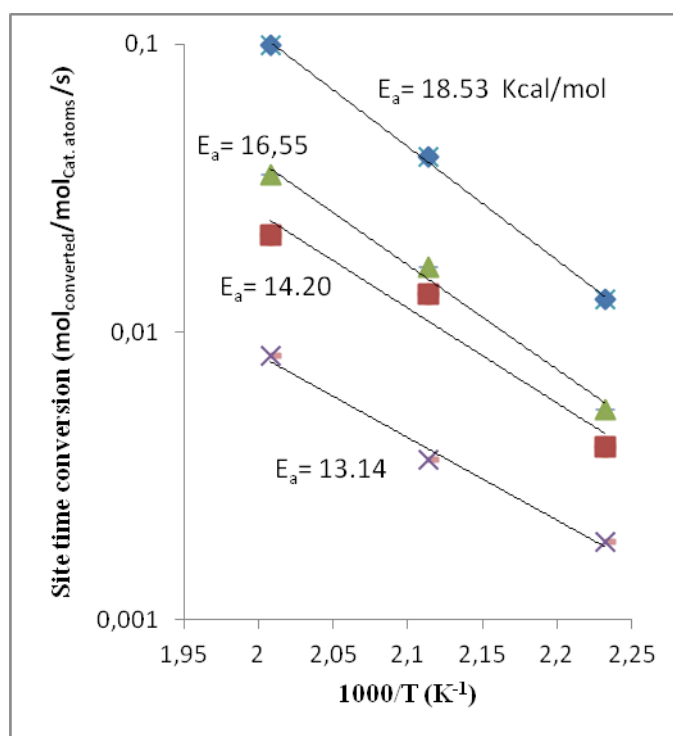


Figure 5- Relation between space-time yield and temperature for hydrogenation site time conversion on Rh(♦) and Co (▲) and hydroformylation site time conversion on Rh(■) and Co (×)

The more pronounced temperature effect on hydrogenation than on hydroformylation can be explained by investigating the selected heterogeneous ethylene hydroformylation mechanism that is shown in Figure 6 in some more detail.

The depicted mechanism is constituted by the following elementary steps:



- 2- Hydrogen dissociative chemisorption : $H_2 + 2M \leftrightarrow 2 MH$
- 3- Partial ethylene hydrogenation : $MM C_2H_4 + MH \leftrightarrow MC_2H_5 + 2M$
- 4- Reductive elimination towards paraffin: $MC_2H_5 + MH \leftrightarrow C_2H_6 + 2M$
- 5- CO molecular chemisorption : $CO + 2M \leftrightarrow MMCO$
- 6- CO insertion: $MC_2H_5 + MMCO \leftrightarrow MC_2H_5CO$
- 7- Hydrogen addition to metal bound carbonyl: $MC_2H_5CO + MH \leftrightarrow MMC_2H_5CHO$
- 8- Desorption of aldehyde: $MMC_2H_5CHO \leftrightarrow C_2H_5CHO + 2M$

With increasing temperature, adsorbed C_2H_4 molecules apparently exhibit a higher affinity towards reductive elimination into ethane (step 4 in Figure 6) than reacting with adsorbed CO molecule (step 6) on the catalyst surface. This can be related to the expected evolution in the hydrogen and CO surface concentrations. Because the chemisorption heat of CO is typically about the double of that of hydrogen, the CO concentration will decrease much faster with increasing temperature than the hydrogen concentration. As a result, the relative importance of hydrogenation in the overall ethylene conversion will increase at the expense of hydroformylation.

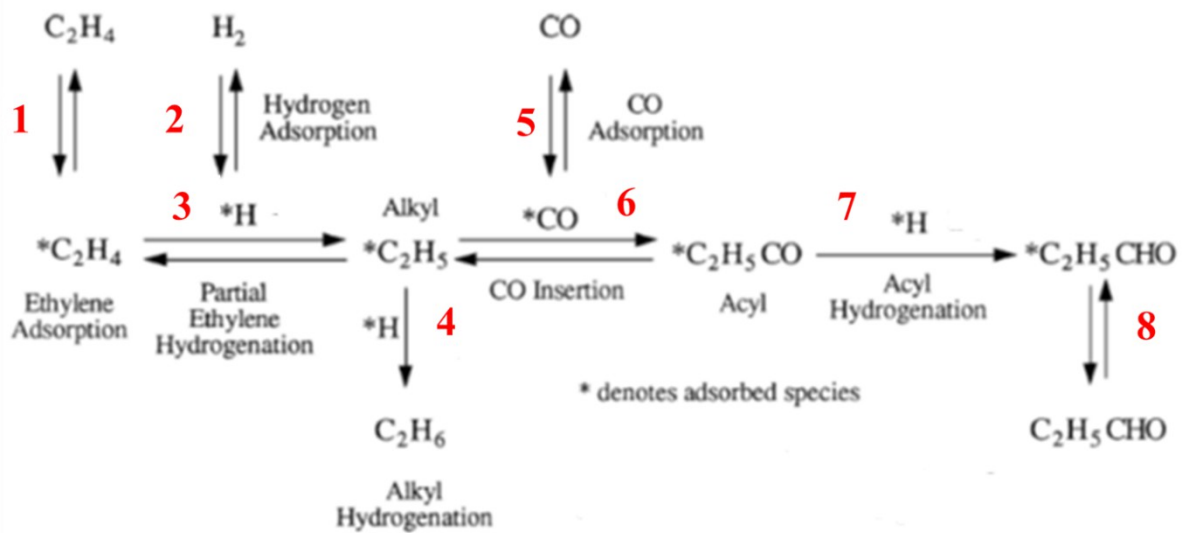


Figure 6: Proposed reaction mechanism for ethylene hydroformylation to propanol [21]

4. Conclusion

Gas phase hydroformylation measurements have been performed on 5%Rh/Al₂O₃, 1%Co/Al₂O₃ and 0.5%Co-0.5%Rh/Al₂O₃ catalysts in a high-throughput set up. The main products observed were ethane, propanal and propanol. The Rh catalyst showed the highest hydroformylation and hydrogenation rates compared to other catalysts at the investigated operation conditions. Bimetallic catalyst shows slightly higher activity than pure cobalt catalyst since the fine Co particles in the Rh-Co catalyst enhances the activity of this catalyst.

On all investigated catalysts, increasing the temperature has a more pronounced effect on the hydrogenation rate than on the hydroformylation rate. The overall activation energy for ethane formation exceeds that for propanal formation which can be related to a higher heat of chemisorption for CO than for hydrogen. In addition, metal particle size effects also play a significant role in the selectivity between hydrogenation and hydroformylation. Whereas small metal particles exhibit high hydroformylation activity, large metal clusters rather favour hydrogenation reactions.

Acknowledgements

This work was supported by the European research project "TOPCOMBI" (contract NMP2-CT2005-515792) and Methusalem program.

References

- [1] Cornils B., H.W.A., Rasch M., *Otto Roelen, pioneer in industrial homogeneous catalysis*. Angewandte Chemie International Edition, 1994. 33(21): p. 2144 - 2163.
- [2] Van Leeuwen P.W.N.M., C.C., *Rhodium catalyzed hydroformylation*. 2002, N.Y Springer.
- [3] Breit, B. and Seiche, W., *Recent advances on chemo-, regio-, and stereoselective hydroformylation*, *Synthesis*, 2001, 1–36
- [4] Otsuka K., Ando T., Yamanaka I., *Hydroformylation of Ethylene via Spontaneous Cell Reactions in the Gas Phase*, *Journal of catalysis* 165, 221-230, 1997.
- [5] Cornils B., H.W.A., *Applied Homogeneous Catalysis with Organometallic Compounds*. 1996, Weinheim: VCH
- [6] Zeelie. H., Root. A., Krause. A.O.I., Rh/fibre catalyst for ethane hydroformylation: Catalytic activity and characterization, *Applied Catalysis A: General* 285, 2005, 96-109
- [7] Ullmann's Encyclopedia of Industrial Chemistry. 6 ed. 2002: John Wiley & Sons.

- [8] Zeelie, T., *Rhodium and cobalt catalysts in the heterogeneous hydroformylation of ethane, propene and 1-hexene*. 2007
- [9] Balakos, M.W. and S.S.C. Chuang, *Dynamic and LHHW Kinetic-Analysis of Heterogeneous Catalytic Hydroformylation*. *Journal of Catalysis*, 1994. 151(2): p. 266-278.
- [10] Haza, U. J., Diaz-Abin. O., Wilhelm, A. M., Delmas, H., *Supported Aqueous phase catalysis in the pores of silica support: kinetics of the Hydroformylation of 1-Octene*, *Ind. Eng. Chem. Res.* 2005, 44, 9636-9641
- [11] Tomishige. K., Furikado. I., Yamagishi. T., Ito. S., Kunimori. K., *Promoting effect of Mo on alcoholformation in hydroformylation of propylene and ethylene on Mo-Rh/SiO₂*, *Catalysis Letters* Vol. 103, Nos. 1-2, 2005
- [12] Brundage. M. A., Balakos. M. W., Chaung. S.S.C., *LHHV and PSSA kinetic analysis of rates and adsorbate coverages in CO/H₂/C₂H₄ reactions on Mn-Rh/SiO₂*, 1998., *Journal of catalysis* 173, 122-133
- [13] Zapirtan. V. I., Mojet. B. L., Ommen. J.G.V., Spitzer. J., Lefferts. L., *Gas phase hydroformylation of ethylene using organometallic Rh-complexes as heterogeneous catalysts*, *Catalysis Letters*. Vol. 101. Nos. 1-2, 2005
- [14] Hanaoka. T., Arakawa. H., Matsuzaki. T., Sugi. Y., Kanno. K., Abe. Y., *Ethylene hydroformylation and carbon monoxide hydrogenation over modified and unmodified silica supported rhodium catalysts*, *Catalysis Today*. Vol. 58, Issue 4, 2000. p: 271-280
- [15] Xiao. F.S., Ichikawa. M., *Catalytic Performance and Mechanism for oxygenated compound formation for ethylene hydrformylation over supported Ru-M bimetallic carbonyl Cluster-Derived catalysts*, *Journal of catalysis* 147, 578-593, 1994
- [16] Pittman, C. U., Jr., and Wilemon, G. M., *1-pentene hydroformylation catalyzed by polymer-bound ruthenium complexes*, *J. Org. Chem.* 46 (1981) 1901–1905.
- [17] Junfan, W., Juntan, S., Hong, L. and Binglin, H., *The stability of a polymersupported Rh complex in the batch hydroformylation of 1-hexene*, *Reactive Polymers* 12 (1990) 177–186.
- [18] Dietz, W. A., *Response factors for gas chromatographic analyses*, *J. Gas. Chromatogr.* 5, 1967 68-71
- [19] Borodzinski. A., Bonarowska. M., *Relation between crystallite size and dispersion on supported metal catalysts*. *Langmuir*, Vol. 13, No. 21, 1997.
- [20] Berger, R.J. et al, *Cattech Journal*. Vol. 5. Issue 1. 2001 30-60
- [21] Brundage. M. A., Chaung. S.S.C., *Experimental and modelling study of hydrogenation using deuterium step transient response during ethylene hydroformylation*, *Journal of catalysis* 164, 94-108 1996.