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KINETICS OF PROPYLENE HYDROFORMYLATION IN THE PRESENCE OF MODIFIED RHODIUM TRIPHENYLPHOSPHINE CATALYST

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Lucrarea prezintă dezvoltarea unui model cinetic pentru procesul de hidroformilare a propenei, plecând de la măsurători efectuate pe un reactor industrial. Cinetica celor trei reacții ce caracterizează procesul chimic de hidroformilare este descrisă prin expresii de tip produs de puteri. Parametrii obținuți prin corelarea datelor experimentale au fost factorii preexponnențiali, energiile aparente de activare şi ordinele parțiale de reacție în raport cu monoxidul de carbon ale celor trei reacții. Modelul cinetic propus asigură o bună concordanță între valorile calculate şi cele măsurate ale vitezelor reacțiilor de formare a n-butiraldehidei, i-butiraldehidei şi, respectiv, propanului.

The paper describes the development of a kinetic model for propylene hydroformilation process, based on measurements from an industrial scale reactor. The kinetics of three main reactions characterizing the propylene hydroformylation process chemistry was empirically described by power law rate expressions. The fitted parameters were the preexponential factors, apparent activation energies and partial orders in respect with carbon monoxide of the three reactions. The proposed kinetic model provided a good adequacy of the calculated and measured values of formation rates for n-butyraldehyde, i-butyraldehyde and propane respectively.

Keywords: propylene, hydroformylation, industrial data, kinetic modeling

1. Introduction

The hydroformylation (oxosynthesis) is probably the most known synthetic method used for carbon chain growth. At the base of the method is the reaction between an olefin (alkene) and an equimolecular carbon monoxide-hydrogen mixture (synthesis gas). Among the olefins, only the terminal ones are active in hydroformilation, examples including the simple terminal olefins in the range of C_2-C_{13} and functional terminal olefins like allyl alcohol. The reaction generates a linear aldehyde and its methyl isomer with an additional carbon atom relative to starting olefin:

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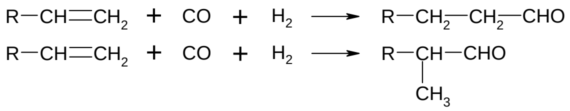

$$R-CH=CH_2 + CO + H_2 \longrightarrow R-CH_2-CH_2-CHO$$

$$R-CH=CH_2 + CO + H_2 \longrightarrow R-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CHO$$

A large quantity of oxo-aldehydes obtained industrially via hydroformylation is hydrogenated to corresponding alcohols used mainly in plasticizers manufacture. The actual worldwide capacity for oxo-aldehydes is around 10^7 tons/year. Among the existent industrial units, over 75% are producing butyraldehydes, using propylene as feedstock. [1-3].

The hydroformylation reactions are catalyzed by complexes of transition metals with different ligands, usually soluble in reaction medium. From the large variety of metals tested, only cobalt and rhodium complexes showed significant activity. In the same time the organic phosphine are the most active ligands, net superior to amines classified on the second place in this way. Beginning with 1974 the old cobalt catalysts were replaced stepwise by new rhodium-based catalysts. Comparing with the cobalt catalyst, the rhodium catalyst is more active and more selective in the preferred linear aldehyde. The activity difference between the rhodium and cobalt complexes was appreciated to be equal with three orders of magnitude. In spite of its high price, nowadays the standard catalyst for propylene hydroformylation is rhodium modified with triphenylphosphine (TPP) as ligand. Newer developments replaced triphenylphosphine with bisphosphites, but such catalysts, extremely active, stable, and straight-chain selective, are applied only in a limited number of units. Some licenses use water-soluble catalyst, for example rhodium modified with the sodium salt of trisulphonated triphenylphosphine (TPPS). The water-soluble catalysts have the advantage of an easy catalyst separation from reaction mixture, as result of a low mutual solubility between the organic phase containing the reaction products and the water phase containing the catalyst. However, the activity of water-soluble catalyst is significantly lower as compared with the standard rhodium/TPP catalyst, the reaction conditions necessary to achieve a reasonable propylene conversion being more severe [1]. The industrial hydroformilation catalysts used across the time are summarized in Table 1 [1]. In practice the propylene is hydroformylated over rhodium/TPP catalyst with conversions and selectivities over 85% and 95% respectively, the linear-to-branched product isomers molar ratio approaching 10:1. Different kinetic studies described the influences of working conditions (temperature, rhodium, TPP and reactants concentrations in catalytic solution) on reaction rates. Most of these studies, refereed by Bohnen and Cornils in their review [3], were used to elucidate the reactions mechanism. The most likely mechanism of olefins hydroformilation on Rh/TPP catalyst supposes the existence of two active species of rhodium complex with triphenylphosphine. The first one, $Rh(CO)(H)(TPP)_3$, stable in a higher excess of phosphine, is responsible for linear aldehyde formation due to the higher hindered arrangement around of central metal atom.

The second species, $Rh(CO)_2(H)(TPP)_2$, favored by a lower TPP concentration, catalyzes the synthesis of branched aldehyde (Fig. 1). For both forms of catalyst, the mechanism supposes the consecutive steps of dissociation, insertion of olefin, insertion of carbon monoxide, carbon monoxide migration and insertion of hydrogen with aldehyde synthesis and catalyst return to its active form.

Table 1

Industrial hydroformilation catalyst data

No.	**Catalyst (active species)**	**Working conditions**		**n/i ratio**	**Developer**
		T [°C]	**P [bar a]**		
1	$CoH(CO)_4$	110 - 180	200 - 350	80 : 20	BASF, Kuhlmann, Ruhrchemie, Exxonmobil
2	$CoH(CO)_3(PR_3)$ R = n-C_4H_9	160 - 200	50 - 100	88:12	Shell
3	$RhH(CO)_4$	100 - 140	200 - 300	50 : 50	-
4	$RhH(CO)(PR_3)_3$ R = C_6H_5	85 - 115	15 - 20	92 : 8	Celanese Union Carbide - Davy PowerGas - Johnson Matthey BASF
5	$RhH(CO)(POR_3)_3$ R = C_6H_5	< 130	< 200	-	Mitsubishi
5	$RhH(CO)(PR_3)_3$ R = m-$C_6H_4SO_3Na$	50 - 130	10 - 100	95 : 5	Ruhrchemie, Rhône-Poulenc
6	RhH(CO)(BIPHOS) BIPHOS = organic biphosphite	85 - 95	15 - 20	30 : 1	Union Carbide Dow Chemical

Rate expressions for propylene conversion to normal and iso-butyraldehyde were recently published by Bernas et al. [4] and Murzin et al. [5]. However, at least a part of the working parameters values are outside the area of practical interest: low TPP and Rh concentrations, high CO partial pressure etc. Therefore, their experimental data do not fully describe the industrial process features; for example the influence of carbon monoxide partial pressure on the product isomers selectivity was not observed in some of these investigations. Another important shortcoming is the missing information regarding the side reactions kinetics, like propylene hydrogenation. Therefore, further process investigations are necessary, in order to improve the understanding of the process kinetics. The aim of this work is to develop a kinetic model of the propylene hydroformilation process, in the domain of practical interest, based on industrial observations.

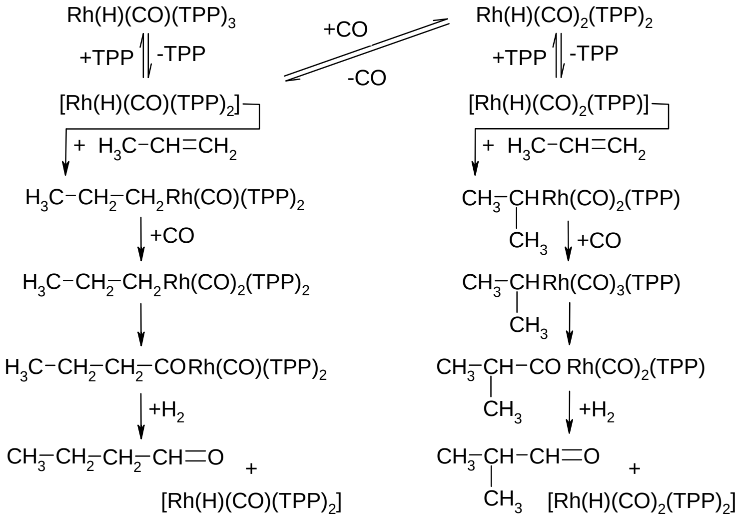

Fig. 1. Mechanism for propylene hydroformilation reactions over Rh/TPP catalyst.

2. Experimental section

In the present work a kinetic model for propylene hydroformylation is developed based on experimental data obtained from an industrial scale oxosynthesis plant having the structure presented in Fig. 2. The main plant components are: two clean-up section, for propylene (a), and for synthesis gas (b), a gas-liquid reactor (c), a product condenser (d), a two phase separator (e), a recycle compressor – oxocycle compressor (f), a stripping column (g), a stabilizing column (h) and its overhead compressor (i). In two clean-up sections (a and b) catalyst poisons and inhibitors are removed from the fresh propylene and synthesis gas streams. The reactor's gas feed (comprising fresh propylene, stripper outlet gas, and recycled synthesis gas) is sparged into the liquid mixture containing the catalyst dissolved in a low volatility products mixture. Due to the relatively high amount of gas bubbled through the liquid reaction mixture, a good liquid mixing intensity is achieved, permitting to consider the reactor as a perfectly mixed one (CSTR). The gas effluent leaving the reactor with an important amount of reaction products is partially condensed and the resulted gas-liquid mixture is split in a separator. The separated gas is recycled to reactor inlet via oxo-cycle compressor, a small part of the gas being purged from compressor suction as off-gas, in order to maintain a constant concentration of inert gases in the recycle loop.

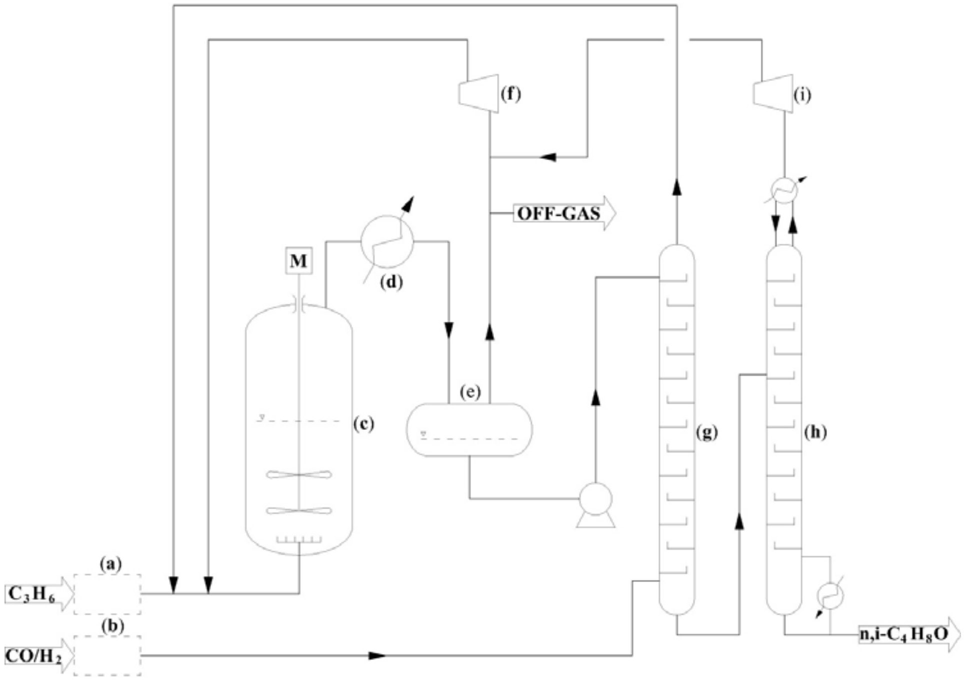

Fig. 2. Schematic of the oxosynthesis plant

The crude butyraldehyde is pumped from separator to the top of the stripping column, where it is contacted counter-currently with the synthesis gas. In this column almost all of the propylene and propane dissolved in the liquid is stripped out by the synthesis gas. The remaining dissolved propylene, propane, and other light gases are removed from the liquid phase in the stabilizing column. The gaseous overhead of the stabilizer, containing valuable reactants, is sent by the second compressor in the suction of the high capacity oxo-cycle compressor. A tight reactor temperature control is insured by DCS system through the variation of the cooling liquid flow and/or its temperature.

A good control of the hydroformylation process is achieved by a distributed control system (DCS), provided with accurate process variable measurements. The flows of propylene stream at inlet and butanals stream at outlet are measured via high accuracy turbine type transmitters, densities of the circulated liquids being software corrected with the temperature. The synthesis gas flow at plant inlet is measured by a differential pressure (DP) transmitter with diaphragm, a pressure – temperature software correction being applied for gas density. The off-gas stream flow purged from the oxosynthesis loop is also accurately measured by a mass flow meter (Coriolis). The catalytic solution level in the oxo-reactor is monitored with a differential pressure (DP) transmitter. The gas phase hydrogen, carbon monoxide, propylene and propane concentrations at reactor outlet are measured by using a gas-chromatograph (GC). In the same point, a supplementary infra-red (IR) analyzer monitors continuously the carbon monoxide concentration. Both analyzers are on-line connected to DCS. The GC, capable to process a gas sample every four minutes is equipped with a number of ten dedicated packed separating columns and TCD detector. Periodically, the GC and IR calibrations are checked switching the sample gas with standard composition gas. The measurements of the main process parameters (inlet gas composition, liquid reaction mixture composition, stripped-off outlet gas composition, pressure, temperature, flow rates) were collected and used to develop a kinetic model of the hydroformylation process. This was possible with good accuracy, thanks to the performance of the plant instrumentation described previously.

3. Results

In the hydroformylation process described above, three chemical reactions were considered: two main reactions for n-butyraldehyde and i-butyraldehyde synthesis from propene and syngas and a side reaction of propene hydrogenation to propane. Other secondary reactions, e.g. liquid by-products resulted from butanals condensation have a low share (typically below 0.5%) under industrial operating conditions. The measurements of the inlet gas composition, liquid reaction mixture composition, stripped-off outlet gas composition, pressure, temperature, and reactor flow rates, allowed to calculate the rate values of the considered chemical reactions. In this aim, 25 experimental operating points were used from industrial steady state plant operation. During data collection period, the composition and activity of catalytic solution was kept constant, by periodical addition of small amounts of fresh rhodium catalytic precursor and triphenylphosphine according to laboratory analysis. Thus, the active rhodium concentration was kept around 250±10 ppm (wt) by using a combination between a flam photometric method and comparative activity tests of fresh catalytic solution and reactor solution respectively. The levels of triphenylphosphine and butanals concentrations (gas-chromatographically analyzed) were situated at approximately 12 wt % and 30-35 wt % respectively. Reagents partial pressures varied between 250 – 600 kPa for propylene, 20 – 80 kPa for carbon monoxide and 140 – 430 kPa for hydrogen respectively, whereas the reactor temperature was modified on the interval 90-110ºC.

The rates of butanals and propane formation reactions were calculated from the mass balance equations around the oxosynthesis reactor, considered as a CSTR:

$$r_A = \frac{DM_{stabilized\ bu\tan als} \cdot X_A}{V_{catalytic\ solution}} \tag{1}$$

$$r_{propane} = \frac{DM_{off-gas\ propane} - DM_{feed\ propane}}{V_{catalytic\ solution}} \tag{2}$$

where:

r_A – rate of formation for butanal isomer A (n-butanal or i-butanal), [mol·L^{-1}·h^{-1}];

$DM_{stabilized\ butanals}$ – stabilized butanals molar flow [mol/h];

x_A – molar fraction of izomer A (n or i-butanal) in the stabilized butanals stream;

$r_{propane}$ – rate of formation for propane, [mol·L^{-1}·h^{-1}];

$DM_{off\text{-}gas\ propane}$ - propane molar flow in the off-gas stream [mol/h];

$DM_{feed\ propane}$ – propane molar flow in the propylene feed stream [mol/h];

$V_{catalytic\ solution}$ – inventory of reactor catalytic solution [L].

The approach is valid if the shares of secondary reactions other than propylene hydrogenation and butanals loses in the discharged off-gas stream are neglected. As shown at the beginning of this chapter, the share of secondary reaction like by-products resulted from butanals condensation is below 0.5% under industrial operating conditions. On the other hand, the concentration of butanals in the off-gas is around 1.4 % vol., total losses of butanal in the off-gas not exceeding 0.15 % of total quantity of produced butanals. In such conditions the above assumptions are acceptable.

4. Kinetic modeling

For the three reactions considered in the present study, the formation rates of n-butyraldehyde ($r_{n\text{-}BA}$), i-butyraldehyde ($ri_{\text{-}BA}$) and propane (r_{propan}), we used power law type expressions (relations 3-5):

$$r_{n-BA} = k_1 \cdot \exp(\frac{-E_{a1}}{R \cdot T}) \cdot p_{C_3H_6} \cdot p_{CO}^{a_1} \cdot p_{H_2} \tag{3}$$

$$r_{i-BA} = k_2 \cdot \exp(\frac{-E_{a2}}{R \cdot T}) \cdot p_{C_3H_6} \cdot p_{CO}^{a_2} \cdot p_{H_2} \tag{4}$$

$$r_{propane} = k_1 \cdot \exp(\frac{-E_{a3}}{R \cdot T}) \cdot p_{C_3H_6} \cdot p_{CO}^{a_3} \cdot p_{H_2} \tag{5}$$

Even that carbon monoxide is not involved as reactant in reaction (3), its partial pressure was included in the rate expression, since it is reported in literature as an inhibitor for catalytic propylene hydrogenation. So the proposed kinetic model is characterized by 9 unknown parameters: three pre-exponential factors, three activation energies and three partial reaction orders for carbon monoxide. The kinetic model parameters were estimated using the least squares method by using the measured plant data, as explained above. The minimization of the sum of squares of residuals (between calculated and measured values of the three considered reaction rates) was performed by nonlinear regression, by means of the Levenberg-Marquardt optimization algorithm, implemented in the MATLAB built-in function *lsqcurvefit*. The kinetic parameters values and the intervals estimated for 95% confidence are given in Table 2.

Table 2

Estimated values of parameters for the proposed kinetic model

Parameter	**Formation of n-BA**	**Formation of i-BA**	**Formation of propane**
Rate constants			
k_1 [mol/(kPa$^{2.407}$·L$_{cat}$·h)]	3443.1 ± 1562.1	-	-
k_2 [mol/(kPa$^{2.898}$·L$_{cat}$·h)]	-	207.8 ± 119.5	-
k_3 [mol/(kPa$^{1.397}$·L$_{cat}$·h)]	-	-	1880369.7 ± 391537.7
Activation energies			
E_{a1}, [KJ/Kmol]	65260.9 ± 1414.7	-	-
E_{a2}, [KJ/Kmol]	-	70519.7 ± 1785.3	-
E_{a3}, [KJ/Kmol]	-	-	83188.5 ± 653.1
Partially reaction orders			
a_1	0.407 ± 0.017	-	-
a_2		0.898 ± 0.027	-
a_3		-	-0.603 ± 0.006

The calculated values of activation energies and the partial orders of carbon monoxide in three rate expression are in expected intervals. In Fig. 3 are given the parity diagrams comparing the calculated and experimental reaction rates values. The values of the 95 % confidence intervals along with the closeness of calculated and measured values of reaction rates, illustrated by the parity diagrams, prove a good quality of the fit, so the proposed kinetic model can be considered as adequate. Finally, it is worth to underline that the accuracy of the kinetic model is dependent on the number of unknown parameters. By introducing variable partial reaction orders also for the other reagents, a better accuracy of the fit could be obtained, but this would lead to an excessive number of model parameters.

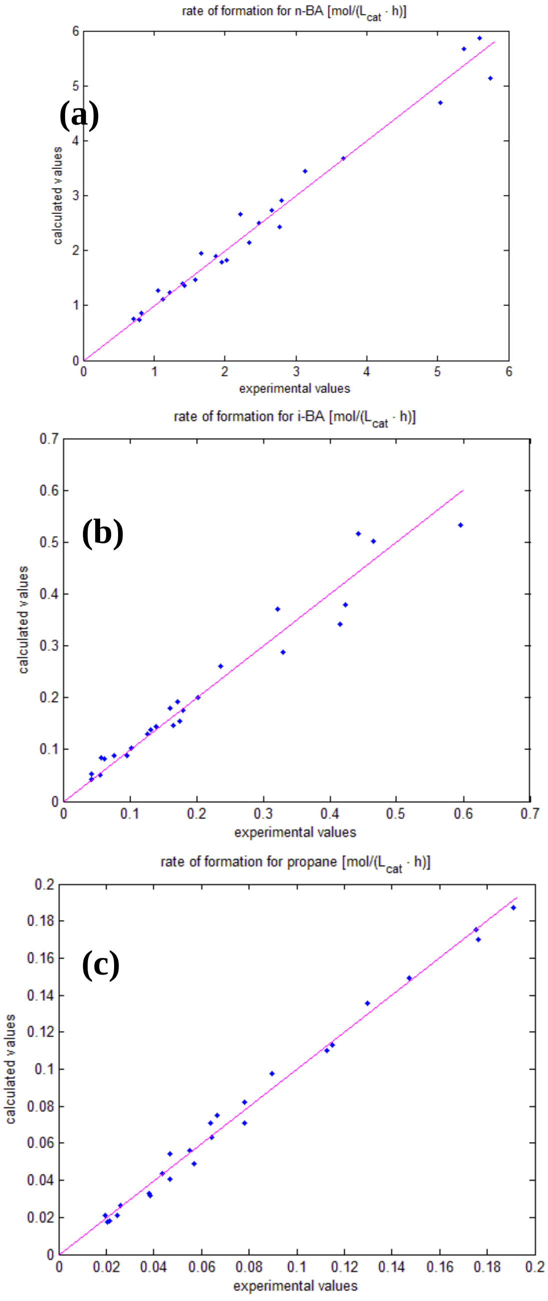

Fig. 3. Parity diagrams comparing calculated and measured reaction rates:
(a) n-butyraldehyde; (b) i-butyraldehyde; (c) propane

5. Conclusions

A kinetic model for propylene hydroformilation process wass developed based on data collected from an industrial oxosynthesis reactor. The kinetics of the main three reactions defining the propylene hydroformylation process was described globally by power law type rate expressions. Unlike other published models, the proposed kinetic model is better, describing the influence of carbon monoxide partial pressure on the main reactions kinetics. It provides a good concordance between the calculated values of the reaction rates and their measured values.

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