KINETICS OF DICYCLOPENTADIENE HYDROGENATION USING PD/C CATALYST

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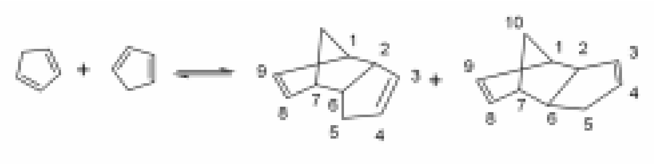
Abstract*. Kinetics of dicyclopentadiene hydrogenation was investigated in laboratory stirred autoclave using a powdered palladium catalyst. Time function of reaction mixture composition for different hydrogen partial pressures, temperatures, catalyst weights and initial concentrations of dicyclopentadiene in a cyclohexane solution was measured.*

Kinetic data were described using Langmuir-Hinshelwood kinetics. Kinetic constant of first reaction step was 5.5 mal higher with respect to second one. Adsorption constant of unsaturated hydrocarbons is proportional to number of double bonds in their molecule. The values of activation energy of both consecutive reactions(25 and 18 kJ/mol) correspond to the interval typical for liquid phase hydrogenation of unsaturated hydrocarbons.

Key words*: hydrogenation, dicyclopentadiene, kinetics, palladium catalyst*

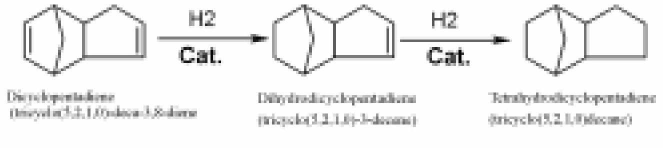
Introduction

Dicyclopentadiene (tricyclo(5,2,1,0)-deca-3,8-diene) is originated by Diels-Alder reaction of cyclopentadiene (see reaction scheme 1) [1]. Reaction heat of this dimerization is – 75.4 kJ/mol and yields two stereo-isomer forms (endo, exo).



Reaction scheme 1. Cyclopentadiene dimerization

Hydrogenation of dicyclopentadiene (DCPD) proceeds according to the following consecutive reaction scheme 2.



Reaction scheme 2. Consecutive dicyclopentadiene (tricyclo(5,2,1,0)-deca-3,8-diene) hydrogenation

The first reaction step takes place in norbornene part of molecule, followed by second double bond in C5 ring hydrogenation. Hydrogenation of double bond molecule in norbornene ring of dicyclopentadiene manifests several times higher reaction rate, than the second one, in cyclopentene ring [2]. Both hydrogenation steps are exothermic ones. Reaction heat of reaction of consecutive reactions is –138.8 kJ/mol and –109.5 kJ/mol, respectively [3].

Dicyclopentadiene and its derivatives are important petrochemical products, their important applications represent syntheses of pharmaceutical intermediates as well.

Selectively hydrogenated dicyclopentadiene results in dihydrodicyclopentadiene which is used in rubber industry, mixed with resin yields special rubber with excellent adhesive features [4]. An other derivative exo-5-(3,3-dimethylureido)-tetrahydro-endo-dicyclopentadiene is used as very a efficient herbicide[5]. By total hydrogenation of DCPD to tricyclo(5,2,1,0)decane and its consecutive izomerization adamantane (tricyclo[3,3,1,1]decane) can be obtained. This substance is used for wide range of drugs synthesis, e.g. aminoadamantane (in form of hydro-chloride) represents a active component as antiviral agent used in healing of disease caused by virus A-2.

Application of palladium black for dicyclopentadiene hydrogenation was studied in paper [6]. At temperature 130°C and pressure 2 MPa 97% of endo –tricyclodecane was obtained.

Application of Pd on γ-alumina catalyst for selective DCPD hydrogenation, in continuous and/or discontinuous arrangement, was described in German patent [7]. Continuous hydrogenation was carried out in trickle-bed reactor at temperature 127°C using co-current down flow of liquid and gaseous phases. Catalyst used was found appropriate for selective hydrogenation; yield of intermediate dihydrodicyclopentadiene was about 98%. Kinetic parameters of dicyclopentadiene hydrogenation, carried out in trickle bed reactor under mass transfer limitation conditions were given in paper [8].

Comparison of activity and selectivity of various metal catalysts (Pd-support, Ni, Raney catalysts, blacks of metals of VIII. Group) was made in papers [9] and [10]. Effects of hydrogen partial pressure, support and active metal nature on consecutive reaction process selectivity were investigated also. It was found, that higher hydrogen partial effect has negative effect on reaction selectivity. This fact was also confirmed during dicyclopentadiene hydrogenation using shaped catalyst extrudates

[11]. Application of Pd/$BaCO_3$ catalyst for dicyclopentadiene hydrogenation was tested also in work [12].

Experimental

Commercial 2 wt.% palladium/charcoal catalyst (Engelhard Co.) was used in this study (for its parameters see Table 1). For powder catalyst experiments original extrudates were crushed and sieved to 45 µm particles in order to eliminate internal mass transfer effect on reaction kinetics.

Table 1. Catalyst properties

Catalyst properties	Dimension	Value
Active metal content	Wt.%	2
Catalyst support	-	Active carbon
Catalyst shape	-	Cylindrical extrudates
Powder particle size	µm	45
Total surface area (B.E.T.)	m^2/g	1100
Pore volume	ml/g	0.62

Laboratory stirred autoclave (Parr Instruments Inc., volume 0.4 l) was used in this study. Experiments were focused on determination of reaction mixture composition on time dependence measured at different hydrogen partial pressure, temperature, catalyst weight and initial concentration of dicyclopentadiene in cyclohexane solution. For experimental conditions see Table 2.

Table 2. Experimental conditions

Parameter	Dimension	Value
Temperature range	^oC	25-40
Pressure range	MPa	1-4
Catalyst weight	g	0.04-0.5
DCPD initial concentration	mol/l	0.15-0.5
Stirring	rpm	1500

Small reaction mixture samples taken in regularly intervals from autoclave via pressure filter (catalyst separation) were analyzed by GC method using Shimadzu GC -17A FID with capillary column (30m) Supelco SB-5.

Results and Discussion

Langmuir-Hinshelwood kinetic model of dicyclopentadiene hydrogenation. A set of 20 experiments measured using powdered catalyst at different conditions has been tested by Langmuir-Hinshelwood kinetic model. The effort was focused on identification of model parameters from complete reaction mixture composition on time data measured at different hydrogen partial pressure, temperature, catalyst weight and initial concentration of dicyclopentadiene in cyclohexane solution.

The following form of kinetic model, supposed surface reaction as rate limiting step and non-dissocative hydrogen adsporption on reaction site, has been used:

$$r_1 = \frac{k_1 * K_H * K_{DCPD} * c_H * c_{DCPD}}{(1 + K_{DCPC} * c_{DCPD} + K_{DHDCPD} * c_{DHDCPD} + K_{THDCPD} * c_{THDCPD} + K_H * c_H)^2} \quad (1)$$

$$r_2 = \frac{k_2 * K_H * K_{DHDCPD} * c_H * c_{DHDCPD}}{(1 + K_{DCPC} * c_{DCPD} + K_{DHDCPD} * c_{DHDCPD} + K_{THDCPD} * c_{THDCPD} + K_H * c_H)^2} \quad (2)$$

where

k1, k2 –stands for kinetic constants (first and consecutive reactions)

K_{DCDP}, K_{DHDCPD}, K_{THDCPD}, K_H – represents adsorption coefficients of starting reaction component - dicyclopentadiene, Intermediate product- dihydrodicyclopentadiene, full saturated product -tetrahydrodicyclopentadiene and hydrogen, respectively

c_{DCPD}, c_{DHDCPD}, c_{THDCPD}, c_H - time functions of reaction components concentrations, i.e. dicyclopentadiene, dihydrodicyclopentadiene, tetrahydrodicyclopentadiene and hydrogen, respectively.

Hydrogen concentration in reaction mixture was calculated using Henry's law. Reaction mixture properties was supposed to be equivalent to pure cyclohexane used as a solvent in this study.

Kinetic parameters, i.e. reaction rate constants of first and consecutive reactions, furthermore adsorption coefficients of reaction components, were evaluated from experimental data using software ERA 2.0 [13]. Using non-linear regression analysis basic kinetic parameters were obtained. An correlation example of experimental data and model solution in case of reaction mixture composition on time dependence is shown in Figures 1-5 corresponding to various initial dicyclopentadiene concentrations and hydrogen partial pressures. Only kinetic constants k1 and k2 were supposed to be temperature dependent during regression analysis procedure. The Table 3 summarizes all kinetic model parameters obtained by regression analysis. The kinetic constants k1 and k2 given in this Table corresponds to temperature 25°C.

Table 3. Regression analysis results

Parameter	Dimensoin	Value
k_1	mol/min*g_{cat}	1.494
k_2	mol/min*g_{cat}	0.265
K_{DCPD}	l/mol	7.989
K_{DHDCPD}	l/mol	4.083
K_{THDCPD}	l/mol	0.0009
K_H	l/mol	14.578
Ea1	kJ/mol	24.7
Ea2	kJ/mol	18.2

Kinetic parameters clearly indicate the difference in reactivity of double bonds in norbornene and cyclopentene ring of dicyclopentadiene molecule. The former is hydrogenated more than 5 times faster. It is also evident that the highest adsorption constant corresponds to hydrogen, on the other hand adsorption constant decreases with the double bonds extent of saturation in substrate molecule. Adsorption constant of hydrocarbons is proportional to number of double bonds, Figure 7.

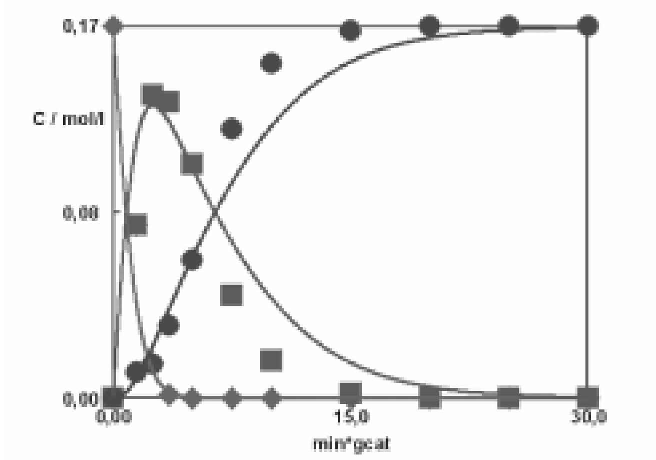


Figure 1. Comparison of experimental (points) and computed (curves) concentrartions p=1 MPa ,T=25°C, c_0=0,15 mol/l,
◆ – Dicyclopentadiene, ■ –Dihydrodicyclopentadiene,
● – Tetrahydrodicyclopentadiene

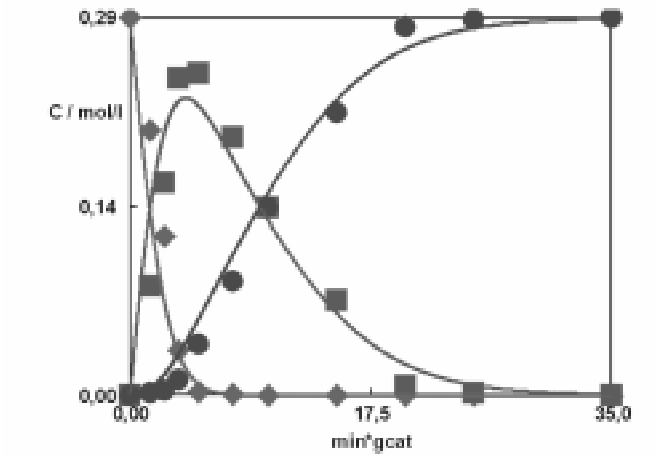


Figure 2. Comparison of experimental (points) and computed (curves) concentrartions p=1 MPa ,T=25°C, c_0=0,29 mol/l,
◆ – Dicyclopentadiene, ■ – Dihydrodicyclopentadiene,
● – Tetrahydrodicyclopentadiene

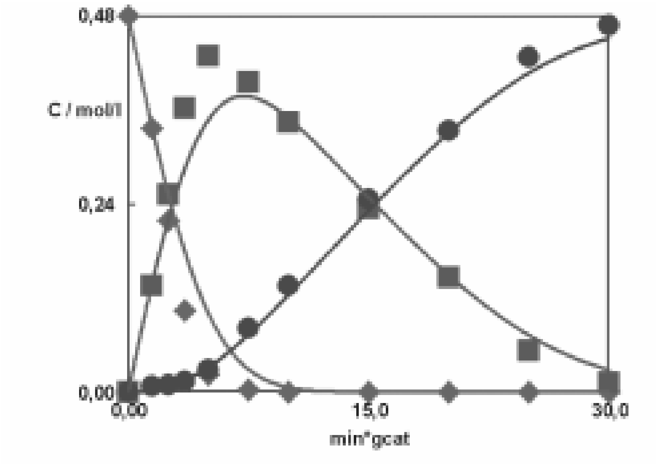


Figure 3. Comparison of experimental (points) and computed (curves) concentrartions p=1 MPa ,T=25°C, c_0=0,49 mol/l,
◆ – Dicyclopentadiene, ■ – Dihydrodicyclopentadiene,
● – Tetrahydrodicyclopentadiene

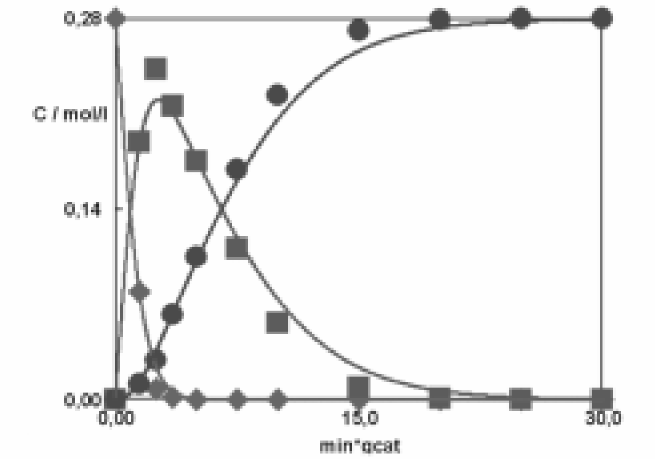


Figure 4. Comparison of experimental (points) and computed (curves) concentrartions p= 2 MPa, T=25°C, c_0=0,29 mol/l,
◆ – Dicyclopentadiene, ■ – Dihydrodicyclopentadiene,
● – Tetrahydrodicyclopentadiene

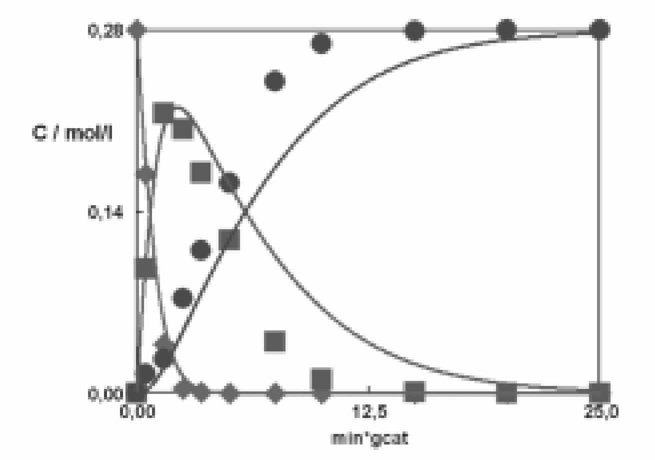


Figure 5. Comparison of experimental (points) and computed (curves) concentrartions p= 4 MPa, T=25°C, c_0=0,29 mol/l,
◆ – Dicyclopentadiene, ■ – Dihydrodicyclopentadiene,
● – Tetrahydrodicyclopentadiene

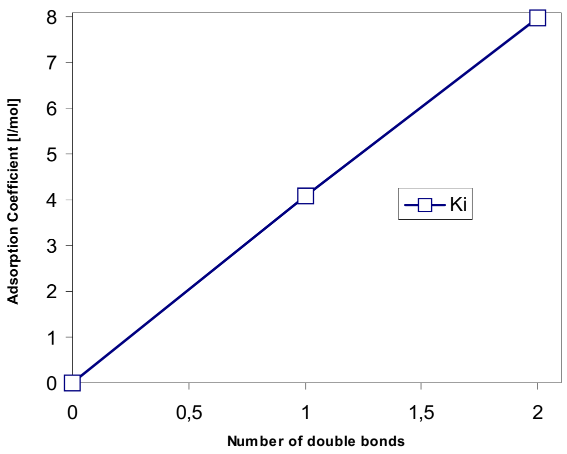


Figure 6. Double bonds effect on adsorption coefficient value

Activation energy determination. Some experiments were carried out at different temperatures. Arrhenius plots of kinetic constants k1 and k2, determined using L-H kinetic model, are given in Figure 7. Corresponding values of activation energy, 24.7 and 18.2 kJ/mol, were determined from the slope of the regression line. The estimated values of activation energy of both consecutive reactions correspond to the interval typical for liquid phase hydrogenation of unsaturated hydrocarbons [14].

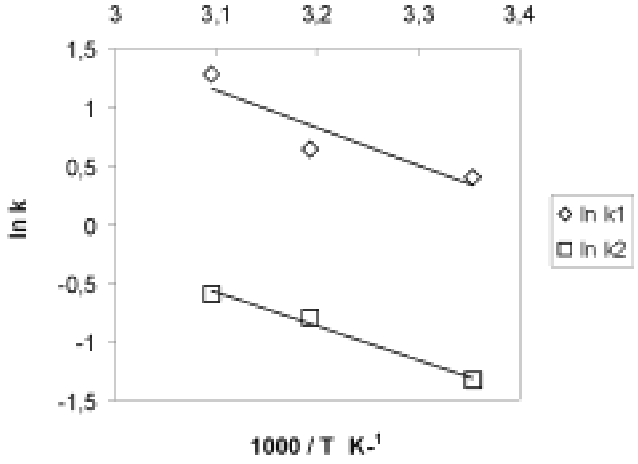


Figure 7. Activation energy determination,
◇ – 1. reaction □ – 2. reaction

Conclusion

Dicyclopentadiene hydrogenation, on powdered palladium on active carbon catalyst, was described using Langmiur-Hinschelwood's equations. Kinetic model considered competitive adsorption of non-dissociated hydrogen and the other components of reaction mixture on catalyst surface.

Based on experimental data, activation energy of both consecutive hydrogenations was evaluated in this study.

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Symbols

k1, k2 – kinetic constants (first and consecutive reactions) [mol/min*g_{cat}]

K_{DCDP}, K_{DHDCPD}, K_{THDCPD}, K_H – adsorption coefficients of dicyclopentadiene, dihydrodicyclopentadiene, tetrahydrodicyclopentadiene and hydrogen, respectively

c_{DCPD}, c_{DHDCPD}, c_{THDCPD}, c_H – concentrations of dicyclopentadiene, dihydrodicyclopentadiene, tetrahydrodicyclopentadiene and hydrogen, respectively

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