

UDC 541.128:547,593.211

THE KINETIC MODEL OF THE REACTION OF OXIDATIVE DEHYDROGENATION OF CYCLOHEXANOL OVER MODIFIED ZEOLITE CATALYST

A.M. Aliyev, Z.A. Shabanova, M.K. Aliyeva, G.A. Alizadeh

Acad. M.F. Nagiyev Institute of Catalysis and Inorganic Chemistry
H. Javid ave., 113, Baku AZ 1143, Azerbaijan Republic, e-mail: kqki@kqki.science.az

Based on experimental data, a probable-stage scheme of the mechanism of oxidative dehydrogenation of cyclohexanol reaction over modified zeolite catalyst suggested. Also, theoretically based kinetic model of the process has been developed and numerical values of the constants of a kinetic model calculated.

Keywords: cyclohexanol, cyclohexanone, oxidative dehydrogenation, kinetics

INTRODUCTION

It should be noted that cyclohexanone is used in the organic synthesis as intermediate in obtaining caprolactam which is manufactured from polymer polyamide fiber, and as a solvent for many substances. One of the major industrial methods for preparing cyclohexanone is the oxidation of cyclohexane by atmospheric oxygen under elevated pressure in the presence of substantially homogeneous catalysts, specifically soluble cobalt salts [1-2]. All of

these catalysts show high activity and selectivity at relatively higher temperatures. We have lately revealed that natural clinoptilolite modified with cations; Cu^{2+} , Zn^{2+} , Co^{2+} and Cr^{3+} by ion-exchange is the active catalyst for the reaction of oxidative dehydrogenation of cyclohexanol into cyclohexanone.

The purpose of the work is to analyze the kinetics and mechanism of the reaction.

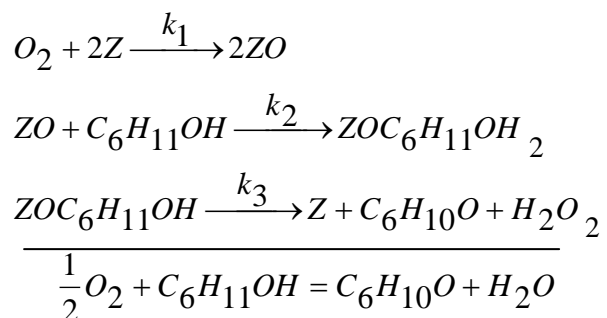
EXPERIMENTAL PART

Results of the experimental analysis to select a catalyst for the reaction of oxidative dehydrogenation of cyclohexanol have shown that the most effective catalysts for this reaction is Cu, Pd, Sn-clinoptilolite (0.5% Cu^{2+} , 0.15% Pd^{2+} , 0.5% Sn^{2+}) [3].

The kinetics of the reaction was examined in the following conditions: temperature - 260-370°C; space velocity of the

reaction mixture (V) - 1036-3109 h^{-1} ; partial pressure (P_{alcohol}) - 0.06-0.24 atm. and (P_{O_2}) - 0.05-0.24 atm.

Proceeding from the analysis of literary materials [3-5] and experimental data, a mechanism of cyclohexanone formation has been suggested. A simplified diagram of the stage mechanism is as follows:



All these stages are practically irreversible. Assuming their simplicity, we find the following expressions for the rates of stages:

$$r_1 = k_1 P_1 \theta_1^2; \quad r_2 = 2k_2 P_2 \theta_2; \quad r_3 = 2k_3 \theta_3 \quad (1)$$

$\theta_1, \theta_2, \theta_3$ - vacancy sections of the modified zeolite coated with atomic oxygen; cyclohexanol molecules and surface intermediate with k_1, k_2, k_3 - rate constants corresponding index stages; r_1, r_2, r_3 -rate index

$$\theta_1 + \theta_2 + \theta_3 = 1 \quad (3)$$

$$k_1 P_1 \theta_1^2 = 2k_2 P_2 \theta_2; \quad \theta_2 = (k_1 P_1) / (2k_2 P_2)$$

$$k_1 P_1 \theta_1^2 = 2k_3 \theta_3; \quad \theta_3 = [(k_1 P_1) / 2k_3] \theta_1$$

From the equations (1):

$$\theta_2 = \frac{k_1 P_1}{2k_2 P_2} \theta_1^2; \quad \theta_3 = \frac{k_1 P_1}{2k_3} \theta_1^2$$

By substituting expression θ_2, θ_3 , in the equation (3) we get:

$$\left(\frac{k_1 P_1}{2k_2 P_2} + \frac{k_1 P_1}{2k_3} \right) \theta_1^2 + \theta_1 - 1 = 0 \quad (4)$$

Solving the equation (4), we obtain the following expression for θ_1 :

$$\theta_1 = \frac{\sqrt{1 + 4 \left(\frac{k_1 P_1}{2k_2 P_2} + \frac{k_1 P_1}{2k_3} \right)} - 1}{2 \left(\frac{k_1 P_1}{2k_2 P_2} + \frac{k_1 P_1}{2k_3} \right)}$$

Therefore, the rate of cyclohexanone equation can be represented as follows:

$$r_4 = k_1 P_1 \left[\frac{\sqrt{1 + 4 \left(\frac{k_1 P_1}{2k_2 P_2} + \frac{k_1 P_1}{2k_3} \right)} - 1}{2 \left(\frac{k_1 P_1}{2k_2 P_2} + \frac{k_1 P_1}{2k_3} \right)} \right]^2 \quad (5)$$

Note that 2-cyclohexen-1-one is produced through the reaction of adsorbed molecules of cyclohexanone with dissociatively adsorbed oxygen molecules. Kinetic equation corresponding to this mechanism

$$r_{2-C_6H_8O-1-on} = r_5 = \frac{dA_2}{d \left(\frac{G_k}{n_{C_6H_{11}OH}^0} \right)} = \frac{k_4 \sqrt{K_2 P_2} \cdot K_3 P_3}{\left(1 + K_1 P_1 + \sqrt{K_2 P_2} + K_3 P_3 + K_4 P_4 + K_5 P_5 + K_6 P_6 + K_9 P_9 + K_{10} P_{10} \right)^2}$$

Total rate of cyclohexanone formation is as follows:

$$r_{C_6H_{10}O} = \frac{dA_1}{d \left(\frac{G_k}{n_{C_6H_{11}OH}^0} \right)} = r_4 - r_5 \quad (6)$$

corresponding stages; P_1 and P_2 - partial pressure oxygen and alcohol.

In steady-state conditions:

$$r_4 = r_1 = r_2 = r_3 \quad (2)$$

where, r_4 -general rate of cyclohexanone formation.

Based on these equations and constancy of total surface areas and formations θ_i overall reaction rate as a function of concentration of reactants is as follows:

Note that cyclohexene is formed by dehydration adsorbed cyclohexanole molecules. This mechanism corresponds to the kinetic equation:

$$r_6 = \frac{k_5 K_1 P_1}{1 + K_1 P_1 + \sqrt{K_2 P_2} + K_3 P_3 + K_4 P_4 + K_5 P_5 + K_6 P_6 + K_9 P_9 + K_{10} P_2}$$

Methylcyclopentene is formed by isomerization of adsorbed cyclohexene molecules. Kinetic equation corresponding to this mechanism is as follows:

$$r_7 = \frac{k_6 K_5 P_5}{1 + K_1 P_1 + \sqrt{K_2 P_2} + K_3 P_3 + K_4 P_4 + K_5 P_5 + K_6 P_6 + K_9 P_9 + K_{10} P_2}$$

Note that CO₂ is formed by the interaction of adsorbed molecules of cyclohexene and oxygen. This mechanism corresponds to the kinetic equation:

$$r_8 = \frac{k_7 K_{10} P_2 \cdot P_5}{1 + K_1 P_1 + \sqrt{K_2 P_2} + K_3 P_3 + K_4 P_4 + K_5 P_5 + K_6 P_6 + K_9 P_9 + K_{10} P_2}$$

where total rate of cyclohexene formation is as follows:

$$r_{C_6H_{10}} = \frac{dA_3}{d\left(\frac{G_k}{n_{C_6H_{11}OH}^0}\right)} = r_6 - r_7 - r_8 \tag{7}$$

Note that methylcyclopentene oxidation takes place through the reaction of adsorbed oxygen and methylcyclopentene molecules:

$$r_9 = \frac{k_8 K_{10} P_2 \cdot P_5}{1 + K_1 P_1 + \sqrt{K_2 P_2} + K_3 P_3 + K_4 P_4 + K_5 P_5 + K_6 P_6 + K_9 P_9 + K_{10} P_2}$$

Total rate of the of methylcyclopentene formation

$$r_{CH_3C_5H_7} = \frac{dA_4}{d\left(\frac{G_k}{n_{C_6H_{11}OH}^0}\right)} = r_7 - r_9 \tag{8}$$

Total rate of the formation of carbon dioxide is presented by the equation as follows:

$$r_{CO_2} = \frac{dA_5}{d\left(\frac{G_k}{n_{C_6H_{11}OH}^0}\right)} = r_8 + r_9 \tag{9}$$

It should be noted that A₁, A₂, A₃, A₄, A₅ generate cyclohexanone, 2-cyclohexen-1-one, cyclohexene, methylcyclopentene and carbon dioxide respectively. Equations (5) - (9) constitute the kinetic model of the process.

The kinetic model of the reaction is subjected to statistical analysis in line with kinetic data. Numerical values of kinetic model constants are presented in the Table.

Table. Numerical values of kinetic model constants

$\ln k_i^0 (\ln K_i^0)$		$E_i (Q_i)$, kcal/mole	
$\ln k_1^0$	7.49	E_1	8.56
$\ln k_2^0$	0.68	E_2	3.0
$\ln k_3^0$	59.29	E_3	9.45

$\ln k_4^0$	22.99	E_4	16.73
$\ln k_5^0$	34.43	E_5	35.96
$\ln k_6^0$	2.73	E_6	16.73
$\ln k_7^0$	33.44	E_7	24.12
$\ln k_8^0$	8.86	E_8	26.95
$\ln K_1^0$	-5.15	Q_1	1.00
$\ln K_2^0$	-9.70	Q_2	8.99
$\ln K_3^0$	-7.93	Q_3	9.00
$\ln K_4^0$	-0.16	Q_4	8.72
$\ln K_5^0$	14.9	Q_5	1.01
$\ln K_6^0$	3.027	Q_6	2.49
$\ln K_7^0$	-0.59	Q_7	1.50
$\ln K_8^0$	-1.75	Q_8	1.56

Calculations have shown that the mean square error of the experiments does not exceed 2%.

REFERENCES

1. Chaudhari S.M., Waghulde A.S., Samuel V., Bari M.L. and Chumbhale V.R. Characterization of ZnO and modified ZnO catalysts for anaerobic oxidation of cycloheksanol . *Res. J. Chem.Sci.* 2013, vol. 3(7), P. 38-44.
2. Vyawahare Y.K., Chumbhale V.R., Pardhy S.A., Samuel V., Aswar A.S. Gas – phase oxidant free oxidation of cyclohexanol over $V_2O_5 - MoO_3 - M_2O$ (M=Na, K,Cs). *IJCT*, 2010, vol.17, p. 43.
3. Aliyev A.M., Shabanova Z.A., Aliyeva M.K., Ali-zadeh G.A. Oxidative dehydration of aliphatic and alicyclic alcohols on modified zeolite catalysts. Proceedings of the Republican Scientific Conference in Commemoration of the 80-anniversary of the M.Nagiyev Institute of Catalysis and Inorganic Chemistry, Baku, 15-16 November, 2016, p.230-231. (In Azerbaijan).
4. Aliyev A.M., Majidova S.M., Saryjanov A.A. et al. Ion-exchanging method of modifying zeolites by metal cations as maximum model of the catalyst. *Azerb. Chem. Journ.* 2011, no. 4, p.9-12. (In Azerbaijan).
5. Shahtakhtinskiy T.N., Aliyev A.M. et al. Selection of active catalyst and the kinetics of partial oxidation reaction of isoamyl alcohol. *Kinetics and Catalysis.* 1996, vol. 37, №2, p.286-290. (In Russian).

TSİKLOHEKSANOLUN MODİFİKASIYA OLUNMUŞ SEOLİT KATALİZATORLAR ÜZƏRİNDƏ OKSİDLƏŞDİRİCİ DEHİDROGENLƏŞMƏSİ REAKSİYASININ KİNETİK MODELİ

A.M. Əliyev, Z.A. Şabanova, M.Q. Əliyeva, G.A. Əli-zadə

AMEA-nın akad. M.Nağıyev adına Kataliz və Qeyri-üzvi Kimya İnstitutu
AZ 1143, Bakı, H.Cavid pr., 113; e-mail: kqki@kqki.science.az

Received 22.06.2017.

Təcrübi nəticələr əsasında tsikloheksanolun oksidləşdirici dehidrogenləşməsi reaksiyanının ehtimal olunan getmə mexanizmi verilmişdir. Prosesin nəzəri cəhətdən əsaslandırılmış kinetic modeli işlənib hazırlanmış və kinetic modelin parametrlərinin ədədi qiymətləri hesablanmışdır.

Açar sözlər: Tsikloheksanol, tsikloheksanon, oksidləşdirici dehidrogenləşmə, kinetika

**КИНЕТИЧЕСКАЯ МОДЕЛЬ РЕАКЦИИ ОКИСЛИТЕЛЬНОГО ДЕГИДРИРОВАНИЯ
ЦИКЛОГЕКСАНОЛА НА МОДИФИЦИРОВАННЫХ ЦЕОЛИТНЫХ КАТАЛИЗАТОРАХ**

А.М. Алиев, З.А. Шабанова, М.К. Алиева, Г.А. Ализаде

*Институт катализа и неорганической химии им. акад. М.Нагиева
Национальной АН Азербайджана
AZ 1143 Баку, пр.Г.Джавида, 113; e-mail: kqki@kqki.science.az*

На основе экспериментальных данных была предложена вероятная схема механизма реакции окислительного дегидрирования циклогексанола. Разработана теоретически основанная кинетическая модель процесса и рассчитаны численные значения констант кинетической модели.

Ключевые слова: *циклогексанол, циклогексанон, окислительное дегидрирование, кинетика*

Redaksiyaya daxil olub 22.06.2017.