# RESEARCH INTO REACTION ABILITY OF CYCLOHEXANOL AND METHYLCYCLOHEXANOLS IN THE OXIDATIVE DEHYDRATION REACTION OVER MODIFIED ZEOLITE CATALYSTS

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*Abstract: The article studied and compared the reactivity of cyclohexanol and methylcyclohexanol isomers in the oxidative dehydrogenation reaction over modified zeolite catalysts. It found that rates of oxidative dehydrogenation of all methylcyclohexanol isomers are practically the same and exceed rates of oxidative dehydrogenation of cyclohexanol into cyclohexanone.*
*Keywords: cyclohexanol, methylcyclohexanol, zeolites, reactivity, reaction mechanism.*

## Introduction

Cyclohexanone and methylcyclohexanones are valuable products of organic synthesis. They are used in organic synthesis as intermediates in the production of caprolactam from the polymer of which polyamide fiber is made and are also used as solvents for many substances. In addition, methylcyclohexanone is the main raw material in the asymmetric synthesis of optically active substances, plasticizers and enanthic acid [1].

The main industrial method for producing of cyclohexanone is the oxidation of cyclohexanol with atmospheric oxygen at high pressure, mainly in the presence of homogeneous catalysts — soluble cobalt salts [2]. Methylcyclohexanone is obtained by oxidation of 2-methylcyclohexanol in the liquid phase at relatively high pressures in the presence of homogeneous catalysts - soluble cobalt salts, and atmospheric oxygen is used as an oxidizing agent [3]. The main disadvantage of liquid-phase processes is the difficulty in separating the catalyst from the liquid catalyzate. Therefore, on an industrial scale, mainly gas-phase processes of oxidative dehydrogenation of cyclohexanol and methylcyclohexanol are used with using as catalysts metals such as nickel, cobalt, iron,

copper, zinc, chromium, ruthenium, rhodium, palladium, etc. on different carriers (silicates, aluminosilicates, aluminum oxides, zirconium and titanium dioxides or their mixtures). The process of oxidative dehydrogenation on these catalysts proceeds at relatively high temperatures [4].

Our previous works [5-6] dealt with the selection of active zeolite catalysts modified by ion exchange method for the reaction of oxidative dehydrogenation of cyclohexanol and 4-methylcyclohexanol. As a result of these studies, it revealed that natural clinoptilolite with a silicate modulus $\lambda = 8.68$ modified by the ion exchange method with cations of $Cu^{2+}- 0.5$ wt. %, $Pd^{2+} - 0.15$ wt. %, $Sn^{2+} - 0.5$ wt. % shows relatively high catalytic activity in the reaction of oxidative dehydrogenation of cyclohexanol to cyclohexanone, and clinoptilolite containing 0.5 wt. % of $Cu^{2+}$ and 0.15 wt. % of $Pd^{2+}$ is an active catalyst for the oxidative dehydrogenation of 4-methylcyclohexanol to 4-methylcyclohexanone. Using these ultradispersed catalysts, the kinetic regularities of the oxidative dehydrogenation of cyclohexanol to cyclohexanone and 4-methylcyclohexanol to 4-methylcyclohexanone were studied and a mechanism and theoretically

grounded kinetic models of these processes proposed [7-8].

    For optimal design of the reactors of large unit power for the above processes, it becomes necessary to study and compare the reactivity of reagents in the oxidative dehydrogenation reaction. However, for a complete comparison of the rate of formation of cyclohexanone and methylcyclohexanones, the kinetic regularities of the processes of obtaining two more isomers of methylcyclohexanol are remained unexplored. These are 2- and 3-methylcyclohexanol.

### Results and discussion

    We carried out additional experiments to study the kinetic regularities of the reactions of oxidative dehydrogenation of 2-methylcyclohexanol and 3-methylcyclohexanol on CuPd-clinoptilolite. The experiments were carried out in keeping with the method described in [8]. The experimental results are presented in Tables 1, 2.

**Table 1.** Results of the study into the reaction kinetics of oxidative dehydrogenation of 2-methylcyclohexanol

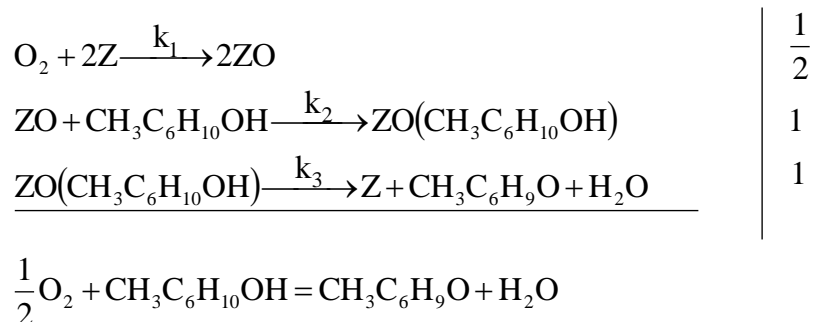| Concentration of cations, wt. % | | $T, {}^0C$ | Volumetric speed, hour$^{-1}$ | Molar ratio, $n_{alcohol}:n_{air}$ | Yield of 2-methylcyclohexanone, % |
|---|---|---|---|---|---|
| $Cu^{2+}$ | $Pd^{2+}$ | | | | |
| 0.5 | - | 210 | 1590 | 0.36:2.64 | 59.0 |
| 0.5 | 0.1 | 210 | 1590 | 0.36:2.64 | 94.9 |
| 0.5 | 0.15 | 210 | 1590 | 0.36:2.64 | 97.3 |
| 0.5 | 0.15 | 200 | 1590 | 0.36:2.64 | 95.8 |
| 0.5 | 0.15 | 180 | 1590 | 0.36:2.64 | 93.0 |
| 0.5 | 0.15 | 190 | 1590 | 0.36:2.64 | 94.0 |
| 0.5 | 0.15 | 210 | 3000 | 0.36:5.18 | 94.1 |
| 0.5 | 0.15 | 230 | 3000 | 0.36:5.18 | 97.4 |
| 0.5 | 0.15 | 200 | 2000 | 0.36:3.88 | 93.7 |
| 0.5 | 0.15 | 210 | 2000 | 0.36:3.88 | 93.6 |
| 0.5 | 0.15 | 210 | 3500 | 0.36:5.21 | 97.3 |
| 0.5 | 0.15 | 220 | 3500 | 0.36:5.21 | 95.2 |
| 0.5 | 0.15 | 210 | 1000 | 0.35:2.45 | 98.6 |
| 0.5 | 0.15 | 230 | 3500 | 0.35:5.21 | 95.5 |
| 0.5 | 0.15 | 210 | 1500 | 0.36:2.56 | 97.9 |

**Table 2.** Results of the study into reaction kinetics of oxidative dehydrogenation of 3-methylcyclohexanol

| Concentration of cations, wt. % | | $T, {}^0C$ | Volumetric speed, hour$^{-1}$ | Molar ratio, $n_{alcohol}:n_{air}$ | Yield of 3-methylcyclohexanone, % |
|---|---|---|---|---|---|
| $Cu^{2+}$ | $Pd^{2+}$ | | | | |
| 0.5 | - | 210 | 1590 | 0.36:2.64 | 60.0 |
| 05 | 0.1 | 210 | 1590 | 0.36:2.64 | 95.2 |
| 0.5 | 015 | 210 | 1590 | 0.36:2.64 | 99.0 |
| 0.5 | 0.15 | 200 | 1590 | 0.36:2.64 | 97.2 |
| 0.5 | 0.15 | 180 | 1590 | 0.36:2.64 | 91.8 |
| 0.5 | 0.15 | 190 | 1590 | 0.36:2.64 | 95.9 |

| 0.5 | 0.15 | 210 | 3000 | 0.36:5.18 | 94.3 |
|-----|------|-----|------|-----------|------|
| 0.5 | 0.15 | 230 | 3000 | 0.36:5.18 | 96.0 |
| 0.5 | 0.15 | 200 | 2000 | 0.36:3.88 | 97.0 |
| 0.5 | 0.15 | 210 | 2000 | 0.36:3.88 | 97.7 |
| 0.5 | 0.15 | 210 | 3500 | 0.36:5.21 | 97.0 |
| 0.5 | 0.15 | 220 | 3500 | 0.36:5.21 | 98.2 |
| 0.5 | 0.15 | 210 | 1000 | 0.35:2.45 | 99.2 |
| 0.5 | 0.15 | 230 | 3500 | 0.35:5.21 | 97.5 |
| 0.5 | 0.15 | 210 | 1500 | 0.36:2.56 | 98.2 |

Based on the literature analysis [4] and carried out the experimental studies, the following mechanism of the oxidative dehydrogenation of 2-, 3-methylcyclohexanol has been proposed: upon the adsorption of 2-, 3-methylcyclohexanol, its protonation occurs with the participation of Bronsted acid sites of the catalyst with further elimination and formation of surface alcoholate. The transformation of the surface alcoholate into 2-, 3-methylcyclohexanone occurs when it interacts with dissociatively adsorbed oxygen atoms through the formation of a ketone-like surface compound on 2-, 3-methylcyclohexanone. In so doing, the initial state of the catalyst is restored. A simplified stage scheme of the mechanism can be represented as follows:

$$O_2 + 2Z \xrightarrow{k_1} 2ZO \qquad\qquad \frac{1}{2}$$

$$ZO + CH_3C_6H_{10}OH \xrightarrow{k_2} ZO(CH_3C_6H_{10}OH) \qquad 1$$

$$\underline{ZO(CH_3C_6H_{10}OH) \xrightarrow{k_3} Z + CH_3C_6H_9O + H_2O} \qquad 1$$

$$\frac{1}{2}O_2 + CH_3C_6H_{10}OH = CH_3C_6H_9O + H_2O$$

Here $k_1$, $k_2$, $k_2$ are reaction rate constants.

It should be noted that the process of formation of cyclohexanone and 4-methylcyclohexanone occurs exactly in line with this mechanism [7, 8]. In general, according to the above mechanism, oxidative dehydrogenation processes occur on modified zeolite catalysts for all cyclic and aliphatic alcohols.

Considering the identity of the mechanism of the above processes, their theoretically based kinetic models are the same as well. Thus, for parametric identification, i.e. for determining constants of the kinetic equation for the rate of formation of 2-, 3-methylcyclohexanone, there could be used the kinetic model of the rate of formation of cyclohexanone [7]:

$$r_{C_6H_{12}O} = k_1 P_2 \left[ \frac{\sqrt{1 + 4\left(\dfrac{k_1 P_2}{2k_2 P_1} + \dfrac{k_1 P_2}{2k_3}\right)} - 1}{2\left(\dfrac{k_1 P_2}{2k_2 P_1} + \dfrac{k_1 P_2}{2k_3}\right)} \right]^2,$$

where $r_{C_6H_{12}O}$ – rate of formation of cyclohexanone; $P_1$, $P_2$ – partial pressures of cyclohexanol and oxygen, respectively; $k_1$, $k_2$, $k_3$ – rate constants of stages corresponding to the index equal to the Arrhenius dependences:

$k_j = k_{0j}e^{-\frac{E_j}{RT}}$. Here $E_j$ – activation energy of the j-th reaction, $k_{0j}$ – pre-exponential factor of the rate constant of the j-th reaction.

On the basis of kinetic studies (Table 1, 2), the constants of kinetic models for processes of oxidative dehydrogenation of 2-, 3-methylcyclohexanol to 2-, 3-methylcyclohexanones have been determined.

Calculations of numerical values of the pre-exponential factors $\ln k_i^0 \left(\ln K_i^0\right)$ and activation energies $\left(E_i\right)$ have been carried out by the "Sliding tolerance" and "Powell" methods using the program "Poisk" system [9]. The numerical values of the constants of kinetic models for the formation of cyclohexanone and methylcyclohexanones are presented in Table 3.

**Table 3.** Numerical values of constants of kinetic models

| $\ln k^0$ | | E, kcal/mol | |
|---|---|---|---|
| Cyclohexanone | | | |
| $\ln k_I^{01}$ | 7.49 | $E_I^1$ | 8.56 |
| $\ln k_I^{02}$ | 0.68 | $E_I^2$ | 3.0 |
| $\ln k_I^{03}$ | 59.29 | $E_I^3$ | 9.45 |
| 2-Methylcyclohexanone | | | |
| $\ln k_{II}^{01}$ | 10.2 | $E_{II}^1$ | 7.0 |
| $\ln k_{II}^{02}$ | 1.15 | $E_{II}^2$ | 3.4 |
| $\ln k_{II}^{03}$ | 65.3 | $E_{II}^3$ | 6.5 |
| 3-Methylcyclohexanone | | | |
| $\ln k_{III}^{01}$ | 10.4 | $E_{III}^1$ | 7.1 |
| $\ln k_{III}^{02}$ | 1.1 | $E_{III}^2$ | 3.6 |
| $\ln k_{III}^{03}$ | 66.5 | $E_{III}^3$ | 6.7 |
| 4-Methylcyclohexanone | | | |
| $\ln k_{IV}^{01}$ | 10.5 | $E_{IV}^1$ | 7.2 |
| $\ln k_{IV}^{02}$ | 1.2 | $E_{IV}^2$ | 3.6 |
| $\ln k_{IV}^{03}$ | 65.6 | $E_{IV}^3$ | 6.8 |

With these numerical values of the kinetic parameters, the relative error of the experimental and calculated data does not exceed 3%. This confirms the correctness of the proposed hypothesis in the course of the said processes.

The reactivity of reagents in the studied oxidative dehydrogenation reactions over modified zeolite catalysts can be revealed on the basis of comparative analysis of their kinetic models. Since the right-hand sides of their kinetic equations have the same form, for comparison, we can use their rate constants as follows: $k_I$, $k_{II}$, $k_{III}$, $k_{IV}$ – the rate constant for the formation of cyclohexanone, 2-, 3-, and 4-methylcyclohexanones, respectively. They have the following Arrhenius dependencies:

$$k_I = k_I^{0i}e^{-\frac{E_I^i}{RT}}, \; k_{II} = k_{II}^{0i}e^{-\frac{E_{II}^i}{RT}}, \; k_{III} = k_{III}^{0i}e^{-\frac{E_{III}^i}{RT}}, \; k_{IV} = k_{IV}^{0i}e^{-\frac{E_{IV}^i}{RT}}$$

Here the value of i varies from one to three, according to the number of elementary stages.

## Conclusion

Since the reactions under consideration proceed on modified zeolite catalysts of the same nature, the numerical values of activation energies differ insignificantly (Table 3). So, for the first stage of the process in all the four processes of oxidative dehydrogenation reactions, we can write:

$$E_I^1 = 8.56; \qquad E_{II}^1 = 7.0; \qquad E_{III}^1 = 7.1; \qquad E_{IV}^1 = 7.2.$$

Hence it follows that to compare the rate of formation of target products, it is sufficient to compare pre-exponential factors of the rate constants. From the data shown in Table 3 this can be concluded for all three isomers of methylcyclohexanol $\ln k_{II-IV}^{01} \approx 10.5$, and for cyclohexanol $\ln k_I^{01} = 7.49$. Thus, all three isomers of methylcyclohexanol are more reactive in the oxidative dehydrogenation reaction than cyclohexanol which is consistent with literature data that substituents on the cyclohexane ring increase the rate of dehydrogenation. In this case, the methyl group accelerates the oxidative dehydrogenation process, and the isomer rates are practically the same, i.e.:

$$r_{2\text{-methylcyclohexsanone}} \approx r_{3\text{-methylcyclohexsanone}} \approx r_{4\text{- methylcyclohexsanone}} > r_{cyclohexsanone}$$

Here r – rate of formation of cyclohexanone, 2-, 3-, 4- methylcyclohexanones, respectively. Therefore, 2-, 3-, 4- methylcyclohexanols are more reactive in the oxidative dehydrogenation reaction than cyclohexanol.

## References

1. Chaudhari S.M., Waghulde A.S., Samuel V., Bari M.L. and Chumbale V.R. Characterization of ZnO and Modified ZnO Catalysts for Anaerobic Oxidation of Cyclohexanol. *Res. J.Chem. Sci*. 2013, vol. 3, issue 7, pp. 38-44.
2. Lebedev N.N. Chemistry and technology of basic and petrochemical synthesis. Moscow : Himiya Publ., 1981. 472 p.
3. Mekhtiev S.J., Aliyev A.F., Samedov Z.J. Oxidation of methylcyclohexane with atmospheric oxygen in the liquid phase. *Izv. AN Azerb. SSR. Ser. Phys.-tech. and chem.* 1958, no.6, pp. 137-149.
4. Fridman V.Z. and Davydov A.A. Dehydrogenation of Cyclohexanol on Copper-Containing Catalysts: I. The Influence of the Oxidation State of Copper on the Activity of Copper Sites. *J.Catal.* 2000, vol. 195(1), pp. 20-30.
5. Aliyev A.M, Majidova S.M., Aliyeva M.G., Ali-zade G.A. Method of obtaining cyclohexanone. Pat. Azerbaijan: a 2011 0183; 30.11.2011.
6. Aliyev A.M., Aliyeva M.G., Najaf-Guliyev U.M., Ali-zade G.A., Shabanova Z.A. Method of obtaining methylcyclohexane. Pat. Azerbaijan: a 2018 0108; 11.09.2019.
7. Aliev A.M., Shabanova Z.A., Alieva M.K., Ali-zade G.A. Selection of active modified zeolite catalyst and reaction kinetics of oxidative dehydrogenation of cyclohexanol to cyclohexanone. *Neftepererabotka i neftechimiya - «Oil Processing and Petrochemistry»*. 2017, no. 2, pp. 38-48. (In Russian).
8. Aliyev A.M., Aliyeva M.G., Ali-zade G.A., Nadzhaf-Kuliyev U.M., Aliyev F.V., Akhmedov R.A., Abbasov M.Ya., Guseynova T.I., Agayeva R.Yu. Oxidative dehydration 4-methylcyclohexanol in 4-methylcyclohexanone on natural clinoptylolite modified by copper and palladium cations. *Neftepererabotka i neftechimiya - «Oil Processing and Petrochemistry»*. 2021, no. 1, pp. 29-31. (In Russian).

9. Shakhtakhtinsky T.N., Bakhmanov M.F., Kelbaliev G.I. Methods for optimizing the processes of chemical technology with computer programs. Baku: Elm Publ., 1985, 260 p.

### *MODİFİKASİYA OLUNMUŞ SEOLİT KATALİZATORLARI ÜZƏRİNDƏ OKSİDLƏŞDİRİCİ DEHİDROGENLƏŞMƏ REAKSİYALARINDA TSİKLOHEKSANOLUN VƏ METİLTSİKLOHEKSANOLLARIN REAKSİYA QABİLİYYƏTİNİN ÖYRƏNİLMƏSİ*

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*Məqalədə seolit katalizatorları üzərində oksidləşdirici dehidrogenləşmə reaksiyalarında tsikloheksanolun və metiltsikloheksanolun izomerlərinin reaksiya qabiliyyətinin öyrənilməsi və müqaisəli tədqiqi göstərilib. Müəyyən olunub ki, metiltsikloheksanolun bütün izomerlərinin oksidləşdirici dehidrogenləşmə reaksiyalarının sürətləri praktiki olaraq bərabərdirlər və tsikloheksanolun tsikloheksanona oksidləşdirici dehidrogenləşmə reaksiyasının sürətindən yüksəkdirlər.*
***Açar sözlər:*** *tsikloheksanol, metiltsikloheksanol, seolitlər, reaksiya qabiliyyəti, reaksiyanın mexanizmi.*

### *ИЗУЧЕНИЕ РЕАКЦИОННОЙ СПОСОБНОСТИ ЦИКЛОГЕКСАНОЛА И МЕТИЛЦИКЛОГЕКСАНОЛОВ В РЕАКЦИИ ОКИСЛИТЕЛЬНОГО ДЕГИДРИРОВАНИЯ НА МОДИФИЦИРОВАННЫХ ЦЕОЛИТНЫХ КАТАЛИЗАТОРАХ*

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*В работе проведено исследование по изучению и сравнению реакционной способности циклогексанола и изомеров метилциклогексанола в реакции окислительного дегидрирования на модифицированных цеолитных катализаторах. Было выявлено, что скорости процессов окислительного дегидрирования всех изомеров метилциклогексанола практически одинаковые и превышают скорость окислительного дегидрирования циклогексанола в циклогексанон.*

***Ключевые слова:*** *циклогексанол, метилциклогексанол, цеолиты, реакционная способность, механизм реакции.*