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STUDY OF KINETIC REGULARITIES OF THE OXIDATIVE CONVERSION OF PROPYLENE TO ACROLEIN ON A MODIFIED CLINOPTILOLITE

Abstract. The kinetic regularities of oxidative conversion of propylene to acrolein with 1 % Ni^{2+}-clinoptilolite catalyst at different temperatures (320–380 °C), volume rates of 700–1 400 h^{-1} and partial pressures ($P_{C_3H_6}$ = 0.36–0.46 atm., P_{O_2} = 0.55–0.64 atm.), have been studied. On the basis of the experimental data, a stepwise scheme of the reaction course was proposed.

Keywords: kinetics, oxidative conversion, propylene, acrolein

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ИССЛЕДОВАНИЕ КИНЕТИЧЕСКИХ ЗАКОНОМЕРНОСТЕЙ ОКИСЛИТЕЛЬНОГО ПРЕВРАЩЕНИЯ ПРОПИЛЕНА В АКРОЛЕИН НА МОДИФИЦИРОВАННОМ КЛИНОПТИЛОЛИТЕ

Аннотация. Изучены кинетические закономерности реакции окислительного превращения пропилена в акролеин на катализаторе 1 % Ni^{2+}-клиноптилолит, при различных температурах (320–380 °C), объемных скоростях |700–1 400 $ч^{-1}$ и парциальных давлениях реагентов ($P_{C_3H_6}$ = 0,36–0,46 атм., P_{O_2} = 0,55–0,64 атм.). На основе экспериментальных данных предложена стадийная схема протекания реакции.

Ключевые слова: кинетика, окислительное превращение, пропилен, акролеин

Для цитирования. Исследование кинетических закономерностей окислительного превращения пропилена в акролеин на модифицированном клиноптилолите / Т. И. Гусейнова, Г. А. Али-заде, М. Г. Алиева, В. М. Ярыев // Весці Нацыянальнай акадэміі навук Беларусі. Серыя хімічных навук. – 2025. – Т. 61, № 1. – С. 24–29. https://doi.org/10.29235/1561-8331-2025-61-1-24-29

Introduction. Acyclic unsaturated hydrocarbons are essential chemical feedstocks for the synthesis of various classes of polyfunctional substances. In particular, catalytic oxidation of propylene is one of the main methods for obtaining monomers and intermediates in organic synthesis, and it is also one of the main methods for obtaining acrolein. Acrolein is an intermediate in the organic synthesis of acrylic acid, glycerol, glutaric aldehyde, allyl ether, methionine, glycidyl alcohol, nicotinic acid, etc. With the increasing demand of the above compounds in the national economy, a lot of attention is being paid to studies on the catalytic oxidation of propylene. The catalytic oxidation of propylene is also of interest from a theoretical point of view.

Acrolein was first produced in industry by the catalytic condensation of acetaldehyde with formaldehyde. This method consists of passing a 30 % aqueous solution of formaldehyde and acetaldehyde over silica gel impregnated with Na_2SiO_3 at 300–320 °C [1]. The main disadvantages of the process are the formation of a large number of by-products and the short lifetime of the catalyst.

The partial vapour phase oxidation of propylene in the presence of heterogeneous catalysts is the main industrial method of acrolein production [2, 3]. This process is the first stage of large-scale industrial production of acrylic acid and its esters. CO_2, CO, acetic aldehyde, acetaldehyde, maleic anhydride are formed as by-products. Among oxides, copper (I) oxide is the most active and selective catalyst for steam-phase oxidation of propylene to acrolein [4]. Among the many complex oxide catalysts for the oxidation of propylene, molybdenum-containing catalysts are the most widely used. These catalysts achieve fairly high selectivity with short contact times and moderate temperatures. The reaction produces propionic aldehyde along with acrolein. The purification of acrolein from near boiling propionic aldehyde increases the cost of acrolein. A disadvantage of the process is that the reaction takes place at high temperature and the yield of acrolein is very low. [5–7]

Molybdenum oxide has low activity in oxidation reaction of propylene to acrolein [8]. Addition of bismuth increases selectivity of acrolein formation in presence of molybdenum catalysts $Mo_{12}Bi_xFe_yTl_z$ and $Mo_{12}Bi_xFe_yTl_zNi_6Zn_3$ [9].

Previously we have conducted studies on the synthesis of modified zeolites with metal cations by ionic exchange method and determination of catalytic activity in the reaction of oxidative conversion of propylene to acrolein [10].

The aim of this work was the synthesis of modified zeolites with metal cations by ion exchange method, determination of their catalytic activity in the reaction of oxidative conversion of propylene to acrolein using a highly active metal zeolite catalyst based on zeolite H-clinoptilolite ($SiO_2 / Al_2O_3 = 10$) modified with 1% Ni^{2+} cation.

We found that, in contrast to wide-porous zeolites, on narrow porous zeolites the catalyst contains a significant amount of appropriate unsaturated hydrocarbons, the proportion of which varies over a wide range depending on the nature of cations. Studies have shown that the selectivity of reaction for acrolein varies depending on the nature of zeolite, the content of cations in zeolite composition and reaction conditions.

In our previous work [10] it was shown that Ni-clinoptylolite exhibits the highest activity and selectivity in the reaction of oxidative conversion of propylene to acrolein.

Experimental. Kinetic experiments were carried out in the flowing apparatus at a temperature range 320–380 °C, volume rates 700–1 400h^{-1}, partial pressures of reagents $P_{C_3H_6} = 0.36–0.46$ atm., $= 0.55–0.64$ atm. By special experiments, the absence of internal and external diffusion inhibition was established, which indicates that the reaction proceeds in the kinetic region.

In our previous works [10, 11], catalysts with particle size 0.25–0.63 mm and 99.2 % propylene; 99.3 % oxygen were used for catalytic activity studies. The obtained catalysts were activated by air purging at temperatures of 300–350 °C and tested on a flow laboratory apparatus, the reaction unit of which was directly connected to the chromatograph. The reaction products were separated under conditions of linearly programmed thermostat temperature rise on an Agilent 7820 GC using a capillary column, HP-5-MS (30 m length).

Catalysts were synthesized using ion-exchange method. In the work we used synthetic zeolites NaY(SiO_2/Al_2O_3 ($\lambda = 4.2$), NaX($\lambda = 2.9$), NaA($\lambda = 2.0$) and natural zeolites clinoptilolite ($\lambda = 10$) and mordenite ($\lambda = 9.6$) from the deposits of Azerbaijan modified by different cations of transition and nontransition elements (Ni, Zn, Cu, Co, Cr, Mn, Fe, Mg, Mn, Bi, Pd and so on). Before ion-exchange natural zeolites were processed with 0.5 N HCl. The amount of introduced cations in the zeolite composition was determined by ion spectral analysis on an “ICP-MS Agilent 7700” instrument.

It follows from the data of Table 1 that the introduction of various cations of transition and non-transition metals (Ni, Zn, Cu, Co, Cr, Mn, Fe, Mg, Mn, Bi, Pd etc.) into the clinoptilolite composition leads to a change in the activity of this catalyst. Thus, it was found that the influence of these metal cations is not the same, since in the reaction each of these cations manifests itself differently.

It was found that the highest yield of acrolein is observed on Ni-clinoptilolite catalyst containing Ni^{2+} 1 % (exp. № 6). Increasing the concentration of this cation in the catalyst leads to a decrease in acrolein yield (exp. № 7, 8).

On the investigated catalyst, the main reaction product of oxidative transformation of propylene is acrolein, and in small amounts – formaldehyde, formic acid carbon oxide (II). The yield of these products depends on the reaction conditions – temperature, molar ratio of the reactants and volumetric feed rate of the reaction mixture.

Table 1. **Oxidative conversion of propylene to acrolein on modified natural clinoptilolite (T = 380 °C, V_0 = 700 hr^{-1}, $C_3H_6 : O_2$ = 1,8 : 1)**

Number of experiment	Composition of zeolite, % mass.	X, %	S, %	Yield of reaction products, %			
				CO_2	HCOH	C_3H_4O	HCOOH
1	Zn (0.2)	37.5	5.25	22.13	13.4	1.97	–
2	Cu (0.5)	58.27	–	38.65	19.6	–	–
3	Co (0.5)	59.81	–	46.37	13.44	–	–
4	Mg (1)	63.03	68.47	8.86	10.31	43.16	0.66
5	Pd (1)	60.37	–	53.37	7	–	–
6	Ni (1)	94.72	85.44	5.44	5.75	80.93	2.6
7	Ni (3)	69.83	68.85	11.96	4.19	48.08	5.6
8	Ni (5)	74.36	48.95	25.74	8.02	36.04	4.2
9	CuFe (0.5 : 0.25)	56.03	18.03	29.8	15.7	10.1	0.4
10	CuPd (0.5 : 0.25)	50.53	–	50.03	–	–	–
11	CoBi (0.5 : 1)	53.83	26.56	24.09	15.07	14.3	0.37
12	ZnCoCr (0.2 : 0.5 : 0.25)	68.35	65	14.96	8.4	44.43	0.56
13	CuPdZn (2 : 1 : 2)	64.52	–	65.52	–	–	–
14	CuMnCo (1 : 0.5 : 0.5)	51.41	16.69	33.25	9.34	8.58	0.24

Results and Discussion. The results of a study of the effect of the partial pressures of the reactants on the reaction are shown in figure 1 below.

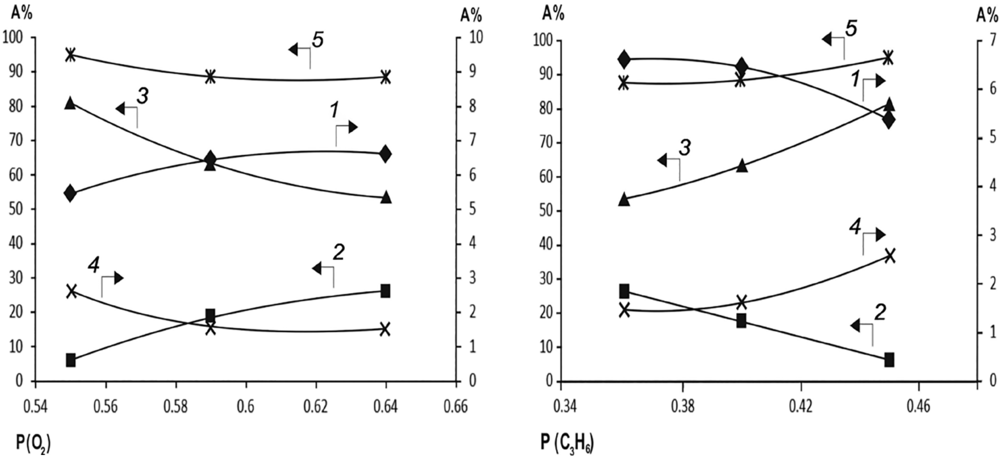
As can be seen from Figure 1, *a* an increase P_{O_2} = 0.55–0.64 atm. leads to a decrease in acrolein yield. In the studied interval the conversion of propylene decreases with increasing partial oxygen pressure.

Figure 1, *b* shows that the acrolein yield dependence has an extreme character at temperature 380 °C, volume rate 700 h^{-1}, at P_{O_2} = 0.55 atm. and varying $P_{C_3H_6}$ from 0.36–0.46 atm. The maximum yield is reached at $P_{C_3H_6}$ = 0.45 atm., its further increase leads to insignificant decrease of acrolein yield. At a given oxygen partial pressure, relatively high partial pressures of propylene prevent coordination of oxygen relative to the active centres of the metal zeolite catalyst.

Similar patterns of dependencies of the reaction product yields on the partial pressures of the reactants are also observed when the reactions are carried out at other temperatures (table 2).

From the above results, it follows that the optimum partial pressures of the reagents, at which the highest acrolein yield is achieved, are: $P_{C_3H_6}$ = 0.45 atm. and P_{O_2} = 0.55 atm.

The effect of temperature and volume feed rate of the reaction mixture on the reaction was investigated under optimum conditions $P_{C_3H_6}$ and P_{O_2}. The results are shown in Fig. 2 and 3. [11]



a *b*

Fig. 1. Dependences of propylene conversion and yields of reaction products on partial pressures of oxygen (*a*) and propylene (*b*) at molar ratio $C_3H_6 : O_2$ = 1,8 : 1 and Ò – 380 °C (*1* – carbon dioxide*, 2* – formaldehyde, *3* – acrolein, *4* – formic acid, *5* – conversion)

Table 2. **Results of investigations of kinetic regularities of propylene oxidative conversion reaction on Ni^{2+}-clinoptilolite catalyst at $V = 700\ h^{-1}$**

T, °C	$P_{C_3H_6}$	P_{O_2}	Reaction product yield, %				X, %
			A_{CO_2}	A_{CH_2O}	$A_{C_3H_4O}$	A_{HCOOH}	
320	0.36	0.64	0.4	18.8	13.4	0.3	32.9
330	0.36	0.64	0.9	19.4	18.3	0.4	39.0
340	0.36	0.64	1.6	20.0	21.2	0.5	43.3
350	0.36	0.64	2.1	22.4	39.4	0.6	64.5
360	0.36	0.64	3.2	23.7	49.8	0.7	77.4
370	0.36	0.64	4.9	24.7	51.8	0.8	82.2
380	0.36	0.64	6.2	26.2	53.5	1.9	87.8
320	0.4	0.6	0.2	10.2	27.4	0.5	38.3
330	0.4	0.6	0.3	12.3	34.1	0.6	47.3
340	0.4	0.6	1.0	13.2	41.3	0.7	56.2
350	0.4	0.6	3.0	14.5	55.6	0.9	74.0
360	0.4	0.6	4.7	15.0	59.4	0.9	80.0
370	0.4	0.6	5.1	16.4	60.4	1.3	83.2
380	0.4	0.6	6.4	17.5	63.2	1.6	88.7
320	0.45	0.55	0.5	3.2	35.1	0.8	39.6
330	0.45	0.55	0.6	3.8	41.7	0.9	47.0
340	0.45	0.55	1.6	4.0	55.0	1.2	61.8
350	0.45	0.55	3.5	4.4	73.5	1.4	82.8
360	0.45	0.55	4.9	5.0	76.7	1.9	88.5
370	0.45	0.55	5.0	5.4	78.5	2.0	90.9
380	0.45	0.55	5.4	5.8	80.9	2.6	94.7

Figure 2 shows that with increasing temperature from 320 to 380 °C the yield of acrolein increases and at 380 °C it reaches 80.93 % and further increasing temperature practically does not change. In the whole temperature range studied the yield of other substances also increases with increasing temperature. The yields of formaldehyde, carbon dioxide and formic acid also increase with increasing temperature. This is due to the deep oxidation of propylene at high temperatures.

With increasing the volumetric rate from 700–1400 h^{-1} at molar ratio $C_3H_6 : O_2 = 1.8 : 1$ and temperature 380 °C, the yield of acrolein, formaldehyde, carbon dioxide and formic acid decreases due to decreasing contact time (Fig. 3).

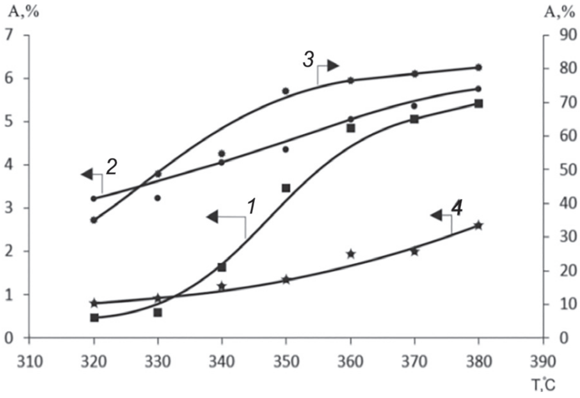


Fig. 2. Dependence of the yield A of the reaction products acrolein (*3*), formaldehyde (*2*), carbon dioxide (*1*) and formic acid (*4*) from reaction temperature at molar ratio $C_3H_6 : O_2 = 1.8 : 1$ and $V_0 = 700\ h^{-1}$

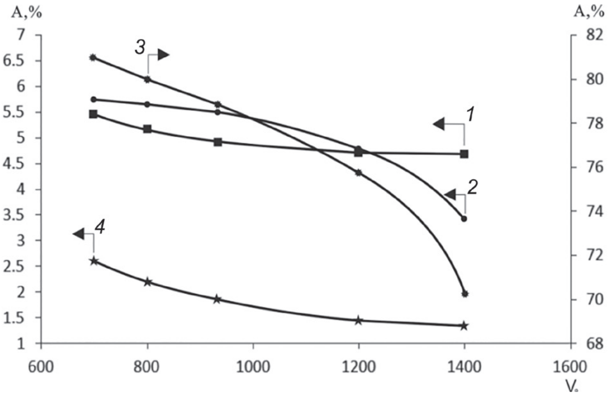
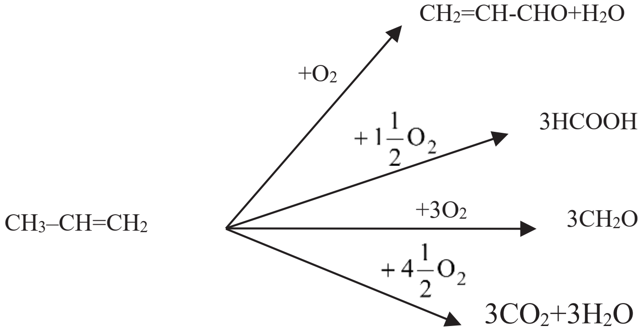


Fig. 3. Influence of the volume rate on the yield A of acrolein (*3*), formaldehyde (*2*), carbon dioxide (*1*) and formic acid (*4*) at a molar ratio $C_3H_6 : O_2 = 1.8 : 1$ and $T = 380$ °C

Based on the experimental data obtained, the following scheme of propylene oxidation reaction on metal-ceolyte catalyst Ni-clinoptilolite is assumed:



The aim was achieved on the basis of zeolite H-clinoptilolite modified with 1% Ni^{2+} cation on the catalyst surface in the temperature range 360–400 °C, molar ratio $C_3H_6 : O_2 = 1.8 : 1$.

Table 3 shows the dependences of propylene conversion, acrolein yield and process selectivity on volume rate and contact time at different temperatures. The highest selectivity of the process is 92–93.1 %, which is observed in the temperature range 360–380 °C, at the volume rate of 1 500 h^{-1}, propylene conversion of 58.6–76.2 % and acrolein yield is 54.6–70.3 %.

Table 3. **Results of experiments on the oxidative conversion of propylene to acrolein on 1 % Ni^{2+}-clinoptilolite**

Catalyst	T, °C	Volume rate velocity V_0, h^{-1}	Contact time, τ, sec.	Propylene conversion, %	Acrolein yield, %	Propylene selectivity, %
1 % Ni^{2+}-clinoptilolite	360	700	5.1	67.2	59.7	88.9
	360	1 125	3.2	63.6	57.4	90.2
	360	1 500	2.4	58.6	54.6	93.1
	370	700	5.1	74.0	64.2	86.7
	370	1 125	3.2	69.6	61.8	88.7
	370	1 500	2.4	65.1	58.7	90.1
	380	700	5.1	84.5	75.6	89.4
	380	1 125	3.2	82.7	74.5	90.1
	380	1 500	2.4	76.2	70.3	92.3
	400	700	5.1	90.3	72.9	80.8
	400	1 125	3.2	86.4	70.7	81.8
	400	1 500	2.4	81.5	69.0	84.7

Conclusions. Thus, the set task was achieved on the basis of H-clinoptilolite zeolite modified with 1 % Ni^{2+} cation on the catalyst surface in the temperature range 360–400 °C, molar ratio $C_3H_6 : O_2 = 1.8 : 1$, volume rate 700–1 500 h^{-1} and at contact time 2.4–3.2 sec.

References

1. Gallagher Milton, Hasche Rudolph Leonard. *Process for the manufacture of unsaturated aldehydes*. Patent US 2245582. Publ. date 17 Juny 1941. Available at: https://patents.google.com/patent/US2245582A/en (accessed 25.05.2023).

2. Alkhazov T. G., Adjamov K. Yu., Khanmamedova A. K. Catalytic oxidation of propylene. *Russian Chemical Reviews*, 1982, vol. 51, no. 6, pp. 950–967. https://doi.org/10.1070/RC1982v051n06ABEH002858

3. Keiko N. A., Voronkov M. G. Methods for the synthesis of acrolein and its α-substituted. *Russian Chemical Reviews*, 1993, vol. 62, no. 8, pp. 796–812. https://doi.org/10.1070/RC1993v062n08ABEH000045

4. Hearne G. W., Adams M. L. Catalytic oxidation of hydrocarbons. Patent US 2486842. Publ. Date 01 November 1949. Available at: https://patents.google.com/patent/US2486842A/en?oq=Catalytic+oxidation+of+hydrocarbons:+pat.+-2486842+US.+%E2%84%96+677530 (accessed 25.05.2023).

5. Yukelson I. I. *Technology of basic organic synthesis*. Moscow, Khimiya Publ., 1968. 507 p. (in Russian).

6. Lebedev N. N. *Chemistry and technology of basic organic and petrochemical synthesis*. Moscow, Khimiya Publ., 1998. 592 p. (in Russian).

7. Boreskov G. K. *Heterogeneous catalysis*. Moscow, Nauka Publ., 1989. 197 p. (in Russian).

8. Volta J.-C., Bertrand O., Floquet N. On the reaction specificity of MoO_3 faces: the role of $Mo_{18}O_{52}$ as a precursor for MoO_3 propylene oxidation catalysts. *Journal of the Chemical Society, Chemical Communications*, 1985, no. 19, pp. 1283–1285. https://doi.org/10.1039/c39850001283

9. Hayakawa T., Tsunoda T., Orita H., Kameyama T., Ueda M., Fukuda K., Takehira K. A solid electrolyte-aided study of alkene oxidation on a molybdate catalyst having the scheelite structure. *Journal of the Chemical Society, Chemical Communications*, 1988, no. 24, pp. 1593–1594. https://doi.org/10.1039/C39880001593

10. Aliev A. M., Najaf-Kuliev U. M., Huseynova T. I., Saryjanov A. A., Safarov A. R., Bakhmanov M. F., Agaeva R. Y., Yaryev V. M. Selection of an active modified zeolite catalyst and studying the kinetics and mechanism of the oxidative conversion of propylene in acrol. *Oil Refining and Petrochemistry*, 2019, no. 5, pp. 25–30.

11. Aliyev A. M., Najaf-Guliyev U. M., Huseynova T. I., Yariyev V. M., Kazimova E. M. Oxidative conversion of propylene to acroleın on metal zeolite catalysts. *Azerbayjan chemical journal*, 2019, no. 1, pp. 28–31. https://doi.org/10.32737/0005-2531-2019-1-28-31

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