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OXIDATIVE CONVERSION OF PROPYLENE TO ACROLEIN ON METAL ZEOLITE CATALYSTS**A.M.Aliyev, U.M.Najaf-Guliyev, T.I.Huseynova, V.M.Yariyev***M.Nagiyev Institute of Catalysis and Inorganic Chemistry, NAS of Azerbaijan**necef-quliyev86@mail.ru*

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Catalytic activity of modified zeolites in the reactions of oxidative conversion of propylene to was studied. It was established that Ni-clinoptilolite (1% Ni²⁺) exhibits high activity in theacrolein reaction. The influence of the reaction temperature and volume rate on product yield on the active catalyst was investigated.

Keywords: oxidative conversion, acrylaldehyde, Ni-clinoptilolite, mordenite activity, NaY, NaX, NaA.

Introduction

Acrolein is an initial raw material for obtaining a wide range of valuable products. The main direction of processing acrolein is the production of acrylic acid used to produce effective sorbents, acrylic emulsions in lacquer dye industry, drilling reagents, polyacrylonitrile fiber and acrylate rubbers, construction mixtures and glues. Acrylaldehyde is used as an intermediate product in production of synthetic glycerin, plastics and other important products. For example, methionine or γ -methylthiol- α -aminobutyric acid which is an effective fodder radiation for poultry is obtained from acrylaldehyde.

For the first time acrylaldehyde was produced by condensation of acetaldehyde with formaldehyde. Presently the only and almost important way of its synthesis is oxidation of propylene which has clear advantages over previous method [1].

Preparation of catalysts directing the oxidation towards primary formation of acrylaldehyde was of great importance for a selective performance of the process. The first of them was cuprous oxide on carriers (0.1–1.5% Cu₂O on pumice, a carborundumsic or Al₂O₃) or even copper tubes of the reactor. Disadvantage of the process is that reaction goes at a high temperature and degree of conversion of propylene to acrylaldehyde is very low.

Contacts were developed later from bismuth molybdate (Bi₂O₃·MoO₃) and bismuth phosphormolybdate (Bi₂O₃·MoO₃·P₂O₅) containing promoters. On these catalysts rather high selectivity is achieved at a short time of contact

and moderate temperature. Disadvantage of the process is that reaction proceeds at a high temperature and yield of acrylaldehyde is very low [2].

From literature data studied by us it was found out that the reaction of oxidative conversion of propylene to acrylaldehyde is mainly performed with the presence of catalysts modified by various metals and containing oxides Bi–Mo. However, oxidative conversion of propylene to acrylaldehyde on metalzeolite catalysts belongs to insufficiently known heterogeneous-catalytic reactions which proceeds with oxygen.

The present work provides the research results of oxidative conversion of propylene to detect the conditions of selective formation to acrylaldehyde in the presence of modified zeolite catalysts. The role of many modifiers used for the preparation of zeolite-containing catalysts has not been clarified. Great problem is the stability of the work of zeolite-containing catalysts which depends on many factors, including resistance to coke formation and regenerability, as well as fixation of modifying additions on zeolite support.

Experimental part

The reaction was performed on the laboratory-scale flowing unit with quartz reactor under stationary layer of a catalyst at atmospheric pressure in the temperature range of 320–380°C, volume rate of 700–1400 h⁻¹ and molar ratio C₃H₆:O₂=1.8:(1–1.8).

In the work we used synthetic zeolites NaY($\text{SiO}_2/\text{Al}_2\text{O}_3=\lambda=4.2$), 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).

Catalysts were synthesized using ion-exchange method [3]. Before ion-exchange natural zeolites were processed by 0.5 N HCl. The amount of introduced elements into the composition of zeolite was determined by ion spectral analysis on "ICP-MS Agilent 7700" and was 0.1–2% from zeolite mass. In the work we used catalysts with the size of particles 0.25–0.63 mm, 99.2% propylene, 99.3% oxygen, 99.9% helium.

Analysis of raw materials and reaction products was performed on gas chromatograph connected directly with a reactionary unit. Separation of reaction products was conducted in a column of 3 min length filled with. Paropac-PC under the conditions of linear programmed rise

of temperature of thermostat chromatograph from 50 to 200°C.

Reaction products were also analyzed on gas chromatograph "Agilent 7890" with mass detector "Agilent 5975" with column HP-5 MS of 30 min length.

Results and discussion

At first catalytic activity of primary zeolites in oxidative conversion reaction of propylene was studied. Table 1 shows the results of studies on zeolites which do not contain metal cations. The results of studies confirmed that Na-forms (NaY, NaX) of zeolites are not practically activated in this reaction. Unlike wide-pore narrow-pore zeolites characterized with less surface (8.0–20.0 m²/g) and small sizes of pores (4.2–4.9 Å) facilitate conversion of propylene to acrylaldehyde.

As follows from Table 1 among cation forms of narrow-pore zeolites the highest yield of acrylaldehyde is observed on natural clinoptilolite.

Table 1. Oxidative conversion of propylene to acrylaldehyde on different initial zeolites ($T=380^\circ\text{C}$, $V_0=700\text{ h}^{-1}$, $\text{C}_3\text{H}_6:\text{O}_2=1.8:1$)

Zeolite	$x, \%$	$s, \%$	Yield of reaction products, %			
			CO_2	HCOH	$\text{C}_3\text{H}_4\text{O}$	HCOOH
NaY	24.7	–	21.5	3.2	–	–
NaX	20.5	–	18.4	2.1	–	–
NaA	11.49	12.18	2.1	7.9	1.4	0.09
Mordenite	13.11	14.49	2.8	8.3	1.9	0.11
Clinoptilolite	19.9	21.1	3.5	10.4	4.2	1.8

Note: x – conversion of propylene, s – selectivity of the process by acrylaldehyde

Table 2. Oxidative conversion of propylene to acrylaldehyde on modified natural clinoptilolite ($T=380^\circ\text{C}$, $V_0=700\text{ h}^{-1}$, $\text{C}_3\text{H}_6:\text{O}_2=1.8:1$)

Number of experiment	Composition of zeolite, mas. %	$x, \%$	$s, \%$	Yield of reaction products, %			
				CO_2	HCOH	$\text{C}_3\text{H}_4\text{O}$	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

Introducing different cations of transition and nontransition metals (Ni, Zn, Cu, Co, Cr, Mn, Fe, Mg, Mn, Bi, Pd and so on) into clinoptilolite leads to the change of activity of this catalyst. It has been established that the effect of cations of these metals is not similar, since each of these cations behave differently in the reaction (Table 2). As a result of studies it is established that the highest yield of acrylaldehyde is observed on catalyst Ni-clinoptilolite containing $\text{Ni}^{2+}=1\%$ (exper. No 6). Increase in concentration of this cation in the composition of catalyst decreases the yield of acrylaldehyde (exper. No 7, 8).

The influence of reaction temperature and volume rate on the yield of products on active catalyst was studied.

As Figure 1 shows when temperature is

Fig. 1. Dependence of yield of A reaction products of acrylaldehyde (3), formaldehyde (2), carbon dioxide (1) and formic acid (4) on reaction temperature at molar ratio $\text{C}_3\text{H}_6:\text{O}_2=1.8:1$ and $V_0=700 \text{ h}^{-1}$.

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METALSEOLİT KATALİZATORLAR ÜZƏRİNDƏ PROPİLENİN AKROLEİNƏ OKSİDLƏŞDİRİCİ ÇEVİRİLMƏSİ

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Modifikasiya olunmuş seolit katalizatorları üzərində propilenin akroleinə oksidləşdirici çevrilmə reaksiyasında katalitik aktivlikləri tədqiq olunmuşdur. Müəyyən olunmuşdur ki, Ni-klinoptilolit ($\text{Ni}^{2+}=1\%$) bu reaksiya üçün yüksək katalitik aktivlik göstərir. Aktiv katalizator üzərində reaksiya məhsullarının çıxımının reaksiyanın temperaturu və həcmi sürətdən asılılığı öyrənilmişdir.

Açar sözlər: oksidləşdirici çevrilmə, akrolein, NaY , NaX , NaA .

increased from 320 to 380°C the yield of acrylaldehyde rises continuously and at 380°C reaches 80.93%, but at further increase in temperature it does not practically change. In studied temperature range at high temperature yield of other substances also increases.

When volume rate increases from 700 to 1400 h^{-1} , the yield of acrylaldehyde and other reaction products decreases (Figure 2).

Thus, the studies showed the opportunity to convert propylene to acrylaldehyde on zeolite catalysts. We determined optimum composition of cation ($\text{Ni}^{2+}=1\%$) introduced into clinoptilolite and optimum conditions for the reaction ($T=380^\circ\text{C}$, $V_0=700 \text{ h}^{-1}$, $\text{C}_3\text{H}_6:\text{O}_2=1.8:1$) under which the yield of acrylaldehyde reaches 80.93%, in conversion of propylene it is 94.72%.

Fig. 2. Effect of volume rate on the yield of A acrylaldehyde (3), formaldehyde (2), carbon dioxide (1) and formic acid (4) at molar ratio $\text{C}_3\text{H}_6:\text{O}_2=1.8:1$ and $T=380^\circ\text{C}$.

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ОКИСЛИТЕЛЬНОЕ ПРЕВРАЩЕНИЕ ПРОПИЛЕНА В АКРОЛЕИН НА МЕТАЛЦЕОЛИТНЫХ КАТАЛИЗАТОРАХ**А.М.Алиев, У.М.Наджаф-Кулиев, Т.И.Гусейнова, В.М.Ярыев**

Исследована каталитическая активность модифицированных цеолитов в реакциях окислительного превращения пропилена в акролеин. Установлено, что Ni-клиноптилолит, (1% Ni^{2+}) проявляет высокую активность в рассматриваемой реакции. Изучено влияние температуры реакции и объёмной скорости на выход продуктов на активном катализаторе.

Ключевые слова: окислительное превращение, акриальдегид, Ni-клиноптилолит, морденит, активность, NaY, NaX, NaA.