UDC 542.943, 547.313.3, 547.211

**OXIDATIVE CONVERSION OF LOWER OLEFINS AND PARAFFINS
OVER THE MODIFIED ZEOLITE CATALYSTS****A.M.Aliyev, F.V.Aliyev, U.M.Najaf-Guliyev, R.I. Akhmadov, T.I.Huseynova, R.Y.Agayeva***M.Nagiyev Institute of Catalysis and Inorganic Chemistry, NAS of Azerbaijan*

With the purpose of development of high efficiency catalysts for reactions of the oxidative conversion of lower olefins and paraffins into the desired products of petrochemical industry it has been synthesized by ion exchange method a range of the metalzeolite catalysts on the basis of synthetic (NaY) and natural (pure and dealuminated clinoptilolite and mordenite) zeolites and the cations of different metals. It has been established that the metalzeolite catalysts prepared on the basis of synthetic zeolite NaY shows relatively high activity in the oxidative conversion of ethylene and propylene into acetaldehyde and acetone accordingly. It has been also synthesized a highly effective metalzeolite catalysts for the processes: oxidative conversion of methane into ethylene; oxidative conversion of propane into acetaldehyde and formaldehyde; oxidative conversion of methane to ethylene and acetylene; oxidative conversion of methane to 1,4-butanediol.

Keywords: zeolites, activity, lower olefins, paraffins, oxidative conversion.

doi

Introduction

The development of high efficiency metalzeolite catalysts for the gas phase reactions of oxidation of ethylene and propylene into acetaldehyde and acetone accordingly as well as for oxidative conversion of methane into ethylene and partial oxidation of propane into acetaldehyde and formaldehyde is of great significance with point of view of industrial realization.

In the literature, by way of the catalysts for oxidation of ethylene and propylene into acetaldehyde and acetone accordingly have been suggested the different salts of palladium on the surface of the different carriers, palladium with additions deposited on surface of aluminum oxide and palladium and copper containing zeolites. From these catalysts, palladium and copper containing zeolites are more perspective which have the relatively high activity [1–4]. Industrial realization of the gas phase oxidation of ethylene and propylene over zeolite catalysts into acetaldehyde and acetone accordingly are required their further improvement by means of selection more efficiency metalzeolites.

Numerous of the literatures data testify that the different mixed oxides of metals show relatively high catalytic activity in the reactions of oxidation of the lower paraffin hydrocarbons [5–7]. Until recently, however little attention

had been given to the possibility of employing of the modified zeolites for promoting these reactions. The use of the modified zeolites with different cations for catalyzing the reactions of oxidative conversion of methane into ethylene, acetylene and partial oxidation of propane into lower carbonyl compounds are not described in the literature.

In the present paper has been given the results of the investigation on selection of high efficiency metalzeolite catalysts of oxidation ethylene and propylene into acetaldehyde and acetone accordingly; oxidative conversion of methane into ethylene; partial oxidation of propane into acetaldehyde and formaldehyde; oxidation of propylene to acrolein; oxidative conversion of methane into ethylene and acetylene and oxidative conversion of methane into 1,4-butanediol.

Experimental part

It has been prepared series of the specimens of metalzeolites modified with cations of the different metals (Pd^{2+} , Cu^{2+} , Mg^{2+} , Ca^{2+} , Sr^{2+} , Ba^{2+} , Sn^{2+} , Li^{+}) on the basis of synthetic zeolite (NaY) and Azerbaijan natural zeolites (pure and dealuminated clinoptilolite and mordenite). Zeolites modified with the cations of the different metals have been synthesized by ion exchange method [8]. The

dealuminated forms of zeolites were obtained by processing of clinoptilolite and mordenite with 0.5N solution of HCl 1–3 times at 98°C for 2 h. After incorporating of ions all of the specimens of the metalzeolite catalysts were activated with air at temperature 350°C and space velocity 2400 h⁻¹ during 30 min.

The test of the activity of the prepared metalzeolite catalysts were carried out for the reaction of oxidation of lower olefins in a flow-circulation apparatus and for the reactions of oxidation of lower paraffins in a flow apparatus with the quartz tube reactors connected directly to the gas chromatographs. The reactor was placed inside the thermostated chamber. Small stainless-steel balls with a 0.2 cm diameter were placed before the catalytic bed in order to obtain plug flow conditions. No catalytic activity was shown by these nonporous balls. A fraction of granulated metalzeolites of about 0.4÷0.8 mm of equivalent diameters was used as the catalyst. The analyses of the products of the reactions of oxidation of ethylene, propylene and propane were performed by gas chromatograph using a column filled with polysorb-1 (length, 3 m). The analyses of the products of reaction of oxidative conversion of methane together with the unreacted reagents were performed by two gas chromatographs LXM-8MD using a hot-wire detector and the columns filled with Na13X (length, 3 m) and polysorb-1 (length, 5 m). Argon was employed as the carrier gas in the first chromatograph. This chromatograph was employed for separating H₂, O₂, CH₄ and CO₂. The second chromatograph helium was employed as the carrier gas and to be analyzed the other products of the reaction with using the program control of the temperature.

The test of the activity of the prepared metalzeolite catalysts for the reactions of oxidative conversion of methane to ethylene and acetylene is carried out in a two-stage reactor with a stepped feed of oxygen. The same experimental method was employed for the reaction of oxidative conversion of methane into 1,4-butanediol.

Type, crystallinity of natural clinoptilolite and mordenite, composition of the zeolite and the metalzeolites have been determined with using of the instruments: BRUKER D2 PHASER and JCP-MS Agilent 7700.

Results and discussion

The experimental data indicated that metalzeolite catalyst PdCuNaY containing 1.5% (wt.) of ions of palladium and 6.0% (wt.) of ions of copper shows relatively high activity in the reaction of oxidation of ethylene and propylene into acetaldehyde and acetone accordingly. Therefore a selection of active catalyst for these reactions was carried out by means modification of this catalyst with ions Ba²⁺, Ca²⁺ and Sr²⁺ by ion exchange method. Some of the results of this investigation are presented in Table 1.

It can be seen from data of Table 1, the best results are obtained at proceeding the reactions over metalzeolite catalyst PdCuCaNaY. Although it has been known from literature that these reactions carry out with formation of intermediate π -complexes but apparently these has been phenomenons which are observed in the reactions proceeding on the carbonium-ion mechanism. Influence of degree of exchange ions of Na with cations of calcium on the catalytic activity is explained by hypothesis according which the activity of the catalyst is determined by existing of the non-compensated electric charge arised because of that one bicharged cation cannot form equivalent bonds with two charged tetrahedron of AlO₄. The observed series of activity Ca²⁺>Sr²⁺>Ba²⁺ on this hypothesis can be explained by change of intensity of fields with increasing of ion radius of cation. Thus the metalzeolite catalyst PdCuCaNaY with degree of exchange ions Na with ions Ca²⁺, 45% containing of ions of Pd²⁺ – 1.5% (wt.) and Cu²⁺ – 6.0% (wt.) shows the highest activity in reactions of oxidation of ethylene and propylene into acetaldehyde and acetone accordingly.

Table 1. The results on the selection of active catalyst for the reaction oxidative conversion of lower olefins

№	Catalyst	Degree of exchange ion of Na	Space velocity, h ⁻¹	Temperature °C	Mole ratio Olefins:H ₂ O:O ₂ :He	Oxidation of C ₂ H ₄			Oxidation of C ₃ H ₆		
						Conversion of C ₂ H ₄ , %	Selectivity on CH ₃ CHO, %	Rate of formation of pdCH ₃ CHO, g/g (Pd)h	Conversion of C ₃ H ₆ , %	Selectivity on CH ₃ COCH ₃ , %	Rate of formation of CH ₃ COCH ₃ , g/g (Pd) h
1	Pd(1.5%)Cu(6%)CaNaY	37	1200	105	1:2:2:3	58.3	96.7	31.8	58.1	98.8	42.7
2		37	1200	115	1:2:2:3	63.3	94.4	33.6	60.6	97.4	43.9
3		37	1200	125	1:2:2:3	64.2	90.0	32.6	63.0	92.1	43.2
4		45	1200	105	1:2:2:3	65.7	96.5	35.8	62.1	98.3	45.5
5		45	1200	115	1:2:2:3	72.8	94.2	38.7	67.9	97.5	49.3
6		45	1200	125	1:2:2:3	74.3	90.5	38.0	71.5	92.0	49.0
7		67	1200	105	1:2:2:3	53.0	95.0	28.4	52.5	98.0	38.3
8		67	1200	115	1:2:2:3	57.1	93.1	30.0	59.3	97.7	43.4
9		67	1200	125	1:2:1:3	60.0	89.2	30.2	63.1	90.2	42.3
10	Pd(1.5%)Cu(6%)CaNaY	45	1200	115	1:2:1:4	63.4	97.3	34.8	66.8	98.0	48.7
11		45	1200	115	1:2:3:2	70.5	91.9	36.6	69.5	96.8	50.1
12		45	1200	115	1:1:2:4	62.7	92.3	32.8	60.3	96.9	43.5
13		45	1200	115	1:3:2:2	67.3	95.6	36.3	63.1	98.0	46.0
14		45	800	115	1:2:2:3	84.5	92.0	29.3	80.9	97.5	39.2
15		45	1600	115	1:2:2:3	55.6	95.3	39.9	53.0	97.8	51.3
16	Pd(1.5%)Cu(6%)SrNaY	29	1200	105	1:2:2:3	36.5	97.8	20.1	34.2	98.3	25.0
17		29	1200	115	1:2:2:3	40.0	95.9	21.7	39.1	97.7	28.4
18		29	1200	125	1:2:2:3	44.3	92.5	23.1	42.5	93.6	29.5
19		41	1200	105	1:2:2:3	41.8	97.0	22.9	37.3	97.8	27.2
20		41	1200	115	1:2:2:3	44.8	94.8	24.0	40.1	97.0	28.9
21		41	1200	125	1:2:2:3	49.8	91.1	25.5	44.9	93.2	31.2
22		57	1200	105	1:2:2:3	43.2	95.5	23.3	40.0	97.3	28.9
23		57	1200	115	1:2:2:3	45.3	93.5	23.9	42.6	96.1	30.4
24		57	1200	125	1:2:2:3	50.4	90.3	25.1	46.3	91.9	31.7
25	Pd(1.5%)Cu(6%)BaNaY	33	1200	105	1:2:2:3	25.3	98.7	14.1	23.0	99.0	17.0
26		33	1200	115	1:2:2:3	30.0	97.0	16.4	27.0	97.3	19.6
27		33	1200	125	1:2:2:3	34.6	93.9	18.3	30.4	94.0	21.3
28		50	1200	105	1:2:2:3	29.5	97.6	16.3	25.9	97.5	18.7
29		50	1200	115	1:2:2:3	34.1	95.6	18.4	31.1	96.2	22.2
30		50	1200	125	1:2:2:3	36.7	92.7	19.2	34.0	94.0	23.8
31		60	1200	105	1:2:2:3	19.4	96.8	10.6	16.5	99.4	12.2
32		60	1200	115	1:2:2:3	21.1	95.0	11.3	19.5	97.2	14.1
33		60	1200	125	1:2:2:3	26.3	92.0	13.7	22.8	95.1	10.2

With the purpose of the development a high efficiency catalyst for the reaction of oxidative conversion of methane into ethylene have been synthesized by ion exchange a range of the metalzeolite catalyst on the basis of natural (pure and dealuminated clinoptilolite and mordenite) zeolites and the cations of different metals (Mg²⁺, Ca²⁺, Ba²⁺, Li⁺). The test of the activity of these catalysts have been carried out at atmospheric pressure in the range

of temperature (700-800)⁰C, space velocity, (7000–18000) h⁻¹ and mole ratio of the reagents CH₄:O₂=1.0:2.5. Some of the results of this investigation are given in Table 2.

Comparative analysis of the data of Table 2 on activity and selectivity of the mordenites and clinoptilolites in the reaction of oxidative conversion of methane shows that the best results are obtained over pure and dealuminated Azerbaijan natural clinoptilolite, with increasing

silicate modulus of the clinoptilolite increases his activity and selectivity.

Therefore the metalzeolite catalysts were synthesized on the basis of dealuminated clinoptilolite with the silicate modulus 10.8. It can be seen from data of Table 2 the best activity shows the dealuminated clinoptilolite containing of ions of calcium. The increasing of concentration of ions of calcium from 5 to 7% (% from weight of catalyst) increases of the activity of metalzeolite catalyst, the further increasing of concentration of ions of calcium does not significantly influence on the activity of metalzeolite catalyst, Clin Ca (exp. 11–14).

With the purpose of the increasing of the selectivity of the process, this catalyst was modified by ions of lithium. In increasing of content of ions of lithium from 3% (wt.) to 8% (wt.) result in the increasing of the selectivity of the process in all of concentration of ions of

calcium (exp. № 20-24). It can be followed from the data of Table 2, the best result are obtained over metalzeolite catalyst – Clin. (silicate module=10.8) Ca Li containing 7.0% (wt.) of ions Ca^{2+} and 8.0% (wt.) of ions Li.

It has also been investigated and activity of these metalzeolite catalysts in the reaction of partial oxidation of propane into acetaldehyde and formaldehyde at atmospheric pressure in the range of change of temperature (320–370) $^{\circ}\text{C}$; space velocity (500–2500) h^{-1} and molar ratio of reagents $\text{C}_3\text{H}_8:\text{O}_2=0.5\text{--}1.2$. Some of results of this investigation are given in Table 3.

It can be seen from the data of Table 4 clinoptilolite containing 1.0% (wt.) of cations Ni^{2+} shows relatively high catalytic activity in reaction of oxidative conversion of propylene to acrolein (exp. 6, 7, 8). Over this catalyst the yield of acrolein is 80.0% at the selectivity of process 85.0%

Table 2. The results on the selection of active catalyst for the reaction oxidative conversion of methane into ethylene at space velocity $V=16000\text{ h}^{-1}$, mole ratio $\text{CH}_4:\text{O}_2=0.402:0.312$

№	Catalyst	$T, ^{\circ}\text{C}$	Conversion of CH_4 mol%	Yield, %		Selectivity, %	
				C_2H_4	C_2H_6	C_2H_4	C_2H_6
1	Clinoptilolite (pure)	800	9.5	3.39	3.35	25.2	35.3
2	Mordenite (pure)	800	5.4	1.30	1.79	24.1	33.3
3	Clinoptilolite (8.68)	800	12.7	3.35	4.64	26.4	36.3
4	Clinoptilolite (9.80)	800	15.8	4.45	6.03	28.2	38.2
5	Clinoptilolite(10.80)	800	19.9	5.93	7.50	29.3	37.7
6	Mordenite I HCl	800	7.3	1.79	2.54	24.6	34.9
7	Mordenite II HCl	800	10.9	2.89	3.65	26.6	33.5
8	Clin(10.8)Mg(5%)	800	36.4	5.64	7.17	15.5	19.7
9	Clin(10.8)Mg(7%)	800	40.2	7.35	7.67	18.3	19.1
10	Clin(10.8)Mg(10%)	800	41.0	7.38	8.40	18.0	20.5
11	Clin(10.8)Ca(5%)	800	35.9	6.64	7.72	18.5	21.5
12	Clin(10.8)Ca(7%)	800	39.8	7.84	8.95	19.7	22.5
13	Clin(10.8)Ca(10%)	800	40.7	8.34	9.40	20.5	23.1
14	Clin(10.8)Sr(5%)	800	33.2	5.04	5.97	15.2	18.0
15	Clin(10.8)Sr(7%)	800	34.3	5.28	6.48	15.4	18.4
16	Clin(10.8)Sr(10%)	800	35.5	5.75	6.46	16.2	18.2
17	Clin(10.8)Ba(5%)	800	31.5	4.44	5.29	14.1	16.8
18	Clin(10.8)Ba(7%)	800	32.0	4.73	5.18	14.8	16.2
19	Clin(10.8)Ba(10%)	800	33.4	5.14	5.64	15.4	16.9
20	Clin(10.8)Ca(7%)Li(3%)	700	58.8	14.31	12.59	26.6	23.4
21	Clin(10.8)Ca(7%)Li(5%)	700	54.9	14.98	13.94	27.3	25.4
22	Clin(10.8)Ca(7%)Li(8%)	700	58.2	17.51	14.55	30.1	25.0
23	Clin(10.8)Ca(5%)Li(8%)	700	53.0	13.80	13.55	26.2	25.2
24	Clin(10.8)Ca(10%)Li(8%)	700	53.8	16.73	10.86	31.1	20.2

It can be seen from data of Table 3 dealuminated clinoptilolite containing of ions of tin and lithium significantly increases of the selectivity of the processed and the yield of formaldehyde and acetaldehyde (exp. 16, 17, 18). The best results are obtained over the metalzeolite catalyst, Clin (10.8) Ca(8%) Sn(7%) Li(7%).

The results on the selection of active catalyst for the reaction of oxidative conversion of propylene to acrolein are presented in Table 4 [9–10].

The reaction of oxidative conversion of methane into ethylene and acetylene is carried out in a two-stage reactor.

Table 3. The results of investigation on selection of active catalyst for the reaction of partial oxidation of propane. Space velocity $V=1000\text{ h}^{-1}$, molar ratio $\text{C}_3\text{H}_8:\text{O}_2=0,5$

№	Catalyst	Temperature °C	Conversion of C_3H_8	Yield, %				
				CH_3OH	CH_3COOH	HCHO	CO_2	CH_2CHO
1	Clin (Pure)	350	5.6	0.6	–	1.6	1.0	2.4
2	Mord (Pure)	350	3.4	0.3	–	0.6	1.4	1.1
3	Clin (10.8)	350	8.4	1.1	–	2.0	2.1	3.2
4	Mord (dealum)	350	6.2	0.9	–	1.4	1.9	2.0
5	Clin (10.8) Mg (5%)	330	35.1	3.8	0.8	9.3	11.0	10.2
6	Clin (10.8) Mg (10%)	330	36.4	2.9	1.2	8.8	13.6	9.9
7	Clin (10.8) Ca (5%)	330	36.6	2.5	1.6	11.8	5.8	15.1
8	Clin (10.8) Ca (10%)	330	37.4	2.2	1.7	12.7	5.2	15.6
9	Clin (10.8) Sr (5%)	330	35.7	2.9	1.0	10.5	10.1	11.2
10	Clin (10.8) Sr (10%)	330	36.0	2.8	1.2	10.2	10.0	10.8
11	Clin (10.8) Ba (5%)	330	33.1	1.7	0.9	11.1	9.5	9.9
12	Clin (10.8) Ba (10%)	330	33.8	1.9	1.0	11.8	9.3	9.8
13	Clin (10.8) Sn (5%)	330	34.5	1.5	2.1	7.9	14.2	8.8
14	Clin (10.8) Sn (7%)	330	35.0	1.8	2.2	7.5	15.1	8.4
15	Clin (10.8) Ca (8%) Sn (7%)	330	52.0	2.1	2.6	10.2	16.9	20.2
16	Clin (10.8) Ca (8%) Sn (7%) Li(3%)	360	56.0	2.0	5.2	15.8	7.8	25.2
17	Clin (10.8) Ca (8%) Sn (7%) Li(5%)	360	60.0	2.1	6.1	18.7	5.0	28.1
18	Clin (10.8) Ca (8%) Sn (7%) Li(7%)	360	63.1	1.8	7.3	20.2	3.6	30.6

Table 4. The results on the selection of active catalyst for the reaction oxidative conversion of propylene to acrolein ($T=380^\circ\text{C}$, $V=800\text{ h}^{-1}$, $\text{C}_3\text{H}_6:\text{O}_2=1.0:1.2$)

№	Catalyst	X, %	S, %	Yield, %			
				CO_2	CH_2O	$\text{C}_3\text{H}_4\text{O}$	HCOOH
1	Zn(0.2%)	37.50	5.25	22.13	13.40	1.97	–
2	Cu (0.5%)	58.25	–	38.65	19.60	–	–
3	Co (0.5%)	59.81	–	46.37	13.44	–	–
4	Mg (1%)	62.99	68.52	8.86	10.31	43.16	0.66
5	Pd (1%)	60.37	–	53.37	7.00	–	–
6	Ni (1%)	94.72	85.44	5.44	5.75	80.93	2.60
7	Ni (3%)	69.83	68.85	11.96	4.19	48.08	5.60
8	Ni (5%)	74.00	48.70	25.74	8.02	36.04	4.20
9	CuFe (0.5:0.25)	56.00	18.03	29.8	15.70	10.10	0.40
10	CuPd (0.5:0.25)	50.03	–	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	65.00	14.96	8.40	44.43	0.56
13	CuPdZn(2:1:2)	65.52	–	65.52	–	–	–
14	CuMnCo(1:0.5:0.5)	51.41	16.69	33.25	9.34	8.58	0.24

The same catalyst were employed in the first and the second reactors with volumes of beds $V'_{\text{cat}} = V''_{\text{cat}} = 0.5 \text{ cm}^3$. At the exit from the stage I contact gas contains C_2H_6 , C_2H_4 , H_2 , CO_2 and trace amount of CO . At the exit of the second stage in the contact gas CO were deleted. The results on the selection of active catalyst for the reaction of oxidative conversion of methane into ethylene and acetylene are presented in Table 5.

It can be seen from the data of Table 5 from not modified with metal cations of zeolites the best activity in this reaction shows natural clinoptilolite (exp. 1–4). The increasing of silicate modulus increases of the catalytic activity of clinoptilolite (exp. 1–2). Modified by cations Mg^{2+} and Ca^{2+} natural clinoptilolite

(silicate modulus=10.8) has relatively high catalytic activity (exp. 5-10). The best results are obtained over metalzeolite catalyst clinoptilolite with silicate modulus 10.8 containing 10.0% (wt.) of Ca^{2+} cations (exp. 10). With the purpose of the increasing of the selectivity of the process this catalyst was modified by cations of lithium (exp. 11-19). It can be seen from these data incorporation of cations on lithium increases of selectivity and activity of the catalyst. It can be explained by decreasing the rate of reaction of deep oxidation. The catalyst were prepared on the basis of clinoptilolite with silicate modulus 10.8 and cations of Mn^{2+} have less activity on comparison with the catalyst (exp. 20-22) containing cations Ca^{2+} and Li^+ .

Table 5. The results on the selection of active catalyst for the reaction oxidative conversion of methane to ethylene and acetylene.

№	Catalyst	$T^1, ^\circ\text{C}$	$T^2, ^\circ\text{C}$	X, %	Yield, %			
					C_2H_4	C_2H_2	C_2H_6	CO_2
1	Clinoptilolite (8.6)	800	600	19.9	5.93	7.50	0.6	5.4
2	Mordenite	800	600	5.4	1.3	1.79	0.3	1.7
3	Clinoptilolite(10.8) HCL	800	600	27.7	6.21	7.10	0.5	13.1
4	Mordenite	800	600	10.9	2.89	3.65	0.2	4.16
5	Clin(10.8)Mg(5%)	800	600	36.4	5.64	7.17	0.2	22.8
6	Clin(10.8)Mg(7%)	800	600	40.4	7.35	7.67	0.2	24.3
7	Clin(10.8)Mg(10%)	800	600	41.0	7.28	8.40	0.3	24.8
8	Clin(10.8)Ca(5%)	800	600	35.9	6.64	7.72	0.25	20.5
9	Clin(10.8)Ca(7%)	800	600	39.8	7.84	8.95	0.3	22.1
10	Clin(10.8)Ca(10%)	800	600	40.7	8.34	9.40	0.4	22.1
11	Clin(10.8)Ca(5%)Li(3%)	800	600	51.1	12.82	11.75	0.5	25.6
12	Clin(10.8)Ca(5%)Li(5%)	800	600	52.2	13.31	12.37	0.5	25.4
13	Clin(10.8)Ca(5%)Li(7%)	800	600	53.0	13.80	13.35	0.6	24.9
14	Clin(10.8)Ca(7%)Li(3%)	800	600	58.8	14.31	12.59	0.65	30.8
15	Clin(10.8)Ca(7%)Li(5%)	800	600	54.9	14.98	13.94	0.67	24.83
16	Clin(10.8)Ca(7%)Li(7%)	800	600	58.2	17.51	14.55	0.81	25.0
17	Clin(10.8)Ca(10%)Li(3%)	800	600	51.5	15.70	9.63	0.64	25.1
18	Clin(10.8)Ca(10%)Li(5%)	800	600	53.5	16.37	9.73	0.57	26.83
19	Clin(10.8)Ca(10%)Li(7%)	800	600	53.8	16.73	10.86	0.9	24.94
20	Clin(10.8)Ca(5%)Li(5%)	800	600	29.7	6.78	6.72	0.41	14.9
21	Clin(10.8)Mn(5%)	800	600	32.8	7.61	6.79	0.42	17.4
22	Clin(10.8)Mn(7%)	800	600	36.3	8.37	6.53	0.50	19.9
23	Clin(10.8)Li(5%)Mg(3%)	800	600	47.0	9.2	7.3	0.8	29.4
24	Clin(10.8)Li(5%)Mg(5%)	800	600	40.7	12.1	8.1	0.74	19.3
25	Clin(10.8)Li(7%)Mg(7%)	800	600	31.3	11.6	7.6	0.73	10.9
26	Clin(10.8) Mg(5%)Mn(7%)	800	600	38.8	7.3	6.8	0.54	23.9
27	Clin(10.8)Mg(7%)Mn(7%)	800	600	41.2	10.9	8.3	0.62	20.83
28	Clin(10.8)Li(7%)Mg(7%)	800	600	65.0	26.0	13.0	0.7	24.9
29	Clin(10.8)Ca(8%) Li(7%)Mg(5%)	800	600	68.2	19.1	13.1	0.76	34.86
30	Clin(10.8)Ca(8%) Li(5%)Mg(8%)	800	600	73.0	20.44	13.2	0.63	38.3
31	Clin(10.8)Ca(8%) Li(7%)Mg(8%)	800	600	79.8	25.0	9.7	0.56	43.97

Table 6. The results on the selection of active catalyst for the reaction oxidative conversion of methane into 1,4-butanediol

№	Catalyst	T ¹ , °C	T ² , °C	V h ⁻¹	X, %	Yield, %		
						A _{BD}	A _{C₂H₂}	A _{C₂H₄}
1	Clin(10.8) Mn(8.0%)	815	600	16000	36.3	2.6	14.9	1.3
2		815	600	16000	35.7	2.2	14.8	1.5
3		815	630	19000	29.7	2.0	13.5	1.0
4	Clin(10.8)Mn(8.0%)Li(7.0%)Ni (8.0%)	800	600	19000	53.8	8.0	11.5	2.8
5		800	700	16000	66.33	8.7	7.0	2.1
6		800	600	16000	46.33	6.2	4.7	1.9
7	Clin(10.8)Mn(8.0%)Li(7.0%)Ni (8.0%)	770	600	16000	80.2	23.1	4.4	2.3
8		670	650	16000	63.3	15.9	2.9	1.5
9		750	650	16000	64.2	17.3	4.4	2.8
10		800	650	16000	72.8	22.3	5.9	3.9
11		800	700	25200	59.4	14.9	3.4	3.0

A_{BD}-yield of 1,4-butanediol

Incorporation of cations of lithium in Mg²⁺ containing clinoptilolite is also increased catalytic activity (exp. 23–25) on comparison with clinoptilolite containing only cations Mg²⁺ (exp. 5–7). It can be explained by decreasing of fraction of reaction of deep oxidation of methane. Clinoptilolite containing cations of Mg²⁺ and Mn²⁺ (exp. 26–27) has relatively high activity on comparison with catalysts containing only cations of Mg²⁺ (exp. 5–7), that can be explained by improving of distribution of the active centers on the surface of catalyst at incorporation in the clinoptilolite of Mn²⁺ cations.

Optimum distribution of the active centers on the surface of catalyst for reaction of oxidative conversion of methane to ethylene and acetylene is reached by modified of natural clinoptilolite with silicate modulus 10.8 with cations: Ca²⁺, Mg²⁺ and Li⁺ (exp. 28–31). By means of variation of concentrations of the cations it has been determined the active consist of the catalyst Clin(10.8) Ca(8.0%) Li(7.0%) Mg(8.0%) (exp. 31) [11–14].

On the basis of natural clinoptilolite with silicate modulus 10.8 we are also synthesized the modified with cations Mn²⁺, Mg²⁺, Li⁺ and Ni²⁺ zeolite catalysts for reaction of oxidative conversion of methane to 1,4-butanediol. Activity of the prepared metalzeolite catalysts were carried out in a two-stage reactor with stepped feed of oxygen volumes of beds $V_{\text{cat}}' = V_{\text{cat}}'' = 0.5 \text{ cm}^3$ of the same catalyst. The analyses of the liquid products of the reaction were performed by gas chromatograph Agilent

7820 using FID, a capillary column, DB-624 (length, 60 m) and helium as the carrier gas.

The results on the selection of active catalyst for this reaction given in Table 6.

It can be seen from data of Table 6 clinoptilolite (silicate module=10.8) containing 8.0% (wt.) of cations Mn²⁺ shows catalytic activity in the reaction of oxidative conversion of methane to 1,4-butanediol (exp. 1–3). The incorporating in this catalyst cations Li⁺ and Ni²⁺ increases its activity (exp. 4–6). The best activity shows the dealuminated clinoptilolite (silicate module=10.8) containing 8.0% (wt.) Mn²⁺, 7.0% (wt.) Li and 8.0% (wt.) Ni²⁺ (exp. 7–11).

Conclusion

It has been synthesized by ion exchange method a range of the metalzeolite catalysts for reactions of the oxidative conversion of the lower olefins and paraffins on the basis of synthetic (NaY) and natural (pure and dealuminated clinoptilolite and mordenite) zeolites and the cations of different metals (Pd²⁺, Cu²⁺, Mg²⁺, Mn²⁺, Ca²⁺, Ba²⁺, Ni²⁺, Sn²⁺, Li⁺). It has been established that the metalzeolite catalysts prepared on the basis of synthetic zeolite NaY and the cations of the metals Pd²⁺, Cu²⁺, Ca²⁺, Sr²⁺ and Ba²⁺ shows relatively high activity in the oxidative conversion of ethylene and propylene into acetaldehyde and acetone accordingly. The results on selection of the active metalzeolite catalyst for the reaction of the oxidative conversion of methane into ethylene have been shown that the best results were obtained over the metalzeolite catalyst contain-

ning dealuminated clinoptilolite (silicate modulus =10.8) and cations Ca^{2+} and Li^+ . It has been also shown that metalzeolite containing dealuminated clinoptilolite (with silicate modulus =10.8) and cations, Ca^{2+} , Sn^{2+} and Li^+ shows the highest activity in oxidative conversion of propane into acetaldehyde and formaldehyde. Propylene is converted to acrolein at 320-380°C with more than 85% selectivity over clinoptilolite containing 1% (wt.) of Ni^{2+} . Natural clinoptilolite with silicate modulus – 10.8 containing cations Li^+ , Ca^{2+} and Mg^{2+} shows relatively high catalytic activity in the oxidative conversion of methane to ethylene and acetylene in a two-stage reactor with stepped feed of oxygen. Oxidative conversion of methane to 1,4-butanediol proceeds in a two-stage reactor with a stepped feed of oxygen over clinoptilolite (10.8) containing cations Mn^{2+} , Li^+ and Ni^{2+} , catalyst.

All of the metalzeolite catalyst presented in the article were tested in a laboratory scale during 300 hours and was not observed any change of catalytic activity for all of the catalyst. The result of the presented experimental investigations show that on the basis of zeolites and metal cations with known catalytic properties by ion exchange method may be synthesized efficiency metalzeolite catalyst for the different reactions.

References

1. Aria H., Lamasharo T., Kubo T., Tominaga H. The catalysis of palladium and cupric ion exchanged zeolite for oxidation of ethylene. Bull. Jap. Petrol. Inst. 1976. 18(1). P. 39–46.
2. Minachev KH.M., Usachev N.Ia., Rodin A.P., Kalinin V.P., Isakov Ia.I. Okisleniia etilena i propilena v karbonilnye soedineniia na tceolitnykh katalizatorakh. Tez. docl. I Neftehim. Simpoz. sotc. stran. Baku, noiabr. 1978. M.: Nauka. S. 92–93.
3. Shakhhtakhtinskii T.N., Benni Kh.F., Aliev A.M., Kuliev A.R., Kasamanskii V.P., Peresada I.M. Podbor Pd- i Su-soderzhashchego tceolitnogo katalizatora dlia gazofaznoi reakcii okisleniia etilena v atcetaldegid.. Azerb. Chem. Journ. 1979. No 2. P. 41–50.
4. Shakhhtakhtinskii T.N., Benni Kh.F., Aliev A.M., Kuliev A.R., Kasamanskii V.P., Mikailov R.Z. Issledovanie reakcii gazofaznogo okisleniia etilena na Pd- i Cu-soderzhashchikh tceolitnykh katalizatorakh. Azerb. Chem. Journ. 1979. No 2. P. 51–57.
5. Sittin M. Protcessy okisleniia uglerodnogo syria. M.:Himiia, 1970. C. 62.
6. Safarov M.G., Balaev F.A. Okislenie propana na vanadiev`kh katalizatorax. Tez. docl. V konf. po okislitel`nomu geterogennomu katalizu. T. 2. 1981. S. 320–321.
7. Avtorskoe svidetel'stvo SSSR №706108. 1978.
8. Shakhhtakhtinskii T.N., Aliev A.M. Pat. (Rossiia) Su1826925 Az 07.07.93. Katalizatory dlia partialnogo okisleniia propana.
9. Aliev A.M., Gusei`nova T.I., Sary`dzhanov A.A., Safarov A.R., Bakhmanov M.F., Agaeva R.Iu., Nadzhaf-Guliev U.M., Iaryev V.M. Podbor aktivnogo modifitsirovannogo tceolitnogo katalizatora i izuchenie kinetiki i mehanizma reakcii okislitel'nogo prevrashcheniia propilena v akrolein. Neftepererabotka i neftehimia. 2019. № 5. S. 25–30.
10. Əliyev A.M., Nəcəf-Quliyev Ü.M., Sarıcanov Ə.Ə., Hüseynova T.İ., Yarıyev V.M., Süleymanov T.Y. Akroleinin alınma üsulu. Patent № İ 2020 0071.
11. Aliyev A.M., Mətiyev K.İ., Aliyev F.V., Ağayeva R.Y. Investigation of mechanism of oxidative coupling of methane to C_2 -hydrocarbons. IX intern. conference mechanism of catalytic reactions. Saint Petersburg, 21–23 October, 2012, 22–24.
12. Aliyev A.M., Shabanova Z.A., Aliyev F.V., Guseynova A.M. Zeolites modified metal cations as catalysts in hydrocarbon oxidation and the alkyl alcohol. European Researcher. International Multidisciplinary Journal. 2014. 82. P. 9–1.
13. Əliyev A.M., Əliyev F.V., Mətiyev K.İ., Al-Dosari M.K. Asetilenin alınma üsulu. Patent № İ 2016 0090.
14. Əliyev A.M., Əliyev F.V., Mətiyev K.İ., Ağayev F.A., Səfərov A.R. 1,4-butandiolun alınma üsulu. Patent № İ 2017 0005.

MODİFİKASIYA OLUNMUŞ SEOLİT KATALİZATORU ÜZƏRİNDƏ AŞAĞI OLEFİNLƏRİN VƏ PARAFİNLƏRİN OKSİDLƏŞDİRİCİ KONVERSİYASI

A.M.Əliyev, F.V.Əliyev, Ü.M.Nəcəf-Quliyev, R.İ.Əhmədov, T.İ Hüseynova, R.Y.Ağayeva

Aşağı olefinlərin və parafinlərin neft-kimya sənayesinin istənilən məhsuluna çevrilmək üçün oksidləşdirici çevrilməsi reaksiyaları üçün yüksək effektivli katalizatorların hazırlanması məqsədi ilə sintetik (NaY) və təbii (təmiz və işlənmiş klinoptilolit və mordenit) seolitlər və müxtəlif metalların kationları əsasında bir sıra metalseolit katalizatorları ion mübadiləsi metodu ilə sintez edilmişdir. Sintetik seolit NaY əsasında hazırlanmış metalzeolit katalizatorlarının etilen və

propilenin asetaldehid və asetona oksidləşdirici çevrilməsində nisbətən yüksək aktivlik göstərdiyi müəyyən edilmişdir. Həm də proseslər üçün yüksək effektivli bir metalzeolit katalizatorları sintez edilmişdir: metanın etilenə oksidləşdirici çevrilməsi; propanın asetaldehidə və formaldehidə oksidləşdirici çevrilməsi; metanın oksidləşmə ilə etilen və asetilenə çevrilməsi; metanın 1,4-butandiol-a oksidləşdirici çevrilməsi.

Açar sözlər: zeolitlər, aktivlik, aşağı olefinlər, parafinlər, oksidləşmə.

ОКИСЛИТЕЛЬНАЯ КОНВЕРСИЯ НИЗШИХ ОЛЕФИНОВ И ПАРАФИНОВ НА МОДИФИЦИРОВАННОМ ЦЕОЛИТНОМ КАТАЛИЗАТОРЕ

А.М.Алиев, Ф.В.Алиев, У.М.Наджаф-Кулиев, Р.И.Ахмедов, Т.И. Гусейнова, Р.Ю.Агаева

С целью разработки высокоэффективных катализаторов реакций окислительного превращения низших олефинов и парафинов в желаемые продукты нефтехимической промышленности был синтезирован ионообменным методом ряд металцеолитовых катализаторов на основе синтетических (NaY) и природных (чистый и деалюминированный клиноптилолит и морденит) цеолитов и катионов различных металлов. Установлено, что металцеолитовые катализаторы, приготовленные на основе синтетического цеолита NaY, проявляют относительно высокую активность в окислительном превращении этилена и пропилена в ацетальдегид и ацетон соответственно. Также был синтезирован высокоэффективный металцеолитовый катализатор для процессов: окислительного превращения метана в этилен; окислительного превращения пропана в ацетальдегид и формальдегид; окислительного превращения метана в этилен и ацетилен; окислительного превращения метана в 1,4-бутандиол.

Ключевые слова: цеолиты, активность, низшие олефины, парафины, окислительная конверсия.