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**OXIDATIVE DEHYDROGENATION OF CYCLOHEXANOL TO CYCLOHEXANONE
CATALYSED BY MODIFIED ZEOLITE CATALYST****Z.A. Shabanova***M. Nagiyev Institute of Catalysis and Inorganic Chemistry, NAS of Azerbaijan**zumrud-042425-@mail.ru*

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Gas-phase oxidative dehydrogenation at atmospheric pressure and a temperature of 260–370°C in the presence of a modified zeolite catalyst clinoptilolite cyclohexanol with a conversion of 90–99 % was oxidized to cyclohexanone with the selectivity of 96–98 %. It has been studied kinetic laws of the reaction.

Keywords: oxidative dehydrogenation, cyclohexanol, cyclohexanone, modified clinoptilolite.

doi

Introduction

Cyclohexanone, a large-capacity product of organic and petrochemical syntheses, is widely used in the production of polyamide plastics, synthetic fibers and biologically active preparations [1]. In this regard, the scale of its production is increasing annually. On an industrial scale, cyclohexanone is mainly obtained by oxidation of cyclohexane with atmospheric oxygen at elevated pressure, mainly in the presence of homogeneous catalysts – soluble cobalt salts [2, 3].

In previous works [3–8] we found that zeolites modified by metal cations by the ion exchange method exhibit relatively high catalytic activity and selectivity in the oxidative reactions of aliphatic alcohols at relatively low temperatures (250–350°C). The use of multifunctional metal-zeolite catalysts in these reactions leads to a reduction in the consumption of raw materials, lower operating costs for the isolation and purification of the resulting product, and environmental protection. The development of these processes requires a detailed study of the mechanism of these reactions proceeding.

The aim of this present work is to study the catalytic activity of the modified zeolite in the oxidative dehydrogenation of cyclohexanol and to investigate the kinetic laws of the reaction.

Experimental part

The test of the activity of the metal-zeolite catalysts and a study of the kinetic regularities of the reactions was carried out in a flow

device with the quartz tube reactor connected directly to the gas chromatograph at atmospheric pressure, in the temperature range 260–370°C, space velocities by the alcohol 0.91–7.0 h⁻¹, molar ratios of reagents C₆H₁₁OH:air = (0.63–1.3): (5.57–8.1).

Chromatographic analysis of oxidation products was carried out on an "Agilent 7890" chromatograph with an "Agilent-5975" mass detector with HP-5 MS column, 30 m long, 0.32 mm in diameter, filled with 5% phenyl, 95% methylpolysiloxane. The carrier gas is helium, flow rate – 2 cm³/min. program control of the temperature from 70 to 180°C at a speed of 15°C per minute.

To prepare a catalyst based on the natural clinoptilolite it was initially dealuminated. A fraction of the initial zeolite with a grain size of 0.25–0.63 mm in a sample of 50 g is taken and processed in a liter flask at stirring with 2 N HCl solution (three times for 2 hours) at *T* = 95–96°C. Cations of transition elements are introduced into the zeolite by the method ion exchange. A specific sample of zeolite with a grain size of 0.25–0.63 mm is placed in a 1-liter round-bottom flask, into which 100 ml of distilled water is added (until the zeolite is coated) and heated at stirring to 95–98°C. Then, in this flask, dropwise, chloride solutions of the corresponding transition element are added. This mixture was stirred for 8–16 hours until the ions were completely exchanged. To determine the

completeness of the exchange, qualitative reactions of the interaction of the introduced ions are used. At the end of the exchange, the catalyst is washed from the Cl^- ions with distilled water and dried at $T=150^\circ\text{C}$. Before the study, the powdery zeolite was pressed into tablets with a diameter of 10 mm, which were crushed with the release of a fraction of 0.25–0.63 mm. Then the catalyst was activated by air purging at a feed rate of 2400 h^{-1} for 2 hours at $T = 350\text{--}400^\circ\text{C}$, then the temperature decreased to the reaction temperature and the system was purged with nitrogen within one hour. The experiments showed that after preliminary processing of the catalyst, the latter worked stably, that was systematically verified during the study by control experiments confirming the reproducibility of the results.

The amount of introduced elements into the clinoptilolite composition was determined by ion spectral analysis on an "Agilent 7700 ICP-MS". We used catalysts with a particle size of 0.25–0.63 mm.

Results and its discussion

Table 1 shows the experiments results of synthesized catalysts in the cyclohexanol oxidation reaction at a space velocity of 2363 h^{-1} and the molar ratio of cyclohexanol: air = 1.1: 6.7.

As can be seen from Table 1, the initial clinoptilolite exhibits a relatively low catalytic activity in the studied reaction. Modification of zeolite leads to an increase the catalyst activity. The results of the studies allow us to conclude that the most highly efficient catalyst for this reaction among the studied catalytic systems at the studied process parameters is the catalyst CuPdSn–clinoptilolite (0.5% Cu^{2+} , 0.15% Pd^{2+} , 0.5% Sn^{2+}).

A study of the kinetic laws of the reaction was carried out under the following conditions: temperature – $260\text{--}370^\circ\text{C}$; the space velocity of reaction mixture (V) is $1036\text{--}3109\text{ h}^{-1}$; partial pressure (P_{alcohol}) – $0.06\text{--}0.24\text{ atm}$ and (P_{O_2}) – $0.05\text{--}0.24\text{ atm}$. Tables 2, 3 present the results of a study of the kinetic laws of the oxidative dehydrogenation of cyclohexanol on the selected active catalyst (CuPdSn-clinoptilolite).

Data in Table 2 that show, at a space velocity of 2073 h^{-1} , at a constant P_{alcohol} (0.12 atm) and a variation of P_{O_2} from 0.05 to 0.24 atm, the maximum ketone yield is reached at $P_{\text{O}_2} = 0.18\text{ atm}$ at all studied temperatures. A further increase in P_{O_2} from 0.18 to 0.24 atm leads to a decrease in the yield of cyclohexanone. In the entire range studied, with an increase in the partial pressure of oxygen, the yields of the reaction products – methylcyclopentene, 2-cyclohexen-1-one, carbon dioxide, and cyclohexene conversion increase, and the cyclohexene yield decreases.

From the Table 3 it can be seen that at constant P_{O_2} (0.17 atm) and with an increasing of P_{alcohol} from 0.06 to 0.12 atm, the yield of cyclohexanone increases and reaches a maximum. A further increase in P_{alcohol} leads to a decrease in the yield of cyclohexanone. A decrease in the yield of ketone is accompanied by an increase in the yield of cyclohexene and methylcyclopentene and a decrease in the conversion of alcohol and the yields of 2-cyclohexen-1-one and carbon dioxide. This is explained by the fact that at a given partial oxygen pressure, the relatively high partial pressures of cyclohexanol prevent the coordination of oxygen with the active sites of the metal zeolite catalyst.

Table 1. Activity of synthesized catalysts

Catalyst	Concentration of cations, %			$T, ^\circ\text{C}$	Conversion, %	Selectivity, %
	Sn	Pd	Cu			
Clin.	–	–	–	300	85.4	17.1
Clin. (treat. NH_4OH)	–	–	–	280	98.0	27.4
Clin. (treat. NH_4OH)	–	–	–	320	96.8	50.9
Clin.		0.1	0.5	330	77.1	75.8
Clin.	0.5	0.15	0.5	245	80.8	92.2
Clin.	0.5	0.15	0.5	335	99.5	96.6

Table 2. The influence of the partial pressure of oxygen on the oxidative dehydrogenation of cyclohexanol ($V=2073 \text{ h}^{-1}$; $V_{\text{O}_2}=0.55 \text{ l/h}$; $n_{\text{O}_2}^0=0.04785 \text{ mole/h}$; $P_{\text{O}_2}=0.17 \text{ atm}$; $G_{\text{cat}}=2.94 \text{ g}$)

$T, ^\circ\text{C}$	Partial pressure, atm.		Conversion, %	The yield of the reaction products, %				
	P_{O_2}	P_{N_2}		Cyclohexene	Cyclohexanone	Methyl cyclopentene	Cyclohexyl cyclohexanone-1	CO_2
260	0.05	0.83	49.7	2.9	38.5	0.9	7.4	–
260	0.13	0.75	75.5	1.8	54.7	1.1	17.9	–
260	0.17	0.71	90.42	1.1	65.5	1.9	21.9	0.02
260	0.24	0.64	94.2	0.5	65.8	3.7	23.8	0.4
320	0.13	0.75	90.41	3.2	81.1	3.6	2.5	0.01
320	0.17	0.71	97.38	1.8	88.7	4	3.3	0.08
320	0.24	0.64	99.4	0.5	89.3	4.9	3.9	0.8
350	0.13	0.75	92.8	2.3	87.9	1.9	0.5	0.2
350	0.17	0.71	99.2	1	94.4	2.1	1.1	0.6
350	0.24	0.64	100	0.1	94.7	2.5	1.5	1.2
370	0.13	0.75	95.4	2	86.6	1.4	–	5.4
370	0.17	0.71	100	0.4	91.8	1.7	0.2	5.9
370	0.24	0.64	100	–	90.5	1.9	0.7	7.3

Table 2. The influence of the partial pressure of cyclohexanol to the oxidative dehydrogenation of cyclohexanol ($V=2073 \text{ h}^{-1}$; $V_{\text{O}_2}=0.55 \text{ l/h}$; $n_{\text{O}_2}^0=0.04785 \text{ mole/h}$; $P_{\text{O}_2}=0.17 \text{ atm}$; $G_{\text{cat}}=2.94 \text{ g}$)

$T, ^\circ\text{C}$	Partial pressure of the reagents, atm		Conversion, %	The yield of the reaction products, %				
	$P_{\text{C}_6\text{H}_{11}\text{OH}}$	P_{N_2}		Cyclohexene	Cyclohexanone	Methyl cyclopentene	Cyclohexyl cyclohexanone-1	CO_2
260	0.17	0.67	84.1	2.1	63.4	2.5	16.1	–
260	0.24	0.59	75.5	3.1	60.2	3.5	8.7	–
290	0.17	0.67	90.72	2.8	79.8	3.3	4.8	0.02
290	0.24	0.59	87.1	4.4	75.6	4.9	2.2	–
320	0.06	0.77	99.1	1.5	79.5	1.7	15.7	0.7
320	0.12	0.74	97.88	1.8	88.7	4	3.3	0.08
320	0.17	0.67	96.75	4.2	85.6	4.7	2.2	0.05
350	0.06	0.77	100	0.8	86.2	1.5	9.8	1.5
350	0.12	0.74	99.2	1	94.4	2.1	1.1	0.6
350	0.17	0.67	97.1	1.7	92.9	2.8	–	0.2
370	0.06	0.77	100	–	84.5	1.1	6.9	7.5
370	0.12	0.74	100	0.4	91.8	1.7	0.2	5.9
370	0.17	0.67	99.8	1.5	90.9	2.5	–	4.9

From the above stated results it follows that the optimal partial pressures of the reagents at which the highest yield of cyclohexanone is achieved, are: $P_{\text{alcohol}}=0.12 \text{ atm}$ and $P_{\text{O}_2}=0.18 \text{ atm}$.

From the data Table 2 and 3 it follows that with increasing temperature from 260 to 350 $^\circ\text{C}$, the yield of cyclohexanone increases and reaches a maximum at 350 $^\circ\text{C}$, and a further increase in temperature to 370 $^\circ\text{C}$ leads to a decrease in yield. Alcohol conversion and CO_2 yield continuously increase throughout the studied temperature range.

The high selectivity (75–97%) of the

formation of cyclohexanone and the conversion of cyclohexanol (77–99%) and moderate temperature suggest the proposed catalyst may be of interest for further practical use.

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MODIFIKASIYA OLUNMUŞ SEOLIT KATALIZATORU ILƏ TSİKLOHEKSANOLUN TSİKLOHEKSANONA KATALİTİK OKSIDLƏŞDIRICI DEHİDROGENLƏŞMƏSİ

Z.Ə.Şabanova

Modifikasiya olunmuş seolit katalizatoru iştirakında 260–370⁰C temperaturda qaz fazada oksidləşdirici dehidrogenləşdirilməklə tsikloheksanol 90–99% konversiya və 96–98% selektivliklə tsikloheksanona oksidləşdirilmişdir. Reaksiyanın getməsinin kinetik qanunauyğunluqları öyrənilmişdir.

Açar sözlər: oksidləşdirici dehidrogenləşmə, tsikloheksanol, tsikloheksanon, modifikasiya olunmuş klinoptilolit.

ОКИСЛИТЕЛЬНОЕ ДЕГИДРИРОВАНИЕ ЦИКЛОГЕКСАНОЛА В ЦИКЛОГЕКСАНОН, КАТАЛИЗИРУЕМОЕ МОДИФИЦИРОВАННЫМ ЦЕОЛИТОМ

З.А.Шабанова

Газофазным окислительным дегидрированием при атмосферном давлении и температуре 260–370⁰C в присутствии модифицированного цеолитного катализатора циклогексанол с конверсией 90–99 % был окислен в циклогексанон с селективностью 96–98 %. Изучены кинетические закономерности протекания реакции.

Ключевые слова: окислительное дегидрирование, циклогексанол, циклогексанон, модифицированный клиноптилит.