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THE USE OF MODIFIED ZEOLITES AS CATALYSTS IN THE GAS-PHASE OXIDATION OF OLEFINIC HYDROCARBONS

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Abstract

The results of studies on the creation of highly dispersed metal zeolite systems and the study of their catalytic action in the oxidation of lower olefinic hydrocarbons (ethylene to acetaldehyde, propylene to acetone) are presented. It has been established that the selectivity of the action of these catalysts is determined by the optimal combination of the metal component in them with the acidity and structure of the zeolite. Based on the results of experimental studies of the kinetic regularities of the oxidation reactions of lower olefinic hydrocarbons on the synthesized catalysts, their probable stepwise mechanisms are presented and kinetic models of the reactions are developed.

Keywords:
Metallzeolite catalysts;
Oxidation;
Hydrocarbons.

Iintroduction

The most important fundamental problem in the field of catalysis is the dependence of the catalytic properties from the metal particle size. Up to now, we studied the effect of dispersion at ≥10Å variations in particle size, including several dozen or more metal atoms. Controlled distribution of the acid sites on the surface of ion-exchange properties, a large internal surface, the molecular sieve selectivity in catalysis, shaped catalyst structure with uniform pores and thermal stability of zeolites create favorable conditions for the creation on the basis of the modified ion-exchanged with metal cations with the known catalytic properties the highly efficient catalyst systems for the different reactions. Furthermore, by reducing cations introduced by ion exchange on the zeolite surface, hydrogen and oxygen, the oxidation can also be obtained finely divided metal oxide and metal zeolite catalyst systems, respectively. Following, it is noted that some reactions such as the partial oxidation of aliphatic alcohols occur with two active sites: metal ions (reduced metals, and metal oxides) and Bronsted acid centers of medium strength, which can also be implemented on the zeolite surface. The study of such complex catalyst systems using zeolite carriers, has not only scientific and practical importance, as this type of catalysts are promising in several refining and petrochemical processes, in particular - in the process of hydrogenation refining of petroleum feedstock [1-4].

This paper presents the results of a study on preparation of highly efficient catalytic systems by ion exchange on the basis of synthetic and natural zeolites and metals with known catalytic properties for the reaction of oxidation of lower olefinic hydrocarbons to carbonyl compounds.

Experimental part

Samples of the catalyst for the gas phase oxidation of lower olefinic hydrocarbons to carbonyl compounds were prepared by ion exchange on the basis of known redox catalyst system for liquid-phase of this process, $PdCl_2$-$CuCl_2$ and a synthetic zeolite NaY with SiO_2/Al_2O_3=4.2, which has a relatively high concentration of medium strength acid centres. Cu^{2+} ions and $[Pd(NH_3)_4]^{2+}$ was introduced by ion exchange from aqueous solutions of $CuCl_2$ and $[Pd(NH_3)_4]Cl_2$, followed by washing and drying at 120 °C for 5 hours.

Testing of the activity of synthesized catalyst samples was performed on a flow-circulation installation with Pyrex reactor; at flow apparatus with a tubular Pyrex reactor; at flow apparatus with two-stage quartz reactor with a stepwise supply of oxygen and flow apparatus with a quartz reactor, respectively. The reaction products were analyzed by gas-liquid chromatography using columns filled polysorb; separon W, GNH zeolite, NaH and Paropak-T in a linear programmed temperature rise. Analysis of the reaction products is also carried out by

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gas chromatography «Agilent 7890» with a mass detector «Agilent-5975» with HP-5 MS column, 30 m length.

Below are the results of research and discussion processes: gas phase oxidation of lower olefinic hydrocarbons to carbonyl compounds and oxidizing dimerization of methane on zeolite catalysts modified with metal cations by ion exchange method.

Results and discussion

For the reaction of gas phase oxidation of ethylene to acetaldehyde were synthesized zeolite catalysts containing various CuPdNaY with palladium and copper. The copper content ranged from 0.1 to 10.0% and palladium - from 0.025 to 2.5% by weight of zeolite [5, 6]. From the synthesized catalyst samples showed the highest activity CuPdNaY, containing 1.5% Pd^{2+} and 6.0% Cu^{2+}.

Test samples of catalyst activity was carried out in the temperature range 105-125 S at atmospheric pressure at partial pressures:

P_{O_2} - (0.125 ÷ 0.275) atm.,
P_{H_2O} -. (0.125 ÷ 0.275) atm. and
$P_{C_2H_4}$ - (0.125 ÷ 0.175) atm. and
contact time - (0.67 ÷ 2.0) g (cat) · h / l.

Shows the results of an experimental study of the kinetics of the reaction of gas-phase oxidation of ethylene to acetaldehyde over the zeolite catalyst CuPdNaY, containing 1.5 wt.% Pd^{2+}, and 6.0 wt.% Cu^{2+} (table 1).

Thus, the known redox catalyst system for liquid-phase oxidation of lower olefinic hydrocarbons to carbonyl compounds, $PdCl_2$-$CuCl_2$, when injected into the main components, Pd^{2+} and Cu^{2+} by ion exchange on the surface of the zeolite exhibits high catalytic activity in the gas phase embodiment this reaction. It have been prepared catalysts for the gas phase oxidation of propylene to butylenes acetone and methyl ethyl ketone by this method, too.

Analysis of the published materials led to the conclusion that the mechanism of the oxidation of ethylene to acetaldehyde in the gas phase heterogenized catalysts similar to the mechanism that is mounted to the liquid phase reaction of an embodiment of a catalytic solution of copper chloride and palladium chloride. Therefore, it can be assumed that the gas-phase oxidation of ethylene flows between the same intermediate complexes that are offered and proved by physical methods to an embodiment of the liquid phase of the reaction. On the basis of the well-known analogy, and we carried out experimental studies

Table 1

Experimental kinetic data for the gas phase oxidation of ethylene to acetaldehyde

T	G_k/F	$P^0_{O_2}$	$P^0_{C_2H_4}$	$P^0_{H_2O}$	Conversion	$r_{CH_3CHO} \cdot 10^{-4}$	$r_{CO_2} \cdot 10^{-4}$
°C	g(cat)·h/l	atм.	atм.	atм.	%	mole/g(cat)·hour	mole/g(cat)·hour
105	1.2	0.200	0.1	0.2	14.63	4.9656	0.1110
105	1.2	0.250	0.1	0.2	14.43	4.8580	0.1492
110	1.2	0.150	0.1	0.2	14.93	4.8788	0.3018
110	1.2	0.175	0.1	0.2	18.81	6.1249	0.3921
120	1.2	0.225	0.1	0.2	22.68	7.1829	0.6870
125	1.2	0.275	0.1	0.2	21.68	6.4785	0.9098
110	1.2	0.1	0.2	0.200	19.44	6.2950	0.4549
120	1.2	0.1	0.2	0.150	21.69	6.2082	1.3229
120	1.2	0.1	0.2	0.225	23.64	7.4582	0.7499
125	1.2	0.1	0.2	0.125	19.99	5.0068	1.9340
125	1.2	0.1	0.2	0.200	21.85	6.6125	0.9799
110	1.2	0.2	0.050	0.2	30.06	4.9929	0.2257
110	1.2	0.2	0.100	0.2	19.44	6.2950	0.4548
120	1.2	0.2	0.050	0.2	33.25	5.4217	0.3507
125	1.2	0.2	0.025	0.2	38.26	3.1803	0.1406
125	1.2	0.2	0.100	0.2	21.85	6.6075	0.9791
120	0.67	0.2	0.1	0.2	11.39	6.5625	0.5562
120	0.8	0.2	0.1	0.2	13.14	6.7969	0.6099
120	1.0	0.2	0.1	0.2	18.94	7.1875	0.7042
120	1.2	0.2	0.1	0.2	23.11	7.2464	0.7778
120	2.0	0.2	0.1	0.2	23.37	4.12500	0.743750

suggested stepwise mechanism of gas-phase reaction of ethylene oxidation to acetaldehyde on the catalyst CuPdNaY considering the by-product - carbon dioxide and reoxidation of palladium.

I

$$Pd^{2+}Z_2 + H_2O \overset{K_1}{\rightleftarrows} Pd^{2+}(H_2O)Z^{-}_{2}$$

II

$$Pd^{2+}(H_2O)Z^{-}_{2} + C_2H_4 \overset{K_2}{\rightleftarrows} Pd^{2+}(H_2O)(C_2H4)Z^{-}_{2}$$

III

$$Pd^{2+}(H_2O)(C_2H4)Z^{-}_{2} + H_2O \overset{K_3}{\rightleftarrows} Pd^{2+}(C_2H_4)(OH^-)Z^- + H_3O^+Z^-$$

IV

$$Pd^{2+}(C_2H_4)(OH^-)Z^- + H_3O+Z^- + H_2O \overset{K_4}{\rightleftarrows} OHCH_2CH_2Pd^{2+}(H_2O)Z^-$$

V

$$OHCH_2CH_2Pd^{2+}(H_2O)Z^- \xrightarrow{k} CH_3CHO + Pd^0 + H_3O + Z^-$$

VI

$$OHCH_2CH_2Pd^{2+}(H_2O)Z^- + 5Z{-}Cu^{2+}O^- \xrightarrow{k_u} 2CO_2 + 2H_2O + Pd^0 + H_3O^+Z^- + 5Cu^+Z^-$$

VII

$$Pd^0 + 2Cu^{2+}Z^{-}_{2} \overset{K_5}{\rightleftarrows} Pd^{2+}Z^{-}_{2} + 2Cu+Z^{-}_{2}$$

VIII

$$Cu+Z- + O_2 \overset{K_6}{\rightleftarrows} Z{-}Cu^{2+}O^{-}_{2}$$

IX

$$Z{-}Cu^{2+}O^{-}_{2} \overset{K_7}{\rightleftarrows} 2Z{-}Cu^{2+}O^-$$

X

$$2Z{-}Cu^{2+}O^- \overset{K_8}{\rightleftarrows} Z{-}Cu^{2+}{-}O{-}Cu^{2+}Z- + \tfrac{1}{2}O_2$$

XI

$$Z^-Cu^{2+}{-}O{-}Cu^{2+}Z^- + 2H_3O^+Z^- \overset{K_9}{\rightleftarrows} 2Cu^{2+}Z^{-}_{2} + 3H_2O$$

By using the method of quasi-stationary concentrations based on the proposed mechanism can obtain the following equation for the rate of formation of acetaldehyde:

$$r_{CH_3CHO} = \frac{kK_1K_2K_3K_4P^3_{H_2O}P_{C_2H_4}}{\left[H_3O^+Z^-\right]\left(1 + K_1P_{H_2O} + K_2P_{C_2H_4}\right) + K_2K_3P_{H_2O}P_{C_2H_4} + K_3K_4P^2_{H_2O}} \quad (1)$$

For the rate of formation of carbon dioxide and the current fraction of the surface occupied by hydronium ions suggested the following equation:

$$r_{CO_2} = k\,\frac{P_{CH_3CHO}P_{O_2}^{\frac{1}{2}}}{P^2_{H_2O}} \quad (2)$$

$$\left[H_3O^+Z^-\right] = \left[H_3O^+Z^-\right]^0 e^{k_1P_{H_2O}} \quad (3)$$

where P_i - partial pressure of the i-substance;

the k, k_n - constant rate of formation of acetaldehyde and carbon dioxide;

$$k = k^0 e^{-\frac{E}{RT}}, \quad k_n = k^0_n e^{-\frac{E_i}{RT}};$$

K_1, K_2, K_3, K_4 – constant adsorption equilibrium elementary stages;

$$K_\gamma = K^0_\gamma e^{\frac{Q_\gamma}{RT}} \quad ;$$

k_1 – empirical coefficient, atm^{-1}.

Equations (1), (2) and (3) constitute a kinetic model of the process.

On the basis of the data presented in table 1 has been checked the compliance of the proposed mechanism to experimental kinetic data. It was found that the numerical values of the constants of kinetic model describes quite well the experimental data. The relative error of the experimental and calculated data does not exceed 6%.

Similar mechanisms occur in the oxidation reaction of propylene and butylenes in acetone and methyl ethyl ketone over modified zeolites [21- 24]. Thus, the ion exchange effective finely

Table 2

Estimated values of the kinetic model of the reaction of ethylene oxidation constants

K^0	E	K^0_n	E_n	K^0_1	Q	K^0_2	Q	K^0_3	Q	K^0_3	Q_4	$[H_3O^+Z^-]^0$
атм ·л ·г(кат)$^{-1}$ч$^{-1}$	ккал/моль	атм$^{1.5}$ л г(кат)$^{-1}$ч$^{-1}$	ккал/моль	атм$^{-1}$	ккал/моль	атм$^{-1}$	ккал/моль	атм$^{-1}$	ккал/моль	атм$^{-1}$	ккал/моль	
$0.238 \cdot 10^{21}$	32.25	$0.879 \cdot 10^{22}$	22.33	$0.9052 \cdot 10^{-9}$	16.48	$0.8071 \cdot 10^{-8}$	17.84	$0.1556 \cdot 10^{-6}$	9.31	0.4601	1.0	0.07993

synthesized CuPdNaY catalyst system for olefin gas phase oxidation reactions to lower carbonyl compounds that lack the disadvantages of liquid-phase process variants: corrosiveness catalytic solutions and steam mixtures (catalytic solution contains hydrochloric acid); the formation of condensation products and organochlorine compounds; a non-refundable rate of the palladium and others.

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Применение модифицированных цеолитов в качестве катализаторов газофазного окисления олефиновых углеводородов

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Реферат

Представлены результаты исследований по созданию высокодисперсных металл-цеолитных систем и изучение их каталитического действия в реакции окисления низших олефиновых углеводородов (этилена в ацетальдегид, пропилена в ацетон). Установлено, что селективность действия этих катализаторов определяется оптимальным сочетанием в них металлического компонента с кислотностью и структурой цеолита. Подобраны высокоэффективные катализаторы для исследуемых реакций. На основе результатов экспериментальных исследований кинетических закономерностей протекания реакций окисления низших олефиновых углеводородов на синтезированных катализаторах представлены их вероятные стадийные механизмы и разработаны кинетические модели реакций.

Ключевые слова: металлеолитные катализаторы; окисление; углеводороды.

Olefin karbohidrogenlərinin qaz-fazada oksidləşməsi üçün katalizator kimi modifikasiya olunmuş seolitlərin tətbiqi

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Xülasə

Yüksək dispers metal seolit sistemlərinin yaradılması və onların olefin karbohidrogenlərin (etilenin asetaldehidə, propilenin asetona) oksidləşməsində katalitik təsirinin öyrənilməsinə dair tədqiqatların nəticələri təqdim olunur. Müəyyən edilmişdir ki, bu katalizatorların təsirinin seçiciliyi onlarda olan metal komponentin seolitin turşuluğu və strukturu ilə optimal birləşməsindən asılıdır. Tədqiq olunan reaksiyalar üçün seçilmiş yüksək effektiv katalizatorlar üzərində reaksiyaların kinetik qanunauyğunluqlarının eksperimental tədqiqatlarının nəticələrinə əsasən onların ehtimal olunan mərhələli mexanizmləri təqdim edilmiş və reaksiyaların kinetik modelləri hazırlanmışdır.

Açar sözlər: metalseolit katalizatorları; oksidləşmə; karbohidrogenlər.