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STUDY ON HETEROGENEOUS CATALYTIC OXIDATIVE DEHYDROGENATION OF ISOPROPYLBENZENE TO α-METHYLSTYRENE

Oleg Fedevych[1], ✉

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Abstract. The influence of the FeBiMoO catalysts composition on their properties in the oxidative dehydrogenation reaction of isopropylbenzene has been studied. The catalyst with the atomic ratio of active components Fe : Bi : Mo = 2 : 1 :2 was found to be the optimum for the maximum yield of *α*-methylstyrene. The assumption that the improvement of catalytic properties is due to the formation of a ternary compound $Fe_2Bi_3Mo_2O_{12}$, which provides optimal acid-base properties of the catalytic surface, has been approved. The kinetic regularities of the process have been investigated on the catalyst of optimal composition and kinetic equations describing the process have been proposed.

Keywords: catalyst, kinetics, α-methylstyrene.

1. Introduction

α-Methylstyrene (MS) is a monomer used to produce various polymeric materials, in particular special rubbers, and a wide range of copolymers.[1-4] MS, like styrene, is produced in industry by catalytic dehydrogenation of cumene[5,6] or ethylbenzene, respectively. However, these processes are thermodynamically limited and the yield of styrene or MS does not exceed 40%.

The processes of hydrocarbons oxidative dehydrogenation, which are effectively realized on molybdates of metals of variable valence, are deprived of this disadvantage.[7] According to Haber,[8] hydrocarbon molecules are adsorbed on active centers (cations Bi^{+3}, Fe^{+3}, Ni^{+2}, Co^{+2}) to form a π-complex with the subsequent rupture of the activated (due to σ-π conjugation) C–H bond in the α-position to the aromatic nucleus with the formation of an aryl radical. In the next stage, these radicals form σ-complexes at the neighboring center (Mo–O polyhedra). The complexes are bound with the oxygen ion and the separation of the hydrogen atom in the β-position leads to the formation of a double bond. Thus, styrene is formed from ethylbenzene and *α*-methylstyrene from isopropylbenzene (IPB). In addition to the main reaction (oxidative dehydrogenation), side reactions (oxidative condensation and complete oxidation) proceed on aprotic active centers with too strong hydrocarbon adsorption.[9,10]

It should be noted that if the oxidative dehydrogenation of ethylbenzene has been studied quite thoroughly,[11-15] then information on the oxidative dehydrogenation of cumene is practically absent. The aim of this work was to study the process of heterogeneous catalytic oxidative dehydrogenation of isopropylbenzene to MS – a valuable intermediate. First of all, it was necessary to select the appropriate catalyst. It is known that catalysts based on iron molybdate are used for selective oxidation.[16,17] The Fe-Bi-Mo-O system exhibits optimal properties for oxidative dehydrogenation of ethylbenzene.[11-13] Therefore, we studied the influence of this system composition on its catalytic properties in the process of oxidative dehydrogenation of IPB and the regularity of this reaction on the catalyst of optimal composition.

2. Experimental

The catalysts were prepared using ammonium heptamolybdate $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (reagent grade), iron nitrate $Fe(NO_3)_3\cdot 9H_2O$ (analytical grade), and bismuth nitrate $Bi(NO_3)_3\cdot 5H_2O$ (reagent grade) according to the method described by Zhyznevskiy *et al.*[9] After preparation, the catalysts were calcined for 5 h at a temperature of 723 K, ground to a grain size of 2–3 mm and activated in a flow reactor at 673 K by a reaction mixture of 5 vol% IPB in the air to achieve the constant activity.

The specific surface area of the investigated catalysts was measured using the thermal desorption of argon. The acidity and basicity of the catalyst surface were determined using pulse chromatography. The temperature of the thermostat was 343 K. The total acidity and basicity of the catalytic surface determined by the

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[1] Lviv Polytechnic National University
12, S. Bandery St., Lviv 79013, Ukraine
✉ *foe69@ukr.net*

difference between the amount of fed and non-chemisorbed NH_3, or CH_3COOH, was expressed in mmol/m^2. The strength of the surface basic and acid centers, which is characterized by the activation energy of thermal desorption of NH_3 or CH_3COOH from the catalyst surface, was determined by the dependence of the desorption rate on temperature. For this purpose, programmed thermal desorption of the compounds was carried out from 343 to 773 K with a thermostat heating rate of 13 K/min. Calculations of thermodesorption activation energy were performed according to the method described by Kharlamov *et al.*[18]

Information about the nature of the catalytic action of the studied catalysts was obtained by studying their phase composition. X-ray diffraction analysis was performed on a DRON-2 diffractometer (copper Kα radiation with a nickel filter in the 2θ range of 20–50°, voltage 40 kV, current 20 mA). Set data[19] were used to decipher the diffractograms.

IPB used was of reagent grade. The reaction was investigated by the micropulse method in a complete-mix differential reactor with the vibrofluidized catalyst bed. The reactor was a stainless-steel tube (l = 180 mm, d_{in} = 5 mm), in which a catalyst layer with a grain size of 1.0–1.5 mm was placed on a mesh grid. The reactor was connected to a mechanical electric vibrator with a frequency of 50 Hz and oscillations amplitude of 2–10 mm. The volume of the catalyst layer increased by 2–3 times, which ensured the absence of concentration and temperature gradients. Previous experiments have shown that under such conditions the reaction takes place under the kinetic mode because its rate does not depend on either the catalyst grain size (if d_{gr} < 4 mm) or the linear velocity of the gas flow through the vibrated liquid catalyst bed.

The experiments were performed as follows. The carrier gas stream (He) was passed through a layer of vibrated liquefied catalyst, for which the definite temperature was sustained. To ensure a steady state of the catalyst surface before the impulse supply (V_{imp} = 5.5 cm^3), the reactor was blown with a standard mixture (5 vol% of IPB in the air) for 15 min at 673 K. The impulse of the reaction mixture was fed into the carrier gas stream, and after leaving the reactor it entered the tee, where was divided into two equal streams for chromatographic analysis on two different columns.[11] Thus, all products were quantified in one pulse. The oxygen concentration in the reaction mixture was regulated by changing the flow rate of oxygen and helium, and the IPB concentration – by changing the evaporator temperature with a constant supply of oxygen-helium mixture. The results of the studies were defined as the average value of 2–3 parallel experiments, the difference between which did not exceed 10 %.

3. Results and Discussion

In the first stage of research, the influence of the catalysts' composition on their catalytic properties during the IPB oxidation was studied. The binary systems Fe-Mo-O, Bi-Mo-O and the ternary system were studied. The studies were performed at 613, 643, and 673 K. Conditions and results of experiments at 673 K are shown in Table 1.

It is noticeable that the increase in iron content in binary Fe-Mo-O catalysts increases the catalytic activity and reduces the formation selectivity and MS yield.

The increase of bismuth content in Bi-Mo-O catalysts leads to an increase in the activity and selectivity of IPB formation. The introduction of iron ions into bismuth molybdenum oxide catalysts promotes the growth of both activity and selectivity. Maximum activity and selectivity are shown by the catalysts with an atomic ratio Fe : Bi : Mo = 2 : 1 : 2.

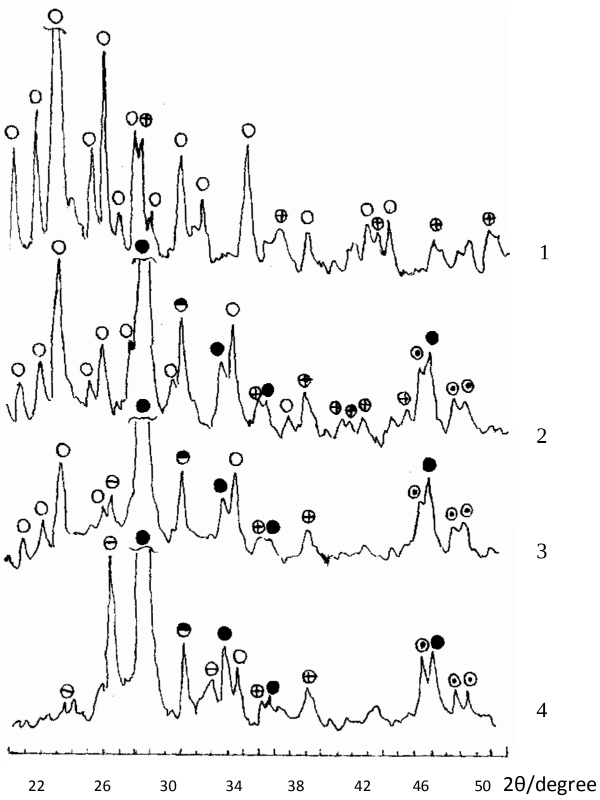

Fig. 1. X-ray spectra of Fe-Bi-Mo-O$_x$ catalysts: FeMoO$_x$ (1) and $Fe_2BiMo_2O_x$ (2) catalysts before activation and operation at a pulse installation; $Fe_2BiMo_2O_x$ catalyst after activation and operation at a pulse installation (3) and reduced by 46 pulses of isopropylbenzene at 693 K (4). Phases: ○ – α-$Fe_2(MoO_4)_3$; ⊘ – MoO_2; ⊖ – α-$Bi_2(MoO_4)_3$; • – γ-Bi_2MoO_6; ⊛ – $Fe_2Bi_3Mo_2O_{12}$; ⊗ – Fe_2O_3·(3–4)MoO_3

Table 1. The influence of the composition of Fe-Bi-Mo-O catalysts on the oxidative dehydrogenation of IPB (V_{imp} = 5.5 cm^3, V = 0.6 cm^3/s, the reaction mixture of 5 vol% IPB in air, T = 673 K)

Catalyst composition	$S_{spec.}$, m^2/g	τ, s	X_{IPB}, %	S_{MS}, %	S_{CO_2+CO}, %	MS yield, %
$FeMo_2O_x$	5.0	2.4	45.3	39.1	60.9	17.7
		3.6	53.1	30.1	69.9	16.0
$Fe_{1.5}Mo_2O_x$	6.3	2.4	72.0	44.1	55.9	31.8
		3.6	83.4	39.0	61.0	32.5
$Fe_2Mo_2O_x$	1.2	2.4	86.1	34.0	66.0	29.2
		3.6	91.2	28.8	71.2	26.3
$Fe_{2.5}Mo_2O_x$	13.4	2.4	82.4	24.0	76.0	19.8
		3.6	91.6	19.1	80.9	17.5
$Bi_{0.5}Mo_2O_x$	2.9	2.4	50.1	39.2	60.8	19.6
		3.6	53.4	36.1	63.9	19.3
$BiMo_2O_x$	4.0	2.4	59.4	44.3	55.7	26.3
		3.6	66.4	39.8	60.2	26.4
$Bi_{1.5}Mo_2O_x$	4.3	2.4	68.4	60.2	39.8	41.2
		3.6	76.4	55.4	44.6	42.3
$FeBiMo_2O_x$	3.6	2.4	81.2	65.6	34.4	53.3
		3.6	85.4	61.4	38.6	52.4
$Fe_{1.5}BiMo_2O_x$	4.1	2.4	84.5	79.3	20.7	67.0
		3.6	91.6	76.2	23.8	69.8
$Fe_2BiMo_2O_x$	5.0	2.4	87.1	86.4	13.6	75.3
		3.6	96.2	83.1	16.9	79.9
$Fe_{2.5}BiMo_2O_x$	8.6	2.4	84.1	81.2	18.2	60.3
		3.6	93.1	78.1	21.9	72.7

Notes: S_{spec} is a specific surface area of the catalyst; X_{IPB} is IPB conversion; S_{MS} is a selectivity of MS formation; S_{CO_2+CO} is a selectivity for the sum CO_2+CO

Information about the nature of the active components of the catalysts under study was obtained on the basis of their phase composition. The radiographs of the studied catalysts (Fig. 1) show that sample 1 with a ratio of Fe :Mo = 1 : 1 is a phase of normal iron molybdate $Fe_2(MoO_4)_3$ with characteristic imprints d/n = 3.80; 3.47; 4.08; and 3.24 Å,[19] with an admixture of the phase $Fe_2O_3{\cdot}(3–4)MoO_3$ with imprints d/n = 3.19; 2.50; 2.31 Å.[19] The spectra of freshly prepared $Fe_2BiMo_2O_x$ catalyst (Fig. 1, sample 2) indicate the phase composition: $Fe_2(MoO_4)_3$, α-$Bi_2(MoO_4)_3$, γ-Bi_2MoO_6 and the ternary compound $Fe_2Bi_3Mo_2O_{12}$ with characteristic imprints d/n = 1.9; 1.88; 1.86 Å,[20] as well as with prints d/n = 2.50; 2.31; 2.17 Å, characteristic of the $Fe_2O_3{\cdot}(3–4)MoO_3$ phase.

After activation and operation at the pulse installation of the sample 3 (catalyst $Fe_2BiMo_2O_x$), the intensity of the peaks corresponding to the phases α-$Bi_2(MoO_4)_3$ and γ-Bi_2MoO_6 almost did not change compared with freshly prepared catalyst (sample 2), but the number and intensity of phases $Fe_2(MoO_4)_3$ and $Fe_2O_3{\cdot}(3–4)MoO_3$ decreased significantly and a low-intensity peak with an imprint d/n = 3.39 Å, characteristic of the MoO_2 phase, appeared. This indicates that during the operation of the $Fe_2BiMo_2O_x$ catalyst, the Mo^{6+} ions are partially reduced to Mo^{4+} with the release of the MoO_2 phase.

This reduction process is clearly manifested when the catalyst is treated with IPB pulses (sample 4). Many peaks characteristic of $Fe_2(MoO_4)_3$ disappear in the spectrum of this sample, and an intense peak with d/n = = 3.40 Å, characteristic of the MoO_2 phase, appears. Peaks characteristic of α- and γ-bismuth molybdates and imprints of the $Fe_2O_3{\cdot}(3–4)MoO_3$ phase also become less intense after the reducing activity of IPB. Thus, it can be considered that the phase of the ternary compound $Fe_2Bi_3Mo_2O_{12}$ is the most stable with respect to the reducing ability of IPB.

Comparing data on the phase composition of the Fe-Bi-Mo-O system and its catalytic properties in the oxidation of IPB (see Table 1), we can assume that the increase in catalytic activity during the reaction of oxidative dehydrogenation is due to the formation of the ternary compound $Fe_2Bi_3Mo_2O_{12}$. This conclusion is also confirmed by the results of differential thermal, thermogravimetric, and IR analyses.[9,21]

It is known that during hydrocarbons oxidation the properties of oxide catalysts are specified by the acidity and basicity of their surface. Acid centers are metal ions with high electronegativity, which activate electron donating reagents (olefins, alkyl aromatic hydrocarbons), and the optimal acidity of these centers ensures the selectivity of oxidative processes.

Tables 2 and 3 show data on the acidity and basicity of the catalyst surface before operation and after reaching a steady state in contact with the reaction mixture.

Table 2. Adsorption and thermal desorption of ammonia on the surface of Fe-Bi-Mo-O catalysts (ΣS = 2 m^2; V_{imp} = 0.5 cm^3; V_{He} = 0.28 cm^3/s; adsorption temperature is 343 K; thermal desorption is 13 K/min)

Symbol	Composition	NH_3 adsorbed, mmol/m^2	$N_c \cdot 10^{-18}$	Peak I		Peak II		S_1/S_2
				T_{max}, K	$E_d \pm 5$, kJ/mol	T_{max}, K	$E_d \pm 5$, kJ/mol	
K_1	$Fe_2Bi_{0.5}Mo_2Ox$	5.6	3.4	423	80	503	131	2.0
K_1*	$Fe_2Bi_{0.5}Mo_2Ox^*$	2.7	1.6	403	137	473	147	1.5
K_2	Fe_2BiMo_2Ox	3.1	1.8	423	34	593	115	14
K_2*	$Fe_2BiMo_2Ox^*$	2.9	1.7	423	31	743	131	8
K_3	$Fe_2Bi_2Mo_2Ox$	2.2	1.3	433	36	543	41	1.9
K_3*	$Fe_2Bi_2Mo_2Ox^*$	3.6	2.2	413	67	483	66	1.1
K_4	$Fe_2Bi_3Mo_2Ox$	1.1	0.7	443	71	493	92	2.0
K_4*	$Fe_2Bi_3Mo_2Ox^*$	3.1	1.9	433	68	523	70	11

Notes: * catalysts after operation at the pulse installation; N_c is the number of active centers on the catalyst surface; E_d is a thermodesorption activation energy; T_{max} is the maximum temperature of the thermal desorption peak; S_1/S_2 is the ratio of the first and second desorption peak areas; ΣS is the total surface area of the loaded catalyst

Table 3. Adsorption and thermal desorption of CH_3COOH on the surface of Fe-Bi-Mo-O catalysts (ΣS = 2 m^2; V_{imp} = 0.39 cm^3; V_{He} = 0.28 cm^3/s; adsorption temperature is 343 K; thermal desorption is 13 K/min)

Symbol	Composition	NH_3 adsorbed, mmol/m^2	$N_c \cdot 10^{-18}$	Peak I		Peak II		S_1/S_2
				T_{max}, K	$E_d \pm 5$, kJ/mol	T_{max}, K	$E_d \pm 5$, kJ/mol	
K_1	$Fe_2Bi_{0.5}Mo_2Ox$	2.3	1.4	398	80	573	132	9
K_1*	$Fe_2Bi_{0.5}Mo_2Ox^*$	4.3	2.6	393	66	573	122	7
K_2	Fe_2BiMo_2Ox	3.8	2.3	393	61	553	111	10
K_2*	$Fe_2BiMo_2Ox^*$	4.1	2.5	408	54	583	79	6
K_3	$Fe_2Bi_2Mo_2Ox$	4.6	2.7	403	83	573	119	14
K_3*	$Fe_2Bi_2Mo_2Ox^*$	3.4	2.0	433	52	583	84	5
K_4	$Fe_2Bi_3Mo_2Ox$	4.6	2.7	413	69	583	86	13
K_4*	$Fe_2Bi_3Mo_2Ox^*$	3.7	2.2	393	64	573	97	8

Note: designations are the same as in Table 2

With increasing bismuth content, the total surface acidity of freshly prepared catalysts decreases, and the basicity increases. The acidity and basicity of the surface in the steady state of the catalysts does not change significantly with increasing bismuth content.

When determining the acidity, we observed a small third peak during thermal desorption on the catalysts K_1, K_2, K_3, in addition to the two main peaks. The first peak of NH_3 thermal desorption is observed at a relatively low temperature. The highest temperature (T_{max} = 443 K) has a catalyst with a maximum bismuth content. The minimum activation energy of the first peak thermodesorption (31 kJ/mol) has a catalyst with an optimal content of bismuth (K_2). This catalyst also has the largest T_{max} of the second peak. This means that the catalyst with optimal catalytic properties binds NH_3 with the least force on weak acid centers and with the largest one – on the moderate acid centers of the surface.

A comparison of the surface basicity of the studied catalysts (Table 3) indicates two forms of CH_3COOH adsorption. The first form has almost the same T_{max} of desorption peak (393–433 K) and the value of E_d. The second form of the thermodesorption peak also has almost the same T_{max} (553–583 K). The maximum E_d is observed for K_1 and the minimum E_d – for K_2, *i.e.*, for the optimal catalyst. The general basicity also practically does not depend on bismuth content.

The number of acid centers on the surface of freshly prepared catalysts decreases with increasing bismuth content (Table 2). After activation and operation at the pulse installation, the number of acid centers is smaller in comparison with freshly prepared catalysts until the ratio of Bi : Mo reaches 0.5 and the number is greater when the Bi : Mo ratio is 1–1.5.

As shown by Zhyznevskiy[9] and Ai,[21] the activation of alkyl aromatic hydrocarbons during partial oxidation is carried out on acid centers and the retention of the reagent molecule depends on their strength. The strength of acid centers can be characterized by the temperature of thermodesorption maximum peak and the activation energy of thermodesorption. The best catalyst (K_2) has the highest S_1/S_2 ratio, from which it can be concluded that the activation of IPB molecules involved in the formation of MS occurs on the acid centers of the first form of adsorption (peak I). In this catalyst the number of acid centers of the second form of NH_3 adsorption (peak II), which strongly bind the reagent molecules resulting in the complete oxidation is an order of magnitude less than the number of centers of the first form of adsorption. One can see from Table 2 that on the $Fe_2BiMo_2O_x$ catalyst, which provides the maximum selectivity of the MS formation the number of such centers is the least.

Acid molecules, in particular O_2, are activated on the basic centers. As can be seen from Table 3 the number of basic centers on the catalysts surface before activation increases slightly with increasing bismuth content, and after activation this value does not change significantly. The strength of the basic active centers, as well as acid ones, are characterized by T_{max} and the activation energy of the desorption peaks of acetic acid. The T_{max} value of the second desorption peak is the largest on the catalyst of optimal composition, but the number of active centers that generate highly active forms of oxygen, causing complete oxidation on this catalyst is insignificant ($S_1 >> S_2$).

Thus, the $Fe_2BiMo_2O_x$ catalyst has a sufficient number of surface acid and basic centers with optimal interaction energy of hydrocarbon and oxygen reagents.

The catalyst of this composition was chosen to investigate the regularities of IPB interaction with oxygen. Kinetic regularities were studied in the range of 633–693 K and contact time of 0.25–2.0 s. Under such conditions, the IPB conversion did not exceed 30%. The oxygen concentration was changed in the range of 7.0–24.0 mol% ($3.1 \cdot 10^{-3}$–$10.6 \cdot 10^{-3}$ mol/L), and the IPB concentrations varied from 1.2 to 10.0 mol% ($0.54 \cdot 10^{-3}$–$4.8 \cdot 10^{-3}$ mol/L). The research results are represented in Table 4 and Figs. 2, 3.

The linear form of data from Table 4 and Figs. 2, 3 in the coordinates lg$W = f$(lg$C$) allowed us to establish that the reaction order of MS and CO_2 formation with respect to IPB is 0.75 and 0.5, respectively, and the reaction order of CO_2 formation with respect to oxygen is 0.9. As can be seen from Fig. 3a, the rate of MS formation does not depend on the oxygen concentration in case of $Co_2 > 4 \cdot 10^{-3}$ mol/L.

Special experiments have shown that the introduction of additional amounts of MS into the reaction mixture does not significantly affect the rate of MS formation in the studied temperature range, *i.e.*, does not have an inhibitory effect. To establish the role of the MS re-oxidation stage, experiments on its oxidation in the absence of IPB were conducted. The results are represented in Table 5.

It is obvious that even in the absence of competitive action of IPB, the rate of CO_2 formation is almost an order of magnitude lower than that during IPB oxidation. Thus, we can assume that during IPB oxidative dehydrogenation under the experimental conditions the products of partial (MS) and complete oxidation (CO_2) are formed in parallel.

Thus, the kinetics of the IPB oxidative dehydrogenation in the investigated concentration and temperature ranges (at $C_{O2} > 4 \cdot 10^{-3}$ mol/L) can be described by empirical equations:

$$W_{MS} = k_{MS} \cdot C_{IPB}^{0.75} \quad (1)$$

$$W_{CO_2} = k_{CO_2} \cdot C_{IPB}^{0.5} \cdot C_{O_2}^{0.9} \quad (2)$$

where W_{MS} and W_{CO2} are formation rates of methylstyrene and CO_2, respectively, mol/m^2·s; C_{O2} and C_{IPB} are concentrations of oxygen and isopropylbenzene in the reaction zone, respectively, mol/L; k_{MS} and k_{CO2} are the rate constants of methylstyrene and CO_2 formation.

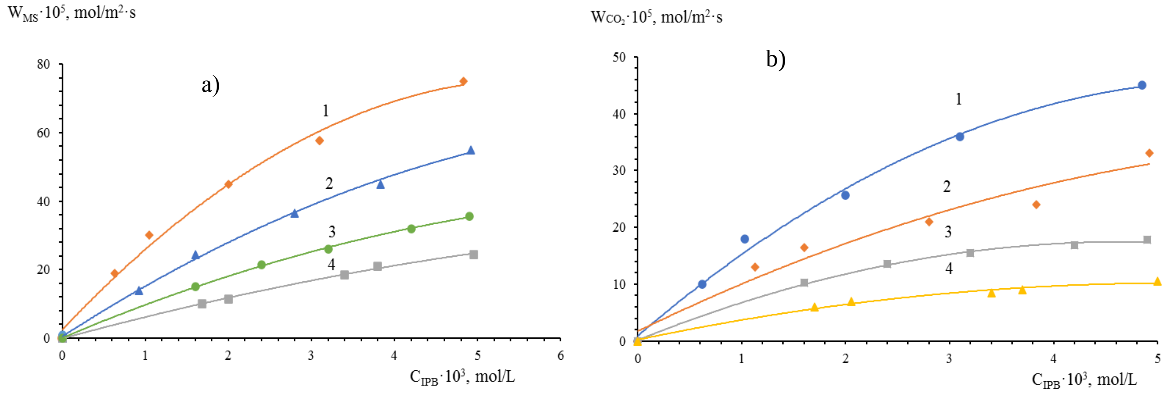

Fig. 2. The effect of IPB concentration on the MS (a) and CO_2 (b) formation rate during isopropylbenzene oxidative dehydrogenation over Fe_2BiMo_2Ox catalyst ($\tau = 0.5$ s; $Co_2 = 10.0 \cdot 10^{-3}$ mol/L) at different temperatures: 693 K (1); 673 K (2); 653 K (3) and 633 K (4)

Table 4. The effect of temperature and reagents concentration on the oxidative dehydrogenation reaction of isopropylbenzene (S_{spec} = 5 m^2/g; τ = 0.5 s)

T, K	$C_{O_2}\cdot 10^3$, mol/L	$C_{IPB}\cdot 10^3$, mol/L	$W_{MS}\cdot 10^5$, mol/m$^2\cdot$s	$W_{CO_2}\cdot 10^5$, mol/m$^2\cdot$s	S_{MS}, %	k_{MS}	k_{CO_2}	$k_{MS}^{aver.}$ k_{MS}^{calc}	$k_{CO_2}^{aver}$ $k_{CO_2}^{calc}$
Effect of IPB concentration									
693	10.4	4.82	69.0	33.9	95.8	0.0477	0.298	0.046±0.0044	0.337±0.036
	10.2	3.10	57.5	30.0	95.5	0.0439	0.334		
	9.8	2.00	45.0	25.8	94.0	0.0474	0.370		
	10.4	1.05	30.0	18.0	93.8	0.0517	0.339		
	10.6	0.61	19.8	14.1	92.7	0.0508	0.342	0.045	0.359
673	10.6	4.96	54.8	26.0	95.0	0.0293	0.221	0.031±0.0021	0.249±0.020
	10.4	3.83	45.0	24.0	94.4	0.0292	0.236		
	10.1	2.80	36.7	21.3	93.9	0.0301	0.252		
	10.0	1.60	24.8	16.5	93.1	0.0310	0.258		
	9.7	0.95	18.0	13.1	92.5	0.0333	0.276	0.030	0.242
653	10.5	4.91	38.0	17.9	95.1	0.0205	0.154	0.0186±0.0018	0.163±0.009
	10.3	4.20	32.1	16.8	94.5	0.0195	0.159		
	10.1	3.20	26.0	15.5	93.8	0.0167	0.171		
	10.3	2.40	19.2	13.2	92.9	0.0178	0.165		
	9.8	1.60	15.0	10.5	92.8	0.0187	0.167	0.0199	0.158
633	10.4	4.98	24.1	10.5	95.6	0.0129	0.0907	0.0130±0.0014	0.092±0.003
	10.1	3.70	20.7	9.0	95.4	0.0147	0.0903		
	10.2	3.40	18.5	8.3	95.3	0.0131	0.0884		
	10.4	2.02	12.0	7.0	93.9	0.0126	0.0951		
	9.9	1.70	10.0	6.1	93.6	0.0119	0.0943	0.0128	0.101
Effect of oxygen concentration									
693	1.53	3.10	22.5	4.3	98.0		0.264		0.330±0.030
	2.01	3.15	24.5	6.0	98.1		0.286		
	2.61	2.95	40.2	8.0	97.8		0.311		
	3.10	3.21	45.1	9.5	97.7	0.0444	0.304	0.045±0.004	
	4.80	3.13	52.4	14.0	97.1	0.0396	0.306		
	7.00	3.05	54.6	20.1	96.1	0.0420	0.317		
	8.80	3.07	52.6	24.4	95.1	0.0405	0.312		
	11.60	3.12	56.0	30.1	94.3	0.0424	0.297	0.044	0.360
673	1.81	3.12	13.1	4.0	96.8		0.210		0.220±0.016
	2.56	3.14	18.3	5.2	96.9		0.201		
	3.50	2.98	25.0	7.1	96.9		0.205		
	4.90	3.10	34.9	10.8	96.6	0.0296	0.232	0.0296±0.004	
	6.10	3.15	34.1	13.0	95.9	0.0256	0.227		
	8.00	3.12	35.8	16.8	95.0	0.0271	0.231		
	10.6	2.99	36.7	21.1	94.0	0.0287	0.231		
	12.1	3.00	37.2	23.0	93.6	0.0291	0.223	0.0303	0.220
653	1.64	3.18	7.0	3.2	95.2		0.180		0.175±0.0080
	2.20	3.06	11.1	4.1	96.1		0.181		
	3.10	3.14	16.2	5.5	96.4		0.178		
	4.70	2.98	23.5	8.0	96.3	0.0184	0.182	0.0193±0.008	
	6.30	3.07	24.2	10.3	95.6	0.0191	0.177		
	8.20	3.11	25.2	12.4	94.8	0.0191	0.167		
	10.3	3.12	26.4	15.5	93.9	0.0200	0.170		
	11.8	3.03	25.9	16.6	93.4	0.0201	0.164	0.0199	0.160
633	1.63	2.95	4.5	1.8	95.7		0.107		0.102±0.005
	2.10	2.98	7.1	2.2	96.6		0.105		
	3.21	2.12	11.5	3.5	96.7		0.110		
	4.82	3.04	16.1	4.7	96.8	0.0125	0.104	0.0134±0.009	
	6.31	3.20	18.1	6.0	96.5	0.0134	0.101		
	8.12	3.00	18.8	7.5	95.8	0.0147	0.104		
	10.42	2.98	16.9	8.3	94.8	0.0132	0.093		
	12.10	3.08	17.6	9.5	94.3	0.0134	0.091	0.0128	0.101

Notes: k_{MS}^{aver} average constant rate of MS formation; k_{MS}^{calc} calculated constant rate of MS formation; $k_{CO_2}^{aver}$ average constant rate of CO_2 formation; $k_{CO_2}^{calc}$ calculated constant rate of CO_2 formation

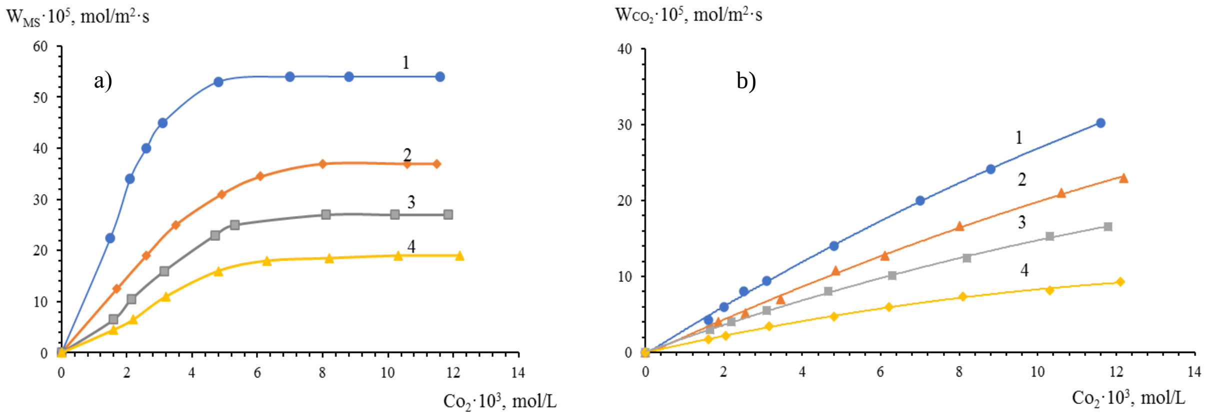

Fig. 3. The effect of oxygen concentration on the MS (a) and CO_2 (b) formation rate during isopropylbenzene oxidative dehydrogenation over Fe_2BiMo_2Ox catalyst ($\tau = 0.5$ s; $C_{IPB} = 3.1\cdot10^{-3}$ mol/L) at different temperatures: 693 K (1); 673 K (2); 653 K (3) and 633 K (4)

Table 5. Oxidation of methylstyrene during isopropylbenzene oxidation over $Fe_2BiMo_2O_x$ catalyst ($S_{spec} = 5$ m²/g; $\tau = 0.5$ s)

T, K	$C_{O2}\cdot10^3$, mol/L	$C_{MS}\cdot10^3$, mol/L	$W_{CO2}\cdot10^5$, mol/m²·s
653	11.0	3.5	2.4
673	10.8	3.6	3.7
693	10.3	3.4	4.6
713	10.5	3.1	6.3

The suitability of Eqs. (1) and (2) for describing the kinetics of IPB oxidative dehydrogenation on the $Fe_2BiMo_2O_x$ catalyst is evidenced by the satisfactory constancy of the rate constants of MS and CO_2 formation (see Table 4).

Using the values of the rate constants at 633, 653, 673 and 693 K and we calculated the values of activation energies and preexponential factors in the Arrhenius equations by the least squares method:

$$k_{MS} = 4.03 \pm 0.30 \cdot 10^4 \cdot e^{-\frac{81200\pm1500}{RT}} \qquad (3)$$

$$k_2 = 4.10 \pm 0.35 \cdot 10^5 \cdot e^{-\frac{82600\pm1600}{RT}} \qquad (4)$$

The values of the rate constants calculated by these equations almost coincide with the experimental data (see Table 4) and can be used to optimize the process. Under optimal conditions ($\tau = 2.8$ s; $T = 683$ K) the yield of α-methylstyrene is 84 %.

The rate of MS formation is determined by the IPB concentration in the reaction mixture (Eq. 1) and does not depend on the oxygen concentration (at $C_{O2} > C_{O2}^{min}$). This allows us to assume that the limiting stage of the process is associated with activated adsorption of IPB and formation of an aryl radical. This radical generates MS, which is practically not oxidized. However, on the centers of destructive and complete oxidation, which require a large excess of oxygen, the order of oxygen is close to unity. Therefore, the increase in IPB concentration and the decrease in the concentration of oxygen contribute to the increase in the selectivity of MS formation.

Since the values of activation energies of oxidative dehydrogenation reactions and complete oxidation of IPB are close (Eqs. 3 and 4), the selectivity of MS formation is not actually changed in the investigated temperature range.

4. Conclusions

The physico-chemical and catalytic properties of the Fe-Bi-Mo-O system during IPB oxidative dehydrogenation were studied. It was found that the catalyst of $Fe_2Bi_3Mo_2O_x$ composition, in which the formation of the chemical compound $Fe_2Bi_3Mo_2O_{12}$ was detected, had the optimum catalytic properties in the reaction of catalytic oxidative dehydrogenation of isopropylbenzene to α-methylstyrene. Using the catalyst of optimal composition, the regularities of IPB oxidative dehydrogenation were investigated. It was established that MS and products of complete oxidation are formed in parallel. On the basis of experimental data we obtained equations, which satisfactorily describe the process kinetics; this allowed to optimize the process.

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ДОСЛІДЖЕННЯ ГЕТЕРОГЕННО-КАТАЛІТИЧНОГО ОКИСНЮВАЛЬНОГО ДЕГІДРУВАННЯ ІЗОПРОПІЛБЕНЗОЛУ ДО α-МЕТИЛСТИРОЛУ

Анотація. *Вивчено вплив складу FeBiMoO каталізаторів на їхні властивості в реакції окиснювального дегідрування ізопропілбензолу і встановлено, що оптимальним для забезпечення максимального виходу α-метилстиролу є каталізатор з атомним співвідношенням активних компонентів Fe : Bi : Mo = 2 : 1 :2. На підставі вивчення фазового складу обґрунтовано припущення, що поліпшення каталітичних властивостей зумовлено утворенням потрійної сполуки складу* $Fe_2Bi_3Mo_2O_{12}$*, що забезпечує оптимальні кислотно-основні властивості каталітичної поверхні. На каталізаторі оптимального складу досліджено кінетичні закономірності перебігу процесу і запропоновано кінетичні рівняння, що задовільно описують його.*

Ключові слова: *каталізатор, кінетика, α-метилстирол.*