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ULTRASONIC ACTIVATION OF THE CATALYSTS OF ETHYLBENZENE DEHYDRATION TO STYRENE

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Abstract. The ultrasonic treatment of Fe_2-Bi-Mo_2-O_x catalyst of ethylbenzene oxidative dehydration to styrene has been studied. Its physico-chemical properties have been compared with those of non-activated catalyst before and after operation. It has been shown that the catalyst prepared from salts solution activated by ultrasound has better activity and increases styrene yield under the same conditions.

Keywords: ultrasound, catalyst, ethylbenzene, styrene.

1. Introduction

Oxidative dehydration of hydrocarbons, olefins namely, has advantages over usual high-temperature catalytic dehydration [1]. First of all, it takes place at lower temperatures ensuring the increase of process selectivity. Secondly, the oxidative dehydration allows to remove thermodynamical restrictions connected with the reversibility of the simple dehydration reaction resulting in the increase of carbon conversion. Moreover, oxygen in the reaction mixture prevents coking of the catalyst surface; therefore the catalyst can work longer without regeneration. In the presence of oxygen the endothermic reaction turns into exothermic one and the obtained heat may be used for technological purposes.

It is well-known [2] that ultrasonic activation of heterogeneous catalysts increases their activity. Therefore the aim of our work is the investigation of ultrasonic (US) treatment of developed by us Fe_2-Bi-Mo_2-O_x catalyst for the oxidative dehydration of ethylbenzene (EB) to styrene (St).

2. Experimental

The catalyst activation was carried out as follows. Solutions of iron and bismuth nitrate and hexamolibdate ammonium in water were treated by ultrasonic oscillations (22 kHz, power 100 W) for 2 h. Then the solutions were evaporated using water bath under stirring till the dry residue was formed. The residue was grinded by a ball mill, moistened and "worms" were formed by means of the gel pressed through a glass tube with the internal diameter of 3 mm. The "worms" were dried first at room temperature for 12 h, then in a drying oven for 5 h with the temperature rising from 320 to 473 K. After this the "worms" were fried at 723 K for 5 h. The same procedure was applied to prepare the untreated catalyst. Then the catalysts were grinded to the sizes of 1-3 mm and activated in a flow reactor at 713 K by the reaction mixture of 5 mol% EB in the air till the constant activity of the catalysts.

The catalytic properties of untreated [3] and treated by ultra-sonic oscillations (US-treated) catalysts were investigated in a flow reactor with the impulse feed of the reaction mixture of 5 mol % EB in the air.

The surface acidity and basicity were determined using the impulse chromatographic method in accordance with NH_3 and CH_3COOH chemosorption (Fig. 1).

3. Results and Discussion

The obtained results of the catalytic and physico-chemical properties of the catalysts are represented in Table 1.

One can see from Table 1 that US-treatment increases the catalysts activity. The temperature at which 50 % conversion of EB is achieved over US-treated catalyst is lower by 21 K than that over untreated catalyst. At 693 K and contact time 3.6 s EB conversion is 100 % over activated catalyst and only 93 % – over non-activated one. The same regularity is observed at other temperatures.
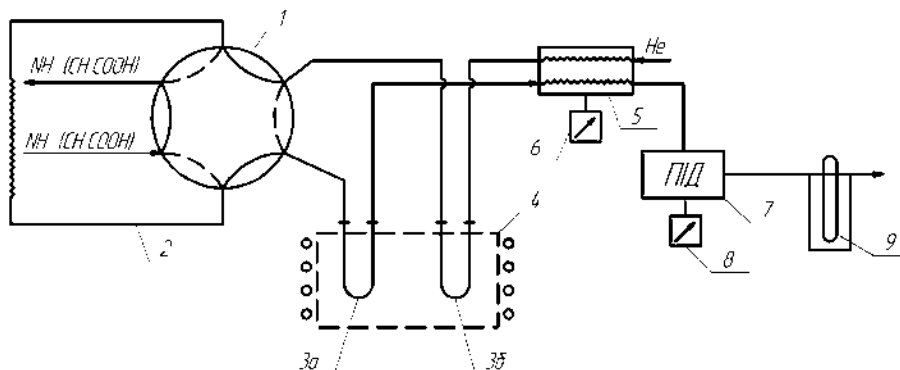
Fig. 1. Scheme of the plant for determination of catalysts surface acidity and basicity: 1 – six-way cock;
2 – dosator loop; 3a – comparative column; 3b – column with the catalyst sample; 4 – chromatographic thermostat;
5 – thermal-conductivity detector; 6 and 8 – recorders; 7 – flame-ionization detector; 9 – rheometer

Table 1

Oxidation dehydration of EB to St over Fe-Bi-Mo-Ox catalysts. Impulse reactor, $V_{imp} = 5.5$ cm^3, $V_f = 0.56$ cm^3/s. The reaction mixture of 5 mol% EB in the air

Catalyst composition and its specific area (m^2/g) before/after operation	T, K	t_c, s	X_{EB}, %	S_{St}, %	$T_{50\%}$, K	Acidity before/after operation
(K$_1$) Untreated Fe$_2$-Bi-Mo$_2$-O$_x$ 2.6/5.0	693	3.6	93.0	83.7	676	$A = 3.1/2.9$ $N_c = (1.8/1.7) \, 10^{18}$ $T_M^{\,I} = 423/423$ $T_M^{\,II} = 473/503$ $E_{des}^{\,I} = 34/31$ $E_{des}^{\,II} = 115/131$
		2.4	80.0	85.7		
	673	3.6	60.0	79.4		
		2.4	44.0	82.9		
	653	3.6	30.0	80.1		
		2.4	10.0	81.0		
(K$_2$) US-treated Fe$_2$-Bi-Mo$_2$-O$_x$ 10/10	693	3.6	100.0	92.6	655	$A = 0.2/3.1$ $N_c = (1.3/1.9) \, 10^{18}$ $T_M^{\,I} = 453/413$ $T_M^{\,II} = 743/503$ $E_{des}^{\,I} = 40/99$ $E_{des}^{\,II} = 140/151$
		2.4	98.0	99.0		
	673	3.6	98.0	91.0		
		2.4	86.0	98.7		
	653	3.6	63.0	94.3		
		2.4	47.0	95.2		

Notes: X_{EB} and S_{St} – EB conversion and selectivity by St, relatively; $T_{50\%}$ – temperature at which 50 % conversion of EB is achieved at contact time (t_c) equaled to 3.6 s; A – surface acidity of the catalyst before/after operation (μmol/m^2); T_M – temperature of the maximum of NH$_3$ thermal desorption peak, K; N_c – amount of acid centers over the catalyst surface; E_{des} – activation energy of thermal desorbtion (kJ/mol) calculated according to the desorbtion rate [2].

The selectivity is higher over treated catalyst. The maximal selectivity regarding St (85.7 %) is achieved at 693 K and t_c= 2.4 s over untreated catalyst. Under the same conditions the selectivity is 99 % over treated catalyst. After operation the specific area of the untreated catalyst increases, perhaps due to the decrease of pores diameter and increase of their amount. The catalyst specific area of US-treated catalyst is constant before and after operation and twice higher than that of untreated catalyst after operation.

Table 1 also represents the parameters of surface acidity. The strength of surface acidic and basic centres is characterized by the temperature of the desorption peal maximum height (T_M) and activation energy of NH$_3$ or CH$_3$COOH thermal desorption from the catalyst surface, which is determined in accordance with the dependence of desorption rate on the temperature. For this purpose the programmed desorption of these compounds has been carried out to the temperature of 773 K with the adsorber heating rate of 12 K/min. The desorption activation energy was calculated using the method of graphical integration of desorption peaks by the procedure described in [4].

NH$_3$ impulses were delivered at 343 K at adsorption plant with the catalyst till its surface was saturated. The control was carried out by the constancy of

chromatographic peak height of non-adsorbed NH_3 at the adsorber exit. The amount of NH_3 and acetic acid (AA) chemosorbed by the catalyst surface was determined by the difference between delivered and non-adsorbed NH_3 or AA. After the saturation of catalyst surface by NH_3 or AA the adsorption column was sustained for 30 min at the adsorption temperature. Then the programmed thermodesorption was carried out to determine the peak T_M and desorption heat.

From the results of Table 1 one can see that the surface acidity (*A*) of untreated catalyst (K_1) is practically the same before and after operation (3.1/2.9 μmol/m^2). The surface activity of the US-treated ctaalyst is small before the operation (0.2 μmol/m^2) and increases till the value of untreated catalyst before operation (3.1 μmol/m^2). The amount of active acidic centres over the catalyst surface calculated according to the amount of NH_3 chemosorbed by the surface in a case of one-centered absorption is practically the same over both catalysts $(1.7–1.9)\cdot10^{18}$ centers/m^2. This value decreases over untreated catalyst from $1.8\cdot10^{18}$ to $1.7\cdot10^{18}$ centers/m^2 and increases from $1.3\cdot10^{18}$ to $1.9\cdot10^{18}$ centers/m^2 over US-treated catalyst. During NH_3 thermal desorption two desorption peaks were observed. Obviously, it is protonic and aprotic acidity.

The strength of acidic centers regarding the temperature of desorption peak maximum height and E_{des}^1 of the first peak are practically the same before and after the operation over the untreated catalysts. For the treated catalyst the strength of acidic centers decreases after the operation (T_M decreases by 40 K) and E_{des}^I increases from 40 to 99 kJ/mol.

The strength of acidic centers increases after the operation regarding T_M^{II} of the second peak (Table 1) over untreated K_1 catalyst and considerably decreases over K_2 catalyst. *Pro tanto*, the activation energy of desorption E_{des}^{II} increases after the operation over K_1 and decreases – over K_2.

The comparison of K_1 and K_2 desorption characteristics show that for the first desorption peak the temperature of the maximum T_M^I is 423 K for K_1 and 453 K for

K_2 before the operation. After the operation they are 423 K for K_1 and 413 K for K_2. Thus, for K_1 the temperatures are the same and for K_2 the temperature decreases from 453 to 413 K, which is less than that for K_1. Obviously, the I type acidic centers have not enough strength to activate the substrate molecules.

The main role in substrate molecules activation belongs to the II type centers. Using K_1 catalyst after its activation by substrate and operation, the temperature of maximum T_M^{II} of the second desorption peak increases from 473 to 503 K. Using K_2 catalyst, the temperature decreases from 743 to 503 K. The latter temperature is in agreement with the temperature for K_1 (503 K). E_{des}^I decreases after the operation from 34 to 31 kJ/mol for K_1 and increases from 40 to 99 kJ/mol for K_2.

Thus the US-treatment increases the strength of the catalyst acidic centers. In the case of US-treated catalyst K_2 the activation of the catalyst by the reaction mixture also increases the strength of the acidic centers. T_M^{II} over $K_1 > T_M^{II}$ over K_2; E_{des}^{II} over $K_2 > E_{des}^{II}$ over K_1.

The II type centers, over which T_M^{II} is equal over both catalysts and E_{des}^{II} over K_2 is considerably higher than that over K_1 after operation, play the main role in the substrate activation. The comparison of catalysts activity shows that K_2 is considerably more active than K_1. Thus the acidic centers of the catalysts are very important for the oxidation process; obviously they activate the chemisorbed substrates. After the catalysts activation by the reaction mixture E_{des}^{II} increases from 115 to 131 kJ/mol over K_1 and from 140 to 151 kJ/mol – over K_2. The activation increases the strength of the acidic centers but it should not be too high. The reason is that the difficulties with the formed products desorption may occur, as well as the problems with their decomposition and forming products of destructive and complete oxidation.

The comparison of catalytic properties of the catalysts K_1 and K_2 shows that US-treatment of the catalysts increases both activity and selectivity of the catalyst in the oxidative dehydration of EB to St.

Table 2

Surface basicity (*B*) and parameters of AA programmed thermal desorption from the surface of untreated (K_1) and US-treated (K_2) catalysts before (K_1, K_2) and after (K_1^*, K_2^*) operation. Impulse reactor, $V_{imp} = 0.39$ cm^3, $V_f = 0.28$ cm^3/s. Thermal desorption 13 K/min

Catalyst	B, μmol/m^2	I peak		II peak		N_c, 10^{-18}	S_1/S_2
		T_M, K	$E_{des}\pm5$, kJ/mol	T_M, K	$E_{\partial ec}\pm5$, kJ/mol		
K_1	3.8	393	61	553	111	2.3	10
K_1^*	4.1	408	54	583	79	2.5	6
K_2	1.6	393	94	583	84	1.0	16
K_2^*	1.4	383	37	573	86	0.8	14

Notes: *B* – chemosorption of acetic acid; S_1/S_2 – ratio between peaks areas of I and II forms of desorption

We also examined the surface basicity of the investigated catalysts using the same method as for the determination of surface acidity ragarding the chemosorption of acetic acid (AA). The obtained results are represented in Table 2.

The surface basicity (B) of the untreated catalyst is higher than the basicity of the activated catalyst. Moreover after the treatment by the reaction mixture of 5 mol % EB in the air the basicity increases over K_1 and decreases slightly over K_2. It is well-known that the oxygen activation takes place over the basic centers of the catalyst surface and oxygen atoms are formed different by their activity: from O_2^- to $2 O^{2-}$. The latter one has the high reactivity and participates in the reactions of complete oxidation; therefore the strong basic centers are undesirable over the catalyst surface. The US-treated catalyst has a lower surface basicity and less T_M^I of the first peak. If these centers are the main for O_2 activation, then S_1/S_2 ratio is larger over US-treated catalyst K_2. After the operation S_1/S_2 ratio is equal to 14 over K_2^* and to 6 over K_1^*. Thus, untreated catalyst has more II type centers, over which the oxygen activation has a higher rate. K_1^* catalyst has a greater amount of active basic centers and, as a result, the lower selectivity regarding styrene (Table 1).

4. Conclusions

1. The US-treatment optimizes the parameters of the catalyst surface acidity after its activation by the reaction mixture, increases the specific surface (twice) and catalytic activity.

2. The US-treatment decreases the amount of strong basic centers and increases the catalyst selectivity regarding styrene.

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УЛЬТРАЗВУКОВА АКТИВАЦІЯ КАТАЛІЗАТОРІВ ОКИСНЮВАЛЬНОГО ДЕГІДРУВАННЯ ЕТИЛБЕНЗОЛУ В СТИРОЛ

Анотація. *Досліджено ультразвукове оброблення Fe$_2$-Bi-Mo$_2$-O$_x$ каталізатора окиснювального дегідрування етилбензолу в стирол та порівняно його фізико-хімічні властивості з неактивованим каталізатором до і після роботи. Показано, що виготовлений з розчину солей і активований ультразвуком каталізатор має кращу активність та підвищує у порівняльних умовах вихід стиролу.*

Ключові слова*: ультразвук, каталізатор, етилбензол, стирол.*