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EFFECT OF BARIUM SALTS ON PHYSICO-CHEMICAL AND CATALYTIC PROPERTIES OF Fe-Te-Mo-O_x CATALYST FOR OXIDATIVE AMONOLYSIS OF ISOBUTYL ALCOHOL

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Abstract. The effect of barium salts (nitrate, sulphate, chloride) on the physico-chemical and catalytic properties of Fe:Te:Mo (1:0.85:1) oxide catalyst has been determined for oxidative amonolysis of isobutyl alcohol (IBA) to methacrylonitrile (MAN). The catalyst doped with BaCl₂ (Ba/Mo = 0.1) was found to be the best catalyst relatively to the MAN yield. It has been shown that the promoters increase the catalyst specific surface and affect catalyst surface acidity improving the catalyst efficiency.

Keywords: catalysis, methacrylonitrile, catalyst, promotor.

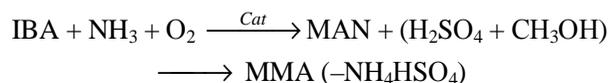
1. Introduction

Isobutyl alcohol (IBA) is a by-product formed during the ethyl alcohol obtained *via* digestion of starch or sugar raw materials. IBA, as well as other alcohols, is a part of fusel oil (FO), the composition of which depends upon the initial material quantity and technological process peculiarities. Thus the content of different alcohols varies (mas %): ethanol 5–7; *n*-propanol 7–15; IBA 10–20; isoamyl alcohol 50–60; water 5–10. Taking into account the productive capacity of distilleries, IBA may be used for production of different important chemical products.

In the present work we suggest to use IBA for obtaining methacrylates which may be used in different branches of industry. Taking into consideration that isobutylene oxidation or oxidative amonolysis (today it is used for the production of branched hydrocarbons – gasoline high-octane components) are the main methods of methacrylates synthesis, a deficit of IB is observed. To our mind, IBA may be a raw material for methacrylates synthesis, namely for MAN production *via* IBA oxidative

amonolysis. IBA converts into isobutylene at high temperatures over acid catalyst and then – into methacrolein (MA) in the presence of oxygen. MA, in its turn, also converts into MAN. Then methylmethacrylate (MMA) is obtained in the presence of H₂SO₄ and methanol. MMA, as well as MAN, are important monomers widely used in industry.

The simplified scheme of IBA conversion into MAN and MMA is:



It is well-known that oxide contact Fe:Te:Mo (1:0.85:1) is the effective catalyst for olefins oxidation, isobutylene (IB) namely [1]. In work [2] authors investigated its doping with alkaline and alkaline-earth metals in the reaction of IB oxidative amonolysis to MAN. The best results relative to the MAN yield were obtained using alkaline-earth metals. The alkaline metals block partial oxidation centers and decrease the catalyst activity. The contact doped with barium nitrate (Ba/Mo = 0.1) was found to be the best catalyst relative to the MAN yield. Over this catalyst the maximum yield of MAN (91.5 %) was obtained at $T = 643 \text{ K}$, $t_c = 0.42 \text{ s}$ and the composition of initial reaction mixture (mol %): IB – 2; NH₃ – 3 in the air [2]. Therefore we used oxide contact Fe:Te:Mo (1:0.85:1) for our investigations in the present work. Barium was a promotor. Such barium salts as sulfate or chloride are more stable and give better results in the processes of oxidative conversion compared with barium nitrate which decomposes to oxide during thermal treatment [3].

Thus, the aim of this work is to investigate the effect of barium salts (nitrate, sulfate, chloride) on the catalytic properties of Fe:Te:Mo:O_x catalyst in the reaction of IBA oxidative amonolysis.

2. Experimental

The procedures of catalyst preparation, experiments and analysis of the reaction products are given in our previous work [4]. The experiments were carried out at $T = 673$ K, $t_c = 2.4$ s in the continuous plant with impulse feed of the following mixture (mol %): IBA – 4; NH_3 – 6 in the air ($V_{imp} = 12.5$ cm³; $V_{flow} = 0.56$ cm³/s).

The size of the catalyst specific surface was determined using the chromatographic method of argon thermal desorption [5].

The catalyst surface acidity was determined using the pulse chromatographic method of NH_3 chemisorption over the catalyst surface. The catalyst sample corresponding to the total surface of the catalyst (5 m²) was loaded to the adsorber. Then the adsorber with the catalyst was involved in the chromatograph gas scheme following a doser and placed into a chromatograph thermostat. It was heated to 673 K and blown by helium for 1 h to release the surface from adsorbed gases. After this the temperature was reduced to 343 K. NH_3 impulses (dose of 1 cm³) were fed till the catalyst surface was saturated by the adsorbate. The control was carried out by the peak area at the output of thermal-conductivity detector. The amount of NH_3 absorbed by the catalyst surface (the difference between supplied and non-absorbed amount of NH_3) was determined by the amount of supplied NH_3 impulses and total area of non-absorbed NH_3 chromatographic peaks in accordance with a calibration sensibility factor of detector under the experimental conditions. After the saturation of NH_3 surface the adsorber was blown by helium for 30 min at the adsorption temperature and then the NH_3 programmed thermodesorption was carried out. Two thermodesorption peaks were observed and they were used to calculate the thermodesorption activation energy considering a thermodesorption rate [5].

3. Results and Discussion

The obtained results at different Ba/Mo ratio are represented in Table 1.

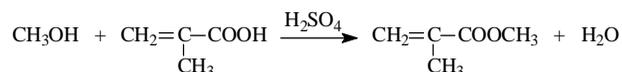
One can see that the ratio Ba/Mo = 0.1 is the optimum one relatively to the MAN yield in all experiments. For the catalysts doped with $\text{Ba}(\text{NO}_3)_2$ and BaSO_4 the MAN yield is 60 % and for BaCl_2 – 70 %.

The increase in contact time to 3.6 s increases the MAN yield to 72 % over the catalyst doped with BaCl_2 . The total MA+MAN yield under the mentioned conditions is 92 % and since IBA conversion is 100 %, 20 % of MA is formed. In the reaction of MA oxidative amination to MAN over doped BaCl_2 the selectivity is 95 % (Table 4). Thus at the recirculation of 20 % of MA the MAN total yield is $72 + 20 \cdot 0.95 = 91$ %.

The interaction between MAN and H_2SO_4 results in the formation of methacrylic acid (MAA) and ammonium hydrosulphate:



MMA is formed from MAN in the presence of CH_3OH and H_2SO_4 as a catalyst



The MMA yield relatively to MAN is 90 % [6]. Then the MMA yield relatively to IBA is $91 \cdot 0.9 = 81.9$ %.

At isobutylene oxidative amination over Fe-Te-Mo-O_x doped with $\text{Ba}(\text{NO}_3)_2$ (Ba/Mo = 0.1) [2] the MAN yield is 91.5 %, then the MMA yield is $91.5 \cdot 0.9 = 82.4$ %. Using IBA the yield is 81.9 %, *i.e.* it is less by 0.5 %. Thus, IBA may be used as a raw material for MMA production.

Table 1

Physico-chemical and catalytic properties of Fe-Te-Mo-O catalysts doped with barium salts (reaction conditions see above)

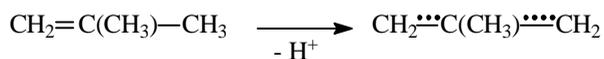
Ba/Mo, atom.	Promoter $\text{Ba}(\text{NO}_3)_2$						Promoter BaSO_4						Promoter BaCl_2						
	S_s	$K \cdot 10^3$	$E_1 \pm 5$	$E_2 \pm 5$	X, %	Y	S_s	$K \cdot 10^3$	$E_1 \pm 5$	$E_2 \pm 5$	X, %	Y	S_s	$K \cdot 10^3$	$E_1 \pm 5$	$E_2 \pm 5$	X, %	Y	
0	0.8	0.15	40	72	90	47													
0.05	0.9	0.2	35	68	82	56	0.6	2.0	30	65	89	53	0.9	0.7	18	54	95	53	
0.1	1.3	0.3	32	60	86	60	0.6	2.8	27	64	87	60	1.75	0.9	16	50	98	70	
0.2	1.2	0.17	25	42	84	57	0.7	2.4	25	68	88	38	2.5	0.8	14	30	96	47	
0.5	1.1	0.15	15	39	80	54	1.4	2.1	17	86	79	40	2.6	0.8	12	18	87	46	

Notes: S_s – catalyst specific surface after activation, m²/g; K – surface acidity, mmol/m²; E_1 and E_2 – activation energies of NH_3 thermosorption from the catalyst surface determined by desorption rate, kJ/mol; X – IB conversion, % (IBA conversion is 100 %); Y – MAN yield, % ($Y = X \cdot S_s$)

Nitrates of alkaline-earth elements are used as promoters in [2]. They decompose to the oxides during a catalyst thermal treatment. In some works [3] it was shown that anion of salt, which is stable under the reaction conditions, also influences the catalytic properties. For example, the efficiency of barium salts relatively to the MAN yield (Table 1) may be represented in a row: (Ba/Mo = 0.1):BaCl₂ > BaSO₄ = Ba(NO₃)₂.

The effect of barium salt concentration on the physico-chemical and catalytic properties of investigated catalysts is given in Table 1. The specific surface (S_s) of the catalysts doped with Ba(NO₃)₂ and BaCl₂ is greater than that of the initial one. The surface of the catalyst doped with BaSO₄ is greater only at higher concentration of the dopant, namely Ba/Mo = 0.5.

Since the oxidative amonolysis takes place over the contact surface [9] during the heterogeneous catalysis, the increase of S_s has to increase the catalyst activity. On the contrary the maximum IB conversion of 90 % is observed over undoped catalyst (IBA conversion is 100 % in all experiments). However IB conversion decreases with the increase of Ba(NO₃)₂ and BaSO₄ concentration. For the catalyst doped with BaCl₂ the conversion increases to 96 % compared with undoped catalyst at the ratio Ba/Mo = 0.2 and decreases to 87 % for the catalyst with the ratio Ba/Mo = 0.5. To our mind this fact may be explained by the blocking of the surface strong acid centers by the dopant, *i.e.* the increase of promoter concentration increases the specific surface and has to increase the conversion, but at the same time the blocking extent increases resulting in the rate deceleration and as a consequence, in the conversion reduction. Using BaCl₂ we observe the triple effect: the increase of specific surface and blocking extent, and the presence of Cl⁻. The latter one weakens C–H bond and in such a way favors the increase of hydrogen detachment rate at the first stage of the process – *p*-allyl radical formation:



The parameters of determined surface acidity are given in Table 1. This value is maximum for the optimum catalysts relatively to the MAN yield (Ba/Mo = 0.1).. Obviously the cation Ba²⁺ of the barium salt plays the main role for the catalyst acidity and promotion mechanism. The catalyst doped with BaCl₂ has the maximum surface acidity (K_s). At the same time this catalyst is the best relatively to MAN yield. The higher selectivity of the catalysts doped with BaCl₂ compared with other dopants was discussed above.

The analysis of the acid centers strength concerning the activation energy of NH₃ thermodesorption shows that dopants considerably decrease the strength of acid centers of both the first and the second peaks for all promoters.

Moreover the strength of acid centers (E_{des}) decreases with the increase of dopant concentration.

The analysis of desorption products shows that MAN was absent in the first peak of desorption. Probably IB and MA are insufficiently active over these centers. The second desorption form is the determinant for MAN production. Moreover, the catalyst doped with BaCl₂ (Ba/Mo = 0.1) has the minimum desorption activation energy and the greatest MAN yield (72 %) at 673 K and contact time of 3.6 s.

We also investigated IBA adsorption and desorption over Fe-Te-Mo-O_x catalyst doped with BaCl₂. The same two thermosorption peaks were observed, *i.e.* two kinds of alcohol adsorption exist. The first one is the centers of weak adsorption ($T_{max} = 368-395$ K; $E_{des} = 22-40$ kJ/mol) and products which are thermally desorbed over them are: IBA, IB, MA, CO and CO₂. Over the second kind of centers the thermodesorption takes place at higher temperatures (620–693 K) and desorption activation energy of 50–75 kJ/mol. The products are: IB, MA, MAN, CO and CO₂. The minimum T_{max} of the first peak has the catalyst with ratio Ba/Mo = 0.05–0.01 and the minimum $E_{des} = 22$ kJ/mol has the undoped catalyst. The maximum $E_{des} = 40$ kJ/mol has the catalyst with ratio Ba/Mo = 0.1 which is the best relatively to the MAN yield. In the case of second desorption peak the best catalyst has minimum $T_{max} = 623$ K and low $E_{des} = 57$ kJ/mol. The minimum E_{des} is observed over the catalyst with the dopant maximum concentration and ratio Ba/Mo = 0.5.

Obviously that at high concentration of dopants both centers of complete and partial oxidation are blocked accompanied by the decrease of catalyst activity and the MAN yield (Table 1). The undoped catalyst has the maximum E_{des} . Thus, the catalyst which is an optimal one relatively to the MAN yield, should have a small amount of dopant and moderate $E_{des} = 55-57$ kJ/mol. The surface acidity should also have the moderate value. We assume that centers of the first type are Lewis ones and stronger centers are Brønsted ones.

One can see from Tables 1 and 2 that the maximum amount of IBA is absorbed over the catalyst doped with BaCl₂ (Ba/Mo = 0.1) which is the optimal one relatively to the MAN yield. This amount of surface covering degree is approximately 1 (Table 2) and amount of NH₃ adsorption centers is maximum as well (adsorption proceeds till NH₃ saturates the catalyst surface). Since the IBA oxidative amonolysis proceeds *via* redox mechanism, the MAN formation takes place without oxygen, *i.e.* *via* interaction between IB (dehydration product of IBA) and oxygen adsorbed on the surface or oxygen of the catalyst lattice. As it was shown in [1], at olefin concentration > 3 mol %, the rate of MA formation depends only on oxygen concentration, *i.e.* the interaction between IB and

oxygen is a limiting stage. Therefore it was advisable to investigate the effect of the reactivation degree of the optimum catalyst Ba/Mo = 0.1 (BaCl₂). Obviously, the reactivation degree of the catalyst surface depends upon the ratio reducing agent : oxygen, concentration of alkaline-earth promoter affecting the mobility of the surface oxygen and the catalyst activity and selectivity.

The experiments were carried out in the flow reactor with a pulsed feed of the initial mixture containing 5 mol % of IBA in helium; $T = 673$ K; $V_{imp} = 5.5$ cm³; $V_{flow} = 0.56$ cm³/s; catalyst total surface $\Sigma S_{cat} = 2.6$ m²; catalyst mass $m_{cat} = 3$ g; $t_c = 3.6$ s (Table 3).

Under the experimental conditions IBA converts completely, thus the calculations were carried out for IB which was present at the reactor outlet. For the first 5 impulses of the initial mixture the products were analyzed in every impulses, then every 5th impulse (till 30) and every 10th impulse till the end of the experiment. The catalyst reactivation degree was determined taking into account the amount of formed oxidation products. The obtained results (Table 3) allow to conclude:

- at the recovery of 70 % of oxygen monolayer in the first impulse (oxygen monolayer is 0.2 cm³/m² [7]) the IB conversion decreases by 10 % and selectivity relatively to MA increases by 17 % in the following impulse;
- in the next 4 impulses (including the 5th one) more than 3 oxygen monolayers are recovered from the surface.

At the same time IB conversion is constant, selectivity relatively to MAN increases from 67.5 to 91.7 % and selectivity relatively to CO+CO₂ decreases from 49.4 to 8.3 %. Hence, there are great amounts of active oxygen on the surface of non-activated catalyst; oxygen converts IBA and IB into the products of complete oxidation. After oxygen recovering (the 5th impulse) to the 25th impulse the yield of the complete oxidation products is constant but IB conversion decreases from 87.6 (the 5th impulse) to 9 % (the 45th impulse). The rate of IB oxidation decreases as well from $1.29 \cdot 10^{-6}$ to $0.15 \cdot 10^{-6}$ mol/m²·s.

- during the following feed of the initial mixture from the 5th to the 45th impulse the IB conversion decreases from 87.6 to 9 %. The oxidation rate decreases from $1.19 \cdot 10^{-6}$ to $0.15 \cdot 10^{-6}$ mol/m²·s.

As it was shown in [1] the catalyst reactivation degree depends on IB concentration in the reaction mixture which is determined in our case by IBA concentration and the rate of its dehydration to IB under the process conditions. According to [1], the optimum catalyst relatively to the MAN yield is the catalyst over which the rate of MA conversion into MAN exceeds the rate of IB formation (Table 4). The catalyst phase composition is formed at IB concentration of 2–7 mol %. Thus the catalyst must work at the presence of the mentioned range of IB concentration.

Table 2

IBA adsorption and thermodesorption over Fe-Te-Mo-O catalysts doped with BaCl₂
($T_{ads} = 343$ K; thermodesorption was carried out at the temperature programming 16°/min)

Ba/Mo, atom.	Volume of adsorbed IBA ($V \cdot 10^3$), mmol/m ²	IBA adsorption centers ($N_c \cdot 10^{18}$), centers/m	Degree of surface covering by IBA (θ), % of monolayer	Thermodesorption			
				First peak		Second peak	
				T_{max} , K	E_{des} , kJ/mol	T_{max} , K	E_{des} , kJ/mol
0	3.8	2.3	0.72	375	22	660	75
0.05	3.5	2.3	0.95	368	29	693	83
0.10	5.4	3.3	1.05	368	40	623	83
0.20	3.0	1.8	0.57	386	27	640	55
0.50	2.8	1.7	0.54	395	26	657	50

Table 3

**Reactivation of FeTe_{0.85}MoBa_{0.1}O_x catalyst
by the impulses of the initial mixture (IM)**

Impulse number	X_{IB} , %	S_{MA} , %	S_{CO} , %	S_{CO_2} , %	$W_{IB} \cdot 10^6$, mol/(m ² ·s)	Reactivation degree, % of monolayer
1	97.2	50.5	40.8	8.6	1.29	70.0
2	88.7	67.5	23.6	8.9	1.20	150.0
3	88.7	76.5	16.5	7.1	1.18	214.0
4	87.2	88.2	5.8	6.0	1.21	289.0
5	87.6	91.7	2.0	6.3	1.19	362.0
15	74.3	91.0	2.4	6.6	0.87	619.0
25	33.9	85.4	4.3	10.3	0.52	745.0
45	9.0	85.0	5.2	8.8	0.15	925.0

Table 4

IB oxidation to MA and oxidative amonolysis of IB, MA and IBA to MAN over Fe-Te-Mo-O_x catalyst doped with BaCl₂ (Ba/Mo = 0.1) in the impulse reactor at 613 K; $t_c = 1.2$ s; $V_{imp} = 12.5$ cm³. The reaction mixture (mol %): RH – 4; NH₃ – 6 in the air

No.	Mixture composition	X_{IB} , %	S_{MAN} , %	S_{MA} , %	W , mol/dm ² ·s		
					MA	MAN	IB
1	IB + O ₂	73.0	–	86.0	13.0	–	14.0
2	IB + O ₂ + NH ₃	65.0	70.0	20.0	3.0	8.5	11.5
3	MA + O ₂ + NH ₃	78.0*	95.0	–	16.0	12.0	–
4	IBA + O ₂ + NH ₃	75.0	30.0	45.0	4.8	7.2	12.0

Notes: for the mixture No. 3: W_{MA} – rate of MA consumption; for the mixture No. 4: $X_{IBA} = 100$ %; RH – IB, MA, IBA; * – MA conversion.

After the feed of the 45th impulse of the initial mixture the impulses of oxidative mixture (OM) with oxygen concentration of 10 mol % and the amount of strongly chemisorbed products on the catalyst surface was determined in accordance with the formed CO₂ to calculate for IB. CO₂ is formed over the time of 4 impulses of OM. The amount of fed oxygen is $5.5 \cdot 4 \cdot 0.1 = 2.23$ cm³. Taking into account the catalyst mass of 3 g and total surface of 2.6 m², 0.189 cm³ of CO₂ was removed; to calculate for IB – 0.047 cm³ or 19 % of monolayer's covering (IB monolayer 0.096 cm³ [8]) calculated for 1 m² of the catalyst surface: $0.047/0.096 \cdot 2.6 \cdot 100$ % = 19 %.

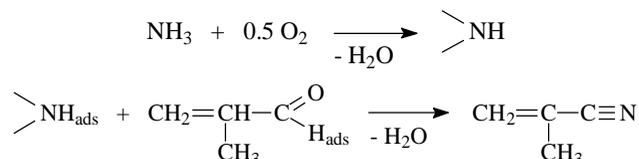
The reactivation of the optimum catalyst relatively to the MAN yield doped with BaCl₂ (Ba/Mo = 0.1) by the mixture IBA+NH₃ has been investigated as well (Fig. 1). The experimental conditions are given above (Table 3).

The IB oxidation rate increases to the 5th impulse and the selectivity relatively to MAN decreases (Fig. 1). After the feed of impulses from the 5th to the 50th the rate decreases from $13.8 \cdot 10^{-7}$ (maximum one) to $2.6 \cdot 10^{-7}$ mol/m²·s but the selectivity increases from 75 to 96 % with 14 monolayers removing.

The comparison of catalyst reactivation by pure IBA (Table 3) and IBA+NH₃ (Fig. 1) shows that NH₃ in the initial mixture retards the rate of IB conversion w (IBA conversion is 100 % in all experiments). Thus in the 1st impulse without NH₃ (Table 3) $w = 12.9 \cdot 10^{-7}$ mol/m²·s, in the presence of NH₃ it is $8.0 \cdot 10^{-7}$ mol/m²·s (Fig. 1) and increases till the 5th impulse. After achieving the maximum value of $13.8 \cdot 10^{-7}$ mol/m²·s the rate decreases to $2.6 \cdot 10^{-7}$ mol/m²·s (the 50th impulse). However this rate is higher than that at the catalyst reactivation by pure alcohol ($1.5 \cdot 10^{-7}$ mol/m²·s in the 45th impulse).

To our mind all these facts may be explained by the following. When the catalyst is reactivated by pure IBA the end-product of partial oxidation is MA; when IBA+NH₃ is used, MAN is the end-product. Therefore in the second case the total rate of alcohol conversion

$w_{al} = w_{MA} + w_{MAN}$. The increase of IBA conversion rate in the first impulses is explained by the fact that the catalyst surface has strong acid centers over which NH₃ converts into N₂. Hence, with the increase of impulses amount the centers are blocked by NH₃, that retards N₂ formation and increases the rate of MAN formation. Moreover, in the reaction of MAN formation NH₃ reacts with oxygen of the catalyst surface and forms =NH particle which further reacts with adsorbed MA and forms MAN.



The results presented in Table 4 confirm the MA conversion into MAN. According to the Table data the rate of this conversion is higher than that of IB conversion into MAN. The selectivity relatively to MAN is higher as well ($X_{IB} = 65$ %, $S_{MAN}^{IB} = 70$ %, $X_{MA} = 78$ %, $S_{MAN}^{MA} = 95$ %). The conversion of IB+O₂+NH₃ is 65 %, less than IB conversion into MAN (73 %). Thus, the presence of NH₃ in the mixture retards IB oxidation into MAN because it blocks not only strong acid centers but the centers of partial oxidation as well. Since the rate of MA conversion into MAN is considerably higher than that of IB into MAN and higher than the rate of IB into MA, we may assume that the formation of intermediate product – MA – is the limiting stage of IB oxidative amonolysis into MAN. While studying the process kinetics we established that the MAN formation from both IB and MA proceeds via redox mechanism and retards by NH₃; at the same time strong acid centers of complete oxidation products are blocked first of all. CO₂ is formed only at low NH₃ concentrations. At the NH₃ excess only MAN is formed.

The results of undoped Fe-Te_{0.85}-Mo-O_x catalyst reactivation by IBA+NH₃ mixture are presented in Fig. 2. The maximum oxidation rate for doped catalyst is $13.8 \cdot 10^{-7}$ mol/m²·s and only $8.5 \cdot 10^{-7}$ mol/m²·s – for undoped

one. For 20 impulses of the initial mixture 10 monolayers are removed from the doped catalyst and 5 ones – from undoped catalyst. After 20 impulses the selectivity relatively to MAN is 75 % for doped catalyst and 20 % – for undoped one. At the same time MAN is formed after the 20th impulse using undoped catalyst and after the first one – using the doped catalyst. Over the undoped catalyst NH_3 converts into N_2 after the 10th impulse.

Thus, the dopant considerably improves the catalytic properties of Fe-Te-Mo- O_x catalyst increasing its activity and selectivity relatively to MAN.

The additional oxygen consumption at the process first stage is also confirmed by the fact that during catalyst reactivation by pure IBA 9.25 monolayers of oxygen are

removed for 45 impulses and in the presence of NH_3 – 13.5 monolayers are removed for the same impulses (Table 3 and Fig. 1, correspondingly). The decrease of the catalyst selectivity relatively to MA (Table 3) from the 15th to the 45th impulses may be explained by the phase composition change of the catalyst surface layer at high reactivation degree.

One can see from Fig. 1 that during the catalyst reactivation for 50 impulses 14 monolayers are removed and 9.5 monolayers are absorbed. Thus, surface reoxidation is slower than the catalyst reactivation. That is why during kinetics investigations of IB oxidation into MA we observe the first order by oxygen and zero order by olefin [1].

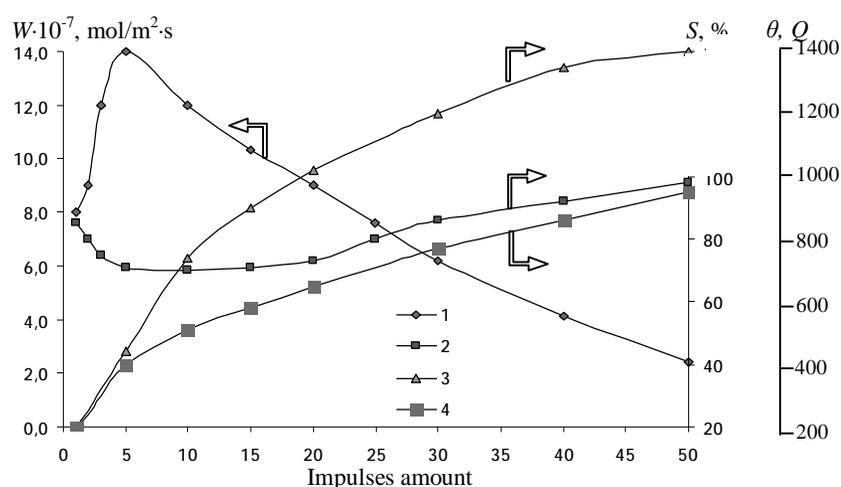


Fig. 1. Catalyst reactivation by IBA+ NH_3 (1 : 1 mol) mixture and reoxidation by oxygen of the reactivated catalyst (doped with BaCl_2 ($\text{Ba}/\text{Mo} = 0.1$)) before its activation: IB conversion rate (1) (IBA conversion is 100 % in all cases); selectivity relatively to MAN (2); degree of oxygen removal by initial mixture impulses (3) and oxygen absorption by the catalyst while feeding reoxidation mixture (4)

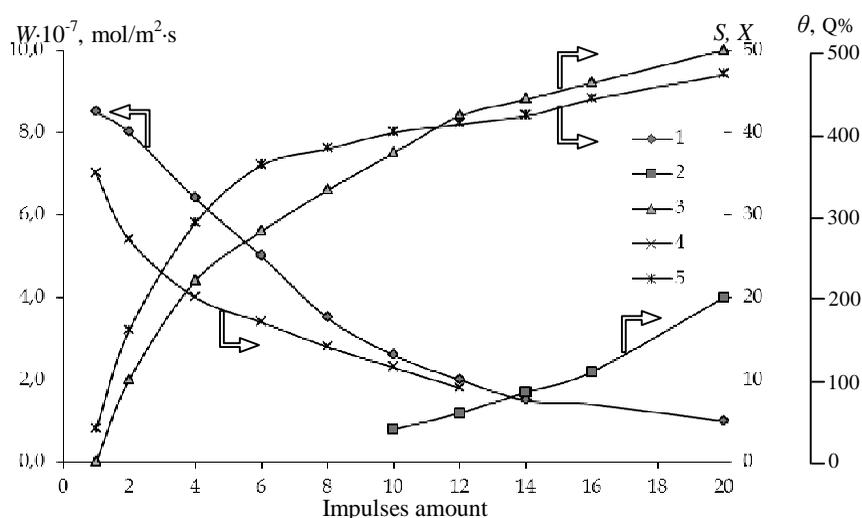
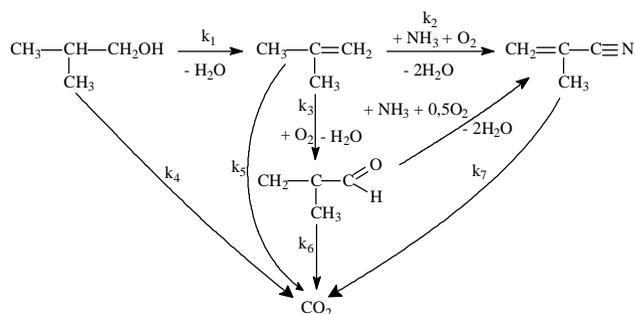


Fig. 2. Catalyst reactivation by IBA+ NH_3 (1 : 1 mol) mixture and reoxidation by oxygen of the reactivated undoped catalyst: IB conversion rate (1) (IBA conversion is 100 % in all cases); selectivity relatively to MAN (2); degree of oxygen removal by initial mixture impulses (3); oxygen absorption by the catalyst while feeding reoxidation mixture (4) and NH_3 conversion (5)

On the basis of obtained results and literature data we propose the following mechanism of IBA oxidative amonolysis:

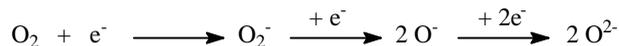


The process intermediate products are: IB obtained *via* IBA dehydration, and MA obtained *via* isobutylene oxidation. The reaction 1 takes place over the catalyst acid centers forming isobutylene which converts into metacrylonitrile by redox mechanism and into the intermediate product – metacrolein – which also converts into into metacrylonitrile by the same mechanism. The complete oxidation product CO₂ is formed from IBA, IB, MA and MAN. The latter one is the most stable in the mentioned reaction.

All reactions proceeding by redox mechanism take place only in the presence of oxygen of the catalyst surface layer. The dopant introduced into the catalyst composition increases the oxygen mobility (Figs. 1 and 2, [2]). CO₂ is formed between chemisorbate over the catalyst surface and oxygen of gaseous phase; it is so called “percussion mechanism”. The dopants block the strong acid centers of the surface over which the complete oxidation products are formed. The same role is for NH₃ in the mixture.

The acid centers of the catalyst surface take part in the activation of organic reagents and form the intermediate activated complex between catalyst active center and reagent, what weakens the chemical bonds participating in the reaction.

Obviously in the oxidation process the activation of the catalyst surface oxygen is necessary. It is assumed that activation proceed [2] over the surface main centers, then Fe-Te-Mo-O_x doped by alkaline-earth element should form additional main centers of oxygen activation and it will be as follows:



The oxygen activity depends upon the quantity of attached electrons. The oxygen high activity is undesirable in the reactions of hydrocarbons partial oxidation because it leads to the formation of complete oxidation products and decreases the process selectivity.

The strength of the catalyst acid centers should not be high because it leads to the formation of destruction products and decreases the selectivity.

4. Conclusions

The effect of barium salts (nitrate, sulphate, chloride) on the physico-chemical and catalytic properties of Fe:Te:Mo catalyst (1:0.85:1 atomic ratio) has been investigated in the reaction of oxidative amonolysis of isobutyl alcohol to methacrylonitrile. BaCl₂ was found to be the best dopant (Ba/Mo = 0.1). The highest methacrylonitrile yield (91 %) is observed over the mentioned catalyst.

Isobutyl alcohol may be the raw material for methacrylates synthesis.

The optimum conditions of MAN production *via* oxidative amonolysis of isobutyl alcohol over Fe-Te-Mo oxide catalyst doped with BaCl₂ are: temperature 673 K and contact time 3.6 s.

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ВПЛИВ СОЛЕЙ БАРІЮ НА ФІЗИКО-ХІМІЧНІ ТА КАТАЛІТИЧНІ ВЛАСТИВОСТІ Fe-Te-Mo-O_x КАТАЛІЗАТОРА РЕАКЦІЇ ОКИСНЮВАЛЬНОГО АМОНОЛІЗУ ІЗОБУТИЛОВОГО СПИРТУ

Анотація. Досліджено вплив солей барію (нітрат, сульфат, хлорид) на фізико-хімічні і каталітичні властивості Fe:Te:Mo (1:0,85:1) оксидного каталізатора реакції окиснювального амонілізу ізобутилового спирту (ІБС) в метакрилонітрил (МАН). Встановлено, що кращим за виходом МАН є каталізатор (Кт), промотований BaCl₂ (Ba/Mo = 0,1). Показано, що промотори збільшують питому поверхню (S_n) Кт та впливають на його поверхневу кислотність, що покращує ефективність каталізатора в реакції окиснювального амонілізу ІБС в МАН.

Ключові слова: каталіз, метакрилонітрил, каталізатор, промотор.