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1,3-BUTADIENE AND METHACRYLONITRILE OBTAINING USING OXIDATIVE CONVERSION OF C₄ OLEFINS OVER Fe-Te-Mo-O_x CATALYST PROMOTED WITH BaCl₂

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Abstract. The effect of BaCl₂ promotor on the catalytic properties of Fe-Te-Mo-O_x catalyst of joint oxidative dehydration and oxidative amonolysis of C₄ olefins has been examined. The optimal composition of promoted catalyst has been established taking into consideration methacrylonitrile and butadiene yields. The process kinetics has been investigated.

Key words: oxidation, dehydration, amonolysis, catalyst, promotor, isobutylene, butadiene, methacrylonitrile

1. Introduction

It is well-known [1] that oxidative catalysts contain thermostable salts of alkali and alkali-earth elements. Moreover, thermostable chlorides and sulphates are used as promoters.

Previously we investigated oxidation of C₄ olefins with air and oxidation of C₄ olefins with mixture of air, metacrolein (MA) and NH₃. Results have shown that NH₃ considerably broke the process. At oxidation of i-C₄ (2 mol. %) with air at 583 K and contact time (τ_k) 2.4 s olefin conversion was 55 %, olefin conversion rate was $1.24 \cdot 10^{-7}$ moles/m²·s and selectivity to MA was 84.8 %. Under similar conditions at addition of NH₃ (3 mol. %) to the air the conversion was 31 %, conversion rate $0.7 \cdot 10^{-7}$ moles/m²·s and summary selectivity to metacrolein + metacrylonitrile (MA+MAN) was 90 %.

Thus, NH₃ brakes gross-reaction of olefin oxidation and full oxidation of MA, MAN and butadiene (BD). The last ones take place over acid centers of strong, irreversible chemisorption of olefins, as well as partial oxidation products [1]. Such acid centers may be blocked by addition of minor amount of alkali or alkali-earth elements to the catalyst. Moreover, these elements may produce additional main centers of oxygen activation [1] what is very important for FeTe_{0.85}MoO_x catalyst, over which i-C₄

oxidation takes place by redox mechanism. The catalyst reoxidation is limited stage of mentioned process.

In order to prove the MAN formation from intermediate product of i-C₄oxidation with MA, we examined the MA oxidation in the presence of NH₃. MA forms MAN in the presence of NH₃ and rate of this process is higher than rate of MAN formation using i-C₄ oxidative amonolysis. The above-mentioned process selectivity is higher too. We explain this fact by presence of full oxidation of i-C₄ by parallel scheme at olefin oxidative amonolysis.

2. Experimental

The experiments were carried out in flow reactor with stationary catalyst, impulse feed of reaction mixture and full chromatographic analysis of reaction products. Reactor was part of gaseous system of chromatograph. Three types of chromatographic columns and two types of detectors (catarometer and flame-ionization detector) were used to analyze reaction products. First column had the length 4 m was filled with chromaton-N and 20 mass % of ether of butyric acid and triethyleneglycol. CO₂ and hydrocarbons were analyzed at first column. The second column had the length 2 m filled with NaX molecular sieve was used for the determination of O₂, N₂ and CO (in order of their appearance). Catarometer was used as detector for both types of columns. The third column had the length 3 m. It was filled with N-DMCS chromaton with 15 mass % of PEG-6000 and was connected with flame-ionization detector. Hydrocarbons, methacrolein (MA) and methacrylonitrile were analyzed at third column at 363 K.

3. Results and Discussion

The effect of BaCl₂ concentration on catalytic properties of investigated catalyst is represented in Table 1.

Table 1

The effect of BaCl_2 on catalytic properties of $\text{FeTe}_{0.85}\text{MoO}_x$ catalyst (K_0) at the reaction of joint oxidative dehydration of butene-1 (B-1) and $i\text{-C}_4$ oxidative amination

Catalyst and its specific surface, S_n , m^2/hour	τ_k , s	T, K	olefins summary conversion ΣX , %	Selectivity, %			
				BD	MA	MAN	$\Sigma(\text{BD}+\text{MAN})$
K_0 $S_n = 0.8$	1.2	673	81.7	10.6	71.6	-	10.6
		643	75.3	5.1	74.9	-	5.1
		613	51.7	2.3	76.3	-	2.3
	3.6	673	97.2	18.3	38.3	33.9	52.2
		643	94.4	18.1	22.3	55.1	73.2
		613	84.9	11.9	22.8	62.5	74.4
$K_0+0.05\text{BaCl}_2$ $S_n = 0.9$	1.2	673	61.8	8.4	72.4	13.6	22.0
		643	56.0	6.4	56.1	33.7	40.1
		613	40.4	5.2	26.8	65.1	70.3
	3.6	673	86.8	14.5	63.4	18.3	32.8
		643	84.3	8.4	29.8	59.8	68.2
		613	77.3	6.2	21.7	70.6	76.8
$K_0+0.1\text{BaCl}_2$ $S_n = 1.9$	1.2	673	76.7	14.6	72.1	5.7	20.3
		643	67.6	12.9	47.6	33.9	46.8
		613	52.5	7.9	32.4	56.6	64.5
	3.6	673	90.3	23.9	43.4	23.1	47.0
		643	86.9	20.1	35.8	38.7	58.8
		613	76.3	12.7	23.0	60.9	73.6
$K_0+0.5\text{BaCl}_2$ $S_n = 2.6$	1.2	673	89.7	13.2	65.2	7.8	21.0
		643	88.0	13.9	47.3	31.8	45.7
		613	79.4	10.7	47.8	36.3	47.0
	3.6	673	100.0	5.6	-	68.7	74.3
		643	97.5	10.8	1.1	67.3	78.1
		613	96.0	16.1	4.7	63.3	79.4

Notes: the reactor is of pulse flow type, $V_n = 0.56 \text{ cm}^3/\text{s}$; $V_p = 6.2 \text{ cm}^3$.

The reaction mixture consists of (mol. %): isobutene – 2, butene-1 – 2, NH_3 – 3, O_2 – 5, the rest is He.

It is obvious, that promoter decreases catalyst activity and increases summary selectivity to BD+MAN, with simultaneously the increase of promoter amount (Ba / Mo ratio) from 0 to 0.1 decreases the reaction rate from $0.9 \cdot 10^{-6}$ to $0.3 \cdot 10^{-6}$ moles/ $\text{m}^2 \cdot \text{s}$.

At higher concentrations of Ba ions the rate practically does not change but olefins conversion increases from 67 % (Ba/Mo = 0.1) to 94 % (Ba/Mo = 0.2-0.5). Obviously it is connected with increase of catalyst specific surface, which in turn, is connected with increase of promoter concentration and surface basicity. Maximal summary yield of MAN+BD (84 %) was obtained over catalyst with Ba/Mo ratio equal to 0.2 (vide Fig. 1). Olefins conversion is 94.4 %, summary selectivity – 89 %, selectivity to MAN – 75 %.

So, it has been established that the optimal conditions of the process: temperature is 613 K, contact time is 2.4 s and Ba/Mo ratio in the catalyst is 0.2. Obtained results show that increase of temperature increases selectivity to MA and decreases selectivity to MAN. It is confirmation of assumption that MAN is formed from MA, which is intermediate product. MAN may be also formed directly from $i\text{-C}_4$.

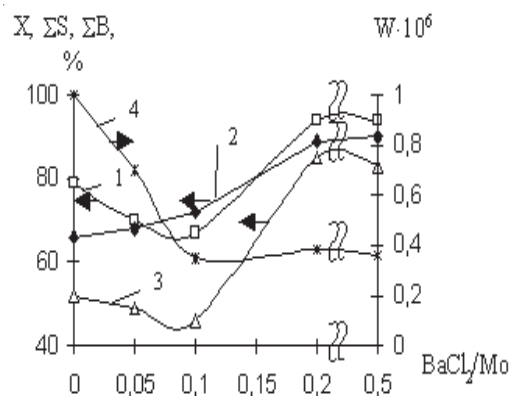


Fig. 1. The effect of BaCl_2 on the catalytic properties of $\text{Fe:Te:Mo}=(1:0.85:1)$ catalyst at $T = 613 \text{ K}$, $\tau_k = 2.4 \text{ s}$
1 – olefins conversion; 2 – BD+MAN summary conversion; 3 – BD+MAN summary yield; 4 – gross-rate of olefins conversion, moles/ $\text{m}^2 \cdot \text{s}$

Investigating NH_3 activation mechanism we may assume [2] that $=\text{NH}$ chemisorbed active particles are formed over catalyst surface as a result of NH_3 oxidation.



Description of NH_3 activation mechanism has been analogous in [3]. Another assumption has been made in [4] at investigations of kinetics and reaction mechanism of MAN formation. NH_3 may add to the olefin double bond and amine is formed with following conversion into nitrile. To our mind, mechanism described in [4] is more reliable because MA is converted into nitrile in the presence of NH_3 .

We examined also the kinetics of joint oxidative amonolysis of isobutylene and oxidative dehydration of butene-1 over catalyst with Ba/Mo optimal ratio (Ba/Mo=0.2). It should be considered that $i\text{-C}_4$ and B-1 are reactive olefins and they may compete for active catalytic surface.

In order to solve the problem under consideration, the olefin concentration's effect on the conversion rate of another one have been investigated. It has been established that $i\text{-C}_4$ has higher reactive ability than B-1. At 583 K under conditions of individual oxidation $s\text{-C}_4$ conversion has been equal to 89.2 % and B-1 conversion has been equal to 82.8 %, because B-1 less affects $i\text{-C}_4$ oxidation rate. The increase of B-1 concentration from 0 to 5 mol. % decreases $i\text{-C}_4$ oxidation rate from $0.145 \cdot 10^{-6}$ to $0.134 \cdot 10^{-6}$ moles/m²·s (i.e. by 7 %) The same increase of $i\text{-C}_4$ concentration decreases B-1 oxidation rate from $0.134 \cdot 10^{-6}$ to $0.088 \cdot 10^{-6}$ moles/m²·s (i.e. by 30 %).

At presence of the oxygen excess into the reaction mixture, the coefficient of reaction brake is expressed by following equation:

$$\frac{1}{W} = \frac{1}{W_0} + \frac{b}{W_0} \cdot C$$

where W , W_0 – rate and initial rate of olefin conversion, correspondingly

b – brake coefficient

C – concentration of component, which has been added to the initial mixture at constant initial concentration of other component

Coefficient “ b ” for both olefins has been found from graphic dependence $\frac{1}{W} - f(C)$ at 583 K. In the case of $i\text{-C}_4$ conversion with butene $b = 26 \text{ dm}^3/\text{mole}$ and in case of B-1 conversion with isobutylene $b = 230 \text{ dm}^3/\text{mole}$. Thus, $i\text{-C}_4$ more considerably brakes the reaction what is connected with its higher reactivity.

Also the NH_3 concentration effect on the rate of olefins conversion in a case of their separate oxidation has been investigated. NH_3 considerably brakes $i\text{-C}_4$ and B-1 oxidation at 583 K. At $i\text{-C}_4$ oxidation $b = 550 \text{ dm}^3/\text{mole}$ and at B-1 oxidation $b = 560 \text{ dm}^3/\text{mole}$, in other words they are practically similar. At 613 K values of

coefficient “ b ” are less: at $i\text{-C}_4$ oxidation $b = 36 \text{ dm}^3/\text{mole}$ and at B-1 oxidation $b = 26 \text{ dm}^3/\text{mole}$. The decrease of “ b ” value with temperature increase may be explained by reduction of blocking of catalyst surface with ammonia. Moreover, in a case of $i\text{-C}_4$ oxidation some part of NH_3 will take place in MAN formation, which accelerates with temperature increase.

Thus, kinetic regularities of $i\text{-C}_4$ and B-1 joint oxidation have been studied taking into consideration their competition for active surface and considerable brake of reaction by ammonia. $\text{FeTe}_{0.85}\text{MoBa}_{0.2}\text{O}$ was the catalyst. The full mixing reactor of differential type with vibroliquefied catalyst has been used. The reaction has been studied by impulse method in the kinetic area, which has been determined by grind of catalyst grains and change of linear flow rate at constant contact time. It has been established that reaction rate does not depend upon size of catalyst grains at their values less than 5 mm and upon linear flow rate within investigated temperature range.

The effect of concentrations of $i\text{-C}_4$, B-1, O_2 and NH_3 compounds upon formation rates of MA, MAN, BD, CO and CO_2 and conversion rates of $i\text{-C}_4$ and B-1 was examined. When concentration of one of the components have been changed, the concentrations of others have been maintained by fixed addition of helium. Concentrations of $i\text{-C}_4$ and B-1 have been changed within the range $(1.12-11.1) \cdot 10^{-4}$ moles/dm³, concentrations of oxygen – $(0.22-8.56) \cdot 10^{-3}$ moles/dm³, concentrations of ammonia – $(4.4-13.4) \cdot 10^{-4}$ moles/dm³.

Following kinetic reactions are used for the reaction rate determination and MA formation:

$$W_{iC_4} = k_1 \frac{C_{iC_4}}{1 + b_1 C_{NH_3}} \quad (1)$$

$$W_{MA} = k_2 \frac{C_{iC_4}}{1 + b_2 C_{NH_3}} \quad (2)$$

The reaction rate of MAN formation may be expressed by:

$$W_{MAN} = k_3 C_{iC_4} \cdot \theta \quad (3)$$

where θ is covering degree of catalyst surface with NH_3 , which may be calculated using equation (1)

$$\theta = \frac{k_4 C_{NH_3}}{k_3 \cdot C_{iC_4} + k_4 C_{NH_3}} \quad (4)$$

Thus, the rate of MAN formation is calculated using following equation:

$$W_{MAN} = \frac{k_3 C_{iC_4} \cdot k_4 C_{NH_3}}{k_3 C_{iC_4} + k_4 C_{NH_3}} \quad (5)$$

B-1 conversion rate and BD formation rate have first order in B-1 and reactions are broken with $i\text{-C}_4$ and NH_3 .

$$W_{B-1} = k_5 \frac{C_{B-1}}{1 + b_3 C_{iC_4} + b_4 C_{NH_3}} \quad (6)$$

$$W_{BD} = k_6 \frac{C_{B-1}}{1 + b_5 C_{iC_4} + b_6 C_{NH_3}} \quad (7)$$

We have been considered that deep oxidation products, such as CO and CO_2 have been formed from $i\text{-C}_4$ and B-1 olefins, as well as from partial oxidation products, such as MA, MAN, BD. The rates of mentioned reactions are broken with NH_3 and may be expressed by following equations:

$$W_{CO} = k_7 \frac{\sum C_{RH}}{1 + b_7 C_{NH_3}} \quad (8)$$

$$W_{CO_2} = k_8 \frac{\sum C_{RH}}{1 + b_8 C_{NH_3}} \quad (9)$$

where $\sum C_{RH}$ is summary concentrations of olefins and partial oxidation products

Rate constants (k_i) of above-mentioned reactions and adsorption coefficients (b_i) have been calculated using experimental data in accordance with equations (1-9). The least correlation coefficient was 0.93. So, we can conclude that proposed equations satisfactorily described obtained experimental results of $i\text{-C}_4$ and B-1 joint oxidation in the presence of NH_3 . Activation energies (E) and adsorption heats of obtained products were determined using graphic dependence $\ln k_i$ (b_i) upon $1/T$. The results are presented in Table 2. The correlation coefficient was within the range 0.95-0.99 at the determination of rate constants and within 0.93-0.9 – at the determination of coefficient “b”.

Table 2

Constants (k_i) and adsorption coefficients (b_i) of equations 1, 2, 5 and 9 activation energies of reactions and adsorption processes

T, K	k_i, s^{-1}								$b_i, dm^3/mole$							
	k_1	k_2	k_3	k_4	k_5	k_6	k_7	k_8	b_1	b_2	b_3	b_4	b_5	b_6	b_7	b_8
613	1,28	1,22	0,92	1,47	1,0	1,0	0,04	0,03	487	1560	220	770	420	770	740	780
583	0,64	0,63	0,19	0,36	0,60	0,6	0,02	0,02	604	1860	250	870	490	870	1900	2200
553	0,3	0,25	0,08	0,1	0,43	0,4	0,01	0,01	810	2200	290	1000	660	990	3600	5000
$E \pm 5$ kJ/ mole	69	66	79	140	67	50	69	46	23	16	13	12	21	12	74	87

4. Conclusion

The optimal composition of $\text{FeTe}_{0.85}\text{MoBa}_{0.2}\text{O}_x$ has been determined using maximal yield of methacrylonitrile and butadiene. Temperature 613 K and contact time 2.4 s have been considered as the optimal process' conditions. The kinetics of the joint process of isobutylene oxidative amonolysis and butene-1 oxidative dehydration has been investigated over the developed catalyst. As the results of kinetic researches it has been established that activation energy of olefines oxidative conversion and energy of methacrolein formation are practically indifferent.

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ОДЕРЖАННЯ БУТАДІЄНУ-1,3 ТА МЕТАКРИЛОНІТРИЛУ ОКИСНЮВАЛЬНИМ ПЕРЕТВОРЕННЯМ ОЛЕФІНІВ C_4 НА FeTe-Mo-O_x КАТАЛІЗАТОРІ, ПРОМOTOВАНOMУ BaCl_2

Анотація. Досліджено вплив промотора BaCl_2 на каталітичні властивості FeTe-Mo-O_x каталізатора сумісного процесу окиснювального дегідрування та окиснювального амонолізу олефінів фракції C_4 . Встановлено за виходом метакрилонітрилу і бутадієну оптимальний склад промоторованого каталізатора, на якому досліджено кінетику процесу.

Ключові слова: окиснення, дегідрування, амоноліз, каталізатор, промотор, ізобутилен, бутадієн, метакрилонітрил