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CATALYTIC OXIDATION OF *tert*-BUTYL ALCOHOL TO METHACROLEIN

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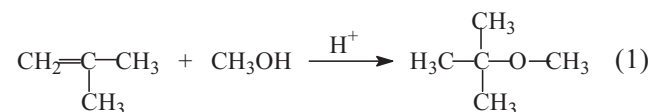
Abstract. Oxidation of *tert*-butyl alcohol (TBA) to methacrolein (MA) over Fe-Te-Mo-O_x catalyst (Cat), promoted by Ca(NO₃)₂ has been investigated. Promoter concentration, which was optimum by the MA yield, has been established (Ca/Mo = 0.05). Using catalyst of such a type the MA yield was 87.1 % (calculated for supplied TBA) at the temperature of 663 K, process time of 2.5 s and TBA concentration of 7.0 % with the concentration of water vapour in the air of 20 %. Under mentioned conditions TBA conversion was 100 %, isobutylene conversion – 95.5 %, selectivity by MA was 87.6 % and by CO₂ – 12.4 %.

Key words: oxidation, catalyst, process, *tert*-butyl alcohol, methacrolein, optimization

1. Introduction

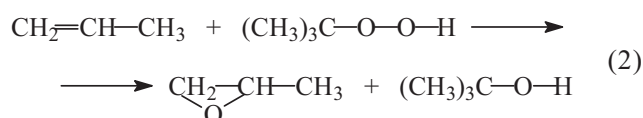
MA is the valuable monomer of chemical industry, used for the production of methacrylic acid (MAA) and its derivatives. Polymeric materials on the basis of MAA derivatives are characterized by transparency, chemical stability and ability to pass through an ultraviolet (UV) radiation. That is why they are used in the production of organic glass, glues, light-optical equipment *etc.*

A present-day production of MAA is based on the catalytic oxidation of isobutylene (*i*-C₄) but its every year increase is restrained because of the *i*-C₄ deficit. The main part of isobutylene is used for the production of methyltertbutyl ether, which is high-octane component of petrol in the presence of acid catalysts (reaction 1)



Hence, the search of alternative raw material for MAA and methacrylates production is the issue of the day, which can be decided, to our opinion, using TBA as a raw material. The considerable amount of TBA is obtained by oxidation of propylene oxide to propylene (reaction 2) and during the extraction of isobutylene,

diluted with H₂SO₄, from gases of the catalytic cracking and hydrocarbons pyrolysis.



Fe-Te-Mo-O_x reveals good catalytic properties as a catalyst for the reaction of *i*-C₄ oxidation. The addition of different promoters, earth-alkali elements in particular, increases its efficiency in the reaction of *i*-C₄ oxidation [1]. There are insufficient literature reports, devoted to the TBA oxidation. That is why, to our opinion, research of catalytic properties of above-mentioned catalyst in the reaction of TBA oxidation and its promotion with different additives is an actual question.

The aim of our work is the research of Ca²⁺ nitrate effect on the catalytic properties of Fe : Te : Mo (1 : 0.85 : 1) catalyst in the TBA oxidation reaction.

2. Experimental

The following reagents were used for the catalysts preparation:

(NH₄)₆Mo₇O₂₄·4H₂O – ammonium hexamolibdate, chemically purified;

H₂TeO₄·2H₂O – *ortho*-telluric acid, chemically purified;

Fe(NO₃)₃·9H₂O – ferric nitrate, chemically purified;

Ca(NO₃)₂ – calcium nitrate, chemically purified.

Corresponding solutions of the above-mentioned components in distilled water were prepared. Then catalysts with calculated atomic ratio between metals were synthesized using calcium nitrate as a promoter. The procedure of catalysts preparation is represented in [2].

Catalyst phase composition was determined by X-ray phase technique using DRON-2 diffractometer. X-ray pictures were decoded using ASTM tables [3].

The specific surface of the catalysts was determined by chromatographic method of argon thermal desorption [3].

The surface acidity of the catalysts was determined using impulse chromatography of NH_3 chemisorption [4].

TBA adsorption over catalyst surface was examined by impulse chromatography. The column filled with the catalyst of the known mass was connected with chromatograph gaseous system and placed into a thermostat, where it was blown through at 723 K during 1 h. Then the temperature was decreased to the adsorption temperature and the given impulse volume of TBA was supplied over the catalyst till the catalyst surface was fully saturated with adsorbate. The saturation was fixed by the constancy of peak area on the potentiometer of the katharometer. The amount of the product chemisorbed by catalyst surface was calculated using known amounts of supplied and non-chemisorbed TBA.

After the saturation of catalyst surface with the adsorbate the column was again blown through with helium till physically adsorbed TBA was removed completely, *i.e.* till the chromatograph recorder showed the zero line. Then the programmed heating of the column was switched on and TBA desorption heat was determined using two different detectors – katharometer and flame-ionization detectors.

Catalytic activity of Fe-Te-Mo- O_x system with $\text{Ca}(\text{NO}_3)_2$ additives was determined by impulse methods using “Viruchrom” chromatograph. A reactor with vibroliquefied catalyst was placed beyond the vaporizer in such a way that it was possible to disconnect the reactor in order to prepare the catalyst and maintain its properties.

All reaction products were controlled by detectors and recorded by potentiometers [2].

3. Results and Discussion

It is known that in the processes of partial oxidation of organic substances the catalyst activity depends on the mobility of surface oxygen [5], as well as on acidity and basicity of catalyst surface [6]. M. Ai [7] considers that acid centers of Cat surface containing cations with high electronic inefficiency favor the activation of electron-donor reagents (olefines, alcohols and others). At the same time catalysts with optimum acidity have the heightened selectivity in the processes of incomplete oxidation. On the basic centers of Cat surface electron-acceptor reagents are activated, *i.e.* oxygen is activated in the oxidation processes. It is also known [1] that at isobutylene oxidation over Fe-Te-Mo- O_x the stage of active centers reoxidation is the limiting stage of the process, that is why elements of basic character (alkaline alkaline-earth ones) may be promoters to such Cat. Investigated Ca^{2+} cation belongs to promoters of above-mentioned type. Its content (calculated for MA yield) is optimum in the Cat promoted by earth-alkaline elements.

For the research of cation effect on catalytic properties of Fe-Te-Mo- O_x the series of Cats with Ca/Mo different ratio were prepared. Catalytic properties of the catalysts were studied in a flow reactor with the stationary Cat and impulse feed of reaction mixture. The impulse dose was 12.5 cm^3 at Cat volume $0.3\text{--}2 \text{ cm}^3$. Under such conditions chromatographic complications were absent – the chromatographic mode of reaction proceeding was not observed.

The composition of investigated Cats and their physico-chemical and catalytic properties at the TBA oxidation are presented in Table 1.

The MA yield achieves maximum (94.5 %) under the conditions of reaction proceeding over the Cat while the Ca/Mo ratio equals to 0.05. Evidently, that over a non-promoted Cat the MA yield is minimum (42 %) compared with the Cat promoted by Ca^{2+} . There is a large yield of products of destructive (acetic aldehyde) and deep (CO , CO_2 , H_2O) oxidation on an initial contact. Selectivity by the sum of destructive and deep oxidation products is over 30 %. The Cat activity is also minor compared with promoted catalysts, but at small contact time. However it should be taken into account that conversion increases but selectivity decreases with the increase of contact time.

The comparison of $i\text{-C}_4\text{H}_8$ and TBA oxidation processes over Fe-Te-Mo- O_x Cat, promoted by earth-alkaline elements shows the following. The effect of earth-alkaline promoters on the Fe-Te-Mo- O_x catalytic properties in the reaction of isobutylene oxidation to MA has been investigated [10]. It was established that at $T = 693 \text{ K}$ and $\tau = 1.4 \text{ s}$ the highest yield by MA (86.1 %), $X_{i\text{C}_4\text{H}_8} = 99.0 \%$ and $S_{MA} = 86.9 \%$ were achieved over the Cat promoted by Mg (Mg/Mo = 0.1). If the Cat is promoted by Ca, then under the same conditions the highest yield by MA (75 %), $X_{i\text{C}_4\text{H}_8} = 91.6 \%$ and $S_{MA} = 81.9 \%$ were achieved over the Cat while Ca/Mo ratio equals to 0.05. Thus, optimum Cats are different for the oxidation of $i\text{-C}_4\text{H}_8$ and TBA. In the first case the Cat is promoted by Mg, in the second – by Ca. The Me/Mo ratio is also different for both cases: Mg/Mo = 0.1 and Ca/Mo = 0.05.

Comparison of the Cat catalytic properties shows that the surface acidity is maximum on the surface of the Cat with Ca/Mo = 0.05, which is the best also by MA yield. It has also minimum parameters of T_m (391 K) and E_a of NH_3 desorption from a surface (68 kJ/mol). The Cat with the ratio Ca/Mo = 1.0 and the non-promoted Cat have the least selectivity by MA. The first one has the minimum acidity ($0.3 \mu\text{mol}/\text{m}^2$) and low T_m (393 K), practically the same as that of the Cat with the optimum composition but the amount of active centers of NH_3 chemisorption is minimum ($0.2 \cdot 10^{-18} \text{ c}/\text{m}^2$) compared with the optimum Cat ($2.8 \cdot 10^{-18} \text{ c}/\text{m}^2$).

Table 1

Effect of calcium concentration (Ca/Mo ratio) in Fe-Te-Mo-O_x Cat on its surface acidity and catalytic properties at the reaction of TBA oxidation

No.	Ca/Mo	S _n	NH ₃ chemisorption				N·10 ⁻¹⁸	X _{iC₄H₈} , %	S _{MA} , %	B _{MA} , %
			K	V _d	T _m	E _a ± 5				
0*	0.0	9.2	3.5	2.5	425	80	1.9	61.0	69.0	42.0
1	0.01	8.7	3.8	2.9	408	75	2.2	97.4	95.6	93.0
2	0.02	8.2	4.0	2.9	398	72	2.4	98.7	92.7	91.5
3	0.05	5.2	4.7	2.7	391	68	2.8	98.8	95.7	94.5
5	0.1	5.0	4.2	2.5	403	76	2.6	98.8	91.6	90.4
5	0.5	8.2	3.3	2.6	393	78	2.0	97.6	67.9	66.3
6	1.0	25.0	0.3	0.3	393	74	0.2	70.0	60.0	42.0

Notes: NH₃ chemisorption at 343 K, V_{imp} = 0.1 cm³, V_f is feed rate = 0.56 cm³/s; desorption 0.27 K/s, Cat amount related to ΣS = 10 m²; S_s is a specific surface up to Cat activation; K is acidity, μmol NH₃/m²; V_d is an amount of desorbed NH₃, μmol/m²; T_m is a temperature of maximum desorption peak, K; E_a is activation energy of NH₃ desorption, kJ/mol; N is an amount of acid centers on the Cat surface, c/m². Catalytic properties (X_{iC₄H₈}, S_{MA}, B_{MA}) are obtained at T = 663 K, τ_c = 3.3 s, 5 mol % of TBA in the air.

* for the initial Cat τ_c = 0.72 s.

Table 2

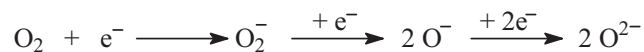
TBA chemisorption over Fe-Te-Mo-O_x with different ratio of Ca/Mo at 343 K

ΣS = 2 m²; V_{He} = 0.4 cm³/s, V_{imp} = 0.1 cm³

No.	Ca/Mo	TBA _{ads} , μmol/m ²	Thermal sorption						N·10 ⁻¹⁸ , c/m ²	θ of mono-layer	
			I peak			II peak					
			T _b	T _m	T _e	E _d	T _b	T _m			E _d
0	0.0	3.2	345	393	440	25	673	765	80	1.8	0.75
1	0.01	4.0		373	423	20	663	723	76	2.4	0.93
2	0.02	4.3		370	403	39	583	723	74	2.6	1.0
3	0.05	5.5		368	403	40	643	723	83	3.3	1.28
4	0.1	3.4		367	403	29	623	723	57	2.0	0.79
5	0.5	2.8		395	443	26	657	723	50	1.7	0.65
6	1.0	0.8		387	443	15	703	723	37	0.5	0.18

Notes: T_b, T_m and T_e are temperatures of beginning, maximum and end of desorption, K; E_d is activation energy of desorption, kJ/mol; θ is a coverage degree of the surface (depending on a monolayer in accordance with S_s and size of TBA molecule cross-section, calculated using [8]).

At first general surface acidity increases with the increase of promoter concentration to optimum ratio and then decreases. High promoter concentrations considerably increase the specific surface (2.5 m²/g) and decrease the Cat acidity and activity. The decrease of selectivity by MA with the increase of Ca/Mo ratio more than optimum value is connected with the fact that the promoter disables the active centers of MA formation and creates the centers of very active oxygen formation.



The two latter forms (O⁻ and O²⁻) are very active in oxidation reaction and mainly form the products of complete oxidation.

As the reaction of TBA oxidation to MA takes place by an adsorptive redox mechanism, TBA chemisorption was investigated over the catalysts promoted with Ca (Table 2).

It was established that TBA maximum amount (5.5 μmol/m²) is chemisorbed over the Cat which is the best by MA yield (catalytic properties are presented in Table 1). At first till the optimum composition of the Cat, its adsorption ability by TBA increases with the increase of promoter concentration and then decreases. The highest T_m in the I peak of desorption is observed over non-promoted Cat, then it decreases to the ratio of Ca/Mo = 0.05–0.1 and increases again in time.

Chromatographic analysis shows that TBA and i-C₄ are present in the I peak of thermal sorption (approximately in equal amount) and MA, i-C₄, CO and CO₂ – in the second peak (MA mostly). Maximum activation energy of desorption of the first form products (40 kJ/mol) is obtained over the optimum Cat. Values of T_m and T_e increase with the increase of promoter concentration, but E_d and i-C₄ concentrations considerably decrease in products. These Cats have the low surface

acidity (Table 1), that is why the velocity of NH_3 dehydration to $i\text{-C}_4$ is insignificant. For the second peak the value of T_m is practically equal to the temperature of heating end of the Cat, which was not heated higher than 723 K, however product E_d is also maximum over the optimum Cat (83 kJ/mol). At first with the increase of promoter concentration this value increases and then decreases. Comparison of centers amount of NH_3 (Table 1) and TBA (Table 2) shows that these values are practically identical. Obviously, under the research conditions TBA is chemisorbed over every acid center.

Researches of the effect of recovery degree of the Cat optimum by MA yield ($\text{Ca}/\text{Mo} = 0.05$) on its catalytic properties in the reaction of TBA oxidation show (Fig. 1) that catalyst activity notably decreases as the catalyst is recovered. The Cat reduction was carried out by mixture consisting of 5 % TBA in the air. After the cycling of 44 impulses of recovery mixture (RM) the conversion degree of isobutylene decreases from 97.0 % to 9.0 % (oxidation rate decreases from 1.2 to $0.15 \cdot 10^{-6} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$), and selectivity by MA, on the contrary, increases from 50 to 83 %. Thus on the graphic chart of selectivity versus degree of catalyst recovery there is a maximum at the recovery degree of 4–5 %. The increase of selectivity in the first impulses of RM is obviously connected with the removal of the more active surface oxygen, which takes part in the reactions of complete oxidation. After that a process selectivity is stabilized.

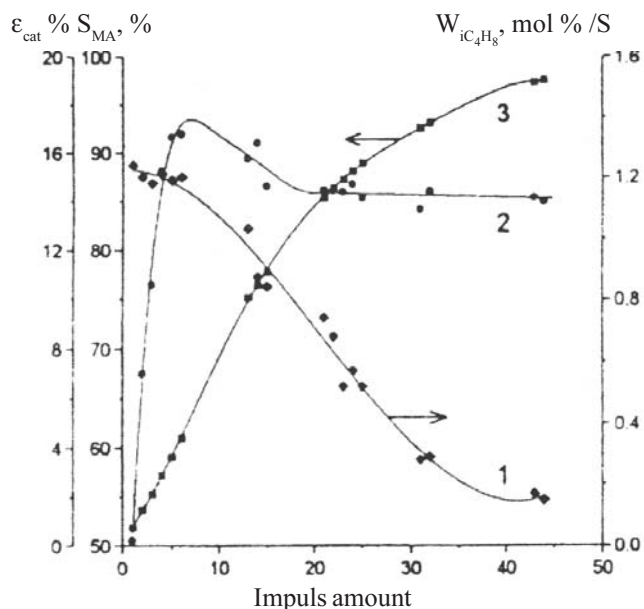


Fig. 1. Recovery of Fe-Te-Mo-O Cat, promoted with Ca ($\text{Ca}/\text{Mo} = 0.05$), by mixture of 5 mol % TBA in the air. Pulse reactor, $T = 663 \text{ K}$, $V_{imp} = 5.5 \text{ cm}^3$; $V_f = 0.55 \text{ cm}^3/\text{s}$.
1 – velocity of isobutylene conversion, $\text{mol}/(\text{m}^2 \cdot \text{s})$;
2 – selectivity by MA, %; 3 – a degree of oxygen removal, mass % (ϵ) calculated for the Cat:
 $0.5\text{Fe}_2\text{O}_3 \cdot \text{MoO}_3 \cdot 0.85\text{TeO}_3 \cdot 0.05\text{CaO}$

However different promoters of alkaline-earth elements influence in a different way the stages of recovery and reoxidation of promoted catalysts (Table 3). All promoted catalysts have higher activity and selectivity both in the first and in the 20th impulse of RM in comparison with an initial catalyst (C_0).

By activity in the 1st impulse of RM they are situated in the following order:

$$\text{Ca} > \text{Sr} > \text{Mg} = \text{Ba} > \text{Be} > C_0,$$

by selectivity in the same impulse:

$$\text{Sr} > \text{Ca} = \text{Ba} > \text{Mg} > \text{Be} > C_0.$$

In the 20th impulse by activity:

$$\text{Ba} > \text{Cr} > \text{Ca} > \text{Mg} > \text{Be} = C_0,$$

by selectivity:

$$\text{Ca} > \text{Be} > \text{Mg} > C_0 > \text{Sr} > \text{Ba}.$$

The obtained results show that addition of alkaline-earth promoters considerably enhances the mobility of surface oxygen. Moreover, they lock the active centers of complete oxidation.

Since catalytic properties of the heterogeneous catalytic system are determined by its phase composition, which substantially changes during the change of reaction mixture composition and conditions of catalyst work, the corresponding researches were conducted. They showed that non-promoted catalyst consists mainly of phase of Fe-Te-Mo-O triple compound and ordinary ferric molybdate. The catalyst promoted with Ca consists of a triple compound, MoO_3 , Fe_2O_3 phases and minor amount of ferric molybdate. After the recovery of this catalyst by the mixture of isobutylene and the air its phase composition differs from the nonrecoverable catalyst by the presence of molybdenum recovery phases – mainly Mo_9O_{26} . After its reoxidation by oxygen it does not return to the initial state. After work of the catalyst with an optimum composition ($\text{Ca}/\text{Mo} = 0.05$) in the flow reactor during about 10 h it consists mainly of a triple compound phase and $\text{Fe}_2(\text{MoO}_4)_3$, as well as initial non-promoted catalyst. Catalysts with higher content of Ca ($\text{Ca}/\text{Mo} = 1.0$; 2.0) have mainly a phase of Ca molybdate and they are inactive in a reaction of TBA oxidation to MA.

Thus, the phase of a triple compound of Fe-Te-Mo oxides with the slight excess of MoO_3 is the active phase of Fe-Te-Mo-O Cat. MoO_3 dissolves in the main phase and causes defectiveness of its structure which favors the formation of oxidation active centers.

3.1. Mechanism and kinetics of TBA oxidation to MA over an optimum catalyst

On the basis of that the process of TBA oxidation over this catalytic system ($\text{Ca}/\text{Mo} = 0.05$) takes place by phasic redox mechanism, which is confirmed by the results of researches (Fig. 1), Mars-van-Krevelen approach which is widely applied for the description of reaction rates of olefins partial oxidation [6] was used for the derivation of kinetic equations.

Table 3

**Recovery and reoxidation of Fe-Te-Mo-O Cats promoted by the cations of alkaline-earth metals,
with optimum ratio Me/Mo (by MA yield) in the pulse reactor
 $V_{imp} = 0.71 \text{ cm}^3$, $V_f = 0.56 \text{ cm}^3/\text{s}$, total surface of the Cat – 10 m^2**

Me/Mo	S_s , m^2/g	1 th impulse of RM					20 th impulse of RM				Together for 20 impulses		In 5 th impulse of OM V'_{O_2}
		V_{MA} , cm^3	V_{C_4} , cm^3	V_{O_2} , cm^3	$W \cdot 10^7$	S_{MA} , %	V_{C_4} , cm^3	V_{O_2} , cm^3	$W \cdot 10^7$	S_{MA} , %	V_{O_2} RM	V'_{O_2} OM	
—	25	0.36	0.60	1.50	44	60	1.1	1.8	0.8	84	5.5	5.0	0.34
Be 0.1	26	0.37	0.62	2.07	46	59	1.2	1.9	0.8	88	4.7	4.9	0.47
Mg 0.2	10	0.41	0.65	1.57	47	63	1.3	2.1	1.2	86	6.0	6.0	0.48
Ca 0.05	5.2	0.45	0.90	2.00	64	66	1.2	1.9	2.9	89	6.4	6.0	0.44
Sr 0.05	4.8	0.46	0.67	1.62	49	68	2.3	4.2	8.0	82	5.9	5.1	0.46
Ba 0.05	4.0	0.42	0.63	1.57	47	66	2.4	4.6	11.0	80	5.7	5.1	0.46

Notes: W – conversion rate of isobutylene, $\text{mol}/(\text{m}^2 \cdot \text{s})$; V_{MA} – a volume of formed MA, cm^3 ; V_{C_4} – a volume of reacted isobutylene, cm^3 ; V_{O_2} – a volume of removed oxygen, cm^3 ; V'_{O_2} – a volume of absorbed oxygen at the feed of oxidizing mixture, cm^3 ; V_{imp} – an impulse volume, cm^3 ; V_f – feed rate, cm^3/s ; OM – oxidizing mixture.

$$r = \frac{k_1[\text{RH}] \cdot k_2[\text{O}_2]}{\nu k_1[\text{RH}] + k_2[\text{O}_2]} \quad (3)$$

where k_1 , k_2 are rate constants of the recovery and reoxidation of catalyst surface centres, correspondingly; ν is a stoichiometric coefficient by oxygen, for the reaction of MA formation, $\nu = 1$.

For the determination of k_1 and k_2 equations result in linear view:

$$\frac{[\text{O}_2]}{r} = \frac{1}{k_2} + \frac{1}{k_1} \cdot \frac{[\text{O}_2]}{[\text{RH}]} \quad (4)$$

Researches are carried out in the kinetic area of reaction proceeding, that was confirmed by crushing the catalyst grains and changing the stream linear velocity at $T = 623$, 643 and 663 K.

Since the TBA oxidation will be realized in industry at large excess of O_2 (5 mol % TBA in the air), we supported the high and permanent concentration of O_2 ($\sim 8.0 \cdot 10^{-3} \text{ mol}/\text{dm}^3$) during the kinetics research; the TBA concentration was changed from $0.2 \cdot 10^{-3}$ to $2 \cdot 10^{-3} \text{ mol}/\text{dm}^3$.

The obtained results show that the increase of isobutylene concentration (TBA in all experiments reacted fully) increases selectivity of MA formation at all explored temperatures, however olefins conversion decreases. The olefin high concentrations miserably affect the selectivity by MA, and at low concentrations the selectivity notably decreases with the increase of temperature. Reaction rates of all oxidation products formation increase with the increase of concentration and temperature.

Dependence of $[\text{O}_2]/r_{MA}$ on $[\text{O}_2]/[i\text{-C}_4\text{H}_8]$ allows to determine the constants of the recovery and reoxidation stages of the catalyst at all explored temperatures (where $[\text{O}_2]$ is a concentration, r is formation rate (Fig. 2)).

Using dependence of rate constants upon temperature in the $\ln k_i \rightarrow 1/T$ coordinates activation energies

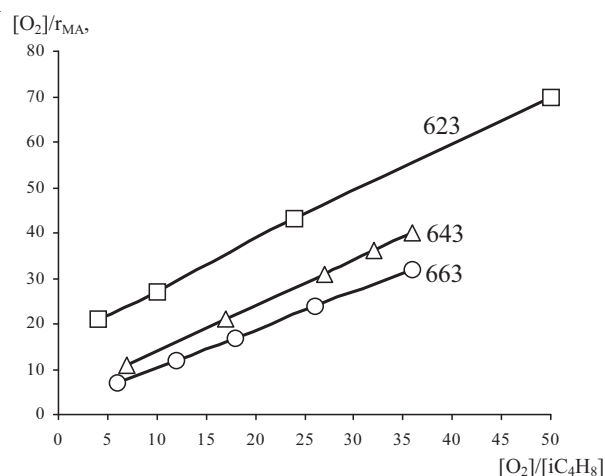


Fig. 2. Dependence of $[\text{O}_2]/r_{MA}$ on $[\text{O}_2]/[i\text{-C}_4\text{H}_8]$ for the reaction of MA formation by TBA oxidation at different temperatures. Reaction conditions for the Figs. 2–4: pulse reactor, $V_{imp} = 5.5 \text{ cm}^3$; $V_f = 0.55 \text{ cm}^3/\text{s}$, $\tau_c = 1.25 \text{ s}$

of these stages (k_i) and adsorption heat (b_i) were determined (Fig. 3).

Comparison of the stages constants shows that the stage of catalyst recovery in the reaction of MA formation has a higher rate comparatively with the stage of catalyst reoxidation, in spite of oxygen excess in the reaction mixture. Obviously the reoxidation stage is a limiting stage that was also observed over a non-promoted catalyst during TBA oxidation to MA. Comparison of activation energies of the limiting stage of the TBA oxidation to MA and effective activation energy of isobutylene oxidation to MA over the non-promoted catalyst shows that higher activation energy of oxidation (150 kJ/mol) is observed at TBA oxidation compared with isobutylene oxidation (130 kJ/mol). Probably there is a competition for an active surface between isobutylene and water vapour which appears during TBA hydration.

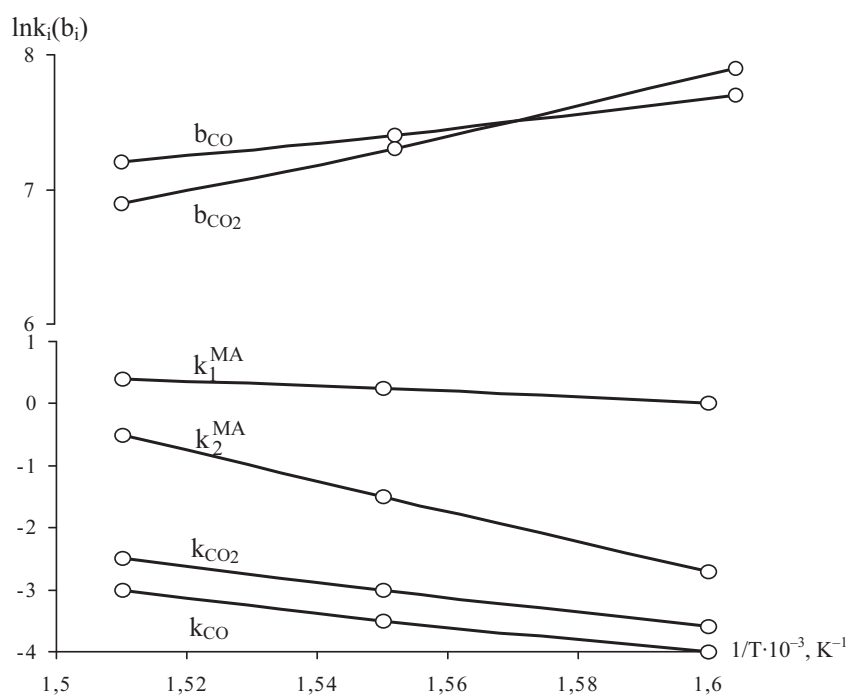


Fig. 3. Dependence of $\ln k_i(b_i)$ upon $1/T$: k_1^{MA} and k_2^{MA} are constants of MA formation stages; k_{CO} , k_{CO_2} , b_{CO} and b_{CO_2} are rate constants and adsorption coefficients of CO and CO₂ formation by TBA oxidation

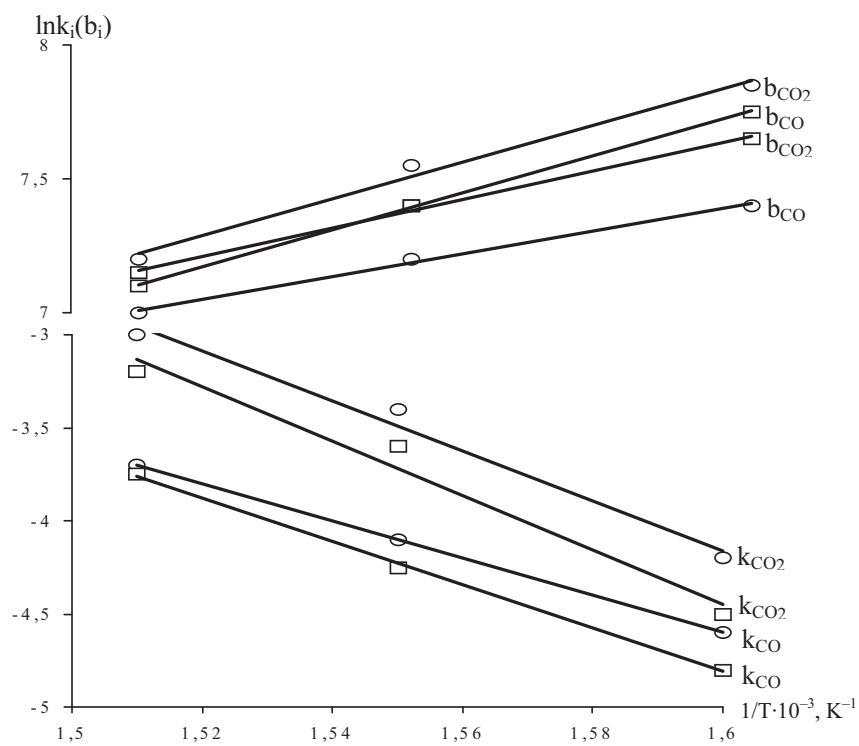
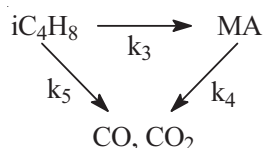


Fig. 4. Dependence of $\ln k_i(b_i)$ upon $1/T$: for the reaction of MA oxidation (O) and isobutylene (\square) into CO and CO₂

The following parallel-serial scheme has been proposed for the formation of deep oxidation products using the results of kinetics investigation.



For the determination of k_3/k_4 ratio kinetics of MA oxidation over the optimum catalyst was investigated (Table 4).

It is accepted that the reaction of CO and CO₂ formation takes place between an organic reagent adsorbed on the surface of the catalyst and oxygen of a gas phase. In such a case the reaction rate can be described by the equation given below [9]:

$$r_c = \frac{K_c b_c [RH][O_2]}{1 + b_c [RH]} \quad (5)$$

where r_c is a gross-rate; K_c is a total constant; b_c is a total adsorption coefficient; $[RH] = [iC_4H_8] + [MA]$.

This equation in a linear aspect is the following:

$$\frac{[O_2]}{r_c} = \frac{1}{K_c} + \frac{1}{K_c b_c [RH]} \quad (6)$$

The equation constants and adsorption coefficients were determined by a graphic method (Figs. 5 and 6), their values are resulted in Tables 5 and 6.

It should be noted that acids (acetic, methacrylic) were also formed during MA oxidation, however only formation rates of CO and CO₂ were taken into account.

During the calculations of rate constants of CO and CO₂ formation from isobutylene the formation rate of these products from MA were calculated depending on the concentration of the latter in the reaction mixture. Then this calculated rate was subtracted from a total rate. Using graphic method rate constants and adsorption coefficients of CO and CO₂ formation from isobutylene were calculated by the difference between the total rate and the rate of CO and CO₂ formation from MA.

On the basis of above-mentioned researches the ratio between constants of consecutive (k_2) and parallel (k_3) ways of formation of isobutylene oxidation products have been calculated. It is established that for the reaction of CO₂ formation from isobutylene or MA k_i constants are practically identical at all temperatures and effective constants ($k_i b_i = k_{ef}$) are practically identical at 663 K. At low temperatures (623 K) more CO₂ is formed by consecutive MA afteroxidation. For the reaction of CO formation ratio $k_{CO}^{MA} / k_{CO}^{iC_4}$ increases with the decrease of temperature and k_{ef} , on the contrary, decreases, that testifies to predominant CO formation from MA at high temperatures.

Table 4

Methacrolein oxidation in CO and CO₂
 $S_s = 0.6 \text{ m}^2/\text{g}$, pulse reactor, $V_{imp} = 5.5 \text{ cm}^3$; $V_f = 0.55 \text{ cm}^3/\text{s}$, $\tau_c = 1.25 \text{ s}$

T, K	$[MA] \cdot 10^3$, mol/l	$[O_2] \cdot 10^3$, mol/l	$[CO_2] \cdot 10^3$, mol/l	$[CO] \cdot 10^3$, mol/l	$W_{CO_2} \cdot 10^3$, mol/l	$W_{CO} \cdot 10^3$, mol/l	X, %
623	1.62	8.88	0.16	0.085	0.135	0.07	5.4
	0.82	8.9	0.144	0.072	0.1	0.055	6.3
	0.49	8.91	0.1	0.04	0.085	0.044	6.1
	0.29	8.91	0.073	0.034	0.063	0.031	8.5
643	1.69	8.92	0.269	0.136	0.224	0.113	6.9
	0.76	8.89	0.197	0.098	0.164	0.08	9.1
	0.45	8.9	0.134	0.073	0.112	0.061	10.0
	0.27	8.91	0.106	0.054	0.088	0.045	14.5
663	1.76	8.83	0.4	0.21	0.25	0.14	9.8
	0.77	8.87	0.26	0.128	0.23	0.108	11.8
	0.49	8.89	0.196	0.096	0.158	0.082	13.6
	0.25	8.9	0.128	0.63	0.102	0.052	17.6

Table 5

Values of rate constant, adsorption coefficient and activation energy of TBA oxidation to MA, CO and CO₂

T, K	MA		CO ₂		CO	
	k_1, s^{-1}	k_2, s^{-1}	$K_c \cdot 10^2, \text{s}^{-1}$	$B_c, \text{l/mol}$	$K_c \cdot 10^2, \text{s}^{-1}$	$B_c, \text{l/mol}$
663	1.45	0.65	8.1	1042	4.8	1302
643	1.23	0.25	4.7	1667	2.99	1768
623	0.98	0.07	2.5	2674	1.87	2289
$E_a \pm 5, \text{kJ/mol}$	31	198	101	-81	82	-48

Table 6

Values of rate constant, adsorption coefficient and activation energy of MA (1) and isobutylene (2) oxidation into CO and CO₂

T, K	CO ₂ (1)		CO (1)		CO ₂ (2)		CO (2)		CO ₂	CO
	$k_4 \cdot 10^2$, s ⁻¹	b_1 , l/mol	$k_4 \cdot 10^2$, s ⁻¹	b_1 , l/mol	$k_5 \cdot 10^2$, s ⁻¹	b_2 , l/mol	$k_5 \cdot 10^2$, s ⁻¹	b_2 , l/mol	k_4/k_5	k_4/k_5
663	4.5	1327	2.5	1097	4.1	1236	2.5	1180	1.1	1
643	2.8	1780	1.9	1307	2.5	1623	1.4	1620	1.12	1.14
623	1.3	2504	0.94	1646	1.05	2113	0.73	2280	1.2	1.3
$E_a \pm 5$, kJ/mol	109	-55	82	35	116	-46	105	-57	—	—
K_{0i} and b_{0i}	$1.74 \cdot 10^7$	$6.16 \cdot 10^{-2}$	$7.22 \cdot 10^4$	1.92	$4.71 \cdot 10^7$	0.294	$4.68 \cdot 10^6$	$3.81 \cdot 10^{-2}$	—	—

Note: k_j/k_3 - constant ratio between consecutive and parallel ways of CO and CO₂ formation

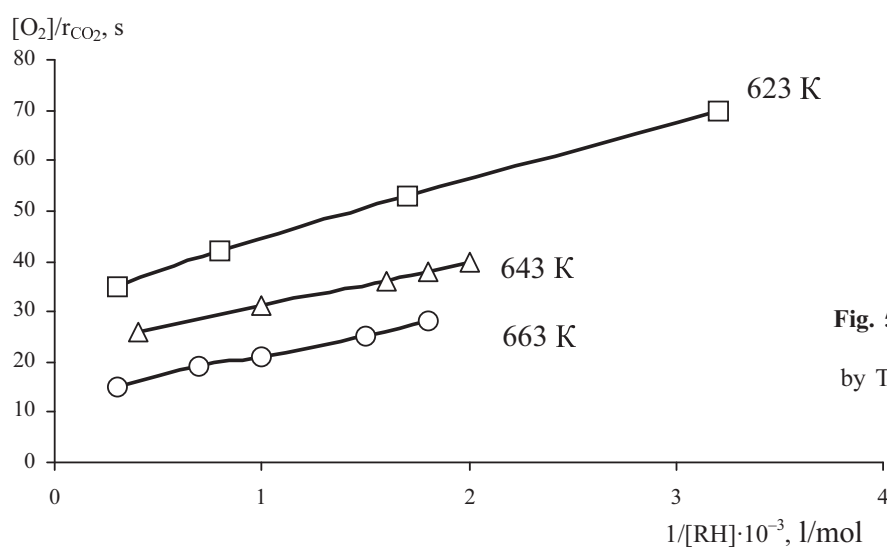


Fig. 5. Dependence of $[O_2]/r_{CO_2}$ upon $1/[RH]$ for the reaction of CO₂ formation by TBA oxidation at different temperatures

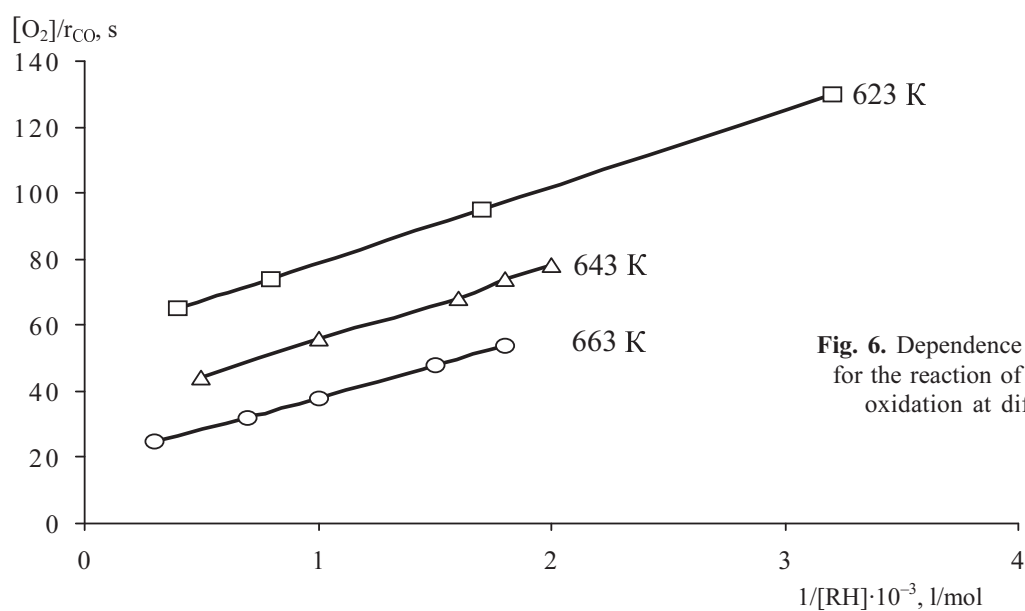


Fig. 6. Dependence of $[O_2]/r_{CO}$ upon $1/[RH]$ for the reaction of CO formation by TBA oxidation at different temperatures

Thus, formation rates of isobutylene oxidation products formed from TBA, can be described by the following kinetic equations:

$$r_{MA} = \frac{2.02 \cdot 10^{17} \cdot \exp(-26461.39/T) \cdot [iC_4H_8] \cdot [O_2]}{2.78 \cdot 10^2 \cdot \exp(-3488.1/T) \cdot [iC_4H_8] + 7.27 \cdot 10^{14} \cdot \exp(-22973.3/T) \cdot [O_2]} \quad (7)$$

$$r_{CO_2} = \frac{7.67 \cdot 10^5 \cdot \exp(-6495.1/T) \cdot [MA] \cdot [O_2]}{1 + 6.14 \cdot 10^{-2} \cdot \exp(-6615.35/T) \cdot [MA]} + \frac{1.25 \cdot 10^7 \cdot \exp(-8419.53/T) \cdot [iC_4H_8] \cdot [O_2]}{1 + 0.29 \cdot \exp(-5532.84/T) \cdot [iC_4H_8]} \quad (8)$$

$$r_{CO} = \frac{7.17 \cdot 10^4 \cdot \exp(-5653.11/T) \cdot [MA] \cdot [O_2]}{1 + 1.91 \cdot \exp(-4209.77/T) \cdot [MA]} + \frac{1.21 \cdot 10^5 \cdot \exp(-5773.4/T) \cdot [iC_4H_8] \cdot [O_2]}{1 + 3.8 \cdot 10^{-2} \cdot \exp(-6855.9/T) \cdot [iC_4H_8]} \quad (9)$$

4. Optimization of the Process

Optimization of the process was carried out on the basis of the obtained kinetic model at temperatures of 643, 673, 693 K and initial concentrations of isobutylene (TBA) in the air of 2.5 and 7.0 mol %. It is established that the maximum MA yield (87.5 %) is obtained at 643 K, the initial concentration of $i-C_4$ (TBA) 7 mol % and contact time 4.4 s. With the increase of temperature the MA yield decreases from 87.5 % (643 K) to 84.1 % (693 K). At the same time the contact time is twice greater at 643 K (4.4 s against 2.2 s). At 673 K and $i-C_4$ concentration 7 mol % the isobutylene conversion is practically complete ($X = 99.5$ %) at $t = 2.5$ s. Selectivity by MA is 87.6 %, yield is 87.1 %. Selectivity by $CO_2 + CO$ is 12.4 % while adding water vapour (20 mol %) to the reaction mixture. It is established that water vapour accelerates a reaction, preventing the formation of high molecular polymerization or pyrolysis products on the surface, and increases selectivity by MA.

So optimum conditions are the following: $[i-C_4] = 7$ mol % in the air + 20 mol % of water vapour; $T = 673$ K; $X_{TBA} = 100$ %, $X_{iC_4} = 99.5$ %, $SMA = 87.6$; $CO + CO_2 = 12.4$ %. MA yield is 87.1 %.

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КАТАЛІТИЧНЕ ОКИСНЕННЯ ТРЕТБУТИЛОВОГО СПИРТУ ДО МЕТАКРОЛЕЇНУ

Анотація. Досліджено процес окиснення трет-бутилового спирту (ТБС) до метакролеїну (МА) на Fe-Te-Mo-O_x каталізаторі (Кт), промотованому Са(NO₃)₂. Встановлено оптимальну за виходом МА концентрацію промотора (Са/Мо = 0,05). На каталізаторі такого типу вихід МА на поданий ТБС при T = 663 K, τ_к = 2,5 с становить 87,1 %, при концентрації ТБС 7,0 % у повітрі з 20 % пари води. За цих умов конверсія ТБС 100 %, ізобутилену – 95,5 %, селективність за МА – 87,6 %; за CO₂ – 12,4 %.

Ключові слова: окиснення, каталізатор, процес, трет-бутиловий спирт, метакролеїн, оптимізація.