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THE USE OF ISOBUTYL ALCOHOL FOR METHACRYLATE SYNTHESIS

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Abstract. Methyl methacrylates synthesis *via* oxidative conversion of isobutyl alcohol has been investigated in accordance with different schemes. The possibility of its use as an alternative raw material instead of isobutylene and *tert*-butyl alcohol has been established. Using the scheme isobutyl alcohol \rightarrow methacrylonitrile \rightarrow methyl methacrylate the product with ultimate yield of 64.8 % has been obtained. Taking into consideration the recirculation of unreacted methacrolein the yield is 81.9 %. This scheme may be recommended for industrial application.

Keywords: oxidation, oxidative amonolysis, catalyst, methacrylonitrile, methyl methacrylate.

1. Introduction

Production of methacrylate monomers and polymeric materials on their basis is among the most important branches of chemical industry of any industrially advanced country. There is a tendency to increase their production capacity, however the lack of raw materials and accompanying ecological problems hinder this process.

The existing acetone cyanohydrine method (ACH) of methyl methacrylate (MMA) synthesis uses extremely poisonous prussic acid (HCN). Moreover, using the existing technology six tons of waste products are formed from one ton of MMA. Ammonium sulphate is the main waste product, which is difficult to utilize.

The best method of MMA production is two-staged process of isobutylene (IB) or *tert*-butyl alcohol (TBA) oxidation to methacrolein (MA) and then to methacrylic acid (MAA). The first stage is sufficiently effective – MA yield is 85 %, IB conversion is 98 %, selectivity by MA is 86.7 % [1]. In the case of TBA oxidation its conversion is 100 %, IB conversion is 99 %, selectivity by MA is 89.5 % (calculated for IB), MA yield is 88.6 % [2]. However, the second stage – MA oxidation to MAA – is insufficiently selective. MAA yield of the both stages is 72 %.

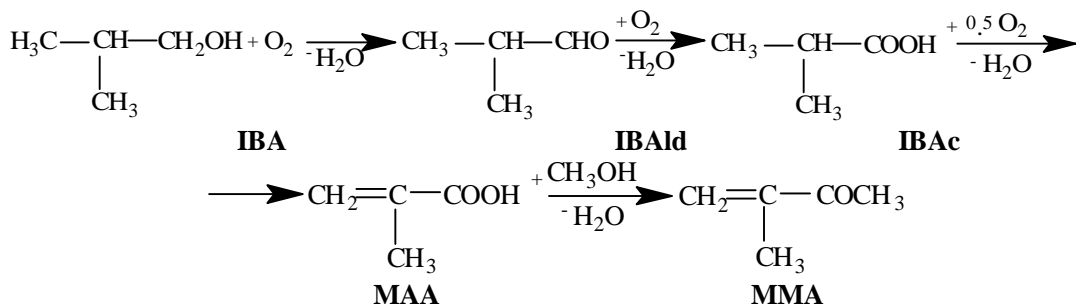
It is known that methyl methacrylates are valuable monomers of chemical industry. Polymethyl methacrylate

(PMMA) is a hard amorphous material characterized by transmittance, atmospheric stability, and good physico-chemical and electroisolated properties. It is frost-resistant (till 213 K) and thermostable at the same time. Under normal conditions it is stable to acids, alkali, light, and oxygen actions. At the heating to 378–383 K PMMA softens, turns into highly plastic state and is easily formed. Therefore, it is widely used for the production of optical and chemical glass, glues, optical instruments, varnish-and-paint materials, *etc.* Apparently the methacrylate production capacity increases every year [3]. At the same time the deficit of the raw material (IB) is observed because the great amount of IB is used for the production of high-octane branched C₈ hydrocarbons *via* the interaction between IB and butenes. Thus the search for alternative raw material instead of IB and TBA is an urgent problem. To our mind, such raw material may be isobutyl alcohol (IBA), which is obtained during alcohols oxysynthesis and which is a component of so-called “fusel oil” during ethanol production *via* fermentation of starch or sugar raw materials (molasses, sugar beet, *etc.*)

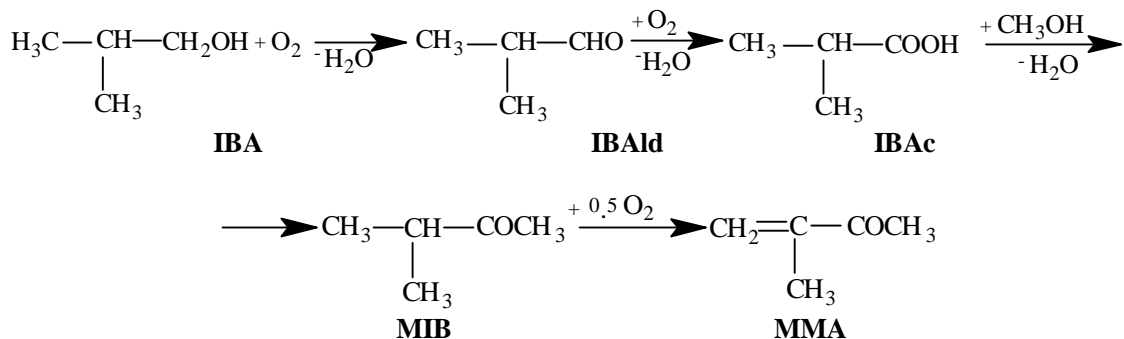
2. Experimental

The process in which IBA is used as raw material for MMA synthesis may proceed by different schemes.

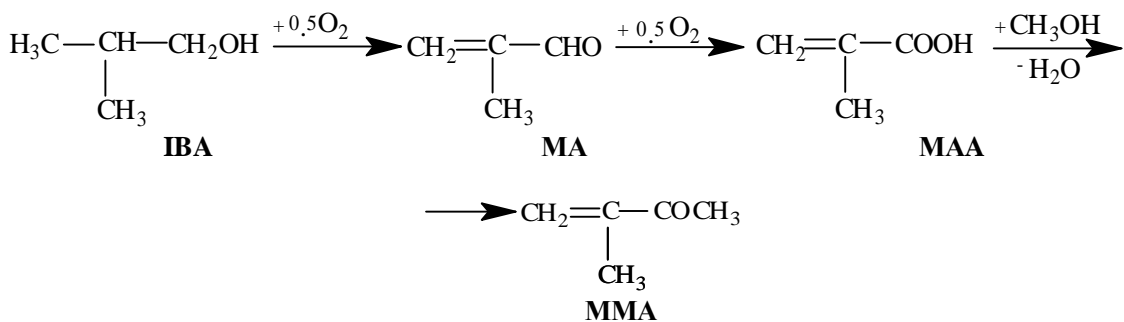
According to Scheme (1) IBA is oxidized to isobutyric aldehyde (IBAlD) and then to isobutyric acid (IBAc), which may be converted to MAA using oxidative dehydration. MMA is obtained by MAA esterification with methanol. It is known [3] that IBAc oxidative dehydration is a low-selective process (~50 %). Methylisobutyrate (MIB) oxidative dehydration to MMA has higher selectivity; therefore we consider this conversion scheme. Moreover, MMA may be obtained by Scheme (2). IBA is oxidized to MA, then to MAA, which is converted into MMA using esterification with methanol. In accordance with Scheme (4) oxidative amonolysis is used to convert IBA into methacrylonitrile (MAN). MAN methanolysis in the presence of sulphate acid and methanol allows to obtain MMA.



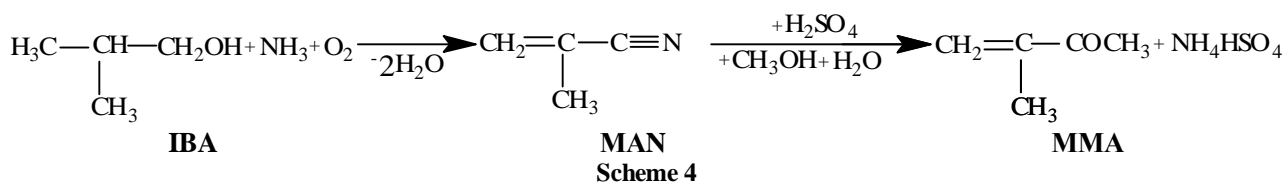
Scheme 1



Scheme 2



Scheme 3



Scheme 4

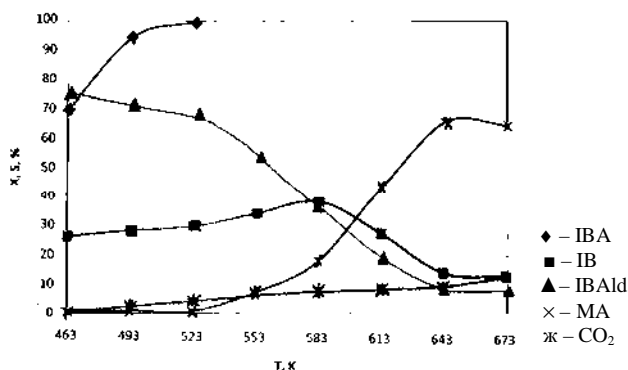


Fig. 1. Dependence of IBA oxidation products selectivity upon the temperature at $t = 1.2$ s. Flow reactor with stationary catalyst Fe:Te:Mo-O_x (1:0.85:1) and impulse feed of reaction mixture (air + 4 mol % IBA).
 $V_{imp} = 12.5 \text{ cm}^3$, $V_{flow} = 0.56 \text{ cm}^3/\text{s}$

For the first stage of Scheme (1) we used Fe:Te:Mo-O_x (1:0.85:1) catalyst (Cat) developed by V. Zhyznivskiy [5] for the oxidation of low-molecular olefins with high yield of unsaturated aldehydes. Experimental results are represented in Fig. 1.

One can see that Cat is effective in the mentioned reaction. The complete IBA conversion is achieved at the contact time (*t*) of 1.2 s and the temperature of 523 K. Under such conditions the reaction products are: IBAlD (the main product), IB, MA (traces), and CO₂.

Thus, the process optimum conditions are: *T* = 523 K, *t* = 1.2 s, and IBA concentration of 4 mol %. Under such conditions IBAlD yield is 97.1 %.

3. Results and Discussion

3.1. Kinetics of IBA Oxidation to MA

To calculate the process it is necessary to know its kinetic regularities. Kinetics of IBA oxidation to MA was

studied using micro-chromatographic method. The complete-mixing reactor with vibro-liquefied catalyst had the pulse feed of the reaction mixture [6] in the reaction kinetic area determined by Cat grains grinding and changing the flow linear rate at the constant contact time. It has been established that using Cat grains size of 1.5–2 mm at reactor shaking frequency of 50 Hz and flow rate *V_{flow}* ≥ 0.35 cm/s the reaction proceeds in the kinetic area. At the mentioned shaking frequency and small doses of reagents fed by one impulse (12.5 cm³) the concentration and temperature drops in Cat layer were absent. The variation interval of temperature and concentrations are represented in Table 1. Since the experiments were carried out at great excess of O₂ in the reaction mixture containing less than 2 mol % of IBA, we changed only IBA concentration in the air. Constants were calculated accordingly to the pseudo-first order reaction by IBA. The experimental results are confirmed by the data represented in Fig. 2.

Table 1

Kinetic regularities of IBA oxidation over Fe:Te:Mo-O_x (1:0.85:1) catalyst at *t* = 1.2 s

<i>T</i> , K	<i>C</i> _{IBA} · 10 ⁴ mol/dm ³	Concentration of the reaction products <i>C_i</i> · 10 ⁵ , mol/dm ³				Rate of products obtaining, <i>Wp_i</i> · 10 ⁵ , mol/dm ³ ·s					Rate constants, s ⁻¹			
		AA	IBAlD	MA	CO ₂	AA	IBAlD	MA	CO ₂	Σ <i>W</i>	AA · 10 ³	IBAlD	MA	CO ₂ · 10 ³
423	2.15	0.06	2.4	3.6	0.06	0.05	1.88	2.81	0.05	4.78	2.11	0.09	0.13	2.18
423	4.30	0.11	4.9	6.8	0.12	0.09	3.83	5.31	0.09	9.32	2.00	0.09	0.12	2.18
423	6.50	0.16	6.8	10.1	0.19	0.13	5.31	7.89	0.15	13.48	1.92	0.08	0.12	2.28
423	8.50	0.22	9.3	13.3	0.24	0.17	7.27	10.39	0.19	18.02	2.02	0.09	0.12	2.21
<i>k_{av}</i>											2.01	0.09	0.12	2.21
453	2.15	0.096	3.8	5.0	0.07	0.08	2.97	3.91	0.05	7.00	3.49	0.14	0.18	2.54
453	4.30	0.196	6.9	7.2	0.15	0.15	5.39	5.63	0.12	11.29	3.55	0.13	0.13	2.73
453	6.50	0.32	11.6	14.7	0.20	0.25	9.06	11.48	0.16	20.95	3.85	0.14	0.18	2.40
453	8.50	0.42	13.4	17.9	0.31	0.33	10.5	13.98	0.24	25.02	3.86	0.12	0.16	2.85
<i>k_{av}</i>											3.69	0.13	0.16	2.63
483	2.15	0.17	6.1	6.9	0.08	0.13	4.77	5.39	0.06	10.35	6.18	0.22	0.25	2.91
483	4.30	0.29	8.4	10.9	0.17	0.23	6.56	8.52	0.13	15.44	5.27	0.15	0.20	3.09
483	6.50	0.40	15.0	19.2	0.24	0.31	11.7	15.00	0.19	27.22	4.81	0.18	0.23	2.88
483	8.50	0.51	16.2	21.8	0.37	0.40	12.7	17.03	0.29	30.38	4.69	0.15	0.20	3.40
<i>k_{av}</i>											5.24	0.18	0.22	3.07
513	2.15	0.29	10.6	9.2	0.10	0.23	8.28	7.19	0.08	15.77	10.510.5	0.39	0.33	3.63
513	4.30	0.58	16.1	18.9	0.20	0.45	12.6	14.77	0.16	27.95		0.29	0.34	3.63
513	6.50	1.01	23.6	30.5	0.33	0.79	18.4	23.83	0.26	43.31		0.28	0.37	3.97
513	8.50	1.14	29.0	36.5	0.42	0.89	22.7	28.52	0.33	52.39		0.27	0.34	3.86
<i>k_{av}</i>											10.9	0.31	0.34	3.77

Note: *C*_{IBA} was calculated as $C_{av} = \frac{C_0 + C_k}{2}$. Since *X*_{IBA} = 100% then $C_{av} = \frac{C_0}{2}$; AA – acetaldehyde

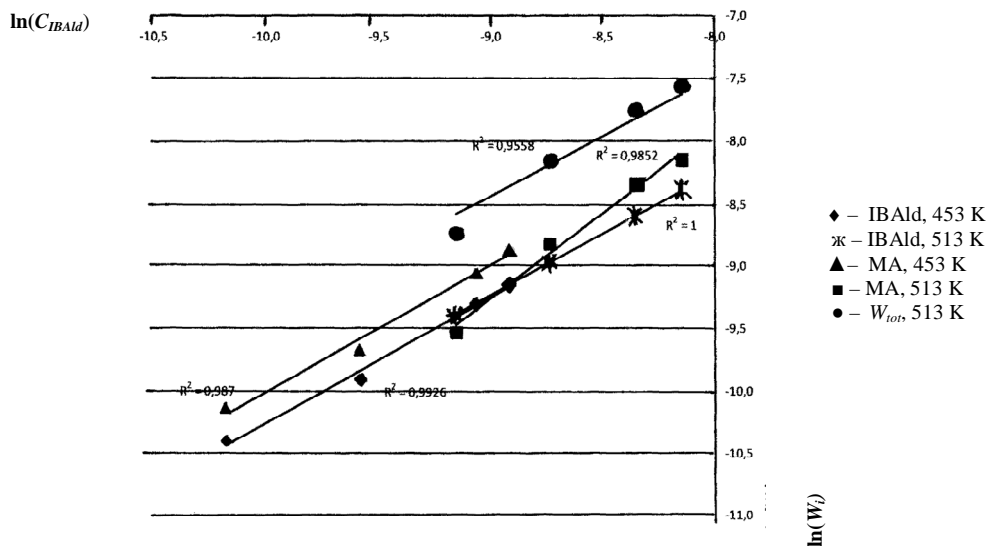


Fig. 2. $\ln(W_i)$ versus $\ln C_{IBAlD}$ at $t = 1.2$ s

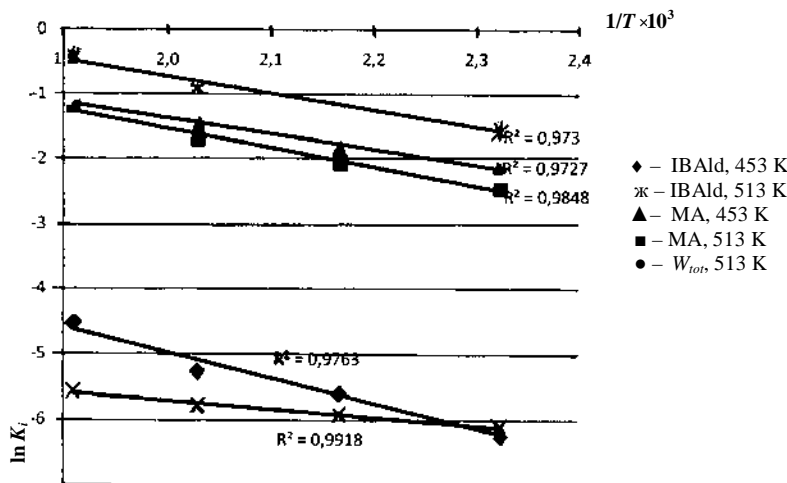


Fig. 3. $\ln K_{iav}$ versus $1/T$ for the reaction of IBA oxidation products obtaining

Using the dependence between $\ln K_{iav}$ and $1/T$ (Fig. 3) the activation energies of oxidation products were calculated by the formula $E_a = -\text{tga} \cdot R$ (where $R = 8.314$ – gas constant):

for IBAlD	$E_a = 24.5$ kJ/mol;
for MA	$E_a = 20.2$ kJ/mol
for AA	$E_a = 32.1$ kJ/mol
for CO ₂	$E_a = 10.7$ kJ/mol
for IMA conversion	$E_a = 21.9$ kJ/mol

The activation energies values show that the increase in temperature increases the selectivity by acetaldehyde, which is confirmed by the experimental result.

3.2. Oxidation of Isobutyric Aldehyde to Isobutyric Acid

This is the second stage of Scheme (1). The experiments were carried out in a flow reactor with stationary catalyst and pulse feed of the reaction mixture ($V_{imp} = 12.5$ cm³, $V_{flow} = 0.56$ cm³/s, $t = 2.4$ s) using different catalysts based on 12-molibdenumphosphoric heteropolyacid ($\text{Cs}_2\text{P}_1\text{Mo}_{12}\text{Pb}_{0.2}\text{Cr}_1\text{O}_x$). The reaction mixture composition (mol %) is: IBAlD 4.0; water steam 20; air 76. The reaction temperature is 613 K, contact time 2.4 s. IBAlD conversion is 70 %, selectivity by IBAc 82 %, its yield is 63 %, acetic acid yield is 63 %, and CO+CO₂ yield 14 %.

Under the same conditions but using another catalyst ($\text{Cs}_2\text{P}_2\text{Mo}_{12}\text{Pb}_{0.2}\text{V}_{1.0}\text{O}_x$) IBAlD conversion is 64 % and selectivity by IBAc is 67 %.

The best results are obtained using the catalyst $\text{Mo}_{12}\text{P}_1\text{As}_{0.6}\text{Cu}_{0.25}\text{O}_x$ (Table 2).

Table 2

IBAlD oxidation to IMAc over $\text{Mo}_{12}\text{P}_1\text{As}_{0.6}\text{Cu}_{0.25}\text{O}_x$

T, K	IBAlD conversion, %	Selectivity, %		IBAc yield, %
		IBAc	CO ₂	
463	6.0	100	-	6.0
493	15.0	99.0	1.0	14.8
523	25.0	97.0	3.0	24.2
553	40.0	96.0	4.0	38.4
583	66.0	95.0	5.0	62.8
613	92.0	92.0	8.0	84.6
643	100.0	80.0	20.0	80.0

Maximum selectivity by IBAc (100 %) is obtained at 463 K but under such conditions IMAld conversion is only 6 %. Increase in the temperature increases IMAld conversion and decreases the selectivity by IMAc. Maximum IMAc yield is 84.6 % obtained at 613 K and contact time of 2.4 s. IMAld complete conversion is achieved at 643 K but IMAc yield decreases to 80 %. Thus the optimal conditions are: $T = 613 \text{ K}$, $t = 2.4 \text{ s}$,

IBAlD concentration in the air 5 mol %. Under these conditions beside IMAc (yield 84.6 %) CO₂ in the amount of 8 % is also formed.

3.3. Obtaining of Methylisobutyrate

The third stage of MMA synthesis is obtaining of methylisobutyrate (MIB). Esterification of IBAc to MIB may be carried out in both gaseous (over KU-2-8- cationic exchanger) and liquid (over toluene sulphate Cat) phases. The results are better for the gaseous phase, MIB yield is above 90 % [3]. In the presence of sulfocationic exchanger the process is carried out at 383–393 K in the flow reactor with stationary catalyst. To increase the acid conversion the excess of methanol with its recirculation is required. The process schematic diagram is represented in Fig. 4 [3].

Under the laboratory conditions (temperature of 393 K, catalyst KU-2-8, $\text{CH}_3\text{OH}:\text{IBAc}$ ratio 1.5:1.0, methanol recirculation and water azeotropic distillation) the results were the following: IBAc conversion 96.5 %, selectivity by MIB 92 %, dimethyl ether 8 %, reaction time 30 min, and MIB yield 88.8 %.

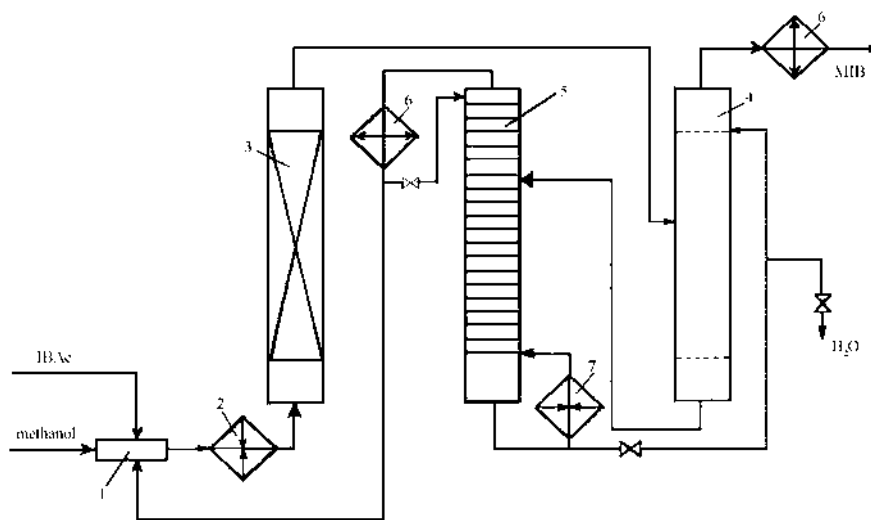


Fig. 4. Schematic diagram of IBAc esterification in the presence of sulfocationic exchanger: mixer (1), evaporator (2), reactor (3), extraction column (4), column for alcohol recuperation (5), condenser (6), and boiler (7)

3.4. Oxidative Dehydration of Methylisoburate to Methacrylate

This is the last stage of MMA synthesis. The catalyst based on 12-molibdeniumphosphoric heteropolyacid ($\text{H}_3\text{PMo}_{12}\text{O}_{40}$) with different promoters which were effective for the reactions of MA oxidation to MAA [9] and the catalyst $\text{Mo}_{12}\text{P}_1\text{As}_{0.6}\text{Cu}_{0.25}\text{O}_x$ [10] (initial one and with Cr addition) were used for the synthesis. Composition and physico-chemical properties of the investigated catalysts are given in Table 3.

Surface acidity has a great influence on oxidation processes proceeding according to adsorption mechanism. The main reagents are activated over these centres. The surface of the catalysts is heterogeneous. Therefore, the reaction products, as well as substrates hold out on the surface with different forces affecting the reaction selectivity. Irreversible chemisorption of organic substrate is observed over strong acid centres resulting in its decomposition, destructive products formation and complete oxidation.

Table 3

**Physico-chemical properties of the catalysts
for oxidative dehydration of MIB to MA**

Catalyst symbol	Atomic composition	S_s , m ² /g	Surface acidity					ΣN_c , 10 ⁻¹⁸
			K , mcmol/m ²	T_{mb} , K	T_{mII} , K	$E_I(\pm 5)$, kJ/mol	$E_{II}(\pm 5)$, kJ/mol	
Cat ₁	CsP ₁ Mo ₁₂ Pb _{0.2} O _x	3.0	5.4	450	705	74.0	300.0	3.2
Cat ₂	Cat ₁ + V _{1.0}	5.0	7.2	440	705	62.0	226.0	4.3
Cat ₃	Cat ₁ + W _{1.0}	3.0	3.2	440	650	57.0	190.0	1.9
Cat ₄	Cat ₁ + Cr _{1.0}	8.0	7.3	403	640	55.0	130.0	4.4
Cat ₅	Cat ₁ + V _{1.0} + Sn _{1.0}	6.0	7.2	423	683	53.0	95.0	4.3
Cat ₆	Mo ₁₂ P ₁ As _{0.6} Cu _{0.25} O _x	5.3	6.3	393	653	33.0	52.0	3.8
Cat ₇	Mo ₁₂ P ₁ As _{0.6} Cu _{0.25} O _x + Cr _{1.0}	4.9	6.9	383	673	27.0	75.0	4.2
Cat ₈	Mo ₁₂ P _{1.2} Sb _{0.5} W _{0.6} K _{0.7} O _x	5.2	4.5	383	663	29.0	58.0	2.7

Notes: K – surface acidity, determined by NH₃ chemisorption using pulse chromatographic method at $T = 343$ K; T_{ml} and T_{mII} – temperature of thermal desorption maxima at Cat programmed heating; E_I and $E_{II}(\pm 5)$ – heats of NH₃ thermal desorption from Cat surface determined by thermal sorption rate at programmed increase of T (0.27 K/s) using the procedure described in [8]; ΣN_c – amount of acid centres calculated by the amount of chemisorbed NH₃ at one-centered chemisorption; S_s – Cat specific surface determined by argon thermal desorption [7].

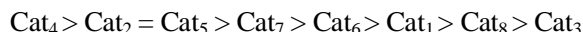
Table 4

Oxidative dehydration of MIB to MMA using mixed oxide catalysts

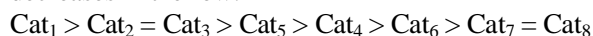
Catalyst symbol	T , K	MIB conversion, %	Selectivity, %				MMA yield, %
			OA	Acetone	MMA	CO+CO ₂	
Cat ₁	553	41.9	9.3	11.3	70.8	8.6	29.7
	563	72.1	21.4	18.0	46.9	13.5	33.7
	593	100.0	33.0	20.3	23.0	23.7	23.0
Cat ₂	533	30.6	4.0	17.5	77.0	1.5	23.8
	573	58.8	5.2	13.8	76.8	4.2	45.1
	603	82.1	7.3	10.5	76.0	6.2	62.4
Cat ₃	533	20.0	15.0	15.0	68.0	2.0	13.6
	563	75.8	18.8	10.9	61.0	9.3	46.2
	573	95.3	34.0	12.8	36.4	16.8	34.7
Cat ₄	513	80.0	0.8	8.3	88.4	2.5	70.7
	523	98.0	1.0	9.1	85.4	4.5	83.7
	533	100.0	1.9	9.9	79.5	8.7	79.5
Cat ₅	533	66.0	0.9	12.2	86.3	0.6	56.8
	553	91.0	0.9	11.4	87.0	0.7	79.2
	573	96.0	1.8	11.7	85.0	1.5	81.6
Cat ₆	493	60.0	-	8.5	90.0	1.5	54.0
	513	74.0	-	7.3	90.0	2.7	66.6
	523	100.0	-	6.2	90.0	3.8	90.0
	533	100.0	-	8.5	86.0	5.5	86.0
Cat ₇	463	63.0	-	4.0	94.0	2.0	59.2
	473	83.0	-	5.1	92.1	2.8	76.4
	483	100.0	-	6.3	90.0	3.7	90.0
Cat ₈	483	70.0	0.4	3.0	96.0	0.6	67.2
	503	90.0	0.4	3.0	96.0	0.6	86.4
	513	100.0	0.6	3.6	95.0	0.8	95.0

Notes: 5 mol % of MIB in the air, $V_{imp} = 9.1$ cm³, $V_{flow} = 0.56$ cm³/s, $\tau = 2.4$ s

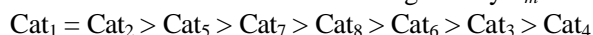
The analysis of surface acidity of investigated catalysts (Table 3) show the total acidity decrease in the following order:



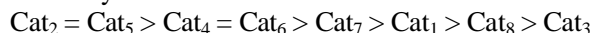
The strength of acid centres of the first genus by T_m decreases in the row:



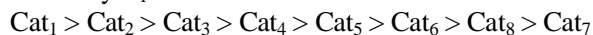
For the centers of the second genus by T_m :



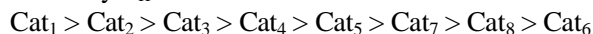
By the amount of active acid centers:



By E_1 :



By E_{II} :



Thus, the obtained rows for the centres of I and II genus are practically identical by activation energy of NH_3 desorption. The maximum strength of acid centres by T_m , E_1 and E_2 has the Cat_1 , whose selectivity by MMA is the least (Table 4). Its surface strongly holds both MIB and products of its conversion followed by their afteroxidation to CO-CO_2 .

Taking into consideration MIB conversion degree at 553 K, for Cat_1 – Cat_5 based on Cat_1 and different promoters the following row is observed: $\text{Cat}_4 > \text{Cat}_5 > \text{Cat}_1 > \text{Cat}_2 > \text{Cat}_3$. The row coincides with the row of total acidity (Table 3). The catalysts Cat_6 – Cat_8 , containing As (Cat_6 and Cat_7) and Sb, W, K (Cat_8) differ from Cat_1 – Cat_5 by their composition, thereby it is incorrect to compare their parameters of surface acidity with those of Cat_1 – Cat_5 . Concerning the amount of acid centres for Cat_1 – Cat_5 , they are situated in the row: $\text{Cat}_4 > \text{Cat}_5 = \text{Cat}_2 > \text{Cat}_1 > \text{Cat}_3$ which also coincides with their activity (Table 3).

IBAc yield at Cat_8 is higher by 5 % compared with that at Cat_7 but the temperature at Cat_8 is also higher (by 30 K). Under experimental conditions Cat_8 has the highest selectivity by MMA among all catalysts.

Thus, surface acidity of the catalyst plays a significant role in heterogeneous catalysis. The increase of surface acidity increases Cat activity as a result of existing chemical bonds weakening at its activation and formation of transitional activated complex.

For the first time the connection between Cat surface acidity and Cat activity in the reaction of methanol oxidation was mentioned by N. Pernikone and co-workers [11]. G. Boreskov [12] noted that heterogeneous catalysts activity correlates with the strength of acid centres for acid-base reactions.

The connection between Cat surface acidity and Cat activity is observed in many works. Surface acid centres participate in activation of substrate molecules forming transition activated complex between substrate and surface acid centre. At the same time there are different

acid centres on the catalyst surface which adsorb reagents with varied strength. Over strong acid centres an irreversible chemisorption may occur, with the formation of destruction products and complete oxidation compounds. To block such centres a small amount of alkali or earth-alkali elements is introduced into the Cat. One can see from Table 3 that Cat_7 has the least temperature at which 80% and 100% conversion of MIB is achieved. But MIB selectivity by MMA is lower by 5 % than that for Cat_8 . Obviously the chrome oxide introduced into Cat_6 , increases surface acidity and activity of the catalyst. Comparison of the temperatures at which MIB conversion is 80 % and selectivity by MMA is high shows that the most active catalysts are Cat_7 and Cat_8 . Using Cat_7 the complete MIB conversion is 100 % at 483 K and using Cat_8 (the most selective one) – at 513 K (Table 5).

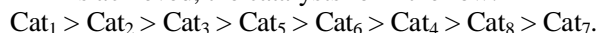
Table 5

Temperature and selectivity by MMA at MIB conversion 80 % (see experimental conditions in Table3)

Catalyst symbol	T , K	S_{MMA} , %	Y_{MMA}^* , % at T_{opt} (K)
Cat_1	580	38.0	33.7 (563)
Cat_2	575	70.0	62.4 (603)
Cat_3	568	55.0	46.2 (563)
Cat_4	513	88.0	83.7 (523)
Cat_5	543	86.0	81.6 (573)
Cat_6	518	90.0	90.0 (523)
Cat_7	468	93.0	90.0 (483)
Cat_8	493	95.0	95.0 (513)

* Maximum yield at temperature optimal for Cat

Based on the temperature at which 80 % conversion of MIB is achieved, the catalysts form the row:



The yield achieved using Cat_8 (95 %) at 513 K is higher than that using Cat_7 (90%). At lower temperature (483 K) MIB conversion is 100 % for the both catalysts.

Obviously the process selectivity may be determined by thermodynamic characteristics of acidity, *i.e.* strength of adsorbate holding on the surface and heat of activated thermal desorption of oxidation products. At MIB conversion of 80 % the selectivity by MMA for the catalysts decreases in the row: $\text{Cat}_4 > \text{Cat}_5 > \text{Cat}_2 > \text{Cat}_3 > \text{Cat}_1$. By E_1 the following row is obtained: $\text{Cat}_1 > \text{Cat}_2 > \text{Cat}_3 > \text{Cat}_4 > \text{Cat}_5$; E_{II} : $\text{Cat}_1 > \text{Cat}_2 > \text{Cat}_3 > \text{Cat}_4 > \text{Cat}_5$. Selectivity by T_{mI} : $\text{Cat}_1 > \text{Cat}_2 = \text{Cat}_3 > \text{Cat}_5 > \text{Cat}_4$; T_{mII} : $\text{Cat}_1 > \text{Cat}_2 > \text{Cat}_3 > \text{Cat}_4 > \text{Cat}_5$.

The comparison of selectivity row with acidity strength (NH_3 adsorption strength) shows that the greater the acidity strength, the less the selectivity of the Cat.

4. Conclusions

1. Cat₈ is the best of all investigated catalysts. The maximum MMA yield (95 %) with complete MIB conversion is achieved over this Cat at 513 K, contact time 2.4 s and MIB concentration in the air 5 mol %.

2. Ether oxidative dehydration gives better results compared with IBAC dehydration. MMA yield calculated for supplied IBA is: 97.3 % (1 stage), 84.6 % (2 stage), 90 % (3 stage), and 95 % (4 stage). The total MMA yield is 70.4 %.

3. Taking into account that acid is an initial material for IBAC dehydration and in our case IBA gives the additional stages 1 and 2 with high yields (97.3 and 84.6 %) the investigated scheme of IBA use for MMA synthesis may be applied in the industry.

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ВИКОРИСТАННЯ ІЗОБУТИЛОВОГО СПИРТУ ДЛЯ СИНТЕЗУ МЕТАКРИЛАТІВ

Анотація. Досліджено синтез метилметакрилатів окиснювальним перетворенням ізобутилового спирту за різними схемами. Встановлена можливість використання його як вихідної альтернативної сировини ізобутилену та трет.бутилового спирту. При одержанні метилметакрилатів за схемою: ізобутиловий спирт → метакрилонітрил → метилметакрилат одержано продукт, сумарний вихід якого на поданий спирт дорівнює 64,8%, а з рециркуляцією непрореагованого метакролеїну – 81,9%. Цю схему можна рекомендувати для впровадження в промисловість.

Ключові слова: окиснення, окиснювальний амонізі, каталізатор, метакрилонітрил, метилметакрилат.