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 → methacrylonitrile → 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. 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.
H$_3$C–CH–CH$_2$OH + O$_2$ $\rightarrow$ CH$_3$–CH–CHO $\rightarrow$ CH$_3$–CH–COOH + 0.5 O$_2$

\[ \text{IBA} \quad \text{IBAld} \quad \text{IBAc} \]

\[ \rightarrow \text{CH}_2=\text{C}–\text{COOH} \]

\[ \text{CH}_3 \quad \text{CH} \quad \text{MMA} \]

\[ + \text{CH}_3\text{OH} \rightarrow \text{CH}_2=\text{C}–\text{COCH}_3 \]

\[ \text{CH}_3 \quad \text{CH} \quad \text{MMA} \]

\[ \text{MIB} \quad + 0.5 \text{O}_2 \rightarrow \text{CH}_2=\text{C}–\text{COCH}_3 \]

\[ \text{CH}_3 \quad \text{CH} \quad \text{MMA} \]

\[ \text{Scheme 1} \]

H$_3$C–CH–CH$_2$OH + O$_2$ $\rightarrow$ CH$_3$–CH–CHO $\rightarrow$ CH$_3$–CH–COOH + CH$_3$OH

\[ \text{IBA} \quad \text{IBAld} \quad \text{IBAc} \]

\[ \rightarrow \text{CH}_3–\text{CH}–\text{COCH}_3 \]

\[ \text{CH}_3 \quad \text{MMA} \]

\[ + 0.5 \text{O}_2 \rightarrow \text{CH}_2=\text{C}–\text{COCH}_3 \]

\[ \text{CH}_3 \quad \text{MMA} \]

\[ \text{Scheme 2} \]

H$_3$C–CH–CH$_2$OH $\rightarrow$ CH$_2=\text{C}–\text{CHO} \rightarrow$ CH$_2=\text{C}–\text{COOH} \rightarrow$ CH$_3$–CH–COCH$_3$

\[ \text{IBA} \quad \text{MA} \quad \text{MMA} \]

\[ + 0.5 \text{O}_2 \rightarrow \text{MA} \quad \text{MAA} \]

\[ \rightarrow \text{CH}_2=\text{C}–\text{COCH}_3 \]

\[ \text{CH}_3 \quad \text{MMA} \]

\[ \text{Scheme 3} \]

H$_3$C–CH–CH$_2$OH$+\text{NH}_3$+O$_2$ $\rightarrow$ CH$_2=\text{C}–\text{C}=$N $\rightarrow$ CH$_2=\text{C}–\text{COCH}_3$+$\text{NH}_3\text{HSO}_4$

\[ \text{IBA} \quad \text{MAN} \quad \text{MMA} \]

\[ +\text{H}_2\text{SO}_4 \rightarrow \text{MAN} \quad \text{MMA} \]

\[ \text{CH}_3 \quad \text{CH} \quad \text{MMA} \]

\[ \text{Scheme 4} \]

Fig. 1. Dependence of IBA oxidation products selectivity upon the temperature at $\tau = 1.2$ 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).

$V_{imp} = 12.5$ cm$^3$, $V_{flow} = 0.56$ cm$^3$/s
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 $V_{flow} \geq 0.35$ 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

<table>
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<tr>
<th>$T$, K</th>
<th>$C_{IBA} \times 10^4$, mol/dm³</th>
<th>Concentration of the reaction products $C_i \times 10^3$, mol/dm³</th>
<th>Rate of products obtaining, $W_p \times 10^5$, mol/dm³/s</th>
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Note: $C_{IBA}$ was calculated as $C_{av} = \frac{C_a + C_l}{2}$. Since $X_{IBA} = 100\%$ then $C_{av} = \frac{C_a}{2}$; AA – acetaldehyde
Using the dependence between \( \ln K_{iav} \) and \( 1/T \) (Fig. 3) the activation energies of oxidation products were calculated by the formula \( E_a = -\Delta G \cdot R \) (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 \( (V_{imp} = 12.5 \) cm\(^3\), \( V_{flow} = 0.56 \) cm\(^3\)/s, \( \tau = 2.4 \) s) using different catalysts based on 12-molibdeniumphosphoric heteropolyacid \( (Cs_2P_2Mo_{12}Pb_{0.2}Cr_1O_{13}) \). 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+CO\(_2\) yield 14%.

Under the same conditions but using another catalyst \( (Cs_2P_2Mo_{12}Pb_{0.2}V_{1.0}O_{13}) \) IBAld conversion is 64% and selectivity by IBAc is 67%.
The best results are obtained using the catalyst 
$\text{Mo}_{12}\text{P}_{3}\text{As}_{0.6}\text{Cu}_{0.25}\text{O}_x$ (Table 2).

### Table 2

<table>
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<tr>
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<th>IBAl oxidation</th>
<th>Selectivity, %</th>
<th>IBAc yield, %</th>
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<td>643</td>
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Maximum selectivity by IBAc (100 %) is obtained at 463 K but under such conditions IMAl conversion is only 6 %. Increase in the temperature increases IMAl conversion and decreases the selectivity by IMAc. Maximum IMAc yield is 84.6 % obtained at 613 K and contact time of 2.4 s. IMAl complete conversion is achieved at 643 K but IMAc yield decreases to 80 %. Thus the optimal conditions are: $T = 613$ K, $\tau = 2.4$ s, IBAl concentration in the air 5 mol %. Under these conditions beside IMAc (yield 84.6 %) CO$_2$ 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 sulfocatonic 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, CH$_3$OH: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](image)

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 $\text{Mo}_{12}\text{P}_{3}\text{As}_{0.6}\text{Cu}_{0.25}\text{O}_x$ [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 chemosorption of organic substrate is observed over strong acid centres resulting in its decomposition, destructive products formation and complete oxidation.
Physico-chemical properties of the catalysts for oxidative dehydration of MIB to MA

<table>
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<tr>
<th>Catalyst symbol</th>
<th>Atomic composition</th>
<th>$S_r$, m$^2$/g</th>
<th>Surface acidity</th>
<th>$\Sigma N_r$ 10$^{-18}$</th>
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<td>$T_{\text{K}}$</td>
<td>$K$, mmol/m$^2$</td>
<td>$T_{\text{mid}}$, K</td>
<td>$T_{\text{fin}}$, K</td>
<td>$E_i$($\pm 5$), kJ/mol</td>
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Notes: $K$ – surface acidity, determined by NH$_3$ chemosorption using pulse chromatographic method at $T = 343$ K; $T_{\text{mid}}$ and $T_{\text{fin}}$ – temperature of thermal desorption maxima at Cat programmed heating; $E_i$ and $E_f$($\pm 5$) – heats of NH$_3$ 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]; $\Sigma N_r$ – amount of acid centres calculated by the amount of chemosorbed NH$_3$ at one-centered chemosorption; $S_r$ – Cat specific surface determined by argon thermal desorption [7].

Oxidative dehydration of MIB to MMA using mixed oxide catalysts

<table>
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<th>Catalyst symbol</th>
<th>$T$, K</th>
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<td>Cat$_8$</td>
<td>483</td>
<td>70.0</td>
<td>0.4</td>
<td>3.0</td>
<td>96.0</td>
<td>0.6</td>
</tr>
<tr>
<td>503</td>
<td>90.0</td>
<td>0.4</td>
<td>3.0</td>
<td>96.0</td>
<td>0.6</td>
<td>86.4</td>
</tr>
<tr>
<td>513</td>
<td>100.0</td>
<td>0.6</td>
<td>3.6</td>
<td>95.0</td>
<td>0.8</td>
<td>95.0</td>
</tr>
</tbody>
</table>

Notes: 5 mol % of MIB in the air, $V_{\text{imp}} = 9.1$ cm$^3$, $V_{\text{flow}} = 0.56$ cm$^3$/s, $\tau = 2.4$ s
The analysis of surface acidity of investigated catalysts (Table 3) show the total acidity decrease in the following order:

\[ \text{Cat}_4 > \text{Cat}_3 > \text{Cat}_2 > \text{Cat}_1 \]

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

\[ \text{Cat}_1 > \text{Cat}_2 > \text{Cat}_3 > \text{Cat}_4 \]

For the centers of the second genus by \( T_m \):

\[ \text{Cat}_1 = \text{Cat}_2 > \text{Cat}_3 > \text{Cat}_4 \]

Thus, the obtained rows for the centres of I and II genus are practically identical by activation energy of \( \text{NH}_3 \) desorption. The maximum strength of acid centres by their composition, thereby it is incorrect to compare their parameters of surface acidity with those of \( \text{Cat}_1 \)– \( \text{Cat}_5 \) by their composition, thereby it is incorrect to compare their parameters of surface acidity with those of \( \text{Cat}_1 \)– \( \text{Cat}_5 \). The catalysts \( \text{Cat}_6 \)–\( \text{Cat}_8 \), containing As (\( \text{Cat}_6 \) and \( \text{Cat}_7 \)) and Sb, W, K (\( \text{Cat}_8 \)) differ from \( \text{Cat}_1 \)–\( \text{Cat}_5 \) by their composition, thereby it is incorrect to compare their parameters of surface acidity with those of \( \text{Cat}_1 \)–\( \text{Cat}_5 \). Concerning the amount of acid centres for \( \text{Cat}_1 \)–\( \text{Cat}_5 \), they are situated in the row: \( \text{Cat}_4 > \text{Cat}_3 = \text{Cat}_2 > \text{Cat}_1 > \text{Cat}_5 \) which also coincides with their activity (Table 3).

IBAc yield at \( \text{Cat}_8 \) is higher by 5% compared with that at \( \text{Cat}_1 \) but the temperature at \( \text{Cat}_8 \) is also higher (by 30 K). Based on the temperature at which 80% conversion of MIB is achieved, the catalysts form the row:

\[ \text{Cat}_1 > \text{Cat}_2 > \text{Cat}_3 > \text{Cat}_4 \]

The yield achieved using \( \text{Cat}_8 \) (95%) at 513 K is higher than that using \( \text{Cat}_7 \) (90%). At lower temperature (483 K) MIB conversion is 100% for 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: \( \text{Cat}_4 > \text{Cat}_3 > \text{Cat}_2 > \text{Cat}_1 \). By \( E_t \) the following row is obtained: \( \text{Cat}_4 > \text{Cat}_3 > \text{Cat}_2 > \text{Cat}_1 \). Selectivity by \( T_m \): \( \text{Cat}_1 > \text{Cat}_2 > \text{Cat}_3 > \text{Cat}_4 > \text{Cat}_5 \). Selectivity by \( T_{m1} \): \( \text{Cat}_1 > \text{Cat}_2 > \text{Cat}_3 > \text{Cat}_4 \). The comparison of selectivity row with acidity strength (\( \text{NH}_3 \) adsorption strength) shows that the greater the acidity strength, the less the selectivity of the catalyst.

### Temperature and selectivity by MMA at MIB conversion 80% (see experimental conditions in Table 3)

<table>
<thead>
<tr>
<th>Catalyst symbol</th>
<th>( T, \text{K} )</th>
<th>( S_{\text{MMA}}, % )</th>
<th>( Y_{\text{MMA}^*}, % ) at ( T_{\text{opt}}, \text{K} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Cat}_1 )</td>
<td>580</td>
<td>38.0</td>
<td>33.7 (563)</td>
</tr>
<tr>
<td>( \text{Cat}_2 )</td>
<td>575</td>
<td>70.0</td>
<td>62.4 (603)</td>
</tr>
<tr>
<td>( \text{Cat}_3 )</td>
<td>568</td>
<td>55.0</td>
<td>46.2 (563)</td>
</tr>
<tr>
<td>( \text{Cat}_4 )</td>
<td>513</td>
<td>88.0</td>
<td>83.7 (523)</td>
</tr>
<tr>
<td>( \text{Cat}_5 )</td>
<td>543</td>
<td>86.0</td>
<td>81.6 (573)</td>
</tr>
<tr>
<td>( \text{Cat}_6 )</td>
<td>518</td>
<td>90.0</td>
<td>90.0 (523)</td>
</tr>
<tr>
<td>( \text{Cat}_7 )</td>
<td>468</td>
<td>93.0</td>
<td>90.0 (483)</td>
</tr>
<tr>
<td>( \text{Cat}_8 )</td>
<td>493</td>
<td>95.0</td>
<td>95.0 (513)</td>
</tr>
</tbody>
</table>

* Maximum yield at temperature optimal for \( \text{Cat}_8 \).
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.

References


ВИКОРИСТАННЯ ІЗОБУТИЛОВОГО СПІРТУ ДЛЯ СИНТЕЗУ МЕТАКРИЛАТИВ

Анотація. Досліджено синтез метилметакрилатів окиснювальним перетворенням ізобутилового спирту за різними схемами. Встановлена можливість використання його як вихідної альтернативної сировини ізобутиловому та треті-бутиловому спиртам. При одержанні метилметакрилатів за схемою: ізобутиловий спирт → метакрілонітрил → 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 амоноліз, каталізатор, метакрілонітрил, метилметакрилат.