**Influence of Various Factors on the Rate of Methyl Acetate Synthesis Process**

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**Abstract.** In industry, methyl acetate is primarily obtained through catalytic esterification of methanol and acetic acid. Methyl acetate was studied using the "Sol-gel" technology based on the heterogeneous-catalytic acetylation reaction. Subsequently, the influence of various factors (temperature, molar ratio of starting materials, space velocity, the effect of reaction products, etc.) on the rate of methyl acetate synthesis was investigated.

**Keywords.** Methyl acetate synthesis, reaction rate, esterification kinetics, methanol acylation, acetic acid esterification, catalytic activity, heterogeneous catalyst, homogeneous catalyst, temperature effect

**INTRODUCTION**

In recent years, the demand for environmentally safe, low-toxic, and highly effective solvents in the field of organic chemistry and chemical technology has been increasing significantly. This need is particularly evident in the paint and varnish industry, polymers, pharmaceuticals, and fine organic synthesis sectors. In this regard, methyl acetate (CH3COOCH3) is an important industrial product and, due to its favorable physicochemical properties, is considered an alternative to many traditional solvents.

In industry, methyl acetate is mainly obtained by catalytic esterification of methanol and acetic acid. This process is based on the classical esterification mechanism described by Fischer-Speier and is represented by the following equilibrium reaction:

CH3COOH+CH3OH⇌CH3COOCH3+H2O (1)

This reaction is reversible, and the main limitation of the process is related to the reaction equilibrium. Therefore, to increase the reaction yield, an excess of methanol is used or the resulting water is continuously removed from the system. Studies conducted based on the Hougen-Watson kinetic model have shown that the esterification rate directly depends on the amount of water in the reaction medium. In this regard, an in-depth analysis of the chemical nature of methyl acetate synthesis reactions, the application of modern catalytic systems, and the implementation of integrated technologies are considered relevant scientific and technical tasks today.

**RESULTS AND DISCUSSION**

Methyl acetate synthesis is carried out in the presence of a heterogeneous catalyst with the composition **Al2O3·ZrO2·SnO2·SiO2/HCS.** The reaction takes place **in the vapor phase,** at a temperature range of **130-140°C** and **under a pressure of 1-2 atm.** Under experimental conditions, **acetic acid and methanol** are used in a 1:2 ratio. These parameters provide optimal conditions for methyl acetate formation, serving to increase the selectivity and yield of the reaction. The heterogeneous-catalytic acetylation reaction of methyl acetate was studied using the "Sol-gel" technology. In this case, sulfate (SO42-)ions were used as promoters to increase the acidity of the medium.

**TABLE 1.** Influence of starting materials on catalyst activity in the catalytic acetylation reaction of methanol (403-413 K, CH3COOH·CH3OH=1·2)

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **No** | **Catalyst composition** | **Total CH3COOH conversion, (%)** | **Conversion to methyl acetate, (%)** | **Selectivity S, (%)** |
| **1** | Al2O3·ZrO2 / **HSZ** | 69.66 | 52.84 | 75.85 |
| **2** | Fe2O3·SnO2 / **HSZ** | 71.48 | 56.98 | 79.71 |
| **3** | Al2O3·SnO2 / **HSZ** | 74.34 | 61.91 | 83.28 |
| **4** | Al2O3·TiO2·SnO2 / **HSZ** | 77.28 | 66.34 | 85.84 |
| **5** | Fe2O3·ZrO2·SiO2 / **HSZ** | 79.63 | 69.66 | 87.48 |
| **6** | Al2O3·SnO2·SiO2 / **HSZ** | 80.24 | 71.84 | 89.53 |
| **7** | Cr2O3·TiO2·SnO2·SiO2 / **HSZ** | 83.42 | 75.43 | 90.42 |
| **8** | Al2O3·ZrO2·PbO2·SiO2 / **HSZ** | 85.6 | 79.33 | 92.67 |
| **9** | **Al2O3·ZrO2·SnO2·SiO2 / HSZ** | **87.20** | **82.80** | **94.95** |
| **10** | Fe2O3·SrO·PbO2·SiO2 / **HSZ** | 82.7 | 75.71 | 91.55 |
| **11** | Cr2O3·TiO2·SnO2·SiO2 / **HSZ** | 79.48 | 70.15 | 88.27 |
| **12** | Fe2O3·ZrO2·PbO2·SiO2 /  **HSZ** | 78.84 | 66.97 | 84.94 |

Under the selected normal reaction conditions, the total conversion of acetic acid was 87.2%, and the conversion to methyl acetate was 82.8%.

The results of the study on the effect of the catalyst on the yield and selectivity of the process with respect to methyl acetate are presented in Table 2.

**TABLE 2.** Effect of catalyst composition on the yield and selectivity of the process with respect to methyl acetate

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| **No** | **(Al2O3)x∙ (ZrO2)y∙ (SnO2)z∙ (SiO2)k amounts** | **Yield relative to methyl acetate, kg (m3∙hour-1)** | | | | **Selectivity, (%)** | **Resistance to spreading, (%)** |
| **115-125°C** | **130-140°C** | **145-160°C** |  | |  |
| 1 | 3:3:2:4 | 45 | 150 | 140 | >98 | | 98 |
| 2 | 3:4:2:4 | 44 | 152 | 150 | >98 | | 98 |
| 3 | 4:2:2:4 | 48 | 158 | 146 | >98 | | 99 |
| 4 | 4:3:1:4 | 43 | 148 | 138 | >98 | | 98 |
| 5 | 4:3:2:3 | 51 | 160 | 147 | >98 | | 99 |
| 6 | 4:3:3:3 | 53 | 163 | 150 | >98 | | 98 |
| **7** | **4**:**3**:**2**:**4** | **55** | **165** | **150** | **>98** | | **99** |
| 8 | 5:2:2:4 | 47 | 155 | 144 | >98 | | 98 |
| 9 | 5:3:2:3 | 52 | 160 | 148 | >98 | | 98 |

**Based on the study of the influence of various factors on the reaction rate in the presence of** the selected (Al2O3)x∙(ZrO2)y∙(SnO2)z∙(SiO2)k/**HCS****catalyst composition, the kinetic regularities of the process were studied and a reaction mechanism was proposed.**

The influence of various factors (temperature, volumetric flow rate, molar ratios of CH3COOH:CH3OH, catalyst preparation method) on the yield of methyl acetate, the selectivity of the process, and the conversion of starting materials was studied using catalyst No. 9 **from the table.**

When studying the influence of the CH3COOH:CH3OH ratio on the yield of methyl acetate formation and the selectivity of the process, it was determined that under optimal conditions, the ratio of CH3COOH:CH3OH is 1:2.

**TABLE 3.** Influence of the CH3COOH:CH3OH ratio on the yield of methyl acetate

(T=403-413 K, catalyst No. 9)

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **No.** | **CH3COOH:CH3OH molar ratio** | **CH3COOH**  **conversion, (%)** | | **Selectivity**  **S %** |
| **Total** | **To methyl acetate** |
| 1 | 4:1 | 69.4 | 52.1 | 75.07 |
| 2 | 3:1 | 70.9 | 56.5 | 79.68 |
| 3 | 2:1 | 75.25 | 66.3 | 88.1 |
| 4 | 1:1 | 77.16 | 70.4 | 91.23 |
| **5** | **1:2** | **87.2** | **82.8** | **94.95** |
| 6 | 1:3 | 80.6 | 73.2 | 90.81 |
| 7 | 1:4 | 74.8 | 65.64 | 87.75 |

As can be seen from the table, with an increase in the molar content of methanol in the reaction mixture, the total conversion of acetic acid increases. When the molar ratio of the starting materials exceeds 1:2, the yield of methyl acetate decreases due to the formation of additional substances (dimethyl ether, acetal compounds, acetic acid anhydride, and others).

**TABLE 4.** Influence of temperature on the yield of the methanol acetylation reaction

(CH3COOH:CH3OH=1:2, catalyst No. 9)

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **No.** | **Temperature, °C** | **CH3COOH**  **conversion, %** | | **Selectivity**  **S %** |
| **Total** | **To methyl acetate** |
| 1 | 90-110 | 70.4 | 56.41 | 80.12 |
| 2 | 115-125 | 78.7 | 70.55 | 89.64 |
| **3** | **130-140** | **87.2** | **82.8** | **94.95** |
| 4 | 145-160 | 80.6 | 73.18 | 90.79 |
| 5 | 165-180 | 74.5 | 62.72 | 84.18 |

As can be seen from the table, the total conversion of acetic acid increases with increasing temperature. The yield of methyl acetate increases up to 130-140°C and decreases above 140°C. At temperatures above 140°C, the reaction yield decreases due to the decomposition of methyl acetate and the formation of additional substances (dimethyl ether, acetal compounds, acetic acid anhydride, and others).

Subsequently, the influence of various factors (temperature, molar ratio of starting materials, space velocity, the effect of reaction products, and others) on the rate of methyl acetate synthesis was studied.

The synthesis of methyl acetate is based on the reversible esterification reaction of methanol and acetic acid in the presence of acid catalysts. The process mainly occurs on the surface of Brønsted acid catalysts (sulfonic acids, ion-exchange resins, zeolites).

CH3COOH + CH3OH ⇌ CH3COOCH3 + H2O (2)

The reaction mechanism consists of several sequential elementary steps, carried out through the active centers of the catalyst.

Step 1. Protonation (activation) of acetic acid. The acidic active site on the catalyst surface (H+) protonates the carbonyl oxygen of acetic acid:

CH3COOH + → CH3C(OH) (3)

At this stage, the electrophilicity of the carbonyl carbon increases, and it becomes active for nucleophilic attack.

Step 2. Nucleophilic attack of methanol. The methanol molecule attacks the carbonyl carbon of protonated acetic acid as a nucleophile, forming a tetrahedral intermediate complex:

CH3C(OH) + CH3OH → CH3C (OH) (OCH3) OH+  (4)

This stage is considered one of the main kinetic steps of the esterification mechanism.

Step 3. Proton exchange and water release. The proton is redistributed within the resulting intermediate complex, leading to the release of a water molecule:

CH3C (OH) (OCH3) OH+ → CH3COOCH3H+ + H2O (5)

This step strongly affects the equilibrium because water, as a reaction product, can accelerate the reverse reaction.

Step 4. Formation of methyl acetate and catalyst regeneration. In the final step, the protonated methyl acetate molecule returns the proton to the catalyst and forms free methyl acetate:

CH3COOCH3H+ → CH3COOCH3 + H+  (6)

With this, the catalyst's active center is restored, and a new cycle begins.

Connecting the mechanism with mathematical modeling. Based on the above mechanism, the rate equation is expressed as follows:

*r = kfCCH3OHCCH3COOH - krCCH3COOCH3CH2O*  (7)

This equation, together with the mass balance and energy balance, allows for the construction of a complete mathematical model of methyl acetate synthesis.

**CONCLUSION**

A new nanocatalyst with the composition Al2O3·ZrO2·SnO2·SiO2 / **HSZ**, which has high productivity and selectivity for the synthesis of methyl acetate from methanol, was created using "sol-gel" technology. For the first time, the influence of the composition of **HSZ** (high-silica zeolite) as a core substance (carrier) on the activity of the selected nanocatalysts was studied.

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