**Preparation of Optimal Catalyst Compositions for Obtaining Methyl Acetate from Methanol**

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**Abstract.** Under the influence of a catalyst, the carbonyl group of acetic acid is protonated, facilitating the interaction with the nucleophilic methanol molecule. The textural and physicochemical properties of a new nanocatalyst with high catalytic activity, developed for the synthesis of methyl acetate from methanol, have been determined. For the first time, improved and low-waste compact technologies for obtaining methyl acetate by acetylation of methanol have been developed.

**Keywords.** Methyl acetate synthesis, methanol acylation, catalyst preparation, optimal catalyst composition, heterogeneous catalysts, homogeneous catalysts, catalyst formulation, metal-based catalysts, acid catalysts

**INTRODUCTION**

The esterification process is carried out in the presence of strong acid catalysts. Under the influence of a catalyst, the carbonyl group of acetic acid is protonated, facilitating the interaction with the nucleophilic methanol molecule. The reaction mechanism occurs in the following sequential steps:

1. Protonation of acetic acid
2. Nucleophilic attack of methanol on carbonyl carbon
3. Formation of an intermediate complex
4. Release of water and formation of methyl acetate

In recent scientific studies, Sundmacher, Taylor, and Doherty employed ion-exchange resins (Amberlyst-15) instead of mineral acids. These catalysts are distinguished by their high selectivity and corrosion resistance. In the presence of these catalytic systems, the reaction proceeds according to the following general equation, but is considered more environmentally friendly and technologically efficient.

At the end of the 20th century, R. Krishna and H. Green proposed a reactive distillation method for methyl acetate synthesis. This method combines the esterification reaction and product separation process in a single apparatus. As a result, water is continuously removed from the bottom of the distillation column, shifting the reaction equilibrium to the right. This approach allows for increasing product yields to 98-99%, reducing energy consumption, and simplifying the technological scheme.

In studies conducted by scientists from CIS countries, including Uzbekistan, the dependence of the esterification process on temperature, catalyst concentration, and raw material ratios has been thoroughly investigated. The results show that conducting the process under optimal conditions significantly increases the economic and environmental efficiency of methyl acetate production.

**RESULTS AND DISCUSSION**

Currently, methanol is obtained directly under catalytic conditions of methane gas synthesis (using catalyst Cu-ZSM-5 and artificial analogues of the enzyme methane monooxygenase (MMO)). Methanol is mainly used as a solvent, and is also used in the synthesis of various organic substances, such as formaldehyde, acetic acid, dimethyl ether, methyl methacrylate, and methyl amines.

Standard indicators of technical methanol obtained as a result of catalytic acetylation according to physicochemical parameters

**TABLE 1.** Physicochemical indicators of methanol

|  |  |  |
| --- | --- | --- |
| **No.** | **Indicator name** | **Standard** |
| 1 | Mass fraction of technical and high-purity methanol, (%) not less than  a) mass fraction of water, (%) not more than  b) mass fraction of ethanol, (%) not more than | 99.85-99.9  0.05-0.1  0.005-0.05 |
| 2 | Mass fraction of free acids relative to formic acid, %, not more than | 0.0015 |
| 3 | Mass fraction of aldehydes and ketones relative to acetone, %, not more than | 0.0015 |
| Note: Methanol is a highly flammable liquid and belongs to the 3rd fire hazard class. Its flash point is in the range of +11°C to +12°C, with a lower explosive limit in air of 6% and an upper limit of 36%. | | |

Acetic acid is a long-known substance, formed during the fermentation of glucose by bacteria in the production of beer and wine. Acetic acid is obtained by oxidation of methanol through the action of carbon monoxide.

CH3OH + CO → CH3COOH (1)

In addition, acetic acid is obtained by catalytic oxidation of acetaldehyde.

CH3CHO + O2 → CH3COOH (2)

In industry, the physicochemical parameters of technical acetic acid obtained by the Kucherov reaction must comply with the following standards.

**TABLE 2.** Physicochemical parameters of acetic acid

|  |  |  |  |
| --- | --- | --- | --- |
| **No.** | **Parameter name** | **Standard** | |
| **Grade 1** | **Grade 2** |
| 1 | Appearance | Clear, colorless liquid without mechanical impurities | |
| 2 | Mass fraction of acetic acid, % | 99.5±0.5 | 70.0±1.0 |
| 3 | Mass fraction of non-volatile residue (%), maximum | 0.008 | 0.008 |
| 4 | Color stability of potassium permanganate solution (min), minimum | 60 | 60 |
| 5 | Mass fraction of organic substances (%) calculated as formic acid, maximum | 0.1 | 0.1 |
| 6 | Mass fraction of sulfates (%), maximum | 0.0002 | 0.0002 |
| 7 | Mass fraction of chlorides (%), maximum | 0.0001 | 0.0001 |
| 8 | Mass fraction of heavy metals (Pb) (%), maximum | 0.00008 | 0.00008 |
| 9 | Mass fraction of iron (%), maximum | 0.0001 | 0.0001 |

**TABLE 3.** 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 conditions of the reaction, the total conversion of acetic acid was 87.2%, and the conversion to methyl acetate was 82.8%.

The rate equation for the esterification reaction is expressed as follows:

*r = kfCMeOHCAc - krCMeAcCH2O*  (3)

*kf*, *kr -* rate constants for forward and reverse reactions;

*CMeOH* , *CAc* - concentrations of methanol and acetic acid;

*CMeAc*, *CH2O* - concentrations of methyl acetate and water;

Rate constants are determined by the Arrhenius equation:

(4)

The mass balance for an ideal mixture in a continuous stirred-tank reactor (CSTR) under constant volume conditions is written as:

(5)

Where:

F - flow rate,

V - reactor volume,

ν - stoichiometric coefficients.

Energy balance

(6)

This equation allows for determining the change in temperature over time.

The process of obtaining methyl acetate (MeOAc) is described as a continuous technological scheme based on the catalytic esterification reaction of methanol and acetic acid. The process consists of a complex of interconnected main apparatuses, where the reaction and product separation stages are carried out simultaneously.

### **1. Raw material feed system.**In the initial stage of the technological scheme, methanol (CH3OH) and acetic acid (CH3COOH) are fed from separate storage tanks to the reactor system using metering pumps. Methanol is usually supplied in excess of the stoichiometric amount, which helps shift the reaction equilibrium towards the products.

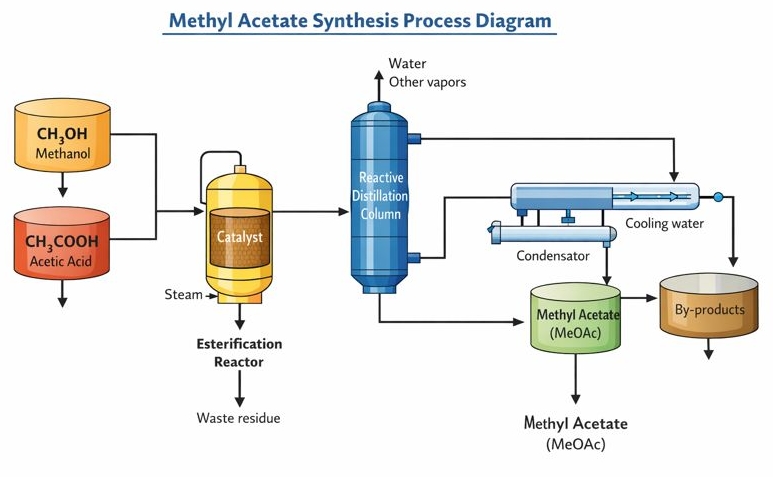
### **2. Esterification reactor.**A mixture of methanol and acetic acid enters an esterification reactor filled with a catalyst. Ion-exchange resins or other solid catalysts Al2O3·ZrO2·SnO2·SiO2/YuKS are placed inside the reactor, which increase the reaction rate. The process is usually carried out at a temperature of 130-140°C and under low pressure conditions. The following main reaction occurs in the reactor:

CH3COOH+CH3OH⇌CH3COOCH3+H2O (6)

The resulting reaction mixture consists of methyl acetate, water, unreacted methanol, and acetic acid.

### **3. Reactive distillation column.**The reaction mixture exiting the reactor is directed to the reactive distillation column. In this apparatus, the reaction and separation processes occur simultaneously. Components with low boiling points, including methyl acetate and methanol, are separated in vapor form at the top of the column, while water and heavier components are collected at the bottom.

The main advantage of the reactive distillation process is shifting the equilibrium towards product formation by continuously removing water from the reaction zone.



**FIGURE 1.** Methyl acetate synthesis technology

### **4. Condenser and cooling system.**The vapors exiting the top of the column are directed to a condenser. In the condenser, the vapors are converted to a liquid state using cooling water. The condensate mainly contains methyl acetate and some methanol.

### **5. Separation of products and by-products.**The condensate is transferred to the product collection tank, and the main product - methyl acetate - is separated. During the separation process, the remaining by-products and unreacted substances are directed to a separate container for processing or disposal. If necessary, methanol is recirculated and fed back into the process.

**CONCLUSION**

The textural and physicochemical properties of a newly composed nanocatalyst with high catalytic activity, developed for the synthesis of methyl acetate from methanol, have been determined. Based on the kinetics of the methyl acetate synthesis process in the presence of this new nanocatalyst, the kinetic models and reaction mechanism were determined, and based on the analysis of these kinetic models, the optimal reactor type was selected. For the first time, improved and low-waste compact technologies for obtaining methyl acetate by acetylation of methanol have been developed.

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