Catalytic synthesis of acetone by direct hydration of acetylene

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Abstract. Background: Replacing the cadmium–calcium phosphate catalyst with a zinc-containing catalyst makes it possible to obtain acetone in good yield with minor changes in technology. Aim: Study the kinetic laws of obtaining acetone by catalytic hydration. Materials and methods: Experiments on the catalytic hydration of acetylene and its derivatives in the gas phase were carried out in a reactor with a diameter of 25 mm, a height of 1000 mm, and made of stainless steel under stationary conditions. Results and discussions: In the reaction of hydration of acetylene and its derivatives, the use of \((\text{Fe}_2\text{O}_3)_{x}:\!(\text{MoO}_3)_{y}:(\text{ZnO})_{z}:(\text{Mn}_2\text{O}_3)_{k}\) catalysts can be highly efficient and promising in production, obtaining high-quality products. Keywords: acetylene, hydration, acetone, catalyst, Gibbs energy, reaction yield.

1 Introduction

Acetone is a valuable product of the chemical industry. It can be obtained by oxidative dehydrogenation of isopropyl alcohol, propylene oxidation, decomposition of acetic acid and ethyl alcohol, cumene oxidation, etc. [1–5].

Among the known processes for the production of acetone, the most promising is the synthesis by hydration of acetylene in the presence of catalysts. The advantage of this method is the possibility of carrying out the process in existing acetaldehyde production plants. On the other hand, the process of simultaneous production of acetaldehyde and acetone under the action of polyfunctional catalysts and the implementation of the process using a flexible technology is promising [6–13].

The vapour phase hydration of acetylene with the formation of acetone on polyfunctional catalysts was studied. Process parameters have been found that ensure the production of acetone with high selectivity and acetylene conversion.

At present, acetaldehyde is mainly produced by two methods: acetylene hydration and ethylene oxidation [14–22].

The process of hydration of acetylene to acetaldehyde in the presence of catalysts has been studied quite well. Numerous catalysts have been proposed for this process [23–29]. Among the known catalysts for the hydration of acetylene to acetic aldehyde, cadmium-calcium phosphate catalyst (CCP) turned out to be the most active, which is recommended for industrial use [29–32]. However, the cadmium-calcium phosphate

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catalyst is not without its drawbacks. The average yield of acetaldehyde per pass of acetylene does not exceed 7.0%. The CCF catalyst is very sensitive to temperature changes; its service life before regeneration does not exceed 72-76 hours.

Hydration of acetylene in the presence of a catalyst can be carried out in order to obtain acetone. The advantage of this method is the possibility of carrying out the process in existing units for the production of acetaldehyde. The replacement of a cadmium–calcium phosphate catalyst with a zinc-containing catalyst makes it possible to obtain acetone in good yield with minor changes in technology [33–55].

2 Materials and methods

Experiments on the catalytic hydration of acetylene and its derivatives in the gas phase were carried out in a reactor with a diameter of 25 mm, a height of 1000 mm, and made of stainless steel under stationary conditions.

The specific surface area, crushing strength, total pore volume, and ash content of the samples were determined.

The specific surface area was determined by the method of thermal desorption of nitrogen in a flow of a carrier gas, helium, at the boiling point of liquid nitrogen; the experimental data were processed according to the BET equation.

The crushing mechanical strength of granules was measured using a Prochnomer PK-1 device designed for testing granular materials for mechanical strength under static conditions by the compression method. The arithmetic mean of 25 individual tests was taken as the result of the analysis.

The phase composition of the samples was determined by X-ray diffractometry, the survey was performed on a DRON-3M diffractometer using CuKα radiation with a Ni filter, X-ray radiation length \( \lambda = 1.54\text{Å} \).

The specific surface area of the obtained catalyst was calculated by the BET method, and the average mesopore size was calculated by the VUA method. The dispersion properties of the catalyst were studied using a scanning electron microscope (JSM -6510 LV). The catalytic activity of the obtained sample was studied in the reaction of hydration of acetylene.

3 Results and discussion

The effect of temperature, water: acetylene ratio, space velocity, catalyst composition on the yield of target products and the degree of acetylene conversion was studied.

The study of the effect of the ratio of water: acetylene on the yield of the target product was carried out in a stainless steel reactor at a temperature of 360-440 °C at a mixture space velocity of 12 0 h⁻¹.

We have studied the catalytic vapour phase hydration of acetylene and its derivatives in the presence of complex mixed polyfunctional catalysts.

In order to establish the technological parameters of the process of obtaining acetone by direct hydration of acetylene, we studied the effect of space velocity, temperature, acetylene: water ratio, and others on the yield of acetone.

As a result of the experiments carried out, an effective catalyst with high activity, selectivity, productivity, and stability was chosen. The developed catalyst retains its activity for a long time.

After that, we carried out studies of processes using catalysts prepared according to the “Sol-gel” technology \((\text{Fe}_2\text{O}_3)_k:(\text{MoO}_3)_y:(\text{ZnO})_z:(\text{Mn}_2\text{O}_3)_k\). With the use of these catalysts, the yield of acetone production from acetylene under the influence of various factors was
studied.

**Effect of temperature on the reaction yield.** The effect of temperature studied 280-475 °C on the yield of the acetylene hydrate reaction using the effective catalyst we developed \((\text{Fe}_2\text{O}_3)_x:(\text{MoO}_3)_y:(\text{ZnO})_z:(\text{Mn}_2\text{O}_3)_k\). The results of the study are shown in table 1.

**Table 1.** Temperature effect on acetylene conversion and acetone yield (cat \((\text{Fe}_2\text{O}_3)_x:(\text{MoO}_3)_y:(\text{ZnO})_z:(\text{Mn}_2\text{O}_3)_k\)).

<table>
<thead>
<tr>
<th>No.</th>
<th>Temperature. °C</th>
<th>Acetylene conversion. %</th>
<th>Acetone output. %</th>
<th>Selectivity for acetone. S %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>280</td>
<td>18.2</td>
<td>10.0</td>
<td>54.9</td>
</tr>
<tr>
<td>2</td>
<td>330</td>
<td>33.5</td>
<td>20.6</td>
<td>61.2</td>
</tr>
<tr>
<td>3</td>
<td>350</td>
<td>48.5</td>
<td>32.6</td>
<td>67.2</td>
</tr>
<tr>
<td>4</td>
<td>375</td>
<td>52.4</td>
<td>41.7</td>
<td>73.4</td>
</tr>
<tr>
<td>5</td>
<td>400</td>
<td>65.8</td>
<td>58.5</td>
<td>88.9</td>
</tr>
<tr>
<td>6</td>
<td>425</td>
<td>92.8</td>
<td>76.4</td>
<td>82.3</td>
</tr>
<tr>
<td>7</td>
<td>450</td>
<td>94.8</td>
<td>81.8</td>
<td>86.3</td>
</tr>
<tr>
<td>8</td>
<td>475</td>
<td>90.8</td>
<td>68.4</td>
<td>75.3</td>
</tr>
</tbody>
</table>

As can be seen from the table, when the temperature reaches 425 °C, the yield of acetone is 86.4%, and the selectivity for acetone is 91.1%.

**Effect of space velocity on methane conversion and acetone yield.** The effect of space velocity on the yield of acetone and acetylene conversion was studied. The results of the study are shown in table 2. As can be seen from the table, with an increase in the space velocity of acetylene, the conversion of acetylene decreases.

**Table 2.** Influence of space velocity on acetone yield and acetylene conversion (cat \((\text{Fe}_2\text{O}_3)_x:(\text{MoO}_3)_y:(\text{ZnO})_z:(\text{Mn}_2\text{O}_3)_k\)).

<table>
<thead>
<tr>
<th>Volumetric speed. hour⁻¹</th>
<th>Acetylene conversion. %</th>
<th>S. %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>General</td>
<td>In acetone</td>
</tr>
<tr>
<td>40</td>
<td>98.2</td>
<td>34.3</td>
</tr>
<tr>
<td>60</td>
<td>97.6</td>
<td>44.8</td>
</tr>
<tr>
<td>80</td>
<td>96.5</td>
<td>55.7</td>
</tr>
<tr>
<td>100</td>
<td>95.2</td>
<td>68.8</td>
</tr>
<tr>
<td>120</td>
<td>94.8</td>
<td>81.8</td>
</tr>
<tr>
<td>140</td>
<td>92.6</td>
<td>69.4</td>
</tr>
<tr>
<td>160</td>
<td>90.2</td>
<td>50.8</td>
</tr>
<tr>
<td>180</td>
<td>87.7</td>
<td>38.2</td>
</tr>
</tbody>
</table>

**Influence of molar ratios of reagents on the yield of acetone and the conversion of acetylene.** We have also studied the effect of \(\text{C}_2\text{H}_2\text{H}_2\text{O}\) molar ratios on the yield of acetone and the conversion of acetylene. The results of the study are shown in table 3.

**Table 3.** The dependence of the degree of conversion, the stability of the catalyst and the yield of the target product on the ratio of water: acetylene.

<table>
<thead>
<tr>
<th>Ratios water: acetylene. moll</th>
<th>Average catalyst run before regeneration</th>
<th>Target product yield. per reacted acetylene. %</th>
<th>Acetylene conversion. %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Acetaldehyde</td>
<td>Acetone</td>
</tr>
<tr>
<td>1</td>
<td>32.0</td>
<td>4.6</td>
<td>55.0</td>
</tr>
<tr>
<td>2</td>
<td>54.0</td>
<td>3.4</td>
<td>66.0</td>
</tr>
<tr>
<td>3</td>
<td>96.0</td>
<td>2.2</td>
<td>76.0</td>
</tr>
<tr>
<td>4</td>
<td>125</td>
<td>1.5</td>
<td>81.8</td>
</tr>
<tr>
<td>5</td>
<td>144</td>
<td>1.2</td>
<td>82.0</td>
</tr>
<tr>
<td>6</td>
<td>132</td>
<td>1.1</td>
<td>76.0</td>
</tr>
</tbody>
</table>

We also studied the preparation of acetone by hydration of methyl acetylene and
methylacetylene-allene fractions with the participation of \((\text{Fe}_2\text{O}_3)_x\) :(\(\text{MoO}_3\))\(_y\) :(\(\text{ZnO}\))\(_z\) :(\(\text{Mn}_2\text{O}_3\))\(_k\) catalyst at 320-475 °C. It has been established that the reaction rate at 450 °C and the molar ratio of acetylene: water = 4:1 is 22 mol/l (l * hour).

At the same time, the reactions of hydration of phenylacetylene with the participation of a cadmium fluoro aluminium catalyst promoted with 5% \(\text{AlF}_3\) were also studied. The reaction of obtaining acetophenone by hydration of phenylacetylene with the participation of this catalyst at a temperature of 300-400 °C increases the yield of the product to 90-92%.

The main goal of thermodynamic calculations is to find the optimal conditions under which the maximum yield of the final product is ensured. The conditions for the reaction to proceed at a maximum rate are found empirically.

The change in the Gibbs energy of the reaction was calculated using the following equation:

\[
\Delta G^0_T = \Delta H^0_{298} - T \cdot \Delta S^0_{298} - \Delta C_p \cdot T \cdot M_0
\]

(1)

Here: \(M_0\) – temperature dependent coefficient. The values of this coefficient at different temperatures are given in the table.

To calculate the change in the Gibbs energy, the Schwartzman-Temkin formula was used:

\[
\Delta G^0_T = \Delta H^0_{298} - T \cdot \Delta S^0_{298} - T \cdot \left(\Delta a \cdot M_0 + \Delta b \cdot M_1 + \Delta c \cdot M_2 + \Delta e' \cdot M_2\right)
\]

(2)

Here: \(M_0, M_1, M_2, M_3\) are coefficients depending on temperature. Their values at various temperatures are given in Table 5,

To calculate \(M_0\) the following equation is used:

\[
M_0 = 1 + \ln \left(\frac{T}{298.2}\right) + \frac{298.2}{298.2} \left(\frac{T}{298.2}\right)
\]

(3)

The temperature dependence of \(M_1, M_2,\) and \(M_3\) is expressed by the following equation:

\[
M_n = \frac{T^n}{n(n+1)} + \frac{298.2^{n+1}}{(n+1)T} - \frac{298.2^n}{2}
\]

(4)

**Table 5.** Meaning of \(M_n\) at different temperatures to calculate \(\Delta G^0_T.\)

<table>
<thead>
<tr>
<th>T. K</th>
<th>(M_0)</th>
<th>(M_1,10^3)</th>
<th>(M_2,10^6)</th>
<th>(M_3,10^{-5})</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>2</td>
<td>0.149</td>
<td>0.0000016</td>
<td>-1.12</td>
</tr>
<tr>
<td>400</td>
<td>2.039</td>
<td>0.162</td>
<td>0.0043025</td>
<td>-1.08</td>
</tr>
<tr>
<td>500</td>
<td>2.113</td>
<td>0.189</td>
<td>0.0188299</td>
<td>-1.03</td>
</tr>
<tr>
<td>600</td>
<td>2.196</td>
<td>0.225</td>
<td>0.0302699</td>
<td>-0.98</td>
</tr>
<tr>
<td>700</td>
<td>2.279</td>
<td>0.264</td>
<td>0.0498321</td>
<td>-0.93</td>
</tr>
<tr>
<td>800</td>
<td>2.360</td>
<td>0.306</td>
<td>0.0732538</td>
<td>-0.90</td>
</tr>
<tr>
<td>900</td>
<td>2.436</td>
<td>0.350</td>
<td>0.1003595</td>
<td>-0.87</td>
</tr>
<tr>
<td>1000</td>
<td>2.508</td>
<td>0.395</td>
<td>0.1310440</td>
<td>-0.84</td>
</tr>
</tbody>
</table>
The calculation of the equilibrium constant at $P < 0.5$ MPa was carried out according to the formula

$$K_p = K_f = e^{-\Delta G/(RT)}$$

Here, $R$ is the universal gas constant.

As a result of thermodynamic calculations, a relationship was established between the equilibrium constant and temperature:

$$\log K_p = \frac{1763.7}{T} - 2.811 \log T + 1.356 \cdot 10^{-3} T - 3.894$$

The equilibrium constant can be used to calculate the yield of a product under certain conditions.

For this reaction:

$$\text{CH} \rightleftharpoons \text{CH} + \text{H}_2\text{O} \rightarrow \text{CH}_3 - \text{C} \equiv \text{O}$$

$$x = \sqrt{\frac{K_p}{P + K_p}}$$

<table>
<thead>
<tr>
<th>T. K</th>
<th>$K_p$</th>
<th>$X$</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>0.0001174</td>
<td>0.0042</td>
</tr>
<tr>
<td>400</td>
<td>0.0000573</td>
<td>0.0309</td>
</tr>
<tr>
<td>500</td>
<td>0.0503615</td>
<td>0.219</td>
</tr>
<tr>
<td>600</td>
<td>0.4763883</td>
<td>0.568</td>
</tr>
<tr>
<td>700</td>
<td>2.0247712</td>
<td>0.818</td>
</tr>
<tr>
<td>800</td>
<td>5.7913784</td>
<td>0.923</td>
</tr>
</tbody>
</table>

In the temperature range from 700 to 800 K $\Delta G < 0$, the process proceeds spontaneously. Max and small output is achieved at a pressure of 0.1 MPa and temperatures of 700-800 K.

### 4 Conclusions

The effect of temperature, water: acetylene ratio, space velocity, catalyst composition on the yield of target products and the degree of acetylene conversion was studied.

The study of the effect of the ratio of water: acetylene on the yield of the target product was carried out in a stainless steel reactor at a temperature of 360-440 °C at a mixture space velocity of 120 h$^{-1}$.

We have studied the catalytic vapour phase hydration of acetylene and its derivatives in the presence of complex mixed polyfunctional catalysts.

In order to establish the technological parameters of the process of obtaining acetone by direct hydration of acetylene, we studied the effect of space velocity, temperature,
acetylene: water ratio and others on the yield of acetone.

Thus, in the reaction of hydration of acetylene and its derivatives, the use of \((\text{Fe}_2\text{O}_3)_x:(\text{MoO}_3)_y:(\text{ZnO})_z:(\text{Mn}_2\text{O}_3)_k\) catalysts can be highly efficient and promising in production, obtaining high-quality products.

As a result of the experiments carried out, an effective catalyst with high activity, selectivity, productivity, and stability was chosen. The developed catalyst retains its activity for a long time.

To find the optimal conditions for the process, it is important to provide a thermodynamic substantiation of the catalytic hydration of acetylene.

The main goal of thermodynamic calculations is to find the optimal conditions under which the maximum yield of the final product is ensured. The conditions for the reaction to proceed at a maximum rate are found empirically.

References