Catalysts of Aldol Condensation of Acetic Acid with Formaldehyde

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Abstract – it had been demonstrated that mechanochemical and hydrothermal treatment of support allows increasing activity and selectivity of the catalyst in the studied process. Hydrothermal treatment (HTT) of silica increases mechanical strength of silica gel granules subjected to hydrothermal treatment, also reduction of coke formation takes place, as well as prolongation of the catalysts life. Similarly, the same approaches allow to optimize the pore structure of titanium phosphates.

Keywords – acrylic acid, aldol condensation, mechanochemical treatment, hydrothermal treatment, porous structure.

I. Introduction

Acrylic acid (AA) is a valuable substance in the industry of organic synthesis and is widely used in the production of high-quality paint and varnish, organic glass, as an auxiliary substance in the textile industry, in the production of superabsorbents, in medicine [1-4]. World production of AA amounts to over 5 million tons per annum, and according to analytical studies, the market of acrylate monomers has a steady upward trend [5]. One of the most promising methods of AA production is aldol condensation of acetic acid (AcA) with formaldehyde (FA) [6]. The production of AA by aldol condensation is not implemented in industry because of comparably low efficiency of known catalysts and short working life due to coke formation on catalysts’ surface [7].

The key for successful implementation of AA production based on AcA and FA is effective catalyst for this process. It is known that the reactions of aldol condensation may proceed through both base and acidic catalysis. We have synthesized the catalysts of both types and found that acid catalysts have higher activity and efficiency than the base ones [8,9]. Also the correlation between the strength of acid sites of the catalysts and their selectivity was found [10]. But despite of some success in the catalysts development, the desirable level of their efficiency isn’t still achieved.

It is well known that porous structure of solid catalysts has a huge effect on their catalytic properties. So we decided to continue our developments of catalytic systems for aldol condensation reaction and to apply different kinds of treatment of the catalysts in order to modify their crystal structure, activate surface and, as a result, change their catalytic properties [11]. This kind of modification also allows to vary parameters of porous structure (specific surface area (S), pore size (d) and pore size distribution (PSD)) in wide limits [12].

II. Results and Discussion

It is well known that efficiency of catalysts of aldol condensation reactions depends on many physical and chemical characteristics, namely specific surface area, porous and crystal structure, surface acidity. So, different kinds of catalysts were tested in this process: acid and basic type catalysts, supported and bulk solid catalysts, the catalysts with various carriers. Recently using of structured carriers for aldol condensation catalysts was reported as well as the huge effect of porous structure of catalysts on their chemical properties. So in this context, application of different kinds of catalysts treatment (hydrothermal, microwave and mechanochemical), which are able to vary the physical and chemical characteristics of catalysts within wide limits, can be considered as the alternative method for porous structure regulation and optimization of the catalytic properties [12]. Therefore, the goal of present work is to study the efficiency of hydrothermal methods for the regulation of porous structure of the catalysts for aldol condensation reaction as well as optimization of their catalytic performance in acrylic acid synthesis, for which we tested the effect of hydrothermal treatment of B₂O₃–P₂O₅–WO₃–V₂O₅/SiO₂ and hydrothermal and mechanochemical treatments of TiPO₄ catalysts which are moderately efficient in gas-phase acrylic acid synthesis via aldol condensation.

It has been found that hydrothermal treatment (HTT) of silica support of B–P–V–W–O₅ catalyst at 150 °C allows increasing the one-pass yield of acrylic acid synthesis from 58 % to 68 % at acrylic acid selectivity of 91 %. In addition to increase of mechanical strength of silica gel granules subjected to hydrothermal treatment, reduction of coke formation takes place, as well as prolongation of the catalysts life.

As expected, mechanochemical and hydrothermal treatment of TiPO₄ catalyst also modifies its porous structure (Table 1). But in this case specific surface area changes are insignificantly.

As for catalytic properties in aldol condensation reaction of AcA with FA, the formation of AA on pure TiPO₄ was negligible (Fig. 2).
Sustainable catalytic hydrogenation of crotonaldehyde over TiPO₄ catalysts

Mechanochemical and hydrothermal treatment of titanium phosphate dramatically changes its catalytic properties in test reaction. Thus both mechanochemically and hydrothermally treated catalysts exhibit much better catalytic performance. On the treated by MChT catalyst AA yield increases to 14 %, and on the treated by HTT catalyst AA yield reaches maximum value 61 % at 623 K.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>SSA. m²/g</th>
<th>V₂, cm³/g</th>
<th>d, nm</th>
<th>Total acidity, mmol/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiPO₄ (Initial)</td>
<td>109</td>
<td>1.60</td>
<td>32; 52</td>
<td>0.434</td>
</tr>
<tr>
<td>TiPO₄ (MChT)</td>
<td>86</td>
<td>1.23</td>
<td>9.0</td>
<td>0.080</td>
</tr>
<tr>
<td>TiPO₄ (HTT)</td>
<td>107</td>
<td>1.72</td>
<td>3.7; 49</td>
<td>0.510</td>
</tr>
</tbody>
</table>

TABLE 1
PARAMETERS OF POROUS STRUCTURE OF THE CATALYSTS

SSA – specific surface area, V₂ – total pore volume, d – pore size

Conclusion

It had been demonstrated that mechanochemical and hydrothermal treatment of support allows increasing activity and selectivity of the catalyst in the studied process. Hydrothermal treatment (HTT) of silica support of B–P–V–W–O₄ catalyst at 150 °C allows increasing the one-pass yield of acrylic acid synthesis from 58 % to 68 % at acrylic acid selectivity of 91 %. In addition to increase of mechanical strength of silica gel granules subjected to hydrothermal treatment, reduction of coke formation takes place, as well as prolongation of the catalysts life. Similarly, the same approaches allow to optimize the pore structure of titanium phosphates. On the treated by MChT catalyst AA yield increases to 14 %, and on the treated by HTT catalyst AA yield reaches maximum value 61 % at 623 K.

References