Synthesis, Porous Structure and Catalytic Properties of Mixed Vanadium-Titanium Phosphates in Aldol Condensation Reaction of Acetic Acid with Formaldehyde

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Abstract – mixed vanadium-titanium phosphates as well as individual vanadium and titanium phosphates were prepared via precipitation from sulfate aqueous solutions. Coprecipitated phosphates were modified through mechanochemical treatment (MChT) and characterized using the adsorption-structural methods. The aldol condensation of acetic acid with formaldehyde has been used as a test reaction. Reduction of optimum reaction temperature from 623 K to 573 K on the treated catalysts is observed.

Key words – acetic acid, aldol condensation, solid catalysts, mechanochemical treatment, porous structure.

I. Introduction

Acrylic acid (AA) is valuable chemical, world production of which amounts to over 4 million tons per annum. One of the most promising methods of AA synthesis which is of great interest to scientists is based on formaldehyde (FA) and acetic acid (AcA) [1]. Both AcA and FA in industry are obtained from methanol (via carbonylation and oxidation reactions respectively) [2–4], and the common raw material for methanol production is synthesis gas which is obtained from natural gas or coal. Considering the largest global reserves of natural gas and coal compared to other fossil fuels, the use of these raw materials for organic synthesis is highly promising.

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 also it was found that acid catalysts have higher activity and efficiency than the base one [1, 5]. Also the correlation between the strength of acid sites of the catalysts and their selectivity was found [6]. But despite some success in the catalysts development the desirable level of their efficiency is still doesn’t 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 apply mechanochemical treatment of the catalysts in order to modify their crystal structure, activate surface and, as a result, change their catalytic properties [7]. 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 [8].

II. Results and Discussion

Mixed vanadium-titanium phosphates containing 40% of vanadium as well as individual vanadium and titanium phosphates (for comparison) were prepared via precipitation from sulfate aqueous solutions. Then coprecipitated phosphates were modified through MChT using planetary ball mill. The catalytic properties of synthesized V-Ti-PO₄ catalytic systems were investigated in aldol condensation reaction of acetic acid with formaldehyde at temperature range from 548 to 648 K, residence time 8 sec at equimolar initial reagents ratio.

Isotherms of nitrogen adsorption-desorption and PSD curves presented in Fig. 1 confirm changing of porous structure of the catalysts. Particularly, value of S has decreased by 1.5-2.5 times as a result of MChT in water and air. Thus, specific surface area for milled catalysts is 47 and 26 m²/g, respectively, while for un-milled catalyst S=70 m²/g. The total pore volume is within 1.2-1.6 cm³/g. It is also important that modification leads to formation of meso-macroporous structure (with a predominance of macropores fraction).

![Fig. 1. The differential pore volume distribution (dV/dd) by pore diameter (d) and isotherms of N₂ adsorption-desorption](image)

As for catalytic properties in aldol condensation reaction of AcA with FA, co-precipitated phosphates exhibit higher performance (Fig. 2). While the formation of AA on pure TiPO₄ does not observed and on pure VPO₄ AA yield is 26 %, on mixed V-Ti-PO₄ AA yield of 31 % is achieved (at 623 K).

Mechanochemical treatment of mixed vanadium-titanium phosphate dramatically changed its catalytic properties in test reaction. Thus at 623 K both V-Ti-PO₄ catalysts subjected to MChT in the presence of air as well as water have over 90 % of AcA conversion, but the selectivity of AA formation radically dropped (to less than 5 %).
Mechanochemical treatment of initial vanadium-titanium phosphate changes its porous structure as well as catalytic performance and allows to reduce optimum reaction temperature from 623 K to 573 K.

Acknowledgements

A part of this research was financially supported by Lviv Polytechnic National University under the grant program for young scientists (project number ГЛП3/2016).

References