

Sulfated Zirconia in n-Pentane Isomerization and Trimethylpentanes Formation

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Skeletal isomerization of n-alkanes has the industrial importance because the branched alkanes are generally useful as clean fuel. Alkilation of isobutene with butanes is an industrial process for the production of high octane gasoline and commercial plants used sulfuric acid and hydrofluoric acid as acid catalysts. Solid superacids, for example sulfated zirconia are among the most promising catalyst for both reactions. In this work the sample of mesoporous ZrO₂ in form of spherical grains was used as precursor for solid acid catalysts preparation. The precursor was suspended for 30 min in a 0.5 M H₂SO₄ (30 ml/g) solution, dried at 110 °C and calcined in air at 200-600 °C.

XRD data shown that the calcination at 600 °C led to zirconia tetragonal modification formation but at low temperature a material was amorphous. The desorption of adsorbed ammonia from surface of ZrO₂/SO₄-600 sample proceeds at low temperature in contrast to ZrO₂/SO₄-350 catalyst, which practically did not desorb the molecule of base (Fig. 1). XPS study of catalysts surface demonstrates that calcinations at 600 °C accompanied by loss of surface sulfur and a decrease of content of oxygen belong to SO₄ groups (Table).

Catalytic activity of the prepared samples was studied in flow type reactors with on-line chromatographic analysis of the products. The results presented in Fig 2 show that the activity in n-pentane isomerization increases with the rise of the calcinations temperature but selectivity to i-C₅H₁₂ decreases. In contrary for catalyst treated at high temperature the cracking function (formation of propylene) increases. Practically analogous dependence observes for isobutene alkylation by 1-butene (Fig. 3). Both the activity of the catalysts and selectivity to cracking products (C₅-C₇) increases with the calcinations temperature. Maximum selectivity to C₈ hydrocarbons formation observes for ZrO₂/SO₄-350 catalyst.

Table. XPS study of ZrO₂/SO₄ catalysts

| Sample | Binding energy, eV | | | | | S/Zr | Relative content O (II), % |
|--|----------------------|-------|-------|-------|-------|------|----------------------------|
| | Zr 3d _{5/2} | S 2p | O 1s | | | | |
| | | | I | II | III | | |
| ZrO ₂ /SO ₄ -350 | 182.2 | 169.1 | 530.5 | 532.2 | 533.8 | 0.59 | 64.8 |
| ZrO ₂ /SO ₄ -600 | 182.3; 179.7 | 169.3 | 530.4 | 532.0 | 533.4 | 0.49 | 53.8 |

