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Propane dehydrogenation on vanadium oxide supported on mesoporous mixed oxide ZrO₂-SiO₂

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Due to the significant increase in the world demand for clean propylene, the obtaining of it by direct dehydrogenation of propane is the most studied catalytic reactions. Earlier it was determined, that in this process of vanadium oxide, supported on mesoporous silicate of structure MCM-41 and modified by introduction of Ti^{4+} ions, shows greater stability with similar performance in comparison with commercially Cr₂O₃- or Pt-containing catalysts supported on Al₂O₃. However, the receipt of MCM-41 and Ti-MCM-41 requires using expensive organic templates. In continuing the search of effective catalyst dehydrogenation of propane in this work as supports of active phase V_2O_5 were tested acidic mixed oxide 0,6 ZrO₂-SiO₂ and its modified form, obtained by introduction 3 wt.% TiO₂. Catalytic characteristics were compared with those obtained on V_2O_5/Ti -MCM-41.

Samples 0,6 ZrO_2 -SiO₂ and 0,6 ZrO_2 -SiO₂-0,03 TiO₂ were synthesized by sol-gel and then were formed into spherical granules by droplet coagulation method. Vanadium oxide was deposited by impregnation with a solution of NH₄VO₃. Reaction of propane dehydrogenation was carried out in a flow quartz reactor at 250 - 675 °C in a reaction mixture of 7 vol. % propane in argon.

It were obtained the amorphous oxide zirconium - silicate systems, having the micro/mesoporous structure with pore diameters ~ 1.4 ; 2.7 and 5 nm, a specific surface area of ~ 300 m²/g and the size of spherical particles of ~ 200 microns. Samples showed catalytic activity in propane dehydrogenation. Supporting 5 and 10 wt. % V_2O_5 on 0.6 ZrO₂-SiO₂ resulted to increase propylene yield, respectively, from 20 to 35 and 40 mol. % at 650 °C and a contact time of 3 s. Upon supporting of 15 and 20 wt. % V_2O_5 on 0.6 ZrO_2 -SiO₂ the yield of propylene dramatically was reduced, that can be attributed to decrease in specific surface of sample and formation phase ZrV₂O₇. The introduction of TiO₂ into the structure 0,6 ZrO₂-SiO₂ contributed to increase the yield of propylene to about 10 mol. % and led to a decrease in its only when it was supported of 20 wt. % V₂O₅. In comparison with 5 % V2O5/Ti-MCM-41, catalysts of 5% V2O5/0,6 ZrO2-SiO2 and 5% V2O5/0,6 ZrO2- $SiO_2-0.03TiO_2$ can significantly reduce the temperature of maximum propylene vield. But it does not grow with an increase in contact time from 3 to 7 s. That can be explained by the smaller ordering of these structures and their influence on reaction passing over homogeneously heterogeneous mechanism.