PROPANE DEHYDROGENATION IN THE PRESENCE OF CO₂ OVER CHROMIUM OXIDE-BASED CATALYSTS

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The dehydrogenation of hydrocarbons in the presence of CO₂ has been recently investigated as an alternative for traditional non-oxidative dehydrogenation. In this process unsaturated hydrocarbons are obtained with simultaneous conversion of CO₂ to CO, which is more useful raw material for a number of chemical processes.

In the present work the results concerning dehydrogenation of propane in the presence of CO₂ over various chromium oxide-based materials are presented. Four series of catalysts with Cr loadings in the range of 0.7 – 7.0 wt. % were obtained with impregnation, characterized with different techniques (chemical analysis with bunsen-rupp method, icp, xrd, uv-vis drs, n₂-sorption and quantitative/qualitative h₂-tpr) and evaluated in dehydrogenation of propane with CO₂. Two commercially available amorphous silicas (SiO₂-p; S₆=261 m²·g⁻¹ and SiO₂-a; S₆=477 m²·g⁻¹) as well as mesoporous siliceous sieves with cubic (SBA-1; S₆=1181 m²·g⁻¹) and hexagonal (SBA-15; S₆=750 m²·g⁻¹) pore structure were applied as the supports.

It was found that at a low Cr tot content, the Cr⁶⁺ species predominate on the surface of all the supports, while at a higher Cr content, the Cr⁶⁺ and Cr³⁺ species coexist above the monolayer coverage. The balance of the Cr⁶⁺/Cr³⁺ species, H₂ consumption (from H₂-TPR) as well as the formation of crystalline Cr₂O₃ strongly depend on the Cr tot loading and the specific surface area of the silica support. In the case of catalysts with a similar Cr tot content, both, the Cr⁶⁺ content and H₂-consumption decrease in the following order: Crₓ/SBA-1 > Crₓ/SBA-15 > Crₓ/SiO₂-a > Crₓ/SiO₂-p. The reaction rate normalized to the catalyst’s weight decreases in the same sequence, what indicates that the catalytic activity in the dehydrogenation of propane with CO₂ is related to the concentration of Cr⁶⁺ species which are the precursors of catalytically active Cr³⁺ and Cr²⁺ sites.

Finally, based on characterization results and catalytic tests the possible pathways of propene formation in the presence of CO₂ were proposed.