

PERSPECTIVES of INDUSTRIAL REALIZATION for PROPANE OXIDATIVE DEHYDROGENATION over CHROMIUM OXIDE CATALYSTS

A.L.Lapidus¹, N.A.Gaidai¹, Yu.A.Agafonov¹, M.A.Botavina^{1,2}, P.Pertici³, D.V.Trushin¹, C.Evangelisti³, N. Panziera³, G.Martra², N.V.Nekrasov¹, K.Tenchev⁴, L.Petrov⁴, S.Coluccia²

¹*N.D.Zelinsky Institute of Organic Chemistry, Russ.Acad.Sci., Leninsky prosp., 47, 119991 Moscow, Russia. Fax: (7-495)1355328, E-mail: gaidai@mail.ioc.ac.ru*

²*Department of Chemistry IFM, via P.Giuria, 7, 10125, Torino, University of Torino, Italy*

³*Chemical Institute of Organometallic Compounds CNR, via Risorgimento 35, 56126, Pisa, Italy*

⁴*Institute of Catalysis, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria*

Propene is one of the important and basic substances used in industrial processes. The demand of propene has increased significantly and the existing production of propene from steam cracking is not sufficient to saturate needs of the market. It is necessary to develop new methods for propene production. A new method which is very promising is the oxidative dehydrogenation (ODH). Designing catalysts, methods of preparation and choosing reaction conditions remain a challenging task. CO₂ is a promising oxidant for ODH of propane. It shifts the equilibrium of the dehydrogenation reaction at the expense of the interaction with hydrogen and it oxidizes the coke, formed during the reaction. All this gives rise to an increase of catalyst activity and stability. Early we have shown [1] that a catalyst CrO_x/SiO₂, containing 5.0 % wt. Cr, prepared by wet impregnation, demonstrated rather high initial propane conversion and selectivity to propene in ODH in presence of CO₂ but its activity decreased during the process which was not fully reversible. In the present paper we have used different methods of metal loading: vacuum evaporation of metallic Cr on SiO₂ and hydrothermal incorporation of Cr in silicas matrix (MCM-41). Besides we changed the conditions of wet impregnation of chromium in order to obtain more active and stable catalysts and to decrease the share of irreversible deactivation. The catalysts were tested in propane ODH in presence of CO₂ or mixture oxidants: CO₂+O₂. The catalytic experiments were carried out in a flow unit at temperature 600°C, volume space velocities 200 h⁻¹ at atmospheric pressure. The initial reaction mixtures were the following (% vol.): C₃H₈ (15), CO₂ (30), N₂ (55) and C₃H₈ (15), CO₂ (30), N₂ (50), O₂ (5.0). Chromium content was changed in the range 0.25 – 10.0 % wt. Catalysts were investigated by TPR, IR- and UV-spectroscopy. The specific surface and total pore volume were measured.

The activity of chromium catalysts prepared by all methods falls in variable extent during the process but only for catalysts on MCM-41 it returned to initial level after regeneration in the air. It means that there is no irreversible deactivation on such catalysts. Application of XRD, TPR and UV-spectroscopy showed that formation of big agglomerates of chromium oxides with low extents of oxidation is the main reason of chromium catalyst deactivation during the process of propane ODH. The formation of such particles was not observed in catalysts prepared by hydrothermal incorporation because of separate chromium ions are fixed in support structure. These catalysts can stably work for a long time with constant activity. The use of mixture of oxidants allows to increase the conversion of propane, the selectivity toward the olefins and the stability of the catalysts under study when the selectivity to propene decreases slightly.

Effective chromium oxide catalysts, methods of preparation and optimal reaction conditions can be recommended for industrial realization of propane ODH.

1. A.L.Lapidus, M.A.Botavina, Yu.A.Agafonov, D.V.Trushin, A.A.Makashov, N.V.Nekrasov, N.A.Gaidai. Proceeding of DGMK/SCI-Conference. Milan, 2005, pp.187-194.