

THE MINISTRY OF EDUCATION AND SCIENCE OF THE RUSSIAN FEDERATION
NATIONAL RESEARCH TOMSK STATE UNIVERSITY

CATALYSIS: FROM SCIENCE TO INDUSTRY

*Proceedings of
V International scientific school-conference for young scientists*

September 25-29, 2018

Tomsk 2018

Comparison of supported CrO_x catalysts in non-oxidative and oxidative dehydrogenation of light alkanes

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A growing demand in the obtaining of high purity olefins requires new technologies of their production in addition to traditional steam and catalytic cracking methods. Olefins are widely used in chemical and pharmaceutical industry to produce a wide range of valuable chemicals. For these purposes, catalytic non-oxidative (DH) and oxidative (ODH) direct dehydrogenation of alkanes into olefins represent wide scientific interest. DH of alkanes is a promising method due to high selectivity toward olefins. In turn, ODH with CO₂ as a mild oxidant is also prospective due to possibility of shifting of the dehydrogenation reaction equilibrium and CO₂ utilization. Both DH and ODH pathways strongly depend on red-ox properties of support and active component. To date, different types of mixed oxides [1, 2] have been studied as catalysts for these processes. In spite of toxicity of chromium compounds, Cr-containing catalysts remain one of the most active among the catalysts for DH. The use of CrO_x as an active component supported on alumina is caused by ability to multiple and reversible oxidation-reduction (Cr^{V/VI} ↔ Cr^{II/III}). Supported Cr-containing catalysts also show high activity in ODH-CO₂ of propane and isobutane. However, the use of oxide supports for Cr catalysts with active oxygen and red-ox properties is preferable for higher activity and stable operation of the catalyst. Alumina shows poor red-ox ability, while ZrO₂, CeO₂ and mixed ceria–zirconia oxides are the best candidates as supports for ODH catalysts due to their unique red-ox properties. Thereby, the purpose of the present work is to compare the activity of Cr-containing systems on different supports in non-oxidative and oxidative dehydrogenation of alkanes.

γ-Al₂O₃, CeO₂, ZrO₂, Ce_xZr_(1-x)O₂, and γ-Al₂O₃, modified with ZrO₂ and/or CeO₂, were used as supports. Cr-containing catalysts with Cr loading corresponding to a monolayer (5 at_{Cr}/nm²) were prepared by incipient wetness impregnation of supports using aqueous solution of H₂CrO₄. The catalysts were dried at 80 °C for 12 h and calcined at 600 °C for 4 h. The catalysts were characterized by low-temperature N₂ sorption, XRD, TPR, DRS, RS and tested in DH of isobutane and ODH-CO₂ of ethane.

According to the results obtained, the state of Cr on the surface is different over different supports. The formation of α-Cr₂O₃ particles is observed only for the CrO_x/CeO₂ catalyst. TPR-H₂ results show that the CrO_x/ZrO₂ and CrO_x/Ce_xZr_(1-x)O₂ contain the highest amount of red-ox Cr^{5+/6+} species. These catalysts are the most active in i-C₄H₁₀ dehydrogenation. Thus, mainly chromium state affects on the catalyst activity in DH of isobutane. The modification of γ-Al₂O₃ by ZrO₂ and/or CeO₂ leads to an increase of Cr^{5+/6+} parts and growth of activity in DH of i-C₄H₁₀ in comparison with unmodified CrO_x/Al₂O₃ catalyst. However, in the case of ODH-CO₂ of ethane the reaction pathway, activity and stability of the catalyst depend on both chromium state and support features (acid-base and red-ox properties) [3]. The CrO_x/γ-Al₂O₃ and CrO_x/ZrO₂ catalysts exhibited the highest ethylene formation rates, but the reaction followed different pathways. On CrO_x/γ-Al₂O₃ catalyst, ethylene is formed via direct dehydrogenation of ethane accompanied by RWGS, while on CrO_x/ZrO₂ ethylene is formed via selective ODH. Addition of ZrO₂ and/or CeO₂ to CrO_x/Al₂O₃ catalyst results in selective ODH. For CrO_x/ZrO₂/Al₂O₃ catalyst, ethylene is additionally formed via selective ODH reaction, while non-selective and/or dry reforming reactions take place on CrO_x/CeO₂/Al₂O₃ as shown by the higher CO formation rate.

This work was supported by “The Tomsk State University Academic D. I. Mendeleev Fund Program” grant № 8.2.31.2018. The authors thank A. Livanova for XRD studies and Dr. E. Fakhrutdinova for DRS studies.

References

1. Sattler, J.J.H.B.; Ruiz-Martinez, J.; Santillan-Jimenez, E.; Weckhuysen, B.M. *Chem. Rev.* **2014**, *114*, 10613-10653.
2. Gartner, C.A.; van Veen, A.C.; Lercher, J. A. *ChemCatChem* **2013**, *5*, 3196-3217.
3. Bugrova, T.; Dutov, V.; Svetlichnyi, V.; Cortés Corberán, V.; Mamontov, G. *Catal. Today* **2018**, in press.