E-ISSN: 2997-9382
American Journal of Technology Advancement
https://semantjournals.org/index.php/AJTA

| Research Article

Check for updates

Theory of the Propane Cracking Catalyst

Nurov Suhrob Qo‘zi o‘g‘li, Farmanov Behzod Ilhomovich
Karshi State Technical University

Annotation
As a result, the activity of the studied catalytic systems decreases, and the reaction mainly proceeds via the mechanism of carbon skeleton destruction. The maximum degree of propane conversion—68% with a selectivity of 65% for propylene—is achieved at a temperature of 700 °C when using a nanocrystalline composite material. It has been established that this composite possesses surface area and acidity values close to those of a titanium-containing zeolite of the MFI type. The composite material promotes better adsorption of propane molecules at the catalytic center and facilitates C–H bond cleavage. The catalytic activity of materials consisting of a mechanical mixture of titanium oxide with aluminum oxide, as well as highly porous titanium oxide, turned out to be significantly lower than that of the composite catalyst. All studied catalytic systems demonstrated high resistance to surface deactivation due to the deposition of amorphous carbon.

Keywords: Aluminum oxide, titanium oxide, heterogeneous catalysts.

This is an open-access article under the CC-BY 4.0 license

Introduction. Currently, various catalytic systems with differing efficiencies are used for the thermocatalytic processing of natural gas [1]. The use of noble metal–based materials (Pt, Pd, Au) as catalysts allows for a significant reduction in the cracking temperature and achieves high conversion and selectivity of the initial feedstock. However, their use is limited by high cost and surface deactivation due to the deposition of amorphous carbon during synthesis [2, 3]. Replacing noble metals with iron-containing materials and using various non-ferrous metals and their oxides significantly reduces the catalyst cost, although with some decrease in process performance [4]. Therefore, the development of new, highly efficient, and deactivation-resistant catalytic systems based on non-ferrous metals and their compounds is a relevant task for petrochemical synthesis [5].

The calculation of the atomic rate of formation of the main components was performed according to the equation:

$$w = \frac{Kw_{\text{вых}}S}{V_{\text{петли}}}$$

where K is the correction factor, K = 1.1 × 10^5 mkmol/(mV·s); w_{out} is the outlet flow rate of the reaction mixture, normalized to the catalyst mass, mkmol/(g·s); S is the chromatographic peak area; V_p is the sampling loop volume, L.

Selectivity for each component

$$S_x = \frac{a_{i/3} n_x}{n_{\text{вых}} - n_{\text{вх}}} \cdot 100\ \%.$$

Here, α_i is the number of carbon atoms in product (i); n_x is the molar flow rate of product (i) at the reactor outlet; n_{out} and n_{in} are the molar flow rates of C_3H_8 at the reactor outlet and inlet, respectively.

The carbon balance (%) makes it possible to estimate the fraction of amorphous carbon formed, which participates in the surface deactivation process (indices: н — unreacted substance; об — formed; исх — initial):

$$\frac{n(C_3H_8)_{\text{н}} + n(C)_{\text{об}} + n(CH_4)_{\text{об}} + n(C_2H_4)_{\text{об}} + n(C_2H_6)_{\text{об}} + n(C_3H_6)_{\text{об}}}{n(C_3H_8)_{\text{исх}}} \cdot 100\ \%.$$

The relative error in determining each component did not exceed 7%.

The acid-base properties of the surface of the studied samples were analyzed by pyridine (Py) adsorption. The concentration in the solutions was determined from UV spectra using a single-beam scanning spectrophotometer SF-103. The concentration of the test substance was determined from the calibration dependence of the optical density of the solution (D) on the pyridine concentration at a wavelength of λ_{max} = 252 nm.

Gibbs adsorption, mol/g:

$$\Gamma = \frac{(C_0 - C_t)V}{m} = \frac{(D_0 - D_t)V}{m\varepsilon l},$$

where V is the volume of the solution (4 mL); m is the sample mass (0.01 g); D_0 and D_t are the optical densities at the absorption maximum of Py (Bac) before and during adsorption; ε is the molar absorption coefficient (extinction), for Py — 2 × 10^6 L/(mol·cm), for Bac — 1 × 10^4 L/(mol·cm); l is the cuvette thickness (1 cm).

The analytical absorption bands λ_{max} (Bac) = 230 nm and λ_{max} (Py) = 253 nm did not change in the presence of the adsorbent. The relative error in determining pyridine adsorption was 5%.

Results and Discussion. The results of numerous studies have shown that the propane cracking process can proceed in two directions. The most promising direction is the formation of propylene via a dehydrogenation mechanism, which occurs at high temperatures (900–1273 K):

$$C_3H_8 \rightarrow C_3H_6 + H_2$$

In the second pathway, ethylene and methane are formed from propane according to a destructive mechanism involving the breaking of carbon–carbon bonds, which predominantly occurs at lower temperatures (700–923 K):

$$C_3H_8 \rightarrow C_2H_4 + CH_4$$

During the experiments, it was found that thermal cracking of propane (the reaction without a catalyst) begins at a temperature above 750 °C, whereas the use of catalysts shifts the process to a lower temperature range. Thus, when using a mixture of oxides (TiO_2/Al_2O_3), the conversion of the initial gas begins at 700 °C and reaches its maximum at 950 °C.

In the case of catalytic systems based on nanofibrous aerogel-type material (TiO_2/Al_2O_3-vol) and active titanium oxide (TiO_2-z-g), a propane conversion of up to 40% is observed at temperatures below 700 °C.

Even higher results were obtained when using nanocrystalline composite (TiO_2/Al_2O_3-cr) and titanium-containing zeolite (Ti-MFI) as catalysts, where conversion $\alpha > 60\%$ was recorded in the same temperature range.

These data are in good agreement with the determined activation energy values for the propane decomposition reaction (see table), which amount to 104 kJ/mol for thermal cracking and decrease noticeably during thermocatalytic processing in the following sequence: $TiO_2/Al_2O_3 > TiO_2$-z-g > TiO_2/Al_2O_3-vol > TiO_2/Al_2O_3-cr = Ti-MFI.

Optimal parameters for the propane cracking reaction (T = 700 °C)

Catalyst	**S_{sp}, m^2/g**	**E_a, kJ/mol**	**w, µmol/(g·s) C_2H_4**	**w, µmol/(g·s) C_3H_6**	**Carbon balance, %**
TiO_2/Al_2O_3	105	91.0	126.9	67.0	96.0
TiO_2-z-g	142	88.1	119.1	90.1	98.1
TiO_2/Al_2O_3-vol	310	77.1	156.9	163.4	98.0
TiO_2/Al_2O_3-cr	145	76.0	190.0	367.0	95.2
Ti-MFI	450	76.0	220.0	117.0	99.0

In the experiments, the maximum rate of ethylene formation (w = 220 µmol/(g·s)) was observed at temperatures above 700 °C for the Ti-MFI catalyst, with a maximum process selectivity of $S_{(C_2H_4)} = 45\%$ and a propane conversion exceeding 60% (Fig. 3).

For the TiO_2/Al_2O_3 catalyst without preliminary hydrogen activation, the propylene yield was 35% with a selectivity of 60%, while after activation with a hydrogen stream, this catalyst ($TiO_2/Al_2O_{3a}c_t$) enabled the process to occur at lower temperatures (see Fig. 3), achieving propylene selectivity of 66% at 873 K. It was noted that the yield of the target product increases with temperature.

The observed changes in the technological characteristics of the process are due to differences in the structure of the catalytic centers. For the nanofibrous aerogel catalyst, this center represents a hydroxyl group chemisorbed on an aluminum atom and titanium oxide, which facilitates propane adsorption followed by hydrogen and propylene formation—as confirmed by the corresponding activation energy values (see table).

During hydrogen activation, the nanofibrous catalysts are transformed into a nanocrystalline form, resulting in the formation of an active center represented by a structural element consisting of aluminum and oxygen atoms of the crystal lattice. This transformation facilitates propane adsorption and its catalytic conversion to propylene.

Conclusion. As a result of studies on the thermocatalytic cracking of propane using catalytic systems containing aluminum and titanium oxides, it was shown that the synthesized materials TiO_2/Al_2O_3-vol, TiO_2/Al_2O_3-cr, and Ti-MFI exhibit high catalytic activity. The highest selectivity for propylene formation was demonstrated by the nanocrystalline catalyst TiO_2/Al_2O_3cr.

References

1. Bricker, C. *Advanced catalytic dehydrogenation technologies for production of olefins.* Topics in Catalysis, 2012, Vol. 55, No. 19–20, pp. 1309–1314. DOI: https://doi.org/10.1007/s11244-012-9912-1
2. Zhu, X., Wang, T., Xu, Z. *Pt–Sn clusters anchored at 3Alpenta sites as a sinter-resistant and regenerable catalyst for propane dehydrogenation.* Journal of Energy Chemistry, 2022, Vol. 65, pp. 293–301. DOI: https://doi.org/10.1016/j.jechem.2021.06.002
3. Cherednichenko, A.G., Markova, E.B., Sheshko, T.F., *et al. Thermal-catalytic destruction of polyolefin polymers in the presence of $LnVO_3$ and $LnVO_4$.* Catalysis Today, 2021, Vol. 379, pp. 80–86. DOI: https://doi.org/10.1016/j.cattod.2021.03.012
4. Kainthla, I., Bhanushali, J.T., Keri, R.S., *et al. Activity studies of vanadium, iron, carbon and mixed oxide-based catalysts for the oxidative dehydrogenation of ethylbenzene to styrene: a review.* Catalysis Science & Technology, 2015, Vol. 5, Issue 12, pp. 5062–5076. DOI: https://doi.org/10.1039/c5cy00996k
5. Bogomolov, B.B., Boldyrev, V.S., Zubarev, A.M., *et al. An intelligent logical–informational algorithm for selecting energy- and resource-efficient chemical technologies.* Theoretical Foundations of Chemical Engineering, 2019, Vol. 53, No. 5, pp. 483–492. DOI: https://doi.org/10.1134/S0040357119050026
6. Hrabánek, P., Zikánová, A., Bernauer, B., *et al. A route to MFI zeolite–alumina composite membranes for the separation of light paraffins.* Desalination, 2008, Vol. 224, Issue 1–3, pp. 76–80. DOI: https://doi.org/10.1016/j.desal.2007.02.082