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Effective perovskite catalysts based on rare earth vanadites for propane cracking in associated petroleum gas processing technologies

Ekaterina B. Markova,*[a] Svetlana O. Kovtun,[a] Alexander G. Cherednichenko,[a] Kristina Vukajlovic,[a] Varvara S. Udalaya[a] and Alexander O. Terent'ev[b]

[a] *Peoples Friendship University of Russia (RUDN University), 117198 Moscow, Russian Federation.*
E-mail: ebmarkova@gmail.com
[b] *N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 119991 Moscow, Russian Federation*

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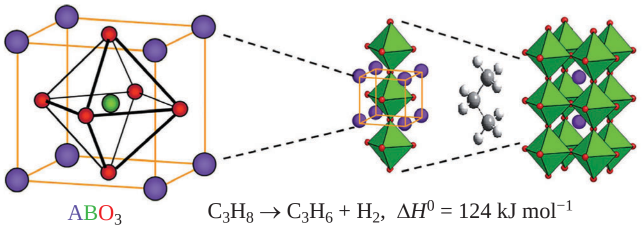
The process of propane cracking in the presence of rare earth vanadites was explored. It was shown that the samples can be attributed to mesoporous catalysts, which also contain a small amount of micropores. It was revealed that the propane conversion and the yield of light olefins grew up with an increase in the molecular weight of a catalyst, while the ethylene and propylene selectivities were enhanced; the propane conversion reached a maximum value of 96.5% with ethylene and propylene selectivities of 69.4 and 26.5%, respectively, when europium vanadite was used as a catalyst.



$C_3H_8 \rightarrow C_3H_6 + H_2$, $\Delta H^0 = 124$ kJ mol^{-1}

Keywords: catalysis, vanadites, perovskite catalysts, associated petroleum gas processing, propane conversion.

This work is dedicated to the famous scientist, talanted and attentive leader, wonderful person and colleague Academician M. P. Egorov.

Associated petroleum gas (APG) is a mixture of saturated gaseous hydrocarbons dissolved in crude oil and released during the oil production in the fields. Development of new technologies for processing APG into a variety of chemical products is an imperative. The burning of APG in the fields without processing leads to significant emissions of solid pollutants and environmental degradation.[1,2] APG can be used to generate electricity. However, the most interesting approach to APG processing is heterogeneous thermocatalytic conversion for light olefins production. Indeed, APG contains about 21% propane, which can be used for propylene synthesis *via* catalytic dehydrogenation of propane. In addition to propylene, ethylene can be obtained as a product of propane cracking. The right choice of a catalyst and conditions of the process makes it possible to reduce the ethylene content in the final reaction products and obtain propylene with high selectivity.[3–5]

The industry uses several proprietary processes to produce propylene, including Catofin, Oleflex and Star.[3] The Catofin method is implemented on CrO_x-based catalysts, and Pt-based catalysts are used for the other two. Although these catalysts have high activity, they still have a few disadvantages, in particular, high cost (in the case of Pt-based catalysts) or excessive toxicity (in the case of CrO_x-based catalysts).

For several decades researchers have been trying to invent relatively inexpensive and environment friendly alternatives based on stabilized V_2O_5, Ga_2O_3 or MoO_3.[6–10] A hypothesis has been put forward according to which lattice defects, being the catalytically active centers, can form in metal oxides, which usually have a constant oxidation state, but at the same time are characterized by increased oxygen mobility under conditions of propane dehydrogenation.[11,12]

It has been shown[6] that vanadium-containing compounds can catalyze dehydrogenation of light hydrocarbons and extend catalyst lifetime. Therefore, development of catalytic systems containing both vanadium and rare earth elements (REEs) has a high potential.

The object of this work are the rare earth vanadites with $LnVO_3$ (Ln = La, Pr, Nd, Sm, Eu) composition obtained by reduction of orthovanadates obtained by solid phase high temperature interaction of stoichiometric amounts of V_2O_5 and rare earth element oxides in accordance with the following reactions:[13–14]

$$V_2O_5 + Ln_2O_3 = 2LnVO_4,$$

$$LnVO_4 + H_2 = LnVO_3 + H_2O.$$

The phase composition of the catalysts was established.[†] All orthorhombic perovskites belong to the space group D^{16}_{2h}-*Pbnm* and the deformation is due to the displacement of heavy lanthanide atom along the *b*-axis direction, while the transition metal atoms are fixed at the centers of symmetry (Table 1). An exception is $LaVO_3$ (Table 1), which pertains to tetragonal system.[9] The texture characteristics were measured.[‡] The catalytic centers of all catalysts have been determined.[§]

[†] X-ray phase analysis of the sample structure was performed using an X-ray diffractometer with an Ultima IV goniometer (Rigaku, Japan). CuKα irradiation was carried out with a scanning step of 0.02° and an exposure time of 1 s. The angle measurement range is $2\theta = 10–100°$.

[‡] The parameters of the porous structure of the samples were determined from nitrogen adsorption–desorption isotherms at 77 K, measured on an automatic high-vacuum Micromeritics ASAP 2020 MP Adsorption Analyzer, USA, within the range of relative vapor pressures from 0.001 to 0.98.

[§] Water vapor adsorption was measured at 293 K on a vacuum weighting unit equipped with a quartz spring balance with a sensitivity of 10 μg with sample masses of up to 100 μg to study the changes in the number of primary adsorption centers (PACs).

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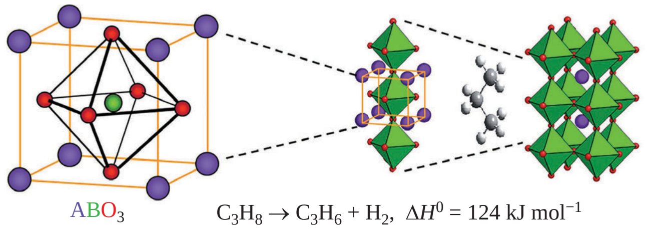

Figure 1 Propane dehydrogenation on $LnVO_3$ systems.

The samples can be described as mesoporous adsorbents, which also contain a small amount of micropores. The mesopore region of the samples is of special interest. The presence of mesopores in the catalyst makes it possible to increase efficiency of the propane dehydrogenation reaction (Figure1).

The most probable pore sizes were determined from the pore size distribution curves calculated by the Barrett–Joyner–Halenda (BJH) method from the desorption branch of the isotherm in the capillary condensation range. The results have shown that vanadites have a nonporous structure (Figure2).

During the research a correlation was established linking a decrease in the total specific surface area and pore volume with a decrease in the ionic radius of a rare earth element (Table 1).

Characteristics of the propane cracking reaction were explored in a flow-through catalytic unit with an U-shaped quartz reactor under stationary conditions at an atmospheric pressure over a wide range of temperatures.

Loading of the reactor was 0.5 g. Propane with a 99.9% content of the main component was used as a feedstock. The flow rate of propane fed into the reactor was constant in all experiments and was 55 mmol min^{-1}. The temperature of propane cracking was gradually increased from 298 to 1143 K with an interval of 50 K. Analytical measurements were carried out at each temperature.

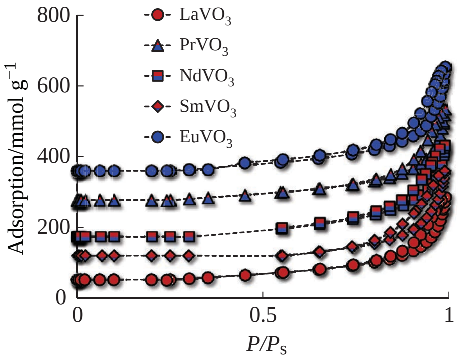

Figure 2 Nitrogen adsorption isotherms at 77 K.

Table 1 Parameters of the porous structure of the investigated nanocrystalline complex oxides.

Catalyst	Unit cell parameters *a*, *b*, *c*/Å			$S_{BET}{}^a$/ m^2 g^{-1}	$W_{BJH}{}^b$/ cm^3 g^{-1}	$2xo_{BJH}{}^c$/ nm	PAC^d/ μmol g^{-1}
$LaVO_3$	3.90 ± 0.02	–	–	3.5	0.044/0.043	12.9/13.1	30.0
$PrVO_3$	5.487 ± 0.005	5.562 ± 0.005	7.751 ± 0.004	3.0	0.050/0.051	13.1/13.3	31.2
$NdVO_3$	5.393 ± 0.008	5.588 ± 0.008	7.583 ± 0.008	2.7	0.046/0.046	13.1/13.2	31.8
$SmVO_3$	5.384 ± 0.008	5.580 ± 0.005	7.667 ± 0.008	2.6	0.045/0.048	13.1/13.2	32.5
$EuVO_3$	5.384 ± 0.008	5.580 ± 0.005	7.667 ± 0.008	2.5	0.047/0.045	13.2/13.3	33.1

[a] S_{BET} is the specific surface area calculated by the BET method. [b] W_{BJH} is the mesopore volume calculated by the BJH method, using the adsorption/desorption data. [c] $2xo_{BJH}$ is the mesopore size calculated by the BJH method, using the adsorption/desorption data. [d] PAC is the number of primary adsorption centers.

During the thermal cracking of propane, the formation of products was observed above 773 K and the conversion of propane was only 2% at 873 K.[7] The temperature regime shifted to a lower temperature range in the process of catalytic cracking, and propane conversion and olefin selectivity increased compared to thermal cracking. In the case of catalytic cracking in the temperature range of 623–1123 K, the yield of olefins constantly increased.

Analysis of the obtained data showed that the yield of ethylene increases when the catalysts with a molecular weight lower than that of lanthanum vanadite were used. The yield of propylene begins to decrease somewhat earlier (Table 2).

The propane catalytic cracking process is a set of chemical transformations that lead to the production of propylene, ethylene, hydrogen, methane, ethane and other products [equations (1)–(5)]:

$$C_3H_8 \leftrightarrows C_3H_6 + H_2, \quad (1)$$

$$C_3H_8 \longrightarrow C_2H_4 + CH_4, \quad (2)$$

$$C_3H_8 + H_2 \leftrightarrows C_2H_6 + CH_4, \quad (3)$$

$$C_2H_4 + H_2 \leftrightarrows C_2H_6, \quad (4)$$

$$C_3H_8 \leftrightarrows 3C + 4H_2. \quad (5)$$

Selectivities of gaseous products are given in Table 2. The lantanide outer orbitals are characterized by the presence of a gradually filling shell 4f, located under a layer of outer shells 5s, 5p and 6s. In general, the electronic configuration of lanthanides can be written as follows: [Xe](4f^n)(5d^x)(6s^2). Valence electrons are 6s^{2}4f, which removal corresponds to the formation of ions with a charge of +3. According to Hund's rule, electronic shells are stable when they are empty, full, or half full. A consistent increase in the number of electrons at the 4f level adds the acidity of REE-containing compounds, increasing the amount of PACs, thus provoking the formation of unsaturated hydrocarbons. There is a correlation between the amount of PACs (Table 1) and the processes of degradation with the formation of ethylene and dehydrogenation with the formation of propylene. The amount of PACs combines weak Brønsted acids and medium Lewis acidity. Simultaneously with the formation of such Lewis centers, the acidity of neighboring Brønsted centers increases due to the possible donor–acceptor interaction.

Its maximum value was obtained using europium vanadite as a catalyst. For the explored vanadites, an increase in the molecular weight of the catalyst leads to an increase in the yield of light olefins. At the same time, the conversion of propane and propylene selectivity increase (Figure 3).

As a result of the conducted research, it was shown that rare earth vanadites can be used as highly effective catalysts for synthesis of light olefins in the process of propane cracking. The propane conversion was 96.5%, with ethylene selectivity reaching 69.4% and propylene selectivity – 26.5% when europium vanadate was used. The results obtained enable us to recommend the synthesized compounds as catalysts for processing components of associated petroleum gas.

Table 2 Catalytic performance of REE vanadites in propane dehydrogenation reaction.

Vanadite catalyst	$LaVO_3$	$PrVO_3$	$NdVO_3$	$SmVO_3$	$EuVO_3$
C_2H_4 selectivity (%)	66.0	67.3	68.0	68.7	69.4
CH_4 selectivity (%)	4.0	3.2	2.5	1.8	1.1
H_2 selectivity (%)	6.0	4.5	4.0	3.5	3.0

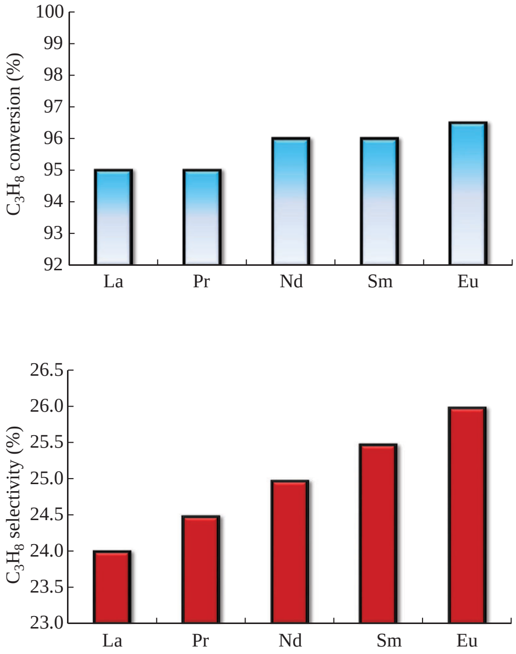

Figure 3 Propane catalytic cracking on $LnVO_3$ systems.

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