CONVERSION PROPANE IN THE PRESENCE OF (La, Sm, Eu) VANADITE AND (La, Sm, Eu) VANADATE

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Abstract

The aim of this work was to investigate features of propane conversion in the presence of samarium, lanthanum, europium vanadate and samarium, lanthanum, europium vanadite. The conversion of propane was studied in the presence of samarium, lanthanum, europium vanadate and samarium, lanthanum, europium vanadite synthesized by solid-phase method. $MeVO_4$ (Me=La, Sm, Eu) crystallized in the zircon structural type, while $MeVO_3$ (Me=La, Sm, Eu) had a perovskite-like structure It was shown that $MeVO_3$ (Me=La, Sm, Eu) catalyzes mainly the process of propane cracking to form methane and ethylene, and $MeVO_4$ (Me=La, Sm, Eu) equally accelerates both cracking and the dehydrogenation of propane.

Keywords: Dehydrogenation, propylene, rare-earth vanadates, cracking, light olefins

1. INTRODUCTION

There has recently been a great increase worldwide in the production of propylene, an important large-scale intermediate product for subsequent synthesis of polypropylene, acrylonitrile, and propylene oxide [1]. There are several methods for the industrial production of propylene; most prominent among these are the cracking of naphta and the FCC process [2]. Several studies [4-6] have shown that compounds with vanadium-containing anions are capable of catalyzing the dehydrogenation of light hydrocarbons. It is also known that rare-earth elements can be used as the components of dehydrogenation catalysts [7-9] and can increase their durability. The development of catalytic systems containing both vanadium and rare-earth elements is thus very promising. Note that rare-earth vanadates have zircon- like structures [10], while rare-earth vanadites have perovskite-like structures [11]. These types of structures have high thermal stability, while perovskite-like structures are permeable to oxygen. The aim of this work was to investigate features of propane conversion in the presence of samarium, lanthanum, europium vanadate and samarium, lanthanum, europium vanadite.

2. METHODS

Catalytic activity of aerogels were studied at atmospheric pressure in a catalytic fluid cracking unit with a quartz reactor, the loading of the catalyst was 0.05 g. Propane of high purity (99.98 mass %) was used as a raw material. The flow rate was 1.25 ml/s. Analysis of the reaction products was carried out by means of a chromatograph Crystal 2000M (Russia). The results of the catalytic conversion were compared with the data of thermal cracking. As-prepared samarium, lanthanum, europium vanadate and samarium, lanthanum, europium vanadite were used as the catalyst in the cracking of pure propane. The catalyst was placed in a U-

shaped quartz reactor, and propane was passed at atmospheric pressure with the flow rate of 1.25 mL/s. The temperature in reactor was set by the electric furnace and checked by the chromel-alumel thermocouple.

The parameters of the porous structure were determined from the nitrogen vapors adsorption isotherms at 77 K using the high-vacuum volumetric equipment ASAP-2020 MP (Micromeritics, USA) in the range of relative pressures from 10^{-6} to 0.99. Before the measurements the samples were outgassed at 473 K.

The chemical composition analysis of catalytic systems was determined using the high-precision X-ray fluorescence (XRF) spectrograph Clever-C31 (Russian Federation).

The X-ray structure analysis (XRD) was performed using the high-precision X-ray diffractometer PANalytical EMPYREAN (Nalkho Techno SA) with monochromatic CuKa-radiation and reflection geometry.

3. EXPERIMENTAL

Analytically pure vanadium(V) and samarium, lanthanum, europium (III) oxides were used as the initial materials for the synthesis of samarium, lanthanum, europium vanadite $MeVO_3$ (Me=La, Sm, Eu). The initial components were preliminarily calcined in a muffle furnace at 450°C for 5 h to remove moisture and adsorbed CO_2. $MeVO_4$ (Me=La, Sm, Eu) was prepared via high-temperature solidphase synthesis, according to the reaction

$$Me_2O_3 + V_2O_5 \rightarrow 2MeVO_4 \qquad Me=La, Sm, Eu$$

This required thorough homogenization of stoichiometric amounts of vanadium(V) and samarium, lanthanum, europium (III) oxides by grinding in the presence of ethyl alcohol in an agate mortar, compression into tablets, and subsequent step annealing in a muffle furnace at 550°C for 3 h, at 650°C for 3 h, and at 750°C for 3 h. The stepwise temperature rise was due to the possibility of V_2O_5 melting (Tmp = 670°C). The annealed samples were grinded again in order to homogenize them and then annealed for another 4 h at a temperature of 950°C to obtain a well-formed structure. Samarium, lanthanum, europium vanadite $MeVO_3$ (Me=La, Sm, Eu) was prepared from $MeVO_4$ (Me=La, Sm, Eu) via high-temperature reduction. A sample of finely-ground $MeVO_4$ (Me=La, Sm, Eu) was placed in a molybdenum boat in a tube furnace, heated in hydrogen to a temperature of 900°C for 1 h, and allowed to stand at this temperature for a further 4 h. The volumetric hydrogen feed rate was 500 h^{-1}.
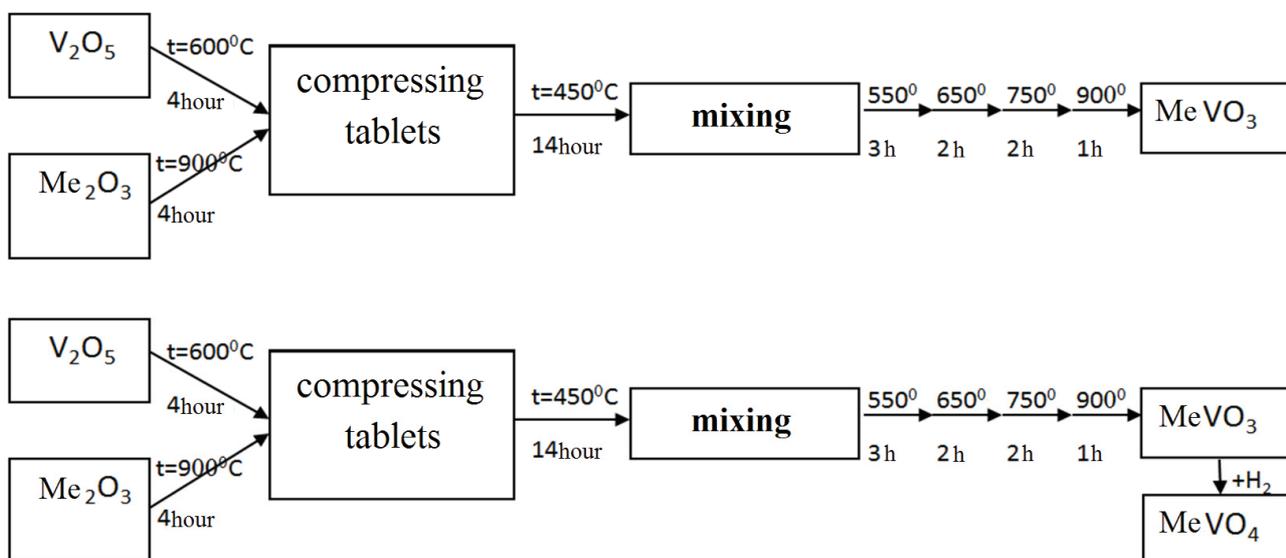
All of the synthesized samples were studied via X-ray powder diffraction (XPD). XPD was performed on a Rigaku X-ray diffractometer (Japan) equipped with an Ultima IV theta-theta goniometer (Cu$K\alpha$ radiation) at a scanning step of 0.02° and a scanning time 1 s. The range of diffraction angle measurement was 2θ = 10°-100°

The X-ray powder diffraction patterns were indexed by means of homology, based on data from the international ICDD PDF-4 database. The crystal lattice parameters were refined using the RTP (X-ray Table Processor) program.

The synthesized samarium, lanthanum, europium vanadate and samarium, lanthanum, europium vanadite were analyzed via X-ray powder diffraction to determine the structure and refine the parameters of the unit cells. $MeVO_4$ (Me=La, Sm, Eu) crystallized in the zircon structural type (space group *I41/amd*, *a* = 7.272 Ѓ} 0.006 A, and *b* = 6.391 Ѓ} 0.006 A), while $MeVO_3$ (Me=La, Sm, Eu) had a perovskite-like structure (space group *Pbnm*, *a* = 5.384 Ѓ} 0.008 A, *b* = 5.580 Ѓ} 0.005 A, and *c* = 7.667 Ѓ} 0.008 A).
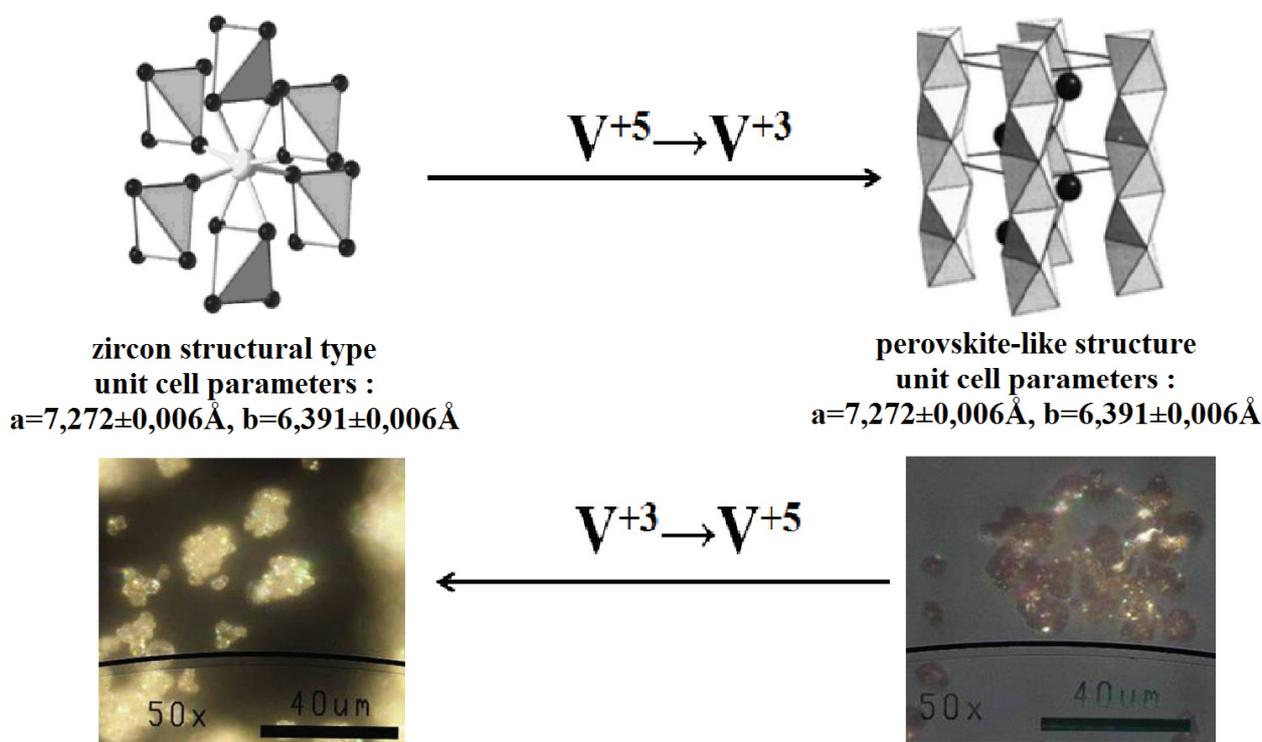
Figure 1 The structure and refine the parameters of the unit cells

The catalyst load was equal in all experiments. The rate of propane conversion was calculated using the equation

$$w = \frac{K \times w_{ex} \times s}{V_{loop}} \; [\mu mol/(g \, s)] \qquad (1)$$

where K is a correction coefficient, w_{ex} - is the exit velocity of the reaction mixture, s - is the area of the peak, and V_{loop} is the loop volume.

The selectivity of each component was calculated according to the formula:

$$Sx = \frac{n_x}{n_{in} - n_{rest}} \times 100\% \qquad (2)$$

where n_{in} - is the amount of propane involved in the reaction (μmol), and n_{rest} - is the amount of unreacted propane (μmol).

The results obtained via catalytic conversion were compared to the thermal cracking data. The degree of propane conversion was determined from the amount of reacted propane when a steady state was achieved:

$$\alpha = \frac{n_{in} - n_{rest}}{n_{in}} \tag{3}$$

4. RESULTS AND DISCUSSION

The equilibrium adsorption isotherms of nitrogen vapors at 77 K exhibited the specific nonporous type features with the well-developed and reversible plateaus and the hysteresis loop in the capillary condensation range (III type). The parameters of porous structure of vanadates and vanadites are presented in **Table 1**. The specific surface area was determined by the BET method [12]. The micropore volume W_o and the conventional surface assigned with micropores, S_{mic}, for the samples under study were calculated using the t-plot and MP comparative methods. The mesopore volume W_{BJH} and the average pore size $(2x_{oBJH})$ in the capillary condensation range were determined by the Barrett-Joyner-Holenda (BJH) method [13]. The pore size (two half pore width for the slit-like pores) $2x_o$ was estimated as $4V/a$ in the BET area, where V is a total pore volume. and a is an adsorption value. The average pore size and the pore size distribution over the area of capillary condensation based on the desorption branch were obtained using the BJH model [13].

Table 1 The parameters of porous structure samarium, lanthanum, europium vanadate and samarium, lanthanum, europium vanadite

Catalysts	Ssp, m²/г	W_o, cm³/g S_{mic}, m²/g	W_{BJH}, см³/г desorption/adsorption	$2x_o$, nm BET	$2x_o$ BJH, нм desorption/adsorption
LaVO$_3$	1.5	24	0.034 / 0.041	10.8	11.2 / 11.4
LaVO$_4$	2.8	40	0.047 / 0.055	14.9	14.2 / 14.3
SmVO$_3$	2.5	39	0.047 / 0.045	12.3	13.2 / 13.3
SmVO$_4$	3.1	42	0.053 / 0.052	18.2	19.6 / 20.2
EuVO$_3$	2.6	39	0.047 / 0.046	13.1	13.9 / 14.3
EuVO$_4$	3.1	42	0.053 / 0.052	18.2	19.6 / 20.2

For comparison, we conducted the noncatalytic conversion of propane. It was shown that propane conversion started at 773 K, was only 2% at 873 K, and raising the temperature to 923 K increased propane conversion to 21%; methane and ethane were the major products (**Figure 2**). Propane dehydrogenation thus does not occur under conditions of noncatalytic thermal cracking. In the presence of MeVO$_3$ (Me=La, Sm, Eu) and MeVO$_4$, (Me=La, Sm, Eu) a considerable increase in propane conversion was observed that reached 50% at 923 K. In addition to shifting the degree of half-conversion toward lower temperatures, the selectivity with regard to olefin changed with respect to thermal cracking.
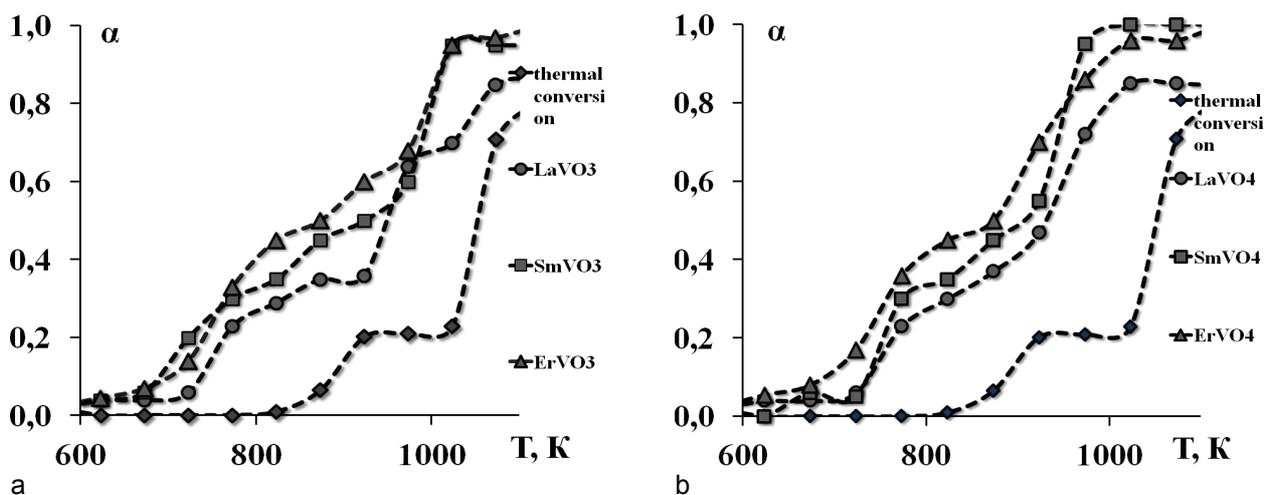
Figure 2 The degree of propane conversion a - samarium, lanthanum, europium vanadite b - samarium, lanthanum, europium vanadate

However, the addition of rare-earth vanadites and rare-earth vanadates catalysts significanltly changed the ratio between the reaction products. In the case of catalytic conversion by activated vanadites of $MeVO_3$ (Me=La, Sm, Eu), the ethylene formation predominated. The mixture of products in almost equal proportions were obtained in the thermal decomposition until the resinification started. Ethylene is the main product of catalytic conversion of propane with usage of $MeVO_3$ (Me=La, Sm, Eu) as catalysts unlike the case of the of $MeVO_4$ (Me=La, Sm, Eu) rare-earth vanadates catalyst employment when the propylene yield prevailed. For all catalysts under study, the yield of light hydrocarbons increased in the temperature range 723-1073 K as compared with that for thermal cracking (**Figure 3**).
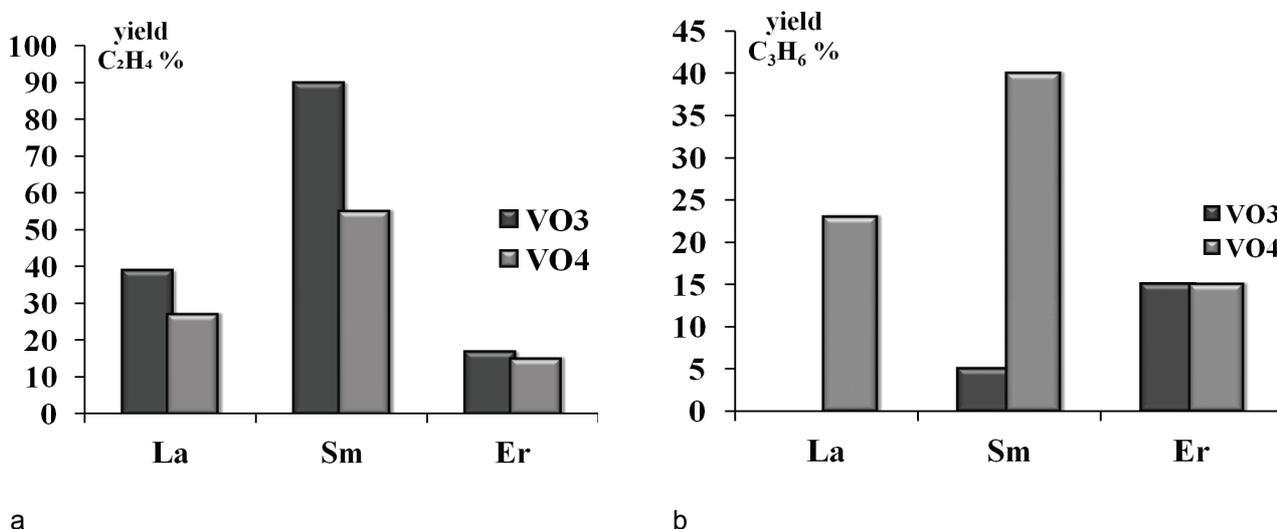
Figure 3 Yields of alkenes: a - ethylene b - propylene

The temperature dependence of ethylene selectivity of reaction (**Figure 4**) showed that the activated of $MeVO_3$ (Me=La, Sm, Eu) had a high selectivity in relation to ethylene formation (**Figure 4**). The yield of ethylene was of about 90% in the catalytic temperature range 773 - 1123 K, with a maximum of 93% at 923 K (before carbonization). In this case, the selectivity for the most important component as ethylene increased.

Figure 4 evidenced that usage of $MeVO_4$ (Me=La, Sm, Eu) led to the change of selectivity, and the basic product was propylene. In the catalytic temperature range 800-1000 K, the selectivity was over 40%. And the

hydrogen activation of the rare-earth vanadates catalyst to a shift of the maximum selectivity at **Figure 4** in the region of lower temperatures, while it increased the selectivity up to 48%. at 923 K.
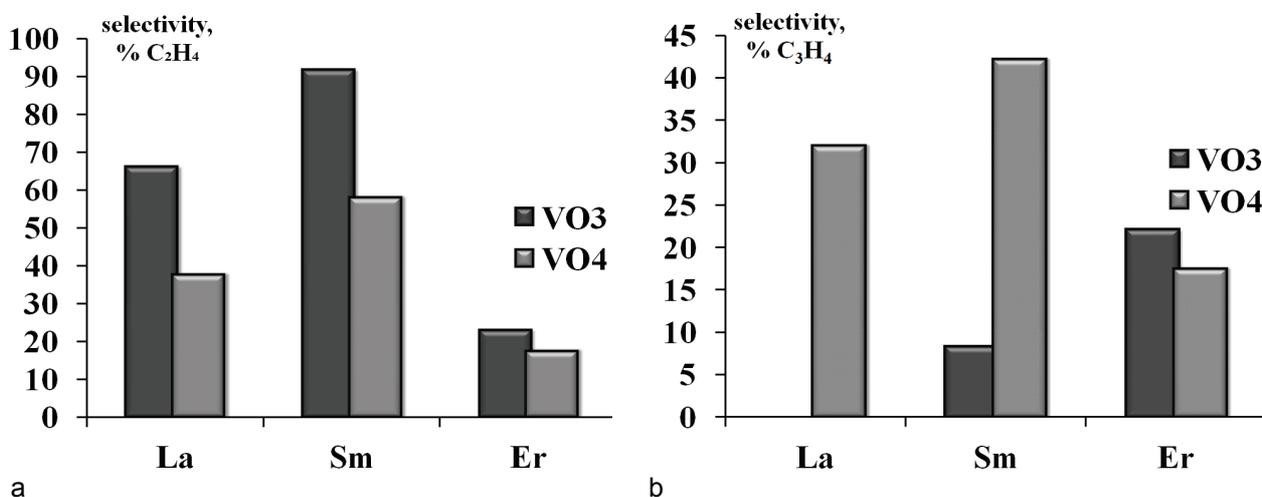
Figure 4 Selectivity for alkenes versus temperature of reaction: for ethylene (a) and for propylene (b)

On the MeVO$_4$ (Me=La, Sm, Eu) catalyst, which has a zircon-like structure, the cracking process and the dehydrogenation of propane proceed equally. Since the cracking of propane is a first order reaction, the energies of activation for the process were calculated for all of the studied catalysts. This required constructing the patterns of the reaction rate logarithm as a function of the reciprocal temperature

Deactivation was much faster with MeVO$_3$ (Me=La, Sm, Eu), and it was observed after 20 h of operation at a rate that was slightly slower than the one for MeVO$_4$ (Me=La, Sm, Eu). These results agree with the data on the selectivity of product formation. It was found that MeVO$_4$ (Me=La, Sm, Eu) better catalyzes the dehydrogenation process, as a result of which the reaction mixture contains hydrogen. To some extent, this prevents the formation of condensation products on the catalyst's surface, which in turn leads to a loss of catalytic activity.

CONCLUSIONS

The conversion of propane was studied in the presence of samarium, lanthanum, europium vanadate and samarium, lanthanum, europium vanadite synthesized by solid-phase method. It was shown that MeVO$_3$ (Me=La, Sm, Eu) catalyzes mainly the process of propane cracking to form methane and ethylene, and MeVO$_4$ (Me=La, Sm, Eu) equally accelerates both cracking and the dehydrogenation of propane.

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