Features of the Catalytic Cracking of Propane with a Step-Wise Change \(Pr_xYb_{2-x}Zr_2O_7\)

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Abstract: In this paper, the features of catalytic cracking of propane with a step-wise change in the composition of the catalyst from \(Pr_2Zr_2O_7\) to \(Yb_2Zr_2O_7\) were considered. For the research, samples of catalysts \(Pr_2Zr_2O_7\), \((Pr_{0.75}Yb_{0.25})_2Zr_2O_7\), \((Pr_{0.5}Yb_{0.5})_2Zr_2O_7\), \((Pr_{0.25}Yb_{0.75})_2Zr_2O_7\) and \(Yb_2Zr_2O_7\) were synthesized and analyzed. Analysis of the results from catalytic experiments showed that for the catalyst \((Pr_{0.25}Yb_{0.75})_2Zr_2O_7\), at a temperature of 700 °C, the conversion of propane reaches values of 100%, but for \(Yb_2Zr_2O_7\), this indicator decreases to 84%. The selectivity for ethylene is consistently reduced from 85% to 28% in several catalysts \((Pr_{0.75}Yb_{0.25})_2Zr_2O_7 > Pr_2Zr_2O_7 > (Pr_{0.5}Yb_{0.5})_2Zr_2O_7 > (Pr_{0.25}Yb_{0.75})_2Zr_2O_7 > Yb_2Zr_2O_7\). An increase in the number of surface adsorption centers leads to a predominant rupture of the C–C bond in the propane molecule with the formation of ethylene. When ytterbium ions are introduced into the catalyst, the amount of ethylene in the reaction products decreases, but the selectivity for propylene increases in the series \(Pr_2Zr_2O_7 < (Pr_{0.75}Yb_{0.25})_2Zr_2O_7 < (Pr_{0.5}Yb_{0.5})_2Zr_2O_7 < (Pr_{0.25}Yb_{0.75})_2Zr_2O_7\), which is associated with a decrease in the binding energy of carbon atoms in propane with the catalytic center during adsorption.

Keywords: heterogeneous catalysis; propane conversion; «light» olefins; adsorption; catalytic centers; \(Ln_2Zr_2O_7\)

1. Introduction

Catalytic cracking of propane is one of the promising methods for obtaining “light” olefins (ethylene and propylene) [1–3]. For a more selective production of propylene, this process is carried out using industrial catalysts containing chromium oxides CrO\(_3\) or platinum Pt and supported on an Al\(_2\)O\(_3\) carrier. However, compounds containing chromium in their composition are highly toxic and endanger human health and the environment. Platinum-based catalysts are less dangerous and more promising for industrial use. However, the technology of using platinum-based catalysts for the synthesis of propylene has several disadvantages associated with their production. For example, to ensure high catalytic activity and propylene selectivity, it is necessary to obtain Pt particles of a certain size, as well as to use additional surface treatment to remove carbon deposits [4]. The high price of platinum is another disadvantage of these catalysts. Therefore, obtaining a catalyst based on the oxides of other metals using an inert, highly porous support is an urgent task. At the same time, the synthesized catalyst should have a lower cost compared to known materials and have high catalytic activity.

Currently, the most active catalysts of dehydrogenation processes are Pt-containing systems [5]. For example, UOP has developed the Oleflex process, in which propane dehydrogenation occurs in the presence of a catalyst, which is metallic platinum and tin deposited on inert aluminum oxide (Pt/Sn/Al\(_2\)O\(_3\)). The process is carried out in an adiabatic reactor with a moving catalyst layer at atmospheric pressure and a temperature...
of 580–650 °C. The addition of inert gas to the raw materials somewhat complicates the technology but contributes to an increase in the conversion of propane into the final reaction products. An example of an industrial process of propane dehydrogenation using catalysts, where chromium (III) oxide is used as an active component, is the “CATOFIN” process of ABB Lummus Crest/United Catalysts [6], as well as the “FBD” process of ABB Lummus Crest/United Catalysts [7,8]. The main disadvantage of such catalysts, as noted earlier, is the high toxicity of chromium (III) oxide and their short service life. A dehydrogenation catalyst is known, which is an aluminum oxide carrier modified with silicon oxide, on which the active component chromium oxide and the promoter potassium oxide are distributed [9].

The catalyst is used for the dehydrogenation of C<sub>4</sub>-C<sub>5</sub> paraffin hydrocarbon and has high activity, selectivity and thermal stability. The disadvantages are the rapid deactivation of the catalyst and the presence of environmentally unsafe chromium compounds in its composition. A hydrocarbon dehydrogenation catalyst consists of platinum, tin and potassium deposited on theta modifications of aluminum oxide [10]. The disadvantage is a large amount of coke formed on aluminum oxide substrates.

It is known that coordinatively unsaturated Zr cations are active sites for the dehydrogenation of various hydrocarbons [11]. The use of pure zirconium dioxide as a catalyst is complicated by the fact that the monoclinic structure of this oxide, which has a high degree of crystallinity and a low specific surface area, is often used for these purposes [12]. Of greatest interest for catalysis are low-temperature metastable phases of ZrO<sub>2</sub> (amorphous, cubic, tetragonal), characterized by high dispersion and a developed surface. The stabilization of such low-temperature phases of zirconium dioxide is promoted by the inclusion of various anions or cations in its structure. 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)):

\[
\begin{align*}
\text{C}_3\text{H}_8 & \rightleftharpoons \text{C}_3\text{H}_6 + \text{H}_2 \\
\text{C}_3\text{H}_8 & \rightarrow \text{C}_2\text{H}_4 + \text{CH}_4 \\
\text{C}_3\text{H}_8 + \text{H}_2 & \rightleftharpoons \text{C}_2\text{H}_6 + \text{CH}_4 \\
\text{C}_2\text{H}_4 + \text{H}_2 & \rightleftharpoons \text{C}_2\text{H}_6 \\
\text{C}_3\text{H}_8 & \rightleftharpoons 3\text{C} + 4\text{H}_2
\end{align*}
\]

(\Delta H_{298} = 124.3 \text{ kJ/mol})

(\Delta H_{298} = 98.9 \text{ kJ/mol})

(\Delta H_{298} = -37.7 \text{ kJ/mol})

(\Delta H_{298} = -136.6 \text{ kJ/mol})

(\Delta H_{298} = 119.5 \text{ kJ/mol})

The most important reactions for producing propylene (Equation (1)) and ethylene (Equation (2)) are endothermic and proceed with an increase in the number of gas molecules. Therefore, an increase in the reaction temperature and a decrease in pressure contribute to higher conversions of propane into the final products. Indeed, the process of propane dehydrogenation at a pressure of 1 bar is usually carried out at a temperature of 550–750 °C. With a further increase in the process temperature, a simultaneous increase in the rate of the dehydrogenation reaction with the C–H bond cleavage (Equation (1)) and competitive reactions with C–C bond cleavage with the formation of ethylene and methane (Equation (2)) is observed. Therefore, the cracking conditions and the properties of the catalyst should affect the reduction in the proportion of side reactions and the increase in propylene selectivity.

It has been suggested that the coordination of unsaturated Zr and oxygen adjacent to the lattice participate in the dehydrogenation reaction. Yet, the promoter used to purposefully create unsaturated Zr increased the activity [13,14]. The presence of unsaturated Zr in the lattice of zirconium oxide ZrO<sub>2</sub> lowers the activation barrier for the formation of hydrogen and propylene from propane (Equation (1)). The conditions of catalyst synthesis make it possible to influence the particle size of ZrO<sub>2</sub> and its crystal structure while simultaneously controlling the number of unsaturated Zr [15,16]. The conditions of catalyst synthesis make it possible to influence the particle size of ZrO<sub>2</sub> and its crystal structure while simultaneously controlling the number of unsaturated Zr [17,18]. In addition, doping
of zirconium compounds and treatment of the material in a reducing agent are effective methods for obtaining unsaturated Zr. Rare-earth metal oxides can be used for doping.

However, despite the high activity achieved for some of the listed catalysts, their stability was often insufficient due to the leaching of the active component in an aggressive oxidizing water environment. The addition of lanthanides to catalytic systems or the creation of complex oxide oxides are among the most promising catalysts for cracking processes due to their high activity and stability in an aggressive environment [19,20]. That is why research is currently being conducted to study the possibility of using complex oxides in catalytic conversion processes. The reason catalytic versatility of such oxides—along with their high stability at a high temperature and in an aggressive environment—consists in the stabilization of transition metal cations at unusual degrees of oxidation, as well as in the high mobility of oxygen in the structure of pyrochlore.

Therefore, complex oxides of the composition Ln$_2$Zr$_2$O$_7$ are significant as materials for the manufacture of catalysts for the dehydrogenation of hydrocarbons. They have high thermal stability, high ionic conductivity, and chemical resistance [21–24]. All zirconates of rare earth metals change their properties upon alloying due to the formation of defects in their structure [25,26]. The study of the catalytic properties of materials with a step-wise change in composition from Pr$_2$Zr$_2$O$_7$ to Yb$_2$Zr$_2$O$_7$ in the process of catalytic propane dehydrogenation can lead to very interesting and practically important results.

2. Results
2.1. Catalyst Characteristics
2.1.1. Catalyst Synthesis

Samples of rare earth element zirconates Ln$_2$Zr$_2$O$_7$ (Ln = Pr, Yb) were synthesized by the well-known method [27,28] from ZrOCl$_2$ and rare earth metal nitrates (Figure 1). To do this, solutions of the initial reagents were mixed at room temperature. A solution of ammonium hydroxide was added to the resulting solution at a pH = 9.0 ± 0.5. The resulting precipitate was filtered and dried at a temperature of 100 °C for 5 h. Then the synthesis was carried out at a temperature of 1000 °C for 3 h. Synthesized rare earth metal zirconate was analyzed and used as a catalyst for propane cracking.

![Figure 1. Adsorption isotherms.](image-url)

Inductively coupled plasma atomic emission spectroscopy (ICP-AES) was used to quantify the concentration of elements in all synthesized catalysts. ICP-AES measurements were carried out on a Vista-PRO spectrometer (Varian, Agilent Technologies Inc., Santa Clara, CA, USA) operating in a simultaneous mode. All selected spectral lines were free from interference. The background emission was compensated by preparing samples and calibration solutions under the same condition.
2.1.2. Catalyst Surface

In the work, the specific BET surface ($S_{\text{BET}}$) of the samples, as well as the parameters of the porous structure (Table 1), are calculated.

Table 1. Textural properties of Ln$_2$Zr$_2$O$_7$ catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>$W_0$, cm$^3$/g</th>
<th>$E_0$, kJ/mol</th>
<th>$a_0$, mmol/g</th>
<th>$S_{\text{BET}}$, m$^2$/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pr$_2$Zr$_2$O$_7$</td>
<td>0.030</td>
<td>18.7</td>
<td>0.88</td>
<td>44.4</td>
</tr>
<tr>
<td>(Pr$<em>{0.75}$Yb$</em>{0.25}$)$_2$Zr$_2$O$_7$</td>
<td>0.033</td>
<td>17.7</td>
<td>0.73</td>
<td>42.5</td>
</tr>
<tr>
<td>(Pr$_0.5$Yb$_0.5$)$_2$Zr$_2$O$_7$</td>
<td>0.028</td>
<td>24.9</td>
<td>0.56</td>
<td>38.1</td>
</tr>
<tr>
<td>(Pr$<em>{0.25}$Yb$</em>{0.75}$)$_2$Zr$_2$O$_7$</td>
<td>0.026</td>
<td>34.7</td>
<td>0.48</td>
<td>24.3</td>
</tr>
<tr>
<td>Yb$_2$Zr$_2$O$_7$</td>
<td>0.024</td>
<td>34.7</td>
<td>0.48</td>
<td>21.1</td>
</tr>
</tbody>
</table>

$S_{\text{BET}}$—specific surface area calculated by the BET method. $W_0$—the adsorption volume in the samples was calculated by t-plot by the comparative method. $E_0$, $a_0$—the characteristic adsorption energy and the monomolecular layer of the adsorbate are calculated by the Dubinin-Astakhov (DA) method.

It can be seen from the table that the gradual substitution of ytterbium for praseodymium in the A position leads to an increase in the adsorption volume. The specific surface calculated by the BET method decreases.

All samples belong to low-porosity samples, and substitution in the A-position of the metal, both partial and complete, does not lead to a sharp change in the surface of the catalytic systems.

In a row Pr$_2$Zr$_2$O$_7$ $\leq$ (Pr$_{0.75}$Yb$_{0.25}$)$_2$Zr$_2$O$_7$ $<$ (Pr$_{0.5}$Yb$_{0.5}$)$_2$Zr$_2$O$_7$ $<$ (Pr$_{0.25}$Yb$_{0.75}$)$_2$Zr$_2$O$_7$ $<$ Yb$_2$Zr$_2$O$_7$ an increase in the characteristic energy from 17.7 to 34.7 kJ/mol is observed. The step-wise change of the metal leads to a decrease in the amount of substance adsorbed in monolayers attributable to the primary, most advantageous catalytic centers.

The textural properties of Ln$_2$Zr$_2$O$_7$ catalysts were also analyzed using N$_2$ (Figure 1) adsorption–desorption with isotherms and pore size distribution profiles.

At the same time, (Pr$_{0.5}$Yb$_{0.5}$)$_2$Zr$_2$O$_7$, (Pr$_{0.25}$Yb$_{0.75}$)$_2$Zr$_2$O$_7$, and Yb$_2$Zr$_2$O$_7$ have much higher pore volumes than Pr$_2$Zr$_2$O$_7$, (Pr$_{0.75}$Yb$_{0.25}$)$_2$Zr$_2$O$_7$.

2.1.3. Catalytic Centers

It is known that the activity of catalysts is affected by the acid–base properties of their surface. During the research, a series of experiments were carried out to test the electron-withdrawing centers of the surface of the synthesized compounds (Figure 2). The efficiency of acid sites was determined from the rate of adsorption of pyridine molecules.

Figure 2. Pyridine adsorption isotherms—(a), the number of electron-withdrawing centers—(b).

The initial section of these curved lines corresponds to adsorption on “strong” acids. The next section of the curve represents adsorption in the “weaker” adsorption centers. The slope tangent of the first section determines the rate of “fast” adsorption $W_1$ in the
adsorption centers of type 1, respectively; the slope tangents of the following sections of the curve determine the rate $W_2$ (that is, “slow” adsorption) (Figure 2a).

The number of electron-withdrawing centers increases in the order $Pr_2Zr_2O_7 < (Pr_{0.75}Yb_{0.25})_2Zr_2O_7 < (Pr_{0.5}Yb_{0.5})_2Zr_2O_7 < (Pr_{0.25}Yb_{0.75})_2Zr_2O_7 < Yb_2Zr_2O_7$ (Figure 2b).

Primary adsorption centers (PACs) were identified to establish the preferred mechanism for the catalytic conversion of propane. The number of primary adsorption centers and the total number of oxygen-containing centers were determined by the adsorption of water from the gas phase (Figure 3).

Figure 3. Isotherms of Water adsorption—(a), comparative adsorption isotherms at low pressures—(b).

It was found that $Pr_2Zr_2O_7$ has the highest absorption of water; substitution of a rare-earth metal cation in the $A$-position leads to a decrease in water capacity. The number of primary adsorption centers decreases from 96 mmol/g for $Pr_2Zr_2O_7$ to 76 mmol/g for $Yb_2Zr_2O_7$.

2.2. Catalytic Tests

Catalytic cracking of propane is a complex process that consists of several series-parallel reactions (Equations (1)–(5)). The selection of the process conditions and the catalyst makes it possible to shift the equilibrium towards the formation of ethylene or propylene.

It is known that during the thermal cracking of propane, the formation of products begins at a temperature above 700 °C with a further increase in temperature to 800 °C, and the conversion of propane reaches 20%. The main reaction products under these conditions are methane and ethane [25].

As a result of the studies, it was shown that when using catalysts based on synthesized REM zirconates, propane conversion also significantly depends on the cracking temperature. At a temperature of 700 °C, the propane conversion value increases in the series $Pr_2Zr_2O_7 \rightarrow (Pr_{0.75}Yb_{0.25})_2Zr_2O_7 \rightarrow (Pr_{0.5}Yb_{0.5})_2Zr_2O_7 \rightarrow (Pr_{0.25}Yb_{0.75})_2Zr_2O_7$. At the same time, to connect the composition $(Pr_{0.25}Yb_{0.75})_2Zr_2O_7$ under such temperature conditions, the maximum value of propane conversion is observed, which is about 100%, which sharply decreases to 84% when switching to unalloyed $Yb_2Zr_2O_7$. The minimum value of propane conversion at a temperature of 700 °C was registered for the compound of the composition $Pr_2Zr_2O_7$ (Figure 4). A further increase in the cracking temperature to 800 °C makes it possible to eliminate the observed differences in the propane conversion for all the studied catalysts except for $Pr_2Zr_2O_7$. Thus, the step-wise composition change from $Pr_2Zr_2O_7$ to $Yb_2Zr_2O_7$ allows you to adjust the value of the degree of propane conversion depending on the cracking temperature. As a result of the analysis of the composition of the final products of cracking, it was shown that when using the studied catalysts, not only does the high values of propane conversion shift to lower temperatures, but also the selectivity for “light” olefins changes (Figures 5 and 6).
The observed effect can be explained by comparing the values of selectivity for ethylene and propylene in the considered temperature range. For example, the maximum yield
of ethylene was obtained using the catalyst \((\text{Pr}_{0.75}\text{Yb}_{0.25})_2\text{Zr}_2\text{O}_7\) or when the selectivity value for ethylene, at a temperature of 700 °C, was 86%. When replacing praseodymium with ytterbium in the series \(\text{Pr}_2\text{Zr}_2\text{O}_7 \rightarrow (\text{Pr}_{0.75}\text{Yb}_{0.25})_2\text{Zr}_2\text{O}_7 \rightarrow (\text{Pr}_{0.5}\text{Yb}_{0.5})_2\text{Zr}_2\text{O}_7 \rightarrow (\text{Pr}_{0.25}\text{Yb}_{0.75})_2\text{Zr}_2\text{O}_7 \rightarrow \text{Yb}_2\text{Zr}_2\text{O}_7\), the ethylene yield decreases significantly (Figure 6) and the propylene selectivity value increases (Figure 5).

Thus, a step-wise change in the composition of the catalyst in the direction of increasing the ytterbium content in the series \(\text{Pr}_2\text{Zr}_2\text{O}_7 \rightarrow (\text{Pr}_{0.75}\text{Yb}_{0.25})_2\text{Zr}_2\text{O}_7 \rightarrow (\text{Pr}_{0.5}\text{Yb}_{0.5})_2\text{Zr}_2\text{O}_7 \rightarrow (\text{Pr}_{0.25}\text{Yb}_{0.75})_2\text{Zr}_2\text{O}_7 \rightarrow \text{Yb}_2\text{Zr}_2\text{O}_7\) changes the direction of the process toward the formation of propylene by accelerating the propane dehydrogenation reaction. The maximum propylene selectivity value of 40% is observed for \((\text{Pr}_{0.25}\text{Yb}_{0.75})_2\text{Zr}_2\text{O}_7\), and the transition to the non-ligated compound \(\text{Yb}_2\text{Zr}_2\text{O}_7\) leads to a slight decrease in this indicator to 38%.

After cracking at a temperature of 700 °C for 72 h, no change in activity was observed for all the studied catalysts. Table 2 shows the correlation between the decrease in activation energy and the value of the increase in the TOF value.

Table 2. Catalytic characteristics of complex oxide systems in the process of propane cracking.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>(\text{TOF}_{\text{surf}} \text{ s}^{-1})</th>
<th>(E_a \text{, kJ/mol})</th>
<th>(\text{CB, %})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Pr}_2\text{Zr}_2\text{O}_7)</td>
<td>4.8</td>
<td>91</td>
<td>96</td>
</tr>
<tr>
<td>((\text{Pr}<em>{0.75}\text{Yb}</em>{0.25})_2\text{Zr}_2\text{O}_7)</td>
<td>4.6</td>
<td>90</td>
<td>98</td>
</tr>
<tr>
<td>((\text{Pr}<em>{0.5}\text{Yb}</em>{0.5})_2\text{Zr}_2\text{O}_7)</td>
<td>4.8</td>
<td>88</td>
<td>95</td>
</tr>
<tr>
<td>((\text{Pr}<em>{0.25}\text{Yb}</em>{0.75})_2\text{Zr}_2\text{O}_7)</td>
<td>6.1</td>
<td>81</td>
<td>96</td>
</tr>
<tr>
<td>(\text{Yb}_2\text{Zr}_2\text{O}_7)</td>
<td>6.0</td>
<td>79</td>
<td>96</td>
</tr>
</tbody>
</table>

On the positive side, the TOF value tends to increase with the conversion rate, which makes it possible to design catalytic systems that are more productive and efficient with existing industrial catalysts.

Studies have shown that during the operation of the catalyst, the accumulation of carbon on its surface is negligible. Table 2 shows the results from calculating the carbon balance of the process, which shows the presence of minor deviations. The increase in carbon deposition increases in the series \(\text{Pr}_2\text{Zr}_2\text{O}_7 < (\text{Pr}_{0.75}\text{Yb}_{0.25})_2\text{Zr}_2\text{O}_7 < (\text{Pr}_{0.5}\text{Yb}_{0.5})_2\text{Zr}_2\text{O}_7 < (\text{Pr}_{0.25}\text{Yb}_{0.75})_2\text{Zr}_2\text{O}_7 \approx \text{Yb}_2\text{Zr}_2\text{O}_7\). These data correlate with catalytic activities, where the highest activity contributes to a greater accumulation of carbon on the catalyst surface.

The regeneration of catalytic systems occurs with airflow at 400 °C for 10 h. The amount of remaining carbon does not exceed 2 wt.% and does not affect the catalytic activity of these systems.

3. Discussion

An analysis of the results of catalytic experiments showed that the selectivity of ethylene with the used synthesized catalysts is not sensitive to cracking temperatures. As shown in Figure 5, the \(\text{C}_2\text{H}_4\) selectivity achieved on the catalysts follows the sequence \((\text{Pr}_{0.75}\text{Yb}_{0.25})_2\text{Zr}_2\text{O}_7 > \text{Pr}_2\text{Zr}_2\text{O}_7 > (\text{Pr}_{0.5}\text{Yb}_{0.5})_2\text{Zr}_2\text{O}_7 > (\text{Pr}_{0.25}\text{Yb}_{0.75})_2\text{Zr}_2\text{O}_7 > \text{Yb}_2\text{Zr}_2\text{O}_7\). Among all catalysts, \(\text{Pr}_2\text{Zr}_2\text{O}_7\) demonstrates the best characteristics associated with high selectivity for \(\text{C}_2\text{H}_4\) (about 86%) at a temperature of 700 °C. At the same time, propane conversion was 48%. The catalyst \((\text{Pr}_{0.25}\text{Yb}_{0.75})_2\text{Zr}_2\text{O}_7\) showed the highest conversion of propane into reaction products at this temperature. This fact indicates that the change in the specific surface area of catalytic systems does not make a decisive contribution to the process of catalytic cracking of propane (Figure 7a). Of considerable interest is the establishment of the relationship between the structure and catalytic properties of compounds with a step-wise change in their composition in the series \(\text{Pr}_2\text{Zr}_2\text{O}_7 \rightarrow (\text{Pr}_{0.75}\text{Yb}_{0.25})_2\text{Zr}_2\text{O}_7 \rightarrow (\text{Pr}_{0.5}\text{Yb}_{0.5})_2\text{Zr}_2\text{O}_7 \rightarrow (\text{Pr}_{0.25}\text{Yb}_{0.75})_2\text{Zr}_2\text{O}_7 \rightarrow \text{Yb}_2\text{Zr}_2\text{O}_7\) with a fixed \(\text{Zr}^{4+}\) center in the B-position and various centers of rare-earth elements in the A-position.
It is known that compounds of the $A_2B_2O_7$ type have high thermal stability, intrinsic oxygen vacancies, and the presence of acid–base sites, which meets the requirements for promising materials for use as propane cracking catalysts. A detailed analysis of the properties of these materials makes it possible to determine the correlations between the presence of active electrophilic oxygen and acid–base centers in the material under study and its catalytic activity. The conducted studies on the adsorption of pyridine show a clear influence of the number of acid centers on the degree of conversion of propane (Figure 7b).

According to Hund’s rule, electron shells are stable when they are empty, full, or half full.

When studying the properties of the surface, all synthesized compounds of the Ln$_2$Zr$_2$O$_7$ series showed the presence of a combined variant of isotherms of types IV–V with a hysteresis loop of type H2. This fact points to close textural characteristics of the investigated samples of materials. However, the results of the quantitative determination of the specific surface area show that its decrease is observed in the series Pr$_2$Zr$_2$O$_7$ > (Pr$_{0.75}$Yb$_{0.25}$)$_2$Zr$_2$O$_7$ > (Pr$_{0.5}$Yb$_{0.5}$)$_2$Zr$_2$O$_7$ > (Pr$_{0.25}$Yb$_{0.75}$)$_2$Zr$_2$O$_7$ ≈ Yb$_2$Zr$_2$O$_7$. In this case, (Pr$_{0.5}$Yb$_{0.5}$)$_2$Zr$_2$O$_7$, (Pr$_{0.25}$Yb$_{0.75}$)$_2$Zr$_2$O$_7$, and Yb$_2$Zr$_2$O$_7$ have much higher pore volumes than Pr$_2$Zr$_2$O$_7$, (Pr$_{0.75}$Yb$_{0.25}$)$_2$Zr$_2$O$_7$. A decrease in the ratio r$_A$/r$_B$ or a decrease in the unit cell volume in the crystal structure in the series Pr$_2$Zr$_2$O$_7$ > (Pr$_{0.75}$Yb$_{0.25}$)$_2$Zr$_2$O$_7$ > (Pr$_{0.5}$Yb$_{0.5}$)$_2$Zr$_2$O$_7$ > (Pr$_{0.25}$Yb$_{0.75}$)$_2$Zr$_2$O$_7$ > Yb$_2$Zr$_2$O$_7$ leads to a change in the position reflections for Ln$_2$Zr$_2$O$_7$ towards larger angles 2θ. This is described in detail in Article [28], which studies our catalytic systems. This indicates the presence of the effect of compression of the unit cell caused by a decrease in the cation radii in the A-position.

The regions 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$4f, the separation of which corresponds to the formation of ions in the state of charge +3, that is, TR$^{3+}$. According to Hund rule a, electronic enclosures are stable when they are empty, full, or half full. Pr$^{3+}$ has two more electrons (4f$^2$) than required for stable electronic configurations, and Yb$^{3+}$ has one electron less (4f$^{13}$) than required for a stable electronic configuration. A sequential increase in the number of electrons at the 4f level increases the acidity of compounds containing REM.

Regarding the selectivity of ethylene, the opposite is observed. This pattern is in good agreement with the presence of available surface oxygen. Surface oxygen properties associated with intrinsic oxygen vacancies.

The general formula Ln$_2$Zr$_2$O$_7$ can be described as a defective solid solution of fluorite, in which cations form a face-centered cubic matrix, and one-eighth of the anions is unoccupied, which ensures charge neutrality. From this point of view, five unique crystallographic positions (Wyckoff symbols) are available: 16d for Ln cations, 16c for Zr cations, 48f for O and 8b (3/8, 3/8, 3/8) are stable and tetrahedrally coordinated cations Ln,
for O', and eight positions a (1/8, 1/8, 1/8) are free and shifted towards the neighboring empty eight a-sites and are associated with two Ln cations and two Zr cations.

The Ln–O and Zr–O bonds have a strong covalent character, and the calculated overlap populations are positive. The Ln–O bonds are divided into O8a–Ln and O8b–Ln, whereas for Zr–O, only one type of bond, O8f–Zr, is characteristic. A decrease in the lengths of the O–Ln bonds in the series Pr2Zr2O7 > (Yb2Zr2O7) is mainly due to the contraction of the 4f shell. These changes entail changes in the mechanisms of the catalytic conversion of propane. Since the distances between the catalytic centers change, the interatomic interactions between atoms decrease in the sequence OO' < OO < Ln–O < Zr–O. This leads to the appearance of various types of defects (Figure 8), and this means the appearance of additional catalytic sites.

Figure 8. Scheme of formation of type of defects.

Due to the deformations of the crystal structure that occur during a step-wise change in the samples’ composition, the geometric dimensions of the propane adsorption site, and the properties of the catalyst surface, change and the process of breaking the C–C bond is replaced by breaking the C–H bond. Crystal lattice distortions are the result of the replacement of Pr ions by Yb, and oxygen vacancies are not formed in this case. This result corresponds to a change in the reactivity of this series of catalysts in reactions proceeding according to the dehydrogenation mechanism C3H8 ⇌ C3H6 + H2. However, if all changes in the catalytic activity of the synthesized catalysts are associated with a change in the geometric dimensions of the crystal lattice, then a single dependence of the selectivity of “light” olefins on the number of primary adsorption centers should be observed. However, when passing to the Yb2Zr2O7 compound, this dependence is disrupted (Figure 9). In this case, the shape of the dependence of propane conversion on the number of catalytic sites of the catalyst (Figure 7a) repeats the shape of the dependence of ethylene selectivity on the number of primary adsorption centers (Figure 9a).

Figure 9. Dependence of selectivity for target products on the number of primary adsorption centers (a)—for ethylene, (b)—for propylene.
It is reasonable to believe that the amount of surfactant oxygen sites may be an important factor in controlling the direction of the reaction to form ethylene. Depending on the surface concentration of PAC, the adsorption of propane molecules will be completed with the formation of either isolated clusters in equilibrium with saturated steam or a continuous adsorption layer in the form of a film on the catalyst surface.

In the first case, the distance between the PACs must be greater than the limiting size of the propane cluster on the surface. In the second case, the minimum distance between PACs ($l_{\text{min}}$) should be less than the limiting size of clusters. The distance between PACs was calculated, assuming their uniform distribution over the catalyst surface. Based on the results of our calculations, a continuous adsorption layer is not formed on the surface since the distance between PACs is greater than 5 nm, which exceeds the limiting value. Such a distribution of PAC makes the C–C bond less strong during the adsorption of a propane molecule, which leads to the formation of predominantly ethylene.

Another important influence is exerted by the interaction strength of the propane molecule with the catalytic site, which depends on the value of the characteristic adsorption energy (Figure 10).

Figure 10. Dependence of selectivity for target products on the strength of the interaction of the reactant with the catalytic center (a)—for ethylene, (b)—for propylene.

The decrease in selectivity for ethylene and the increase in the amount of propylene in the reaction products observed in the series of propane cracking $\text{Pr}_2\text{Zr}_2\text{O}_7 \rightarrow (\text{Pr}_{0.75}\text{Yb}_{0.25})_2\text{Zr}_2\text{O}_7 \rightarrow (\text{Pr}_{0.5}\text{Yb}_{0.5})_2\text{Zr}_2\text{O}_7 \rightarrow (\text{Pr}_{0.25}\text{Yb}_{0.75})_2\text{Zr}_2\text{O}_7 \rightarrow \text{Yb}_2\text{Zr}_2\text{O}_7$ catalysts are associated with an increase in the interaction of propane carbon atoms with catalytic sites.

4. Materials and Methods
4.1. Synthesis Details

In the first stage, an ammonia solution was added to a solution of a mixture of Ln(NO$_3$)$_3$ and ZrOCl$_2$ salts (atomic ratio Ln:Zr = 1:1) with vigorous stirring. The resulting suspensions (pH = 9.0 ± 0.5) were filtered, and the precipitates were washed and dried at 100 °C. This technique provides the most uniform distribution of cations over the volume of precursor particles. The details of the synthesis procedure are described in [27]. In the second stage, a sample of powders was prepared from each type of the synthesized precursor by isothermal annealing in air for 6 h at a temperature of 1000 °C.

4.2. Physical Characteristics of Catalyst
4.2.1. X-ray Diffraction

The X-ray diffraction (XRD) of the Ln$_2$O$_3$ and ZrO$_2$ powder samples annealed at various temperatures was carried out using a Rigaku MiniFlex 600 diffractometer (CuKα-radiation, Tokyo, Japan). The patterns were recorded at room temperature in the Bragg–Brentano
reflection geometry for \(2\Theta = 10^\circ - 110^\circ\) using a step angle of 0.05\(^\circ\), with an exposure time of 3 sec. per step [28].

4.2.2. Specific Surface Area  

The parameters of the porous structure of the samples were determined from nitrogen vapor adsorption isotherms at 77 K, measured on an ASAP 2020-MR Micromeritics, Norcross, GA, USA, automatic high-vacuum setup in the relative pressure range from 0.001 to 0.98. The samples were preliminarily evacuated to a residual vacuum of less than 10–7 mmHg at 400 °C.

To do this, when processing experimental data, the BET Equation:

\[
a = \frac{a_m C_p}{p_s} \frac{p}{(1 - \frac{p}{p_s}) + [1 + (C - 1) \frac{p}{p_s}]
\]

To determine the porosity of the sample, the model proposed by Barrett, Joyner, and Halenda (BJH) was used, which allows you to calculate the pore volume and plot the pore size distribution. The calculation was made according to the Equation:

\[
w = \left( \frac{r_{pm}}{r_{mn} + \frac{\Delta t}{2}} \right)^2 \left( V_n - \Delta t \sum_{j=1}^{n-1} A_{C_j} \right)
\]

In this formula, \(w\) is the pore volume (cm\(^3\)/g), \(r_{mn}\)—pore radius (nm), \(r_{pm}\)—adsorbate molecule radius (nm), \(V\)—adsorbate volume (cm\(^3\)/g), \(t\)—adsorption layer thickness, and \(A_{C_j}\)—empty pore area.

4.2.3. Analysis of Catalytic Sites

Comparative evaluation of the number of primary adsorption centers of the samples obtained. Water adsorption isotherms were measured at 293 K on a vacuum weighing unit with McBain quartz spring balances with a sensitivity of 10 µg with a weight of up to 100 mg.

The determination of acid sites was controlled by UV absorption spectra of catalytic systems of pyridine molecules. The concentration was determined using a single-beam scanning spectrophotometer Agilent Cary 60 UV-Vis (Santa Clara, CA, USA).

The formula by which the Gibbs adsorption was determined (g × mol/g):

\[
N = \frac{(C_0 - C_T) \times V}{m} = \frac{(D_0 - D_T) \times V}{m \times \varepsilon \times l}
\]

where \(V\) is the volume of the solution (4 mL); \(m\) is the mass of the sample (0.01 g); \(D_0\) and \(D\)—optical density at the absorption maximum Py (Bac) before and during adsorption; \(l\) is the cell thickness (1 cm); \(\varepsilon\)—molar absorption coefficient (extinction, \(\varepsilon_{Py} = 2 \times 10^6 \text{ L/(mol·cm)}\), \(\varepsilon_{Bac} = 1 \times 10^4 \text{ L/(mol·cm)}\)).

The analytical absorption bands \(\lambda_{max}(\text{Bac}) = 230\text{ nm}\) and \(\lambda_{max}(\text{Py}) = 253\text{ nm}\) did not change in the presence of the adsorbent.

4.3. Catalytic Studies

Catalytic cracking of propane was carried out in a temperature range of 100–900 °C with a step of 50 °C on a bench-top unit with a flow reactor. The reaction was monitored at each temperature point using a Kristall 5000M chromatograph (Yoshkar-Ola, Russia) equipped with a flame ionization detector and a thermal conductivity detector.
The calculation of the atomic rate of formation of the main components (value \( w \)) is performed according to the Equation:

\[
\dot{w} = K \frac{w_{\text{out}} \times s}{V_{\text{sample}}} \text{[\( \mu \text{mol/g} \times \text{s} \)}
\]

where \( K \) is the correction factor of the detector sensitivity to analytes; \( w_{\text{out}} \)—is the rate of exit of the reaction mixture, referred to as the mass of the catalyst \( \mu \text{mol/(g \cdot s)} \); \( s \)—is the area of the chromatographic peak; \( V_{\text{sample}} \) is the volume of the injected mixture.

Selectivity for each component is calculated by the formula:

\[
S_x = \frac{a_i \times n_x}{n_{\text{in}} - n_{\text{res}}} \times 100\%
\]

where \( a_i \) is the number of carbon atoms in the product (i), \( n_x \) is the molar flow of product (i) at the reactor outlet, \( n_{\text{in}} \) and \( n_{\text{res}} \) are the molar flow of \( \text{C}_3\text{H}_8 \) at the inlet to the reactor and the molar flow of \( \text{C}_3\text{H}_8 \) at the outlet of the reactor.

The degree of propane conversion was determined when the steady state was reached by the amount of propane that reacted:

\[
a = \frac{n_{\text{in}} - n_{\text{res}}}{n_{\text{in}}} \times 100\%
\]

Since the number of active centers is not known for certain, the surface turnover frequency (TOF_{surf}) was calculated; the number of catalytic conversion events per unit time per unit surface was measured by nitrogen adsorption by the BET method.

\[
\text{TOF}_{\text{surf}} = \frac{1}{\tau} \times \frac{n_{\text{C}_3\text{H}_8}}{N_{\text{kat}}} \text{[s}^{-1}\text{]}
\]

the number of reacted propane molecules on the catalyst surface per unit time of.

The carbon balance (“carbon balance”, %), which makes it possible to estimate the proportion of formed amorphous carbon involved in the process of surface deactivation, was calculated by the formula:

\[
\frac{n(\text{C}_3\text{H}_8)_{\text{res}} + n(C)_{\text{rec}} n(\text{CH}_4)_{\text{rec}} + n(\text{C}_2\text{H}_4)_{\text{rec}} + n(\text{C}_2\text{H}_6)_{\text{rec}} + n(\text{C}_3\text{H}_6)_{\text{rec}}}{n(\text{C}_3\text{H}_8)_{\text{source}}} \times 100
\]

Using the dependence of the reaction rate on temperature:

\[
\ln \dot{w} = \ln A - \frac{E_a}{RT}
\]

where \( E_a \) is the observed activation energy of the process (kJ/mol).

5. Conclusions

In the course of the study, catalysts with a step-wise measurement of the composition of \( \text{Pr}_2\text{Zr}_2\text{O}_7; (\text{Pr}_{0.75}\text{Yb}_{0.25})_2\text{Zr}_2\text{O}_7; (\text{Pr}_{0.5}\text{Yb}_{0.5})_2\text{Zr}_2\text{O}_7; (\text{Pr}_{0.25}\text{Yb}_{0.75})_2\text{Zr}_2\text{O}_7 \) and \( \text{Yb}_2\text{Zr}_2\text{O}_7 \) for propane cracking were synthesized. Inductively coupled plasma atomic emission spectrometry (ICP-AES) was used to quantify the concentration of elements in all synthesized catalysts. In order to estimate the number of primary adsorption centers of the obtained samples, water adsorption isotherms were measured at a temperature of 293 K. It is shown that an increase in the number of primary adsorption centers leads to the predominance of the destruction mechanism. The location of the catalytic centers becomes closer, which contributes to the alignment of the propane molecule with the localization of all carbon atoms on the surface and the breaking of the C–C bond. The formation of propylene decreases in the series \( \text{Yb}_2\text{Zr}_2\text{O}_7 > (\text{Pr}_{0.25}\text{Yb}_{0.75})_2\text{Zr}_2\text{O}_7 > (\text{Pr}_{0.5}\text{Yb}_{0.5})_2\text{Zr}_2\text{O}_7 > (\text{Pr}_{0.75}\text{Yb}_{0.25})_2\text{Zr}_2\text{O}_7 \approx \)}
When ytterbium ions are introduced into the catalyst, the amount of ethylene in the reaction decreases, but the selectivity for propylene increases in the series \( \text{Pr}_2 \text{Zr}_2 \text{O}_7 \) - \( \text{Yb}_0.25 \text{Zr}_2 \text{O}_7 \) - \( \text{Yb}_0.5 \text{Zr}_2 \text{O}_7 \) - \( \text{Yb}_0.75 \text{Zr}_2 \text{O}_7 \). The selectivity for ethylene is consistently reduced from 85% to 28% in several catalysts \( \text{Pr}_2 \text{Zr}_2 \text{O}_7 \) - \( \text{Yb}_0.25 \text{Zr}_2 \text{O}_7 \) - \( \text{Yb}_0.5 \text{Zr}_2 \text{O}_7 \) - \( \text{Yb}_0.75 \text{Zr}_2 \text{O}_7 \) - \( \text{Yb}_2 \text{Zr}_2 \text{O}_7 \). When ytterbium ions are introduced into the catalyst, the amount of ethylene in the reaction decreases, but the selectivity for propylene increases in the series \( \text{Pr}_2 \text{Zr}_2 \text{O}_7 \) - \( \text{Yb}_0.25 \text{Zr}_2 \text{O}_7 \) - \( \text{Yb}_0.5 \text{Zr}_2 \text{O}_7 \) - \( \text{Yb}_2 \text{Zr}_2 \text{O}_7 \), which is associated with a decrease in the binding energy of carbon atoms in propane with the catalytic center during adsorption and breaking of the C–H bond.

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