Effect of Alkaline Additives over V-Based Catalysts Supported on γ-Al₂O₃ for Propane Oxidative Dehydrogenation

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ABSTRACT

The olefins product are more reactive than the corresponding alkanes, and may easily be superoxidised into CO and CO₂ in selective oxidation of alkanes. The proper balance of acid and base sites on the V-based catalyst surface plays a decisive role in limiting the complete oxidation of alkanes. Therefore, our goal was to evaluate the promoting effect of alkali metals and the support effect using boehmite as precursor for the propane oxidative dehydrogenation (ODH) reaction. Catalysts were prepared via co-impregnation of V and Na or K on a synthesized alumina support. The following characterization techniques were used: N₂ adsorption-desorption, X-ray diffraction (XRD), temperature programmed reduction (TPR) and isopropanol decomposition tests to evaluate the acid-base character. The catalyst performance in the propane ODH reaction was evaluated at the O₂:C₃H₈:He molar ratios of 5:2:4, 6:1:4, and 4:3:4. The K-doped catalysts exhibited higher propene selectivity owing to the modification of acid-base character that rendered the weaker interaction between olefinic intermediate and more basic catalyst surface. A high molar fraction of O₂ of the reaction mixture minimized coke formation and a high reoxidation rate possibly increased catalytic activity and propene selectivity.

Keywords: Propane oxidative dehydrogenation; alumina; V; Na; K.

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1. INTRODUCTION

Propene is one of the most important feedstocks in the petrochemical industry to produce mainly polypropylene, propylene oxide and acrylonitrile [1]. The main commercial processes for producing propene are steam cracking, fluid catalytic cracking (FCC) and catalytic dehydrogenation [2-4]. However, the capacity of the aforementioned processes to produce propene is limited, owing to their high-energy requirements and coke formation and so frequent catalytic regeneration is required. Catalytic dehydrogenation is a reversible reaction due to the hydrogen involved, and therefore the production of olefins is limited by thermodynamic equilibrium [4].

Recently, the growing global olefins demands has stimulated the search for environmental-friendly and exothermic processes for reducing energy costs [4,5]. In this scenario, propane oxidative dehydrogenation (ODH) has been pointed out as an alternative method for propene production that has the advantage of being an exothermic reaction; moreover it overcomes the thermodynamic restrictions of non-oxidative dehydrogenation owing to the formation of water ending the process. In addition, the use of O₂ in the reaction mixture minimizes the deposition of coke and ensures a long catalyst lifetime. However, the greatest challenge lies in obtaining selective catalysts that can inhibit the complete oxidation of olefins that leads to the formation of CO and CO₂ as by-products [5-7]. The propene yields reported in propane ODH reactions (less than 30%) are still not sufficient to satisfy economic feasibility [5].

Propene is a low-cost feedstock that can be found as a component of natural gas and it is easy to separate, making it a valuable but non-renewable gas. On the other hand, an emerging technology for the production of renewable “green” propane or bio-propane is gaining notoriety where it is already being operated on a large-scale production. Green propane has the potential to be produced from biomass, including as a side-product in the production of biodiesel, from glycerol and other substrates [8]. Therefore, there is a trend in the search for green and renewable routes to meet environmental concerns.

Boron-based catalysts have emerged as one of the most active and selective catalysts. The inhibition of the further dehydrogenation reaction of propene by a large energy barrier has revealed the cause of a high selectivity [9,10]. On the other hand, the supported vanadium species are particularly one of the active components with redox properties of the greatest interest for hydrocarbons partial oxidation reactions; moreover, vanadium is a transition metal easily found in nature [11,12]. The change in the oxidation state of vanadium during the propane ODH reaction has been better understood by the Mars-van-Krevelin (MVK) mechanism, which involves two steps [13,14]:

(i) the reduction of $V^{5+}$ to $V^{4+}$ by the reaction of propane with catalyst oxygen, forming propene and water molecules;
(ii) the subsequent re-oxidation of the catalyst by $O_2$, completing the redox cycle $V^{5+}/V^{4+}$.

Recently, spectrometric measurements during the propane ODH reaction have allowed the identification of reaction intermediates to uncover reaction mechanisms. The most recent research findings are reported in paper published by Ternero-Hidalgo et al. [15]. The proposed mechanism was the propane activation, as the rate determining step in the reaction, that occurs via the irreversible formation of isopropoxide species, which can be desorbed as propylene or further oxidized to chemisorbed acetone. The latter can be converted into acetate (CH₃CHOO⁻) and formate (CHOO⁻) species, which would be the precursors of CO₂. The propene formed during reaction can be adsorbed again on the surface and oxidized to isopropoxide species via neighboring V-OH groups such as Brønsted acid sites and continues with the subsequent steps for CO₂ formation.

The use of CO₂ instead of O₂ has received considerable attention, as a mild oxidant, preventing deep oxidation, and consequently increasing the propene selectivity. Under these conditions, higher degree of reduction of vanadia species during the propane ODH reactions has been linked to higher selectivity [16,17]. Nevertheless, the low olefin yield, poor catalyst stability and the demand for heating source due to the endothermic nature of the reactions constrain the CO₂-ODH process [17]. Therefore, the use of O₂ as an oxidant in this study was more appropriate, in addition to being an abundant and low-cost feedstock. Changes in the O₂:CH₃H₈ molar ratio, also proposed in this study, can affect the reoxidation rate and, therefore, the ratio of the $V^{5+}/V^{4+}$.
Supported vanadium oxide catalysts are the conventional metal-based catalysts of the propane ODH reactions. However, its high reactivity deals with the formation of excess electrophilic oxygen species that increases the formation of CO and CO₂, decreasing the selectivity to propylene [5,6]. The balance of acid and base sites on the V-based catalyst surface via the addition of alkaline and alkaline earth promoters has been a crucial parameter for propene selectivity control. The use of modifiers, such as alkali metals, can weaken the adsorption of propene on the less acidic and more basic surface of catalysts, avoiding the deep oxidation [18-20]. Teixeira-Neto el al. [21] studied the behavior of V-modified MCM-22 zeolite toward propane ODH reaction and noted that ion-exchange with alkaline ions led to a decrease in cracking reactions, by removing the strong Brønsted acid sites. Furthermore, the changes in the physical-chemical and structural properties of different V-based catalysts have been studied for understanding the influence of promoters on catalytic performance [18,22].

The support effect is also an important factor. The textural properties and lower acidity of Al₂O₃ than that of other oxides, such as TiO₂ and ZnO, has favored the dispersion of superficial V species [11]. The formation of isolated tetrahedral V⁵⁺ species seems to be the most suitable for higher propene selectivity [23]. For this reason, the use of alumina as an oxide support for V-containing catalysts for propane ODH reactions has provided higher propene selectivity [24-26]. Several methods can be used for the synthesis of aluminum hydroxide precursors, Al(OH)₃, or aluminum hydroxide oxides, AlO(OH), which generate transition alumina when it subjected to a heat treatment, [27,28].

Our goal of this study was to evaluate the promoting effect of K and Na as additive and the effect support using boehmite as precursor to increase propene selectivity of the propane ODH reaction. The effect of changing acid-base properties, via alkali metals addition, on V-based catalyst activity was essentially evaluated. Unlike the use of commercial alumina, this work also proposed the synthesis of an efficient alumina for use as a support. The reaction conditions were taken into account, modifying the O₂/propane molar ratio of the reaction mixture.

2. MATERIALS AND METHODS

2.1 Synthesis

The aluminum hydroxide precursor was prepared using the precipitation method via the addition of AlCl₃ (pH = 0.5) into a NaOH solution (pH = 12.9), which was placed in a batch reactor at 65 °C under mechanical stirring until the pH was approximately 9.5. The obtained precipitate was washed with distilled water, dried, and calcined at 600 °C for 5 h to obtain the alumina support, which was denoted as Al₂O₃ (B). To synthesize alumina-supported V catalysts, the support was subjected to wet impregnation with excess solvent (water). Half-monolayer impregnation of 4 V atoms per square nanometer of alumina was performed by mixing a NH₄VO₃ solution heated to 70 °C and powder carrier in a vacuum rotary evaporator. Thereafter, the residual powder was dried and calcined at 450°C for 5 h, and the prepared catalyst was denoted as 4V-Al (B). The alkali-metal-doped catalysts were prepared via the co-impregnation of V (half monolayer) and alkali metals (x = 0.5 and 1.0 Na or K atoms per square nanometer of support) on alumina. The doped catalysts were synthesized according to the aforementioned method using a mixture of NaOH or KOH aqueous solutions and NH₄VO₃ for co-impregnation. The prepared catalysts were denoted as 4V-xNa-Al (B) and 4V-xK-Al (B).

2.2 Physicochemical Characterization

The specific surface areas and pore volume (Brunauer–Emmett–Teller method) and pore volume distribution (Barrett–Joyner–Halenda method) were determined using N₂ adsorption–desorption isotherms, which were obtained at -196 °C using a Belsorp-mini-II instrument. The samples were pretreated in situ under vacuum and were subsequently heated at 200°C for 2 h.

X-ray diffraction (XRD) analyses were performed using a PANalytical Empyrean instrument with Cu Kα radiation (λ = 0.1544 nm) at a power of 30 kV, current of 20 mA, and goniometer angular velocity of 0.02°/s in the 2θ range of 10-80°. Temperature programmed reduction (TPR) experiments were performed using a Quantachrome, ChemBET-3000 system equipped with a thermal conductivity detector (TCD). Samples (0.05 g) were dried in situ at 200°C for 2 h under a He flow. Next, the solids were cooled to room temperature and reduced at 900 °C (temperature ramp of 10 °C/min) with a 5% H₂/N₂ mixture (flow rate of 30 mL/min).
Isopropanol decomposition tests were performed at atmospheric pressure in a fixed-bed borosilicate glass reactor to evaluate the acid-base surface properties of the samples. The reactor was fed with isopropanol (99.7%), which was injected using a Thermo Separation Products P100 pump at a flow rate of 0.02 cm$^3$min$^{-1}$ and was diluted with a He and N$_2$ mixture at a flow rate of 37.5 cm$^3$min$^{-1}$. The effluent gases were analyzed on line using a Varian 3380 chromatograph equipped with a TCD and a Poropak-Q column (4.5 m). The reaction was evaluated in the temperature range of 100-300 °C using 150 mg of catalysts and the residence time (W/F$\text{isop}$) of 6.3 ghmol$^{-1}$. The conversion of isopropanol ($X$$_{\text{isop}}$), product selectivity ($S$$_j$), specific reaction rate ($S$RR), and the specific rate of product formation ($S$RP) were calculated as follows:

$$X_{\text{isop}}(\%) = \frac{\sum z_j n_j}{3 n_{\text{isop}} + \sum z_j n_j} \times 100$$  \hspace{1cm} (3)

$$S_j(\%) = \frac{z_j n_j}{\sum z_j n_j} \times 100$$  \hspace{1cm} (4)

$$S_{\text{RR}} = \frac{x_{\text{isop}}(\%) \times F_{\text{isop}}}{W \times S_g}$$  \hspace{1cm} (5)

and

$$S_{\text{RP}} = \frac{S_j(\%) \times S_{\text{RR}}}{S_g}$$  \hspace{1cm} (6)

where $n_{\text{isop}}$ is the number of moles of unconverted isopropanol in the product stream, $n_j$ is the number of moles of gaseous carbon in product “j”, $z_j$ is the number of carbon atoms in gaseous carbon-containing product “j”, $F_{\text{isop}}$ is the reactor outflow of isopropanol, W is the catalyst weight, and $S_g$ is the specific surface area.

### 2.3 Catalytic Test

The catalytic activity of the prepared catalyst samples for the propane ODH reaction was tested at atmospheric pressure at a range temperature of 300-500°C in a fixed-bed quartz microreactor (Fig. 1). The thermocouple placed inside the catalyst (0.15 g) was used to measure and control the temperatures and mass flow controller was used to control the gas flow (O$_2$, He and propane). The O$_2$:C$_3$H$_8$:He molar ratios were 5:2:4, 6:1:4, and 4:3:4 and the total flow rate was 48 ml.min$^{-1}$. The molar fraction of He and the total flow rate was maintained constant to determine the effect of the O$_2$:C$_3$H$_8$ molar ratio on the catalytic activity of the catalyst samples. The concentrations of unconverted propane and products were analyzed on line using a Varian 450 chromatograph equipped with a TCD using two 1/8" diameter columns. The stationary phases consisted of HS-N (80/100) and MS-13X (45/60).
The performance of the catalysts was assessed using the conversion of propane \( X_{C_3H_8}(\%) \), product selectivity \( S_i \), and propene yield \( Y_{C_3H_6} \), which can be calculated as follows:

\[
X_{C_3H_8}(\%) = \frac{\sum z_i n_i}{3n_{propane}+\sum z_i n_i} \times 100
\]

(7)

\[
S_i(\%) = \frac{x_i n_i}{\sum x_i n_i} \times 100
\]

(8)

and

\[
Y_{C_3H_6}(\%) = \frac{X_{C_3H_8}(\%) \times S_{C_3H_6}(\%)}{100}
\]

(9)

where \( n_{propane} \) is the number of moles of unconverted propane in the product stream, \( n_i \) is the moles of gaseous carbon in the product “i”, and \( z_i \) is the number of carbon atoms in the gaseous carbon-containing product “i”. These equations were considered suitable for evaluating the performance of the catalysts because they provide accurate results, which depend on the reaction products measured using TCD analysis [29].

3. RESULTS AND DISCUSSION

3.1 Physicochemical Characterization

The textural characteristics of the transition alumina and vanadium-and-alkali-metal-based catalysts are summarized in Table 1. The impregnation of vanadium oxide onto the alumina support caused a reduction in the values of the specific area \( S_{BET} \) and pore volume \( V_p \). The \( S_{BET} \) value decreased with increasing Na content. Conversely, \( S_{BET} \) increased with the addition of 1.0 K atom per square nanometer of alumina and can be attributed to the greater pore blockage caused by K⁺ ions, whose ionic radius is higher than that of Na⁺ ions.

Fig. 2 illustrates the \( N_2 \) adsorption-desorption isotherms of the samples. The undoped and alkali-metal-doped V catalysts (Fig. 2b-c) and \( Al_2O_3 \) (B) support (Fig. 2a) presented similar \( N_2 \) adsorption-desorption isotherms, which were type-IV isotherms with H-2 hysteresis loops according the IUPAC classifications, indicating that they had an ink-bottle mesoporous structure. In addition, the hysteresis loops length and pore volume decreased with addition of V and alkali metals, indicating the modification of texture properties.

Fig. 3 presents the \( V_p \) distribution curves of the alumina and respective catalysts. The radius of most pores of the alumina support was between 1 and 3 nm (Fig. 3a). However, the V-based catalysts presented the radius of most pores between 1 and 5 nm (Fig. 3b-d); possibly, the radius of pores increased because of the accommodation of V species and alkali metal ions into the pores.

Fig. 4 shows the XRD profiles of the alumina support and catalysts. The alumina precursor presented orthorhombic aluminum hydroxide oxide (boehmite) structure (ICCD: 05-0190, \( 2\theta = 13.46°, 28.08°, 38.58°, 49.1°, 64.94°, 71.90° \)). Upon calcination at 600 °C, the boehmite precursor formed \( \gamma-Al_2O_3 \) (ICCD: 10-0425, \( 2\theta = 46.12°, 66.86° \)), which presented low crystallinity. The XRD profiles of the catalysts impregnated with vanadium oxide and alkali metals were very similar to that of the alumina support. The absence of peaks related to bulk compounds indicated a good dispersion of superficial VO₂ species. However, the formation of possible clusters of V nanoparticles (<4 nm), which are detectable by spectroscopic analysis, such as Raman and UV-Vis, could not be ruled out [29,30], although the total V + K or V + Na coverage was below a monolayer. Furthermore, the dispersion of vanadium oxide depends on the textural properties, concentration of surface hydroxyl groups of oxide support for anchoring V species, synthesis methods and vanadium precursors [5,12]. For us, the purpose of catalyst synthesis was achieve a better dispersion of V species for a half-monolayer, which are possibly the most selective for propane oxidative dehydrogenation reactions.

<table>
<thead>
<tr>
<th>Support/ Catalysts</th>
<th>( S_{BET} ) (m²g⁻¹)</th>
<th>( V_p ) (cm³g⁻¹)</th>
<th>( R_p ) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( Al_2O_3 ) (B)</td>
<td>330</td>
<td>0.54</td>
<td>2.36</td>
</tr>
<tr>
<td>4V-Al (B)</td>
<td>176</td>
<td>0.27</td>
<td>3.12</td>
</tr>
<tr>
<td>4V-0.5Na-Al (B)</td>
<td>182</td>
<td>0.25</td>
<td>2.41</td>
</tr>
<tr>
<td>4V-1.0Na-Al (B)</td>
<td>169</td>
<td>0.24</td>
<td>2.41</td>
</tr>
<tr>
<td>4V-0.5K-Al (B)</td>
<td>159</td>
<td>0.26</td>
<td>3.12</td>
</tr>
<tr>
<td>4V-1.0K-Al (B)</td>
<td>180</td>
<td>0.25</td>
<td>2.41</td>
</tr>
</tbody>
</table>
Fig. 2. \( N_2 \) adsorption-desorption isotherms of the Al\(_2\)O\(_3\) (B) support and catalysts loaded with vanadium oxide and alkali metals

Fig. 3. \( V_p \) distribution curves of the Al\(_2\)O\(_3\) (B) support and catalysts loaded with vanadium oxide and alkali metals
Fig. 4. X-ray diffractograms of catalyst samples. The □ and ■ peaks represent gibbsite and \( \gamma \)-\( \text{Al}_2\text{O}_3 \) phases, respectively.

The TPR profiles of the catalysts are presented in Fig. 5. The undoped V catalyst exhibited a single reduction temperature peak (532°C), which corresponded to the reduction of \( \text{V}_2\text{O}_5 \) to \( \text{V}_6\text{O}_{13} \). However, the same reduction peak shifted to higher temperatures (538-557°C) for doped V catalysts that indicated a decrease in reducibility, owing to the higher inhibition of vanadium active sites by the alkali metal ions [19]. A second reduction peak emerged at 570°C for 4V-0.5K-Al (B) catalyst, which could be associated with the formation of vanadium oxide aggregates that were caused by less dispersion of surface V species or compounds that were formed between potassium and vanadium.

The SRR and SRP values for the decomposition of isopropanol at 280 and 300°C are summarized in Tables 2 and 3, respectively. For the evaluation of acid-base properties, the product distribution was analyzed according to the nature of surface sites. The formation of propene via isopropanol dehydration requires the presence of Lewis or Bronsted acid sites, whereas the formation of acetone via isopropanol dehydrogenation occurs at basic or redox sites. Diisopropyl ether are formed via intermolecular dehydration at strong and medium strength Lewis sites and basic sites [31,32]. The addition of V to alumina support increased substantially the catalytic activity and propene production. The high propene SRP and onset of acetone formation indicated the strong acid and redox character of V species. In contrast, the addition of alkali metals led to a decrease in SRR and propene SRP, being proportional to alkali metal content of the catalysts. The inhibition of acid sites by K was more pronounced that of Na, because the ionic radius of \( \text{K}^+ \) is higher than that of \( \text{Na}^+ \). The acetone production, which occur preferentially at basic sites, increased for the doped catalysts. Only traces of diisopropyl ether were observed during the tests.

Table 2. Specific reaction rate (SRR) and specific rate of product formation (SRP) of the support and catalysts at 280 °C

<table>
<thead>
<tr>
<th>Support/ Catalysts</th>
<th>SRR (μmolm⁻²min⁻¹)</th>
<th>SRP (μmolm⁻²min⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Al}_2\text{O}_3 ) (B)</td>
<td>1.71</td>
<td>1.71</td>
</tr>
<tr>
<td>4V-Al (B)</td>
<td>16.1</td>
<td>14.3</td>
</tr>
<tr>
<td>4V-0.5Na-Al (B)</td>
<td>12.7</td>
<td>10.4</td>
</tr>
<tr>
<td>4V-1.0Na-Al (B)</td>
<td>10.7</td>
<td>7.4</td>
</tr>
<tr>
<td>4V-0.5K-Al (B)</td>
<td>10.4</td>
<td>6.9</td>
</tr>
<tr>
<td>4V-1.0K-Al (B)</td>
<td>6.72</td>
<td>4.1</td>
</tr>
</tbody>
</table>
Fig. 5. Temperature programmed reduction curve of the catalysts

Table 3. Specific reaction rate (SRR) and specific rate of product formation (SRP) of the support and catalysts at 300 °C

<table>
<thead>
<tr>
<th>Support/Catalysts</th>
<th>SRR (μmolm⁻²min⁻¹)</th>
<th>SRP (μmolm⁻²min⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Propene</td>
<td>Acetone</td>
</tr>
<tr>
<td>Al₂O₃ (B)</td>
<td>4.4</td>
<td>4.4</td>
</tr>
<tr>
<td>4V-Al (B)</td>
<td>30.9</td>
<td>27.3</td>
</tr>
<tr>
<td>4V-0.5Na-Al (B)</td>
<td>25.9</td>
<td>22.1</td>
</tr>
<tr>
<td>4V-1.0Na-Al (B)</td>
<td>21.3</td>
<td>15.7</td>
</tr>
<tr>
<td>4V-0.5K-Al (B)</td>
<td>20.8</td>
<td>14.5</td>
</tr>
<tr>
<td>4V-1.0K-Al (B)</td>
<td>15.3</td>
<td>9.9</td>
</tr>
</tbody>
</table>

3.2 Catalytic test

Fig. 6 shows the catalytic performance of the undoped and alkali-metal-doped V catalysts for the propane ODH reaction at the O₂: C₃H₈:He molar ratio of 5:2:4. The highest propene yields were observed at the beginning of the experiments (300 °C) for all catalysts (Fig. 6b). In contrast, the propane conversion increased (Fig. 6a) and propene yield decreased at higher temperature (500 °C) owing to the olefin combustion process to form CO and CO₂. However, the propane conversion at 300 °C and 500 °C decreased with the addition of alkali metals, because of the effect of the dopants on the redox properties of V. Furthermore, a certain number of propane adsorption centers were blocked by the alkali metal ions, affecting reagent accessibility [33].
Fig. 6. Propane conversion (a) and propene yield (b) of the catalysts during propane oxidative dehydrogenation

The start of the combustion processes is depicted in Table 4. The production of CO, over the alkali-metal-doped catalysts started at higher temperatures than that of the undoped catalyst. These results were attributed to the alkali metal ions blocking the strong acid and nonselective sites that favor the formation of CO. [19]. This effect was more significant for the K-doped catalysts because of the ion radius of K⁺ being larger than that of Na⁺. The higher inhibition of the acidic sites by K is confirmed by the lowest propylene production, since propylene production during the isopropanol decomposition reaction require the presence of acid sites.

Table 4. Catalytic activity for the propane oxidative dehydrogenation reaction

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Initial propane conversion (%)</th>
<th>Initial propene yield a (%)</th>
<th>Initial combustion temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4V-Al (B)</td>
<td>64.8</td>
<td>64.8</td>
<td>322</td>
</tr>
<tr>
<td>4V-0.5Na-Al (B)</td>
<td>61</td>
<td>61</td>
<td>356</td>
</tr>
<tr>
<td>4V-1.0Na-Al (B)</td>
<td>44.5</td>
<td>44.5</td>
<td>357</td>
</tr>
<tr>
<td>4V-0.5K-Al (B)</td>
<td>53.4</td>
<td>53.4</td>
<td>380</td>
</tr>
<tr>
<td>4V-1.0K-Al (B)</td>
<td>49</td>
<td>49</td>
<td>370</td>
</tr>
</tbody>
</table>

aThe highest propene yields were observed at the beginning of the reactions.
Fig. 7. Propene selectivity during propane oxidative dehydrogenation

Fig. 8. Propane conversion (a) and propene yield (b) of the 4V-0.5K-Al(B) catalyst at different O₂:C₃H₈:He molar ratios

Interactions of propane molecules with a large number of oxygen active sites restored to the catalytic structure that were sufficient to selectively convert propane to propylene [6]. Conversely, the catalytic performance decreased when the molar fraction of O₂ was lower (O₂:C₃H₈:He = 4:3:4); catalytic activity and propene yield decreased owing to a possible
insufficient O replacement in the catalytic structure [6]. Moreover, at the O₂:C₃H₈:He molar ratio of 4:3:4, catalyst deactivation increased with the coke formation, in that the catalyst samples appeared blackened after the catalytic test. Therefore, O₂ played an important role for preventing the deposition of coke on the catalyst surface [7] with increasing O₂ molar fraction.

The propene selectivity curves of the 4V-0.5K-Al(B) catalyst at different O₂:C₃H₈:He molar ratios are presented in Fig. 9. The increase in O₂ molar fraction improved the propylene selectivity. Some studies have reported a greater reduction of V cations with decreasing amount of O₂, which favored selectivity to olefins [6,7,35-37]. In this specific study, however, a higher O₂ molar fraction facilitated catalytic regeneration, providing an increase in propene yield and decreased production of CO and CO₂. Therefore, the propene selectivity depends on the oxygen/alkane feeding ratios and the composition and physicochemical properties of the prepared catalysts during the catalytic test usually carried out at atmospheric pressure. Thus, the O₂:C₃H₈:He molar ratio of 6:1:4 was the most suitable for the propene ODH reaction.

![Propene Selectivity Curves](image)

**Fig. 9.** Propene selectivity of the 4V-0.5K-Al (G) catalyst at different O₂:C₃H₈ molar ratios

Higher reaction temperatures may promote the adsorption of oxygen on the surface of catalysts, and therefore higher rates of re-oxidation may have favored the increase in propane conversion (Fig. 6a and Fig. 8a) [38]. However, higher reaction temperatures favored the undesired reactions that decreased the propene selectivity (Fig. 9).

The alkali metal dopants have been reported to improve propene selectivity but have been associated with a decrease in catalytic activity and can be attributed to the alkali metal ions blocking the strong acid and nonselective sites [18,19]. The catalysts prepared in this study presented same behavior, with the important contribution of alkali metals and O₂ in the selectivity to propylene.

4. CONCLUSION

The precipitation method was satisfactory, since the synthesized alumina support presented specific area and pore volume suitable for the dispersion of surface V species; the XRD analyzes did not indicate the significant agglomeration of such species. The change in acid-base properties with the addition of potassium, as a promoter, provided better propene selectivity and can be attributed to the weak interaction between the olefinic intermediates and more basic catalyst surface. The change in C₃H₈:O₂ molar ratios during the propane ODH tests revealed the importance of the availability of oxygen of the reaction mixture for replacement in the catalytic structure and prevention of coke formation. The 4V-0.5K-Al (B) catalyst was the most selective (high initial conversion of propane of approximately 63% at 300°C and the O₂:C₃H₈:He molar ratio of 6:1:4) eliminating the complete oxidation to CO and CO₂. The performance of the K-doped catalysts was superior to previously published results [18,19,39,40] in that the combustion catalysts were partially inhibited with the presence of the alkali metal promoters. Therefore, further detailed studies should be performed to elucidate the interactions of alkali metals with support materials prepared in this paper and the influence of O₂:C₃H₈ molar ratio for a promising catalytic efficiency.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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