

Oxidative Dehydrogenation of Propane over Vanadium Catalyst Supported on Alkali-Modified χ -Al₂O₃

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Authors' contributions

This work was carried out in collaboration among all authors. All authors read and approved the final manuscript.

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ABSTRACT

The propane oxidative dehydrogenation (ODH) reaction has been considered as an alternative method for propene production owing to its exothermic nature, which renders it environmentally friendly. The use of alkaline promoters for supported V catalysts can increase propene selectivity and partially inhibit the formation of CO and CO₂. Our goal was to evaluate the promoting effect of K and Na and the support effect using gibbsite as precursor for the propane ODH reaction. Catalysts were prepared via co-impregnation of V and alkali metals on a previously prepared alumina support and were characterized using N₂ adsorption-desorption, X-ray diffraction, temperature-programmed reduction, and isopropanol decomposition tests to evaluate their acid-base properties. The activity of the synthesized catalysts for 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 addition of alkali metals to the V catalysts increased propane conversion and propene selectivity; moreover, both parameters increased with increasing molar fraction of O₂ in the reactants. K doping increased the propene selectivity of the doped catalysts, because it inhibited a large fraction of catalytic surface acidic sites. A high molar fraction of O₂ in the reactants facilitated the regeneration of the catalyst, whereas a high reoxidation rate improved catalytic activity and propene selectivity.

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1. INTRODUCTION

Propene is the main chemical for the synthesis of a wide variety of petrochemical derivatives, mainly polypropylene, propylene oxide, and acrylonitrile [1]. The conventional processes for producing propene are steam cracking, fluid catalytic cracking (FCC), and catalytic dehydrogenation [2-5]. Recently, the conversion of propane to propene has received increasing attention because of the limited capacity of the aforementioned processes to produce propene, which cannot meet the growing global demands [5,6]. Oxidative dehydrogenation (ODH) is a promising alternative process for the synthesis of propene from propane, which is a low-cost feedstock. Unlike conventional alkene production methods, the propane ODH reaction requires much lower temperatures; moreover, the use of O₂ as a reactant minimizes the formation of coke and ensures a long catalyst lifetime.

In addition, as an exothermic reaction, the propane ODH reaction overcomes the thermodynamic restrictions of non-oxidative dehydrogenation owing to the formation of water at the end of the process. However, because of the side reactions leading to the formation of CO_x, the propene yield of the propane ODH reaction is not sufficient for industrial production. The olefins product are more reactive than the corresponding alkanes, and may easily be super-oxidised into CO₂ [6-9]. The design of efficient catalysts and selection of appropriate reactors are key factors for the commercial implementation of the propane ODH reaction and can increase its propylene yield [5, 9-11].

Several studies have focused on the development of catalysts with high activity–selectivity relationships for selective oxidation reactions. The speciation of vanadium oxide from the interaction with support oxide has been the differential for the catalytic performance [12,13]. The versatility in obtaining porous structures with different alumina transition phases allows the selection of appropriate supports for active phase dispersion. Therefore, the methodology and synthesis conditions of aluminum hydroxide precursors and subsequent calcination are crucial for obtaining alumina supports with specific properties [14-16].

The acid-base and redox properties of catalysts are important parameters for propene selectivity control and can be modified *via* the addition of

alkaline promoters. In particular, the promoter effect of K on the V₂O₅/Al₂O₃ catalysts for the alkane ODH reaction has been studied [17-21]. The promising improvement in selectivity was attributed to the modification of acidic sites into basic sites, although a better understanding of the role of alkali dopants on the structure and properties of supported vanadia catalysts is required [19,20]. It has been reported that the interaction of K or Na with vanadia led to the weakening of the terminal V=O bonds [20,22].

The Mars–van Krevelen (MvK) redox mechanism has often been referred to as the appropriate model to describe the alkane ODH reaction over transition-metal-based catalysts, such as V [23,24]. This mechanism involves the reduction of the catalyst by adsorbed alkane with participation of the lattice oxygen forming olefin and water. Then, gas-phase oxygen re-oxidizes the reduced catalytic sites. Chen et al. [25] have proposed the following mechanistic sequences for the propane ODH reaction over V-based catalysts:

- I) $C_3H_8 + O^* \rightarrow C_3H_8O^*$ (adsorption of propane molecule by interaction with lattice oxygen (O^{*}) in the V=O, V-O-V or V-O-Support bonds of structures VO_x species);
- II) $C_3H_8O^* + O^* \rightarrow C_3H_7O^* + OH^*$ (propane H-abstraction by neighboring lattice oxygen (O^{*}) (C-H bond cleavage) to produce propyl radicals (C₃H₇O^{*}) and OH^{*} groups);
- III) $C_3H_7O^* \rightarrow C_3H_6 + OH^*$ (desorption of propene by OH^{*} elimination from adsorbed alkoxide species);
- IV) $OH^* + OH^* \rightarrow H_2O + O^* + *$ (recombination of OH^{*} groups to form partially reduced V centers (*));
- V) $O_2 + * + * \rightarrow O^* + O^*$ (re-oxidation of reduced V centers (*) *via* dissociative chemisorption of O₂).

The changes in the O₂:C₃H₈ molar ratio can affect the re-oxidation rate and, therefore, the synergistic effect between the V⁵⁺/V⁴⁺ species and, consequently, catalytic performance. A few studies reported a greater reduction of V cations with decreasing amount of O₂; however, this did not observe the same results in terms of propene selectivity of the catalysts for the propane ODH reaction [8, 26-28].

In this study, our goal was to evaluate the promoting effect of K and Na as additive to increase propene selectivity of the propane ODH

reaction. The differential of this study was the evaluation of the effect of the interaction of alkali metals with V and transition alumina support that was prepared from gibbsite as precursor. Generally, the V-based catalysts reported in the others research papers [13,20] were prepared by impregnation of vanadium on a commercial γ -Al₂O₃ support. We also proposed to evaluate the change of the O₂/propane molar ratio of the reaction mixture, modifying molar flow rates of reagents.

2. MATERIALS AND METHODS

2.1 Synthesis

The aluminum hydroxide precursor was prepared using a precipitation method *via* the continuous injection of CO₂ at a flow rate of 48 mLmin⁻¹ into a solution of NaAlO₄ (3.3 M), which was placed in a batch reactor at 348 K under mechanical stirring until the pH was approximately 10.8. The obtained precipitate was washed with distilled water, dried, and calcined at 873 K for 5 h to obtain the alumina support, which was denoted as Al₂O₃ (G). 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 343 K and powder carrier in a vacuum rotary evaporator. Thereafter, the residual powder was dried and calcined at 723 K for 5 h, and the prepared catalyst was denoted as 4V-Al (G). 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 (G) and 4V-xK-Al (G).

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 77 K using a Belsorp-mini-II instrument. The samples were pretreated *in situ* under vacuum and were subsequently heated at 473 K for 2 h.

X-ray diffraction (XRD) analyses were performed using a PANalytical Empyrean instrument with Cu K α radiation ($\lambda = 0,1544$ nm) at a power of 30

kV, current of 20 mA, and goniometer angular velocity of 0.02°/s in the 2 θ 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 473 K for 2 h under a He flow. Next, the solids were cooled to room temperature and reduced at 1173 K (temperature ramp of 10 K min⁻¹) with a 5% H₂/N₂ mixture (flow rate of 30 mLmin⁻¹).

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 cm³min⁻¹ and was diluted with a He and N₂ mixture at a flow rate of 37.5 cm³min⁻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 373–573 K using 150 mg of catalysts and the residence time (W/F_{A0}) of 6.3 ghmol⁻¹. The conversion of isopropanol (X_{isop}), product selectivity (S_j), specific reaction rate (SRR), and the specific rate of product formation (SRP) were calculated as follows:

$$X_{isop}(\%) = \frac{\sum_j z_j n_j}{3n_{isop} + \sum_j z_j n_j} \times 100 \quad (3)$$

$$S_j(\%) = \frac{z_j n_j}{\sum_j z_j n_j} \times 100 \quad (4)$$

$$SRR = \frac{X_{isop}(\%) \times F_{isop}}{W \times S_g} \quad (5)$$

and

$$SRP = \frac{S_j(\%) \times SRR}{S_g} \quad (6)$$

where n_{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_{A0} 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 573–773 K 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 $O_2:C_3H_8:He$ 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 $O_2:C_3H_8$ 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:

$$X_{C_3H_8}(\%) = \frac{\sum_i z_i n_i}{3n_{propane} + \sum_i z_i n_i} \times 100 \quad (7)$$

$$S_i(\%) = \frac{z_i n_i}{\sum_i z_i n_i} \times 100 \quad (8)$$

and

$$Y_{C_3H_6}(\%) = \frac{X_{C_3H_8}(\%) \times S_{C_3H_6}(\%)}{100} \quad (9)$$

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 specific surface area (S_{BET}), pore volume (V_P), and average pore radius (R_P) of the alumina

support and vanadium-and-alkali-metal-based catalysts are summarized in Table 1. The impregnation of vanadium oxide onto the alumina support caused a decrease in S_{BET} and V_P . Furthermore, S_{BET} decreased with increasing Na content. The S_{BET} values of the K-doped catalysts were lower than that of the undoped catalyst; however, the S_{BET} values of both K-doped catalysts were similar. In general, the S_{BET} values of the alkali-metal-doped catalysts were slightly lower than those of that of the undoped catalysts. This was attributed to the preparation procedure and, in particular, to the low amounts of dopants used [20,21].

The V_P distribution curves of the catalysts are presented in Fig. 2. The radius of most pores of the alumina-supported V catalysts was between 1 and 4 nm (Fig. 2(b)-(d)). The Al_2O_3 (G) catalyst support exhibited a shoulder that extended to 10 nm radius pores (Fig. 2(a)) which was eliminated after the impregnation of vanadium oxide and alkali metals. This was attributed to vanadium oxide and alkali metal species promoting the collapse of small pores in pure alumina during calcination.

The XRD profiles of the support and catalysts are illustrated in Fig. 3. The alumina precursor presented monoclinic aluminum hydroxide (gibbsite) structure (ICDD 00-033-0018), and its XRD profile presented very narrow and defined peaks at 18.31° and 20.37° owing to its highly crystalline structure; other peaks with lower intensity were also observed. Upon calcination at 873 K, the gibbsite precursor formed χ - Al_2O_3 (ICDD 04-0880, $2\theta = 37.74^\circ, 39.57^\circ, 42.91^\circ, 45.68^\circ, \text{ and } 67.68^\circ$), which presented low crystallinity. The XRD profiles of the catalysts impregnated with vanadium oxide and alkali metals did not include any peaks related to bulk compounds. This indicated a good dispersion of surface vanadium species; however, the formation of V-associated nanoparticles could not be ruled out because of the limitations of the XRD analysis [30,31].

Table 1. Specific area (S_{BET}), pore volume (V_P), and average pore radius (R_P) of catalysts

Support/ Catalysts	S_{BET} (m ² g ⁻¹)	V_P (cm ³ g ⁻¹)	R_P (nm)
Al_2O_3 (G)	197	0.31	2.35
4V-Al (G)	105	0.22	2.74
4V-0.5Na-Al (G)	104	0.21	2.41
4V-1.0Na-Al (G)	96	0.19	2.41
4V-0.5K-Al (G)	98	0.20	2.74
4V-1.0K-Al (G)	100	0.20	2.41

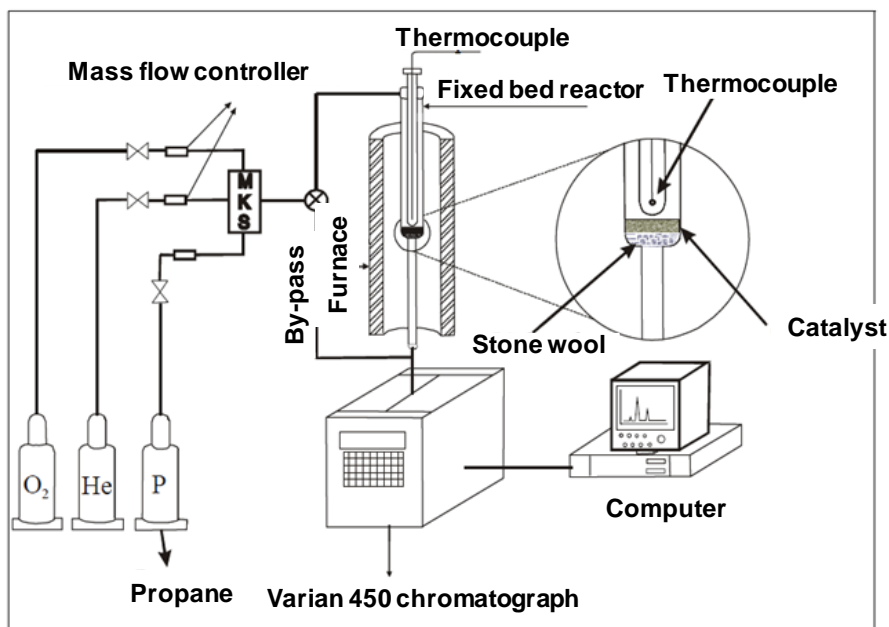


Fig. 1. Experimental set-up diagram of the propane ODH reaction

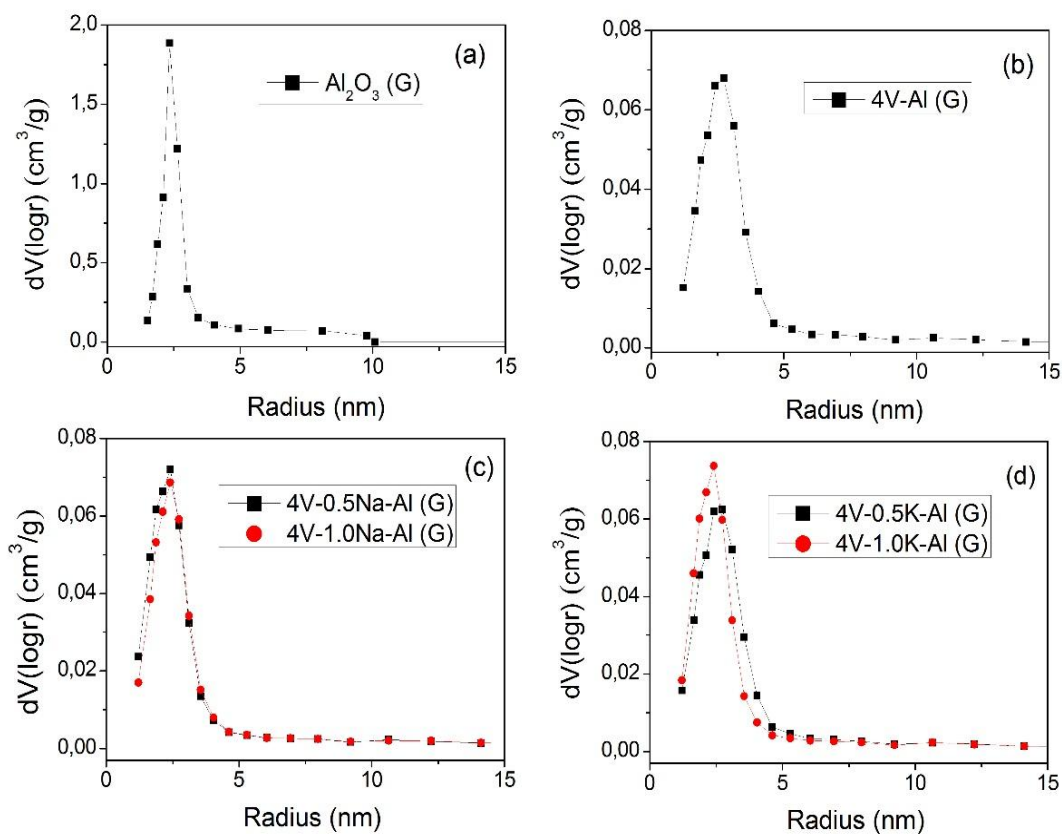


Fig. 2. Pore volume distribution dependence of pore radius for Al₂O₃(G) support and catalysts loaded with vanadium oxide and alkali metals

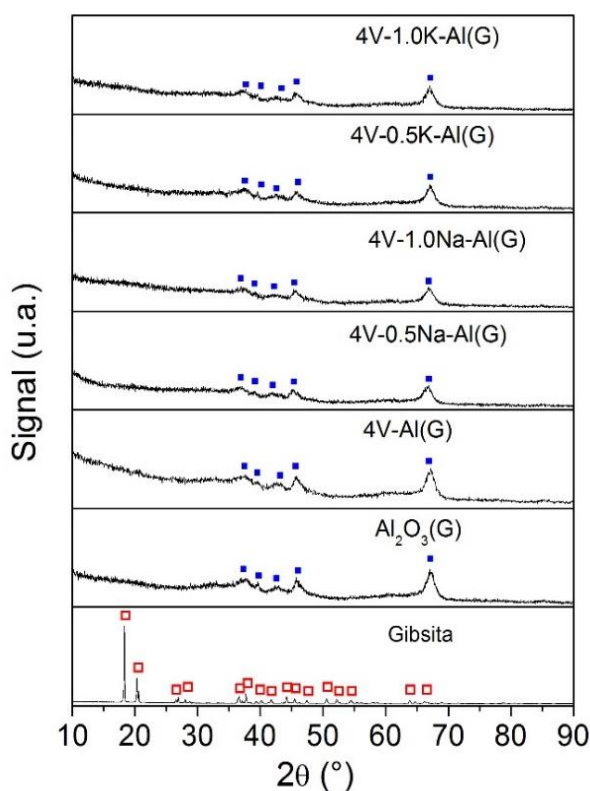


Fig. 3. X-ray diffractograms of catalyst samples. The ■ and □ peaks represent gibbsite and γ - Al_2O_3 phases, respectively

The TPR profiles of the catalysts are illustrated in Fig. 4. The undoped V catalyst presented a single reduction peak (787 K) which corresponded to the reduction of V_2O_5 to V_6O_{13} . The addition of alkali metals shifted this peak to higher temperatures (785-819 K), which indicated a decrease in reducibility. The stronger interactions between the acidic V sites and basic alkalis can hinder V reduction [21]. But, the reduction temperature of the 4V-0.5Na-Al (G) catalyst (785 K) was similar to that of the undoped catalyst (787 K), this may be associated with a lower dispersion of sodium ions during their impregnation, not inhibiting active sites. The reduction temperature of the 4V-1.0Na-Al (G) catalyst was the highest of all catalyst samples, and the reduction temperatures of the 4V-0.5 K-Al (G) and 4V-1.0K-Al (G) catalysts were similar. This suggested that catalyst reducibility did not change significantly with increasing K content. Conversely, Cortez et al. [20] reported that the maximum H_2 consumption temperature of K-doped $\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$ catalysts increased with K loading irrespective of the preparation method. Lemonidou et al. (2000) [21] analyzed the effect of alkali metals (Li, Na, and K) on the reducibility

of V species and reported that reduction temperature did not depend on the nature of alkali metal used for doping. The morphological properties of the support material, content of impurities, and method used to prepare vanadia to affect V reducibility [32].

The SRR and SRP values for the decomposition of isopropanol at 553 and 573 K are summarized in Tables 2 and 3, respectively. The formation of propene *via* isopropanol dehydration requires the presence of Lewis or Brønsted acid sites, whereas the formation of acetone *via* isopropanol dehydrogenation occurs at basic or redox sites [33,34]. The catalytic activity and production of propene increased significantly when V was added to the alumina support. 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 decreased the SRR and propene SRP; moreover SRR and propene SRP decreased with increasing alkali metal content of the catalysts. The inhibition of acid sites by K exceeded that of Na at the same Na and K content because the ionic radius of K^+ is higher than that of Na^+ . The

production of acetone, which depended on the availability of basic sites, was higher for the doped catalysts. However, the change in basicity with increasing alkali metal content of the catalysts was insignificant and the inhibition of acidic sites was more noticeable. Cortez et al. (2003) [20] reported that a fraction of acid sites was converted into basic sites with increasing K content. This observation was supported by the progressive decrease in dimethyl ether formation (acid sites) with increasing K loading followed by an increase in CO₂ production (basic sites) during methanol chemisorption and its temperature-programmed surface reaction.

3.2 Catalytic Test

Table 4 and Fig. 5 illustrate the 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 (573 K) for all catalysts. Initially, catalytic activity decreased at higher temperatures for all catalysts except for the undoped one. The catalytic deactivation can be associated with the onset of coke deposition

owing to the start of the combustion process [8]. After, the doped catalysts become more markedly active with the formation of CO and CO₂ by-products, in which the combustion process is more thermodynamically favorable at higher temperatures, i.e., the olefins are more susceptible to undergo complete oxidation to form CO_x [9].

The combustion of propene over the 4V-Al (G) catalyst started instantaneously (573 K), indicating that 4V-Al (G) was very active. Conversely, the production of CO_x over the alkali-metal-doped catalysts started at high temperatures (643-658 K). This can be attributed to the alkali metal ions blocking the strong acid and nonselective sites, which favored the olefins combustion reaction [21]. This effect was more significant for the 4V-1.0K-Al (G) (658 K) catalyst because the ion radius of K⁺ being larger than that of Na⁺. The higher inhibition of these sites by K was confirmed by the lowest propene production during the isopropanol decomposition reaction to evaluate their acid-base properties; the propene production requires the presence of acid sites [33,34].

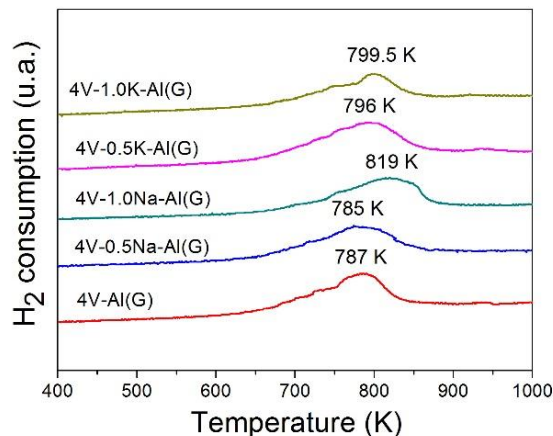


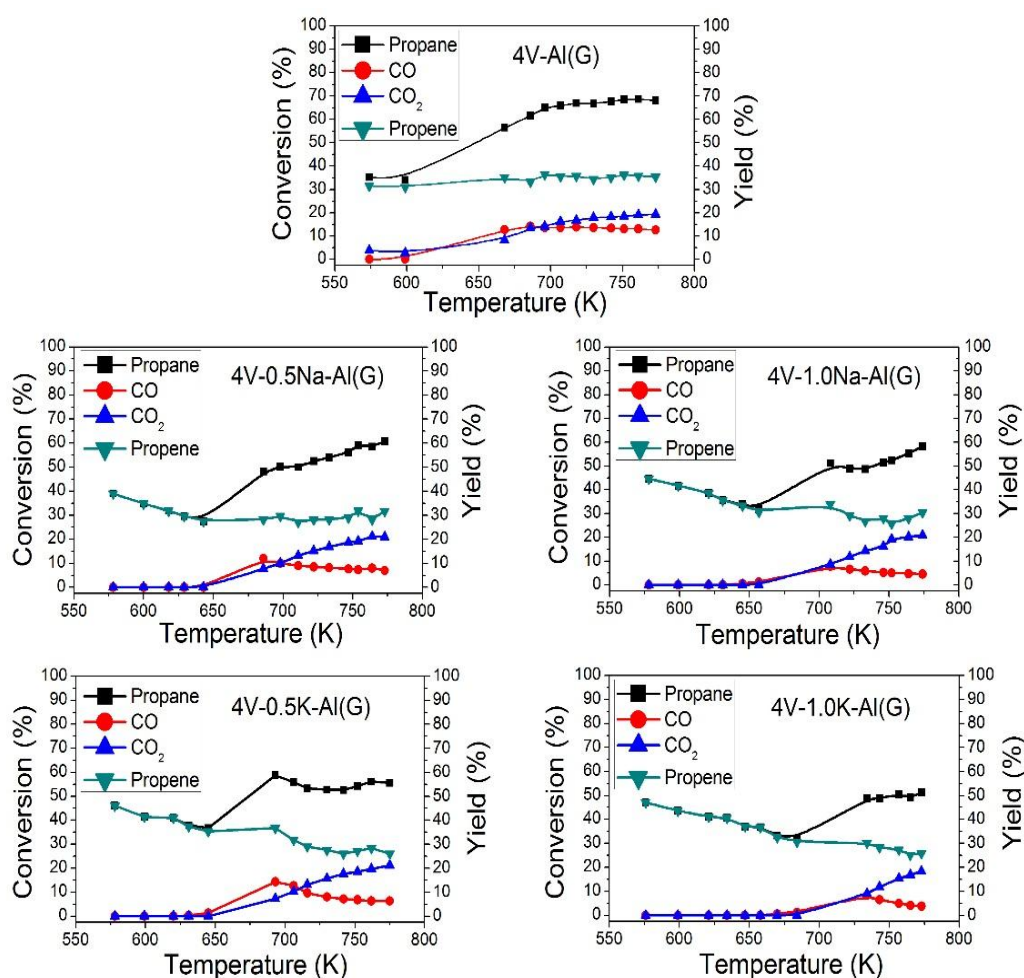
Fig. 4. Temperature programmed reduction curve of the catalysts

Table 2. Specific reaction rate (SRR) and specific rate of product formation (SRP) of the support and catalysts at 553 K

Support/ Catalysts	SRR ($\mu\text{molm}^{-2}\text{min}^{-1}$)	SRP ($\mu\text{molm}^{-2}\text{min}^{-1}$)	
		Propene	Acetone
Al ₂ O ₃ (G)	1.75	1.63	0.01
4V-Al (G)	27.63	23.03	4.21
4V-0.5Na-Al (G)	21.33	15.37	5.85
4V-1.0Na-Al (G)	15.80	9.64	5.72
4V-0.5K-Al (G)	16.61	10.61	5.96
4V-1.0K-Al (G)	14.08	7.99	5.89

Table 3. Specific reaction rate (SRR) and specific rate of product formation (SRP) of the support and catalysts at 573 K

Support/ Catalysts	SRR ($\mu\text{molm}^{-2}\text{min}^{-1}$)	SRP ($\mu\text{molm}^{-2}\text{min}^{-1}$)	
		Propene	Acetone
Al ₂ O ₃ (G)	4.63	4.46	0.1
4V-Al (G)	49.14	43.73	5.23
4V-0.5Na-Al (G)	38.50	28.28	10.09
4V-1.0Na-Al (G)	32.57	21.35	10.84
4V-0.5K-Al (G)	36.13	24.78	11.36
4V-1.0K-Al (G)	27.30	16.08	11.15

**Fig. 5. Catalytic activity for the propane oxidative dehydrogenation reaction****Table 4. Catalytic activity for the propane oxidative dehydrogenation reaction**

Catalysts	Initial propane conversion (%)	Initial propene yield ^a (%)	Initial combustion temperature (K)
4V-Al (G)	31.5	31.5	573
4V-0.5Na-Al (G)	40	40	643
4V-1.0Na-Al (G)	44.6	44.6	645
4V-0.5K-Al (G)	46.1	46.1	643
4V-1.0K-Al (G)	49	49	658

^aThe highest propene yields were observed at the beginning of the reactions

Conversely, propane conversion over the alkali-metal-doped catalysts was higher than that over the undoped catalyst. The less reducible character of the doped catalysts, which was demonstrated using TPR analysis, did not lead to their lower activity for the propane ODH reaction. Therefore, when the propane ODH reaction was performed over the alkali-modified catalysts it did not follow the Mars–van Krevelen mechanism; moreover, the effect of the dopants on the redox properties of V was not observed for these reactions.

Putra et al. [35] studied the promoter effect of Sr over V-Mo oxide catalysts supported on γ -Al₂O₃ and observed that the presence of Sr enhanced the propane conversion and propene selectivity. In kinetic investigations, they observed that the Sr-Mo-V catalysts with low reducibility fitted well Langmuir–Hinshelwood (LH) mechanism, but the typical mechanism, Mars–van Krevelen, was more appropriate for Mo-V-catalyst (higher reducibility). For LH mechanism, propane and oxygen are adsorbed on the catalyst surface and they react to give propene. Therefore, this study indicated that other reaction models can be more appropriate for alkali-modified catalysts with lower reducibility prepared in this work, that require further detailed kinetic studies.

The addition of alkali metals to the V catalysts increased propene selectivity (Fig. 6), and the 4V-1.0K-Al (G) catalyst was more selective than the other alkali-metal-doped catalysts over almost the entire reaction duration. A significant decrease in selectivity was observed only after the temperature reached 684 K for the 4V-1.0K-Al (G) catalyst owing to the olefin combustion process, which occurred at higher temperatures. Lemonidou et al. [21] reported the beneficial effect of alkali metal (Li, Na, and K) addition to V₂O₅/Al₂O₃ catalysts on propylene selectivity; however, they did not observe a difference in propene selectivity among the alkali-metal-doped catalysts. In general, the more pronounced decrease in acidity with the addition of K compared with Na was attributed to the electronic density caused by K⁺ ions in the V–O groups, that served as active sites, being greater than that of Na⁺ ions [36]. The most significant neutralization of the acid sites by K⁺ ions was confirmed by the greatest decrease in propene production during the isopropanol decomposition test. The higher basicity provided better desorption of propene for the propane ODH reaction and rendered the olefins less susceptible to undergo complete oxidation to form CO and CO₂ [20].

In addition to the promoting effect of alkali metals on the catalytic properties of V catalysts, the effect of the O₂:C₃H₈ molar ratio on catalytic performance were also evaluated. The most selective catalyst, 4V-1.0K-Al (G), was evaluated using the O₂:C₃H₈:He molar ratios of 6:1:4 and 4:3:4; the molar fraction of He and the total flow rate was maintained constant. The experimental results are illustrated in Fig. 7. The catalytic activity of the 4V-1.0K-Al (G) catalyst increased with increasing O₂ molar fraction, as demonstrated by the increase in propane conversion (Fig. 7(a)) and propene yield (Fig. 7(b)). Excess and non-stoichiometric amounts of non-selective and poorly adsorbed species (O₂, O²⁻, and O⁻) and O in the catalyst has been reported in the literature to increase catalytic activity and propene combustion rate [8]. The increase in propane conversion reported in this paper can be attributed to the interactions of propane molecules with a large number of oxygen active sites restored to the catalytic structure. On the other hand, the high olefin yield showed that this oxygen actives were sufficient to selectively convert propane to propylene, i.e., higher O₂ molar fraction may not have led to an excess of non-selective O species. In contrast, the catalytic performance decreased when the molar fraction of O₂ was lower (O₂:C₃H₈:He molar ratio of 4:3:4); catalytic activity and propene yield decreased owing to a possible insufficient O replacement in the catalytic structure. Moreover, at the O₂:C₃H₈:He molar ratio of 4:3:4, catalyst deactivation increased with the deposition of coke on the catalyst surface, which was confirmed by the blackened appearance of the catalyst after the propane ODH reaction, in which O₂ plays an important role in eliminating carbonaceous species [8]. Therefore, the large amount of O₂ minimized coke formation, increased catalytic activity, and favored propene formation. It is important to note that the propane conversion increased at higher temperatures (773 K) at the different O₂:C₃H₈:He molar ratios; however, the propene yield decreased owing to the olefin combustion process to form CO and CO₂.

The propene selectivity curves of the 4V-1.0K-Al(G) catalyst at different O₂:C₃H₈:He molar ratios are presented in Fig 8. Propene selectivity increased with increasing O₂ molar fraction that is in agreement with higher propene yield and decreased production of CO and CO₂. Høj et al. (2013) [26] reported different results for the propane ODH reaction on alumina-supported V catalysts. The X-ray absorption spectroscopy

results demonstrated the reduction of V^{5+} to V^{4+} owing to the low concentration of O_2 in the reaction mixture favoring propene selectivity particularly for oligomerized V species. Gao et al. (2002) [27] also confirmed the significant effect of the $C_3H_8:O_2$ molar ratio on propene selectivity over the V_2O_5/ZrO_2 catalyst. The ultraviolet–visible diffuse reflectance spectroscopy and Raman spectroscopy analysis results revealed that a greater fraction of V^{5+} species were reduced to V^{4+} species with increasing $C_3H_8:O_2$ molar ratio. However, when an O_2 -rich mixture was used ($C_3H_8:O_2$ molar ratio of 1:10), propene selectivity was high, which suggested that olefin production was favored by high-oxidation-state V species (V^{5+}). The same results were observed in this study, in which the reaction mechanism

can be related to propene formation at the V^{5+} active sites, whereas the reduced V species (V^{4+}/V^{3+}) can favor CO_x formation. These byproducts can be formed *via* the decomposition of a small amount of acrolein, the organic intermediate formed during the activation of the C–H bonds of propylene in the presence of reduced vanadia sites [27]. Conversely, Cortez and Bañares (2002) [28] analyzed the Raman spectra and catalytic activity of alumina-supported vanadium oxide during the propane ODH reaction and reported that the effect of the $O_2:C_3H_8$ molar ratio on the selectivity–activity ratio was negligible. In this work, the $O_2:C_3H_8:He$ molar ratio of 6:1:4 was the most suitable for the propene ODH reaction.

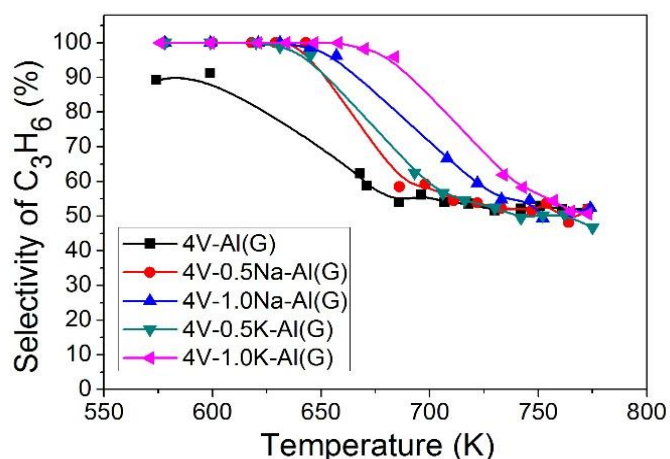
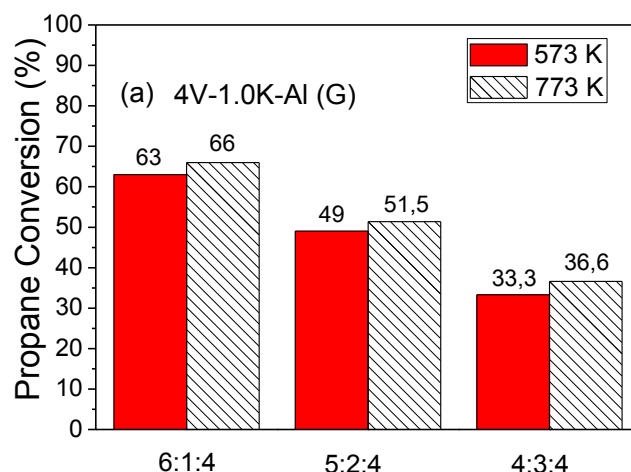


Fig. 6. Propene selectivity during propane oxidative dehydrogenation



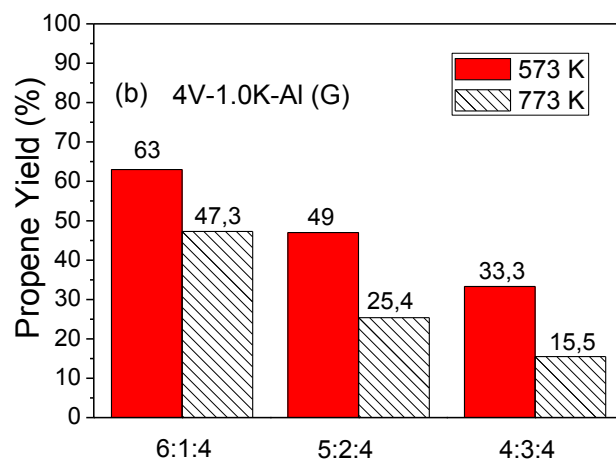


Fig. 7. Propene conversion (a) and propene yield (b) of the 4V-1.0K-Al (G) catalyst at different O₂:C₃H₈ molar ratios of 6:1:4, 5:2:4 and 4:3:3

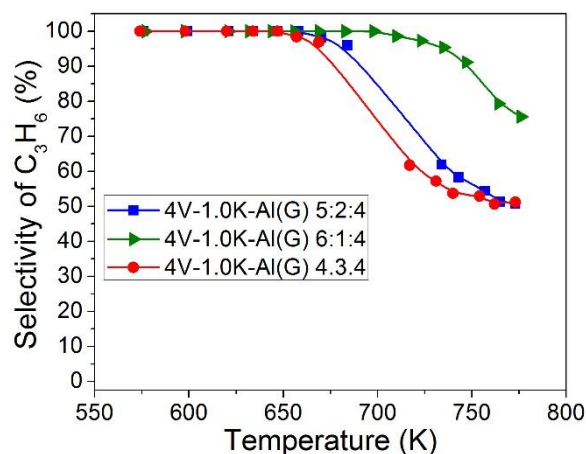


Fig. 8. Propene selectivity of the 4V-1.0K-Al (G) catalyst at different O₂:C₃H₈ molar ratios

Ermini et al. [18] also doped the alumina-supported V catalyst with potassium and noted that addition of K decreased activity, but increased significantly the propene selectivity. This result was ascribed to the blocking of acid sites of the alumina support that converted propene in organic by-products. Under conditions of higher propene production, it was reported that the propene selectivity increased from 16.6% (13V-Al) to 39.9% (13V-0.5K -Al) at the respective propane conversion values of 50.2% and 41% (V₂O₅ = 13 wt.%; K₂O = 0.5 wt.%). Lemonidou et al (2000) reported the same trend with the increase in the propene selectivity of 39.8% (V-Al) to 57.2% (KV-Al) at propane conversion of 20.3% and 16.9 %, respectively, at

773 K (V₂O₅ = 4 wt.%; K₂O/V₂O₅ = 0.25). Overall, alkali metal dopants have been reported to improve propene selectivity but have been associated with a decrease in catalytic activity [18-21]; however, the catalysts prepared in this study presented opposite behavior. The V–O–support bonds have been identified as the active sites for propane activation [37-40], which suggested that the presence of alkali metal additives induced changes in the vanadium species of the catalysts prepared using gibbsite as the precursor. Therefore, the changes in the acid-base properties and active site–support interactions with the addition of alkali metal ions indicated that further detailed studies should be performed to elucidate the promising catalytic

efficiency of alkali-metal-doped V catalysts. Furthermore, the high propene selectivity at high propane conversions suggested control over the strong oxidizing action of O₂, because the olefins are able to form CO and CO₂ byproducts very easily [8].

The alkali metal ions tend to coordinate to surface V species by altering the V-O bond [34,41]; moreover, the alkali doping can increase propene selectivity and activity in propane ODH reaction, while preventing the transformation phase, inhibiting sintering and creating basic centers on the catalyst surface [42]. In this study, it was demonstrated that the changes in catalytic performance associated with the addition of alkali metals were not caused by the formation of bulk V–K–Al or V–Na–Al compounds. The XRD profiles of the catalyst samples revealed that the vanadium oxide species were dispersed and the total V + K or V + Na coverage was below a monolayer [20,43]. Therefore, the changes in acid-base properties and binding strength of the surface lattice oxygen can be considered the most relevant factors for selectivity control [9].

4. CONCLUSION

The textural properties of the alumina carrier synthesized using the precipitation method favored the uniform dispersion of vanadium species on the catalyst surface; however, the formation of possible clusters of V nanoparticles could not be ruled out because of the limitations of the XRD analysis. The incorporation of alkali metal ions and V on the alumina support improved the propene selectivity of the propane ODH reaction; in particular, the inhibitory effect of K⁺ ions on the acid sites were stronger than that of Na⁺ ions. The addition of alkali metals to the alumina-supported V catalysts considerably improved catalytic performance in terms of propane conversion and propene selectivity. In this study, the C₃H₈:O₂ molar ratio was an important factor for selectivity control, since the high O₂ molar fraction could minimize the formation of coke and favor the propene formation. Therefore, the 4V-1.0K-Al (G) catalyst was the most efficient and selective with high initial conversion of propane of approximately 63% at 573 K at the O₂:C₃H₈:He molar ratio of 6:1:4, suppressing the complete oxidation to CO and CO₂. By comparison, the catalytic performance of this catalyst was superior to previously published results in that the combustion process was predominant [17-21]. Consequently, further studies should be

conducted to elucidate the interactions of alkali metals with support materials described in this paper for a promising catalytic efficiency.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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