

Operating condition effect on achieving higher propene yield in propane oxidative dehydrogenation process

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ABSTRACT

Supported vanadia catalyst was successfully synthesized using wet impregnation of γ -alumina to study Propane Oxidative Dehydrogenation (POD). The prepared catalysts were characterized with XRD, BET, and TPR tests. In a broad temperature range (340 °C to 630 °C), effects of vanadia loading (2.7, 5.4, and 9 wt%) and propane to oxygen ratio (3/1 to 1/3) were investigated on propane conversion as well as propene yield at atmospheric pressure. Results indicate that by increasing the vanadia content the activity of catalyst increases while selectivity to propene decreases monotonically. As the temperature increases from 340 °C to 630 °C, yield to propene shows ascending behavior in case of all catalyst samples. Yield to propene shows a climax with changing propane to oxygen ratio from 3/1 to 1/3. The yield increases with increase in oxygen partial pressure of feed until equimolar ratio of propane and oxygen, then it declines with further increase of oxygen partial pressure. Higher propene yields were observed at higher temperatures and equimolar feed ratio of propane and oxygen ($C_3/O_2=1/1$). A maximum propene yield of 17% was experienced on catalyst with 2.7 wt% vanadia at temperatures at 550 °C.

Keywords: Propane oxidative dehydrogenation, Vanadia loading, γ -Alumina, Temperature, Feed composition.

1. Introduction

Propene as a commodity product is an important feed stock in chemical and petrochemical industries. Propene is used in production of 2-propanol, acrylonitrile, propylene oxide, and epichlorohydrin but its main use is in polypropylene production [1]. Conventional processes including thermal and catalytic cracking of naphtha and dehydrogenation of propane suffer from technical and economical drawbacks [2-4]. Furthermore a consumption increase of about 5% per year due to polypropylene market increase [5,6] makes it crucial to develop new routes and processes for propene production. Due to inherent beneficial characteristics of non-equilibrium exothermic reactions, propane oxidative dehydrogenation (POD) seems to be a promising route to fill the gap between the increasing demand and the capacity of existing plants. Despite of these tempting benefits, low yield of propene prevents commercially development of POD [7,8].

Vanadia has shown to be selective in oxidative dehydrogenation of alkanes [9-13]. So impact of vanadia catalysts, supported on metal oxides, has been

studied for POD [14-24]. Focused on the dispersion and morphology of vanadia over different supports, Khodakov et al. [14] reported that among different forms of vanadia, polyvanadate monolayer is more selective in POD reactions. Diversity in the structure of vanadia depends on its dispersion which mainly arises from loading as well as support characteristics such as surface area and acid/base property [2,24-26]. Martra et al. [2] studied acid/base property of impregnated vanadia on Al_2O_3 , H-Na/Y zeolite, MgO , SiO_2 , TiO_2 and ZrO_2 . In a similar work but with more emphasis on the effect of support, Dinse et al. [27] examined CeO_2 , TiO_2 , Al_2O_3 , ZrO_2 and SiO_2 with low loading of vanadia. Although catalysts with acidic supports show higher conversions in comparison with more basic ones, they have lower selectivity [8]. In attempt to enhance reducibility of active sites and increase the selectivity to propene, some researchers modified the acid/base properties of surface by adding different alkali and alkaline earth metals (Li [28], Na [28], K [8,18,28,29], and Mg [30]).

Beside aforementioned factors, operating conditions and feed composition are decisive parameters in product distribution/catalytic performance of POD reactions [30-32]. POD is a set of consecutive reactions of oxydehydrogenation of propane and further oxidation of propene to CO and CO_2 according

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to Mars van Kerevelen (MvK) mechanism [33-36]. Whether the reaction proceeds under propane rich or propane deficient atmosphere, the controlling step changes and so does product distribution. To the best knowledge of authors, not so much works have been done to thoroughly explore the effect of propane to oxygen ratio (C_3/O_2) and reaction conditions on overall propene yield. Most of the works are at stoichiometric or propane rich atmosphere [2,3,14,16, 19,20,24,37,38] and relatively fewer works have been based on the results obtained in oxygen rich condition [15,17,21,39] with the perspective to investigate reaction kinetics and mechanism, so they almost are reported at low conversions and low temperatures. Given very different conditions and even inconsistent results in various studies, it is not possible to reach a concrete understating on the role of operating condition and feed composition from published works. According to Creaser et al. [37] at low propane concentrations or low propane conversions, oxygen deficient atmosphere is beneficial for higher propene yield but no data at higher propane concentrations or conversions have been reported. In contrary, the results of Jibril et al. [39] showed that higher yields of propene can be achieved at moderately oxygen rich feed.

Major works have been done over last decades on POD; as it is cited; but mostly emphasizing on the effect of catalyst design at first, secondly on the kinetics of POD reactions, and with a little attention on the reactor mode, but ignoring the effect of operating condition as design parameter on the propene yield. From engineering point of view, tailoring operating condition is a way to achieve higher efficiency. So seeing this untouched area, the aim of present study is to examine the effect of operating condition and feed composition over a catalytic bed of V_2O_5/γ -alumina on propene yield. A comprehensive study have been done to explore the effects of vanadia loading over γ -alumina, temperature and feed composition on overall propene yield, propane conversion and propene selectivity.

2. Experimental

2.1. Catalyst preparation

All catalysts were prepared by wet impregnation of γ -alumina (Merck) support with aqueous solution of ammonium monovanadate (Merck). Impregnation was carried out in a rotary evaporator (Biby Strilin Ltd., RE200) at reduced pressure and low temperature. The impregnated samples were dried over night at 383 K and further treated by heating up to 873 K during 3 h and then calcined at this temperature for 6 h. Three catalysts, VAl-01, VAl-02, and VAl-03, with different vanadia loadings of 2.7, 5.4, and 9 wt% respectively were prepared following this procedure.

2.2. Catalyst characterization

Catalyst and support surface area was determined by nitrogen adsorption-desorption at liquid nitrogen temperature (77 K), using a ChemBET-3000 (Quanta Chrome Instrument). To ensure a clean and dry surface, samples were first degassed for 1 h at 300 °C and 0.15 mbar. Surface areas were calculated using the method of Brunauer, Emmett and Teller (BET) method.

XRD patterns were recorded on an X-Pert Philips diffractometer on powdered samples. The scans were collected within the range 10–110° (2 θ) (0.01° (2 θ) s⁻¹) using Cu-K α radiation.

The reducibility of catalysts was studied by temperature programmed reduction (TPR) with a ChemiSorb 2750 (Micromeritics) apparatus. 50 mg of catalysts were oxidized in a O₂-He mixture (20 vol.% O₂) with a flow rate of 30 cc/min at 550 °C for 30 min and then cooled to 50 °C. Successively samples were degassed with nitrogen (20 cc/min) for 2 h at 250 °C to remove the non-binding oxygen. After cooling to 25 °C, TPR tests were carried out under a 20 cc/min flow of 5 vol.% H₂/Ar mixture through a microreactor heating at a constant rate of 10 °C/min up to 950 °C.

2.3. Catalytic test

A one meter long quartz tube with internal diameter of 6 mm, installed in a furnace, was used as a reactor. At every test 100 mg of catalyst was loaded in the reactor and feed mixture was introduced to catalytic bed at a total flow rate of 100 cc/min STP. Feed ratio was varied from N₂:O₂:C₃= 6:3:1 (lean of propane) to 6:1:3 (rich of propane) to investigate the effect of feed composition. A thermometer was adjusted in the bed in order to precisely monitor the temperature of reaction bed. After quenching and removing water from the flow exiting the reactor, it was analyzed with an online Thermofinigan GC (Model No. KAV00109) equipped with TCD and FID detectors. A schematic of used set-up for catalytic test is shown in Fig. 1. Conversion ($X_{propene}$), selectivity ($S_{propene}$), and yield ($Y_{propene}$) were calculated according to the following equations where $F_{propene,i}$ is inlet molar flow rate of propane (mol/min), $F_{propene,e}$ is outlet molar flow rate of propane (mol/min) and $F_{propene}$ is outlet molar flow rate of propane (mol/min).

$$X_{propene} = \frac{(F_{propene,i} - F_{propene,e})}{F_{propene,i}} \times 100$$

$$S_{propene} = \frac{F_{propene}}{(F_{propene,i} - F_{propene,e})} \times 100$$

$$Y_{propene} = \frac{(S_{propene} \times X_{propene})}{100}$$

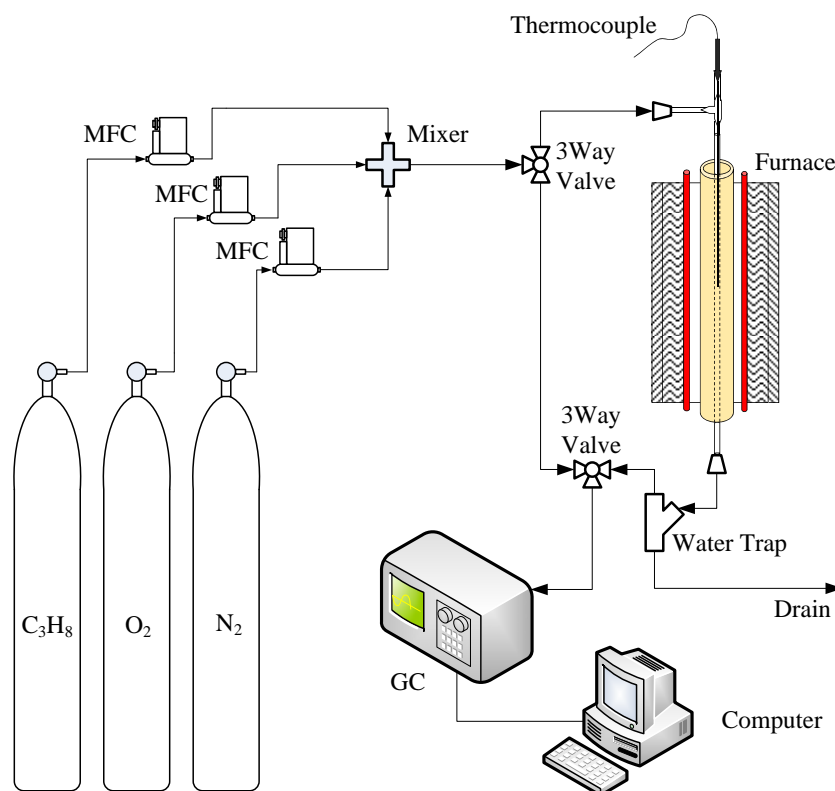


Fig. 1. Schematic of catalytic test set-up.

3. Results and Discussion

Catalyst surface areas and calculated VO_x surface coverage, θ_s (fraction of a theoretical monolayer), are shown in Table 1 as a function of V_2O_5 content.

The coverage was calculated using 4.98×10^{14} V_2O_5 molecules/ cm^2 required for full coverage of the surface [28] and the initial BET area of the used $\gamma\text{-Al}_2\text{O}_3$. Theoretically 18.1 wt.% V_2O_5 loading is sufficient to form a monolayer of vanadia over $\gamma\text{-Al}_2\text{O}_3$ support.

As can be seen in Table 1, in all cases, vanadia loading is well below than that of theoretically required for monolayer coverage; thereby no drastic change is observed in BET results. This may be attributed to good dispersion of vanadia on γ -alumina surface. A vanadia loading of 2.7 wt.% slightly increased surface area but further increase of vanadia loading led to approximately 10% decrease in surface area.

According to XRD patterns (Fig. 2) only the peaks related to the support is detectable and no V_2O_5 -related peaks can be observed. Small V_2O_5 crystallites may be formed on the surface but they are not detectable by X-ray diffraction method due to their poor crystallinity, small unit cell size, and low concentration [14,27]. In accordance with BET results, it can be confirmed that a monotonous dispersion of V_2O_5 species was obtained. Fig. 3 represents TPR results. All catalysts start to be reduced at about 350°C . By increasing the vanadia content, the maximum reduction temperature peak shifts slightly to the left, from 537°C to 528°C and 522°C for VAI-01, VAI-02, and VAI-03 respectively, indicating better reducibility and higher activity.

As mentioned, vanadia loading increase led to increased catalyst activity. Fig. 4a shows conversion profile for three different catalysts at stoichiometric feed ratio ($\text{N}_2/\text{O}_2/\text{C}_3$: 7/1/2).

Table 1. Vanadium content, surface area, calculated VO_x surface density, and TPR for supported vanadium oxide catalysts studied.

Sample	Loading (wt%)	Specific surface area (m^2/g)	θ (coverage%)	T_{TPR} ($^\circ\text{C}$)
γ -Alumina	-	120	-	-
VAI-01	2.7	122	15	537
VAI-02	5.4	104	30	528
VAI-03	9	104	50	522

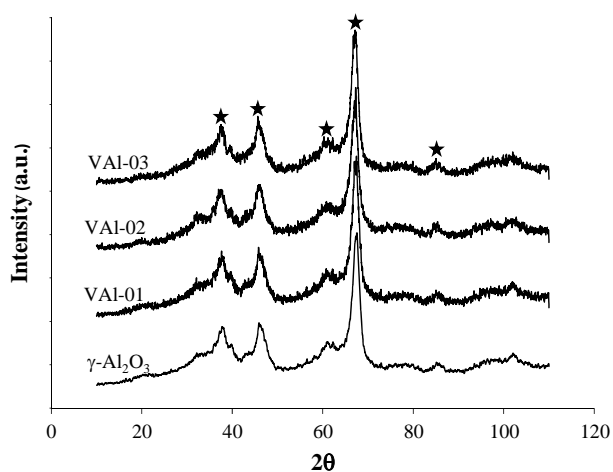


Fig. 2. XRD pattern of the catalyst samples (★: γ -alumina).

As the vanadia content of the catalyst increases, the reaction temperature decreases. In other words, an increase in the loading of vanadia on the surface results in increased catalyst activity. This result is consistent with the TPR test result whereas by increasing vanadia content the reduction temperature decreased. On the other hand, as the vanadia content increases the selectivity to propene decreases (Fig. 4b) High surface area of γ -alumina improves the dispersion of active sites over the surface with enough distance from each other to depress extent of deep oxidation of species to CO_x . As the loading of vanadia increases, the probability of formation of adjacent Bronsted containing active sites increases [2,19]. This may be presumably due to the formation of microcrystallites of vanadia on the surface of γ -alumina by increasing the loading [14,20,27]. Consequently, deep oxidation to CO_x leads to decreased selectivity towards propene. A thorough investigation on the conversion profile versus temperature shows a transient behavior from

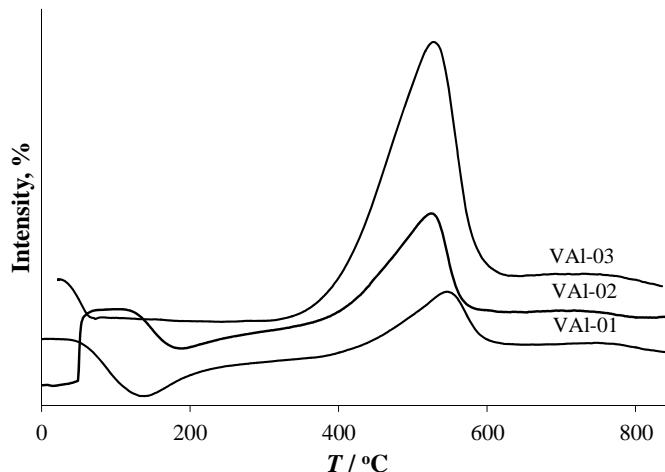


Fig. 3. TPR pattern of the catalyst samples.

low conversions to high conversions as temperature increases. The same transient behavior happens for selectivity to propene but with transition from high selectivities to low selectivities (Fig. 5). All three catalysts showed same behavior with changing temperature at different feed composition from propane rich, stoichiometric, and propane deficient condition. The temperature at which transition occurs, T_{tran} , for each catalyst is almost constant at different feed condition but by increasing vanadia loading, T_{tran} reduces. This can be related to higher activity of higher loaded catalysts. Whether feed is reducing (high C_3/O_2 ratio) or oxidizing (low C_3/O_2 ratio), conversion and selectivity shows different profiles beyond T_{tran} . As the feed composition approaches high C_3/O_2 ratio, the step change caused by increasing temperature is hindered. The performance of all three catalyst samples is similar at low C_3/O_2 ratios and they show same conversion and selectivity. Whilst as the C_3/O_2 ratio increases different catalysts show distinguishable performance.

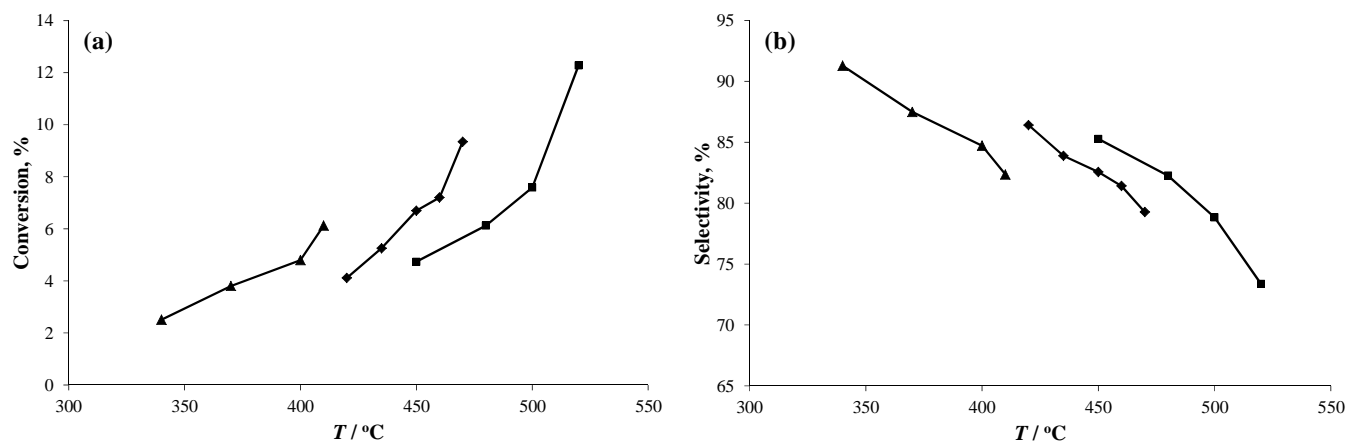


Fig. 4. Propane conversion (a) and propene selectivity (b) over catalysts.

Reaction condition: GHSV= 60000 $\text{cm}^3 \text{gr}^{-1} \text{hr}^{-1}$, Feed composition: $\text{N}_2/\text{O}_2/\text{C}_3= 8/1/1$ (■: VAI-01, ◆: VAI-02, ▲: VAI-03).

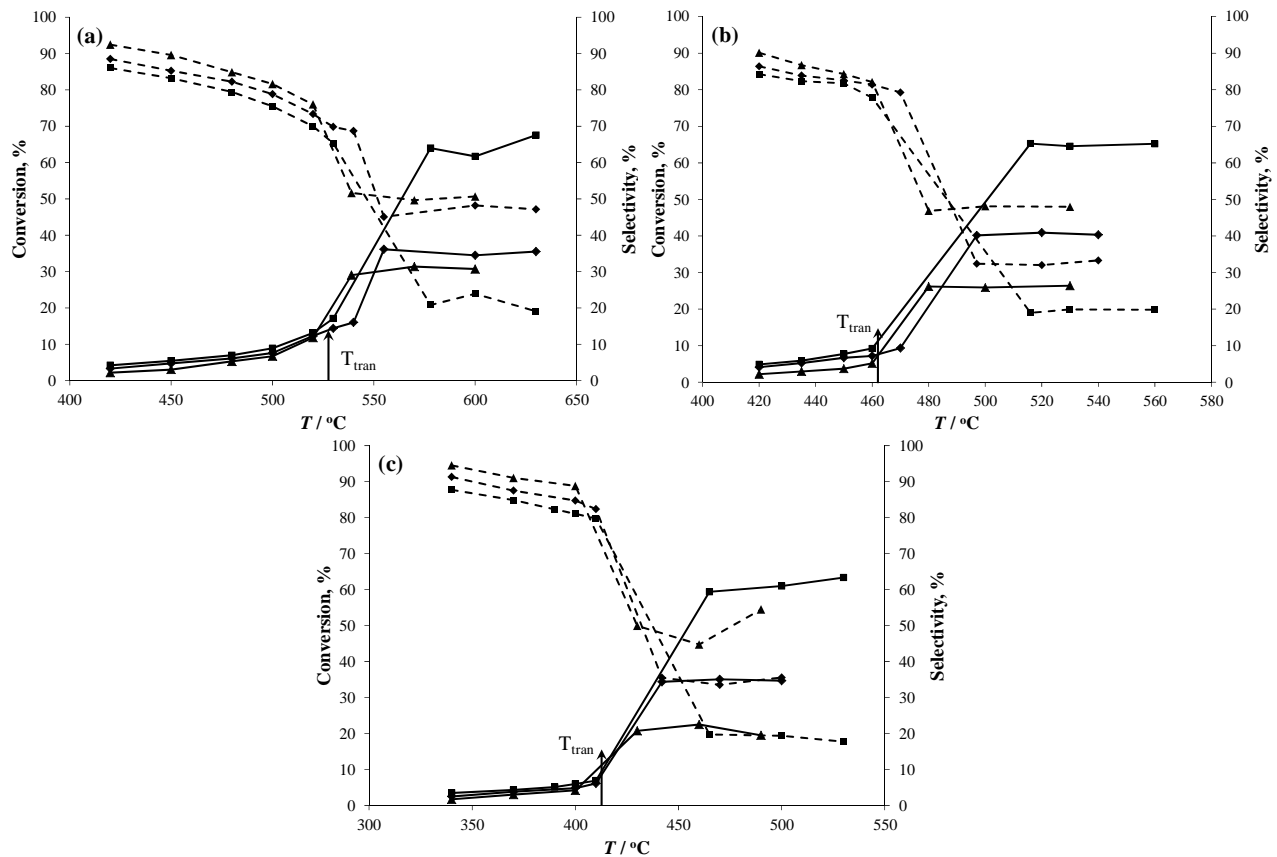


Fig. 5. Feed composition ($N_2/O_2/C_3$) effect on propane conversion (solid line) and propene selectivity (dashed line) over the catalyst samples (a: VAI-01, b: VAI-02, c: VAI-03). Reaction condition: $GHSV = 60000 \text{ cm}^3 \text{ gr}^{-1} \text{ hr}^{-1}$ (■: $N_2/O_2/C_3 = 7/2/1$, ◆: $N_2/O_2/C_3 = 8/1/1$, ▲: $N_2/O_2/C_3 = 7/1/2$).

Fig. 6 shows yield profile versus temperature. Yield increases with temperature, undergoes a sudden increase at T_{tran} , and then remains almost constant. Although VAI-01 exhibits lowest activity amongst catalyst samples, it shows highest yield as the temperature increases beyond T_{tran} . Investigation of Y_{tran} (yield beyond T_{tran}) at different feed composition indicates existence of a maximum value for yield by increasing C_3/O_2 (Fig. 7a). The lowest yield occurs at C_3/O_2 ratio of 1/3. As C_3/O_2 reaches 1/2, a sharp increase in yield is observed. The highest yield happens at the C_3/O_2 of 1/1 and the yield decreases with further increase of C_3/O_2 . The highest yield occurs at propane deficient condition in the range of $1/2 < C_3/O_2 < 2/1$ (Fig. 7b). VAI-01 shows the highest yield amongst three catalysts so that a maximum yield of 17% can be achieved at C_3/O_2 ratio of 1/1 above 550°C . In spite of different catalysts studied, which makes the results incomparable, but these results in accordance with reported by Jibril et al. [39] that states operating at higher temperatures and moderately oxygen rich conditions are beneficial in achieving high

propene yield rather than operating at low temperatures and stoichiometric or propane rich feed compositions.

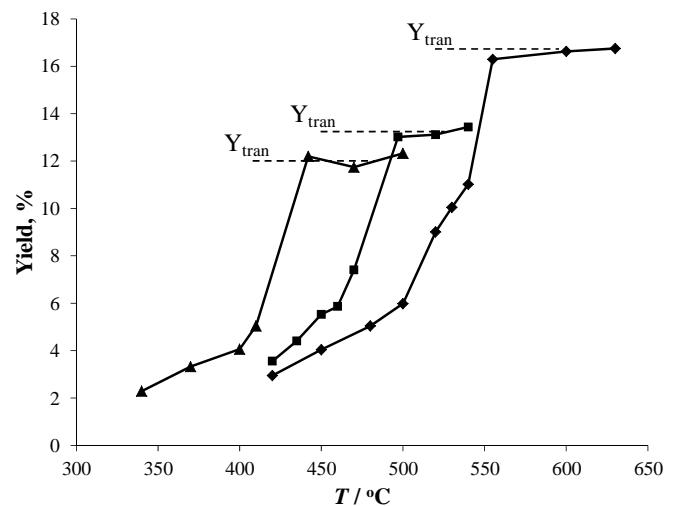


Fig. 6. Propene yield variation with temperature. Reaction condition: $GHSV = 60000 \text{ cm}^3 \text{ gr}^{-1} \text{ hr}^{-1}$, Feed composition: $N_2/O_2/C_3 = 8/1/1$ (◆: VAI-01, ■: VAI-02, ▲: VAI-03).

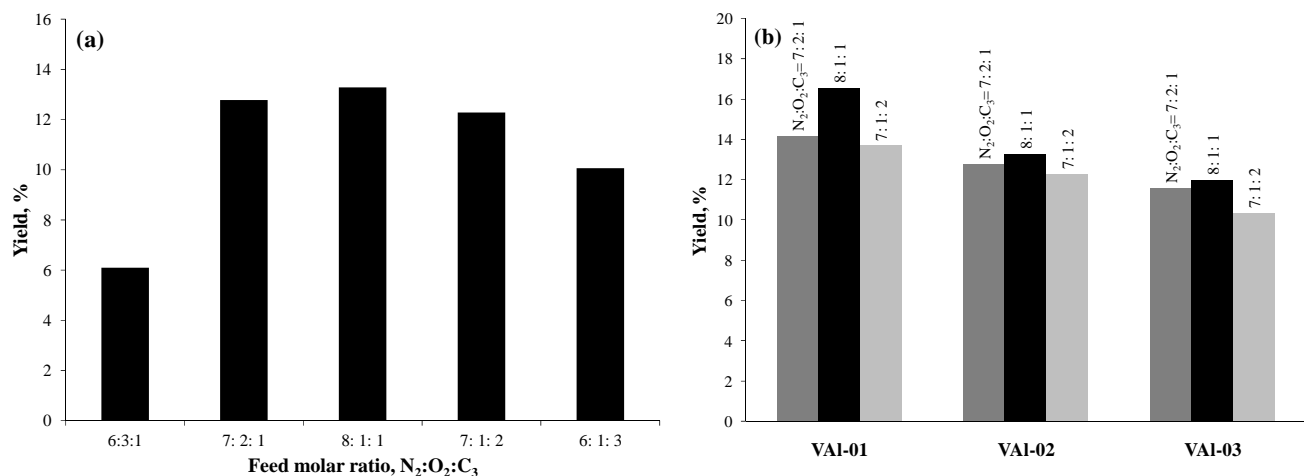


Fig. 7. (a) Variation of maximum propene yield with feed ratio with VAI-02 catalyst, (b) Comparison of maximum propene yield amongst the catalyst samples at different feed ratio. Reaction condition: GHSV= 60000 $cm^3\ gr^{-1}\ hr^{-1}$.

Yield to propene is the result of propane conversion and propene selectivity. Thus, to investigate yield variations, the separate effect of temperature and partial pressure of species on the POD network reaction rates must be taken into account. As said, it is believed that POD reactions take place via MvK mechanism in which abstraction of hydrogen from propane is rate determining step, in other words, the activation energy of selective oxidation of propane to propene is greater than the activation energy of deep oxidation of propene [15,40]. Therefore, the selective oxidation of propane is more sensitive to temperature so that higher temperatures elevate the selectivity to propene at constant conversion. On the other hand, higher partial pressure of reacting species accelerates reaction rate and conversion. Since oxygen is consumed in both selective and deep oxidation, operation at higher oxygen partial pressure ($C_3/O_2 \leq 1/2$) eases re-oxidation of reduced surface and consequently encourages undesired deep oxidation of produced propene, which means reduced selectivity. Although at stoichiometric/propane rich condition ($C_3/O_2 \geq 2/1$) selectivity to propene is relatively higher, but catalyst surface is at reduced state which limits conversion. It seems at $C_3/O_2=1/1$ surface reduction and re-oxidation are balanced in a way that propane oxydehydrogenation reaction, which determines conversion, and further deep oxidation of produced propene, which controls selectivity, are leveled. So overall yield at $C_3/O_2=1/1$ is superior to other conditions.

4. Conclusions

Support, active metal, and promoter have a determining role in the performance of catalysts for achieving higher conversion and selectivity towards desired product. But it is not all which can affect the performance of catalysts. Tuning operating temperature and feed composition as well as so

mentioned parameters can help to increase the overall yields.

Increasing the vanadia content leads to higher activity of catalyst concluded from higher conversion at lower temperatures but as the activity increases by vanadia content, the selectivity to propene declines. The extent of conversion and selectivity highly depends on temperature and feed composition. Due to competitive nature of reactions in the POD process, and considering different effect of reaction atmosphere on the reaction rates of selective oxidation and deep oxidation, as the temperature increases, selective oxidation dominates deep oxidation.

Although oxygen deficient atmosphere leads to higher propene selectivity but because of decelerated re-oxidation step of surface, the conversion at this condition is limited. As the oxygen partial pressure increases in the feed, the reoxidation step of gets accelerated. Consequently the propene selectivity decreases in the expense of increase in conversion. But the extent of selectivity and conversion change depends on feed composition.

In conclusion, by adjusting the feed composition at propane deficient condition and operation at higher temperature, the overall yield increases. The highest propene yield of about 17% is achieved using VAI-01 with 2.7 wt% vanadia content and operation at C_3/O_2 ratio of 1/1 and temperatures above 550 °C.

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