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Higher propene yield by tailoring operating conditions of propane oxidative dehydrogenation over $V_2O_5/\gamma-Al_2O_3$

YOUSEF ZAYNALI and SEYED MEHDI ALAVI*

*Chemical Engineering Department, Iran University of Science and Technology,
P. O. Box 16765-163, Tehran, Iran*

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Abstract: Supported vanadia catalysts were successfully synthesized using wet impregnation of γ -alumina to study propane oxidative dehydrogenation (POD). The prepared catalysts were characterized by X-ray diffraction analysis, specific surface area determination, and temperature programmed reduction tests. Over a broad temperature range (340 to 630 °C), the effects of vanadia loading (2.7, 5.4, and 9 wt. %) and propane to oxygen ratio (3:1 to 1:3) were thoroughly investigated on propane conversion as well as propene yield at atmospheric pressure. The results indicated that on increasing the vanadia content, the activity of catalyst increased while the selectivity to propene decreased monotonically. With increasing temperature from 340 to 630°C, the yield to propene showed an ascending behavior for all catalyst samples. The yield to propene exhibited a maximum on changing the propane to oxygen ratio from 3:1 to 1:3. The yield increased with increasing oxygen partial pressure in the feed until an equimolar ratio of propane and oxygen and then it declined with further increase in the oxygen partial pressure. A maximum propene yield of 17 % was experienced on the catalyst with 2.7 wt. % vanadia at a temperature of 550 °C.

Keyword: propane oxidative dehydrogenation; vanadia loading; propane to oxygen ratio; feed composition.

INTRODUCTION

Propene as a commodity product is an important feedstock in the chemical and petrochemical industries. Propene is used in the production of 2-propanol, acrylonitrile, propylene oxide and epichlorohydrin but its main use is in the production of polypropylene.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 expansion of the polypropylene market^{5,6} makes it crucial to

* Corresponding author. E-mail: alavi.m@iust.ac.ir
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develop new routes and processes for propene production. Due to the 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. However, despite these tempting benefits, the low yield of propene prevents the commercial development of POD.^{7,8}

Vanadia was shown to be selective in the oxidative dehydrogenation of alkanes.^{9–13} Thus, the impact of vanadia catalysts supported on metal oxides was studied for POD.^{14–24} Focused on the dispersion and morphology of vanadia over different supports, Khodakov *et al.*¹⁴ reported that among the different forms of vanadia, a polyvanadate monolayer is more selective in POD reactions. The 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 properties.^{2,24,27–30} Martra *et al.*² studied the acid/base properties of vanadia impregnated on Al₂O₃, H–Na/Y zeolite, MgO, SiO₂, TiO₂ and ZrO₂. In a similar work but with more emphasis on the effect of the support, Dinse *et al.*³¹ examined CeO₂, TiO₂, Al₂O₃, ZrO₂ and SiO₂ with low loadings of vanadia. Although the catalysts with acidic supports showed higher conversions in comparison with more basic ones, they had lower selectivity.⁸ In attempts to enhance the reducibility of the active sites and increase the selectivity to propene, some researchers modified the acid/base properties of the surface by adding different alkali and alkaline earth metals (Li,³² Na,³² K^{8,18,32,33} and Mg³⁴).

Besides the aforementioned factors, the operating conditions and feed composition are decisive parameters in product distribution/catalytic performance of POD reactions.^{34–36} POD is a set of consecutive reactions of oxydehydrogenation of propane and further oxidation of propene to CO and CO₂ according to the Mars van Kerevelen (MvK) mechanism.^{37–40} Whether the reaction proceeds under propane rich (propane to oxygen ratio greater than stoichiometry) or propane deficient (propane to oxygen ratio less than stoichiometry) atmosphere, the controlling step changes and so does the product distribution. To the best of our knowledge, not so many studies thoroughly explore the effect of the propane to oxygen ratio (C₃/O₂) and reaction conditions on overall propene yield. Most of the studies were under stoichiometric or propane rich atmospheres^{2,3,14,16,19,20,24,41–44} and in relatively fewer studies were the results obtained under oxygen-rich condition.^{15,17,21,45,46} Given the very different conditions and even inconsistent results in various studies, it is not possible to reach a concrete understanding of the roles of the operating conditions and feed composition from the published works. According to Creaser *et al.*⁴¹ at low propane concentrations or low propane conversions, a propane-rich atmosphere is beneficial for higher propene yield but no data at higher propane concentrations or conversions were

reported. On the contrary, the results of Jibril *et al.*⁴⁵ showed that higher yields of propene could be achieved at moderately propane deficient feeds.

The aim of present study was to examine the effect of the operating conditions and feed composition over V_2O_5/γ -alumina catalysts to achieve high propene yields. A comprehensive study was performed to explore the effects of vanadia loading over γ -alumina, temperature and feed composition on the overall propene yield, propane conversion and propene selectivity.

EXPERIMENTAL

Catalyst preparation

All catalysts were prepared by wet impregnation of γ -alumina (Merck) support (average particle diameter of 131 μm and density of 2250 kg m^{-3}) with aqueous solution of ammonium monovanadate (Merck). The impregnation was performed in a rotary evaporator (Biby Strilin Ltd., RE200) at reduced pressure and low temperature. The impregnated samples were dried overnight at 110 $^\circ\text{C}$, further treated by heating up to 600 $^\circ\text{C}$ during 3 h, and then calcined at this temperature for 6 h. Three catalysts, VAI-01, VAI-02 and VAI-03, with different vanadia loadings of 2.7, 5.4 and 9 wt. %, respectively, approximately 8 to 10 g of each, were prepared following this procedure.

Characterization

The surface areas of the catalysts and support were 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, the samples were first degassed for 1 h at 300 $^\circ\text{C}$ and 0.15 mbar. The surface areas were calculated using the Brunauer, Emmett and Teller (BET) method.

The X-ray diffraction (XRD) patterns were recorded on an X-Pert Philips diffractometer on powdered samples. The scans were collected within the 2θ range 10–110 $^\circ$ in 0.01 $^\circ$ steps with a 1 s step time using CuK_α radiation.

The reducibility of the catalysts was studied by temperature-programmed reduction (TPR) with a ChemiSorb 2750 (Micromeritics) apparatus. 50 mg of the catalysts were oxidized in an O_2 –He mixture (20 vol. % O_2) with a flow rate of 30 $\text{cm}^3 \text{min}^{-1}$ at 550 $^\circ\text{C}$ for 30 min and then cooled to 50 $^\circ\text{C}$. Successively, the samples were degassed with nitrogen (20 $\text{cm}^3 \text{min}^{-1}$) for 2 h at 250 $^\circ\text{C}$ to remove the non-bound oxygen. After cooling to 25 $^\circ\text{C}$, TPR tests were performed under a 20 mL min^{-1} flow of a 5 vol. % H_2/Ar mixture through a micro-reactor heating at a constant rate of 10 $^\circ\text{C min}^{-1}$ up to 950 $^\circ\text{C}$.

Activity test

A one meter long quartz tube with an internal diameter of 6 mm, installed in a furnace, was used as a reactor. For every test, 100 mg of catalyst diluted with SiC was loaded in the reactor and feed mixture was introduced to catalytic bed at a total flow rate of 100 $\text{cm}^3 \text{min}^{-1}$ at standard temperature and pressure (STP). The feed ratio was varied from $\text{N}_2:\text{O}_2:\text{C}_3 = 6:3:1$ (lean in propane) to 6:1:3 (rich in propane) to investigate the effect of feed composition. A thermometer was installed under the catalytic bed to monitor precisely the temperature of the reaction bed. After quenching and removal of water, the flow exiting the reactor was analyzed with an online Thermofinigan GC (model No. KAV00109) equipped with HayeSep Q, MolSieve 13X columns and in line thermal conductivity detector (TCD) for the detection of permanent gasses, *i.e.*, oxygen, nitrogen, and carbon oxides and Q-Plot column in line with a

flame ionization detector (FID) to detect the hydrocarbons, *i.e.*, propane and propene. The conversion, selectivity, and yield were calculated according to the following equations:

$$\text{Propane conversion: } X_{\text{propane}} = \frac{(F_{\text{propane,i}} - F_{\text{propane,e}})}{F_{\text{propane,i}}} \times 100, \quad (1)$$

$$\text{Propene selectivity: } S_{\text{propene}} = \frac{F_{\text{propene}}}{(F_{\text{propane,i}} - F_{\text{propane,e}})} \times 100, \quad (2)$$

$$\text{Propene yield: } Y_{\text{propene}} = \frac{(S_{\text{propene}} \times X_{\text{propane}})}{100} \quad (3)$$

where $F_{\text{propane,i}}$, $F_{\text{propane,e}}$ and $F_{\text{propene,e}}$ stand for the molar flow rate of propane at the inlet, the molar flow rate of propane at the outlet and the molar flow rate of propene at the outlet, respectively.

RESULTS AND DISCUSSION

The surface areas of the catalysts and the calculated VO_x surface coverage, θ_s (fraction of a theoretical monolayer), are given in Table I as a function of the 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 and the initial BET area of the used $\gamma\text{-Al}_2\text{O}_3$.³² Theoretically, a V_2O_5 loading of 18.1 wt. % is sufficient to form a monolayer of vanadia over the $\gamma\text{-Al}_2\text{O}_3$ support. As can be seen from Table I, in all cases, the vanadia loading was well below that theoretically required for monolayer coverage; thereby, no drastic changes were observed in the BET results. This could be attributed to the good dispersion of vanadia on the γ -alumina surface. A vanadia loading of 2.7 wt. % slightly increased the surface area but a further increase in the vanadia loading led to an approximately 10 % decrease in the surface area. It could be stated that at first, on introduction of vanadia species to the surface of the alumina support, new pores were formed that led to a slight increase in the surface area. With further increase in the surface density of vanadia, although new pores and surfaces were formed, due to blockage of pore opening at the surface and exclusion of the interior surface area, the total surface area decreased.

TABLE I. Vanadium content, surface area (S_{BET}), calculated VO_x surface density (θ_s), and T_{TPR} for the studied supported vanadium oxide catalysts

Sample	Loading, wt. %	$S_{\text{BET}} / \text{m}^2 \text{g}^{-1}$	$\theta_s / \%$	$T_{\text{TPR}} / ^\circ\text{C}$
γ -Alumina	–	120.15	–	–
VAI-01	2.7	122.24	15	537
VAI-02	5.4	104.39	30	528
VAI-03	9	104.20	50	522

According to the XRD patterns presented in Fig. 1, only peaks related to the support were detectable and no V_2O_5 -related peaks could be observed. Small

V_2O_5 crystallites may be formed on the surface but they are not detectable by the X-ray diffraction method due to their poor crystallinity, small unit cell size and low concentration.^{14,31} In accordance with the BET results, it was confirmed that a monotonous dispersion of V_2O_5 species was obtained.

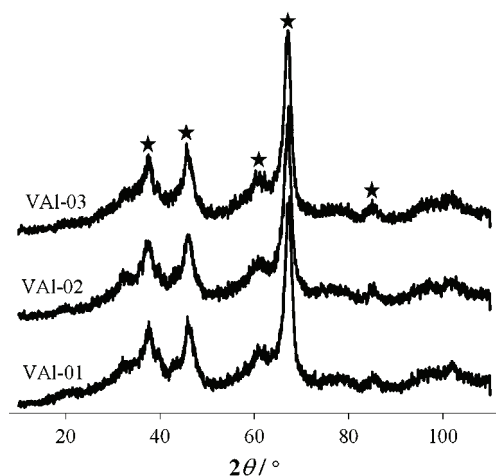


Fig. 1. XRD patterns of the catalyst samples (★: γ -alumina).

The TPR results are presented in Fig. 2. All catalysts start to be reduced at about 350 °C. On increasing the vanadia content, the maximum reduction temperature peak shifted slightly to the left, from 537 °C for VAI-01 to 528 °C and 522 °C for VAI-02, and VAI-03, respectively, indicating better reducibility and higher activity.

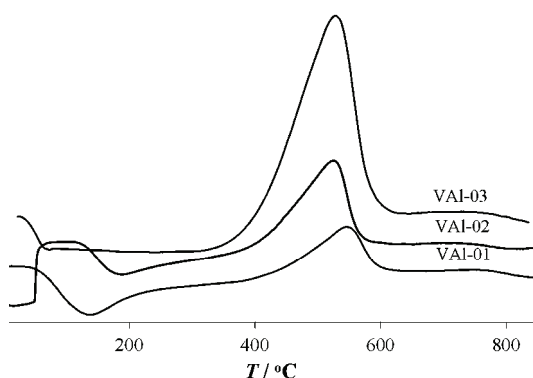


Fig. 2. TPR patterns of the catalyst samples.

The conversion profiles for the three different catalysts at the stoichiometric feed ratio ($N_2:O_2:C_3 = 7:1:2$) are shown in Fig. 3a. As the vanadia content of the catalyst increased, the reaction temperature decreased. This could be interpreted as increasing activity with increasing vanadia loading. This result is consistent with the result of the TPR test. On the other hand, as the vanadia content inc-

reased, the selectivity to propene decreased (Fig. 3b). The large surface area of γ -alumina improves the dispersion of active sites over the surface with sufficient distance between them to depress the extent of deep oxidation of species to CO_x . As the loading of vanadia increased so did the probability of the formation of adjacent Brønsted-containing active sites.^{2,19} This may be due to the formation of micro-crystallites of vanadia on the surface of γ -alumina on increasing the loading.^{14,20,31} Consequently, deep oxidation to CO_x leads to a decreased selectivity towards propene.

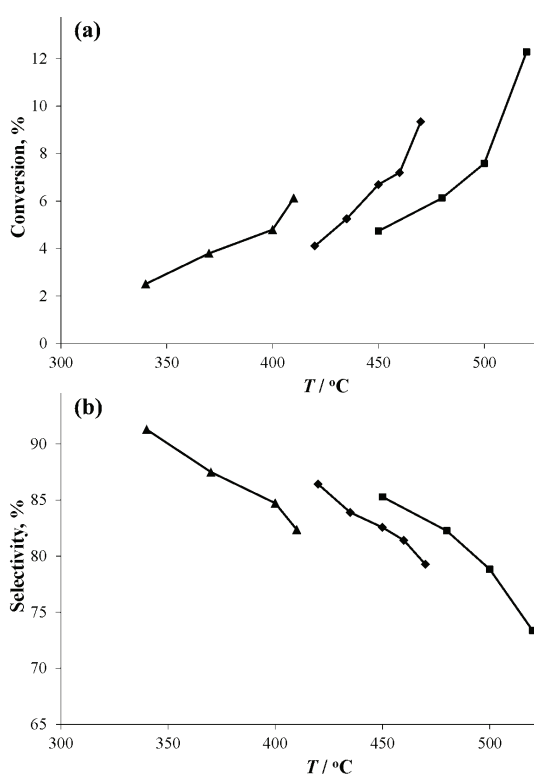


Fig. 3. a) Propane conversion and b) propene selectivity over the studied catalysts. Reaction conditions: gas hourly space velocity = $1.67 \times 10^{-2} \text{ m}^3 \text{ kg}^{-1} \text{ s}^{-1}$, feed composition: $\text{N}_2:\text{O}_2:\text{C}_3 = 8:1:1$. ■) VAI-01, ◆) VAI-02 and ▲) VAI-03.

A thorough investigation of the conversion profile vs. temperature showed that as the temperature increases a shift from low conversions to high conversions occurs. The same transient behavior was observed for selectivity to propene but with the transition from high selectivities to low selectivities (Fig. 4). All three catalysts showed same behavior at different feed compositions from propane rich, stoichiometric, to propane deficient conditions. The temperature at which the transition occurred, T_{tran} , for each catalyst was almost constant under different feed conditions but on increasing the vanadia loading, T_{tran} decreased. This could be related to the higher activity at higher catalyst loadings. Irrespective of whether the feed was reducing (propane rich, high C_3/O_2 ratio) or oxi-

dizing (propane deficient, low $C_3:O_2$ ratio), the conversion and selectivity showed different trends above T_{tran} . The performances of all three catalysts were

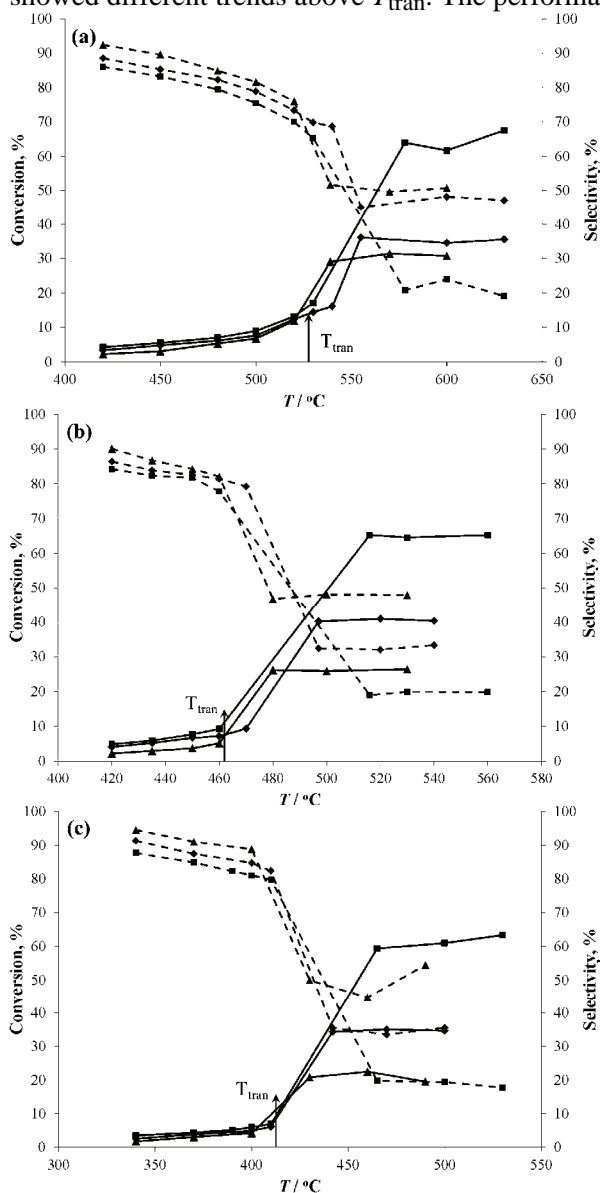


Fig. 4. The effect of the feed composition ($N_2:O_2:C_3$) on propane conversion (solid line) and propene selectivity (dashed line) over the catalyst samples: a) VAl-01, b) VAl-02 and c) VAl-03). Reaction condition: GHSV = $1.67 \times 10^{-2} \text{ m}^3 \text{ kg}^{-1} \text{ s}^{-1}$; $N_2:O:C_3$ – ■) 7:2:1, ♦) 8:1:1 and ▲) 7:1:2.

similar at low $C_3:O_2$ ratios and they show same conversion and selectivity. Whilst with increasing $C_3:O_2$ ratio, the different catalysts show distinguishable performances. As the feed composition approached the high $C_3:O_2$ ratio, the step change caused by increasing temperature was hindered.

The yield profile vs. temperature is shown in Fig. 5. The yield increased with temperature, underwent a sudden increase at T_{tran} and then remained almost constant. Although VAI-01 exhibited the lowest activity amongst catalyst samples, it showed the highest yield as the temperature increased above T_{tran} . Investigation of Y_{tran} (yield above T_{tran}) at different feed compositions indicated the existence of a maximum value for yield on increasing C_3/O_2 (Fig. 6a). The reaction feed compositions varied from $\text{N}_2:\text{O}_2:\text{C}_3 = 6:1:3$ to $6:3:1$, but except for VAI-02, all tests were performed in the range $\text{N}_2:\text{O}_2:\text{C}_3 = 7:1:2$ to $7:2:1$. In comparison with the UEL (upper explosion limit) of propane (9.5 %), all propane mole fractions in reaction mixtures were above the UEL except for $\text{N}_2:\text{O}_2:\text{C}_3 = 6:3:1$. The low yield of propene above T_{tran} at a $\text{C}_3:\text{O}_2$ ratio of 1:3 could be due to operating at temperatures above the AIT (auto ignition temperature) of propane (470 °C), which resulted in homogeneous combustion. As $\text{C}_3:\text{O}_2$ reaches 1:2, a sharp increase in yield was observed. The highest yield was attained at a $\text{C}_3:\text{O}_2$ of 1:1 and the yield decreased with further increasing of $\text{C}_3:\text{O}_2$. The highest yield occurred under propane deficient conditions in the range of $1:2 < \text{C}_3:\text{O}_2 < 2:1$ (Fig. 6b). VAI-01 showed the highest yield amongst the three catalysts so that a maximum yield of 17 % could be achieved at a $\text{C}_3:\text{O}_2$ ratio of 1:1 above 550 °C.

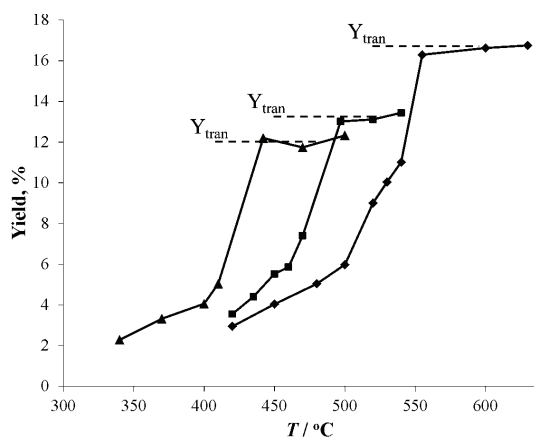


Fig. 5. Propene yield variation with temperature. Reaction conditions: $\text{GHSV} = 1.67 \times 10^{-2} \text{ m}^3 \text{ kg}^{-1} \text{ s}^{-1}$ and feed composition: $\text{N}_2:\text{O}_2:\text{C}_3 = 8:1:1$. (◆) VAI-01, (■) VAI-02 and (▲) VAI-03).

The yield to propene is the result of propane conversion and propene selectivity. Thus, to investigate yield variations, the separate effects of temperature and partial pressure of species on the reaction rates of the POD network must be taken into consideration. As stated, it is believed that the POD reactions occur *via* the MvK mechanism in which abstraction of a hydrogen from propane is the rate determining step; in other words, the activation energy of the selective oxidation of propane to propene is greater than the activation energy of deep oxidation of propene.^{15,47} 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, a higher partial pressure of the reacting spe-

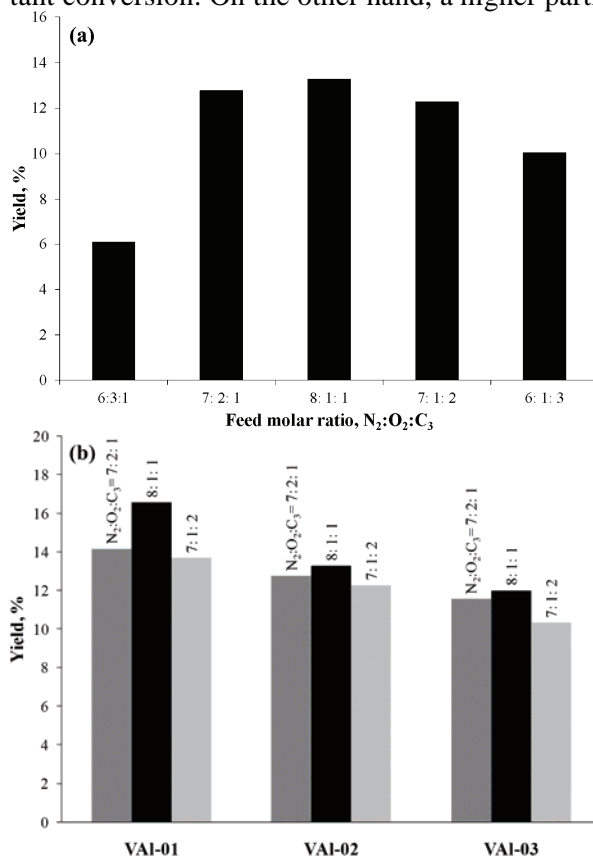


Fig. 6. a) Variation of the maximum propene yield with feed ratio in the case of the VAI-02 catalyst and b) comparison of the maximum propene yield amongst the catalyst samples at different feed ratios. Reaction condition: gas hourly space velocity = $1.67 \times 10^{-2} \text{ m}^3 \text{ kg}^{-1} \text{ s}^{-1}$.

cies accelerates the reaction rate and conversion. Since oxygen is consumed in both selective and deep oxidation, operation at higher oxygen partial pressure ($\text{C}_3:\text{O}_2 \leq 1:2$) eases the re-oxidation of the reduced surface and consequently encourages the undesired deep oxidation of the produced propene, which means reduced selectivity. Although under stoichiometric/propane rich conditions ($\text{C}_3:\text{O}_2 \geq 2:1$), selectivity to propene is relatively higher, the catalyst surface is in a reduced state which limits conversion. It seems that at $\text{C}_3:\text{O}_2 = 1:1$, surface reduction and re-oxidation are balanced in such a way that the propane oxydehydrogenation reaction, which determines conversion, and further deep oxidation of the produced propene, which controls selectivity, are leveled. Hence, the overall yield at $\text{C}_3:\text{O}_2 = 1:1$ was superior to those obtained under other conditions.

CONCLUSION

The support, active metal, and promoter have determining roles in the performance of catalysts in terms of the achievement of higher conversions and selectivity towards the desired product. However, these are not all that can affect the performance of catalysts. Tuning the operating temperature and feed composition could also help to increase the overall yields.

Increasing the vanadia content leads to higher activity of catalyst as concluded from the higher conversion at lower temperatures. However, as the activity increases with vanadia content, the selectivity to propene declines. By adjusting the feed composition at propane deficient conditions and operation at higher temperatures, the overall yield increases. The highest propene yield of about 17 % was achieved using VAl-01 with 2.7 wt. % content of vanadia and operating at a C₃:O₂ ratio of 1:1 at temperatures above 550 °C.

ИЗВОД

ДОБИЈАЊЕ ВЕЋЕГ ПРИНОСА ПРОПЕНА ПОДЕШАВАЊЕМ РАДНИХ УСЛОВА
ОКСИДАТИВНЕ ДЕХИДРОГЕНИЗАЦИЈЕ ПРОПАНА НА V₂O₅/γ-Al₂O₃

YOUSEF ZAYNALI и SEYED MEHDI ALAVI

*Chemical Engineering Department, Iran University of Science and Technology,
P. O. Box 16765-163, Tehran, Iran*

Чврсти катализатор ванадијум-пентоксид је успешно синтетисан импрегнацијом γ-глинице ради испитивања оксидативне дехидрогенизације пропана. Добијени катализатор је окарактерисан следећим методама: XRD, BET и TPR. У широком опсегу температура (340 до 630 °C), испитиван је утицај различитих количина ванадијум-пентоксида (2,7, 5,4, и 9 мас. %) и односа кисеоник:пропан (3:1 до 1:3) на конверзију пропана, као и на принос пропена на атмосферском притиску. Добијени резултати указују на то да са порастом садржаја ванадијум-пентоксида расте активност катализатора док селективност за пропен монотонно опада. Принос пропена расте са порастом температуре од 340 до 630 °C у случају свих испитиваних катализатора. Принос пропена достиже максимум при промени односа пропан:кисеоник од 3:1 до 1:3. Принос расте са порастом парцијалног притиска кисеоника до еквимоларног односа пропан:кисеоник, а затим опада са даљим порастом парцијалног притиска кисеоника. Максимални принос пропена од 17 % је добијен у случају катализатора који садржи 2,7 мас. % ванадијум-пентоксида на температури од 550 °C.

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