

RESEARCH PAPER

Propane Oxidative Dehydrogenation over Vanadium Oxide Nanostructures Supported on Porous Graphene Prepared by Hydrothermal Method

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ABSTRACT

In this study at first, in laboratory, three types of vanadium oxide were produced by using porous graphene and amine framework in hydrothermal method nanostructures such as: vanadium oxide - octadecyl amine - graphene, vanadium oxide - dodecyl amine - graphene and vanadium oxide - aniline - graphene (V-ODA-G, V-DDA-G, V-A-G). Then their structures and functions in propane dehydrogenation reactions were studied and productivity and efficiency of these catalysts in mentioned reactions were compared with each other. In order to notice and compare the structures and properties of synthesized catalysts, some methods such as Field Emission Scanning Electron Microscope (FE-SEM), X Ray Diffraction (XRD), Thermo Gravimetric Analysis (TGA), Fourier Transform Infrared Spectrometry (FTIR), Gas Chromatography (GC) have been used. The obtained results show that vanadium oxide nanostructures have great opportunities to be oxidatively dehydrogenation (ODH) and make sciences explore the use of porous graphene as catalysts for propane oxidative dehydrogenation.

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INTRODUCTION

Due to the growing need to use light olefins in various industries, demand, is growing for light olefins (alkenes) such as propene, butane and isobutene and olefin products. Propylene is one of the most important building blocks in different petrochemical and polymer processes. Fossil fuels (natural) lack the light olefin and most of them include saturated hydrocarbons and aromatics, since we are forced to use synthesis approach to produce light olefin [1-5]. Unsaturated hydrocarbons such as ethylene and propylene, are important classes of materials that are used in chemicals and polymers production. Between the

light olefins, propylene can be used in high scale in polypropylene, acrylonitrile, propylene oxide production and etc. polypropylene is also one of the key products of petrochemical that is used as food for the production of numerous polymers and intermediate products [6-7]. The wide range of using oxidation states and polyhedral coordination in vanadium-oxide system as well as the use of soft chemistry methods makes synthesis of a large amount of metastable vanadium oxides possible with open structures containing organic species or simple metal cations [8]. Vanadium oxides, the class of transition metal oxides with vanadium, have various valence states and result in a number

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of oxide forms of vanadium oxides. These oxide materials show different properties with various compositions and have fascinating technological applications and they attract academic interests [8–14]. The most important derivatives of propylene are polypropylene, acrylonitrile, propylene oxide, phenol, Oxo-alcohol, acrylic acid Isopropyl alcohol, oligomers and various intermediate materials that are finally used as the materials needed in electronics, machinery, construction, packaging and so on [15-16].

Several techniques are available to achieve different levels of polypropylene. Considering the low efficiency and some problems including surplus products such as ethylene and propylene, development of new technologies is essential in polypropylene production [17-18]. One of these new technologies, which is invented in famous companies, is the dehydration of propane which is done in two ways: (a) Non-oxidative dehydrogenation or catalytic (b) oxidative dehydrogenation (ODH). In this method, oxygen is used to prevent coking and deactivating the catalyst [19-20].

Supported vanadium oxide (vanadium) is a commonly employed catalyst for several reactions and is most extensively studied in oxidative dehydrogenation of propane ODHP [21].

In this paper vanadium oxide Nano catalysts (V-ODA-G·V-DDA-G·V-A-G) were produced by using porous graphene and amine framework in hydrothermal method. Then catalytic performance has been determined by some techniques, such as Field emission Scanning Electron Microscope (FE-SEM), X Ray Diffraction (XRD), Thermo Gravimetric Analysis (TGA), Fourier Transform Infrared Spectrometry (FTIR), Gas Chromatography (GC). The obtained results show that vanadium oxide nanostructures have great opportunities for oxidative dehydrogenation (ODH) and encourage us to explore the use of porous graphene as catalysts for propane oxidative dehydrogenation.

MATERIALS AND METHODS

All of vanadium pentoxides (V_2O_5), octadecyl amine ($C_{18}H_{37}NH_2$), dodecyl amine ($C_{12}H_{25}NH_2$), aniline ($C_6H_5NH_2$), benzyl amine ($C_6H_5CH_2NH_2$), ethanol, n-hexane, ethyl alcohol were prepared by Merc Company and Mesoporous Graphene and multi-walled carbon nanotubes (MWCNT) were prepared by RIPI Company.

Synthesis of nanocatalysts

In order to get sample of V-ODA-G, first the vanadium oxide (0.9 g) and octadecyl amine (1.35 g) and mesoporous graphene (0.06 g) were mixed completely with a molar ratio of (1: 1: 1) in 200 ml of ethanol, and then the obtained mixture was stirred for 120 minutes at a temperature 80 °C. Then, a small amount of water (50 ml) was added to the obtained mixture and it was put in an autoclave for 24 hours under the temperature 200 °C. At the end, autoclave was kept in room temperature and cooled. Then, content of autoclave was rinsed as the obtained product, by using n-hexane and ethyl alcohol for several times. At the end, the rinsed product was put in a vacuum oven to dry at 80 °C temperature for 24 hours. The final obtained product is nanostructured vanadium oxide based on graphene and octadecyl amine (V-ODA-G) (Fig. 1).

In order to prepare samples of **V-DDA-G** and **V-A-G**, above mentioned technique can be used (preparing sample of V-ODA-G) but instead of octadecyl amine, dodecyl amine and aniline were used, respectively.

Determine the oxidation reaction mechanism

In this study, a vitro system was used in order to measure the selectivity, conversion and efficiency of synthesized catalysts. This vitro system is shown in Fig. 2. First, certain amount of catalyst with equivalent weight of quartz powder was put in the reactor, and then some rock wool were placed in the middle part of the reactor and both sides of catalyst in order to prevent the outflow of catalyst



Fig. 1. Monomer and Dimer structure of catalyst (s = graphene)

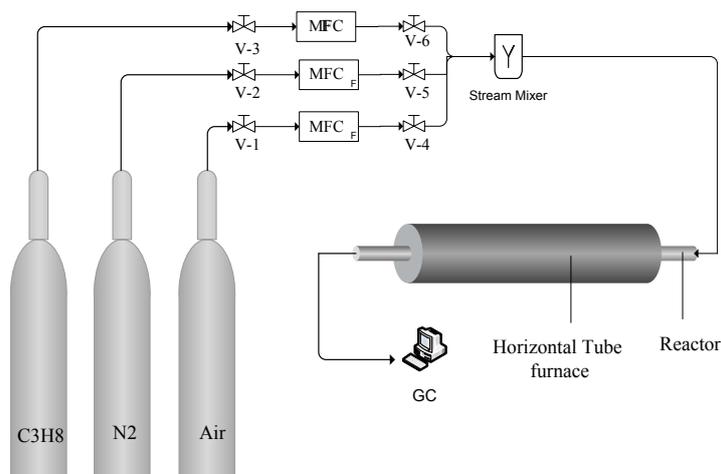


Fig. 2. Used reactor system to determine the oxidation reaction mechanism

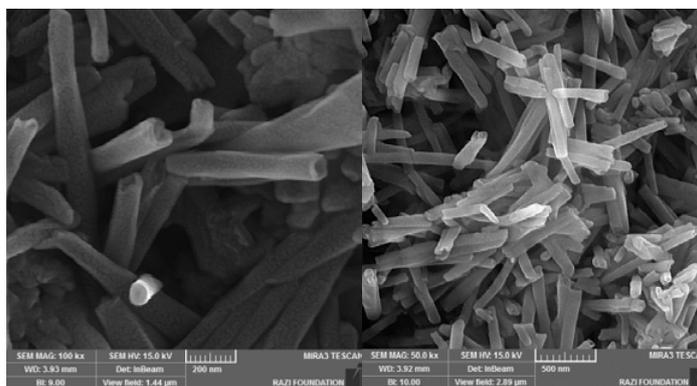


Fig. 3. SEM image of the V-ODA-G.

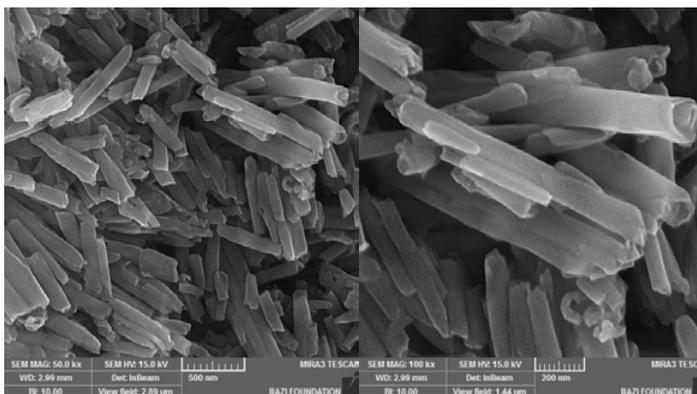


Fig. 4. SEM image of the V-DDA-G.

which is influenced by the gas flow. [22-23]. After setting the input gas flow by controller, all three streams were crossed the mixer and then entered into the reactor. The temperature of the reactor

was increased from 25 °C to 500 °C.

In order to analyze the gaseous outcomes of reaction, given amount of emission gas was gathered in a special bag. For analysis of gas

chromatography, some equipment including Agilent 6890 GC with FID and TCD columns were used. To measure the percentage of conversion of propane and selectivity, the carbon balance of inputs and outputs were used:

C_c was pieces with carbon atoms in the emissions gas, m_c was number of carbon atoms, f_c was intensity of partial molar flow.

RESULTS AND DISCUSSION

Characterization of the catalysts

All of the vanadium oxide nanocatalysts (V-ODA-G·V-DDA-G·V-A-G) have been produced by using porous graphene and amine frameworks such as octadecyl amine, dodecyl amine, and aniline, then the obtained nanocatalysts have been researched by some techniques, such as Field emission Scanning Electron Microscope (FE-SEM), X Ray Diffraction (XRD), Thermo Gravimetric Analysis (TGA), Fourier Transform Infrared Spectrometry (FTIR) and Gas Chromatography (GC).

Field emission Scanning Electron Microscope (FE-SEM)

In Fig. 3 to Fig. 5 the FESEM images of synthesized vanadium pentoxide catalyst based on porous graphene and amine frameworks such as octadecyl amine, dodecyl amine, and aniline, are shown respectively. According to Fig. 3 and Fig. 4, it can be understood that, synthesized vanadium pentoxide catalyst based on porous graphene and octadecyl amine and dodecyl amine frameworks, has got a structure near to nanotubes. Based on Fig. 5, the structure of synthesized nanocatalyst with aniline is a needle-shaped morphology, one-dimensional and uniform. In general, according

to the forms and comparing the size of the synthesized particles, it is seen that, synthesized catalyst based on graphene has a particle size smaller than the other catalysts.

X-ray diffraction analysis

XRD technique was employed to investigate the phase structure of the nanocatalysts. There is a widespread disagreement in attributing the structure of titanate nanotubes to the XRD frameworks.

In Fig. 6a to Fig. 6c the XRD spectra of synthesized vanadium pentoxide catalyst based on porous graphene and amine frameworks such as octadecyl amine, dodecyl amine, and aniline, are shown, respectively. In XRD spectra of the samples, the greatest peak and size is related to the alkyl chains. In fact, alkyl groups of CH_3 are controller for the distance between layers of nanotube VOx.

TGA analysis

TGA graphs for all mentioned nanocatalyst were recorded in Fig. 7 to Fig. 9. As it is clear in these graphs, there is weight loss (approximately 5%) in the temperature range of 50 to 100 ° C, which is related to evaporation and outflow of water molecules from the samples. In fact, this weight loss is indicative to desorption of water molecules within the sample structure. Also, according to graphs, there are weight losses (approximately 10 to 12%) in the temperature range of 100 to 430 ° C, which is related to the decomposition of remaining organic molecules in the sample structure. At the end of the graph, there is a weight loss (approximately 2%) in the

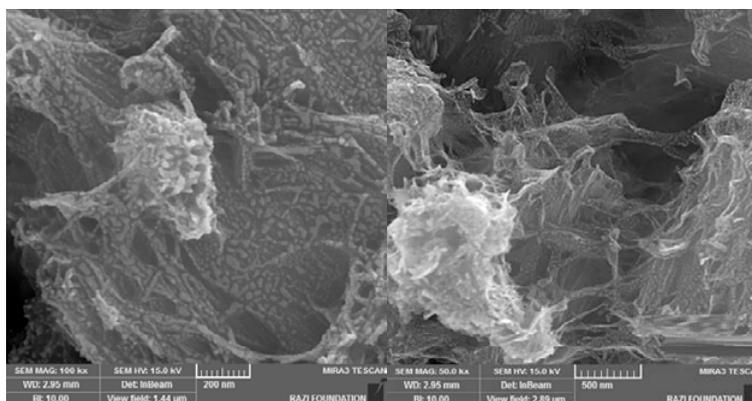


Fig. 5. SEM image of the V-A-G.

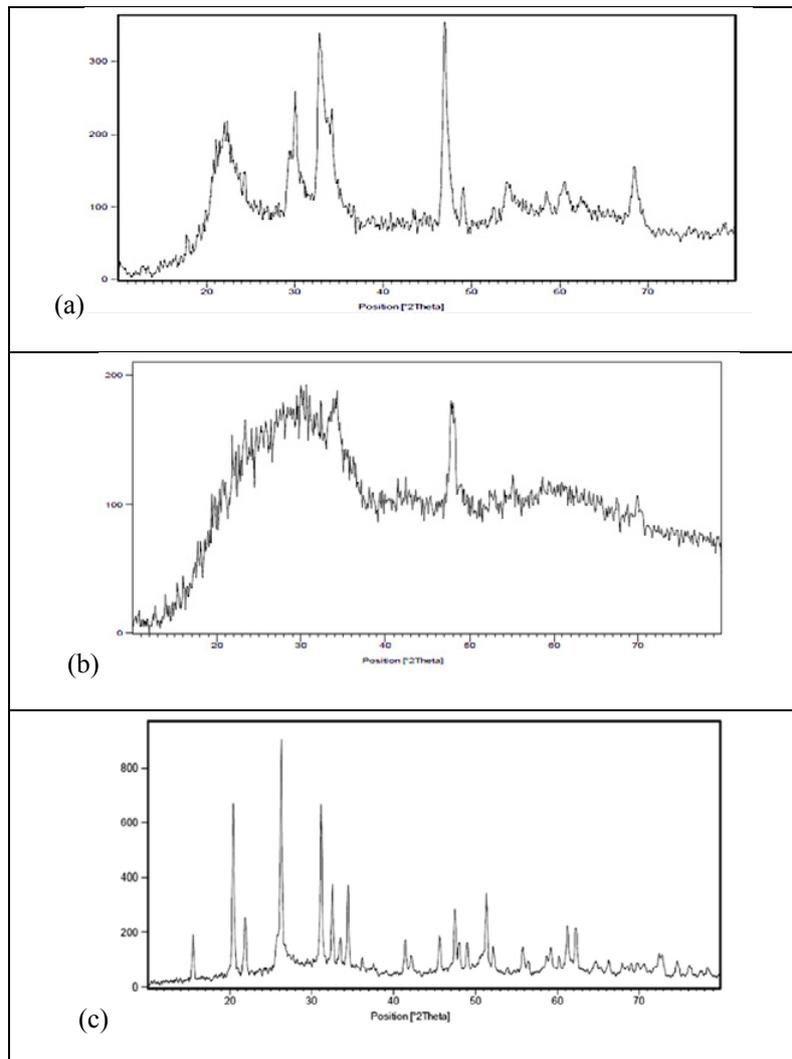


Fig. 6. XRD spectra for sample of V-ODA-G(a), V-DDA-G(b)and V-A-G(c).

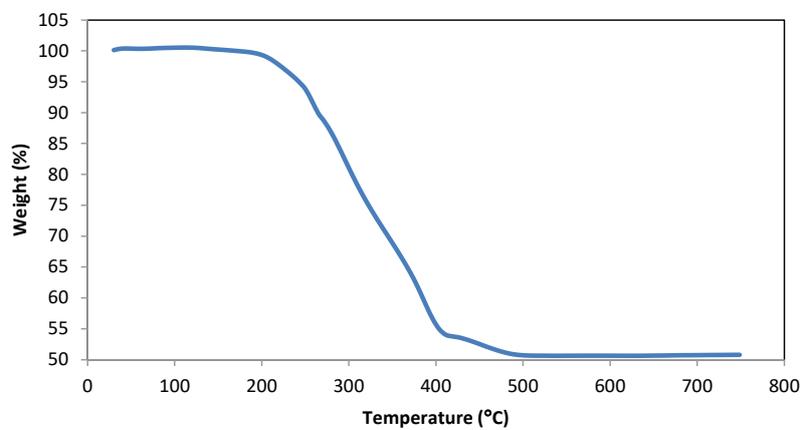


Fig. 7. TGA profiles for sample of V-ODA-G.

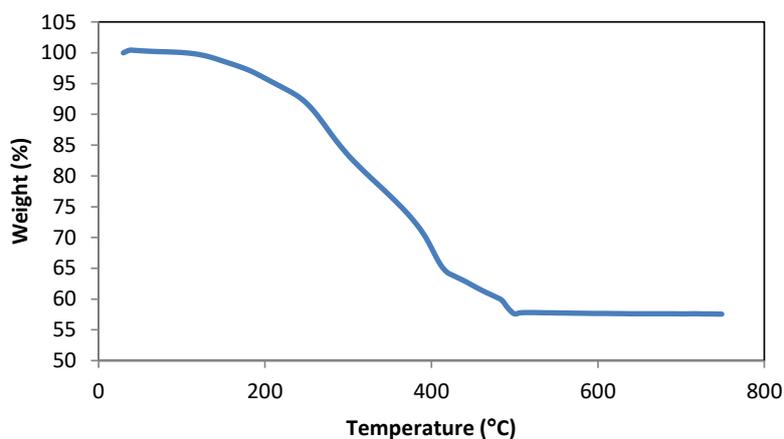


Fig. 8. TGA profiles for sample of V-DDA-G.

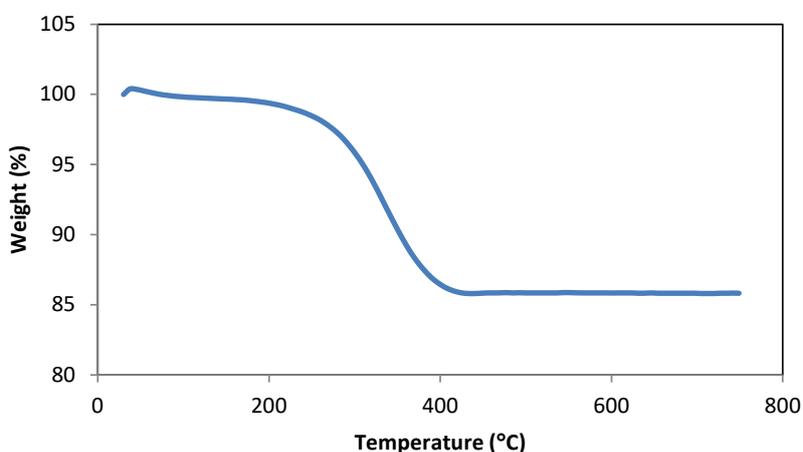


Fig. 9. TGA profiles for sample of V-A-G.

temperature range of 450 °C, that represents the oxidation process of vanadium V^{4+} and formation of yellow Vanadium pentoxide particles according to the following formula:

FTIR analysis

The structure of the prepared catalysts was investigated by IR spectroscopy as presented in Fig. 10a to Fig. 10c the FTIR spectra of synthesized vanadium pentoxide catalysts based on porous graphene and amine frameworks such as octadecyl amine, dodecyl amine, and aniline, are shown, respectively. Investigation and analysis of these FTIR spectrums reveals that, the forecasted structure for each of the nanocatalysts is true. In these Spectra there are signals between the 400 to 1000 cm^{-1} , that they are related to V-O vibrations,

In fact, the broad spectrum of absorption in the range 528 to 541 is related to symmetric and asymmetric stretching vibration of VOV groups in the VOx layers. The signal in the range 915 to 924 cm^{-1} is indicated the vanadyl group V = O. A weak bond in the range 1003 to 1008 is related to the initial deviation of octahedral rearrangement VO_2 . This peak shows the layered structure of vanadium is reorganized on carbon nanostructure samples. C-C stretching bonds in the range 1550-1650 cm^{-1} are related to nanotubes. Very low intensity bands of phenone, around 3400 cm^{-1} , is related to the H_2O or OH groups, that they are absorbed in the sample surface. Due to the influence of the interaction between carbon nanostructures with vanadium metal species, all peaks have shifted to the right slightly.

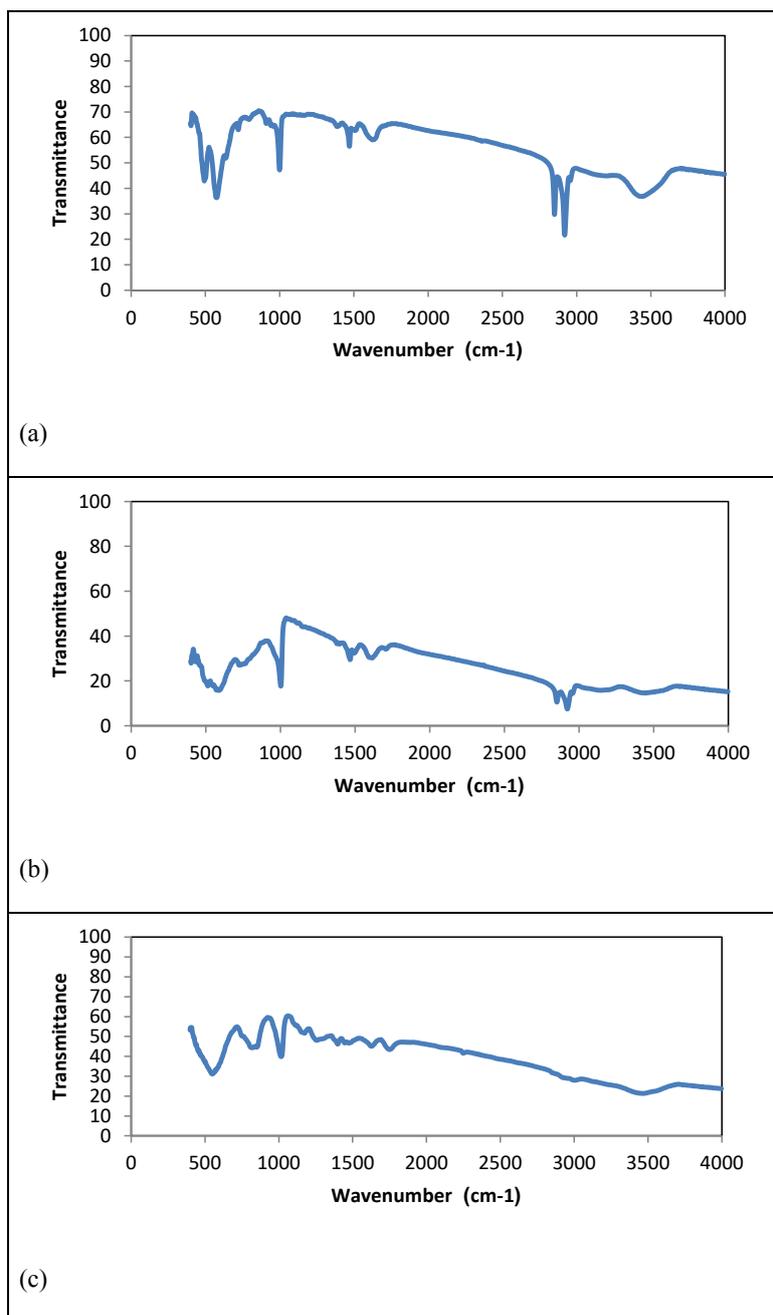


Fig. 10. FTIR spectrum for sample V-ODA-G(a), V-DDA-G(b) and V-A-G(c).

GC analysis

All of the vanadium pentoxide catalysts based on porous graphene and amine frameworks have been studied by Gas Chromatography (GC) technique. In order to do better and easier comparison, the results of GC test are given in Table 1. According to this table, in experimenting of a catalyst, when the temperature was

increased from 450 °C to 600 °C, the selectivity towards ethylene was raised, while selectivity towards propylene was reduced. Because raising the temperature can be lead to oxidation of propane and propylene production, thus it can be seen that, the total selectivity is decreased. In the low temperature, necessary energy for dehydrogenation reaction is not provided, and a

Table 1. The Laboratory results of gas chromatographic analysis

Catalyst	Temperature (°C)	The conversion of propane Percent	CO _x	Selectivity percent			propylene yields Percent
				C ₂ H ₄	C ₃ H ₆		
V-ODA-G	600	58	35.5	23.1	40.56	23.53	
	550	51.3	32.3	20.9	46.62	23.92	
	500	49.1	30.4	19.1	49.77	24.44	
	450	49.1	28.9	18.3	52.14	18.40	
V-DDA-G	600	35.3	35.2	21.3	43.19	25.87	
	550	59.9	32.1	19.7	47.28	26.19	
	500	55.4	29.9	18.1	51.87	26.76	
	450	51.6	27.7	16.9	55.12	20.39	
V-A-G	600	37	18.2	25.7	56.05	37.56	
	550	67	13.6	22.1	64.16	37.92	
	500	59.1	12.1	21.4	66.35	37.56	
	450	56.3	10.5	19.9	68.76	32.86	
	450	47.8	10.5	19.9	68.76	32.86	

V-ODA-G

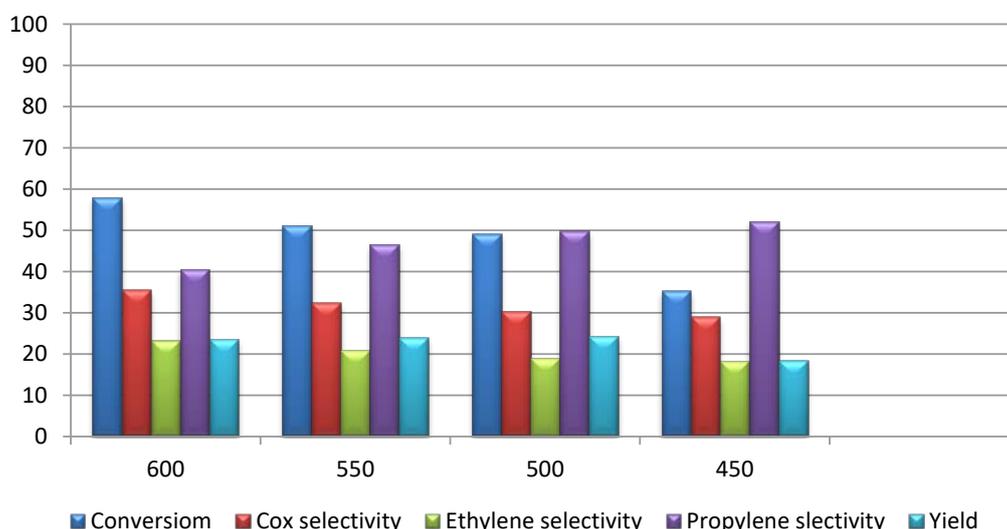


Fig. 11. Selectivity values of ethylene, propylene and carbon dioxide, propylene yields for catalysts of V-ODA-G at different temperatures (°C)

greater deal of adsorbed propane on the catalyst participates in the combustion reaction because produced propylene in low temperature can go out of reaction place with much more difficulty. In this case, increasing the temperature leads to the increase of CO_x production. Also both of the conversion percentages and efficiency will be improved by temperature increase. According to Table 1, it can be noticed that, the selectivity towards ethylene always increases by the increase of temperature. Unlike ethylene, selectivity towards CO_x shows sharp decline by the increase of temperature. This is because, increasing

temperature leads to less propane burning.

Propane conversion and propylene selectivity are related to the type of prior structure, and the presence of any impurities on the surface of the catalyst may act as a diluent of site and it causes to the increase of selectivity in dehydrogenation reaction. Carbon bases can operate as inactive particles and lead to increase of selectivity towards propylene. The selectivity charts of ethylene, propylene and carbon dioxide, and charts of propylene yields for catalysts of V-ODA-G, V-DDA-G and VAG are shown in Fig. 11 to Fig. 13 respectively.

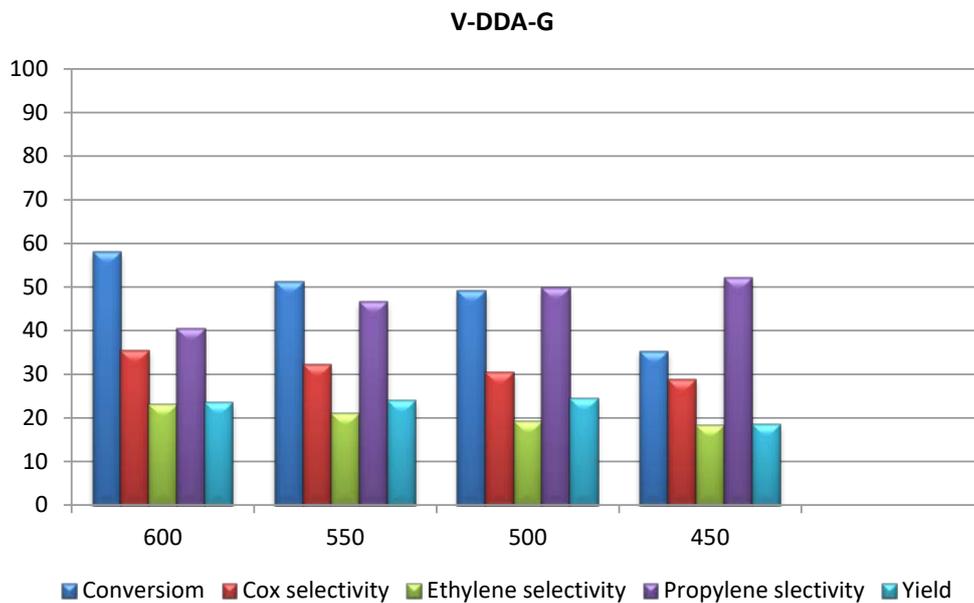


Fig. 12. Selectivity values of ethylene, propylene and carbon dioxide, and propylene yields for catalysts of V-DDA-G at different temperatures (°C)

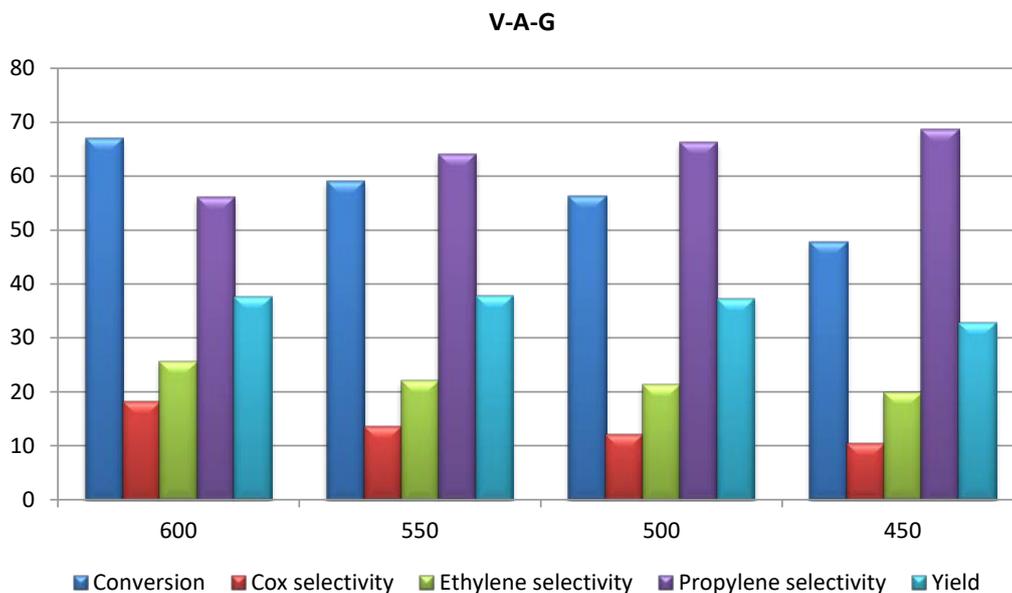


Fig. 13. Selectivity values of ethylene, propylene and carbon dioxide, propylene yields for catalysts of V-A-G at different temperatures (°C)

CONCLUSION

In this paper, first the vanadium oxide nanocatalysts (V-ODA-G, V-DDA-G, V-A-G) was produced by using porous graphene and amine framework in hydrothermal method in the lab, and these nanocatalysts are made use of in oxidative

dehydrogenation reaction of propane. Then, the structure and catalytic function of these compounds were studied by using different techniques. The results show that, the obtained catalysts have an excellent active surface area (surface available for reaction) and they have controllable shape and

size to achieve the maximum of activity, and also they have high selectivity and efficiency. The result reveals that vanadium oxide nanocatalysts on Graphene could be an effective catalyst for ODP when the gasification reaction is prohibited and vanadium oxide nanocatalysts on Graphene can be a good alternative and an affordable catalysts for oxidative dehydrogenation.

CONFLICT OF INTEREST

The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

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