



## Preparation, Characterization and Evaluation of a V<sub>2</sub>O<sub>5</sub>/CNT Catalyst for the Oxidative Dehydrogenation of Propane

M. Fattahi, M. Kazemeini\*, F. Khorasheh, A.M. Rashidi

Department of Chemical and Petroleum Engineering, Sharif University of Technology, Tehran, Iran  
kazemini@sharif.edu

### Abstract

Samples of the V<sub>2</sub>O<sub>5</sub> catalysts supported on multiwall as well as; singlewall carbon nanotubes (MWCNT and SWCNT) were synthesized via hydrothermal method for the oxidative dehydrogenation of propane (ODHP) to propylene. The vanadium catalysts supported on CNTs with the C/V molar ratio of 1:1 were prepared. The catalysts were characterized by the XRD, FTIR, H<sub>2</sub>-TPR, FESEM and UV-vis diffuse reflectance spectroscopy. The performance of the prepared catalysts and the bare supports were subsequently examined in a fixed-bed reactor. The main products were propylene, ethylene, and CO<sub>x</sub>. The vanadium catalyst synthesized had the best performance under the reactor test conditions of 450°C, feed C<sub>3</sub>H<sub>8</sub>/Air molar ratio of 0.6 and the total feed flow rate of 90ml/min resulting in average values of 37.97% and 30.59% for propylene selectivity and propane conversion, respectively. Results under conditions in comparison with open literature values revealed satisfactory performance.

**Keywords:** Oxidative dehydrogenation, Nanostructure, V<sub>2</sub>O<sub>5</sub>, Hydrothermal method, CNT.

### Introduction

Oxidative conversion of light alkanes to olefins is still a challenging approach not only from a fundamental but also from an applied point of view. Investigations on the catalytic oxidative dehydrogenation of propane (ODHP) have been undertaken since this route is expected to lead to lower costs of propylene production as compared with the non-catalytic and non-oxidative processes. The presence of oxygen limits coking and extends the catalysts lifetimes [1-5]. Two most prominent catalytic systems studied for the catalytic ODHP are molybdenum based and vanadium based catalysts [2-4]. The main challenge is minimizing the formation of carbon oxides (CO<sub>x</sub>) in favor of selective products. Propane is dehydrogenated to propylene, and in parallel, to oxidation products. Carbon monoxide is generally produced by oxidation of propylene, while carbon dioxide is generated by oxidation of both propane and propylene. Ethylene is also produced by cracking of both propane and propylene.

In this research, the catalytic activity of a V<sub>2</sub>O<sub>5</sub> over CNTs prepared by hydrothermal as well as; pristine CNTs in the ODHP reaction was demonstrated. The effects of the CNT type including the SWCNT and MWCNT at 450°C, C<sub>3</sub>H<sub>8</sub>/Air=0.6 and total feed flowrate of 90ml/min were investigated in a conventional fixed-bed reactor. The synthesized catalysts were characterized by the XRD, FTIR, H<sub>2</sub>-TPR, FESEM and UV-vis diffuse reflectance. This

investigation provided a simple yet effective catalyst synthesis route towards a better performance for the ODHP reaction.

### Experimental

The MWCNT and SWCNT were calcined under air atmosphere at  $400^\circ\text{C}$  for 2h and were designated as MWCNT-1 and SWCNT-1; respectively, for subsequent reactor tests. Both vanadium pentoxide ( $V_2O_5$ ) and MWCNT as well as, SWCNT produced in-house [6, 7]. This was done in carbon to vanadium (C/V) molar ratio of 1:1 dissolved in 200ml of ethanol. The solution temperature was raised to  $90^\circ\text{C}$  under vigorous stirring for 120 minutes. This solution and 50ml of water were added to a Teflon-lined autoclave with a stainless steel shell kept at  $180^\circ\text{C}$  for 48h. After quenching to room temperature, the autoclave was heated up again to  $180^\circ\text{C}$  for an additional 24h. The resulting precipitate was filtered and washed to get neutralized. This precipitate was then washed with a solution of ethanol and n-hexane then dried at  $100^\circ\text{C}$  for 24h to ultimately obtain the vanadium oxide over the MWCNT and SWCNT. The samples were subsequently calcined at  $500^\circ\text{C}$  for 2h under nitrogen atmosphere and under air atmosphere at  $500^\circ\text{C}$  for an additional 2h. The resulting catalysts prepared by the hydrothermal method were designated as V-MWCNT-1 and V-SWCNT-1. The prepared catalysts were then characterized by the FESEM, XRD, TPR, FTIR, and UV-vis diffuse reflectance. Catalyst performance tests were carried out in a conventional tubular fixed-bed quartz reactor.

### Results and Discussion

Figure 1 illustrated the FESEM micrographs for samples V-MWCNT-1 and V-SWCNT-1; respectively. This figure revealed a porous network of entangled CNTs with diameters of about 40 to 120nm and lengths up to the micron scale. The growth of the  $V_2O_5$  within the porous CNTs networks by the hydrothermal method led to the formation of flexible nanomaterials with a dark-green color where the  $V_2O_5$  loading could be readily controlled by tuning the ratio of the CNTs to the  $V_2O_5$ .

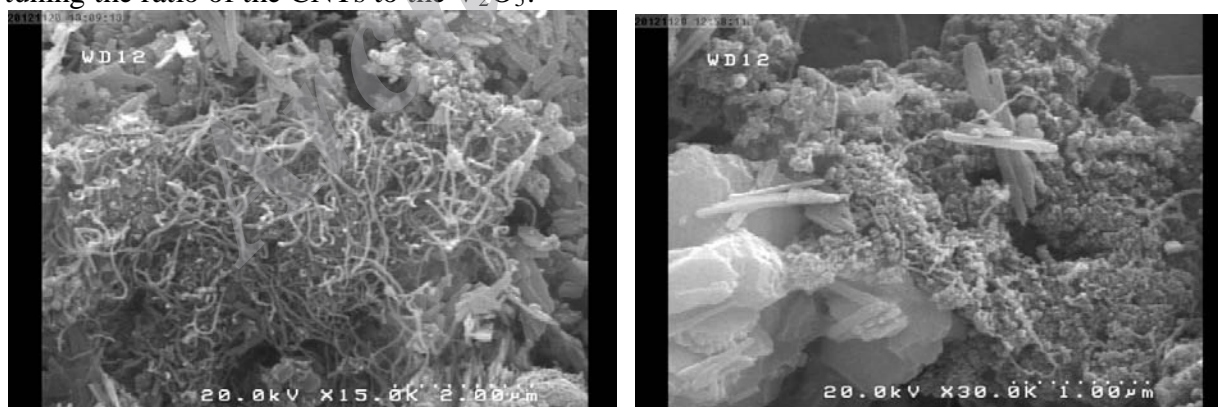


Figure 1: FESEM micrographs of the  $V_2O_5$  nanostructures a) V-MWCNT-1 and b) V-SWCNT-1

Figure 2(a) showed the FTIR spectra of catalysts prepared through the hydrothermal method. It was observed that, the *in-situ* growth of the vanadium within the CNTs led to an interpenetrating network structure. The X-ray diffraction (XRD) patterns for these catalysts were presented in Figure 2(b). The reduction behavior of the catalysts was investigated through the  $H_2$ -TPR technique and the results for some of the samples presented in Figure



2(c). UV-vis spectra provided useful information about the structure and characteristics of vanadium understudied. The UV-vis diffuse spectra of the V<sub>2</sub>O<sub>5</sub> over carbon nanocomposites presented in Figure 2(d).

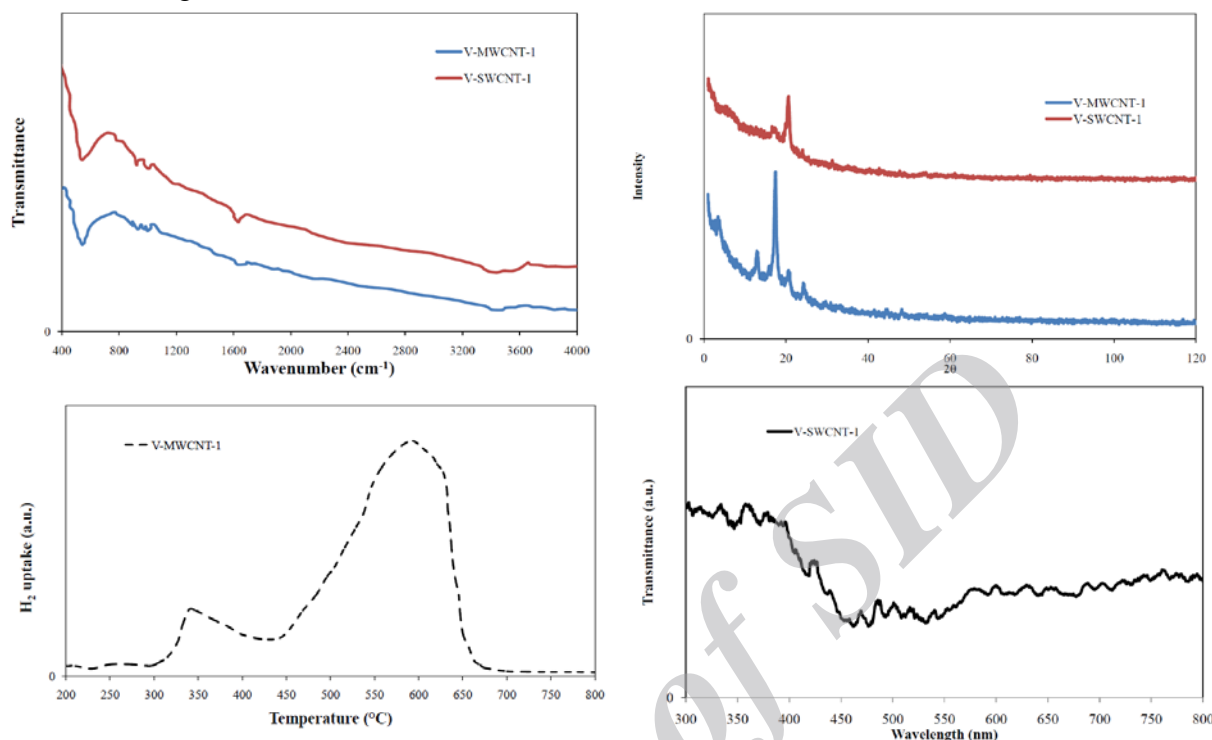


Figure 2: a) FTIR spectra, b) XRD patterns, c) H<sub>2</sub>-TPR results for V-MWCNT-1 and d) DR-UV-vis spectra catalysts prepared by the hydrothermal method

The prepared catalysts including V-MWCNT-1 and V-SWCNT-1 as well as; the bare supports of MWCNT and SWCNT, were evaluated in an experimental reactor setup at the ODHP reaction temperature of 450°C, C<sub>3</sub>H<sub>8</sub> to air molar ratio of 0.6 and a total feed flowrate of 90ml/min. Figure 3 presented propane conversions versus time-on-stream for different catalysts indicating a stable trend. Mean values of propane conversions and product selectivities during a 6h run over pristine catalysts (*i.e.*; MWCNT-1 and SWCNT-1) were summarized in Table 1.

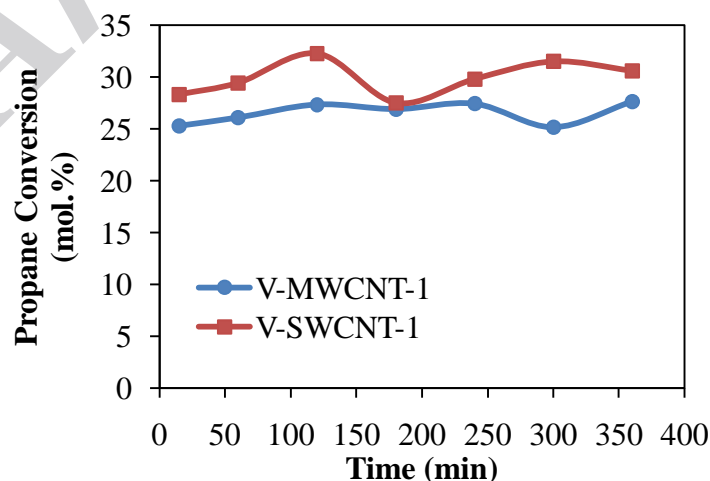


Figure 3: Propane conversions at 450°C, C<sub>3</sub>H<sub>8</sub>/Air=0.6 and feedrate of 90ml/min



Table 1: Mean values of propane conversions and product selectivities over pristine nanocatalysts, at  $T=450^\circ\text{C}$ ,  $C_3H_8/\text{Air} = 0.6$  and total feed rate of 90ml/min

Time (min)	Propane Conversion (%)	Propylene Selectivity (%)	Ethylene Selectivity (%)	$CO_x$ Selectivity (%)	Propylene Yield (%)
MWCNT-1	23.09	24.32	6.54	68.59	5.62
SWCNT-1	24.67	34.97	10.89	53.54	8.63

### Conclusions

This research demonstrated a facile hydrothermal synthesis of the  $V_2O_5$  material over carbon-based nanostructures for the ODHP reaction. The bare carbon-based nanocatalysts were also tested and their performance compared with those of the synthesized catalysts. Prepared catalysts characterized through the XRD, FTIR, TPR, FESEM and UV-vis diffuse reflectance. These materials produced through the hydrothermal method were stable. Oxidation and oxy-cracking reactions also competed with the main ODHP reaction leading to the formation of ethylene and  $CO_x$  as the side products. Ultimately, the performance of the aforementioned catalyst prepared in the present investigation under the ODHP reaction conditions demonstrated to be superior to those reported in the open literature.

### References

- [1] F. Cavani, F. Trifiro, The oxidative dehydrogenation of ethane and propane as an alternative way for the production of light olefins, *Catalysis Today* 24 (1995) 307-313
- [2] L. M. Madeira, M. F. Portela, Catalytic oxidative dehydrogenation of n-butane, *Catalysis Reviews: Science and Engineering* 44 (2002) 247-286
- [3] M.M. Bettahar, G. Costeintin, L. Savary, J.C. Lavalley, On the partial oxidation of propane and propylene on mixed metal oxide catalysts, *Applied Catalysis A: General* 145 (1996) 1-48
- [4] E.A. Mamedov, V. Cortes Corberan, Oxidative dehydrogenation of lower alkanes on vanadium oxide-based catalysts. The present state of the art and outlooks, *Applied Catalysis A: General* 127 (1995) 1-40
- [5] S. Fuchs, L. Leveles, K. Seshan, L. Lefferts, A. Lemonidou, J. A. Lercher, Oxidative dehydrogenation and cracking of ethane and propane over  $LiDyMg$  mixed oxides, *Topics in Catalysis* 15 (2001) 169-174
- [6] A. Rashidi, R. Lotfi, E. Fakhmosavi, M. Zare, Production of single-walled carbon nanotubes from methane over  $Co-Mo/MgO$  nanocatalyst: A comparative study of fixed and fluidized bed reactors, *Journal of Natural Gas Chemistry* 20 (2011) 372-376
- [7] Z. Sadeghian, A.M. Rashidi, Synthesis optimisation and characterisation of multiwalled carbon nanotubes produced by spray pyrolysis of hexane, *Materials Science and Technology* 26 (2010) 1191-1196