Oxidative dehydrogenation of propane over V_2O_5 and K_2O-V_2O_5 impregnated $MgAl_2O_4$ catalysts

Serkan Naci KOÇ*, **Kübra DAYIOĞLU**, **Hasan ÖZDEMİR**
Department of Chemical Engineering, Faculty of Engineering, İstanbul University, İstanbul, Turkey

Abstract: V_2O_5 and K_2O-V_2O_5 impregnated $MgAl_2O_4$ catalysts were prepared and tested for the oxidative dehydrogenation of propane. The as-synthesized catalysts were characterized by using the XRD, BET, NH_3-TPD, TPR, and XPS methods. The catalytic tests were performed in a fixed bed tubular quartz reactor system between 450 and 550 °C. It was observed that the conversion of propane increased but hydrocarbon selectivity decreased with increasing temperature over the $V_2O_5/MgAl_2O_4$ catalysts. The BET surface area values and surface acidities decreased upon potassium addition for the K-$V_2O_5/MgAl_2O_4$ catalysts, which resulted in a drastic drop in the conversion values obtained. The propylene and total hydrocarbon selectivities increased with increasing temperature.

Key words: Selective oxidation, catalysts, propane, vanadium oxide

1. Introduction

Heterogeneous catalyst design for petrochemical selective oxidation reactions is a fundamental research field in catalysis, and oxidative dehydrogenation (ODH) of propane has gained great importance for lower alkane utilization in recent years.[1,2] Endothermic direct dehydrogenation of propane is an equilibrium reaction; thus its conversion is temperature limited, the enthalpy of the reaction is high, and catalyst coking is commonly observed. However, there is no equilibrium problem in the ODH of propane since the reaction is exothermic.

Usually redox metal oxides such as vanadium, molybdenum, and niobium oxides are used for the ODH reactions, and there are a few parameters that affect the catalyst properties. The acidic sites of redox catalysts activate propane by hydrogen abstraction. Further abstraction of hydrogen leads to C_3H_6 formation. However, the allylic C–H bond of propylene is weaker than the secondary C–H bond of propane.[3−9] For this reason, the selectivity of propylene is the main problem in the ODH of propane. The reduction properties and the acidities of catalysts are very important in these types of selective oxidation reactions. Catalysts used in the ODH of propane should desorb the formed propylene easily because strong adsorptions cause propylene combustion to CO and CO_2. Therefore, studies related to the ODH of propane focus on the propane activation mechanism, effect of the oxygen type (adsorbed or lattice), reaction conditions, and catalyst compositions.[8]

Numerous catalysts such as Mg-V-O, V-Silica, V-MCM-41, V-SBA-15, Ce-V-O, V-TiO_2/SiO_2, and V-graphene have been investigated for propane oxidative dehydrogenation.[10−14] In addition, for these vanadium-oxide-based catalysts, different support materials such as Al_2O_3, ZrO_2, HfO_2, TiO_2, and SiO_2 have been tested as well.[15−17] The synergy between different phases affects the catalyst properties. The surface acidity

*Correspondence: nacik@istanbul.edu.tr

changes depending on the type and concentration of the surface VO_x species and concentration, which in turn affect the catalytic activity and the product selectivity.[10,18]

In the present study, novel $V_2O_5/MgAl_2O_4$ and K-$V_2O_5/MgAl_2O_4$ catalysts were synthesized, characterized, and catalytically tested in the ODH of propane.

2. Results and discussion

The XRD results of pure and 15% V_2O_5 loaded $MgAl_2O_4$ are shown in Figure 1. V_2O_5 crystalline phases were observed in vanadium-loaded catalysts. Peaks related to K_2O were not observed upon potassium addition (not shown), which indicated that potassium was mostly distributed in the pores of the catalyst.[19]
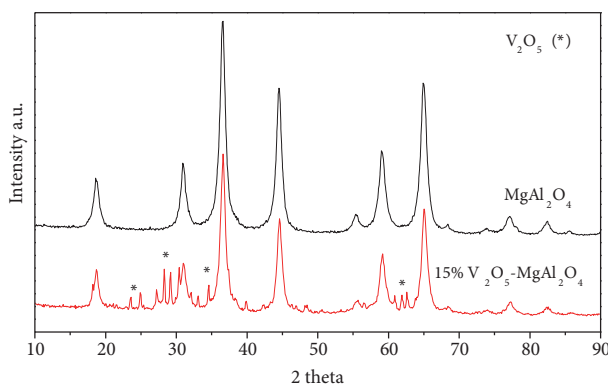

Figure 1. XRD pattern of 15% $V_2O_5/MgAl_2O_4$ and pure $MgAl_2O_4$.

The results of surface area measurements are given in Table 1. The BET surface area of the pure $MgAl_2O_4$ support material is 68 m^2/g (not given). BET surface area values corresponding to 10% and 20% V_2O_5 incorporated samples are 77.5 and 66.5 m^2/g, respectively. As is obvious from these results, the surface areas of catalysts slightly decrease with potassium addition. This indicates that some pores are plugged upon K_2O incorporation.[20]

Table 1. Surface area results of some catalysts.

Catalyst	Surface area (m^2/g)
10% $V_2O_5/MgAl_2O_4$	77.5
20% $V_2O_5/MgAl_2O_4$	66.5
K-10% $V_2O_5/MgAl_2O_4$	57.7
K-20% $V_2O_5/MgAl_2O_4$	32.1

NH$_3$-TPD measurements, which enable the estimation of surface acidity for catalysts, are shown in Table 2. The amount of desorbed NH$_3$ is 58 μmol/g for the 10% V_2O_5 loaded catalyst and 31.7 μmol/g for the 20% V_2O_5 loaded catalyst. Thus it could be concluded that the total acidity decreases with increasing vanadium content. The acidity difference may be due to vanadium dispersion on the surface and different types of VO_x species involved.[10,21] Moreover, the total surface acidity of the catalysts decreases with the alkaline K_2O addition to 16.8 and 6.6 μmol/g for 10% to 20% V_2O_5 loaded catalysts, respectively. Since potassium addition increases the alkaline properties of the catalysts, total acidity decreases as well. NH$_3$-TPD curves of the 10% and 20% V_2O_5 loaded catalysts are given in Figure 2. As seen in these curves, the peaks around 130

and 380 °C correspond to weak and strong acid sites, respectively, and the shoulder in between corresponds to the mild acid sites.[5] The effect of potassium addition on catalyst acidity is shown in Figure 3. As seen, potassium addition mainly decreases the number of mild acidic sites. These curves are consistent with the NH_3 amounts depicted in Table 2.

Table 2. Acidity of catalysts.

Catalyst	Total acidity (μmol/g)
10% V_2O_5/MgAl$_2$O$_4$	58.0
K-10% V_2O_5/MgAl$_2$O$_4$	16.8
20% V_2O_5/MgAl$_2$O$_4$	31.7
K-20% V_2O_5/MgAl$_2$O$_4$	6.6
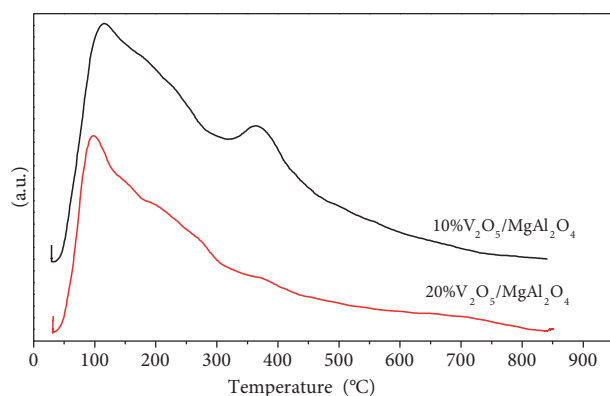
Figure 2. NH_3-TPD spectra of 10% V_2O_5/MgAl$_2$O$_4$ and 20% V_2O_5/MgAl$_2$O$_4$.
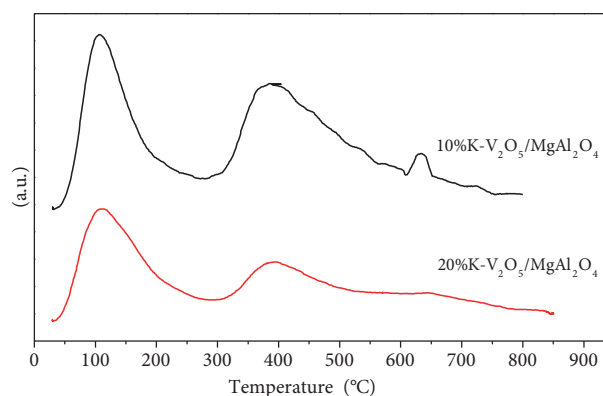
Figure 3. NH_3-TPD spectra of K-10% V_2O_5/MgAl$_2$O$_4$ and K-20% V_2O_5/MgAl$_2$O$_4$.

Temperature programmed reduction (TPR) results of the 10% and 20% V_2O_5 incorporated catalysts are shown in Figure 4. There are two main peak maxima and these two peaks around 580 and 720 °C occur due to reduction of V5+ to V4+ and V4+ to V3+, respectively. The TPR peaks of potassium added 10% and 20% V_2O_5 catalysts are given in Figure 5. In this figure it is seen that the first reduction peak has shifted to 670 and 680 °C, respectively.[6,22]
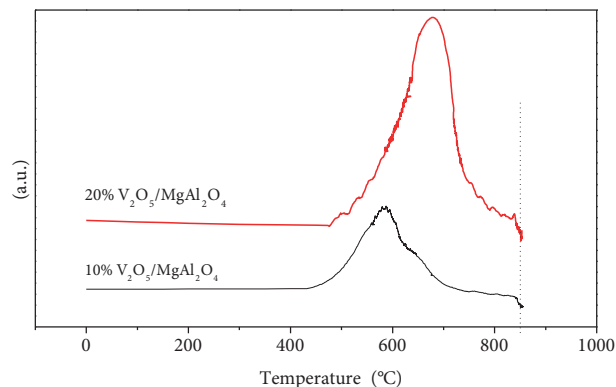

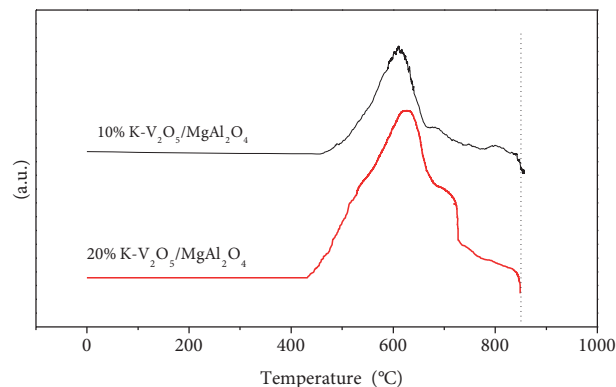**Figure 4.** TPR results of 10% V_2O_5/MgAl$_2$O$_4$ and 20% V_2O_5/MgAl$_2$O$_4$.

Figure 5. TPR results of K-10% V_2O_5/MgAl$_2$O$_4$ and K-20% V_2O_5/MgAl$_2$O$_4$.

The XPS spectra of the 10% V_2O_5 and potassium promoted 10% V_2O_5 catalysts are given in Figure 6. It is observed that $V2p_{1/2}$ and $V2p_{3/2}$ energy regions were obtained for both catalysts. The presence of the $V2p_{3/2}$ energy region occurring at 517 eV indicates that both catalysts contain V^{5+} species.[23] Upon potassium addition the location of this peak did not shift; in other words, the valence state of the vanadium species did not change.
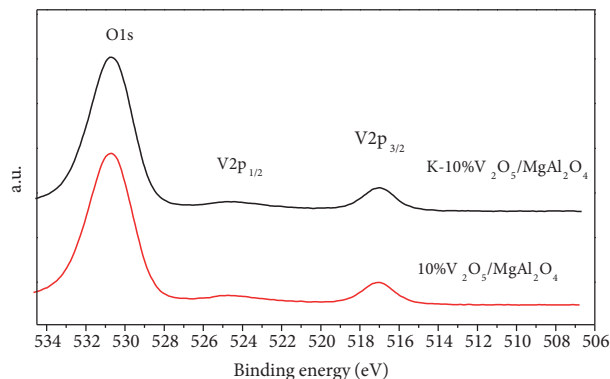

Figure 6. XPS spectra of 10% $V_2O_5/MgAl_2O_4$ and K-10% $V_2O_5/MgAl_2O_4$.

Catalytic activity results of 5%, 10%, 15%, and 20% V_2O_5 loaded catalysts are shown in Table 3. Experiments were run between 450 and 550 °C. The main products of the ODH of propane are propylene, methane, ethylene, and ethane. As seen in this table, propane conversion increases and the total hydrocarbon product selectivity decreases with increasing temperature. Maximum selectivity to propylene and total hydrocarbon products was achieved with the 5% V_2O_5 catalyst at 450 °C as 72.7% and 76.0%, respectively. In these types of selective oxidation reactions, the partial and total combustion products CO and CO_2 form as undesired products. Therefore, the total hydrocarbon selectivity is very important and decreases with increased combustion at higher temperatures.[3−5]

Table 3. Catalytic activity results of $V_2O_5/MgAl_2O_4$ catalysts.

C (%)	S (%)								
Catalyst	T (°C)	C_3H_8	C_3H_6	C_2H_6	C_2H_4	CH_4	CO_2	CO	Hydrocarbon
5% $V_2O_{5/}$ $MgAl_2O_4$	450	4.7	72.7	1.3	0	2.0	6.2	17.8	76.0
	500	14.1	64.9	0.6	0.3	1.1	12.8	20.3	66.9
	550	40.5	36.7	0.20	0.6	0.5	34.2	27.8	38.0
10% $V_2O_5/$ $MgAl_2O_4$	450	9.3	71.2	1.0	0	1.8	9.0	17.1	74.0
	500	37.1	30.0	0.2	0.2	0.5	38.0	31.1	30.9
	550	37.6	31.1	0.2	0.3	0.5	36.3	31.6	32.1
15% $V_2O_5/$ $MgAl_2O_4$	450	25.0	30.4	0.5	0.1	0.9	43.2	24.9	31.9
	500	32.8	28.1	0.1	0.2	0.2	37.9	33.6	28.6
	550	37.5	28.2	0.2	0.4	0.5	36.8	33.9	29.3
20% $V_2O_5/$ $MgAl_2O_4$	450	9.4	62.6	0.9	0	1.3	13.4	21.9	64.8
	500	36.1	24.7	0.2	0.2	0.3	41.5	33.0	25.4
	550	38.5	26.9	0.2	0.5	0.4	38.5	33.5	28.0

C: conversion and S: selectivity

Catalytic activity results of potassium loaded vanadium oxide catalysts are shown in Table 4. Alkali metal promotion compensates and slows down the reduction cycle of the vanadium species in these types of

redox catalysts.[24] As seen in Table 4, propylene selectivity and total hydrocarbon selectivity increase with increasing temperature. This trend is contrary to the results obtained for vanadium oxide catalysts with no potassium addition (Table 3). In particular, propylene is strongly adsorbed on the acid sites of the catalysts and then is converted to the combustion products CO and CO_2. The increasing propylene and hydrocarbon selectivity at 550 °C are due to alkali promotion upon addition of K_2O. Alkali addition increases the surface potential of the catalyst surface, the acidity of the catalyst decreases, and the desorption of hydrocarbons from the catalyst surface becomes easier,[6,8] suppressing further combustions more easily.[6,8] Despite the fact that the propylene and total hydrocarbon selectivities increases with potassium addition, propane conversion decreases greatly compared to the catalysts with no potassium incorporation at all temperatures most probably due to the decreased BET surface areas and surface acidities. Thus, propylene yields are higher with $V_2O_5/MgAl_2O_4$ catalysts at all temperatures and it is concluded that potassium addition is not beneficial for V_2O_5 incorporated catalysts.

Table 4. Catalytic activity results of $K-V_2O_5 MgAl_2O_4$ catalysts.

Catalyst	T (°C)	C (%)	S (%)						
		C_3H_8	C_3H_6	C_2H_6	C_2H_4	CH_4	CO_2	CO	Hydrocarbon
K-5% $V_2O_5/$ $MgAl_2O_4$	450	1.5	2.9	5.6	0	15.0	29.3	52.7	23.5
	500	1.6	8.3	5.4	0	9.0	24.8	52.5	22.7
	550	1,6	24.8	5.1	4.8	8.5	35.7	20.9	43.2
K-10% $V_2O_5/$ $MgAl_2O_4$	450	2.2	23.7	3.9	0	6.6	19.5	46.3	34.2
	500	2.7	55.9	3.2	0	5.5	19.8	15.5	64.6
	550	4.0	44.2	2.1	1.2	3.0	31.9	17.7	50.5
K-15% $V_2O_5/$ $MgAl_2O_4$	450	1.3	13.4	6.5	0	10.9	27.3	41.9	30.8
	500	1.6	35.0	5.5	0	9.2	23.1	27.2	497
	550	3.6	48.0	2.3	1.0	4.1	15.2	29.4	55.4
K-20% $V_2O_5/$ $MgAl_2O_4$	450	1.0	17.4	8.4	0	12.5	28.8	33.4	38.3
	500	2.2	27.7	4.1	0	5.6	19.0	43.8	37.4
	550	3.4	53.1	2.4	0.8	3.6	24.5	15.5	59.9

C: conversion and S: selectivity

3. Experimental

3.1. Catalyst preparation

Catalysts with 5, 10, 15, or 20 (% by weight) $V_2O_5/MgAl_2O_4$ were prepared by the wet impregnation method. Ammonium vanadate (Merck) and oxalic acid (2/1 mol)[17] were dissolved in water and $MgAl_2O_4$ powder was added to this solution at 25 °C. The mixture obtained was heated at 70 °C for 3 h. Samples were dried at 120 °C for 24 h, then heated at 5 °C/min to 550 °C, and calcined for 3 h. Next 3% potassium containing catalysts were prepared with 0.5 M KNO_3 (Merck) solution. The 0.5 M KNO_3 solution was introduced into the ammonium-vanadate, oxalic acid, and $MgAl_2O_4$ solution dropwise by continuous stirring at 25 °C.

3.2. Catalyst characterization

Nitrogen physisorption measurements were carried out at –196 °C using a Quantachrome Nova 3200e BET surface area analyzer after high-vacuum degassing of the catalysts at 300 °C. XRD results were obtained on a Rigaku D/Max-2200 diffractometer using Cu-K_α irradiation ($\lambda = 1.5404$ Å). X-ray photoelectron spectroscopy (XPS) measurements were obtained with a Cratos XPS in fixed transmission mode. Temperature-programmed

reduction (TPR) experiments were carried out in a CATLAB-MS system with 200 mg of catalyst powders placed in a quartz reactor under atmospheric pressure. The reactor was heated up to 900 $^\circ$C at a rate of 20 $^\circ$C/min under a H_2/N_2 flow of 20 mL/min with 5% H_2. The hydrogen amount was monitored by an on-line HIDEN QIC-20 mass spectrometer. NH_3-TPD analysis was carried out after flushing a 200-mg catalyst sample with N_2 at 300 $^\circ$C and cooling to room temperature. Catalysts were treated with 10% NH_3/N_2 mixture for 1 h at this temperature and flushed with N_2 for 30 min. Then the NH_3 signal was recorded with a mass spectrometer up to 700 $^\circ$C with a heating rate of 20 $^\circ$C/min.

3.3. Catalytic activity tests

The ODH reactions were carried out in a fixed bed tubular quartz reactor. Propane (99.95%, Linde), oxygen (99.99%, Linde), and nitrogen (99.99%, Linde) were fed at atmospheric pressure with a total flow rate of 75 mL/min and a composition of 8:8:59, respectively. Next 250–355 micron size catalysts were diluted with quartz chips at a weight ratio of 1:1 to provide a 400-mg catalyst charge. The dead volume of the reactor was filled with quartz chips in order to avoid homogeneous reactions. An Agilent on-line GC system with TCD and FID detectors; a molecular sieve 5A column for N_2, O_2, and CO; and a PoraPLOT Q column for hydrocarbons and CO_2 were used for the analysis.

4. Conclusion

In this study, $V_2O_5/MgAl_2O_4$ catalysts and their potassium promoted forms were prepared and tested for oxidative dehydrogenation of propane. The conversion of propane increases with temperature but propylene and total hydrocarbon selectivity decreases with temperature. The maximum conversion and hydrocarbon selectivity achieved with 5%(wt.)$V_2O_5/MgAl_2O_4$ catalyst at 550 $^\circ$C are 40.5% and 38.0%, respectively. The propylene and total hydrocarbon selectivity increases with temperature due to the addition of potassium. Hydrocarbon products desorb easily from catalytic active sites because of decreasing acidity with potassium. However, propane conversion decreases greatly compared to the catalysts without potassium at all temperatures and potassium addition is not beneficial for V_2O_5 included catalysts. Further studies will be done with different support materials and alkali metal oxides.

Acknowledgments

References

1. Graaf, E. A.; Zwanenbur, G.; Rothenberg, G.; Bliek, A. *Org. Process. Res. Dev.* **2005**, *9*, 397-403.

2. Rossetti, I.; Fabbrini, L.; Ballarini, N.; Oliva, C.; Cavani, F.; Cericola, A.; Bonelli, B.; Piumettid, M.; Garrone, E.; Dyrbeck, H.; et al. *Catal. Today* **2009**, *141*, 271-281.

3. Bodet, H.; Lofberg, A.; Pirovano, C.; Steil, M.C.; Vannier, R.N.; Bordes-Richard E., *Catal. Today* **2009**, *141*, 260-263.

4. Stern, D. L.; Grasselli, R. K. *J. Catal.* **1997**, *167*, 550-559.

5. Heracleous, Ei.; Machli, M.; Lemonidou, A.; Vasalos, I. A. *J. Mol. Catal. A-Chem.* **2005**, *232*, 29-39.

6. Koc, S. N.; Gurdag, G.; Geissler, S.; Guraya, M.; Orbay, M.; Muhler, M. *J. Mol. Catal. A-Chem.* **2005**, *225*, 197-202.

7.   Botavinaa, M. A.; Martra, G.; Agafonov, Yu. A.; Gaidai, N. A.; Nekrasov, N. V.; Trushin, D. V.; Coluccia, S.; Lapidus, A. L. *Appl. Catal. A-Gen.* **2008**, *347* 126-132.

8.   Kung H. H. *Adv. Catal.* **1994**, *40*, 1-40.

9.   Koc, S. N.; Gurdag, G.; Geissler, S.; Muhler, M. *Ind. Eng. Chem. Res.* **2004**, *43*, 2376-2381.

10. Liu, Y. M.; Feng, W. L.; Li, T. C.; He, H. Y.; Dai, W. L.; Huang, W.; Cao, Y.; Fan, K. N. *J. Catal.* **2006**, *239*, 125-136.

11. Liu, Y. M.; Cao, Y.; Zhu, K. K.; Yan, S. R.; Dai, W. L.; He, H. Y.; Fan, K. N. *Chem. Commun.* **2002**, *23*, 2832.

12. Taylor, M. N.; Carley, A. F.; Davies, T. E.; Taylor, S. H. *Top. Catal.* **2009**, *52*, 1660-1668.

13. Chakraborty, S.; Nayak, S. C.; Deo, G. *Catal. Today* **2015**, *254*, 62-71.

14. Fattahi, M.; Kazemeini, M.; Khorasheh, F.; Rashidi, A. *Chem. Eng. J.* **2014**, *250*, 14-24.

15. Gao, X.; Xin, Q.; Guo, X. *Appl. Catal. A* **1994**, *114*, 197-204.

16. Chen, K.; Iglesia, E.; Bell, A. T. *J. Catal.* **2000**, *192*, 197-203.

17. Khodakov, A.; Olthof, B.; Bell, A. T.; Iglesia, E. *J. Catal.* **1999**, *181*, 205-216.

18. Chen, K.; Xie, S.; Bell, A. T.; Iglesia, E. *J. Catal.* **2001**, *198*, 232-242.

19. Watson, R. B.; Ozkan, U. S. *J. Catal.* **2000**, *191*, 12-29.

20. Chen, K.; Xie, S.; Bell, A. T.; Iglesia, E. *J. Catal.* **2000**, *189*, 421-430.

21. Al-Ghamdi, S. A.; de Lasa, H. I. *Fuel* **2014**, *128*, 120-140.

22. Xu, J.; Chen, M.; Liu, Y. M.; Cao, Y.; He, H. Y.; Fan, K. N. *Micropor. Mesopor. Mat.* **2009**, *118*, 354-360.

23. Courcot, D.; Ponchel, A.; Grzybowska, B.; Barbaux, Y.; Rigole, M.; Guelton, M.; Bonnelle, J. P. *Catal. Today* **1997**, *33*, 109-118.

24. Swierkosz, B. G., *Top. Catal.* **2000**, *11-12*, 23-42.