Oxydehydrogenation of Propane over Vanadium Oxide Supported on Kieselguhr or MCM-41

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Abstract: Supported vanadium oxide (5 wt%) on either Kieselguhr or mesoporous MCM-41 was prepared using impregnation method and tested as a catalyst in propane oxidative dehydrogenation (POD). The catalyst samples were characterized using X-ray elemental analysis, Brunauer-Emmett-Teller (BET) physisorption, and Z-ray Photoelectron Spectroscopy (XPS). After impregnation, the catalyst surface area decreased compared with that of the support. More drastic decrease was observed in the case of MCM-41 (77%) than the Kieselguhr supported sample (48%). There are also different degrees of vanadium oxide-support interaction as reflected by the XPS result. Si-O binding energy of 531.5 eV was observed on MCM-41-supported sample compared with 529.5 eV for the Kieselguhr-supported sample. The catalyst tests were conducted at atmospheric pressure, with a propane to oxygen ratio of 0.7 - 3.6 and a reaction temperature of 400 - 700 °C. Oxidative dehydrogenation and combustion products were observed. Minor cracking reaction products (methane, ethane, and ethene) were also produced above 550 °C. The highest propene yield of 14% was obtained from the Kieselguhr-supported sample at 700 °C and with a C_3H_8/O_2 ratio of 1.5.

Keywords: Oxidative dehydrogenation, Propane, Propene, Vanadium oxide, Kieselguhr, MCM-41

نزع الهيدروجين بالأكسدة من البروبان باستخدام أكسيد الفاناديوم المحضر على الكيسيلغر أو أم سي أم –٤١

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الملخص: تم إعداد أكسيد الفاناديوم المدعم (٥٪ بالوزن) على عينه كيسيلغر "Kieselguhr" أو متوسط المسامية (MCM-41) باستخدام أسلوب التشريب واختبارها كعامل محفز في أكسدة البروبان بنزع الهيدروجين. وشخصت هذه العينات باستخدام الأشعة السينية ومقياس المساحة السطحية. بعد التشريب، انخفضت مساحة الحافز بالمقارنة مع الداعم. ولوحظ انخفاض حاد في حالة متوسط المسامية (٧٧٪) عن كيسيلغر (٤٨٪). ولوحظت أيضا درجات مختلفة من تفاعل أكسيد الفاناديوم مع الداعم على نحو ما تعكسه نتيجة الأشعة السينية. كما لوحظ أن طاقة الرابطة (0-SI) هي ٥٣١,٥ إلكترون فولت بالنسبة لعينة متوسط المسامية مقارنة مع ٥٢٩,٥ إلكترون فولت للعينة كيسيلغر. حيث أجريت التجارب تحت الضغط الجوي وكانت نسبة البروبان – الأكسجين ٠,٧–٣,٦، ودرجة حرارة التفاعل ٤٠٠–٧٠٠ درجة مئوية. وقد رصدت الأكسدة الهيدروجينية و احتراق المنتجات. كما تم تصنيع منتجات تفاعل التكسير الصغيرة (الميثان ، الإيثان، الإيثين) على درجات أعلى من ٥٥٠ درجة مئوية. وتم الحصول على أعلى محصول من البروبان بنسبة ١٤٪ للعينة كيسيلغر المدعمة على درجة حرارة ٧٠٠ درجة مئوية، وبلغت نسبة البروبان إلى الأكسجين ١,٥.

الكلمات الدالة: نزع الهيدروجين بالأكسدة، البروبان، البروبين، أكسيد الفاناديوم، الكيسيلغر، ام سي ام –٤١

1. Introduction

Propene is an important link between relatively cheap and abundant natural gas and many petrochemicals and intermediates such as propylene oxide, acrylonitrile and isopropyl alcohol. This importance has spurred a seires of recent research efforts towards developing catalysts for oxidative dehydrogenation of propane as an alternative route to creating propene (Mamedov, Cortes 1995).   The alternative route has the potential to lower reaction temperatures and pressure due to the absence of a thermodynamic equilibrium, which is a major limitation of the non-oxidative route. However, thus far the catalysts proposed for

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oxydehydrogenation of propane to propene have exhibited low yields. As of publication, there is no economic motivation for developing the process on a commercial scale due to low yields (Cavani *et al.* 2007).

Because of this low yield, the current research effort is toward developing active catalysts to conduct the reaction at temperatures lower than 600 ºC with low selectivity to undesired products. To this end, a large number of supported oxides and mixed-oxides have been reported as summarized in recent reviews (Mamedov, Cortes 1995; Blasco, Lopez-Nieto 1997; Centi *et al.* 2001). Most of the catalysts reported, such as V-Mg-O (Mamedov, Cortes C 1995; Centi *et al.* 2001), Mg-V-Sb-O (Michaels *et al.* 1996a; Michaels *et al.* 1996b) and V-Nb-O (Smits *et al.* 1993) are based on vanadium. Others, such as those based on molybdenum, have also been shown to be active for the reaction (Stern *et al.* 1997). For the vanadium-based system, high selectivity to propene has been associated with the presence of monomeric or oligo-metric tetrahedral V^{5+} species. The bridging oxygen between vanadium and the support activates propane (Christodoulakis *et al.* 2004; Routray *et al.* 2004). In the case of V-Mg-O, three different phases - $Mg_3V_2O_8$, $Mg_2V_2O_7$ and MgV_2O_6 - have been identified. Two of them - orthovanadate (Chaar *et al.* 1987) and pyrovanadate (Siew *et al.* 1990; Ruiz-Guerrero *et al.* 1992) - are associated with the activation of alkane.

In both phases, the catalysts reactivities depend on the difference in the nature and surface density of V-O bonds (Mamedov, Cortes 1995; Blasco, Lopez-Nieto 1997). Furthermore, the nature of the support influences the surface density and reducibility of the V-O bond (Mamedov, Cortes 1995; Tsilomelekis *et al.* 2007; Xie *et al.* 2000). Silica was identified as exhibiting higher selectivity to propene than more acidic supports such as alumina and titania (Kondratenko *et al.* 2006; Singh *et al.* 2005; Grabowski 2004). High vanadia dispersion was realized on high surface mesoporous silica such as M41S (Pena *et al.* 2001; Buyevskaya *et al.* 2001), HMS (Knotek *et al.* 2007) and MCM-41 (Karakoulia *et al.* 2008; Jibril, Ahmed 2006; Shanahan, Holder 1999). Our previous study demonstrated the effect of intra and extra-framework positions of the Co, Ni or Mo in MCM-41 on the selectivity to propene (Jibril, Ahmed 2006). The aim of this work was to further explore the effects of silica-based supports - (*i.e.*, Kieselguhr and MCM-41 - on the vanadium species and their catalytic performances in the oxidative hydrogenation of propane. Kieselguhr is diatomaceous earth (primarily silica dioxide based) that has been demonstrated to be effective as a support in oxidative dehydrogenation of propane (Jibril *et al.* 2006) and other reactions (Wells

1991). In addition to the catalytic test, the properties of a sample of the catalysts were studied using Brunauer-Emmett-Teller (BET), surface area, (X-Ray Fluorescene (XRF), and X-Ray Photoelectron Spectroscopy (XPS). The catalysts were found to be active for the reaction.

2. Experimental

2.1 Preparation of Catalysts

The materials used in the experiment were: cetyltrimethyl ammonium chloride (C16TMACl) (Sigma) tetraethoxysilane (TEOS) (Sigma, 98%), sodium aluminate (Fluka, 98%), ammonium vanadate [(NH4)VO3] (Aldrich, 99%) and commercial Kieselguhr (BDH). High purity propane (99.95%), oxygen (99.995%), and helium (99.999%) were obtained from a local supplier and used as received. The mesoporous MCM-41 support was prepared according to a procedure reported earlier (Berndt *et al.* 2000): 2 g of C16TMACl was dissolved in 500 ml of distilled and deionized water containing 50 ml of 0.125 M of NaOH at room temperature. The mixture was stirred for 2 hours. To the above solution, 8 grams of sodium aluminate in 50 ml water and 5 grams of TEOS were added. The mixture was continuously stirred for 48 hours at ambient temperature. A precipitate was formed, filtered, washed with distilled and deionized water and dried for 10 hours at 100 ºC in a vacuum oven. To remove the organic surfactant templates, the synthesized sample was refluxed in 200 ml of ethanol for 12 h. The extracted material was filtered, washed with ethanol and dried for 10 hours at 100 °C in a vacuum oven.

MCM-41 and Kieselguhr supported vanadium oxide catalysts were prepared by wet impregnation of MCM-41 and commercial Kieselguhr with an aqueous solution containing ammonium vanadate with a concentration calculated to give a total loading of 5 w% of vanadium as an oxide. The prepared catalysts were dried at 100 °C in a vacuum oven for 16 hours before calcination in the air at 700 °C for 3 hours. In the subsequent discussion, the catalysts V-oxide/MCM-41 and V-oxide/Kieselguhr are represented as V/M and V/K respectively.

2.2 Catalyst Characterization

The nitrogen adsorption-desorption isotherm of MCM-41, commercial Kieselguhr, or supported vanadium oxide catalysts samples were measured with the Micromeritics ASAP-2010 system using nitrogen sorption at 77 K. Prior to the experiments, approximately 0.2 g of sample was degassed at 523 K for 10 hours. The surface areas and porosities were obtained. The surface area was calculated using a multipoint

Table 1. **BET surface areas, pore volumes and average pore diameters of the supports and catalysts**

Sample	S_{BET} [a] $(m^2 \, g^{-1})$	V_p [b] $(cm^3 \, g^{-1})$	APD [c] (nm)	APD [d] (nm)
MCM-41	882	0.92	32.1	31.3
Kieselguhr	166	0.56	98.5	97.4
5%V_2O_5 / MCM-41	201	0.41	71.3	70.9
5%V_2O_5 / Kieselguhr	110	0.53	182	173

(a) BET surface area
(b) Pore volume
(c) Average pore size determined based on the BET method
(d) Average pore size determined based on the BJH method

BET model. The pore sizes were obtained using Berrett-Joyner-Halenda (BJH) and BET models. The total pore volumes were estimated at a relative pressure of 0.99 atm, assuming full surface saturation with nitrogen.

XPS studies were recorded with a Jeol JPS 9010MC photoelectron spectrometer using MgKα (1253.6eV) radiation from an X-ray source operated at 10KV and 20 mA. The measurements were performed at room temperature and the working pressure was lower than 3.5×10^{-7} Pa. X-ray elemental analysis studies were taken at 30 KV at room temperature using a Jeol element analyzer JAX-3201.

2.3 Catalyst Evaluation

The catalyst was tested in a laboratory bench scale pilot plant fitted with mass flow meters and a fixed bed down pass flow stainless steel reactor (inside diameter = 8 mm, and length = 300 mm) placed in a cylindrical furnace equipped with a coaxial thermocouple. The catalyst zone (about 30 mm) in the middle of the reactor was filled with 1.0 g of catalyst diluted with an equal amount of quartz particles (100-600 mesh) in order to minimize temperature gradients. In the center of the catalyst bed, a thermocouple was installed so that it was in contact with the catalyst particles were measure the reaction temperature. The heating zones at the inlet and the outlet of the reactor was measured in a thermocouple located inside the furnace and were controlled by a temperature controller (Cole Parmer, Digi-Sense). Quartz wool was placed in the empty space in the reactor to minimize gas-phase reactions. A feed flow of 83 ml/minute with -propane to oxygen ratios ranging from 0.7 - 3.6 - at atmospheric pressure was used with helium employed as a diluent. The catalyst zone of 30 mm mades the contact time 4.4 seconds. The activities of the catalysts and product distribution were studied at 400, 500, 600 and 700 °C. Blank reactor runs were conducted as described above in the absence of catalysts. No significant conversions of C_3H_8 or O_2 were observed. Carbon mass balance obtained was within ± 8%.

The reactants and reaction products were passed through a heated-line to an online RGA Varian 3800 series gas chromatography equipped with a flame ionization detector (FID) to analyze hydrocarbon products (CH_4, C_2H_6, C_2H_4, C_3H_8 and C_3H_6) and thermal conductivity detectors (TCD) to analyze O_2, C_O and CO_2. The analyses were based on external standard calibration.

Conversions, selectivity, and carbon balance are defined below:

Conversion = [Propane (in) - Propane (out)] x 100/Propane (in)

Selectivity = [moles of product / moles of products] x 100

Carbon balance = [moles of C atoms (out) / moles of C atoms (in)] x 100

3. Results and Discussion

3.1 Catalyst Characterization

BET surface area, pore volume, and average pore size based on the BET and BJH methods for the catalysts and bare MCM-41 and Kieselguhr are shown in Table 1. The impregnation of the active component and calcinations causes reductions in the BET surface areas and pore volumes of the supports. For the less porous Kieselguhr; the decrease in the area (48%) is much lower than that of mesoporous MCM-41 (77%). There are corresponding decreases in pore volumes and increases in pore diameters as was found in an earlier report (Liu *et al.* 2008). This suggests a blockage of narrow pores by vanadium oxides dispersed on the surface of the supports.

X-ray elemental analysis studies are recorded using X-ray source operating at 30 kV. The analysis of sup-

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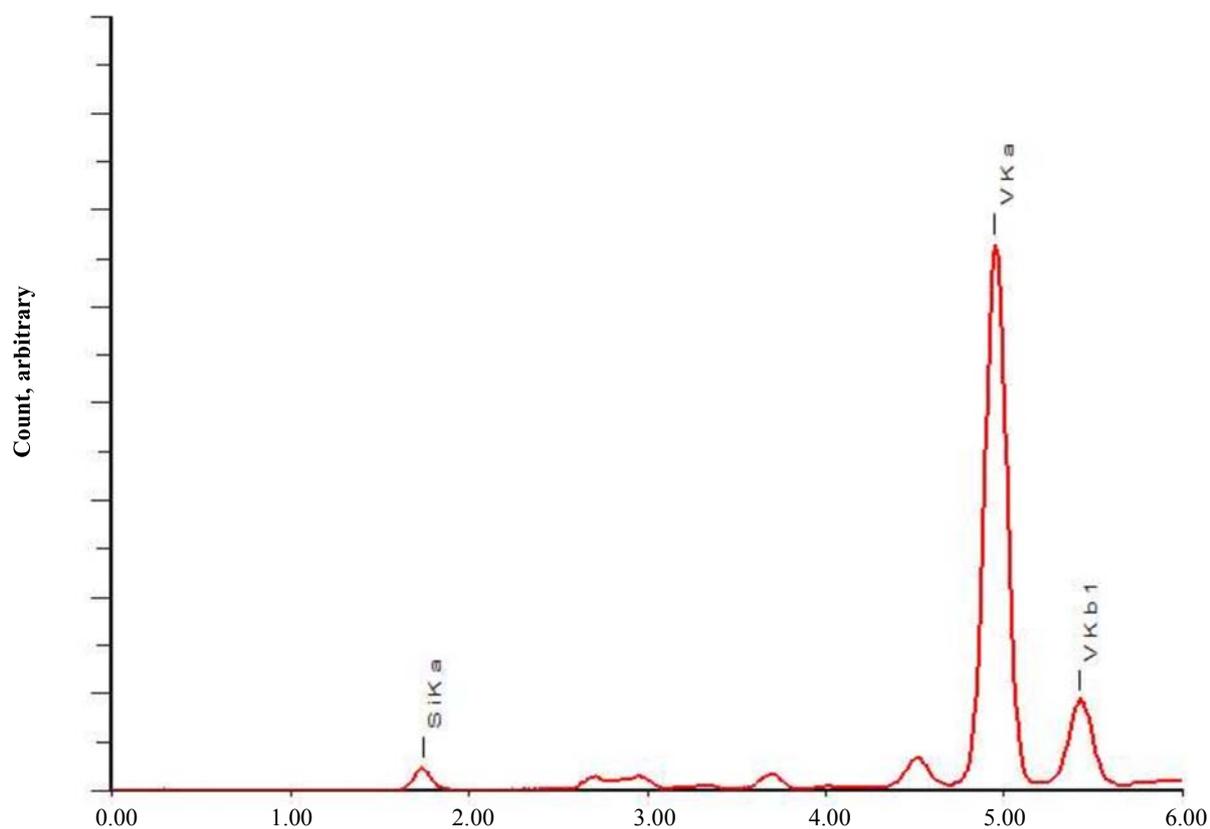
Figure 1a. X-Ray elemental analysis of V-oxide/Kieselguhr support
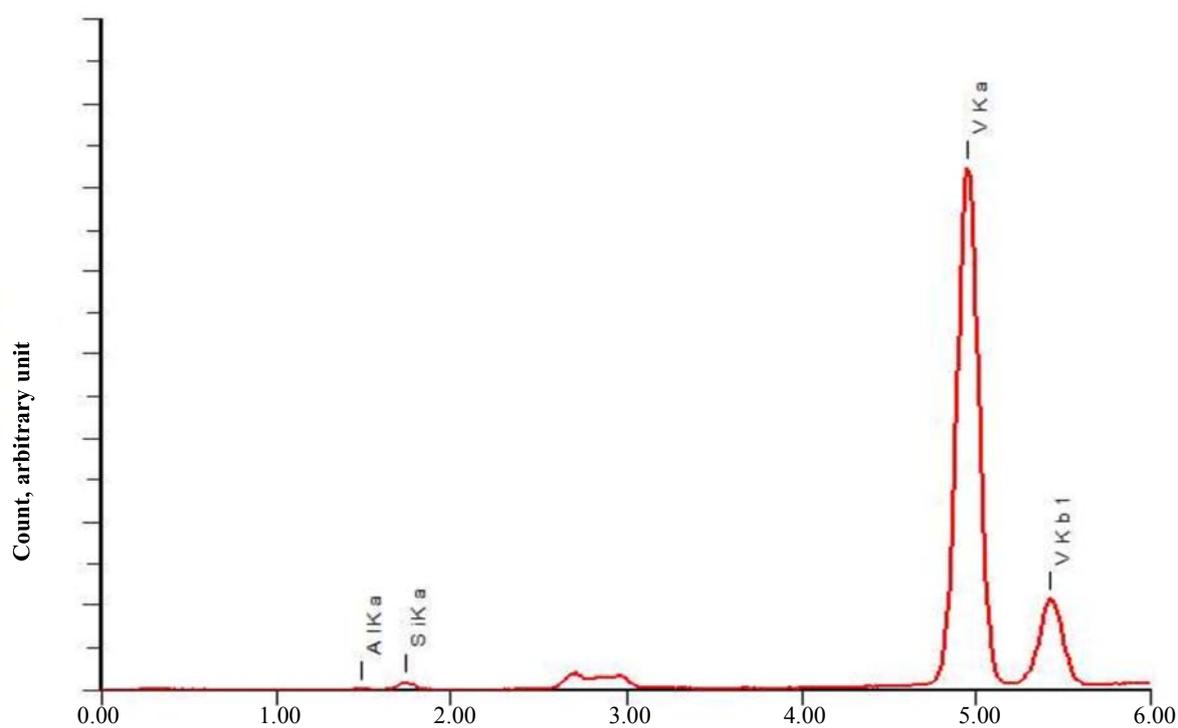
Figure 1b. X-Ray elemental analysis of V-oxide/MCM-41 support

ported vanadium oxide on Kieselguhr showed two major peaks in SiKα attributed to Kieselguhr (SiO₂) and VKα attributed to metal oxide as shown in Fig. 1a.

Also the analysis of supported vanadium oxide on MCM-41 showed three major peaks SiKα and AlKα attributed to MCM-41 support and VKα attributed to

Table 2. X-Ray elemental analysis

	V-Oxide/Kieselguhr		V-Oxide/MCM-41	
	wt(%)	atom/mol (%)	wt(%)	atom/mol(%)
Al_2O_3	---	---	36.4047	26.3826
SiO_2	94.6622	98.1713	58.0189	71.3519
V_2O_5	5.3378	1.8287	5.5764	2.2655

Table 3. X-Ray photoelectron spectroscopy analysis of the standard, support and the supported 5% V-oxide catalysts

Sample	Binding Energy (eV)			
	V $2p_{3/2}$	Si $2p_{3/2}$	Al $2p_{1/2}$	O 1s
Kieselguhr	---	102.1	---	531.9
MCM-41	---	102.5	74.5	532 , (531.5 , 532.2)[a]
V_2O_5	519.1	---	---	531.9
5 wt%V_2O_5/Kieselguhr	520.1	101.5	---	532 , (529.5 , 531.5)[a]
5 wt%V_2O_5/MCM-41	518.1	102.4	74.5	532, (531.9, 532.7, 531.5)[a]

(a) Curve fitting of the 0 1s binding energy

metal oxide as shown in Fig. 1b. The quantitative analysis as summarized in Table 2 shows that the composition of vanadium oxide on each support is about 5 wt% after the calcinations.

The results in Table 3 shows the results of XPS for the catalysts and supports. Figures 2a and 2b show two of the XPS spectra, as samples of wide and narrow scan spectra (O1s, Si$2p_{3/2}$ and V $2p_{3/2}$) of V2O5/Kieselguhr. It can be speculated that the V$2p_{3/2}$ binding energy of 519.1 +1eV for the V-line is due to the presence of vanadium species in an oxidation state V^{5+} in the vanadium samples. Its variation in the catalysts indicates the effect of V-O-support interactions. The XPS of the Si$2p_{3/2}$ energy region shows the presence of a well defined line at 102.1eV characteristics of SiO_2 state of Kieselguhr and MCM-41 supports.

The Al2p photoelectron spectra exhibit Al $2p_{1/2}$ at 74.5 eV, which shares characteristics of Al_2O_3. A strong O 1s spectral line recorded at 532 eV is attributed to oxygen from the supports and supported vanadium oxides. The O 1s line for MCM-41 support could be divided into two bands (in the curve fitting) at 531.5 eV (Si-O) and 532.2 eV (Al-O). In the case of V-oxide/Kieselguhr the two bonds are identified at 529.5 eV (Si-O) and 531.5 eV (V-O), while in the case of V-oxide/MCM-41 the three bonds are identified at 531.5 eV (V-O), 531.2 eV (Si-O) and 532.7 eV (Al-O). The variations in oxygen binding energies reflect the effects of the supports on the catalysts surface properties.

3.2 Tests of Catalysts

The performances of the catalysts in propane oxidative dehydrogenation were studied. Figure 3 summarizes the effects of temperature and feed compositions on propane conversions and products distributions. Propene is the desired product. In the oxidative dehydrogenation reaction, we expect carbon poisoning effects to be minimized. This is because the oxygen in the feed stream reacts with the carbon or its precursor to produce CO/CO_2. The catalysts exhibit low conversions at 400 °C. Both propene and CO_2 appear to be primary products on V/K while only propene is a primary product on V/M. The occurrence of the two reactions suggests the presence of sites of different reducibilities on the catalysts (Klisinska 2006). On V/K, the conversion increases exponentially to 60% at 700 °C, with a corresponding linear decrease in propene selectivity. CO was produced at 500 °C and higher temperatures with selectivities of 5 - 15%. It is perhaps a secondary product of propene further reactions. When the conversion increases to 5%, selectivity to CO_2 increases about six fold that of CO. The high selectivity to CO_2 is in line with the presence of highly reducible sites. These attack the electron-rich region of propyl or propane species to produce CO_2.

The exponential increase in propane conversion is due to cracking of propane as evidenced by the high selectivities to methane and ethane. However, the cracking seems to be catalyst surface mediated due to

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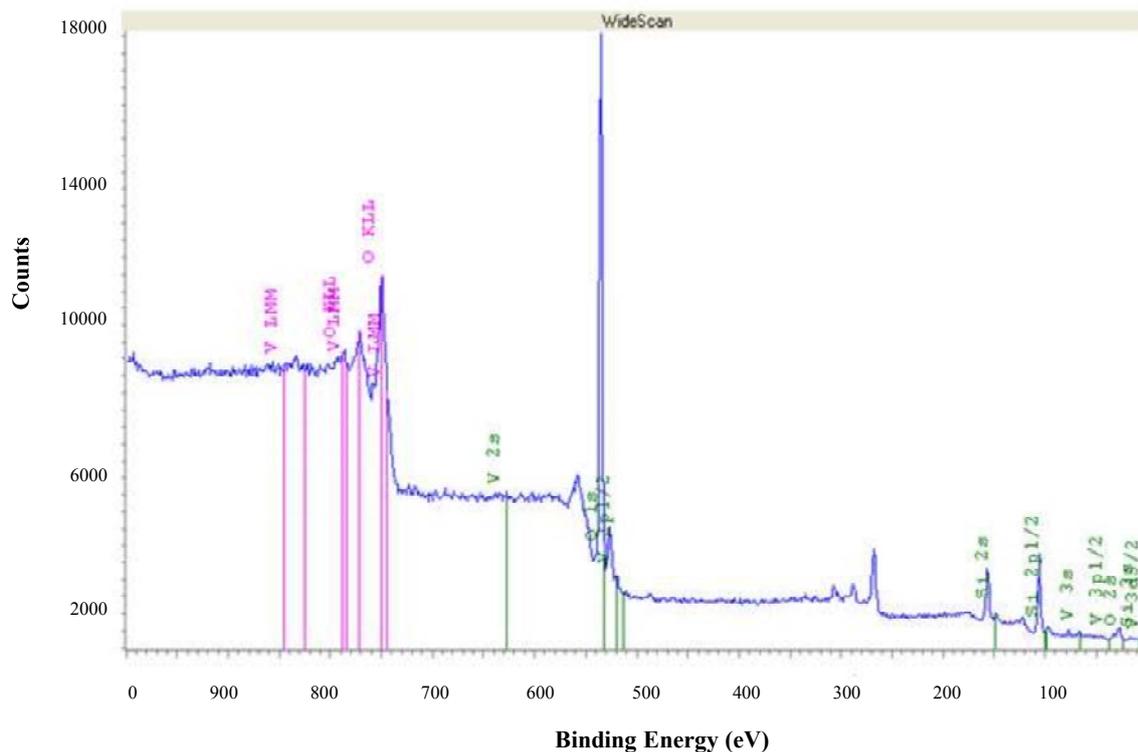
Figure 2a. Wide scan XPS spectrum of supported 5% V205 on Kieselguhr
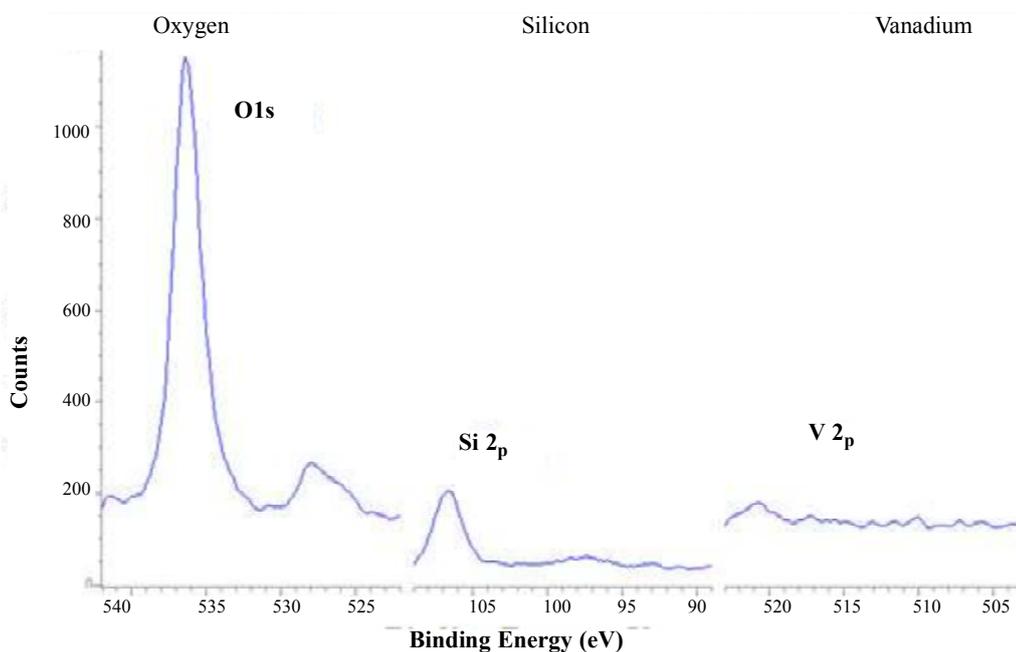
Figure 2b. Narrow scan XPS spectrum of 0 1s, Si $2_{p/32}$ and V $2_{p3/2}$ of 5% V_2O_5 / Kiesel

lower levels of conversion and selectivity to CO_2 observed on V/M (Ji *et al*. 2008). On the V/M, propene is the only primary product. Its further reaction led to CO instead of the CO_2 observed in the case of V/K at 500 °C. At 600 °C, selectivity to CO_2 of 66% was obtained. Thus, there was CO to CO_2 switch between the temperatures of 500 and 600 °C. This suggests the dynamic change in reducibilities of the catalyst's surface. It may also be associated with an increase in oxygen mobility at higher temperature,
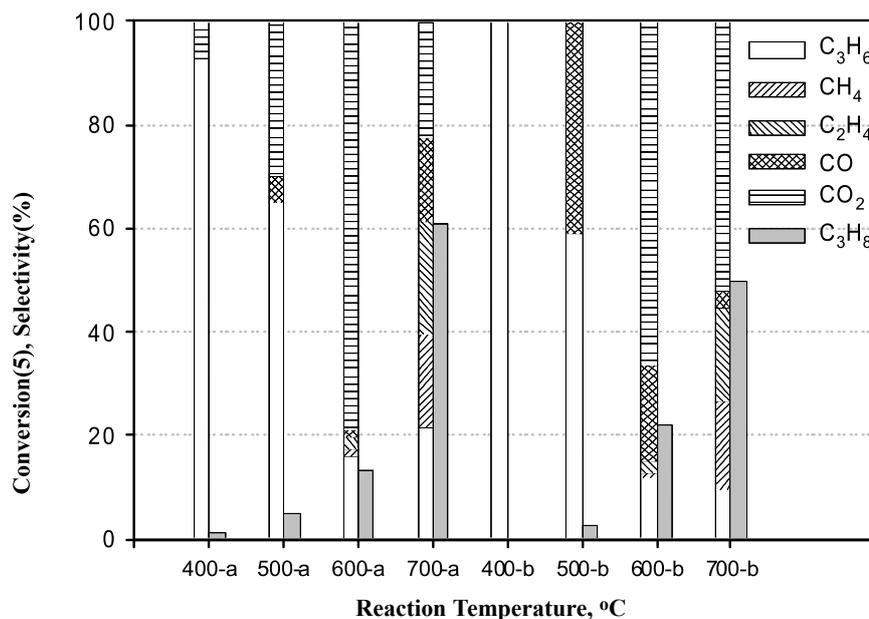
Figure 3. Effect of temperature on propane conversion and products selectivities for (a) V_2O_3/Kieselguhr and
V_2O_3/MCM-41
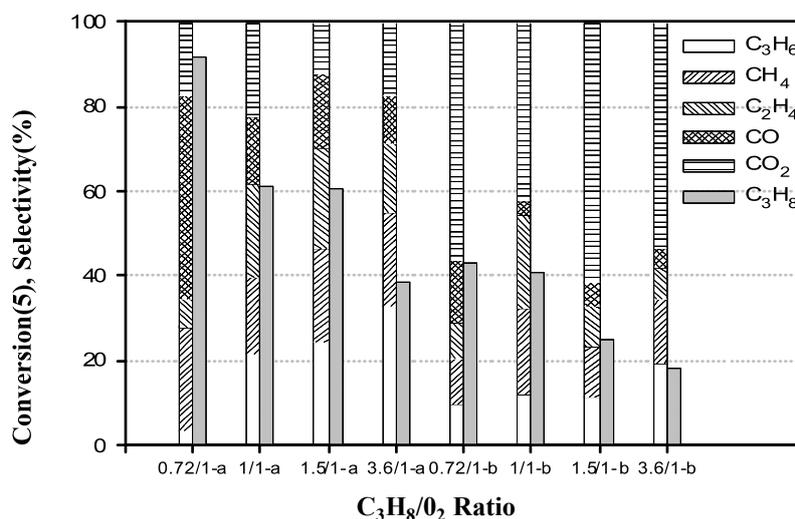
Figure 4. Effect of propane / oxygen ratio on propane conversion and products selectivities for (a) V_2O_5 /
Kieselguhr and (b) V_2O_5 / MCM-41

with concomitant higher selectivity to CO_2 rather than CO, depending on the nature of the catalysts (Owen *et al*. 2008).   Similar to V/K, a substantial amount of cracking products with selectivity of about 35% was observed.

In order to gain further insight into the effects of catalysts on the cracking reaction, the propane/oxygen ratio was varied at 700 °C (Fig. 4). As the ratio increases (0.7 - 3.6), the conversion and selectivities to CO_x decrease with corresponding increase in selectivities to propene. The relative amount of oxygen in the feed determines the selectivity to propene. For the oxygen-rich feed; V/K exhibits selectivity to propene of 3%. This improves to 23% when the amount of

propane increases five times at a constant oxygen flow. The ratio of CO/CO_2 also changes (2.8-0.7) from low to high propane flow. The distribution is different on V/M catalysts. The dominant product is CO_2 at all feed compositions. The differences in CO_X distributions by the catalysts are in line with differences in oxygen binding   energy   in   V/K   and   V/M http://(srdata.nist.gov/xps/ (NIST X-ray photoelectron spectroscopy database).

4. Conclusions

Vanadium-oxide supported on Kieselguhr is more active than that supported on MCM-41 in propane

oxidative dehydrogenation at the conditions explored. The latter's surface area was more drastically decreased when it was impregnated with the vanadium oxide. Both propene and CO_2 appeared to be primary products on vanadium-oxide/Kiesulguhr while only propene was the primary product on vanadium-oxide/MCM-41, suggestive of sites of different reducibilities on the catalysts. The superior performance was maintained when the catalysts were further tested in both oxygen-rich and oxygen-deficient feedstock. The higher activity and different products distributions of Kieselguhr supported samples is associated with its lower Si-O binding energy as evidenced by XPS. The different extent of vanadium oxide interaction with supports affects both its surface properties and catalytic activities.

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