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OXIDATIVE DEHYDROGENATION OF PROPANE AND n-BUTANE OVER ALUMINA SUPPORTED VANADIUM CATALYSTS

V. MURGIA[1,2], E. SHAM[1,2], J. C. GOTTIFREDI[1,2]and E. M. FARFAN TORRES[1,3]

[1]INIQUI - [2]Facultad de Ingeniería – [3]Facultad de Ciencias Exactas, Universidad Nacional de Salta, Buenos Aires 177, 4400-Salta, Argentina.
sham@unsa.edu.ar

Abstract - **Structural properties of vanadium dispersed species on γ-Al_2O_3 are investigated with the scope to detect changes related with V loading in the oxidative dehydrogenation (ODH) of propane and n-butane. XPS, FTIR, and FTIR of absorbed pyridine were used to study the nature of vanadium supported species.**

Tetrahedral V^{5+} and probably V^{4+} species were detected. For vanadium loadings higher than 4.3 % wt octahedral species were also observed.

In the n-butane ODH reaction, the selectivity to ODH products decreases when vanadium content increases. However, for propane ODH, the selectivity seems to be independent of vanadium loadings.

Low oxygen/alkane feeding ratios favor selectivity to olefins. It is also shown that low V loading catalysts reach selectivities as good as best reported V-Mg-O catalyst.

Keywords – **Oxidative Dehydrogenation; Vanadium Catalysts; propane; n-butane.**

I. INTRODUCTION

Vanadium oxide dispersed on metal oxide supports exhibits interesting catalytic properties for partial oxidation of alkanes, aromatics and olefins (Bielanski and Haber, 1979; Dadyburjor at al., 1979; Mamedov and Cortés Corberán, 1995; Blasco *et al.*, 1995). The activity and selectivity of vanadia supported catalysts are deeply modified by the structure and physicochemical properties of the dispersed species supported on the surface (Dadyburjor *et al.*, 1979; Mamedov and Cortés Corberán, 1995; Yoshida *et al.*, 1988; Eon *et al.*, 1992; Koranne *et al.*, 1994).

MgO supported vanadium was reported as a very selective catalyst in the oxidative dehydrogenation of propane and n-butane (Kung and Chaar, 1988), while γ-Al_2O_3 supported vanadium catalyst was found to present a good selectivity to olefin products for ethane ODH but a poor selectivity in the ODH of n-butane (Concepcion *et al.*, 1994).

The acid-base character of the support explained this different behavior. On MgO, a support with basic properties, the interaction between vanadium species and the supports leads to the formation of vanadate compounds. In the case of more acid supports, such as SiO_2 or Al_2O_3 a weak interaction is expected leading to less dispersed vanadium species on the surface which, in turns favors the formation of V_2O_5 crystallites (Blasco at al., 1995; Galli at al., 1995).

Alumina-supported vanadia has been the object of several structural investigations (Haber *et al.*, 1986; Nag *et al.*, 1988; Eckert and Wachs, 1989; Andersen and Kung, 1992; Michalakos *et al.*, 1993). These studies show, in general, that at low loading vanadium form highly dispersed amorphous phases, whose structure changes from isolated tetrahedral vanadium, to polyvanadates species at medium loading. Crystalline V_2O_5 also appears at high loading in addition to amorphous vanadia phases.

The binding strength of oxygen lattice has been postulated as the parameter that governs activities and selectivities of these catalysts (Yoshida *et al.*, 1988). In this way VO_4 tetrahedra formed at low vanadium contents are related with high selectivities to alkenes because all the oxygen ions in these species are bridged between V and the metal ions of the support oxide (Michalakos *et al.*, 1993; Corma *et al.*, 1993a).

Other authors considered that -V_2O_7- units favor alkane ODH and suggested that the bridging oxygen ion between two vanadium ions (V-O-V) plays an important role in the propane ODH. The removal of' this oxygen results in a local structural change from the -V_2O_7- unit to two edge-sharing square-based -VO^{3-}- units where vanadium is present as V^{4+} cations (Eon *et al.*, 1994). These stabilized V^{4+} ions were postulated as responsible for the dehydrogenation selectivity of pyrovanadate structure.

As V^{4+} ions are also present in selective ODH catalysts like Mg pyrovanadate and Mg orthovanadate (Kung and Kung, 1992; Gao *et al.*, 1994), Mamedov and Cortés Corberán (1995) suggest that a certain extent of reduction is needed for the selective dehydrogenation of alkanes. But they also emphasize that a good selectivity can be achieved by controlling reaction conditions (temperature and alkane to oxygen ratio).

The aim of this paper is to further study the nature of active sites and the influence of the acid-base character of the vanadium supported catalysts on the selectivity for the ODH of propane and n-butane. For this purpose V/γ-Al_2O_3 catalysts have been prepared with different degrees of coverage using incipient wet impregnation techniques.

II. EXPERIMENTAL

A. Catalyst Preparation

Alumina support was Aldrich, surface area 132 m^2g^{-1}. Catalysts were prepared by impregnation of the support with an aqueous solution of ammonium metavanadate (from Fluka p.a.). The impregnated samples were dried at 110 °C over night, and then calcined at 550 °C in air 16 hours. Catalysts having loadings of 1.4, 2.7, 4.3 and 5.1 wt % of V were prepared with alumina by successive impregnation cycles. They will be denoted as $Vx/A1_2O_3$, being x the vanadium wt % content.

B. Catalyst Characterization

Infrared spectra were recorded between 1200 and 800 cm^{-1} using a Bruker IFS 88B on samples dispersed in KBr.

The catalysts acidity was also studied using pyridine as probe molecule. FTIR spectra of adsorbed pyridine were obtained from wafers of self supported samples mounted in a pyrex vacuum cell with KRS-5 windows.

The samples were degassed out for 1,5 h at 450°C and then cooled at room temperature (RT) to obtain the reference spectra. Then, pyridine was adsorbed at room temperature and desorbed at different temperatures from RT to 250°C for 30 minutes in each case. The spectra were taken at room temperature and the reference spectra substracted in all cases.

The XPS spectra were taken in a Physical Electronics 5700 ESCA spectrometer. The exciting radiation was Mg Kα (1253.6 eV). The binding energies (BE) were calculated with respect to C_{ls} peak set at 284.5 eV.

C. Catalytic Test

The catalytic studies were performed in a fixed bed tubular reactor. The samples were diluted with quartz. The catalytic volume was 1.2 cm^3. Reactants and reaction products were analyzed by online chromatography using a Varian 3700 and a Shimadzu GC-3BT chromatographs for heavy and light products respectively.

For n-butane test, the reactor was fed with a mixture 20/15/65 of n-butane, oxygen, and nitrogen respectively at a constant flow rate of 150 mL min^{-1}.

The weight of catalytic samples (155-255 µm) was varied to achieve different contact times. Experiments were carried out at constant temperature (703 and 773K). No noticeable deactivation was observed over a period of 24 hours of reaction at the maximum temperature. Blank tests on the reactor showed no activity in the range of temperatures studied.

For propane reaction, two different mixtures of propane, oxygen and nitrogen 20/15/65 and 4/8/88 were fed. The flow rate of the reactants was varied (150-250 mL/min) to achieve different contact times.

III. RESULTS

A. Catalyst Characterization

Surface area, vanadium weight content and the resultant theoretical coverage for the catalysts are given in Table 1.

Table 1. Characteristic of supported vanadium catalysts

Sample	V (wt %)	Theoretical Monolayer coverage [a] (%)	Sg (m^2/g)	V $2p_{3/2}$ BE (eV)
Al_2O_3	-	-	132	-
$V1.4/Al_2O_3$	1.4	12.7	133	515.7
$V2.7/Al_2O_3$	2.7	24.9	131	516.0
$V4.3/Al_2O_3$	4.3	40.2	103	516.2
$V5.1/Al_2O_3$	5.1	48.1	125	516.6
V_2O_5[b]	-	-	-	516.9

[a] Assuming a surface area of 0.10 nm^2 per VO_4^{3-} species (F.Roozeboom et all., 1980)

[b] FLUKA p.a. reactive

XPS spectra show that $V2p_{3/2}$ signals are broadened in the case of supported samples compared to the corresponding signal of bulk vanadium pentoxide. This broadening is more noticeable for low vanadium loadings samples ($Vl.4/A1_2O_3$, $V2.7/A1_2O_3$) and can be correlated with the formation of highly dispersed vanadium species over the carrier.

The assignment of vanadium oxidation state was made by assuming that lines with high BE values (516.9-517.2 eV) could be related to the presence of V^{5+} and those with low BE (515.6-5l6.3 eV) to the presence of some reduced species, probably V^{4+} (Gao *et al.* (1994) and Matralis *et al.*, 1995).

As can be seen in Table 1 samples with very low vanadium coverage ($V1.4/A1_2O_3$, $V2.7/A1_2O_3$ and $V4.3/A1_2O_3$) present $V2p_{3/2}$ lines more related to values of V^{4+} oxidation state. However, V2p3/2 bands are asymmetric suggesting that both V^{4+} and V^{5+} species are present. When the vanadium coverage increases ($V5.1/A1_2O_3$) the measured BE increases to 516.6 eV indicating that V^{5+} species are predominant.

The FTIR spectra of the V*x*/Al_2O_3 catalysts along with that of unsupported V_2O_5 are presented in Fig.1. Bulk V_2O_5 presents two peaks, one at 1018 cm^{-1} which has been assigned to the stretching of the short double bond $(V=O)^{3+}$ (Matralis *et al.*, 1995), and a second absorption at 835 cm^{-1} corresponding to V-O vibrational modes (Gao *et al.*, 1994). The IR spectrum of V1.4/Al_2O_3 catalyst shows essentially a broad absorption band at 991 cm^{-1} which has been assigned to two-dimensional vanadium oxide amorphous phases (Matralis *et al.*, 1995; Miyata *et al.*, 1997). This band has also been correlated with the vibration of isolated V=O bonds of the type VO^{2+} (Corma *et al.*, 1993b). When vanadium loading increases broad bands with maxima centered at 1010-1016 cm^{-1} are observed showing the beginning of V_2O_5 phase formation. The shifting to lower frequencies indicates a weakening of the $(V=O)^{3+}$ bonding coincident with an amorphous oxide phase or the presence of neighboring V^{4+} ions.

In Figure 2 the infrared spectra of pyridine adsorbed on V2.7/$A1_2O_3$ (A), V4.3/$A1_2O_3$ (B) and V5.1/$A1_2O_3$ (C) catalysts after evacuation at temperatures of 150°C (a) and 250°C (b) are presented.

Bands related to physisorbed and coordinately bonded pyridine are observed for all catalysts. After evacuation at 250°C, bands at 1452, 1493, 1577 and 1624 cm^{-1}, characteristic of pyridine retained on Lewis acid sites, are only observed.

The peak at 1539 cm^{-1} associated to pyridine adsorbed on Brönsted acid sites is observed only for V5.1/$A1_2O_3$. This band disappeared after evacuation at 250 °C.

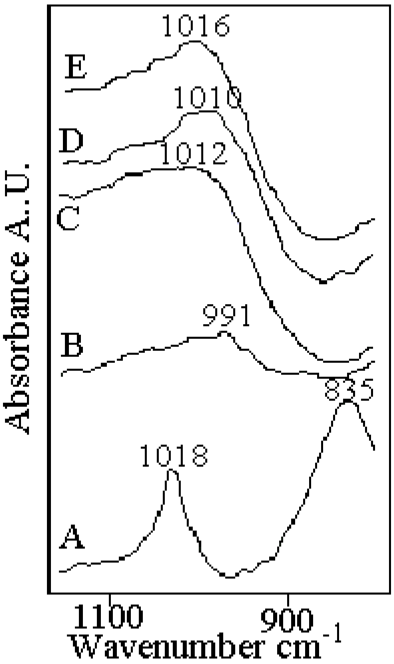

Fig. 1- FTIR spectra of: (A) V_2O_5, (B) V1.4/Al_2O_3, (C) V2.7/Al_2O_3, (D) V4.3/Al_2O_3 and (E) V5.1/Al_2O_3.

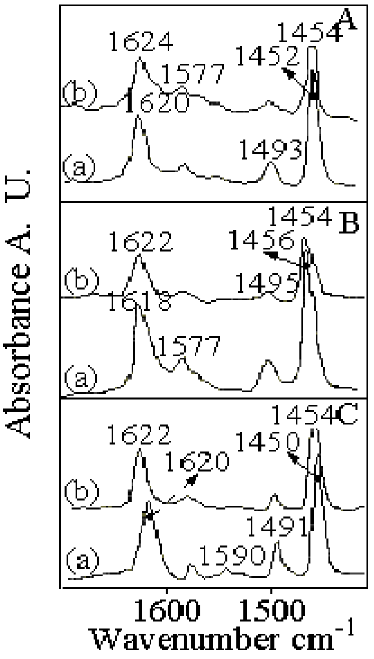

Fig. 2- FTIR spectra of pyridine adsorbed on: (A) V2.7/Al_2O_3, (B) V4.3/Al_2O_3 and (C) V5.1/Al_2O_3 samples obtained at evacuation temperatures of 150°C (a) and 250°C (b).

B. Catalytic Study

The catalytic testing results for the oxidative dehydrogenation of n-butane are presented in Table 2. In general C_4-olefins (l-butene, cis-2-butene, trans-2-butene and butadiene), CO and CO_2 are the main reaction products, while cracking products are minor or absent. The carbon balance is satisfactory in all the cases with differences lower than 1%.

It can be seen that, in all cases, selectivity decreases when conversion increases. However, significantly, the higher selectivities are observed with low vanadium content catalysts. The Rv and Rv x Selectivity ODH at 500°C is higher for lower vanadia loadings.

Also selectivity slightly increases when the temperature increases from 430°C to 500°C. The effect of O_2/C_4 ratio was investigated for V1.4/Al_2O_3 at different temperatures. As O_2/C_4 ratio varies from 0.8 to 1.5, at a given temperature, overall n-butane conversion is increased, while ODH selectivity decreases. However, as shown in Table 3, C_4 olefins yield is almost unaffected.

To compare the catalytic behavior of V1.4 and V5.1/Al_2O_3 solid olefin selectivity, results at 500°C and 430°C are presented in Fig. 3 and 4, respectively. For both catalysts it was observed that the selectivity to l-butene and 2-butenes decreases with the conversion, while butadiene selectivity slightly increases. For low vanadium content, the predominant isomer was 1-butene, and the ratio cis-2/trans-2-butene was near 1. For V5.1/Al_2O_3 catalysts the molar ratio 1-butene/cis-2-butene/trans-2-butene was closer to the equilibrium predictions (1/1/1.1).

Table 2. Oxidative dehydrogenation of n-butane on supported vanadium catalysts

Sample	W/F gcat/mol C4	T (°C)	Conversion (%)	Rv molC4/h molV	Rv x Sel ODH	Selectivity % ODH	Selectivity % COMB.
V1.4/Al_2O_3	6.25	430	5.03	29.28	19.31	64.95	34.05
	12.50		6.84	19.85	12.90	65.01	34.99
	15.63		15.63	19.21	11.62	60.49	39.51
V5.1/Al_2O_3	0.78	430	4.49	57.41	21.52	37.48	62.52
	1.56		7.51	47.99	12.06	25.12	74.88
	3.13		13.39	42.81	10.74	25.09	74.90
	6.25		18.50	29.57	5.91	19.97	80.03
	12.50		18.40	14.68	4.51	30.69	69.31
V1.4/Al_2O_3	1.56	500	5.51	128.22	94.50	73.70	26.3
	3.13		9.22	107.39	68.20	63.51	36.49
	6.25		13.30	77.43	40.92	52.85	46.02[a]
	12.50		21.19	61.67	30.21	48.98	50.18[b]
V5.1/Al_2O_3	0.78	500	16.81	214.96	57.37	26.69	73.31
	1.56		18.84	120.43	32.97	27.38	72.62
	3.13		19.11	61.08	17.66	28.91	70.82[c]
	6.25		19.52	31.19	9.09	29.13	70.87
	12.50		20.65	16.50	6.13	37.17	62.83

[a] 1.13% of propane; [b] 0.84% of propilene; [c] 0.37% of propilene

Table 3. V1.4/Al_2O_3 changes of the selectivity and yield to C4 olefins with O2/C4 ratios

Temperature (°C)	O2/C4=0.8 Conversion (%)	 Selectivity (%)	 Yield (%)	O2/C4=1.5 Conversion (%)	 Selectivity (%)	 Yield (%)
440	4.9	66.1	3.3	5.0	55.4	2.8
485	11.7	54.5	6.4	12.5	51.0	6.4
500	13.3	52.9	7.0	16.0	49.3	7.9
566	28.1	51.5	14.5	36.1	41.3	14.9
584	30.4	50.0	15.2	40.4	39.9	16.1

From Table 2 it can be seen that combustion products (CO and CO_2) selectivity increases up about 18% conversion level. For V2.7, V4.3 and V5.1/Al_2O_3 catalysts cracking products, less than 1%, are observed for conversions higher than 20%. Also for V5.1/Al_2O_3 and conversion higher than 18 %, the selectivity to ODH increases with conversion. For this solid the CO and CO2 selectivities initially increase and then decrease when conversions are higher than 18%.

Figures 5 and 6 show the changes in selectivity to olefins with C_3H_6 conversion for V2.7 and V5.1/Al_2O_3 catalysts at 430 and 470°C, with two different O_2/C_3H_8 feed ratios. It was observed that the selectivity decreases when the conversion increases. However, for propane ODH the selectivity seems to be independent of both, temperature and vanadium loadings, in the studied range which is in agreement with previously reported results (Mamedov and Cortés Corberán, 1995; Eon *et al.*, 1992).

In Table 4, it is shown that the specifc rate per vanadium mol,Rv, and Rv x Selectivity ODH at 500°C reach a maximum for V2.7/Al_2O_3 catalysts. In this table, the effect of the O_2/C_3H_8 ratio at constant temperature is also observed. In general, it can be seen, that increasing this ratio from 0.75 to 2, the propane conversion increases and the selectivity decreases. This decrease could be only related with the conversion and not with the feed ratio. As can be seen in Table 5 when the conversion level is constant, the selectivity and yield show to be independent of this ratio, except for V1.4/$Al_2O_{3.}$ For this catalyst the higher selectivity is achieved at the higher conversions levels when O_2/C_3H_8 ratio is low. On the other side, for this catalyst at low conversion levels the selectivity to ODH products is favored for high O_2/C_3H_8 ratios.

Table 4. Oxidative dehydrogenation of propane on supported vanadium catalysts

Sample	W/F gcat/mol C4	T (°C)	Conversion (%)	Rv molC4/h molV	Rv x Sel DHG	Selectivity (%) ODH	COMB.
O_2:C_3 = 2							
1.4V/Al_2O_3	30.77	430	1.78	2.11	2.11	100	-
2.7V/Al_2O_3			6.31	3.87	3.45	89.09	10.91
4.3V/Al_2O_3			21.75	8.37	3.91	46.64	53.36
5.1V/Al_2O_3			26.72	8.67	2.66	30.69	69.31
1.4V/Al_2O_3	30.77	500	6.68	7.90	6.19	77.93	22.07
2.7V/Al_2O_3			35.97	22.06	7.92	35.93	64.07
4.3V/Al_2O_3			51.75	19.92	3.39	16.99	83.01
5.1V/Al_2O_3			56.25	18.26	2.58	14.12	85.88
O_2:C_3 = 0.75							
1.4V/Al_2O_3	6.25	430	1.57	9.12	7.62	83.55	16.45
2.7V/Al_2O_3			5.91	17.85	12.63	70.79	29.21
4.3V/Al_2O_3			13.97	26.48	14.01	52.88	47.12
5.1V/Al_2O_3			19.56	31.26	13.40	42.87	57.13
1.4V/Al_2O_3	6.25	500	9.24	53.79	30.03	55.83	44.17
2.7V/Al_2O_3			26.34	79.51	37.43	47.08	52.91
4.3V/Al_2O_3			27.38	51.90	21.22	40.88	59.12
5.1V/Al_2O_3			27.21	43.48	17.68	40.67	59.33

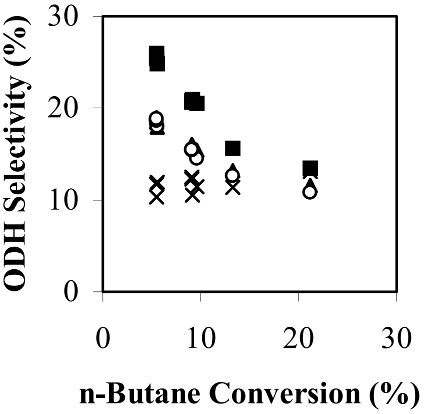

Fig. 3- Selectivity to olefins versus conversion of n-butane at 500°C for V1.4/Al_2O_3: ■ 1-butene; ▲ 2-t-butene; ○ 2-c-butene; × butadiene.

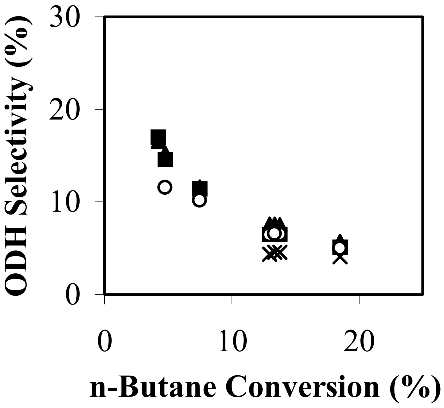

Fig. 4- Selectivity to olefins versus conversion of n-butane at 430°C for V5.1/Al_2O_3: ■ 1-butene; ▲ 2-t-butene; ○ 2-c-butene; × butadiene.

IV. DISCUSSION

A. Structure of V/Al_2O_3 catalysts

Our XPS and IR studies confirm the presence of V^{5+} and probably V^{4+} supported species on the surface of catalysts.

An interesting fact is that catalysts with low vanadium coverage (V1.4/Al_2O_3 and V2.7/Al_2O_3) present a more pronounced shift in the BE for the V2$p_{3/2}$ line confirming the presence of both V^{4+} and V^{5+} surface species. It is known from literature (mostly from studies using XPS, ESR, and chemical titration) that V^{4+} species are stabilized, when vanadium is in strong interaction with the carrier for V_2O_5/TiO_2 and V_2O_5 / Al_2O_3 systems (Matralis *et al.*, 1995 and references there in).

From IR and XPS results we can conclude that formation of this partially reduced vanadium species, in low loading catalysts, could be correlated with the formation of isolated VO_x species where the vanadium is in strong interaction with the support surface. Under these conditions there are very few possibilities of side interactions that could favor the formation of polyvanadates or V_2O_5 crystallites. In the opposite side the formation of polyvanadates like species is favored when vanadium loading increases leading to predominance of V^{5+} species in tetrahedral or octahedral environment.

IR results of adsorbed pyridine indicate that only Lewis acid sites are present in the low vanadium content catalysts, being mainly related to γ-Al_2O_3. At higher vanadium loadings, Lewis and Brönsted acid sites are both present. Brönsted sites are related with octahedral V^{5+} species, for vanadium contents higher than 4 wt %. Thus, a lower selectivity for butane ODH could be correlated with a higher acid character of the vanadium surface species present in the catalyst.

Table 5. Variation of the selectivity and yield to C3 olefins from propane with O_2/C_3 ratio

Sample	Temperature (°C)		O_2/C_3=2			O_2/C_3=0.75	
		Conversion (%)	Selectivity (%)	Yield (%)	Conversion (%)	Selectivity (%)	Yield (%)
$V1.4/Al_2O_3$	550	18.62	39.34	7.33	18.24	51.70	9.43
	500	6.68	77.93	5.21	6.75	60.22	4.06
		5.12	81.38	4.16	5.21	59.84	3.12
$V2.7/Al_2O_3$	430	12.57	61.71	7.75	12.59	58.31	7.34
		8.27	70.45	5.83	8.21	69.90	5.73
		10.83	64.67	7.01	10.11	64.23	6.5
	500	25.83	43.40	11.21	25.01	49.30	12.33
		29.74	44.03	13.10	29.61	46.68	13.82
$V4.3/Al_2O_3$	430	13.63	51.77	7.05	13.97	52.85	7.39
$V5.1/Al_2O_3$	430	7.52	84.23	6.33	7.14	84.55	6.03
		18.84	42.36	7.98	18.18	45.02	8.18
	470	25.65	36.79	9.44	25.42	39.84	10.13

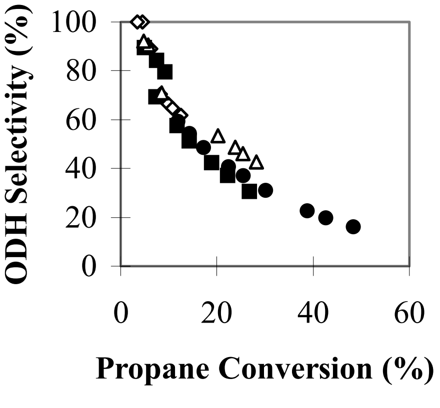

Fig. 5- Selectivities to olefins versus propane conversion for 2/1 O_2/C_3 ratio: ◊ $V2.7/Al_2O_3$ and ■ $V5.1/Al_2O_3$ at 430°C; Δ$V2.7/Al2O3$ and □ $V5.1/Al_2O_3$ at 470°C.

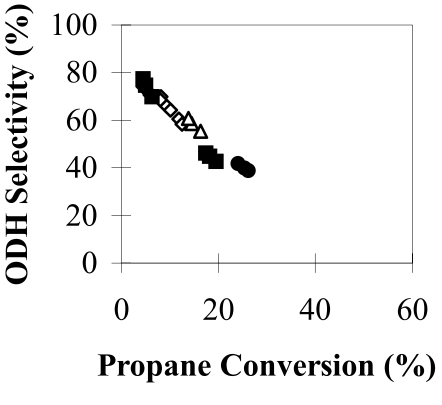

Fig. 6. Selectivities to olefins versus propane conversion for 0.8/1 O_2/C_3 ratio:◊ $V2.7/Al_2O_3$ and ■ $V5.1/Al_2O_3$ at 430°C; Δ$V2.7/Al2O3$ and □ $V5.1/Al_2O_3$ at 470°C.

B. Catalytic Behavior

n-Butane ODH

Since ODH reactions involve redox mechanisms, the catalytic behavior could be associated with the redox behavior of the vanadium species dispersed on the catalyst surface. According with Mamedov and Cortés Corberán's conclusions (1995), a certain extent of V reduced ions species is needed to achieve good activities and selectivities to olefin products. These authors also stated that using low oxygen-to-alkane ratios an optimum extent of reduction could be achieved. For this reason, in the case of n-butane ODH reaction, the reactor was fed with a reaction mixture of this characteristic (15% oxygen, 20% n-butane and 65% nitrogen) instead of those classically used in literature. In Table 2, if we compare ODH selectivity for similar conversion values, it can be observed that selectivity to olefin products increases when the V content decreases. Characterization results show that low vanadium content catalyst (V1.4/A1$_2$O$_3$) presents isolated VO$_x$ species with an important fraction of V^{4+}. While the higher vanadium content catalyst (V5.1 /Al$_2$O$_3$) presents polyvanadates with a predominant V^{5+} oxidation state. For this catalyst, when conversion levels are near 15-18 % and oxygen conversion is higher than 99% the selectivity to ODH is increased. This improvement could be correlated with changes in both the surface structure of vanadate species and in their V^{4+} /V^{5+} ratio (Eon *et al.*, 1992 and Mamedov and Cortés Corberán, 1995) due to the reducing character of the reaction atmosphere. In this way V5.1 /Al$_2$O$_3$ catalyst improves its ODH selectivity.

C. Low Vanadium Content Catalysts

If we consider the results of low content catalysts (V1.4/Al$_2$O$_3$ and V2.7/Al$_2$O$_3$) it is observed that the selectivity to 1-butene and 2-butenes decreases with the conversion while the selectivity to butadiene increases. This behavior suggest that l-butene is a primary product as was early reported. The same conclusion can be derived for 2-butenes. At low conversion the formation of these primary products is predominant.

On the other hand, butadiene can be considered a secondary product formed from butenes since selectivity to butadiene slightly increases with conversion.

Selectivity to CO and CO$_2$ increases with the conversion for these catalysts showing the same trend of' butadiene. This result could indicate that they are also secondary products. As CO production increases with the conversion and begins to be detected at the same time that olefins, its formation could be related with the combustion of olefins strongly adsorbed on the catalyst surface.

The high selectivity to 1-butene for low vanadium content could also be related to the high rate of the second hydrogen abstraction, producing a 1-butene/cis-2-butene/trans-2-butene ratio of 1.4/1/1, which responds to a probabilistic distribution.

D. High Vanadium Contents Catalyst

For high vanadium loadings the selectivity to 1-butene and 2-butenes decreases with the conversion up to near 15-18%. For higher conversion levels, the oxygen conversion is higher than 99%, the selectivity to butenes (1 and 2-butenes) increases and the formation of CO and CO$_2$ of decreases. In this case a kinetic effect could be related with the observed results. In fact as conversion increases oxygen availability becomes the limiting factor. Under these conditions the olefins formation is favored.

Experimentally it was confirmed that no reaction takes place in complete absence of oxygen, showing that both reduced and oxidized species are necessary to sustain ODH reaction.

Assuming that the rate of the second hydrogen abstraction is the selectivity determining step, the result suggests that this is slower for acid catalyst, that is to say those with higher vanadium content. In this case the product distribution follows the equilibrium ratio (1butene / cis-2-butene / trans-2-butene, 1 /1 /1.1). Another possible selectivity determining step is the olefinic intermediates desorption, determined by the interaction of the alkenes with the catalyst surface. This interaction will depend on the acid-base character of both, the products and the catalyst. As olefins interact more strongly with acid catalysts than with basic ones, the desorption rate will decreased, favoring high selectivities to 2-butene and C$_4$ olefins distribution must be close to the equilibrium ratio.

E. Propane ODH

Selectivity results to propene at different temperatures show that all points fit the same selectivity-conversion curve. That could mean that at constant conversion, the selectivity does not depend on the temperature and on vanadium concentration, in the range of coverages studied. This behavior could be related with the fact that propane is more acidic than n-butane and in consequence the interaction between the active sites on the catalysts and the reactant molecule is lower. Also in this case there are no possibilities of equilibrium reactions, because the only two possible ODH products are the olefin or carbon oxides.

An interesting fact is that although the same selectivity is obtained at a constant conversion level with samples having different vanadia loadings, the specific activity per vanadium mol and Rv x Selectivity ODH values reach a maximum for V2.7/Al$_2$O$_3$.

V. CONCLUSIONS

Our studies allow concluding that both reduced and oxides species are necessary to obtain good selectivities to olefins in the case of the n-butane ODH. In this way low loading vanadium catalysts present the best selectivities. In this way when ODH reactions is conducted under reductive conditions reduced species are favored and then alkene selectivities must be enhanced.

For propane ODH the vanadium catalyst content do not affect the selectivity.

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