

Oxidative dehydrogenation of propane on VAPO-5, V_2O_5 /ALPO₄-5 and V_2O_5 /MgO catalysts. Nature of selective sites

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Abstract

The catalytic properties for the oxidative dehydrogenation of propane of selective VAPO-5, V_2O_5 /ALPO-5 (V/AP) and V_2O_5 /MgO (V/MgO) catalysts have been compared in the following reaction conditions: atmospheric pressure, C_3H_8/O_2 /He molar ratio of 4/8/88, in the 475–550°C temperature range. The catalysts have also been characterized by several techniques (S_{BET} , XRD, FTIR, H_2 -temperature programmed reduction, UV-Vis). It was found that isolated tetrahedral V^{5+} species are mainly present on VAPO-5 (0.5 wt% of V atoms) and on V/MgO (8.8 wt% of V atoms) catalysts, while isolated and associated V^{5+} species are present on V/AP samples with vanadium contents between 0.8–2.2 wt% of V atoms. The better catalytic properties for the oxidative dehydrogenation of propane of VAPO-5 are related to the presence of isolated VO_4 tetrahedron in the framework which, in absence of vanadium, exhibits a very low activity. However, the existence of Mg^{2+} sites free of vanadium on the surface of the V/MgO sample favours the direct formation of carbon oxides from propane. In the case of V/AP samples the presence of polymeric vanadium species favours the degradation of the formed propene to carbon oxides.

Keywords: ALPO₄-5 supported vanadium; Dehydrogenation; Oxidative dehydrogenation; Magnesium oxide; Propane; Supported catalysts; Vanadium; VAPO-5

1. Introduction

Mixed vanadium–magnesium oxides are interesting catalysts for the oxidative dehydrogenation (ODH) of alkanes, specially for the transformation of propane and n-butane [1–7]. However, the nature of the active and selective sites for the oxidative dehydrogenation of alkanes is still under discussion.

Kung et al. [1–3,6] proposed that isolated vanadium species in a $Mg_3V_2O_8$ structure are the

selective sites for the ODH of propane, while the presence of V=O bonds favours the formation of carbon oxides from alkanes. Volta et al. [4] proposed that the active and selective phase they found, α - $Mg_2V_2O_7$, is characterized by the presence of both single and double vanadium–oxygen bonds in V–O–V pairs. Recently, it has been proposed that the catalytic properties of V–Mg–O catalysts for the ODH of propane are strongly influenced by the preparation procedure [5,8] and both activity and selectivity depends of the vanadium content on the catalyst surface. In this way, the selective sites in V_2O_5 /MgO catalysts have been related to isolated vanadium species (with a

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Table 1
Characteristics of calcined catalysts

Sample	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	Micropore volume ($\text{cm}^3 \text{g}^{-1}$)	Vanadium content (wt%) ^a	Crystalline phases ^b
ALPO ₄ -5	168	0.066	0	ALPO ₄ -5 (100)
1V/AP	—	—	0.87	ALPO ₄ -5 (100)
2V/AP	67.9	0.023	2.2	Trydimite
VAPO-5	207	0.087	0.47	ALPO ₄ -5 (100)
V/MgO	108	0.001	11.0	MgO + Mg ₃ V ₂ O ₈

^a Chemical composition was determined, in wt% of V atom, from atomic absorption spectrometry.

^b Crystalline phases in calcined samples. The crystallinity referred to as-synthesized ALPO₄-5 (AFI) is in parenthesis.

tetrahedral coordination) on the surface of the catalysts [5,7].

On the other hand, vanadium-substituted aluminophosphate molecular sieve with AFI structure (VAPO-5) present high activity and selectivity for the ODH of propane [9] but they show a low selectivity for the ammoxidation of propane [10] or the oxidation of toluene [11]. The best catalytic properties for the ODH of propane on vanadium substituting molecular sieve have been related to the presence of isolated tetrahedral V⁵⁺ species in the framework of the molecular sieve [9,12]. In this way, amorphous aluminophosphate-supported vanadium catalysts have been also studied, and they show interesting catalytic properties for the ODH of propane [13,14] although the selectivity to propene on these catalysts is lower than on VAPO-5.

VAPO-5 and ALPO₄-5 supported vanadium catalysts have also been studied for the catalytic dehydrogenation of ethylbenzene in absence of molecular oxygen [15–17]. Although the vanadium species on both catalytic systems show a similar activity for the ethylbenzene conversion, the benzene/styrene ratio obtained on VAPO-5 is lower than on ALPO₄-5 supported vanadium catalysts [16,17].

From these results it appears that the main goal to be achieved is to find among the different vanadium species, the ones that are responsible for the selective oxidative dehydrogenation of propane.

In this paper, we present the preparation and the characterization of VAPO-5, V₂O₅/MgO (V/MgO) and V₂O₅/ALPO₄-5 (V/AP) catalysts and their catalytic properties for the oxidative dehydrogenation of propane.

From the comparison between the vanadium species present on each catalyst and their catalytic behaviour, the nature of selective sites for the oxidative dehydrogenation of propane is proposed.

2. Experimental

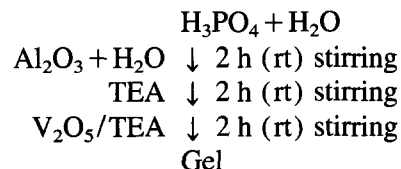
2.1. Catalyst preparation

Pure ALPO₄-5 and VAPO-5 were synthesized hydrothermally from gels with the following molar composition:



with $x=0$ (ALPO₄-5) or 0.117 (VAPO-5).

26 g of orthophosphoric acid (Riedel, 85 wt%) was mixed with 13.5 g of pseudoboehmite (Vista, 70 wt% Al₂O₃) and 60 g of water. After 2 h, 15 g of triethylamine, TEA, (Aldrich, 99 wt%) was added. Finally, a solution of 2.4 g of V₂O₅ (Merck, pro analisis), 5 g of triethylamine and 20 g of water was also added according to the synthesis procedure as follows:



(rt) = room temperature

The reaction mixture obtained was introduced in 60 ml PTFE-lined stainless steel autoclaves and heated at 200°C for 16 h. After this, the autoclaves were quenched in cool water, centrifuged at 10 000 rpm, washed and dried at 80°C. The solid products were calcined in air at 550°C for 8 h, and they are referred as VAPO-5 (with vanadium) or ALPO₄-5 (without vanadium) samples.

ALPO₄-5 supported vanadium catalysts were prepared by a 'wet' impregnation method using an aqueous vanadyl oxalate solution (V₂O₅/oxalic acid molar ratio of 1:3) [8]. The impregnated samples were dried at 80°C and 27 kPa. Finally they were calcined in air at 550°C for 3 h. They are referred as V/AP catalysts.

MgO ($S_{\text{BET}} = 141 \text{ m}^2 \text{ g}^{-1}$) was obtained from magnesium oxalate by calcination at 600°C for 3 h [5]. MgO-supported vanadium sample was prepared with an aqueous ammonium metavanadate solution, according to the preparation procedure described previously [1]. The sample was dried at 80°C overnight and further calcined in air at 550°C for 8 h. It is referred as V/MgO.

The chemical composition and surface area of VAPO-5, as well as of V/AP and V/MgO catalysts, are given in Table 1.

2.2. Characterization

Chemical analysis of Mg, Al and V were done by atomic adsorption, while P was determined by a colorimetric method using the complex formed between phosphorus and molybdovanadic acid [18].

X-ray diffraction (XRD) was performed on a Philips 1060 diffractometer provided with graphite monochromator employing nickel-filtered Cu K α radiation ($\lambda = 0.1542 \text{ nm}$). The crystallinity of VAPO-5 or V/AP samples was determined by measuring the intensity of the characteristic peaks of AFI (ALPO₄-5) structure, appearing at $2\theta \approx 19.8^\circ$, 21.1° and 22.4° , and comparing them with the pure ALPO₄-5.

The infrared spectra were recorded at room temperature on a Nicolet 710 FT-IR spectrometer

with a resolution of 2 cm^{-1} and 1024 scans were averaged. 20 mg of dried samples was mixed with 100 mg of dry KBr and pressed into a disk (600 kg/cm^2).

TPR results were obtained in a Micromeritics apparatus. Samples of 100 mg (VAPO-5 and V/AP samples) and 20 mg (V/MgO sample) were first treated in argon at room temperature during 1 h. The samples were subsequently contacted with a H₂/Ar mixture (molar ratio of 0.15 and a total flow of 50 ml min^{-1}) and heated, at a rate of $10^\circ\text{C min}^{-1}$, to a final temperature of 1000°C.

Diffuse reflectance (DR) spectra in the UV-Visible region (190–800 nm) were collected with a Shimadzu UV-2010 PC spectrophotometer equipped with a reflectance attachment. The samples were pressed into a disk (600 kg/cm^2). In order to study the nature of vanadium species, different reference compounds, i.e., vanadyl acetylacetonate, V₂O₅, and NH₄VO₃ commercial products, were used [8].

2.3. Catalytic test

The catalytic test for the oxidative dehydrogenation (ODH) of propane were carried out in a fixed bed quartz tubular reactor (16 mm i.d. 500 mm length) equipped with a coaxial thermocouple for temperature profiling, operating at atmospheric pressure.

Catalyst samples 0.5 to 1.7 g (particle sizes 0.25–0.42 mm) were mixed with variable amounts of SiC (0.59 mm particle size) to keep a constant volume in the catalyst bed (3 cm^3). The reaction temperature was varied between 450–540°C. A propane/oxygen/helium mixture, molar ratio of 4/8/88, was fed in all the experiments. The total flow was varied from 6 to 12 l h⁻¹ in order to obtain different contact times ($W/F = 20$ to $170 \text{ g}_{\text{cat}} \text{ h} (\text{mol}_{\text{C}_3})^{-1}$). Analysis of reactants and products were carried out by gas chromatography, using two columns: (i) Porapak Q ($3.0 \text{ m} \times 1/8 \text{ in.}$); (ii) 5A molecular sieve ($1.5 \text{ m} \times 1/8 \text{ in.}$).

Yield of product i (Y_i), conversion of propane (x_T , %) and selectivity to product i (S_i , %) were defined as follows:

$$Y_i = \frac{(\text{mol h}^{-1} \text{ formed of } i) (\text{C atoms of } i)}{(\text{mol h}^{-1} \text{ of fed propane} \times 3)} \times 100 (\text{mol}\%)$$

$$x_T = \sum Y_i$$

$$S_i = (Y_i/x_T) \times 100$$

The low conversion rates (in $\text{mol h}^{-1} \text{ g}^{-1}$) for the oxidative dehydrogenation of propane were obtained from the variation of the alkane conversion with the contact time (at an alkane conversion level < 10%).

Blank runs in the temperature interval 450–600°C were carried out replacing the catalyst by SiC, at the maximum contact time. In our reaction conditions the presence of homogeneous reaction can be neglected.

3. Results

3.1. Catalyst characterization

The vanadium content, the surface area and the crystalline phases obtained for each catalyst are shown in Table 1.

The V/MgO catalyst has less surface area than pure MgO. On the other hand, MgO in addition to $\text{Mg}_3\text{V}_2\text{O}_8$ (with a very low crystallinity) are the crystalline phases observed by XRD.

AFI (microporous aluminophosphate with an ALPO_4 -5 structure) was the only crystalline phase in VAPO-5 and 1V/AP samples. However, in the 2V/AP sample, the dense phase of a tridymite type (with characteristic peaks at $2\theta = 20.4$, 21.5 and 22.9) was also observed by XRD. The presence of ALPO_4 tridymite in $\text{V}_2\text{O}_5/\text{ALPO}_4$ -5, resulting from the collapse of the microporous ALPO_4 -5 structure, has also been observed by Whittington and Anderson [11].

On the other hand, the surface area and micropore volume of VAPO-5 are higher than the 2V/

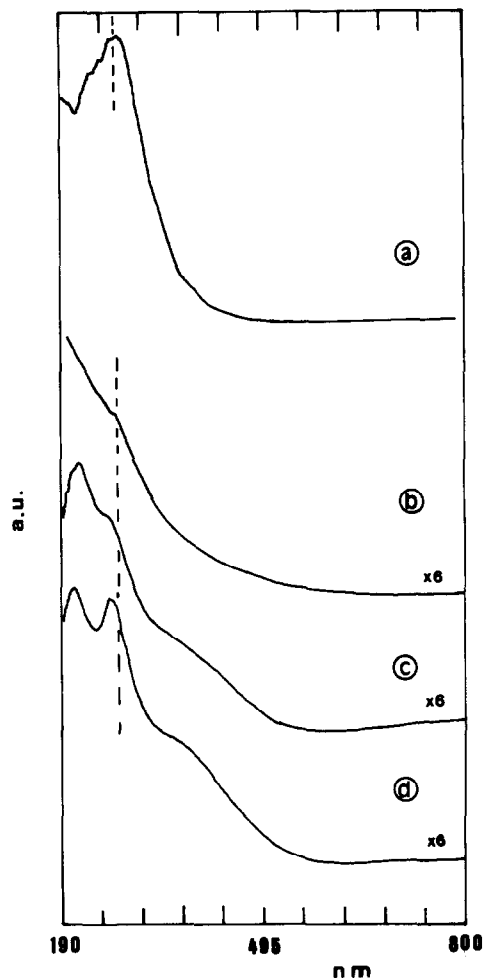


Fig. 1. DR spectra of V/MgO (a), VAPO-5 (b), 1V/AP (c) and 2V/AP (d) catalysts.

AP sample. The low micropore volume observed in the 2V/AP samples is due to the low crystallinity and the presence of a dense phase (without microporous structure).

The diffuse reflectance (DR) spectra in the UV–Vis region of catalysts are shown in Fig. 1. V/MgO (Fig. 1a) shows an absorption band at about 270 nm, indicating the presence of isolated VO_4 tetrahedron [8,19,20].

Since it has been observed [21] that VAPO-5 samples rapidly hydrate at room temperature (ca. 15% of total weight), modifying the coordination of vanadium, dehydrated VAPO-5 sample was used. DR spectra of VAPO-5 sample (Fig. 1b) shows a band at 270 nm, which can be assigned to tetrahedral V^{5+} species [15–17]. However, it

has been observed that, in VAPO-5, the amount of vanadium (V^{5+}) ions with a coordination higher than 4 increases when increasing the vanadium content [21]. For this reason, the existence of vanadium species other than tetrahedral V^{5+} , although in minor amounts, cannot be completely ruled out.

Spectra of $ALPO_4$ -5 supported vanadium, V/AP, samples (Fig. 1c and 1d) show the presence of both tetrahedral (band at 270 nm) and octahedral (broad band in the 350–450 nm region) V^{5+} species. In addition, it can also be seen that the higher the vanadium content the higher the presence of vanadium species with high coordination number is. From the presence of a band at 500 nm in the DR spectra of the 2V/AP sample it can also be concluded that V_2O_5 crystallites are present.

Infrared spectra of VAPO-5 and V/AP samples in the lattice vibration region are depicted in Fig. 2. The IR spectrum of the V/MgO sample [5] shows an intense band at 860 cm^{-1} , in addition to bands at 690 and 916 cm^{-1} , which indicates the presence of $Mg_3V_2O_8$.

The IR spectrum of calcined $ALPO_4$ -5 (Fig. 2a) shows the presence of bands at 1122, 712, 620 and 480 cm^{-1} . This spectrum is similar to that obtained for the as-synthesized $ALPO_4$ -5. The bands between $1000\text{--}1200\text{ cm}^{-1}$ are assigned to the asymmetric stretching of PO_4^{3-} tetrahedra, while the bands at 712 and 459 cm^{-1} are attributed to symmetric stretching and to P–O bending, respectively [14,22,23]. The absorption band in the region $500\text{--}650\text{ cm}^{-1}$ has been assigned to vibration in the double ring region.

In addition to the above bands, new bands in the region $800\text{--}1030\text{ cm}^{-1}$ are observed for the vanadium containing samples. For the VAPO-5 sample, a new band at 836 cm^{-1} is observed (Fig. 2b). Tetrahedral V^{5+} species in V_2O_5 /MgO samples is characterized by the presence of an intense band at 860 cm^{-1} , in addition to bands at 690 and 916 cm^{-1} [5,24]. However, it has been observed that the band at 860 cm^{-1} shifts to 849 cm^{-1} when the catalyst vanadium content decreases [24]. For this reason, and in agreement with DR results, the

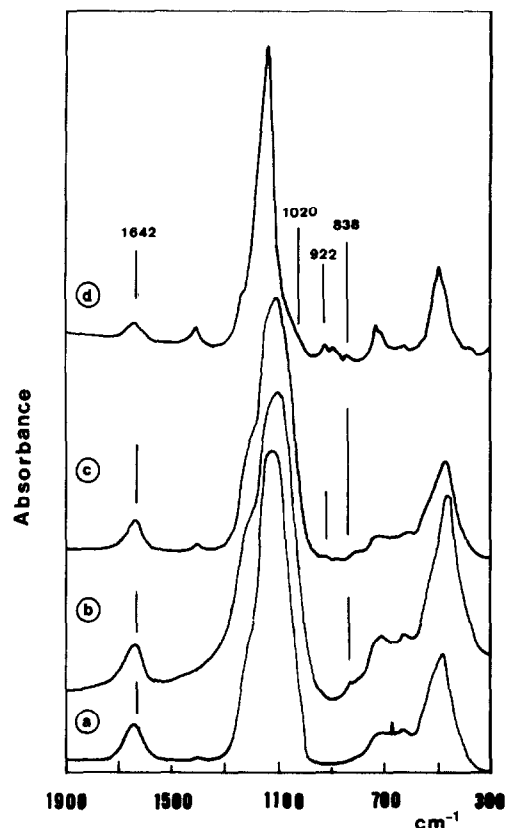


Fig. 2. IR spectra of $ALPO_4$ -5 (a), VAPO-5 (b), 1V/AP (c) and 2V/AP (d) samples.

band at 836 cm^{-1} can tentatively be assigned to isolated tetrahedral V^{5+} species.

In addition to this, new bands at 888 and 922 cm^{-1} , intensities of which increase with the vanadium loading, are observed in the V_2O_5 /AP samples. In the case of the 2V/AP sample (Fig. 2d), the band at 1029 cm^{-1} indicates the presence of crystalline V_2O_5 [25].

The assignment of bands at 888 and 922 cm^{-1} is still under discussion. An intense band at 885 cm^{-1} , in addition to bands at 678, 557 cm^{-1} , is assigned to Mg–metavanadate (with isolated octahedral vanadium species) [24]. On the other hand, a band at $923\text{--}929\text{ cm}^{-1}$ has been related to the presence of $V=O$ species adsorbed on basic sites [15] or highly dispersed vanadyl species in aluminophosphate-supported vanadium catalysts [13]. However, a band at 960 cm^{-1} is observed in vanadium silicates with a ZSM-48 structure, which is assigned to isolated V^{5+} ions in a nearly

symmetrical tetrahedral environment in the framework [26], while the corresponding band is observed at 950 cm^{-1} in AlVO_4 [27].

It has been suggested that the nature of the support can influence the coordination number of vanadium species [28]. In this way, it has been proposed that different vanadium species could appear at the same wavenumber depending on the nature of the support.

According to DR results, it can be proposed that isolated and associated (tetrahedral and/or octahedral) vanadium species are present on V/AP samples. For this reason, the IR band at 888 and 923 cm^{-1} can be related to the presence of isolated and polymeric vanadium species with a coordination number higher than 4. In addition, the intensities of these bands increase with the vanadium loading, and crystalline V_2O_5 is also observed on the 2V/AP sample.

Temperature programmed reduction (TPR) patterns are shown in Fig. 3. The H_2 -TPR pattern obtained from the MgO-supported vanadium sample shows two peaks for H_2 consumption. The maximum of each peak appears at 375 and 575°C . According to previously reported data, these peaks have been related to the presence of two types of V^{5+} species [7,29]. The H_2 consumption of these peaks corresponds to the hypothetical reduction, $\text{V}^{5+} \rightarrow \text{V}^{3+}$, in accordance with previously reported data for V/MgO catalysts [29]. In addition, from the comparison of the H_2 consumption related to each peak, and considering the reduction, $\text{V}^{5+} \rightarrow \text{V}^{3+}$, as total it can be concluded that the vanadium amount associated with the first peak corresponds to about 10% of the total vanadium, i.e., 1.07×10^{20} V-atoms $\text{g}_{\text{cat}}^{-1}$.

VAPO-5 and 1V/AP samples show two peaks for the hydrogen consumption. The maximum of the first peak appears at about 470 and 490°C , respectively. However, we must indicate that the H_2 consumption associated with the first reduction step corresponds to about fifty per cent of the hypothetical hydrogen for a total reduction of V^{5+} to V^{3+} . Then, as it has been proposed for V-silicalite [30], this peak should correspond to a $\text{V}^{5+} \rightarrow \text{V}^{4+}$ reduction. In fact, we must indicate

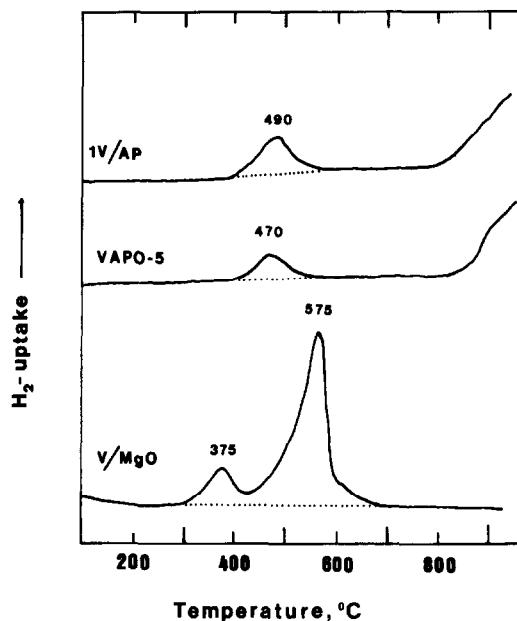


Fig. 3. H_2 -TPR patterns of V/MgO, VAPO-5 and 1V/AP samples.

that a high stability of V^{4+} species in a $\text{AlPO}_4\text{-5}$ framework has been proposed by several authors [10,11,15,16].

At temperatures higher than 850°C , the reduction from V^{4+} to V^{3+} occurs in both VAPO-5 and V/AP samples. This reduction may be associated with the formation of reducible compounds during the thermal decomposition of the molecular sieve, as it has been observed in other MeAPO-5 [31].

3.2. Oxidative dehydrogenation of propane

The catalytic results obtained during the oxidative dehydrogenation of propane on VAPO-5, 2V/AP and V/MgO samples are shown in Fig. 4. Propene, CO and CO_2 were the main products. Oxygenated products other than carbon oxides were not detected. Ethane and methane were only observed, as traces, at high reaction temperature and high conversion levels of propane.

The catalytic activity (and the relative activity), per gram of catalyst, for the conversion of propane of both the supports and the catalysts are shown in Table 2. From these results it can be concluded that the propane conversion is higher on the V/MgO catalyst than on VAPO-5 or V/AP samples. In addition, pure $\text{AlPO}_4\text{-5}$ shows a very

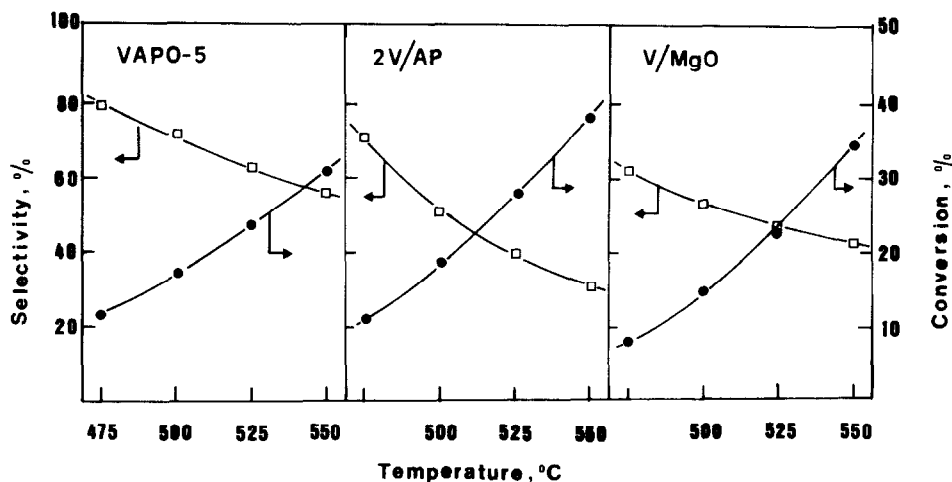


Fig. 4. Variation of the propane conversion (●) and the selectivity to propene (□) with the reaction temperature during the oxydehydrogenation of propane on VAPO-5, 2V/AP and V/MgO catalysts. Contact time, W/F in $\text{g}_{\text{cat}} \text{h} (\text{mol}_{\text{C}_3})^{-1}$, of 90 (VAPO-5), 80 (2V/AP) and 23 (V/MgO).

low activity respect to VAPO-5 or V/AP samples. For this reason it can be concluded that the catalytic activity of vanadium containing samples is related to the presence of vanadium species.

On the other hand, MgO is relatively active but non-selective for the ODH of propane when compared to the V/MgO sample. From the XPS results of MgO-supported vanadium catalysts [5] it has been proposed that vanadium-free Mg sites are present on the catalyst surface, due to the fact that vanadium is partially incorporated into the support. For this reason, the influence of Mg sites (vanadium-free) on the catalytic properties of V/MgO catalysts must be considered, as will be discussed later.

From the results of Fig. 4 it can be seen that the selectivity to propene decreases when increasing the reaction temperature, but, this effect is only a consequence of the variation of the propane conversion. In addition, it can be concluded that the selectivity to propene decreases in the order VAPO-5 > V/AP > V/MgO.

Fig. 5 shows the variation of the selectivities to propene, CO and CO₂ with the propane conversion level of the three catalysts (VAPO-5; 1V/AP and V/MgO samples). In all the range of the propane conversion studied the higher selectivity to propene is obtained on the VAPO-5 sample, while the lower selectivity to propene is obtained on the V/MgO (at low conversion of propane) or

Table 2
Catalytic activity for the oxidative dehydrogenation of propane of supports and catalysts

Sample	W/F	Temperature (°C)	Conversion (%)	Catalytic activity ($\text{mol h}^{-1} \text{g}^{-1}$)	Relative activity ^a	Relative turnover
ALPO ₄ -5	164	500	0.09	5.49×10^{-6}	3×10^{-3}	
VAPO-5	90	500	18.5	2.06×10^{-3}	1.3	
	90	475	8.4	0.93×10^{-3}		5.55
1V/AP	160	500	13.1	0.82×10^{-3}	0.5	
	160	475	7.6	0.47×10^{-3}		1.5
2V/AP	80	500	19.1	2.38×10^{-3}	1.5	
	80	475	12.2	1.52×10^{-3}		1.94
MgO	47	500	7.5	1.60×10^{-3}	1	
V/MgO	23	500	14.5	6.30×10^{-3}	3.9	
	23	475	8.7	3.78×10^{-3}		1.0

^a The relative activity is determined from the catalytic activity and comparing with that of MgO.

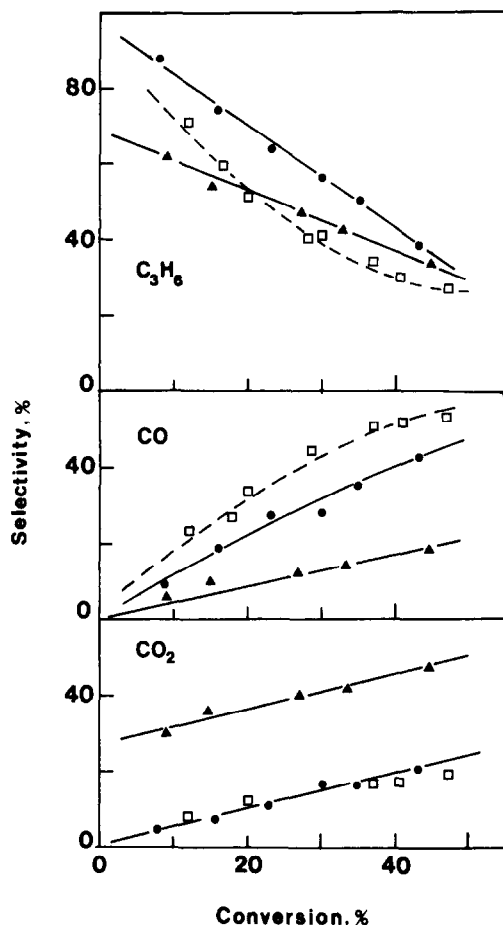


Fig. 5. Variation of the selectivities to propene, CO and CO₂ with the conversion of propane on VAPO-5 (●), 2V/AP (□) and V/MgO (▲) catalysts. Experimental conditions: reaction temperature = 540°C; propane/oxygen/helium molar ratio of 4/8/88.

on the V/AP (at high conversion of propane) catalysts. In addition to this, it can be noticed that on V/MgO sample a CO/CO₂ ratio lower than 1 is observed, while on VAPO-5 and V/AP catalysts CO/CO₂ ratios higher than 1 are obtained.

In Table 3 are shown the selectivities to propene, CO and CO₂ obtained at low ($X_T = 10\%$) and high ($x_T = 45\%$) propane conversion. In addition, the variations of the selectivities (ΔS_i) to the main reaction products have also been included.

From the results obtained at low conversion, it can be concluded that propene is a primary product while CO practically is not formed. On the other hand, CO₂ appears as primary product only when the reaction is carried out on V/MgO or MgO.

The selectivity to propene decreases (unstable product) and the selectivities to CO and CO₂ increase (secondary products) when increasing the conversion of propane. Moreover, a similar variation for the selectivity to CO₂ (ΔS_{CO_2}) with the conversion of propane is obtained on the three catalysts. However, the higher the degradation of propene the higher is the formation of CO.

4. Discussion

4.1. Catalytic activity of vanadium species

According to previously reported data of vanadium based catalysts a correlation between the reducibility of active sites and the catalytic activity for oxidation reactions is generally observed [32,33]. In our case, the TPR results indicate that the reducibility of vanadium species decrease in the following trend: V/MgO (first type of V species) > VAPO-5 > V/AP > V/MgO (second type of V species). However, although the catalytic activity per gram of catalyst shows a similar trend to that above, the catalytic activity per vanadium atom decreases in the order: VAPO-5 > V/AP > V/MgO. This could indicate that a parallelism between catalytic activity and reducibility is not observed.

However, some considerations about the type of vanadium species must be indicated. XPS

Table 3
Selectivities to the main products for the oxidative dehydrogenation of propane on vanadium based catalysts

Sample	Selectivity (%) ($x_T = 10$)			Selectivity (%) ($x_T = 45\%$) ^a		
	C ₃ H ₆	CO	CO ₂	C ₃ H ₆	CO	CO ₂
V/MgO	66	3	31	32 (-34)	20 (+17)	48 (+17)
2V/AP	86	11	3	25 (-61)	55 (+44)	20 (+17)
VAPO-5	91	6	3	35 (-56)	45 (+39)	20 (+17)
MgO	19	9	72			

^a Variation of selectivities to each product is given in parenthesis.

results of V/MgO catalysts have shown that only a portion of the vanadium atoms are present on the surface of the support [5] and a Mg/V surface atomic ratio of 10–20 is found. In this way, and taking into account the relative activity of Mg sites observed on pure MgO (Table 2), the participation of Mg sites, free of vanadium, on the surface of the V/MgO catalyst cannot be ruled out. For this reason, three type of active sites have been considered in the V/MgO sample: (i) Easily reducible surface vanadium species, (ii) vanadium species in a crystalline $\text{Mg}_3\text{V}_2\text{O}_8$ (of low reducibility), and (iii) Mg sites, free of vanadium, on the surface of catalyst. The last active site is only related to hydrocarbon combustion.

Accordingly, if only the most easily reducible vanadium species are considered as responsible for the catalytic activity of the V/MgO catalyst, a similar turnover than VAPO-5 is obtained.

On the other hand, and according to the TPR results, only one type of vanadium species is present in VAPO-5, which corresponds to tetrahedral V^{5+} species in the framework [9,11,13,15–17]. In addition to this, polymeric vanadium species (V_2O_5 is observed in the 2V/AP sample) are also formed on V/AP samples. These results are consistent with those of other authors [11,13].

Thus, from the characterization results it can be concluded that the number of effective vanadium species and the reducibility of vanadium on V/AP samples is lower than on VAPO-5.

4.2. On the nature of selective sites for the ODH of alkanes

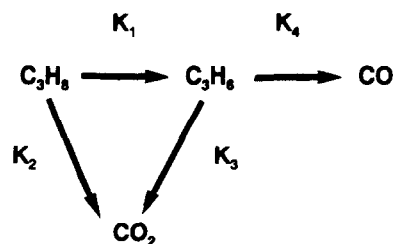
From our results, a network for the oxidative dehydrogenation of propane is proposed in Scheme 1, where K_1 , K_2 , K_3 and K_4 are kinetic constants. The initial selectivity to propene is related to the K_1/K_2 ratio while at high propane conversion level the selectivity to propene will be related to the $K_1/(K_2 + K_3 + K_4)$ ratio.

According to the results presented in Table 3 it can be concluded that the K_1/K_2 ratio in V/MgO is lower than in VAPO-5 or V/AP samples.

The importance of the presence of Mg sites, free of vanadium, on the surface of the catalyst on the catalytic properties of V/MgO catalyst must be considered. Taking into account the non-neglectable activity and the low selectivity to propene observed on pure MgO (Table 3), it can be proposed that Mg^{2+} sites on the catalyst surface of V/MgO can be responsible for the direct degradation of propane into CO_2 . In fact, the higher selectivity to CO_2 is obtained for the oxidation of propane on pure MgO. Moreover, it has been observed that on V/MgO catalysts the selectivity to propene increases and the selectivity to carbon dioxide decreases when increasing the vanadium content, showing the highest selectivity to propene on catalysts with vanadium content between 20–30 wt% of V_2O_5 [5]. However, we must indicate that the optimum vanadium content in selective V–Mg–O catalysts can change depending on the preparation procedure, as a consequence of changes in the V/Mg ratio on the catalyst surface.

For VAPO-5 and V/AP catalysts the direct formation of carbon oxides from propane is very low. In these catalysts, vanadium species are the only active and selective sites for the transformation of propane to propene. This is due to the very low activity of pure ALPO_4 -5.

At high conversion levels of propane, the behaviour of V/MgO and VAPO-5 and V/AP catalysts is different. Thus, the selectivity to propene decreases and the selectivity to CO increases in accord with the follow trend: $2\text{V}/\text{AP} > \text{VAPO-5} > \text{V}/\text{MgO}$. It has been previously proposed that isolated tetrahedral vanadium species show a selectivity to propene that is higher than that of octahedral (isolated or associated) vanadium spe-



Scheme 1. Reaction network for the oxidative dehydrogenation of propane.

cies [10,34]. This can explain why V/AP catalysts, which possess both octahedral and tetrahedral vanadium species (V_2O_5 is detected on the 2V/AP sample by IR) show a degradation of propene higher than that of VAPO-5 or V/MgO catalysts, which possess mainly tetrahedral VO_4 species.

In conclusion, VAPO-5, V/AP and V/MgO have been prepared and characterized and their catalytic properties for the ODH of propane have been studied. These catalysts are active and selective for the ODH of propane. However, the catalytic behaviour of each catalyst can be explained on the basis of both the nature of the vanadium species and the reactivity of support. In this way, the best catalytic properties of VAPO-5 are related to the presence of isolated tetrahedral V^{5+} species in the framework of a molecular sieve which has, in absence of vanadium, very low activity.

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