

RESEARCH NOTE

Nature of Vanadium Sites in V/ α -Ti Phosphate Catalysts for the Oxidative Dehydrogenation of EthaneJ. Santamaría-González,* M. Martínez-Lara,* M. A. Bañares,† M. V. Martínez-Huerta,†
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INTRODUCTION

The selective conversion of ethane into ethylene is currently being studied because of the economic impact of using natural gas and LPG's raw materials to produce chemicals and polymers (1). The available technology for the production of ethylene is the steam cracking of ethane, although it is a highly energy-intensive process. Several approaches to this problem have been considered, although ethane dehydrogenation (ODH) remains prominent. The principal reason for this lies in the fact that dehydrogenation in the presence of oxygen is thermodynamically favored and coking side reactions are minimized.

The selective oxidation of ethane to ethylene is rather limited due to the much lower stability of the product as compared to ethane (2). Thus, an intense search for an efficient catalyst is necessary. Among the many oxide catalysts used for ODH of ethane, vanadium oxide is the most used due to the ability to tune its activity by using different supports and additives (3–5). The catalytic behavior of V₂O₅ is, in general, modified when it is deposited on metal oxide carriers where various vanadium oxide structures can be developed (6). For instance, Al₂O₃-supported V₂O₅ catalysts have been found to display specific vanadium environments which make the catalysts more selective for ODH of ethane than bulk V₂O₅ (5). High and stable ethylene yields seem to be characteristic of appropriate combinations of V₂O₅ with other metal oxides. This is the case of vanadia catalysts to which small amounts of phosphorus have deliberately been added (7).

The approach undertaken in the present work was somewhat different as the vanadium oxide was incorporated on a layered α -Ti phosphate substrate. Accordingly, the present note reports preliminary results in the performance for the

ODH reaction of ethane of a new family of vanadium-loaded α -Ti phosphate catalyst. Moreover, although these catalysts show modest activity with negligible production of CO₂, a second objective was to report data on the genesis of surface sites during on-stream operation.

EXPERIMENTAL

α -Ti phosphate was synthesized using a sol-gel method (8). Basically, a Ti(OCH(CH₃)₂)₄ solution in propanol was hydrolyzed with H₃PO₄ 1M in propanol. The resulting gel was redissolved in concentrated H₃PO₄ (85%) to obtain a molar ratio P/Ti equal to 10. After 5 h of stirring at 295 K, a white gel appeared which was stirred for 70 h at room temperature. The solid was recovered and repeatedly washed with distilled water by centrifugation, and finally air-dried at 333 K. Vanadium oxide was incorporated to α -Ti phosphate by chemical grafting of hydroxyl groups with VOCl₃ (9, 10). The procedure was as follows: a volume of VOCl₃ solution of concentration ranging from 0.004 M to 0.04 M in dry *n*-hexane was added to a suspension of α -Ti phosphate, dried previously at 473 K during 20 h, in dry *n*-hexane while stirred at room temperature for 24 h. After that, the suspensions were centrifuged, washed with *n*-hexane, and the solids air-dried at 333 K. The solids used in the catalytic reaction were previously calcined at 923 K for 4 h. The catalysts are referred to hereafter as *n*V/ α -TiP, where *n* denotes the wt% of V₂O₅. Crystalline phases of both α -Ti phosphate and vanadium-loaded Ti phosphate were studied by X-ray diffraction using a Philips PW1010 powder diffractometer provided with a graphite monochromator. Chemical and structural information of V/ α -Ti phosphate catalysts was obtained by X-ray photoelectron spectroscopy (XPS) using a PHI 5701 electron spectrometer (AlK α = 1486.6 eV). The spectra were decomposed with the least squares fitting routine provided by the manufacturer with a variable Gaussian/Lorentzian ratio and after subtraction of a linear

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background. The C 1s line at 284.8 was taken as an internal standard for binding energy measurements.

The Raman spectra were run with a single monochromator Renishaw system 1000 equipped with a cooled CCD detector (200 K) and a holographic Notch filter. The elastic scattering is filtered by the holographic Notch filter, and the Raman signal remains higher than when triple monochromator spectrometers are used. The samples were excited with the 514 nm Ar line in a *in-situ* treatment cell (Linkam, TS-1500) which allows temperature treatments under flowing gases, the spectral resolution is better than 2 cm^{-1} , and the spectra acquisition consisted of 5 accumulations of 60 s. Unless otherwise stated, the spectra were acquired at 773 K (reaction temperature) under flowing air for the dehydrated samples.

The partial oxidation of ethane was studied in a tubular quartz microreactor (4-mm ID) at nearly atmospheric pressure with no void volume to prevent the interference of homogeneous gas-phase reaction. The powder catalysts were pressed, crushed, and sieved in the particle size range of 0.125–0.250 mm. The catalyst loading in the reactor was in the range of 20–60 mg and the reaction feed consisted of $\text{O}_2 : \text{C}_2\text{H}_6 : \text{He} = 2 : 1 : 8$ mole ratio for a total flow in the range of 30–90 mL(STP)/min. The effluents of the reactor were analyzed by on-line gas chromatography (Hewlett-Packard 4900) equipped with TCD detector. The selectivity to the different products was calculated based on the number of carbon atoms converted to the different products.

RESULTS AND DISCUSSION

The adsorption isotherm of vanadium by α -Ti phosphate as a function of the VOCl_3 added is displayed in Fig. 1. Initially, the amount of vanadium incorporated is high in respect of the vanadium added to the solution, but at loading values higher than 50 mg V/g catalyst the adsorption isotherm reaches a plateau with the amount of vanadium taken up. This VOCl_3 is incorporated into α -Ti phosphate

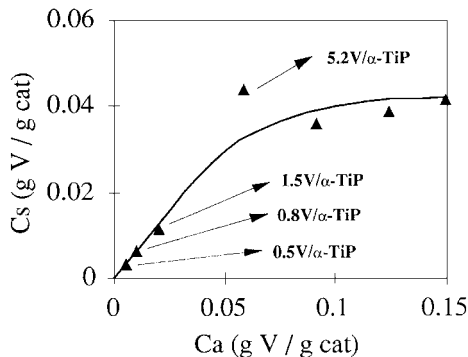


FIG. 1. Adsorption isotherm of vanadium on α -Ti phosphate. C_a is the amount of V added to the suspension per gram of dry substrate, and C_s is the amount of V incorporated per gram of dry support.

TABLE 1
Surface Properties of Catalyst Calcined at 923 K

Sample	%V ₂ O ₅ added (wt%)	S _{BET} (m ² g ⁻¹)	T _C (K) ^a	Ti/V (at. ratio) ^b	IO 1s _(531.6) /IO 1s _(533.3) (peak areas)
Lamellar TiP ₂ O ₇	0	—	1123	—	3.67
0.4V/ α -TiP	0.4	31	1122	29.9(130) ^c	3.71
0.8V/ α -TiP	0.8	31	1092	17.1(64.1) ^c	4.09
1.5V/ α -TiP	1.5	27	1059	8.3(37.2) ^c	4.4
5.2V/ α -TiP	5.2	23	1018	3.4(9.6) ^c	5.1

^a T_C temperature of cubic pyrophosphate formation.

^b From XPS analysis.

^c Values in parentheses are bulk ratios.

by the hydrolytic reaction with P-OH to produce P-O-V linkages and releasing HCl.

The XRD patterns of synthesized α -Ti phosphate showed a low crystallinity, although there were clearly observable diffraction lines at 7.6, 4.2, and 3.4 Å assigned to (001), (111), and (202) reflections (11). Calcination of α -Ti phosphate at 1173 K gives rise to highly crystalline TiP₂O₇ (12). XRD patterns of V-loaded α -Ti phosphate are coincident with those of pure α -Ti phosphate. The intercalation of the vanadium moieties in the interlayer space can be discarded since no increment in the basal spacing is observed. Consequently, the hydrolysis reaction must take place essentially with P-OH located on the edges of the crystallites. This agrees well with the limited amount of VOCl_3 which reacts with α -Ti phosphate. Furthermore, the composition of superficial (from XPS analysis) and bulk Ti/V atomic ratios (Table 1) indicate that vanadium is mainly located on the external surface of the phosphate. Possibly, the VOCl_3 molecules are totally or partially hydrolyzed by POH groups located on the edges of neighboring layers; thus, the vanadyl moiety acts as bridge. This connectivity between layers could explain the decrease of temperature of formation of the cubic pyrophosphate, which appears at 1123 K for the pure α -Ti phosphate and diminishes to values as low as 1018 K in samples with loading higher than 40 mg V/g catalyst.

The O 1s core-level spectra of α -Ti phosphate heated at 473 K can be deconvoluted into two components: the more intense one at 531.2 eV can be assigned to PO₃ oxygen species; the weak peak at 532.8 can be ascribed to POH groups (13). The relative intensity of these two components is 2.9 and agrees very well with the expected value (3.0). When α -Ti phosphate and V/ α -Ti phosphate are heated at 873 K, the formation of lamellar pyrophosphate occurs, with P-O-P bridges appearing between the layers. The O 1s profile for lamellar pyrophosphate can also be deconvoluted into two components at 531.6 eV and 533.3 eV, the latter being assigned to oxygen bridging the layers in the lamellar pyrophosphate. For vanadium-doped α -TiP samples,

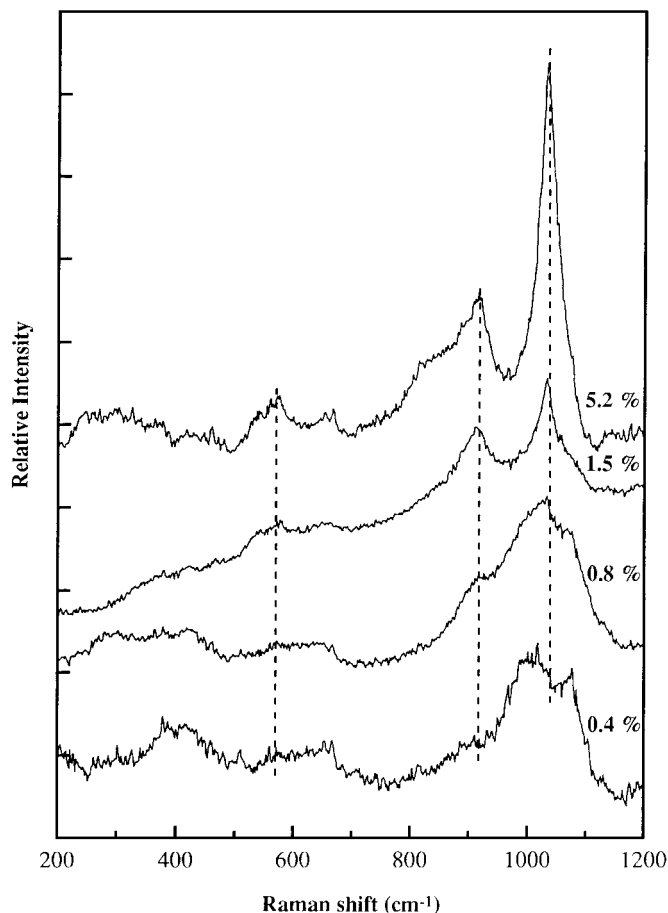


FIG. 2. Raman spectra of fresh V/ α -Ti phosphate catalysts at 773 K after subtraction of the spectrum of α -Ti phosphate support at 773 K.

calcined at 873 K, the atomic ratio of both types of oxygen, $O_{531.6}/O_{533.3}$ (Table 1), increased with the incorporation of cross-linking vanadyl moieties as a consequence of the substitution of P-O-P bridge by vanadyl bridges. It confirms the assigned location of these groups on the edges of crystallites. From the XPS intensity ratios and published sensitivity factors (14), the atomic ratios Ti/V have been calculated which decreased up to 40 mg V/g catalyst.

The Raman spectrum of the α -Ti phosphate support under dehydrated conditions presents bands at 284, 426, 520, 618, and 1030 cm^{-1} (Fig. 2). In order to avoid the contribution of the bands of the substrate of the whole spectrum, subtraction of the background spectrum of the α -Ti phosphate was done in all the spectra. As the V-loading increases, two weak features near 919 and 1031 cm^{-1} become evident. The Raman band at 1030 cm^{-1} , which is characteristic of surface isolated vanadium oxide species, has been previously observed on V/TiO₂ catalysts (15). The band near 921 cm^{-1} is assigned to P-O-P bonds (16). The net spectra for the 0.4 and 0.8 V/ α -Ti phosphate display bands near 536, 571, and a broad band in the 800–1200 cm^{-1} region which can be deconvoluted into contributions from 906,

1020, and 1079 cm^{-1} (Gaussian + Lorentzian). Although bands at 1079 and 892 cm^{-1} are expected for a β -VOPO₄ structure, the observed bands do not match with any well-defined VPO phase (15–17); however some interaction between V and P would be developed. It is inferred that a mixture of surface vanadium oxide species and some type of V-P interacting phase dominate at this loadings. At higher loading (1.5 V/ α -TiP and 5.2 V/ α -TiP), the Raman bands observed near 540, 570, 919, and 1031 cm^{-1} resemble those reported for the α_1 -VOPO₄ phase at 541(s), 579(s), 928(vs), and 1038(s) cm^{-1} (17). However, the presence of some surface-isolated V oxide species, along with VPO, cannot be excluded since those exhibit a Raman band at 1031 cm^{-1} . This may explain why the Raman band near 1038 cm^{-1} is more intense than that at 928 cm^{-1} . Deo and Wachs reported that the addition of V on a P-containing titania substrate did not form VPO compounds upon calcination and that V remained as a surface interacting species (15); however, this work uses a different substrate.

The Raman spectra of fresh and used 1.5 V/ α -Ti phosphate under dehydrated conditions are presented in the Fig. 3.

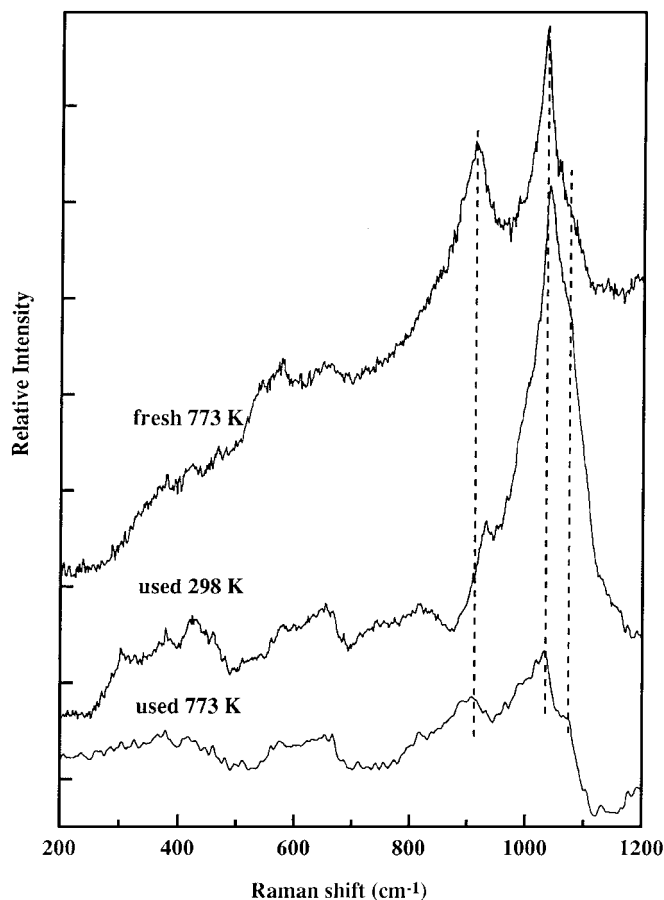


FIG. 3. Raman spectra of dehydrated 1.5 V/ α -Ti phosphate: fresh dehydrated, 773 K; used, dehydrated, 298 K; and used, dehydrated, 773 K. All of them are plotted after subtraction of the spectrum of α -Ti phosphate support at 773 K.

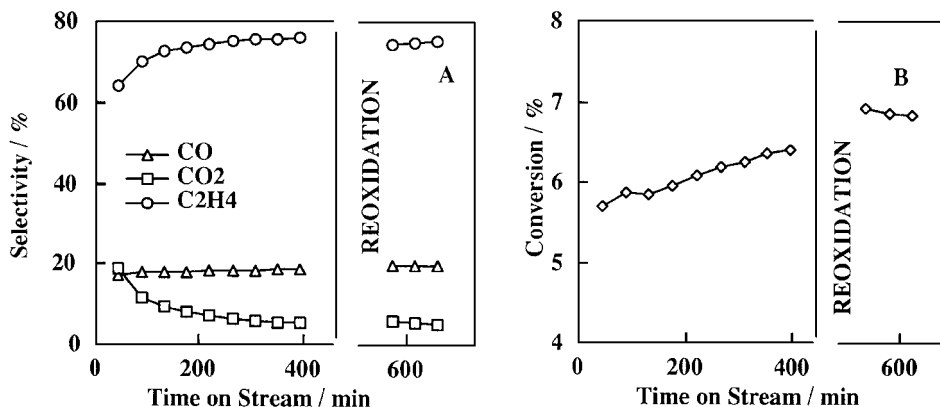


FIG. 4. (A) Selectivity of ethylene (circles), of carbon monoxide (triangles) and of carbon dioxide (squares). (B) Activity of 1.5 V/ α -Ti phosphate during time on stream. Reaction conditions: catalyst loading was 60 mg, total flow was of 30 mL/min with a O₂ : C₂H₆ : He = 6 : 1 : 8 mole ratio. Temperature range 723–863 K.

The fresh catalyst shows the intense bands near 919 and 1031 cm⁻¹ already mentioned. However, the spectrum at room temperature of the dehydrated used catalyst displays a band at 577 cm⁻¹, a broad feature 653 cm⁻¹, and sharper bands near 931 and 1038 cm⁻¹, which do correspond with those characteristic of α_1 -VOPO₄ phase (17). The shoulder near 1070 cm⁻¹ and the feature near 432 cm⁻¹ could be due to some contribution of the β -VOPO₄ phase (17). The spectra of the used catalyst (reaction temperature, 773 K) displays Raman features near 430, 892, 986, and 1070 cm⁻¹ which correspond to that reported for β -VOPO₄ at 435(s), 892(s), 986(vs), and 1075(s) cm⁻¹. The band at 1032 cm⁻¹ evidences the coexistence of highly dispersed surface vanadium oxide species along with β -VOPO₄ phase.

The partial oxidation of ethane on the V/ α -Ti phosphate catalyst yields mainly ethylene, smaller amounts of CO, and negligible amounts of CO₂ after a transient period. Figure 4A shows the selectivity to CO, CO₂, and ethylene versus time-on-stream. The selectivity of ethylene increases at the expense of CO₂, whereas the CO selectivity remains unaltered. For periods on-stream of 400 min, the activity is continuously increasing (Fig. 4B), but it becomes stable and somewhat higher (ca 6.7% conversion) upon reoxidation of the catalyst. Similarly, no change in selectivity is observed after reoxidation. The reaction temperatures needed to reach 1% conversion of ethane at steady state are summarized in Table 2. This temperature decreases with increasing V-loading. However, the activity does not appear to directly correlate with V-loading; this may be due to the interaction of V with P species. The O₂ : ethane mole ratio from 6 : 1 to 2 : 1 has a negligible effect on the activity and selectivity. The selectivity versus conversion profiles for 1.5% V/ α -Ti phosphate are presented in Fig. 5. Selectivity to ethylene for all the V/ α -TiP catalysts is high, whereas that of CO is low. The selectivity of CO increases with conversion at the expense of ethylene. Interestingly, hardly any CO₂ is produced, which is attractive from the

point of view of separation of the ethylene. The selectivity at 1% ethane conversion at steady state is also included in Table 2. The catalysts with the lower V-loading present very high selectivity of ethylene (near 93%), while the catalyst with the highest V-loading, exhibits the lowest selectivity. The formation of surface VPO phases under reaction conditions, as suggested by transient activity experiments and Raman spectra of the fresh and used catalysts, appears to be directly related with the decrease in the production of CO₂.

Activity and characterization results strongly suggest that surface V and P species react under reaction conditions yielding VPO phases. This dynamic behaviour of VPO phases by interaction with the reactants agrees with previous observations by Hutchings *et al.* (18) during the *n*-butane oxidation on VPO catalyst. The results by *in situ* Raman spectroscopy reveal that the incorporated vanadium oxide interacts with the phosphate layer forming a α -VOPO₄ phase. The formation of this phase is associated to the transient activity period during which not only conversion increases but also selectivity to CO₂ remarkably decreases with the simultaneous increase of ethylene selectivity. Our proposal is that the new vanadyl phosphate is mainly developed during on-stream reaction but to a small

TABLE 2

Behavior of V/ α -TiP Catalysts in Oxidation of Ethane

Catalyst	Temperature (K) (1% con. C ₂ H ₆)	Percentage of selectivity (1% Conversion C ₂ H ₆)		
		C ₂ H ₄	CO	CO ₂
0.4 V/ α -TiP	853	92.3	7.7	0.0
0.8 V/ α -TiP	811	93.4	6.6	0.0
1.5 V/ α -TiP	781	92.6	7.4	0.0
5.2 V/ α -TiP	784	84.9	15.1	0.0

Note. Total flow: 30 mL/min; W_{cat} = 30 mg; feed ratio C₂H₆ : O₂ : He = 1 : 2 : 8 mol.

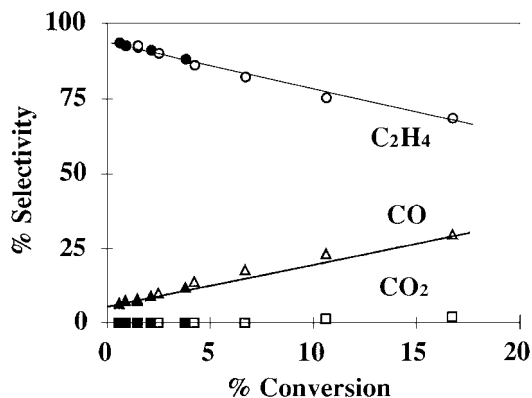


FIG. 5. Selectivity of ethylene (circles), of carbon monoxide (triangles), and of carbon dioxide (squares) with a catalyst loading of 30 mg (solid symbols) and 60 mg (open symbols). 1.5 V/ α -Ti phosphate catalyst, total flow was of 30 mL/min with a O₂:C₂H₆:He = 2:1:8 mole ratio.

extent under calcination conditions and that the new phase is more active and selective than dispersed V₂O₅ species on the carrier.

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