Vanadyl phosphate dihydrate supported on oxides for the catalytic conversion of ethane to ethylene

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Dedicated to Professor Renato Ugo on the occasion of his 65th birthday

Abstract

VOPO$_4 \cdot$2H$_2$O supported as a mono-layer on TiO$_2$, Al$_2$O$_3$ and SiO$_2$ and as a multi-layer on TiO$_2$ has been investigated for the oxidative dehydrogenation of ethane to ethylene in the temperature range 450–550 °C. The catalysts have been characterized with X-ray diffraction patterns (XRD), BET surface area measurements and electron paramagnetic resonance (EPR) and temperature programmed reduction (TPR) techniques comparing their properties to those of bulk VOPO$_4 \cdot$2H$_2$O. TiO$_2$ promotes the best dispersion of vanadyl phosphate for mono-layer catalysts, whereas the formation of VOPO$_4$ bulk-like particles has been detected for SiO$_2$ supported mono-layer catalyst or when the coverage far exceeds the mono-layer on TiO$_2$. A fraction of vanadium is present as V(IV) in all catalysts, probably as VO(H$_2$O)$^{2+}$–O–P species. Reducibility of vanadium phosphate is enhanced by deposition on supports in extent depending on the strength of the interaction support-active phase, TiO$_2$ mono-layer catalyst being the most reducible. The improvement of catalytic activity for supported catalysts has been related to the increase of both surface area and reducibility with respect to bulk VOPO$_4$. Ethylene selectivity increases with the temperature only for well dispersed samples due to a significant increase of V(IV) containing sites at 550 °C observed for these samples.
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1. Introduction

Several processes of partial oxidation of C$_2$–C$_4$ hydrocarbons to produce olefins or organic intermediates are successfully carried out on vanadyl phosphate based catalysts [1]. Although interesting yields have been obtained for some processes, as production of maleic anhydride from *n*-butane, for oxidative dehydrogenation of light alkanes high selectivity is achieved only at low alkane conversion, resulting in alkene productivity far from that required for industrial applications. This is also the case of bulk and TiO$_2$ supported (VO)$_2$P$_2$O$_7$ pyrophosphate, investigated as catalyst for the oxidative dehydrogenation of ethane [2] and propane [3]. The effect of supporting vanadium pyrophosphate on different oxides such as alumina, silica or titania has been investigated, TiO$_2$ promoting the best dispersion [4–6]. However, less attention has been addressed to other vanadium phosphate phases, such as dihydrate vanadyl phosphate VOPO$_4 \cdot$2H$_2$O [7–9].

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In this work, $VOPO_4 \cdot 2H_2O$ either as bulk or as supported phase has been studied as catalyst for ethane ODH. A comparative study of the effect of the vanadium phosphate interaction with three different supports (TiO_2, Al_2O_3, SiO_2) on the physico-chemical and catalytic properties of the materials has been reported reviewing the most remarkable results obtained trying to draw general conclusions on the dispersion of vanadyl phosphate on high surface area supports.

2. Experimental

2.1. Preparation of materials

The vanadyl phosphate dihydrate, $VOPO_4 \cdot 2H_2O$, thereinafter indicated as VOP, was prepared by refluxing for 16 h 10 g of V_2O_5 (Fluka puriss. Grade) in 300 ml of 3.3 mol dm^{-1} H_3PO_4 (Carlo Erba RPE, highest purity product) solution according to Ladwig's method [10].

The supported materials were prepared by impregnation method, where suitable amounts of VOP active phase (9.6, 14 and 14.6 wt.%, respectively) were contacted with high surface area TiO_2 (pure anatase phase, Tioxide Specialties, s.a. $= 125 \, m^2 \, g^{-1}$), γ-Al_2O_3 (AKZO CK-300, s.a. $= 190 \, m^2 \, g^{-1}$), SiO_2 (Sigma, s.a. $= 200 \, m^2 \, g^{-1}$) and drying at 80 °C. For the preparation of TiO_2 supported multilayer VOP 40 wt.% VOP was used.

All these catalyst precursors were afterward calcined at 550 °C for 3 h in air flow.

2.2. Physico-chemical analysis

Vanadium and phosphorus content of the catalyst precursors was determined by dissolving a 100 mg sample with 5 ml of concentrated sulphuric acid in a water boiling bath and diluting the resulting solution to 100 ml. Vanadium was determined by inductively coupled plasma emission spectroscopy (ICPES) technique with a Varian Liberty 150 Model at $\lambda = 309.311$ nm, while phosphorus was determined colorimetrically with a Perkin-Elmer 555 Model Spectrophotometer at $\lambda = 430$ nm, according to the method described in [11].

A Philips PW 1100 diffractometer was employed for obtaining X-ray diffraction patterns (XRD) of calcined samples at room temperature. Ni-filtered Cu Kα radiation was used and the 2θ measurements were accurate to 0.05°. BET surface areas were measured by N_2 adsorption at 77 K with a Quantachrom CHEM-BET 300 instrument.

The electron paramagnetic resonance (EPR) spectra were obtained at X-band frequency with a Varian E-9 spectrometer equipped with a standard Oxford instrument low-temperature attachment.

Temperature programmed reduction (TPR) with hydrogen were carried out using a Micromeritics TPD/TPR 2900 analyser equipped with a TC detector and coupled with a Hiden HPR 20 mass spectrometer reducing the sample with a 2% H_2/Ar mixture (25 cm^3 min^{-1}) and heating at 10 °C min^{-1} to 650 °C. The samples were treated in flowing air at 550 °C for 2 h before the experiment.

2.3. Catalytic tests

Catalytic activity tests were carried out with the experimental apparatus described in [12], equipped with a fixed bed quartz micro-reactor operating under atmospheric pressure. The reaction products were analysed with a Hewlett Packard series II 5890 gas-chromatograph equipped with a thermal conductivity detector for the analysis of O_2, CO and CO_2 and a flame ionization detector for the analysis of hydrocarbons. The concentrations of O_2, CO and CO_2 were also measured on line with a Hartmann & Braun URAS 10E continuous analyser. Water produced during the reactions was kept by a silica gel trap in order to avoid condensation in the cold part of the experimental apparatus. The feed composition was 4% C_2H_6 and 2% O_2 in a balance of He. The reaction temperatures were 450 or 550 °C. The contact time ranged from 0.006 to 0.12 g s N cm^{-3}. Carbon balance was closed within 3% error in all experiments.

3. Results and discussion

3.1. Physico-chemical analysis

The chemical composition of catalysts investigated is reported in Table 1 as VOP weight percentage of the catalyst precursor. VOP content corresponds to the theoretical mono-layer coverage, evaluated according

Table 1
VOP content, BET surface area, results of TPR experiments and rate of C_2H_6 consumption and C_2H_4 formation evaluated from the catalytic activity data

Catalysts	VOP content (wt.%)	Surface area[a] $(m^2 g^{-1})$	H_2 uptake ($\times 10^4$) (mol g^{-1})	V/H$_2$ (mol mol^{-1})	Reaction rate ($\times 10^6$)[b] (mol g^{-1} s^{-1})			
					450 °C		550 °C	
					C_2H_6	C_2H_4	C_2H_6	C_2H_4
VOP	100	<1	15.5	4.0	–	–	–	–
9VOP/Ti	9.6	125	4.3	1.4	1.7	1.2	16.2	11.3
40VOP/Ti	40.0	45	3.5	1.8	1.9	1.2	4.7	3.5
14VOP/Al	14.0	183	4.4	1.5	0.4	0.2	7.5	5.5
15VOP/Si	14.6	162	3.4	1.8	–	–	0.9	0.5

[a] Surface area of TiO_2, Al_2O_3 and SiO_2 are 125, 190 and 200 m^2 g^{-1}, respectively.
[b] Reaction rate of VOP at 450 and 550 °C and of 15VOP/Si at 450 °C has not be evaluated due to the very low activity.

to the surface area of the supports and the cell parameters of VOPO$_4$·2H$_2$O [13], for all supports except for 40VOP/Ti which has a VOP loading far exceeding that corresponding to the mono-layer.

The XRD patterns of the catalysts were recorded after thermal treatment of the precursors at 550 °C for 3 h. VOP shows typical signals of VOPO$_4$·2H$_2$O phase [14]. The supported catalysts revealed only signals of the corresponding supports except for 40VOP/Ti and 15 VOP/Si samples which showed the formation of bulk-like VOP structures (Fig. 1) hydrated [14] and anhydrous [15] thus suggesting that segregation of VOP phase occurs when loading exceeds mono-layer coverage or when the strong acid character of the support, as for SiO$_2$, inhibits a good dispersion of the active phase.

Values of surface areas of the catalysts are reported in Table 1. The 9VOP/Ti sample has the same value of TiO$_2$, indicating that this support promotes the best dispersion, whereas a slight reduction of the surface area with respect to that of the corresponding supports was observed for both Al$_2$O$_3$ and SiO$_2$ samples. The presence of VOP aggregates significantly decreases the surface area as observed for 40VOP/Ti catalyst.

The EPR spectra of bulk VOP and of the different supported VOP precursors show identical features
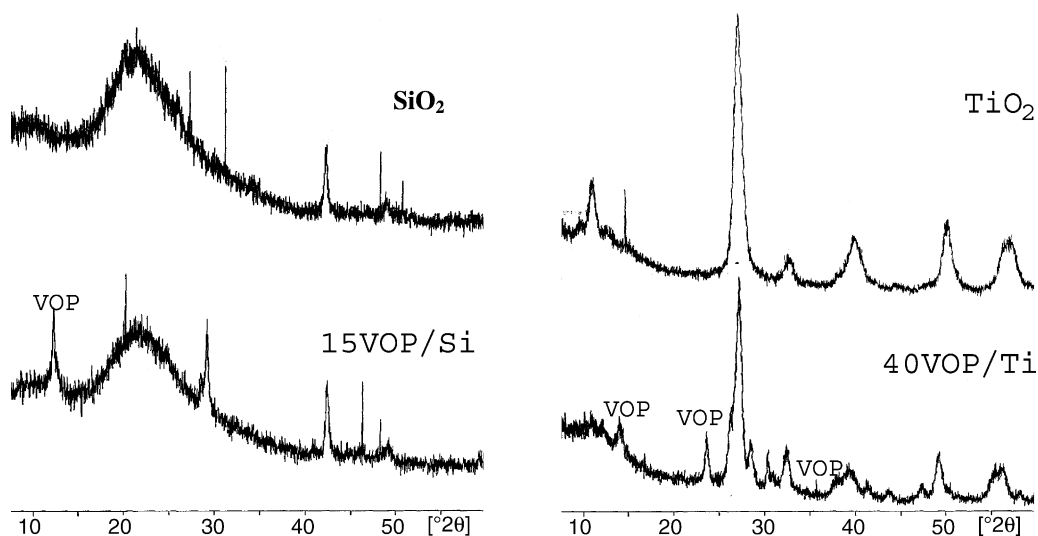

Fig. 1. XRD patterns of 15VOP/Si and 40VOP/Ti catalysts compared with those of the corresponding supports.
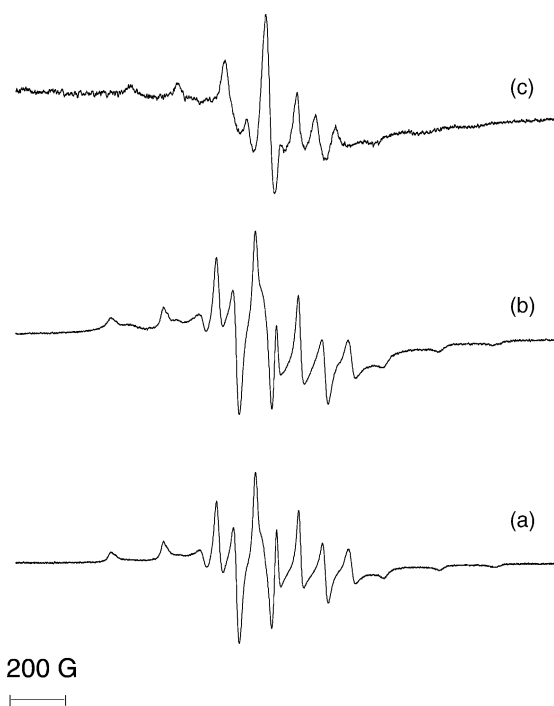
Fig. 2. EPR spectra of 9VOP/Ti: (a) at room temperature as precursor, (b) after air treatment at 550 °C followed by immediate sealing of the cell, (c) at room temperature after ODH reaction at 550 °C.

indicating the presence of vanadium (IV) in a fraction not less than 5% in all samples investigated. Spectrum of 9VOP/Ti precursor, chosen as representative, is reported in Fig. 2 (spectrum a). The signals are axially symmetric and exhibit a fairly good resolution, suggesting chemical equivalence and magnetic dilution of V^{4+}. The average magnetic parameters of the materials reported in Table 2 are almost superimposed to those reported for $VO(H_2O)_5^{2+}$ [16] thus suggesting that tetravalent vanadium should be likely present as a VO^{2+} hydrated species hexa-coordinated to both lat-

tice and water molecules oxygens. Furthermore, since the magnetic parameters are practically identical to those of 1–2% $V^{4+}/VOPO_4 \cdot 2H_2O$, the formation of a $VO(H_2O)^{2+}$–O–P species in the materials can be supposed [17].

When the precursor is heated at 550 °C water molecules are completely removed and the dehydrated solid (the catalyst) gives an EPR spectrum (spectrum b, Fig. 2) indicating a new magnetic VO^{2+} site. The new VO^{2+} species exhibits an axial hyperfine line and the EPR parameters reported in the last row of Table 2 as $g_{//}$, $g_{\perp}$ and $A_{\perp}$ are quite similar to those of the two above mentioned reference compounds confirming the octahedral geometry of the new vanadyl group. The lower value of $A_{//}$, that could be produced from the saturation of the sixth co-ordination of vanadyl species with the oxygen of TiO_2 support, should indicate a tetragonally distortion of the primary octahedral co-ordination.

After the catalytic experiment at 550 °C, the material has been left in air and a new EPR measurement has been done. Signals evidencing the presence of two V^{4+} sites corresponding to hydrated and anhydrous phases are clearly observed (spectrum c, Fig. 2). This result indicates not only that a reversible hydration process occurs, but also that a pyrophosphate phase is not produced during the catalytic reaction.

TPR profiles of VOP and supported catalysts are reported in Fig. 3. The H_2 uptake was totally ascribed to vanadium reduction since supports undergo a negligible reduction. Unsupported VOP is reduced at high temperature (peak value >650 °C), whereas its dispersion on support results in an easier reduction, as shown by the lower values of peak temperature. Also, the extent of reduction increases when VOP is supported as it can be inferred from the amount of H_2 uptake evaluated from the integration of the curves reported in Table 1. This could have been attributed to limited diffusion of H_2 across the VOP particle, however, TPR

Table 2
EPR parameters for some vanadium (IV)-containing species and for the 9VOP/Ti precursor and catalyst

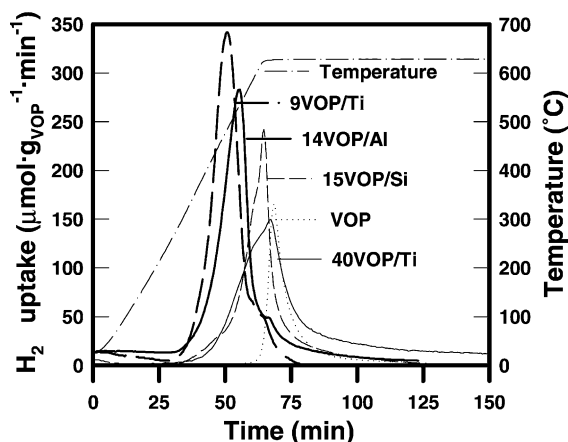| Species and catalysts	$g_{//}$	$g_{\perp}$	$A_{//}$ (cm^{-1})	$A_{\perp}$ (cm^{-1})
$VO(H_2O)_5^{2+}$ [16]	1.936	1.982	−0.0178	−0.0070
1–2% $V^{4+}/VOPO_4 \cdot 2H_2O$ [17]	1.935	1.977	−0.0175	−0.0063
9VOP/Ti (precursor)	1.932	1.975	−0.0175	−0.0076
9VOP/Ti (calc. 550 °C)	1.936	1.990	−0.0161	−0.0066

Fig. 3. TPR curves of bulk VOP and supported catalysts.

measurements carried out on bulk VOP with different particle dimension gave the same result of the first experiment suggesting that the reducibility of VOP has been intrinsically modified by interaction with the support. All supported catalysts show values of V/H_2 ratio ranging from 1 to 2 indicating an average oxidation state of vanadium in the calcined samples lower than $+5$ if $+3$ is the assumed oxidation state of vanadium after the TPR experiment. The possible presence of V^{4+} is in agreement with EPR analysis and with XPS results reported by Casaletto et al. [8] for Al_2O_3 supported VOP samples. The reducibility decreases for catalysts having a supposed worse dispersion suggesting that VOP aggregates have a redox behaviour close to that of bulk VOP as shown by both temperature and extent of reduction.

3.2. Catalytic activity tests

In all catalytic tests, only C_2H_4, CO and CO_2 were produced, no oxygenated compounds being detected in the reaction products. Moreover, O_2 conversion was always far from 100%. The catalytic activity of the supports is negligible if compared to that of the catalysts, moreover, unsupported VOP gave rise to a almost undetectable ethane conversion at $550\,^\circ C$. In Fig. 4, the conversion of C_2H_6 and the selectivity to C_2H_4, CO and CO_2 at $550\,^\circ C$ are reported for the two TiO_2 supported catalysts, chosen as representative, as a function of the contact time. For all catalysts, the C_2H_4 selectivity decreases and that to CO_x increases by increasing the contact time suggesting that C_2H_4 produced by C_2H_6 ODH is further oxidised to CO_x at high contact time. The same behaviour was observed at $450\,^\circ C$. In Table 1, the rate of ethane consumption and that of ethylene formation at 450 and $550\,^\circ C$, evaluated under differential conditions, are reported for all catalysts. The catalytic activity is dramatically enhanced when VOP is supported (more than two order of magnitude), much more than that expected due to the enhanced surface area suggesting that the
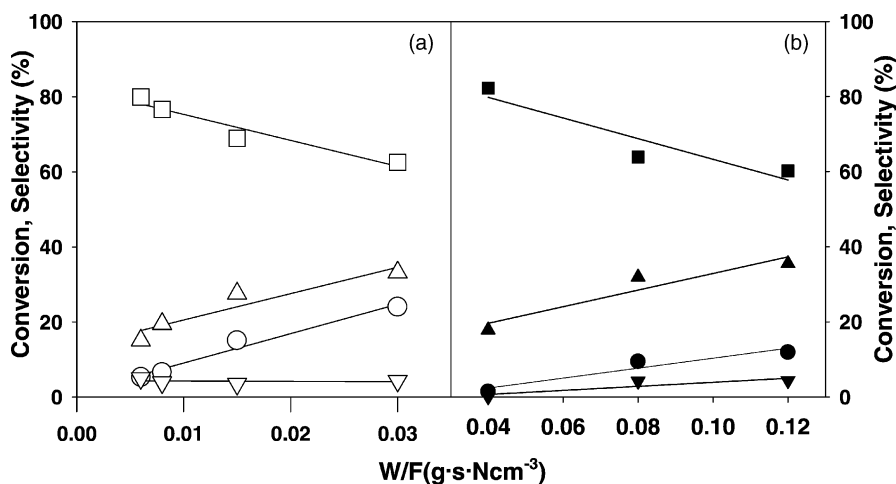

Fig. 4. C_2H_6 (circles) conversion and selectivity to C_2H_4 (squares), CO (up-triangles), CO_2 (down-triangles) as a function of contact time at $550\,^\circ C$ for 9VOP/Ti (a) and 40VOP/Ti (b).

interaction between VOP and the support results in a deep modification of the catalytic properties. Moreover, the nature of the support markedly affects the specific activity of VOP phase as evidenced by the different values of reaction rate, especially at 550 °C, obtained for catalysts with different supports not attributable to the different amount of VOP present in the sample. The increase of catalytic activity with the temperature is much more significant for the TiO_2 supported mono-layer catalyst with respect to the other samples. Nevertheless, the lower performances of 40VOP/Ti compared to those of 9VOP/Ti catalyst, despite the higher VOP loading, confirms that bulk-like VOP structures have a poorer activity. Finally, it should be noted that an easier reducibility corresponds to a better catalytic activity as it can be deduced by the comparison between TPR and catalytic test results.

The selectivity to ethylene increases with the reaction temperature for 9VOP/Ti and for 14 VOP/Al supported mono-layer catalysts, as shown in Fig. 5, in contrast with bulk 40VOP/Ti catalyst promoting the oxidation to CO_x at high temperature [9]. At variance, a similar behaviour was observed by Blasco et al. [18] and Le Bars et al. [19] in ethane ODH and by Dejoz et al. [20] in the oxidation of *n*-butane for vanadium oxide supported catalysts.

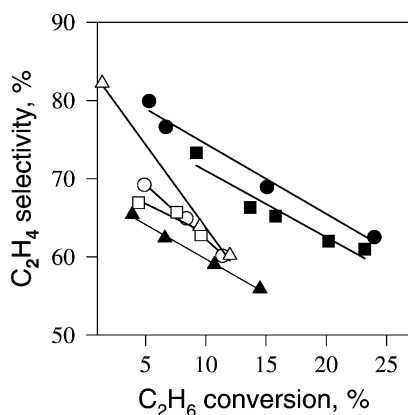The effect of the temperature could have been explained by a possible modification of the active

Fig. 5. C_2H_4 selectivity as a function of C_2H_6 conversion for the 9VOP/Ti (circles), 40VOP/Ti (triangles) and the 14VOP/Al (squares) catalysts at 450 °C (open symbols) and 550 °C (full symbols).

phase under the reaction conditions as reported by Santamarìa-González et al. [21] for V-α-Ti phosphate catalysts who observed the formation of α_I-VOPO$_4$ under reaction conditions leading to an increased ethylene selectivity. In our case, however, any modification of active phase should not be involved since catalytic activity at 450 °C was restored cooling down the catalyst after the test at 550 °C. Furthermore, the transient period observed by Santamarìa-González et al. [21] during the ethane ODH was not detected for our catalysts suggesting that a phenomenon different from a structure rearrangement occurs determining the different catalytic behaviour at high temperature. Since both Le Bars et al. [19] and Dejoz et al. [20] explained the increase of selectivity to ODH products at high temperature with a greater reducibility of vanadium, the effect of temperature on the catalytic properties of VOP/Ti samples was further investigated carrying out TPR experiments immediately after a catalytic test (12 h at either 450 or 550 °C with 15% constant ethane conversion) cooling down the catalyst under He flow and without performing any thermal pre-treatment. The results showed that the H_2 consumption of fresh catalysts is unchanged upon ODH reaction at 450 °C, while it is strongly decreased after reaction at 550 °C (from 4.3 mol $H_2\,g^{-1}$ after catalytic tests at 450 °C to 3.2 mol $H_2\,g^{-1}$ after catalytic test at 550 °C for 9VOP/Ti). As a consequence, the reduction of vanadium is promoted by high temperatures and sites containing reduced vanadium are more active and selective, since the formation of ethylene is enhanced at higher temperature.

Catalysts reduced by H_2 in the TPR experiments were reoxidised at 550 °C and then catalytic tests at 450 and 550 °C were carried out. The results obtained in these tests were the same as obtained with fresh catalysts, suggesting that the reduction of VOP occurring during the reaction is reversible at all.

In order to verify that finely dispersed vanadium phosphate can be reduced also by ethane, a TPR of 9VOP/Ti was performed after treating the sample at 550 °C in flowing ethane and in the absence of oxygen. Ethylene, CO and CO_2 were detected in the reactor outlet during the treatment until lattice oxygen was available. The H_2 uptake calculated from the TPR curve after this treatment is lower (2.1 mol $H_2\,g^{-1}$) than both that consumed by the fresh catalyst and that

consumed by the catalyst after the ODH reaction at 550 °C, indicating that ethane is able to reduce vanadium and that, as expected, the reduction is limited by the presence of O_2.

Due to the difficulty to fully investigate on the catalytic behaviour of bulk VOP because of its too low activity related to the very poor surface area, the same experiments carried out on TiO_2 and Al_2O_3 supported mono-layer samples were performed on 40VOP/Ti and 15VOP/Si catalysts which both showed the presence of VOP bulk-like structures not strictly interacting with the support surface. It was assumed, on the base of the results of physico-chemical characterisation, that the catalytic behaviour of these aggregates was very close to that of bulk VOP. C_2H_4 selectivity at 450 and 550 °C of 40VOP/Ti catalyst is reported in Fig. 5. This catalyst shows an opposite behaviour with respect to the highly dispersed VOP samples being more selective at lower reaction temperature. A TPR experiment carried out on 40VOP/Ti sample after catalytic test at 450 and 550 °C gave the same hydrogen uptake of the fresh sample in both cases. As a consequence, it has been concluded that the enhancement of ethylene selectivity with reaction temperature is related to supported VOP phase strongly interacting with the support which modifies the redox behaviour of bulk VOP. The results obtained for poorly dispersed VOP catalysts do not exclude the occurrence of a redox mechanism of the ODH reaction also for these samples but suggests that the reaction temperature range investigated (450–550 °C) represents a critical range for the well dispersed VOP samples since their reduction takes place just under these temperature conditions. On the contrary, the oxidation state of vanadium in the catalysts having a bad VOP dispersion is not significantly modified at $T < 550$ °C under reducing atmosphere. In conclusion, it has been hypothesised that a lower vanadium oxidation state is stabilised at 550 °C in the presence of hydrogen or ethane, resulting in increasing the number of selective sites, for well dispersed VOP phase, whereas this temperature is not enough high to modify the oxidation of vanadium for bulk-like VOP aggregates. Being unchanged, the number of selective sites in this latter case in the whole range of temperature the further oxidation of ethylene to CO_x prevails at higher reaction temperature determining a decrease of selectivity.

4. Conclusions

Supported $VOPO_4$ catalysts are active and selective in the oxidative dehydrogenation of ethane showing performances dramatically enhanced with respect to bulk $VOPO_4$. The dispersion of $VOPO_4$ results, in addition to a large increase of the surface area, in a strong modification of the redox properties. The higher reducibility, whose extent depends on the nature of the support, results in enhancing both activity and selectivity to ethylene. The catalyst showing the best performances is mono-layer TiO_2 supported sample, this support promoting the highest dispersion of the active phase. Furthermore, the dependence of ethylene selectivity on the reaction temperature in the range 450–550 °C is different for highly dispersed and bulk-like particles of vanadium phosphate due to the formation of a further fraction of V^{4+} containing sites for the former which are more selective in the ODH reaction.

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