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Effect of the preparation technique on the catalytic performances of TiO_2 supported vanadium phosphate in the oxidative dehydrogenation of ethane

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Abstract

TiO_2 supported $VOPO_4$ catalysts, prepared by direct impregnation of TiO_2 with $VOPO_4$ or by dispersing a V_2O_5 precursor on previously phosphated titania, have been investigated for the oxidative dehydrogenation of ethane to ethylene at 823 K. The catalysts have been characterised with XRD, BET surface area measurements, XPS, TPR and NH_3 TPD techniques. Preparation method influences surface composition of the sample, formation of V^{5+} oxide being favoured with respect to V^{4+} oxide for the catalyst prepared in two steps, whereas a comparable fraction of $VOPO_4$ is formed on both samples. Results of catalytic tests suggests that the presence of V^{4+} strongly improves performances leading to higher ethylene yields.

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1. Introduction

Selective oxidation of C_2–C_4 alkanes is catalysed by vanadium-based catalysts. It is reported that the co-presence of V(IV) and V(V) promotes the selective oxidation to olefin or to the desired oxygenated compound [1,2]. Good catalytic performances in the oxidative dehydrogenation (ODH) of ethane have been shown by supported $VOPO_4$, TiO_2 supported catalysts giving the best activity [3] whereas α-Al_2O_3 [4] and, above all, SiO_2 [5] supported catalysts showing poorer performances due to the worse dispersion of the active phase.

The great increase of activity with respect to bulk vanadyl orthophosphate has been attributed to the strong interaction between support and active phase which leads to the formation of different surface species [3,4]. In particular, Casaletto et al. [4] detected the presence of different surface vanadium oxides, in addition to $VOPO_4$, by XPS studies on alumina supported vanadyl orthophosphate catalysts, whose contribution to catalytic activity is still not clear.

In this paper the effect of preparation of TiO_2 supported $VOPO_4$ on the surface chemical composition of the active phase and on the catalytic performances in the ODH of ethane has been investigated.

2. Experimental

2.1. Preparation of catalysts

Two methods have been used to support $VOPO_4{\cdot}2H_2O$ (thereinafter indicated as VOP) on pure anatase TiO_2 ($125\,m^2\,g^{-1}$). In the first one vanadyl phosphate, prepared according to Ladwig's method [6], was supported by impregnating TiO_2 with a suitable amount of water solubilised VOP. Two steps has been used in the second method: (i) TiO_2 was firstly phosphated with $NH_4H_2PO_4$ water solution and calcined at 723 K; (ii) the phosphated titania was impregnated with a NH_4VO_3 water solution, molar concentration of $(VO)^{3+}$ ions being equal to that of $(PO_4)^{3-}$ groups. Catalyst precursors were calcined at 823 K for 3 h in air flow. A VOP amount corresponding to monolayer coverage (9.6 wt.%) [3] was supported according to the

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two techniques described above. A catalyst prepared using the single step method containing 7.0 wt.% VOP has been also studied in order to investigate the properties of a sub-monolayer sample. Catalysts will be indicated as *x*VOP/Ti ss or ds, where *x* represents the $VOPO_4$ weight percentage and ss or ds the single step or the double step preparation, respectively.

2.2. Characterisation of catalysts

A Philips PW 1100 diffractometer was employed for obtaining X-ray diffraction patterns (XRD) of the materials 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 Carlo Erba 1900 Sorptomatic instrument. Photoemission spectra were collected by a VG Microtech ESCA 3000 Multilab spectrometer, equipped with a standard Al Kα excitation source ($h\nu = 1486.6$ eV) and a nine-channeltrons detection system. The binding energy (BE) scale was calibrated by measuring C 1s peak (BE = 284.6 eV) from the surface contamination and the accuracy of the measure was ±0.1 eV. A non-linear least-square peak fitting routine was used for XPS data analysis, separating elemental species in different oxidation states. Relative concentrations of chemical elements were calculated by a standard quantification routine, including Wagner's energy dependence of attenuation length [7] and a standard set of VG Escalab sensitivity factors. The standard error of XPS quantification was lower than ±10% [8]. Temperature programmed reduction (TPR) with H_2 and temperature programmed desorption (TPD) of NH_3 were carried out using a Micromeritics TPD/TPR 2900 analyser equipped with a TC detector and coupled with a Hiden HPR 20 mass spectrometer as described in [3].

2.3. Catalytic tests

Catalytic activity tests were carried out with the experimental apparatus described in Ref. [9], 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 ionisation 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 10 E 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 temperature was 823 K whilst the contact time ranged from 0.006 to 0.04 g s N cm^{-3}. Carbon balance was closed within 3% error in all experiments.

3. Results and discussion

3.1. Characterisation of catalysts

Values of surface area of the samples are reported in Table 1. In contrast with results obtained for the catalysts prepared in one step, showing that original surface area of TiO_2 is preserved up to the monolayer loading, a loss of surface area, even upon phosphatation of titania, can be noticed for samples prepared by double step method. Nevertheless, only signals of the anatase phase of the support are detectable in XRD patterns of all catalysts, as expected since the temperature of calcination was below that promoting transformation to rutile phase. Furthermore, this suggests that vanadium phosphate or oxides aggregates, possibly formed on the surface, should have very small dimensions and formation of Ti phosphate should be limited to the surface, since no signals attributable to these phases were detected.

XPS results expressed as binding energies (BE) of the main photoelectronic peaks (Ti 2p, O 1s, P 2p, V 2p) and the relative chemical composition of the samples, obtained for catalysts prepared by different methods, are listed in Table 2. Elemental concentrations are expressed as atomic percentage (at.%) and calculated both before and after ODH test. The surface (P/V) atomic ratio, determined by XPS, ranges from 1.2 to 0.8 and these values correspond to the stoichiometric bulk one (P/V = 1), at least within the experimental error, in good agreement with literature results [10]. The curve-fitting of the V $2p_{3/2}$ peak of all the samples evidenced the presence of three components at BE = 518.2, 516.9 and 515.8 eV, which can be assigned to V^{5+} phosphate species as detected in $VOPO_4$, to V^{5+} oxide species as in V_2O_5 and to V^{4+} oxide species as in V_2O_4 [4,11], respectively. Quantitative information on the relative surface amount of vanadium species are also reported in Table 2,

Table 1
Surface area, H_2/V ratio (as evaluated from TPR and XPS), NH_3 desorption (evaluated from TPD) and rate of ethane consumption and ethylene formation for catalysts and phosphated TiO_2 evaluated at 823 K under differential conditions

Sample	SA ($m^2 g^{-1}$)	H_2/V		NH_3 ($\mu mol\ m^{-2}$)	$r_{C_2H_6}$ ($\mu mol\ m^{-2}\ s^{-1}$)	$r_{C_2H_4}$ ($\mu mol\ m^{-2}\ s^{-1}$)
		TPR	XPS			
9.6VOP/Ti ss	125	0.71	0.77	2.3	0.16	0.11
7.0VOP/Ti ss	125	0.76	0.79	2.7	0.11	0.069
PO_4/TiO_2	110	–	–	3.2	<0.005	<0.005
9.6VOP/Ti ds	75	0.93	0.87	4.0	0.075	0.044

Table 2
Relative concentration of different chemical species and of different types of vanadium for catalysts as calcined and after ODH test

Sample	Ti 2p (BE = 458.5 eV)	O 1s (BE = 530.1 eV)	P 2p (BE = 134.0 eV)	$V\ 2p_{3/2}$ (BE = 516.5 eV)	C 1s (BE = 284.6 eV)	P/V	V^{5+} phosphate (BE = 518.2 eV)	V^{5+} oxide (BE = 516.9 eV)	V^{4+} oxide (BE = 515.8 eV)
9.6VOP/Ti ss	6.7	31.9	1.1	1.0	54.0	1.1	13.2	42.5	44.3
After ODH	9.0	36.5	1.1	1.3	47.6	0.8	13.3	39.1	47.6
7.0VOP/Ti ss	15.2	48.7	1.8	2.0	32.3	0.9	9.5	48.8	41.7
After ODH	15.1	48.6	1.6	1.9	32.8	0.8	11.2	39.6	49.2
9.6VOP/Ti ds	15.3	45.8	2.1	2.0	34.7	1.0	12.0	61.6	26.4
After ODH	17.3	51.8	2.2	2.0	26.7	1.1	9.3	53.4	37.4

concentrations being expressed as percentage of the total area of $V\ 2p_{3/2}$ peak (taken as 100%). A major amount of V(V) is detected in the samples prepared by the double step method, mostly as V^{5+} oxide and partly as V^{5+} phosphate species, likely due to a weaker interaction of vanadium oxide with the phosphorous, which could stabilise vanadium as V^{4+}. The reduction of vanadium oxidation state, likely occurring during the preparation procedure, was confirmed by TPR results (Table 1) which, in good agreement with XPS data, suggest an oxidation state lower than +5, corresponding to a theoretical H_2/V ratio equal to 1. The dispersion of a precursor of vanadium oxide on a phosphated titania support involves the formation of surface $VOPO_4$ species, as also observed by Santamaría-González et al. [12]. A comparable quantity of V^{5+} phosphate species was found on the surface of the samples prepared by direct dispersion of vanadyl phosphate on titania. The presence of V^{5+} and V^{4+} oxide species on the surface of these samples hints to a partial phosphatation of TiO_2, also confirmed by the shift towards higher BE of the Ti 2p peak, as already observed [13]. In conclusion, dispersion of VOP by double step technique does not significantly affect the amount of $VOPO_4$ deposed on the support but partially inhibits reduction of V_2O_5 to V_2O_4 during the preparation. This phenomenon should be related to the presence of phosphate groups since no formation of V(IV) was observed for V_2O_5/TiO_2 catalysts with different vanadium content by TPR experiments [9]. Moreover, in contrast with results obtained for Al_2O_3 supported VOP [4], no formation of V^{3+} oxide was detected. On the other hand, Al_2O_3 supported sample does not promote the formation of V_2O_5, always representing the main component for TiO_2 supported catalysts. For all catalysts XPS analysis performed after catalytic runs evidenced a reduction of vanadium species, the amount of V^{4+} oxide species increasing mostly to the detriment of V^{5+} oxide species.

Surface acidity of the samples is enhanced by changing the preparation techniques, as detected by NH_3 TPD analysis. Catalysts prepared into two steps give rise to a significantly higher value of NH_3 desorption, even larger than that of phosphated titania, suggesting that a modification of acid sites occurs during the second step of the preparation.

3.2. *Catalytic tests*

Activity of pure and phosphated TiO_2 was found negligible compared to that of vanadium containing catalysts under the same experimental conditions. CO and CO_2 were produced in addition to ethylene, representing the main product for all catalysts in the whole range of conversion explored, CO_2 being always produced with a selectivity lower than 5%. In Fig. 1(a) and (b) the dependence of ethane conversion on W/F and that of ethylene selectivity on C_2H_6 conversion are compared for the two monolayer catalysts prepared with different techniques. CO selectivity, not reported in the figure, roughly balances C_2H_4 selectivity, suggesting a consecutive reaction path for both catalysts. However, the catalyst prepared in one step is either more active and more selective. The higher activity cannot be only attributed to the larger surface area of 9.6VOP/Ti ss catalyst with respect to 9.6VOP/Ti ds, as shown by the values of reaction rate referred to unit area reported in Table 1, but should be related also to the different surface composition. TiO_2 supported V_2O_5 can activate ethane under the same experimental conditions used in this work [9,14], showing a specific activity very similar to that of 7.0VOP/Ti ss and 9.6VOP/Ti ss catalyst (about 3×10^{-2} mol C_2H_6 mol^{-1} V s^{-1}) and this suggests that activation of ethane has a low dependence on the nature of vanadium provided that it is well dispersed. On the contrary, formation of ethylene should be very sensitive to the nature of the surface species, as shown by the much lower selectivity (37% at 12% conversion [9]) provided by a V_2O_5/TiO_2 catalyst with a vanadium content close to that of 9.6VOP/Ti samples but also by the lower selectivity of 7.0VOP/Ti ss [3] and 9.6VOP/Ti ds catalysts. As a consequence, phosphate and/or V^{4+} species should play a role in determining the better selectivity observed for 9.6VOP/Ti ss. Different hypotheses can be made to explain this effect: (i) phosphate can dilute vanadium by generating small domains, which are more selective on the base of the principle of site isolation [15,16]; (ii) V^{4+} species or the couple V^{4+}–V^{5+} are more selective due to a lower oxygen availability. In both cases, a lower selectivity of ds sample, containing either vanadium oxide aggregates and a lower amount of V^{4+}, is expected. Nevertheless, the good dispersion of vanadium in 7.0VOP/Ti ss catalyst but its quite

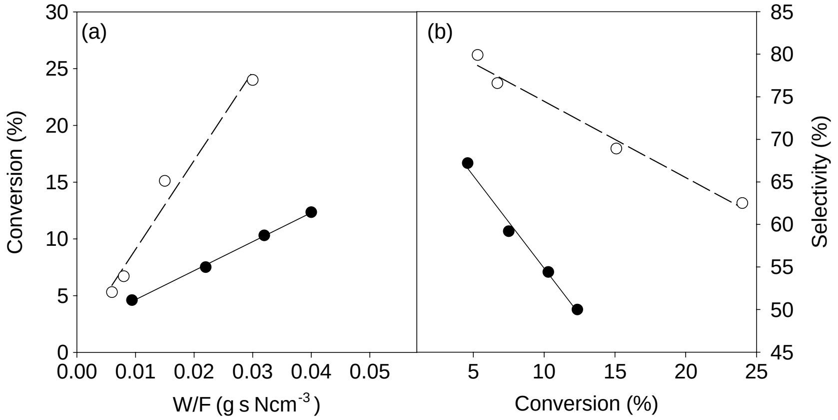

Fig. 1. Ethane conversion as a function of W/F (a) and ethylene selectivity as a function of ethane conversion for (b) 9.6VOP/Ti ss (○) and 9.6VOP/Ti ds (●).

low absolute V^{4+} amount could suggest that V^{4+} inhibits ethylene combustion directly or, indirectly, providing a better isolation of V^{5+} centres. Finally, it cannot be excluded that a higher surface acidity could promote ethylene surface adsorption favouring its oxidation to carbon oxides.

4. Conclusions

Both V(IV) and V(V) oxides are formed, in addition to $VOPO_4$, by contacting TiO_2 with phosphate and vanadium precursors. A better dispersion and a greater amount of V(IV) are obtained by direct dispersion of $VOPO_4$ on the support. These features are responsible of better catalytic performances in the oxidative dehydrogenation of ethane.

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