Comparative study of catalytic behaviour of bulk-like and highly dispersed supported vanadyl orthophosphate catalysts in the oxidative dehydrogenation of ethane

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Received 5 December 2000; accepted 23 January 2001

The catalytic behaviour in the oxidative dehydrogenation of ethane of TiO_2- and SiO_2-supported catalysts containing bulk-like $VOPO_4$ particles has been compared to that of TiO_2-supported highly dispersed $VOPO_4$. The catalysts have been characterised by XRD analysis and BET measurements. Redox properties have been studied by TPR experiments. A correlation of catalytic activity and C_2H_4 selectivity with redox properties has been proposed.

KEY WORDS: vanadyl orthophosphate; oxidative dehydrogenation; ethane; dispersion; reducibility

1. Introduction

Oxidative dehydrogenation (ODH) of light hydrocarbons is a potential alternative to industrial dehydrogenation processes for olefins production [1]. Among transition metal oxides vanadium-oxide-based catalysts are the most widely employed in the ODH of ethane, propane and butane showing high activity associated, however, to a poor selectivity [1,2]. On the other hand, bulk and TiO_2-supported $(VO)_2P_2O_7$ have been proposed for the ODH of C_2–C_4 hydrocarbons [3,4] with a quite good selectivity but low activity. In our previous studies [5,6] we reported that good catalytic performances in the ODH of ethane have been shown by submonolayer and monolayer TiO_2- and γ-Al_2O_3-supported $VOPO_4$. The great increase of activity, observed at 550 °C, with respect to bulk vanadyl orthophosphate, significantly higher than that expected by the enhanced surface area of the supported catalyst, was attributed to the strong interaction occurring between the active phase and the support leading to a deep modification of redox properties of $VOPO_4$. The greater reducibility of supported $VOPO_4$ was supposed to be also related to the higher ethylene selectivity observed at 550 °C with respect to 450 °C hypothesising that high temperature stabilises an increased number of active centers producing selectively C_2H_4. A complete comparison of catalytic activity of highly dispersed vanadyl orthophosphate with bulk $VOPO_4$ should require a much higher surface area of the latter. Nevertheless, this feature is not easily obtainable using usual preparation techniques. Therefore, in order to better investigate the modification of catalytic behaviour in the oxidative dehydrogenation of ethane promoted by the formation of vanadium–support bonds in monolayer TiO_2-supported catalyst, suitable reference compounds with bulk-like $VOPO_4$ structure and significant surface area at the same time are needed. Ruitenbeek et al. [7] investigated the dispersion of vanadium phosphorus oxide (VPO) on TiO_2 and SiO_2 by EXAFS and ESR. They found that silica promotes the formation of a phase close to amorphous bulk VPO as concerns both the local structure of vanadium and the catalytic properties of the sample towards partial oxidation of n-butane to maleic anhydride. Supports such as SiC have been also proposed [8] in order to minimise the interaction between dispersed phase and support leading to significant modifications of the nature of bulk vanadium phosphorus oxide.

In this paper finely dispersed vanadyl orthophosphate particles have been obtained supporting $VOPO_4$ (a) in amount corresponding to the monolayer coverage on SiO_2 which inhibits good dispersion due to its surface acidity, and (b) in amount far exceeding the monolayer coverage on TiO_2. A comparative investigation of both redox and catalytic properties of these samples with those of a highly dispersed TiO_2-supported $VOPO_4$ monolayer catalyst has been done.

2. Experimental

$VOPO_4\cdot 2H_2O$, herein after indicated as VOP, was prepared by refluxing V_2O_5 in H_3PO_4 (85%) and distilled water for 16 h according to the Ladwig method [9].

The supported catalysts were prepared by wet impregnation dissolving suitable amounts of VOP in water in the

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1011-372X/01/0400-0207$19.50/0

presence of the support and then drying at 80 °C and calcining under flowing air at 550 °C for 3 h. Amorphous SiO_2 (Sigma) and pure anatase TiO_2 (Tioxide Specialties) have been used as supports. VOP loading and the catalysts code, indicating both the VOP percentage and the support, are reported in table 1.

A Philips PW 1100 diffractometer was employed for the X-ray diffraction (XRD) patterns at room temperature using a Ni-filtered Cu Kα radiation. BET surface areas were measured by N_2 adsorption at 77 K with a Carlo-Erba 1900 Sorptomatic instrument. Temperature-programmed reduction (TPR) with hydrogen was carried out using a Micromeritics TPD/TPR 2900 analyser equipped with a TCD and coupled with a Hiden HPR 20 mass spectrometer. The sample was reduced by a 2% H_2/Ar mixture (25 $cm^3\,min^{-1}$) heating 10 $°C\,min^{-1}$ up to 650 °C. Before TPR experiments the sample was treated in a flowing air at 550 °C for 2 h.

The catalytic activity tests were carried out in a fixed-bed quartz microreactor operating under atmospheric pressure. The reaction products were analysed by a Hewlett–Packard series II 5890 gas chromatograph equipped with thermal conductivity and flame ionization detectors for the analysis of O_2, CO and CO_2 and for that of hydrocarbons, respectively. The concentration of O_2, CO and CO_2 were also measured by an on-line Hartmann & Braun URAS 10 E continuous analyser. Water produced by the reaction was kept by a silica gel trap in order to avoid condensation in the cold parts of the experimental apparatus. The feed composition was 4% C_2H_6 and 2% O_2 in a balance of He. The reaction temperature ranged from 450 to 550 °C and the space time from 0.003 to 0.18 $g\,s\,Ncm^{-3}$. Carbon balance was closed within 3% error in all experiments.

Table 1
Composition and surface area of the catalysts.

Catalyst	VOP content (wt%)	Surface area ($m^2\,g^{-1}$)
SiO_2	–	200
TiO_2	–	125
15-VOP/Si	14.6[a]	183
9-VOP/Ti	9.6[a]	125
40-VOP/Ti	40.0	45

[a] Corresponding to theoretical monolayer coverage.

3. Results and discussion

The XRD pattern of bulk VOP shows signals of a $VOPO_4{\cdot}2H_2O$ phase [10]. The presence of the two coordination water molecules is likely due to re-hydration of the sample upon exposure to air moisture. Results of XRD analysis confirmed that bulk-like VOP structures have been formed either for 15-VOP/Si and 40-VOP/Ti, notwithstanding the way to obtain them. In fact, the presence of signals corresponding to a dihydrated $VOPO_4$ phase, in addition to those of the supports, detected in the XRD patterns of 15-VOP/Si and 40-VOP/Ti catalysts (figure 1), indicated that segregation of the VOP phase occurred. This was expected due to the strong acidity of SiO_2, inhibiting dispersion of the active phase, as also reported for supported vanadium phosphate and vanadium oxide systems [2,7], for 15-VOP/Si catalyst, and to the VOP coverage far exceeding the monolayer for the 40-VOP/Ti catalyst. In contrast, the XRD pattern of 9-VOP/Ti revealed only signals of the support, indicating a good dispersion of the active phase as also confirmed by the unchanged value of the original surface area of the TiO_2 (table 1). A small reduction of surface area has been observed for the 15-VOP/Si sample. The strong decrease observed for 40-VOP/Ti is related to the very high VOP loading (table 1).

The TPR curves of the samples are reported in figure 2 while the amount of H_2 uptake obtained from the integration of the curves and the peak temperature are reported in ta-

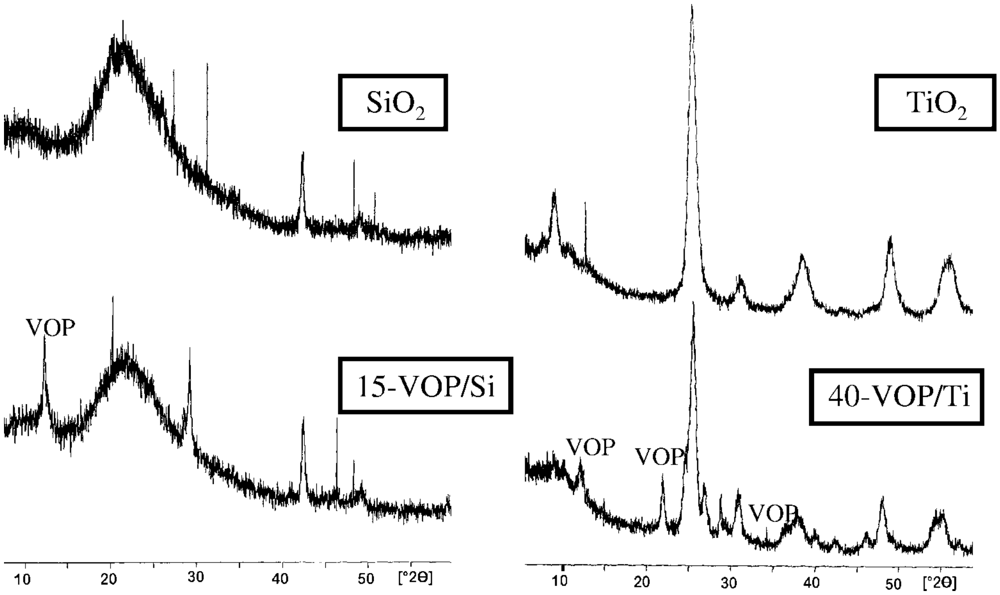

Figure 1. XRD patterns of SiO_2, 15-VOP/Si, TiO_2 and 40-VOP/Ti.

ble 2. Both supports show a negligible reduction compared to that of the catalysts. Supported bulk-like VOP shows a redox behaviour markedly different from that of well dispersed VOP. In fact, although the extent of the reduction, expressed as H/V ratio, of 15-VOP/Si and 40-VOP/Ti is quite close to that of well dispersed VOP supported catalysts, suggesting that reduction of bulk VOP is probably affected by diffusion limitations, the reduction of bulk and poorly dispersed VOP mainly occurs during the isothermal step of the TPR experiment in contrast with that of well dispersed VOP which is almost completed within 650 °C. The H/V ratio values are lower than 2 for all samples. By supposing that vanadium is completely reduced to V^{3+} by H_2 in a single step as observed for supported V_2O_5 catalysts [11] in about the same range of temperature, this implies that V^{4+} should be present in addition to V^{5+} in all catalysts. This hypothesis was confirmed for both bulk VOP and 9-VOP/Ti by EPR measurements [5].

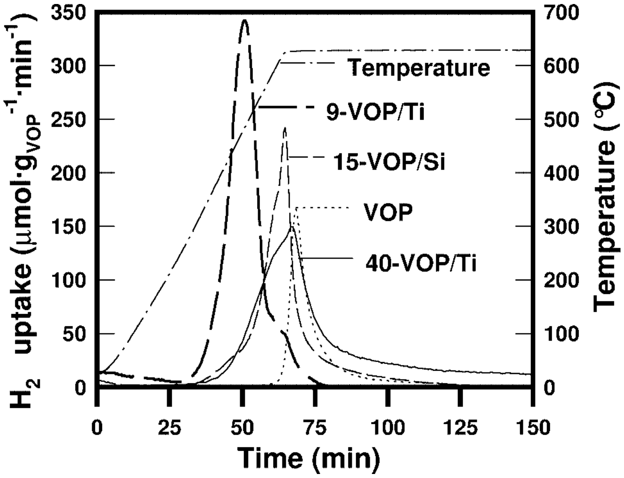

Figure 2. TPR curves of bulk and supported VOP catalysts.

Table 2
Results of TPR experiments.

Catalyst	H_2 uptake $\times 10^3$ (mol g_{VOP}^{-1})	H/V	T_{max} (°C)
VOP	1.5	0.5	>650
15-VOP/Si	3.4	1.1	>650
9-VOP/Ti	4.5	1.4	509
40-VOP/Ti	3.5	1.1	>650

Before carrying out catalytic tests, blank runs in absence of catalysts were performed under the same experimental conditions. No detectable ethane conversion was obtained. Under the experimental conditions investigated in the ODH catalytic tests the oxygen conversion is always <60%. In all catalytic tests only C_2H_4, CO and CO_2 were detected. Unsupported VOP shows a very low catalytic activity with a high selectivity at 550 °C (C_2H_6 consumption rate $<10^{-8}$ mol m^{-2} s^{-1}). It gives undetectable ethane conversion at 450 °C. The catalytic activity of the supports is negligible if compared to that of the catalysts. For all catalysts the conversion of C_2H_6 and the selectivity to C_2H_4 decrease while the selectivity to CO increases by increasing the contact time (figure 3) both at 450 and 550 °C suggesting the consecutive oxidation to CO of ethylene produced.

For ethane conversion not exceeding 20% the ethylene selectivity is in the range 60–80% for all samples. Monolayer TiO_2-supported catalyst shows an activity markedly higher (about two orders of magnitude) of 40-VOP/Ti and 15-VOP/Si which, on the other hand, have a specific activity comparable to that of bulk VOP. The 40-VOP/Ti sample shows an activity slightly higher than that of 15-VOP/Si, likely due to the greater fraction of the active phase. These results confirm that for the highly dispersed system a deep modification of the active phase occurs leading to a significant improvement of the catalytic performances.

In figure 4 ethylene selectivity has been reported as function of ethane conversion at 450 and at 550 °C for the 40-VOP/Ti and 9-VOP/Ti catalysts.

In the range of ethane conversions investigated 40-VOP/Ti is more selective at lower temperature indicating that further ethylene oxidation is favoured at 550 °C. An opposite trend was observed for the monolayer 9-VOP/Ti catalyst and associated to vanadium reduction under reaction conditions at higher temperature generating more selective

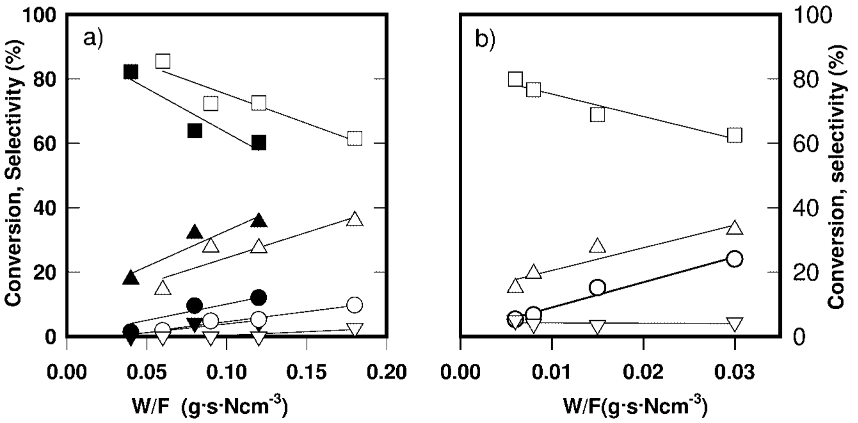

Figure 3. $X_{C_2H_6}$(•, ○), $S_{C_2H_4}$(■,□), S_{CO}(▲,△) and S_{CO_2} (▼,▽) as function of W/F for (a) 40-VOP/Ti (closed symbols) and 15-VOP/Si (open symbols) and (b) 9-VOP/Ti catalysts at 550 °C.

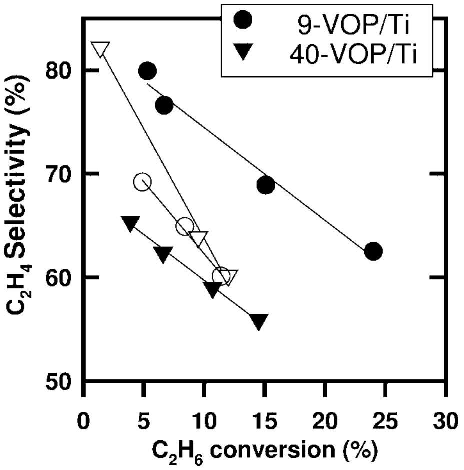

Figure 4. C_2H_4 selectivity as a function of C_2H_6 conversion for 40-VOP/Ti and 9-VOP/Ti catalysts at 450 °C (open symbols) and 550 °C (closed symbols).

sites, as shown by TPR experiments carried out after catalytic tests, suggesting that the catalyst is markedly reduced after the reaction at 550 °C [5]. This hypothesis has been confirmed by the results of a TPR experiment carried out after catalytic tests at 450 and 550 °C on 40-VOP/Ti sample which gave the same hydrogen uptake and the same peak temperature of TPR curve of the fresh sample in both cases. A possible reason of this behaviour could be related to the quite high temperature required for reduction of bulk-like VOP, significantly far from the reaction temperature range investigated. As a consequence, the average oxidation state of 40-VOP/Ti catalyst does not undergo any significant modification in the range 450–550 °C and the number of centres producing ethylene remains unchanged. Under these conditions we just observe the expected greater enhancement of reaction rate of total oxidation reaction compared to that of the ODH reaction at higher temperature. In contrast, the reaction of ethylene formation prevails for 9-VOP/Ti at 550 °C due to the considerable increase of reduced sites probably involved in this selective reaction.

4. Conclusions

Monolayer dispersion of $VOPO_4$ on a suitable support provides an enhanced vanadium reducibility related to a great increase of activity in the oxydative dehydrogenation of ethane, TiO_2 being the support giving the best results. The deep modification of the active phase, induced by the strong interaction with the support, also affects the dependence of ethylene selectivity on the reaction temperature.

Supports inhibiting dispersion, such as SiO_2 or $VOPO_4$ loading far exceeding the monolayer coverage, promote the formation of bulk-like $VOPO_4$ aggregates showing a lower reducibility and giving worse catalytic performances.

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