Catalysis Letters Vol. 82, No. 3–4, October 2002 (©2002)

$VOPO_4 \cdot 2H_2O$ and $Fe(H_2O)_x(VO)_{1-x}PO_4 \cdot 2H_2O$ supported on TiO_2 as catalysts for oxidative dehydrogenation of ethane

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Received 11 April 2002; accepted 21 May 2002

The effect of iron substitution on bulk and TiO_2-supported $VOPO_4 \cdot 2H_2O$ on the catalytic performances in oxidative dehydrogenation of ethane has been studied in a fixed-bed reactor at 550 °C. The samples have been characterized by XRD, BET measurements, TPR and ammonia TPD experiments. A uniform dispersion of the active phase on the support has been obtained. Both iron substitution and dispersion on TiO_2 significantly modify redox and acid properties of vanadyl orthophosphate. A good correlation between the acid and redox properties of the catalysts and their catalytic performances has been observed.

KEY WORDS: vanadyl orthophosphate; oxidative dehydrogenation; ethane.

1. Introduction

Oxidative dehydrogenation (ODH) of light hydrocarbons is a potential alternative to the industrial dehydrogenation process to produce olefins [1]. This reaction can be catalyzed by several metal oxides, vanadium-based catalysts being the most active at temperature as low as 400 °C. The effect of addition of other elements such as Mo, Nb or P to vanadium oxide has been investigated in order to improve the poor selectivity of these catalysts [2]. Bulk and TiO_2-supported $(VO)_2P_2O_7$ have been proposed for the ODH of C_2–C_4 hydrocarbons [3,4] showing a quite good selectivity but low activity. For these materials it has been also reported that the addition of several metals can improve the catalytic properties of VPO systems in oxidation reactions [5]. Less attention has been paid to vanadium–phosphorus oxides different from pyrophosphate. However, recently it has been reported that the low activity in ethane ODH of bulk vanadyl orthophosphate, coupled however to a high selectivity, can be dramatically improved by supporting $VOPO_4$ on TiO_2 yet still preserving a very good selectivity. The increase of activity has been attributed to the enhanced reducibility of $VOPO_4$ when supported on TiO_2 [6]. The role of acid centers has not been investigated although it is reported that for vanadium-oxide-supported catalysts both activity and selectivity to ethylene can be promoted by a high surface acidity [2,7]. Recently new materials have been obtained by isomorphous substitution of some (VO) groups of $VOPO_4 \cdot 2H_2O$ with trivalent metals, such as Fe, Cr, Me, Al and Ga [8,9]. Such substitution modifies the adsorption properties of the $VOPO_4$ phase [10,11].

On the basis of these considerations and taking into account that it is reported [11] that isomorphous substitution of Fe^{3+} ions for VO^{3+} groups in vanadyl orthophosphate can modify the surface acidity, in this paper a comparative study of catalytic behavior of bulk and TiO_2-supported $VOPO_4 \cdot 2H_2O$ and $Fe(H_2O)_{0.23} \cdot (VO)_{0.77}PO_4 \cdot 2.3H_2O$ in ethane ODH have been performed. The physicochemical properties of the catalysts have also been investigated in order to define the features determining the best catalytic performances.

2. Experimental

The vanadyl phosphatedihydrate, $VO(PO_4) \cdot 2H_2O$ (VOP), was prepared by refluxing 10 g of V_2O_5 (Fluka puriss. grade) in 300 ml of a 3.3 $mol\,dm^{-1}$ H_3PO_4 (Carlo Erba RPE, highest purity product) solution according to the Ladwig method [12]. The mono-substituted iron vanadyl phosphate compound of formula $Fe(H_2O)_{0.23} \cdot (VO)_{0.77}PO_4 \cdot 2.3H_2O$ was prepared according to Melanova *et al.* [8], by adding to the previous suspension the appropriate amount of $Fe(NO)_3 \cdot 9H_2O$ such that the V/Fe molar ratio was 10/3, denoted in the text as FeVOP. After 16 h reflux time, both suspensions were hot filtered, the yellow-green solid washed in cold distilled water and dried in air. Chemical analyses

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1011-372X/02/1000-0243/0

of the compounds were carried out as described in ref. [9]. The iron-substituted compound has a tetragonal layered structure and is isomorphous with VOP [8,13].

Pure anatase TiO_2 (s.a. $= 120\,m^2\,g^{-1}$), supplied by Tioxide Specialties, was employed for the preparation of supported catalysts. Water-solubilized VOP (9.6 wt%) and water-suspended FeVOP (9.6 wt%) were contacted at 60 °C with the TiO_2 support so as to obtain a surface coverage corresponding to the theoretical monolayer. This was evaluated by taking into account the cell parameters of VOP [13] and FeVOP [8] and the surface area of the support. The supported samples will be referred to as VOP/Ti and FeVOP/Ti respectively. All catalysts were obtained by calcining the precursors at 550 °C, under flowing air, for 3 h.

A PW 1100 Philips diffractometer was employed for the X-ray diffraction (XRD) patterns. BET surface areas were measured by N_2 adsorption at 77 K with a Carlo Erba 1900 Sorptomatic. Temperature programmed reduction (TPR) and temperature programmed desorption (TPD) of NH_3 were carried out using a spectrometer. The sample was reduced by a 2% H_2/Ar mixture ($25\,cm^3\,min^{-1}$) or treated with flowing He ($25\,cm^3\,min^{-1}$) after saturation with pure ammonia and heating at $10\,^{\circ}C\,min^{-1}$ up to 650 °C in TPR or TPD experiments respectively. Before either TPR and TPD experiments the sample was treated in flowing air at 550 °C for 2 h.

The catalytic activity tests were carried out in a fixed-bed quartz micro-reactor operating under atmospheric pressure at 550 °C. The reaction products were analyzed 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 & Braunn URAS 10 E continuous analyzer. 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 contact time ranged from 0.006 to $0.03\,g\,s\,N\,cm^{-3}$ for supported catalysts and from 0.3 to 1.2 for bulk systems. These values have been obtained fixing the catalyst weight (about 1.5 g for bulk and 120 mg for supported materials) and changing the flow rate.

In order to limit the homogeneous contributions to ethane conversion, α-Al_2O_3 pellets were loaded on the catalytic bed and the reactor diameter was reduced in the post-catalytic zone. The contribution of homogeneous reactions and/or of the α-Al_2O_3 was verified by performing blank runs up to 700 °C under the same reaction conditions of catalytic tests with the reactor containing only α-Al_2O_3. No significant ethane conversions were obtained in the blank experiment up to 700 °C. No significant deactivation effects of the catalysts were observed in 12 h runs.

3. Results and discussion

3.1. *XRD and BET analysis*

XRD analysis of bulk samples revealed the signals of anhydrous pyrophosphate, indicating that water was lost after the 3 h thermal treatment at 550 °C, in agreement with Benes *et al.* [14], who reported that coordinated water is lost in the temperature range 250–600 °C. Only signals of the support are present in the XRD patterns of supported samples, indicating a good dispersion of the active phase also for the sample prepared by chemical mixing. In contrast to Bagnasco *et al.* [15], who prepared FeVOP/Ti catalysts by dissolving the FeVOP precursors in an aqueous suspension of TiO_2 powder, no titanium phosphate, whose formation is promoted by TiO_2 refluxing with H_3PO_4, was detected due to the preparation techniques used that avoid this step.

The higher surface area of the bulk FeVOP sample (table 1) compared with that of bulk VOP could be likely due to the lower crystallinity of the iron-substituted catalyst. The values of surface area of supported catalysts confirm the very good dispersion of the active phase obtained for VOP/Ti and the slightly worse effectiveness of mechanical mixing to dispersed FeVOP on TiO_2.

3.2. *TPR experiments*

TPR profiles of bulk and supported catalysts are reported in figure 1. The results of the integration of the TPR curves are reported in table 1. The support

Table 1
Results of physicochemical characterization

Catalysts	Surface area ($m^2\,g^{-1}$)	H_2 uptake × 10^3 ($mol\,g_{VOP}^{-1}$)	H/V (mol/mol)	T_{max} (°C)	$NH_3{\cdot}$des. × 10^5 ($mol\,m^{-2}$)
TiO_2	125	–	–	–	3.5
VOP	0.8	1.6	0.5	>650	–
FeVOP	5	1.6	0.6	595	2.4
VOP/Ti	125	4.5	1.4	509	2.4
FeVOP/Ti	103	4.3	1.8	522	3.3

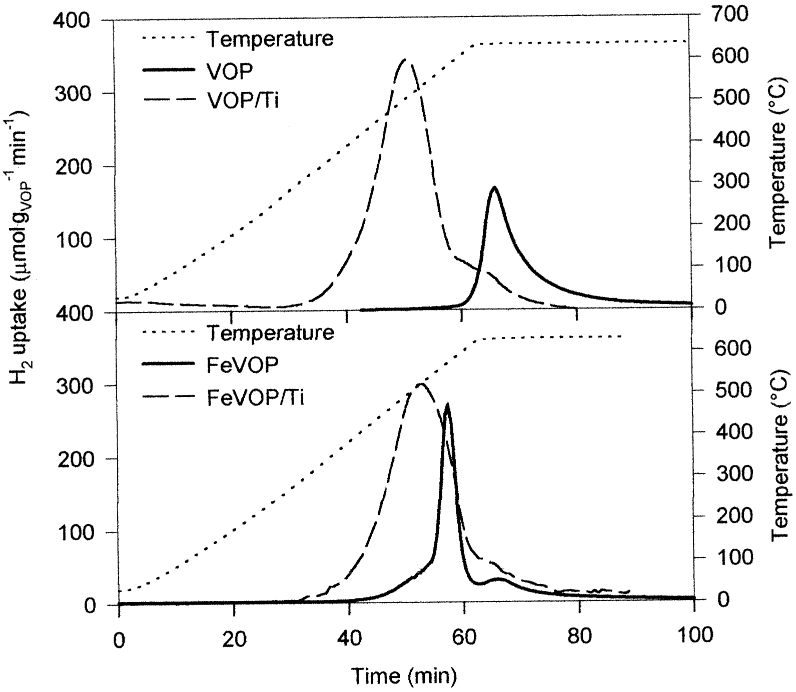

Figure 1. TPR curves of bulk and supported catalysts.

does not undergo significant reduction. For all catalysts the values of an H/V ratio lower than 2 indicate the presence of V^{4+} in addition to V^{5+}. Bulk VOP is reduced at very high temperature (>650 °C under the isothermal step). By supposing that Fe^{3+} is not involved in the reduction, the partial substitution of the VO^{3+} group with Fe^{3+} does not change the amount of H_2 consumed with respect to vanadium. However, the value of the peak temperature obtained for the FeVOP catalyst is 50 °C lower than that of VOP. This result is probably due to the higher porosity of FeVOP, which enhances the diffusion of H_2 in the sample.

The dispersion on support strongly changes the redox properties of active phases. Supported catalysts are more reducible than bulk samples as concerns both the temperature and the extent of the reduction.

The values of peak temperature obtained for supported samples are 100–150 °C lower than those reported for the corresponding bulk catalysts. Moreover, the value of H_2 uptake, about three times higher, indicates a deep reduction of vanadium interacting with TiO_2.

3.3. Ammonia TPD experiments

Ammonia desorption curves of samples are reported in figures 2(a) and 2(b). In table 1 the amount of NH_3 desorbed by the catalysts and by the support, resulting from the integration of the signal, is shown.

No desorption of NH_3 was observed for unsupported VOP under our experimental conditions, in contrast to Bagnasco *et al.* [11], who detected a significant adsorption

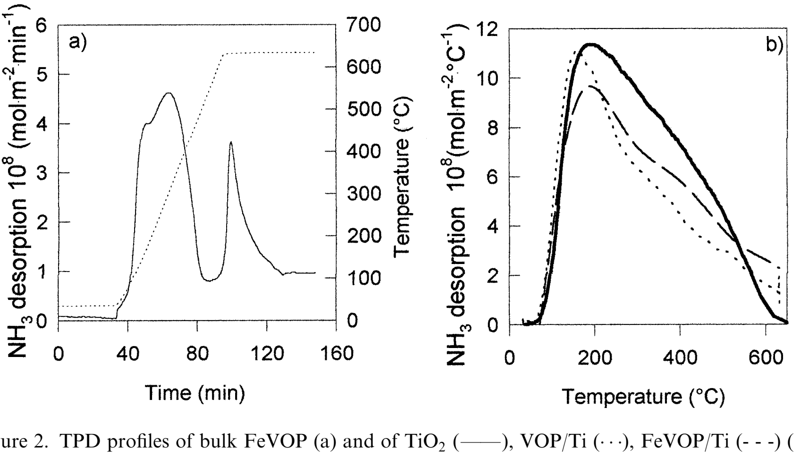

Figure 2. TPD profiles of bulk FeVOP (a) and of TiO_2 (——), VOP/Ti (···), FeVOP/Ti (- - -) (b).

of ammonia on a VOP sample treated at 400 °C by intercalation of NH_3 molecules between two successive layers which collapse upon our treatment at 550 °C. The presence of iron provides some surface acidity which cannot be justified only by the enhanced surface area of the Fe-containing bulk sample with respect to VOP but should be related to the formation of new acid centers not present on the VOP sample. In the FeVOP profile (figure 2(a)) two different contributions can be clearly observed. The first evolution is related to desorption of NH_3, whereas the second evolution, mainly occurring under the isothermal step, is related to desorption of N_2, as detected by the mass spectrometer, probably coming from ammonia oxidation occurring on the catalyst surface at high temperature due to the oxidation properties of FeVOP-based catalysts [15].

TiO_2 shows a large number of acid sites of different types, as shown by the TPD curve extending from about 80 to 600 °C [7]. Its surface acidity is partially decreased by dispersion of the active phase, which is anchored to TiO_2 through hydroxyl groups. For both supported samples desorption of ammonia still occurs at 600 °C, suggesting the formation of strong acid centers not present on TiO_2. Only NH_3 has been detected by mass spectrometer, suggesting that no ammonia oxidation occurs on both supported catalysts. Therefore, the great difference observed between the surface acidity of the two bulk samples is extremely reduced for supported catalysts, although the iron-substituted sample remains slightly more acid than the unsubstituted one also for supported catalysts. Therefore, since any important additive effect of acidity related to the Fe substitution and to interaction with TiO_2 was observed in the FeVOP/Ti sample, a deep modification of dispersed active phase can be supposed also for Fe-substituted catalyst. In particular, for FeVOP/Ti the effect of the interaction between vanadyl phosphate and TiO_2 prevails over that of iron substitution, making the two supported catalysts much more similar than bulk ones.

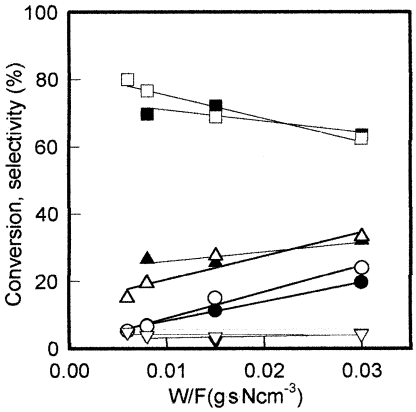

Figure 3. $X_{C_2H_6}$ (●, ○), $S_{C_2H_4}$(■, □), S_{CO} (▲, △) and S_{CO_2} (▼, ▽) as a function of W/F (g s N cm^{-3}) for VOP/Ti (open symbols) and FeVOP/Ti (closed symbols). T_r: 550 °C. Feed composition O_2 2 vol%, C_2H_6 4 vol%, balance of He.

3.4. Catalytic tests

Oxygen conversion ranged from 5 to 60%, whereas ethane conversion ranged from 3 to 24% in the catalytic tests according to the catalysts' activity and the contact time used. In all catalytic tests only C_2H_4, CO and CO_2 were detected as expected at 550 °C and in the presence of oxygen. In fact, under these experimental conditions other partial oxidation products, which can be formed in low amount, such as acetic acid, are completely oxidized to CO_x as reported by Lopez-Sanchez *et al.* [16] on analogous materials. The experimental data have been collected about 3 h after the introduction of the reactants in the reactor previously heated up to reaction temperature in helium flow. The catalytic activity of the supports is negligible if compared with that of the catalysts. Unsupported VOP shows a very low catalytic activity with a high selectivity, while a non-negligible activity was observed for the FeVOP sample. This could be related both to the enhanced surface area of the Fe-substituted bulk sample and to the possible involvement of acid sites, not present for the unsubstituted catalyst, in ethane activation.

For all catalysts the conversion to C_2H_6 and the selectivity to C_2H_4 decrease and the selectivity to CO increases by increasing the contact time (figure 3) in agreement with the reaction pathway proposed for metal transition oxide-based catalysts [1,2,7].

In table 2 the values of C_2H_6 consumption and C_2H_4 formation rate referred either to weight of the active

Table 2

Rate of ethane consumption and ethylene formation evaluated under differential conditions. T_r: 550 °C. Feed composition O_2 2 vol%, C_2H_6 4 vol%, balance of He. $W/F = 1.2\,\mathrm{g\,s\,N\,cm^{-3}}$ for bulk VOP, 0.47 g s N cm^{-3} for FeVOP, and 0.015 g s N cm^{-3} for supported materials respectively

Catalyst	$r\mathrm{C_2H_6} \times 10^6$ ($\mathrm{mol\,g_{VOP}^{-1}\,s^{-1}}$)	$r\mathrm{C_2H_4} \times 10^6$ ($\mathrm{mol\,g_{VOP}^{-1}\,s^{-1}}$)	$r\mathrm{C_2H_6} \times 10^6$ ($\mathrm{mol\,m^{-2}\,s^{-1}}$)	$r\mathrm{C_2H_4} \times 10^6$ ($\mathrm{mol\,m^{-2}\,s^{-1}}$)
VOP	0.02	0.018	0.02	0.018
FeVOP	0.30	0.22	0.06	0.04
VOP/Ti	162	113	0.13	0.09
FeVOP/Ti	120	90	0.12	0.08

phase or to the catalyst surface, evaluated at 550 °C under differential conditions, are reported for all systems.

The catalytic activity of bulk catalysts is dramatically increased by dispersing the active phase on a support due not only to the enhanced surface area but also to the interaction between active phase and support, resulting in a higher reducibility of vanadium for supported catalysts. VOP/Ti catalyst is more active than FeVOP/Ti catalyst if the reaction rate is referred to the total amount of active phase, but the two samples show similar activity if reaction rate is referred to the surface. Finally, if Fe^{3+} is supposed inactive for the reaction, the value of TOF for the FeVOP/Ti catalyst is slightly higher than that for the VOP/Ti catalyst (3.8×10^{-2} mol C_2H_6 mol^{-1} V s^{-1} for FeVOP/Ti, 3.3×10^{-2} mol C_2H_6 mol^{-1}V s^{-1} for VOP/Ti) suggesting that the activity of vanadium-containing sites is a little improved by the presence of Fe^{3+} ions.

4. Conclusions

Partial Fe^{3+} substitution for VO^{3+} groups in vanadyl orthophosphate results in a considerable modification of both redox and acid properties for bulk materials, which leads to an improvement of catalytic performances in the oxidative dehydrogenation of ethane. This effect is less significant for TiO_2-supported catalysts due to the dominance of the strong effect of vanadium–titanium interaction which markedly influences both the reducibility and acidity of vanadyl phosphate, providing an activity more than two orders of magnitude higher than that shown by the corresponding bulk catalysts.

Acknowledgments

Pasquale Patrono wishes to thank CNR and MURST (5% Programma Chimica, contract 98.03746 PF28) for financial support.

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