VANADIUM PHOSPHATE SUPPORTED CATALYSTS FOR ETHANE OXIDATIVE DEHYDROGENATION

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Abstract TiO₂ and Al₂O₃ supported VOPO₄ was studied as catalyst for the oxidative dehydrogenation of ethane in the temperature range 450-550°C. The catalytic performances were dramatically enhanced with respect to bulk VOPO₄ as result of modified redox properties. Catalytic activity and selectivity to ethylene are associated to the presence of reduced vanadium, whose formation occurs during the reaction and is favoured by high temperature.

INTRODUCTION

Oxidative dehydrogenation (ODH) of light hydrocarbons is a potential alternative to dehydrogenation process for olefins industrial production¹. Vanadium oxide based catalysts investigated for the ODH of ethane, propane and butane showed high activity but poor selectivity^{1,2}, while quite a good selectivity but low activity has been reported for bulk and TiO₂ supported (VO)₂P₂O₇^{3,4}.

In this paper the catalytic performances of VO(PO₄)·2H₂O supported on TiO₂ and γ-Al₂O₃ have been investigated for ethane ODH. Catalytic activity and physico-chemical properties of bulk VOPO₄·2H₂O were also investigated for comparison.

EXPERIMENTAL PROCEDURE

Bulk vanadium phosphate, $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ (VOP), was prepared by refluxing V_2O_5 in H_3PO_4 (85%) and distilled water for 16 hours according to Ladwig method⁵. Three supported catalysts were prepared by contacting one anatase TiO_2 sample ($125 \text{ m}^2\text{g}^{-1}$ surface area) and two $\gamma\text{-Al}_2\text{O}_3$ samples (100 and $190 \text{ m}^2\text{g}^{-1}$ surface area) with water solutions of VOP, drying at 80°C and calcining in flowing air at 550°C for 3 hours.

A Philips diffractometer PW 1100 was employed for X-ray diffraction (XRD) analysis. BET surface areas were measured by N_2 adsorption at 77 K with a CHEMBET 300 Quantachrom instrument. Electron paramagnetic resonance (EPR) spectra were obtained with a Varian E-9 spectrometer equipped with a standard Oxford instrument low-temperature attachment. 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 TCD and coupled with a Hiden HPR 20 mass spectrometer. The samples were reduced by a 2% H_2/Ar mixture ($25 \text{ cm}^3 \text{ min}^{-1}$) in TPR or treated with flowing He ($25 \text{ cm}^3 \text{ min}^{-1}$) heating $10^\circ\text{C min}^{-1}$ up to 650°C after ammonia adsorption in TPD experiments. Before either TPR and TPD experiments the samples were treated in flowing air at 550°C for 2 hours.

Catalytic activity tests were carried out with a fixed bed quartz microreactor. The reaction products were analysed by Hewlett Packard series II 5890 gas-chromatograph equipped with thermal conductivity and flame ionization detector for the analysis of O_2 , CO and CO_2 and for that of hydrocarbons, respectively. The feed composition was 4% C_2H_6 and 2% O_2 in a balance of He. The reaction temperature was 450 or 550°C . The space time ranged from 0.006 to $0.12 \text{ g s Ncm}^{-3}$. Carbon balance was closed within 3% error in all experiments.

RESULTS AND DISCUSSION

The catalysts composition is reported in table 1. On the basis of VOPO_4 cell parameters⁶ the VOP content of VOP/Ti catalysts corresponds to sub-monolayer (VOP 7.0 wt %) and monolayer (VOP 9.6 wt %) coverage, while that of VOP/Al samples corresponds to monolayer (VOP 7.9 wt %) and over-monolayer coverage (VOP 14 wt

%). XRD spectra revealed only the signals of the supports denoting high surface dispersion of VOP, also shown by the surface areas very similar to those of the supports.

The EPR spectra indicate the presence of V^{4+} both in bulk and supported $VOPO_4$. The axial symmetry and the good resolution of the signals suggest chemical equivalence and magnetic dilution of V^{4+} . The magnetic parameters of the samples are almost superimposable to those reported⁶ for $VO(H_2O)_5^{2+}$ ion, suggesting that VO^{2+} is six-coordinated to lattice oxygens and water molecules of VOP. Furthermore, the formation of $VO(H_2O)_4^{2+}$ -O-P species can be supposed if one compares the parameters values with those found⁷ for 1-2% $V^{4+}/VOPO_4 \cdot 2H_2O$.

All samples show a single TPR peak associated to vanadium reduction, while the supports do not undergo significant reduction. The peak temperature of the unsupported VOP is markedly reduced (100-150°C lower) in the VOP supported catalysts. Moreover, the hydrogen consumption, reported in table 1 in terms of V/ H_2 ratio, shows that the extent of vanadium reduction of unsupported VOP is much lower than that of the supported ones, likely due to a limited diffusion of H_2 through the particle bulk. Vanadium reducibility of VOP/Ti catalysts appears something higher than that of VOP/Al samples. Finally, the V/ H_2 values greater than 1 indicate the presence of V^{4+} in addition to V^{5+} in all samples, in agreement with EPR characterization.

TABLE 1 Composition and surface area of the catalysts and results of TPR and TPD experiments.

Catalyst	VOP content (wt %)	Surface Area (m ² g ⁻¹)	V/ H_2 from TPR	des.NH ₃ from TPD x 10 ⁶ (mol m ⁻²)
VOP	100	<1	4.0	-
VOP/Ti-7	7.0	125	1.3	1.9
VOP/Ti-9	9.6	125	1.4	2.3
VOP/Al-7	7.9	101	1.6	1.5
VOP/Al-14	14.0	162	1.7	3.2

No desorption of NH_3 was observed for the unsupported VOP. Bagnasco et al.⁸ reported a value of about 10^{-3} mol NH_3 per gram of hydrated $VO(PO_4) \cdot 2H_2O$ due to ammonia intercalation between the layers of phosphate. Therefore, the treatment at 550°C carried out for our samples should have resulted in hindered intercalation due to layered

structure-collapse. For the supported catalysts, ammonia is desorbed in a wide range of temperatures (100-600°C) due to the presence of different types of adsorbed species. However, it should be noticed that both supports have a strong surface acidity and, therefore, they could give a significant contribution to the TPD signal.

In the experimental conditions of the catalytic test C_2H_6 was only converted to C_2H_4 , CO and CO_2 , the O_2 conversion being always far from 100%. The catalytic activity of both supports is negligible if compared to that of all supported catalysts. Unsupported VOP shows a very low catalytic activity (C_2H_6 consumption rate at 550°C $< 10^{-8} \text{ mol g}^{-1} \text{ s}^{-1}$) with high selectivity to ethylene. The activity was dramatically enhanced (three orders of magnitude higher) by supporting VOP on titania or alumina. The effect of ethane conversion on ethylene selectivity is shown in figure 1. For all catalysts, by increasing the contact time the conversion of C_2H_6 and the selectivity to CO increase, the selectivity to C_2H_4 decreases, while that to CO_2 is only slightly changed. This suggests that CO is produced by further oxidation of C_2H_4 , while CO_2 is mainly formed by ethane oxidation, as also found for V_2O_5/TiO_2 catalysts either for ethane⁹ and for propane¹⁰ ODH. In table 2 the rates of C_2H_6 consumption and C_2H_4 formation at 550°C are reported. With both catalytic systems all the rates increase with VOP content, the specific reaction rate of ethane per vanadium atom being mostly constant. The VOP/Ti catalysts are more active and selective than the VOP/Al ones.

For all catalysts both activity and selectivity to ethylene are enhanced by increasing the reaction temperature (figure 1), in contrast with the general behaviour of catalysts containing transition metal oxides, which at high temperature promote the oxidation of ethane to CO_x ². In order to elucidate the effect of temperature on the catalytic properties, further TPR experiments were carried out with VOP/Ti samples immediately after the catalytic test (12 h at either 450 or 550°C) and without performing any thermal treatment before TPR measurement. The results reported in table 3 show that the H_2 uptake of both VOP/Ti catalysts after reaction at 550°C is lower than that of the fresh sample, suggesting that the catalysts are reduced during the ODH reaction. When the reaction temperature was 450°C the oxidation state of vanadium was unchanged, indicating a marked effect of the temperature on the reduction process. All the samples were reoxidised by air treatment. Therefore, it can be assumed that vanadium phosphate is more active and is more active and selective at high temperature as result of vanadium

reduction: As a further confirm of this interpretation a TPR experiment was carried out with VOP/Ti-9 after treating the sample in flowing ethane at 550°C. The H₂ uptake resulted lower than that consumed by the fresh catalyst but also that consumed by the catalyst after the ODH reaction at 550°C, suggesting that ethane is able to reduce the catalyst during the reaction.

FIGURE 1. C₂H₄ selectivity as a function of C₂H₆ conversion for supported VOP catalysts at 450°C (open symbols) and 550°C (full symbols).

Catalyst	$r_{C_2H_6} \times 10^6$ (mol g ⁻¹ s ⁻¹)	$r_{C_2H_4} \times 10^6$ (mol g ⁻¹ s ⁻¹)	$r_{C_2H_6} \times 10^2$ (mol molV ⁻¹ s ⁻¹)	$r_{C_2H_4} \times 10^2$ (mol molV ⁻¹ s ⁻¹)
VOP/Ti-7	11.2	7.0	2.6	1.6
VOP/Ti-9	16.2	11.3	2.7	1.9
VOP/Al-7	4.9	3.5	1.0	0.72
VOP/Al-14	7.5	5.5	0.84	0.66

TABLE 3 H₂ uptake resulting from TPR experiments with used catalysts.

Catalyst	H ₂ uptake x 10 ⁴ (mol.g ⁻¹)
VOP/Ti-7 after reaction at 450°C	3.2
VOP/Ti-7 after reaction at 550°C	2.5
VOP/Ti-9 after reaction at 450°C	4.3
VOP/Ti-9 after reaction at 550°C	3.2
VOP/Ti-9 after C ₂ H ₆ treatment at 550°C	2.1

SUMMARY Supported VOPO₄ catalysts are active and selective in the oxidative dehydrogenation of ethane showing dramatically enhanced performances with respect to bulk VOPO₄. The dispersion of VOPO₄ on titania or alumina results in a significant modification of the vanadium redox properties. The higher reducibility of vanadium enhances both activity and selectivity to ethylene, the vanadium reduction being favoured at increased reaction temperature.

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