Catalysis Letters 42 (1996) 93–97

Vanadium–molybdenum phosphates supported by TiO_2-anatase as new catalysts for selective oxidation of ethane to acetic acid

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Received 11 June 1996; accepted 8 August 1996

Dispersion of vanadium and molybdenum phosphates on titanium oxide (anatase) below the monolayer gives good catalysts for direct oxidation of ethane to acetic acid. By comparison with the dispersion of only vanadium phosphate, the higher selectivity to acetic acid for vanadium and molybdenum phosphates has been explained by an interaction between molybdenum and vanadium as it can be deduced from electron spin resonance and laser Raman spectroscopy studies.

Keywords: ethane oxidation; acetic acid; vanadium–molybdenum phosphates; TiO_2-anatase

1. Introduction

The different systems which catalyze the direct oxidation of light alkanes are, up to now, rather limited. The oxidation of *n*-butane to maleic anhydride has been studied so far on vanadium phosphate oxides catalysts [1] and there are some examples for the oxidation of other alkanes like propane to acrylic acid [2–4] or pentane to maleic and phthalic anhydrides [5]. The direct oxidation of ethane to an oxygenate like acetic acid appears to be difficult on the vanadyl pyrophosphate catalyst [6]. This correlates with the fact that this type of catalyst is less active when the number of carbon atoms decreases from C_5 to C_2 alkanes [7]. Nevertheless, there is a limited number of examples in the literature for the production of acetic acid by direct oxidation of ethane at low temperature (200–350°C) and generally with low conversions [8–11]. Among these studies, the work of Thorsteinson and collaborators has to be considered specifically. These authors used a catalyst based on mixed vanadium–molybdenum–niobium oxides with an optimal formula $Mo_{0.73}V_{0.18}Nb_{0.09}O_x$ [8]. Their study evidenced the determining role of the total pressure and of the addition of water which increases the production of acetic acid. While niobium was considered to have a stabilizing effect on the structure, the determining role of both molybdenum and vanadium was also demonstrated for this catalytic oxidation on other industrial applications [12–15]. More recently, a dispersion of vanadium and phosphorus oxides on TiO_2 appeared as a promising candidate [9–11]. This is the reason why we now probed a combination of vanadium and molybdenum as phosphates on the TiO_2 system for the direct oxidation of ethane to acetic acid.

2. Experimental

For the preparation of the $VOPO_4{\cdot}2H_2O$ precursor, V_2O_5 (12.0 g) was refluxed with H_3PO_4 (115.5 g) in water (24 cm^3 H_2O/g solid) for 8 h. The resulting $VOPO_4{\cdot}2H_2O$ was recovered by filtration and washed with water [16]. $(VO)_2P_2O_7$ catalyst was obtained by calcination at 500°C under nitrogen of $VOHPO_4{\cdot}0.5H_2O$ prepared under an organic route [17]. Molybdenum phosphate with the formula $Mo(OH)_3PO_4$ was prepared by dissolving 30 g MoO_3 in 45 cm^3 H_3PO_4 at 180°C following previous descriptions [18,19]. A white precipitate was obtained when adding 50 ml HNO_3. Calcination under air at 400°C changed its structure to $(MoO_2)_2P_2O_7$, as evidenced by XRD. Active phases (vanadium and molybdenum phosphates) were supported on TiO_2 anatase DT51 from Rhône-Poulence ($S_{BET} = 93$ $m^2\,g^{-1}$, a pore volume of 0.35 cm^3/g and a mean particle size of 20–30 nm). Impregnation was done by dissolving in water $VOPO_4{\cdot}2H_2O$ and $Mo(OH)_3PO_4$ in stoichiometric quantities. After drying at 100°C, the catalysts were calcined under flowing air at 500°C for 3 h and then tested.

Different catalysts were synthesized modifying:

(i) the amount of the phosphate supported ($(Mo + V)/Ti = 0.8$–3.2 mol%) below a monolayer covering [11,20];

(ii) the Mo/V ratio ($Mo/V = 10$–0.1) the $P/(Mo + V)$ ratio was then imposed (around 1.5) by the phosphate stoichiometry.

The effect of phosphorus was investigated by impregnating V and Mo ammonium salts for $P = 0$ mol% and by adding P (through H_3PO_4) on the supported MoVPO catalyst.

The oxidation of ethane was performed in a temperature range of 250–310°C. Reaction conditions were as

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Table 1
Catalytic results as a function of the (Mo + V)/Ti molar ratio. (Feed (mol%): $C_2/O_2/N_2/H_2O = 62/17/11/10$, GHSV = 480 h^{-1}, T = 275°C, $P = 7 \times 10^5$ Pa)

(Mo + V)/Ti ($\times 10^{-2}$)	Conv. (%)		Product selectivity (%)			
	C_2	O_2	C_2H_4	AcOH	CO	CO_2
Mo/V = 10						
0.75	0.2	2	traces	13	40	47
1.5	0.7	5	6	48	28	18
3	0.5	5	10	45	30	15
Mo/V = 4						
0.8	0.6	2.5	1	32	31	36
1.6	1.5	12	6	34	34	26
3.2	1.1	8	11	36	34	19
Mo/V = 1						
0.8	2	20	0.5	8	44	47.5
1.6	3.2	29	8	21	44	27
3.2	3.0	21	17	22.5	42	18.5

follows: feed (mol%): $C_2/O_2/N_2/H_2O$: 62/17/11/10; GHSV: 480 h^{-1}; P: 7×10^5 Pa. We used a continuous fixed bed stainless steel reactor (Hastelloy C22) which was filled with 1 g of the catalyst diluted in 4 cm^3 SiC. Analysis of reactants and products was performed using on-line gas chromatographs equiped with one FID and two TCD detectors.

Catalysts were characterized by XRD (using a Siemens diffractometer and Cu Kα radiation), by laser Raman spectroscopy (using a DILOR OMARS 89 spectrophotometer equipped with intensified photodiode array detector – experiments were performed at 200°C under flowing air in an in situ cell previously described [21]), by ESR (using a Varian E9 spectrometer with a dual cavity for g value determination with DDPH ($g = 2.0036$) as reference) and by XPS (with a VG ESCALAB 200 R machine using the Mg Kα radiation). Charging of catalyst samples was corrected by setting the binding energy of adventitious carbon (C_{1s}) at 284.5 eV.

3. Results and discussion

3.1. Unsupported catalysts

$(VO)_2P_2O_7$ and $(Mo_2)_2P_2O_7$ were tested in the conditions previously described. The same results were observed with no production of acetic acid (conversion of ethane: 0.2% at 275°C).

3.2. MoVPO/TiO_2

The results presented here correspond to performances for which catalysts were observed to be stable for at least 30 h without any deactivation.

Table 1 shows the influence of the percentage of the supported MoVPO phase for different Mo/V ratios. Higher ethane conversion and selectivity to AcOH are obtained for the composition (Mo + V)/Ti = 1.6 mol%, which is clearly below the theoretical monolayer which was estimated at (Mo + V)/Ti = 5.2 mol% [11,20].

Fig. 1 shows the results obtained at 275°C for the

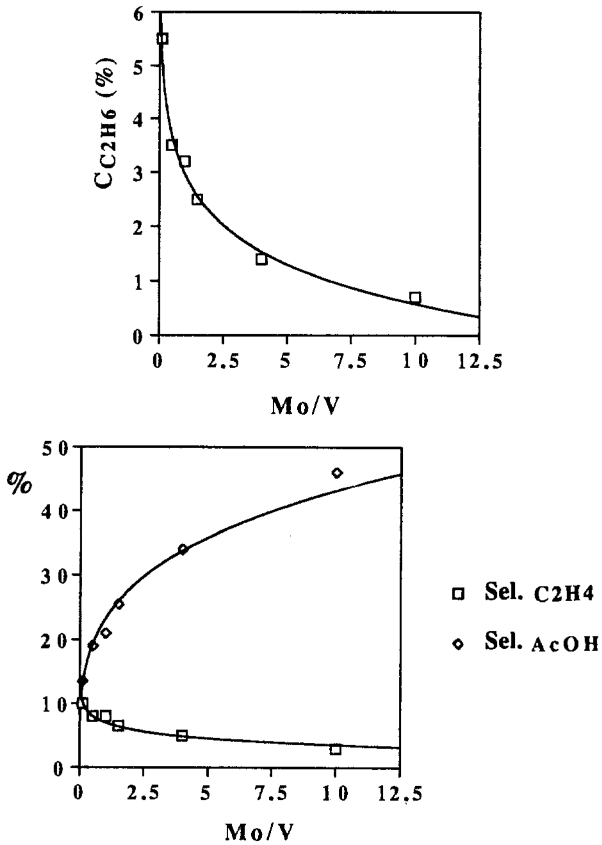

Fig. 1. Performance of MoVPO/TiO_2 catalysts as a function of the Mo/V ratio. (Feed (mol%): $C_2/O_2/N_2/H_2O = 62/17/11/10$, GHSV = 480 h^{-1}, T = 275°C, $P = 7 \times 10^5$ Pa.)

Table 2
Catalytic results as function of the P/(Mo + V) ratio. (Same conditions as in table 1)

P/(Mo + V)	Conv. (%)		Product selectivity (%)			
	C_2	O_2	C_2H_4	AcOH	CO	CO_2
0	4.5	38	3	10	48	39
1.4	1.5	13	6.5	34	34	25.5
2.3	0.8	6	5	39	33	23
4.7	0.5	2	28	19	32	21

same percentage of supported MoVPO phase, ($(Mo+V)/Ti = 1.6 \times 10^{-2}$) as a function of Mo/V ratio. C_2 conversion decreases with the Mo/V ratio while selectivity to acetic acid increases.

If we compare the results obtained for different Mo/V ratios at the same conversion, it is noticeable that selectivities to AcOH are almost the same.

3.3. Influence of P/(Mo + V) ratio

The effect of phosphorus was investigated on the MoVPO/TiO_2 catalyst corresponding to $Mo/V = 4$ with $(Mo+V)/Ti = 1.6 \times 10^{-2}$. Results are summarized in table 2. Results obtained at $P = 0$ wt% clearly show that P moderates the ethane conversion. The addition of P increases the AcOH yield, which goes to a maximum when P/(Mo + V) increases.

3.4. Characterization of MoVPO/TiO_2 catalysts

Whatever the loading, X-ray diffraction patterns for MoVPO/TiO_2 samples show only the spectrum of TiO_2-anatase without detection of any vanadium or molybdenum phosphate phases.

XPS studies (table 3) clearly indicate an enrichment in molybdenum and phosphorus on the surface of TiO_2. For example, in the case of the MoVPO/TiO_2 sample with $(Mo+V)/Ti = 1.6\%$ and $Mo/V = 1$, Mo/Ti was observed to be 4.2×10^{-2} by XPS against $Mo/Ti = 0.85 \times 10^{-2}$ by chemical analysis, while P/Ti was observed to be 10×10^{-2} by XPS against $P/Ti = 1.8 \times 10^{-2}$ by chemical analysis. For vanadium, this enrichment is less significant ($V/Ti = 1.5 \times 10^{-2}$ by XPS against 0.8×10^{-2} by chemical analysis). The V $2p_{3/2}$ signal is difficult to analyse because of the small quantities of vanadium, but we can estimate from the large contribution near 516.7 eV [22] that vanadium is mainly V^{4+} (about 75–80%). These results are confirmed by ESR and ^{51}V NMR which respectively show the presence of V^{4+} and V^{5+} species.

ESR spectra are presented in fig. 2. Molybdenum phosphate supported alone on TiO_2 (fig. 2a) is partially reduced to Mo^{5+} but when it is added to vanadium phosphate (figs. 2c and 2d) only Mo^{6+} remains. The ESR signal of VPO/TiO_2 (fig. 2b) shows that V^{4+} ions are well dispersed (hyperfine structure $g_{\parallel} = 1.93$ and $g_{\perp} = 1.98$, $A_{\parallel} = 2.0 \times 10^{-2}$ T and $A_{\perp} = 10^{-2}$ T). With the simultaneous presence of molybdenum (MoVPO/TiO_2) (figs. 2c and 2d), a new signal of V^{4+} ions appears ($g_{\parallel} = 1.93$ and $g_{\perp} = 1.99$, $A_{\parallel} = 1.85 \times 10^{-2}$ T and $A_{\perp} = 0.7 \times 10^{-2}$ T). It clearly indicates an influence of molybdenum on the state of vanadium.

This vanadium–molybdenum interaction is also evidenced by laser Raman spectroscopy in fig. 3. Small bands at 955 and 973 cm^{-1} are due to TiO_2 (fig. 3a). A band at 997 cm^{-1} is characteristic of molybdenum phosphate in MoPO/TiO_2 (fig. 3b), while a band at 1041 cm^{-1} is typical of vanadium phosphate in VPO/TiO_2 (fig. 3c). In the case of the mixed MoVPO/TiO_2 phosphate, besides the characteristic bands at 997 cm^{-1} (MoPO/TiO_2) and 1041 cm^{-1} (VPO/TiO_2), new bands appear at 987 cm^{-1} (evidenced for $Mo/V = 4$ (fig. 3d)), and $Mo/V = 1$ (fig. 3e)) and at 1030 cm^{-1} (evidenced mainly for $Mo/V = 1$ (fig. 3e)). The band at 1030 cm^{-1} is typical

Table 3
XPS results compared to chemical analysis ones

Samples MoVP/TiO_2	Molecular ratio obtained by chemical analysis ($\times 10^{-2}$)			Molecular ratio obtained by XPS ($\times 10^{-2}$)		
	Mo/Ti	V/Ti	P/Ti	Mo/Ti	V/Ti	P/Ti
(Mo+V)/Ti = 1.6%						
Mo/V = 4	1.3	0.3	1.8	4.6	–	7.2
Mo/V = 1	0.85	0.8	1.8	4.2	1.5	10
(Mo+V)/Ti = 3.2%						
Mo/V = 4	2.6	0.65	3.7	10.7	0.45	21.5
Mo/V = 1	1.6	1.65	3.4	8.15	5.6	17.9

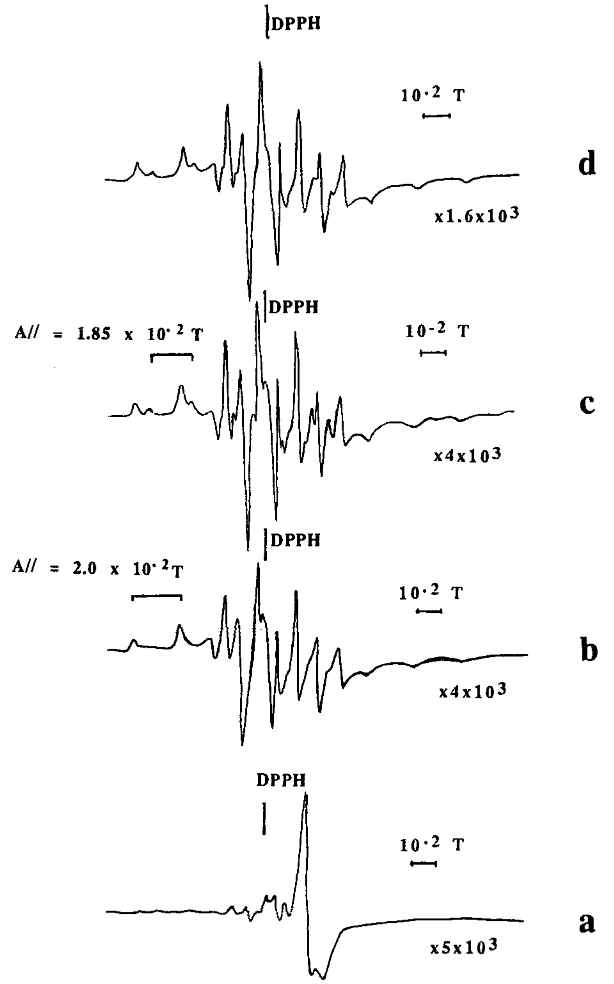

Fig. 2. ESR spectra recorded at room temperature. (a) $MoPO/TiO_2$; (b) VPO/TiO_2; (c) $MoVPO/TiO_2$, Mo/V = 4; (d) $MoVPO/TiO_2$, Mo/V = 1.

of a high dispersion of VO_x species on TiO_2, while the band at 987 cm^{-1} is typical of oligomeric species of MoO_x on TiO_2.

4. Conclusions

These results confirm the value of supporting TiO_2-anatase by a mixed MoVPO formulation to obtain good catalysts for ethane oxidation to acetic acid. The addition of molybdenum phosphate to vanadium phosphate, below the monolayer, improves the catalytic performance for the direct oxidation of ethane to acetic acid. This appears clearly in table 4 in which are compared the performance at 275°C and 7×10^5 Pa for the $MoVPO/TiO_2$ catalyst and for the VPO/TiO_2 catalyst for the same ethane conversion (2%): the $MoVPO/TiO_2$ formulation favors strongly the $AcOH/C_2H_4$ balance.

The fact that, for the $MoVPO/TiO_2$ catalyst, the selectivity to acetic acid is the same at isoconversion whatever the Mo/V ratio is consistent with participation only of vanadium sites in the formation of acetic acid.

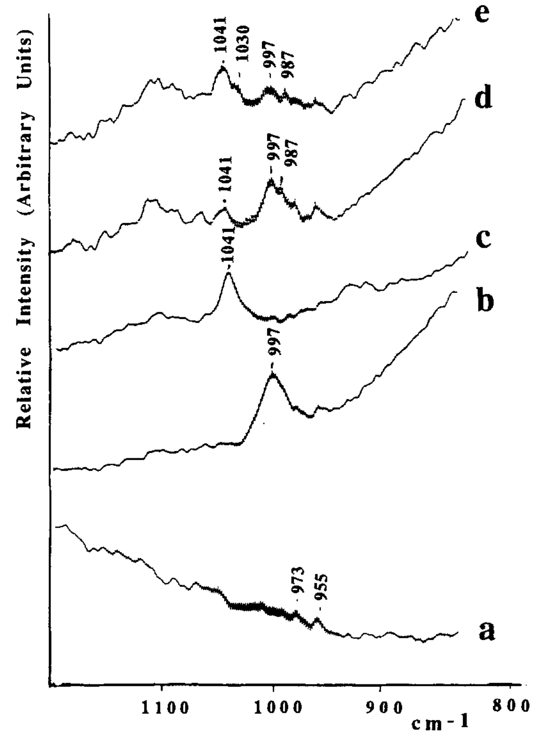

Fig. 3. Laser Raman spectroscopy spectra recorded at 200°C under dynamic air. (a) TiO_2 DT51; (b) $MoPO/TiO_2$; (c) VPO/TiO_2; (d) $MoVPO/TiO_2$, Mo/V = 4; (e) $MoVPO/TiO_2$, Mo/V = 1.

The XPS study of the $MoVPO/TiO_2$ catalyst has shown an enrichment in molybdenum and phosphorus which is mainly not observed for vanadium. This should be in favour of a higher density of molybdenum and phosphorus around vanadium atoms which should explain a better isolation of the working vanadium sites favouring further oxidation of the intermediates to acetic acid.

A local molybdenum–vanadium interaction appears from the electronic spin resonance studies. Indeed V^{4+} and V^{5+} on one hand, and Mo^{6+} species on the other hand are observed which evidence that electronic transfers may occur in the case of the $MoVPO/TiO_2$ formulation, changing the electronic density around vanadium and thus favouring the catalytic scheme towards acetic acid.

Raman spectroscopy confirms the existence of a specific interaction between molybdenum and vanadium from the new features which are observed on the spectra

Table 4
Comparison of the catalytic results for VPO/TiO_2 and $MoVPO/TiO_2$

Catalysts	T (°C)	P (bar)	Conv. (%)	Selectivities (%)	
				AcOH	C_2H_4
VPO/TiO_2	275	7	2	20	20
$MoVPO/TiO_2$ [a]	275	7	2	32	6

[a] Mo/V = 4, (Mo + V)/Ti = 1.6×10^{-2}, GHSV = 334 h^{-1}.

of the mixed supported phosphate oxides catalysts, which is consistent with the observation of V^{4+} by ESR.

TiO_2-anatase appears to be important in this catalytic system. Indeed, it is well known that this support favours the interactions with the supported phases and improves the dispersion [23]. The high oxidizing power of TiO_2 [24] and its peculiar electrical conductivity properties should also play a determining role favouring the oxygen transfers. All these aspects are presently under study and will be the object of a forthcoming publication.

Acknowledgement

We thank Rhône-Poulenc Company for financial support of this study.

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