ELSEVIER

Catalysis Today 24 (1995) 335–340

CATALYSIS TODAY

Active specie on vanadium-containing catalysts for the selective oxidation of ethane to acetic acid

L. Tessier [a], E. Bordes [a], M. Gubelmann-Bonneau [b]

[a] *Département de Génie Chimique, Université de Technologie de Compiègne, B.P. 649, 60206 Compiègne Cédex, France*

[b] *Rhône–Poulenc, Centre de Recherches d'Aubervilliers, 52 rue de la Haie-Coq, 93308 Aubervilliers Cédex, France*

Abstract

Catalytic experiments on pure VPO phases and titania supported VPO_x and VO_x are presented for the selective oxidation of ethane to acetic acid. The effects of temperature, pressure, contact time and feed conditions are examined. The characterization of catalysts by several methods shows that different specie are present on titania according to the loading V/Ti. The correlation with catalytic results allows to propose that polyvanadates are the active specie responsible for the formation of acetic acid from ethane.

1. Introduction

Compared to the chemical processes of naphtha oxidation and methanol carbonylation presently used to obtain acetic acid, the direct selective oxidation of ethane would be very attractive. Ethane is indeed a cheap raw material and has little application except vapocracking. The process itself would be of low cost, owing to the easy separation of products. Partial oxidation of ethane is however very difficult because of its low reactivity. The break of C–H is supposed to happen on a hard base like an oxygen of the catalytic oxide linked to a hard acid cation [1], but after this initial attack the difficulty is to insert two oxygens in the intermediate molecule to get acetic acid and to avoid deeper oxidation.

After the pioneering work made by Thorsteinson et al., on Mo–V–Nb–O catalysts [2], the mild oxidation of ethane has been recently studied on several catalytic systems [3–12]. The main reaction products are ethylene and CO_x with oxygen as oxidant. The formation of significant amounts of acetic acid has been recently claimed for titania supported catalysts [9–11] or solids containing vanadium with other elements. The best performance is generally obtained at superatmospheric pressure (10-30 bars) at 250–320°C in fixed or fluidized bed reactors. Except in the work presented by Merzouki et al., who found acetic acid at atmospheric pressure and studied several catalysts [12,13], no information is given in the literature about relations between structural properties and catalytic behavior. In this paper we report the results obtained with pure and titania supported VO_x and VPO_x catalysts in the oxidation of ethane to acetic acid (AcOH). The influence of experimental parameters on the catalytic properties will be examined and a description of active sites will be proposed.

SSDI 0920-5861(95)00055-0

2. Experimental

$VOPO_4 \cdot 2H_2O$ was prepared by refluxing H_3PO_4 (85%) and V_2O_5 in water [14], and used as such in the reactor. $VOHPO_4 \cdot 0.5H_2O$ and $VO(H_2PO_4)_2$ were obtained by reduction of a mixture of V_2O_5 and H_3PO_4 (85%) in alcoholic media [15]. The calcination of precipitates in N_2 at 500°C (24 h) led respectively to $(VO)_2P_2O_7$ and $VO(PO_3)_2$. Titania used to support active phases was anatase DT51 (Rhône–Poulenc), with a surface area of 86 m^2/g, a pore volume of 0.30 cm^3/g and a mean particle size of 20–30 nm. VO_x/TiO_2 and VPO_x/TiO_2 were synthesized by impregnation of titania, the first one by NH_4VO_3 (V/Ti = 1.6-20.0 mol.%), and the second by a solution of $VOPO_4 \cdot 2H_2O$ reduced with oxalic acid, at a fixed loading of V/Ti = 5.2 mol.%. Calcination was performed in air at 500°C (4 h). Catalysts were characterized by several methods (XRD, FT-IRS, TEM and XPS).

A continuous flow Inconel microreactor (80 mm length and 16 mm diameter) containing typically 3 cm^3 of powdered catalyst was heated by means of a fluidized sand bath furnace in the range 175-375°C. C_2H_6, O_2 and N_2 were controlled by mass-flow rates and mixed in a preheater before feeding the fixed bed reactor. Water could be cofed by means of a HPLC pump and directly vaporized in the preheater. Total pressure was regulated between 1 and 20 bars (abs). The analysis of products was performed on two gas chromatographs, one to detect AcOH (H_3PO_4 modified LAC 446 column and FID) and the other to separate O_2, N_2, CO, CO_2, CH_4, C_2H_6 and C_2H_4 (Hayesep A column and TCD). Owing to the low reactivity of ethane, its conversion was calculated from the sum of the yields of reaction products. Productivity is expressed as the weight of AcOH per liter of catalyst and per hour ($g_{AcOH} \cdot l_{cat}^{-1} \cdot h^{-1}$).

Catalytic tests were generally conducted at $C_2/O_2/N_2 = 85/5/10$ at a total flow rate of 10 Nl/h. Contact time was 1.1 s (NCTP), and total pressure between 1 and 16 bars (abs). In these strongly reducing conditions the maximum theoretical yield of AcOH is 3.9 mol.%, with conversions of ethane and oxygen $C_{C2} = 3.9$ and $C_{O2} = 100\%$ respectively, for a selectivity in acetic acid $S_{AcOH} = 100\%$.

3. Results

3.1. Unsupported catalysts

Among the three phases α-$VOPO_4$, $(VO)_2P_2O_7$ and $VO(PO_3)_2$, only the latter oxidizes ethane to AcOH. The reaction takes place at 1 bar and 200-300°C and no product other than AcOH is detected. This confirms the results already published (S_{AcOH} ca. 100 mol.%) using different conditions [12,13]. In the present case the conversion is lower ($C_{C2} < 0.1$ mol.%) and decreases rapidly with time.

Above 300°C, CO and ethylene are formed at the expense of AcOH. Combustion is very low up to 375°C. At this temperature, conversion of ethane is $C_{C2} = 0.25$ mol.%, $S_{AcOH} = 4$ mol.% and selectivity in ethylene and CO_x are respectively 82 and 14 mol.%. A similar trend is observed when the amount of ethane in the feed is decreased ($C_2/O_2/N_2 = 75/15/10$), except that C_{C2} is higher and that ethylene occurs at a lower temperature (275°C). A lower C_2/O_2 ratio favors the formation of ethylene.

3.2. VPO_x/titania catalyst

At atmospheric pressure, VPO_x/TiO_2 (V/Ti = 5.2 mol.%) exhibits the same behavior than pure $(VO)_2P_2O_7$, but no deactivation is observed for five days. Higher conversions of ethane are obtained, and AcOH is formed at temperature as low as 200°C with a good selectivity. Conversion increases with temperature, and S_{AcOH} decreases while selectivities in ethylene and CO_x increase (Fig. 1). The productivity in AcOH is maximum at 275°C and amounts to 19 $g_{AcOH} \cdot l_{cat}^{-1} \cdot h^{-1}$.

An increase of total pressure at 250°C results in the increase of C_{C2} and slow decrease of S_{AcOH} (C_{C2} and S_{AcOH} 0.5 and 51 mol.% at P = 1 and 1.1

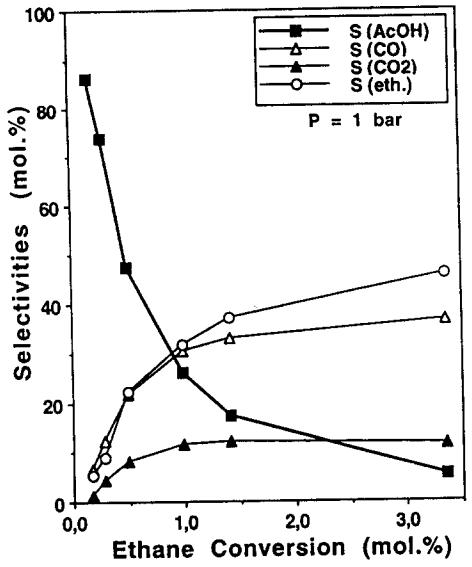


Fig. 1. VPO_x/TiO_2 catalyst. Selectivities products vs. conversion of C_2H_6 at different temperatures (200–300°C, P = 1 bar, $C_2/O_2/N_2 = 85/5/10$).

and 39 at P = 10 bars respectively), but yields of AcOH increase. At a given temperature and same conversion however, the selectivities in AcOH are always higher at superatmospheric pressure (Fig. 2). Productivity in AcOH is also higher, 32 at P = 16 bars instead of 19 $g_{AcOH} \cdot 1_{cat}^{-1} \cdot h^{-1}$ (P = 1) for example.

The best performance is observed by combining the effects of pressure and steam. For example at 275°C and 10 bars, a feed containing steam ($C_2/O_2/N_2/H_2O = 85/5/10/9$) is converted at $C_{C2} = 3.3$ mol.%, with $S_{AcOH} = 29$ mol.% and a good productivity, $P_{AcOH} = 72$ $g_{AcOH} \cdot 1_{cat}^{-1} \cdot h^{-1}$ (see Table).

The effect of the contact time τ on the yields of products has also been examined. At 250°C and 1 bar an increase of τ leads to a non linear behavior of the yield of AcOH, which reaches a plateau when $\tau \geq 1.1$ s, while yields in other products are normally increasing (Fig. 3).

3.3. *VO_x/titania catalysts*

Five VO_x/TiO_2 catalysts with various loadings (V/Ti = 1.6-19.8 mol.%) have been studied in the range 175-275°C, at atmospheric pressure and in the usual conditions as described above. The composition V/Ti = 11.4 mol.% for a theoretical monolayer of VO_x has been calculated by the method of Bond et al. [16].

Increasing the vanadium loading up to the value of theoretical monolayer leads to an improvement of selectivity in AcOH (at the same conversion) (Fig. 4), which reaches a plateau for V/Ti>11.4 mol.%. The same trend is observed for productivity which can be very low at low loadings.

The distribution of reaction products is similar for all five catalysts. AcOH is selectively produced at a temperature as low as 175°C, but CO appears at 200°C, and ethylene, CO_2 at 225°C. The catalytic activity is high since conversion of oxygen is 100 mol.% above 250°C. When temperature increases, S_{AcOH} decreases rapidly while selectivities of ethylene and CO_x increase.

The comparison with VPO_x/TiO_2 shows that VO_x/TiO_2 catalysts are generally more active. Restricting ourselves to samples which composition corresponds to the theoretical monolayer (V/Ti = 5.2 and 11.4 mol.% for VPO_x and VO_x respectively), selectivities are higher at similar conversion (Table). However at the same temperature the productivity can be higher (at 250°C

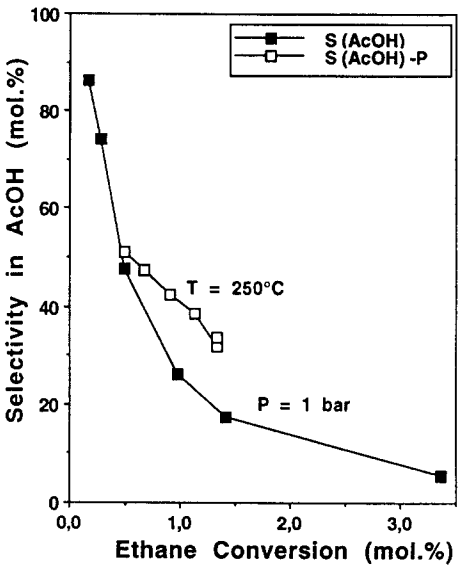


Fig. 2. VPO_x/TiO_2 catalyst. Selectivity in AcOH vs. conversion of C_2H_6, (a) variable T (200–300°C) at P = 1 bar, (b) 250°C and variable pressure (1–16 bars); $(C_2/O_2/N_2 = 85/5/10)$.

Table
Comparison of performance of VPO_x/TiO_2 and VO_x/TiO_2

Temp (°C)	C_2 Conv. (mol.%)		S_{eth} (mol.%)		S_{AcOH} (mol.%)		P_{AcOH} $g_{AcOH}.l_{cat}^{-1}.h^{-1}$	
	VPO_x	VO_x	VPO_x	VO_x	VPO_x	VO_x	VPO_x	VO_x
225	-	0.5	-	8	-	73	-	25
250	0.5	1.0	22	18	48	36	18	26
275	1.0	3.2	32	25	26	3	19	7

P = 1 bar, $C_2/O_2/N_2$ = 85/5/10. Loadings (V/Ti, mol.%): VPO_x: 5.2, VO_x: 11.4.

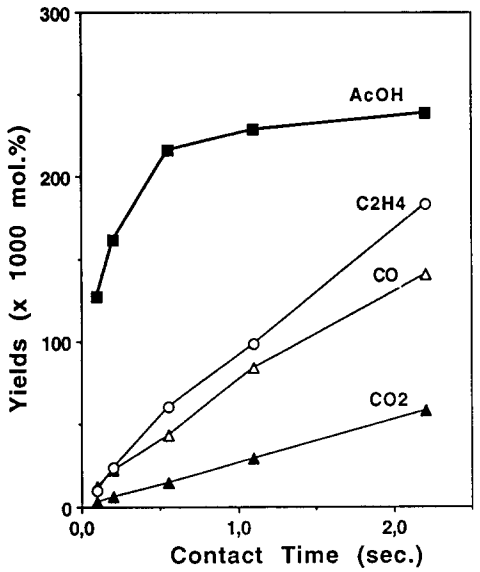


Fig. 3. VPO_x/TiO_2 catalyst. Yields of products vs. contact time (T = 250°C, P = 1 bar, $C_2/O_2/N_2$ = 85/5/10).

P_{AcOH} = 18 and 26 $g_{AcOH} \cdot l_{cat}^{-1} \cdot h^{-1}$ respectively), or lower if production of CO_x becomes too large. The influence of contact time is similar to that observed with VPO_x/TiO_2.

3.4. Characterization of catalysts

The XRD patterns of unsupported VPO phases are in good agreement with those in literature [15]. Even after a long exposure to X-rays (15 h), only TiO_2 anatase is detected in patterns of supported catalysts. No change was observed after catalytic experiments.

XPS experiments performed on VPO_x/TiO_2 and VO_x/TiO_2 (V/Ti = 11.4%) before reaction show that surface V/Ti ratio is significantly higher than the one used for preparation. This indicates an enrichment in active VO_x or VPO_x specie on the surface of anatase. An improved analysis of the spectra leads to the conclusion that, in spite of the oxidising conditions of calcination, vanadium is partially reduced: 38 and 29% of total vanadium is V(IV) for VPO_x/TiO_2 and VO_x/TiO_2 respectively. X-emission (TEM) experiments on VPO_x/TiO_2 clearly show the homogeneous distribution of V, P, specie on the surface, but with local enrichment in vanadium.

The FT-IR spectrum of VO_x/TiO_2 is different according to the loading. A band at 1014-1020 cm^{-1} assigned to vanadyl groups in V_2O_5 crystallites appears progressively for loadings higher than V/Ti = 6.6 mol.%. Vanadyl bond wave-

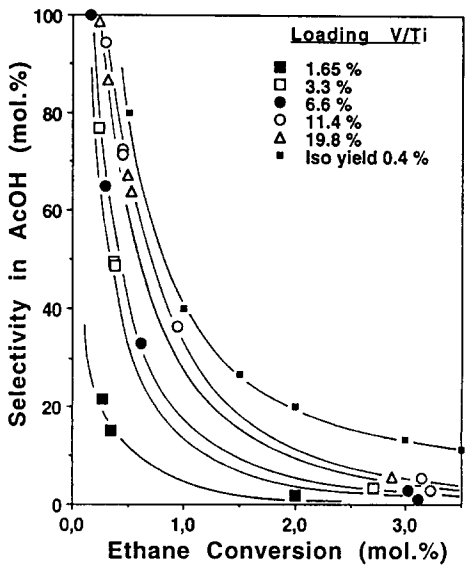


Fig. 4. VO_x/TiO_2 catalyst. Selectivity in AcOH vs. conversion of C_2H_6 for various V/Ti loadings (P = 1 bar, $C_2/O_2/N_2$ = 85/5/10).

number is usually at 1028 cm^{-1} in V_2O_5 [17], but a shift towards lower wavenumbers is observed for loadings 19.8 (1020 cm^{-1}) and 11.4 mol.% (1015 cm^{-1}). This shift, which corresponds to the weakening of V=O bond, could be related to the existence of V^{4+} and to a stronger interaction between VO_x specie and TiO_2. Bands in the range 970-995 cm^{-1} are detected for all samples except for V/Ti=1.65%, and are assigned to bidimensional polyvanadates containing vanadyl groups [18]. These $[VO_x]_\infty$ polyvanadates seem to coexist with V_2O_5 crystallites for loadings 11.4 and 19.4 mol.%. Isolated vanadyl groups (band at 952 cm^{-1}) are present at low coverages, like in the case of V/Ti=1.65 mol.%.

4. Discussion

4.1. Nature of the active sites

Catalytic experiments on VO_x/TiO_2 show an improvement of the performance as the vanadium coverage increases up to the monolayer. For higher loadings (e.g. V/Ti=19.8 mol.%), no change in catalytic behavior occurs, whereas for very low loading (V/Ti=1.65 mol.%), a high degradation of ethane to CO_x is observed (S_{COx}=85 mol.%). According to these results, the optimum loading V/Ti for good performance lays between 6.6 and 11.4%.

FT-IR study shows that isolated vanadyl specie with very weak V=O bonds are present in compounds with V/Ti=1.65 mol.%. At higher loadings, condensation of isolated vanadyl groups to bidimensional polyvanadates happens, up to the real monolayer which corresponds approximately to 70% of the theoretical value [19,20]. These $[VO_x]_\infty$ polyvanadates could also be present on VPO_x/TiO_2 since X-emission revealed a partial segregation between vanadium and phosphorus. When more than a real monolayer is concerned, crystallites of V_2O_5 can coexist with the bidimensional polyvanadates, and this results in no more increase of catalytic performance. Such a situation has already been observed with $VO_2(B)/TiO_2$ [12]. The loss of activity and selectivity observed because of its instability on stream was correlated with the fact that $VO_2(B)$ was reoxidized to V_2O_5.

By comparing these data, it seems now quite clear that $[VO_x]_\infty$ polyvanadates are responsible for the formation of AcOH from ethane. In the case of VPO_x/TiO_2, the same specie may exist and be active for the reaction. The high selectivity in AcOH observed could be due to the isolation [21] of active vanadium sites by phosphate groups, as already proposed for VPO catalysts in the oxidation of butane to maleic anhydride. Moreover, among the pure phases we studied, only $(VO)_2P_2O_7$ is able to transform ethane to AcOH, at very low conversion but with a very good selectivity. Its structure differs from those of α-$VOPO_4$ and $VO(PO_3)_2$ by the presence of pairs of edge-sharing vanadium octahedra [15] (Fig. 5). Therefore one can correlate the presence of these vanadyl dimers to the high selectivity in AcOH observed. This suggests that the $[VO_x]_\infty$ polymeric specie just described for the supported catalysts could be as small as these dimers (Fig. 5).

4.2. Influence of operating conditions

For all catalysts, selectivity in AcOH decreases by increasing temperature, while ethylene and CO_x become the main reaction products. This fact was already noted in the case of $(VO)_2P_2O_7$ [12,13]. It seems that two mechanisms exist according to temperature, one leading to AcOH at low temperature (180–250°C), and the other to ethylene and CO_x at higher temperature (>250°C). This hypothesis is confirmed by recent experiments performed on VPO_x/TiO_2 [22], which indicate that ethylene is not a major intermediate leading selectively to acetic acid, and that the latter is not transformed to CO_x in catalytic conditions.

On the other hand, catalytic experiments clearly show an inhibition of the formation of acetic acid. Experiments consisting in feeding some acetic acid together with the usual ethane/oxygen/nitrogen do not result in an increase of the amount of

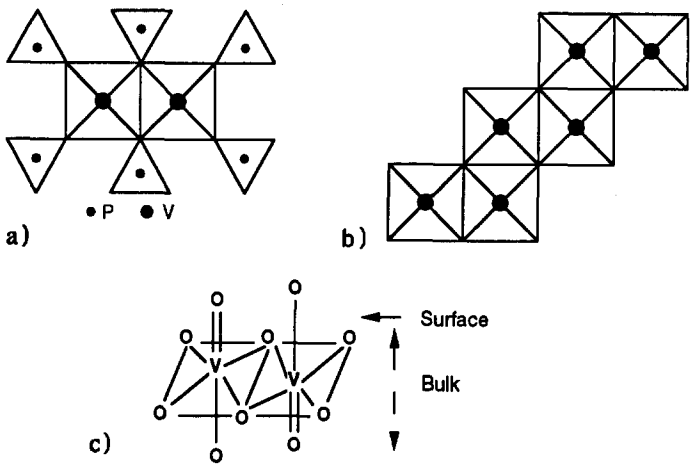
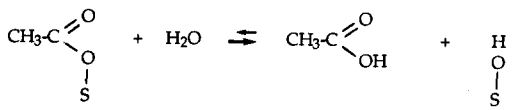


Fig. 5. Hypothetic polyhedral active sites, a) basic unit for $(VO)_2P_2O_7$ and VPO_x/TiO_2, b) VO_x/TiO_2; c) sites common to $(VO)_2P_2O_7$ (bulk) and V_2O_5.

AcOH formed. This means that the step of desorption of acetic acid could be rate-determining. This inhibiting step would explain why the AcOH yield reaches a plateau when contact time increases. Moreover, the action of steam which contributes to the increase in selectivity of AcOH could be explained by using the same hypothesis. Steam would indeed be responsible for the shift of the adsorption–desorption equilibrium of AcOH towards desorption, according to the following scheme:



where S is a catalytic site. The beneficial influence of steam in production of organic acids like acrylic or methacrylic acids is indeed well known. A kinetic investigation is presently on the way to account for this hypothesis.

5. References

[1] E. Bordes, in Elementary Steps in Catalysis, R.W. Joyner and R.A. van Santen, Eds., Kluwer Academic Publishers, 1993, pp.137-153.
[2] E.M. Thorsteinson, T.P. Wilson, F.G. Young, P.H. Kasai, J. Catal., 52 (1978) 116
[3] V.R. Choudhary and V.H. Rane, J. Catal., 135 (1992) 310.
[4] R. Burch and R. Swarnakar, Appl. Catal., 70 (1991) 129.
[5] G. Centi and F. Trifiro, Catal. Today, 3 (1988) 151.
[6] K. Otsuka, Y. Uragami and M. Hatano, Catal. Today, 13 (1992) 667.
[7] S.T. Oyama, J. Catal., 128 (1991) 210.
[8] K. Wada, K. Yoshida, Y. Watanabe and T. Suzuki, Appl. Catal., 74 (1991) L1.
[9] P. Barthe and G. Blanchard, Eur. Pat. 479,692 (1992)
[10] L. Tessier, E. Bordes, F. Blaise, M. Gubelmann-Bonneau, Fr. Pat. Appl. 06,475 (1993).
[11] BP Chem., Eur. Pat. 407,091 (1991), Eur. Pat. 480,594 (1992); Sohio, Eur. Pat. 546,677 (1993).
[12] M. Merzouki, B. Taouk, L. Monceaux, E. Bordes and P. Courtine, Stud. Surf. Sci. Catal. 72 (1991) 165.
[13] M. Merzouki, B. Taouk, L. Tessier, E. Bordes, P. Courtine, Proc. 10th Int. Cong. Catal., 753 (1992).
[14] G. Ladwig, Z. Anorg. Allg. Chem., 338 (1965) 265.
[15] E. Bordes, Catal. Today, 1 (1987) 499; ibid., 3 (1988) 163-174.
[16] G.C. Bond, K. Bruckmann, Faraday Disc. Chem. Soc., 72 (1981) 235.
[17] R.Y. Saley, I.E. Wachs, S.S. Chan and C.C. Cherish, J. Catal., 98 (1986) 102.
[18] G.T. Went, L.J. Leu and A.T. Bell, J. Catal., 134 (1992) 579.
[19] G.C. Bond, J.P. Zurita and S. Flamerz, Appl. Catal., 22 (1986) 361.
[20] J.M. Lopez-Nieto, G. Kremenic and J.L.G. Fierro, Appl. Catal., 61 (1991) 235.
[21] R.K. Grasselli, Surface Properties and Catalysis by Non Metals, Elsevier, Amsterdam, 273 (1983).
[22] M. Gubelmann-Bonneau, unpublished results.