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Effects of the structural and cationic properties of $AV_2P_2O_{10}$ solids on propane selective oxidation

L. Savary [a,*], G. Costentin [a], M.M. Bettahar [a], A. Grandin [b], M. Gubelmann-Bonneau [c], J.C. Lavalley [a]

[a] *Laboratoire Catalyse et Spectrochimie, ISMRA, 6 Bd du Maréchal Juin, 14050 Caen Cedex, France*
[b] *CRISMAT, ISMRA, 6 Bd du Maréchal Juin, 14050 Caen Cedex, France*
[c] *Rhône-Poulenc Recherches, 52 rue de la Haie Coq, 93308 Aubervilliers, France*

Abstract

The activity performances of five $AV_2P_2O_{10}$ compounds of either orthorhombic (A = Cd, Ca), or monoclinic (A = Cd, Ba, Pb) symmetry types, have been compared for propane partial oxidation. They present a rather good activity (9% of propane conversion at 460°C) and a high selectivity (60% of propene selectivity). Results are discussed as a function of the differences in the structural properties. Kinetic studies were also performed for propane and propene oxidation reaction.

Keywords: Structural properties; Cationic properties; $AV_2P_2O_{10}$ solids; Propane selective oxidation

1. Introduction

Vanadium stabilized in a low oxidation state in a suitable crystalline matrix seems to be a key element for the selective oxidation of light alkanes [1]. This feature prompted us to study new VPO oxides: we report here results obtained over $AV_2P_2O_{10}$ oxides in the selective oxidation of propane. Indeed, in these compounds, the vanadium ion is maintained in the V^{4+} state in either an isostructural orthorhombic (o) symmetry framework (A = Ca, Cd) [2,3], or monoclinic (m) symmetry frameworks (A = Cd, Ba, Pb) [4–6]. The aim of this study is to obtain information on a possible relation between structural and/or cation properties and catalytic propane oxidation performances. These performances are compared with propene oxidation results obtained under the same conditions and kinetics experiments were performed with the two reactions.

2. Experimental

The $AV_2P_2O_{10}$ compounds were prepared by solid–solid reactions at high temperature [2–7] in order to obtain well-defined structures as verified by XRD. The surface areas are therefore quite low ($\approx 1\ m^2/g$). No structural modifications have been detected by XRD after catalytic tests.

The catalytic experiments, previously related in [7], were carried out in a quartz continuous fixed bed reactor under the following conditions: $C_3H_8\ (C_3H_6)/O_2/N_2 = 3/1/1$, $W/F =$

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[*] Corresponding author.

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2.1 g l^{-1} h, in the temperature range of 310 to 460°C, after catalyst (1 g) pretreatment (300°C, 2 h) under the reactant feed. Kinetic studies have been performed on the Cd(o) catalyst at 410°C, by plotting selectivities as function of contact time.

3. Results and discussion

3.1. *Structural effects in propane selective oxidation*

Under propane feed (Table 1a) the conversions increase with temperature (reaching 6–8.5% at 460°C). Propene is the main product formed and obtained with good selectivities even at high conversions (up to 55% at 8.5% conversion for $CdV_2P_2O_{10}$(m)). The $AV_2P_2O_{10}$ system is therefore quite good in the oxydehydrogenation reaction (ODHR) of propane as compared to other VPO systems [8–11]. Acrolein appears as minor product, mainly at high temperature (6% selectivity at 411°C for $CdV_2P_2O_{10}$(o)). Balance is CO_x. The reported results show a marked effect of both the general arrangement of the host lattice, and the nature of the inserted cation.

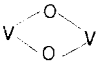
3.1.1. *Organization of the host lattice polyhedra*

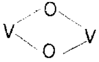
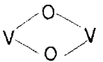
Comparison between the two $CdV_2P_2O_{10}$ phases which only differ by the symmetry of their host lattice, shows that the monoclinic phase is sensibly more reactive than the orthorhombic phase (propane conversion: 8.5% against 6.5% at 460°C). Propene selectivity decreases when temperature increases in the case of the orthorhombic phase, whereas it passes

Table 1
Catalytic results in the oxidation of propane and propene, W/F = 2.1 g l^{-1} h

	Temperature (°C)	Ca	Cd(o)	Cd(m)	Ba	Pb
(a) Propane: Test conditions: $C_3H_8/O_2/N_2 = 3/1/1$						
C_3H_8 conversion	310	0.6	0.9	0.6	0.65	1
	360	1.6	1.85	1.8	1.1	3.6
	411	3.3	3.6	3.8	3	5
	460	6.3	6.5	8.5	7.6	5.9
Propene (acrolein) selectivity	310	86 (1)	73 (1)	68 (1.1)	59 (1)	0
	360	84.5 (2)	64.5 (3)	80 (1)	65 (0.5)	0
	411	73.5 (2)	37 (6)	74 (1.5)	72.5 (1.5)	0
	460	61 (2.5)	42 (4)	55 (2)	59 (1.5)	17 (0.5)
CO_x (* $= CO_2$) selectivity	310	12	21	20	18	99*
	360	11.5	28	18.5	31	99*
	411	23.5	55	24	25	99*
	460	37	51	42	39	82*
(b) Propene: test conditions: $C_3H_6/O_2/N_2 = 3/1/1$						
C_3H_6 conversion	311	1.6	1.1	1.2	1.8	0.9
	360	9.5	7	6.5	9	3.3
	411	18.5	17	20	19	8.9
	460	21.5	20	23	21	16.7
Oxygenated products (acrolein) selectivity	311	56(24)	43 (26)	50 (25)	56 (24)	53 (26)
	360	42.5 (23.5)	33 (20)	34 (22.5)	33 (21)	45 (37.5)
	411	29 (22.5)	20 (16.5)	23.5 (20)	19.5 (16)	36 (33)
	460	30 (27)	21 (19)	28 (26)	19.5 (17.5)	31 (30)
CO_x selectivity	311	44	57	50	44	47
	360	55	65	65	65	52
	411	68.5	78.5	75	80	62
	460	67	77	70	78	67

through a maximum in the case of the monoclinic phase.

These results could be related to the V–O bonding types and size of the vanadium clusters present in the two frameworks. Indeed, we have shown that, if both matrices exhibit a 'linked vanadyl bond' (V = O bond in a V–O–V bridge), the 'free' vanadyl bond (its O atom is only linked in a covalent way to one vanadium atom) only exists in the monoclinic framework. Moreover, the monoclinic host lattice is also characterized by the existence of the double bridge  groups [7].

Many authors have discussed about the role of such entities in selective oxidation [12–15]. As far as our catalysts are concerned, if the highest propane conversion and propene selectivity is obtained when both V · · · O = V and  entities are present, lower activity and propene selectivity are obtained when only the V · · · O = V bridge is present. Therefore, it seems that the two latter entities act at the opposite: if the V · · · O = V bridge may, as suggested by Corma [13], enhance alkene degradation, the double bridge  and/or the 'free' vanadyl bond site lead to an increase of alkane conversion and alkene selectivity.

Another way to analyze the structural differences between the two phases is the size of the vanadium atoms groups: the monoclinic phase consists in clusters of four vanadium atoms[4], whereas the orthorhombic phase consists in V_∞ infinite chains [3], these two kinds of V units being connected together through PO_4 tetrahedra. We can note that the more limited the size of the V unit, the higher the selectivity in propene is. This feature is in agreement with observations previously reported on other systems [16].

3.1.2. Inserted cation effect

To evaluate this effect correctly, it is necessary to consider the isotypic compounds separately, thus the orthorhombic and monoclinic isotypic phases are compared successively.

The $CaV_2P_2O_{10}$ and $CdV_2P_2O_{10}$ isotypic orthorhombic compounds exhibit the same activity in the whole range of temperature but the former is more selective in propene (86–61% against 73–42%) than the latter. As the two ions have the same ionic radius, and therefore the same environment, they only differ by a higher covalent character of the Cd–O bond as compared to the Ca–O one. This particularity could induce some different electronic effects on the neighbouring vanadium atoms and modify the redox properties in such a way the Ca phase is more selective than the Cd one.

The $CdV_2P_2O_{10}$ monoclinic compound cannot be considered for the cation effect because its structure results from the ones of $BaV_2P_2O_{10}$ and $PbV_2P_2O_{10}$ by important distortions [4]. The two latter isotypic compounds behave strongly differently in the selective oxidation of propane. Indeed, their activity depends on the reaction temperature. In addition, the Ba compound is much more selective in propene (up to 59% against up to 17%) whereas the Pb compound mainly leads to a total oxidation (82–99% against 18–39%). The electronic effect inherent to the higher covalent character of the Pb^{2+}–O bond as compared to the exclusively ionic character of the Ba^{2+}–O bond leads to results in agreement with those deduced above. The geometric effect of the size of the inserted cation has also to be considered. Because of the smaller size of Pb(II) as compared to that of Ba(II), and of the steric effect of its $6s^2$ lone pair, the two cations exhibit significantly different environments [6], with in particular, an important anisotropy in the arrangement of the oxygen atoms around Pb^{2+} in opposite to a quite isotropic environment for the Ba cation. This particularity could induce some differences in the oxygen mobility of the two phases.

In order to verify if the propene is the intermediate in acrolein formation, propene oxidation was performed under the same conditions as propane oxidation.

Under propene feed (Table 1b), the conversion increases with the reaction temperature up

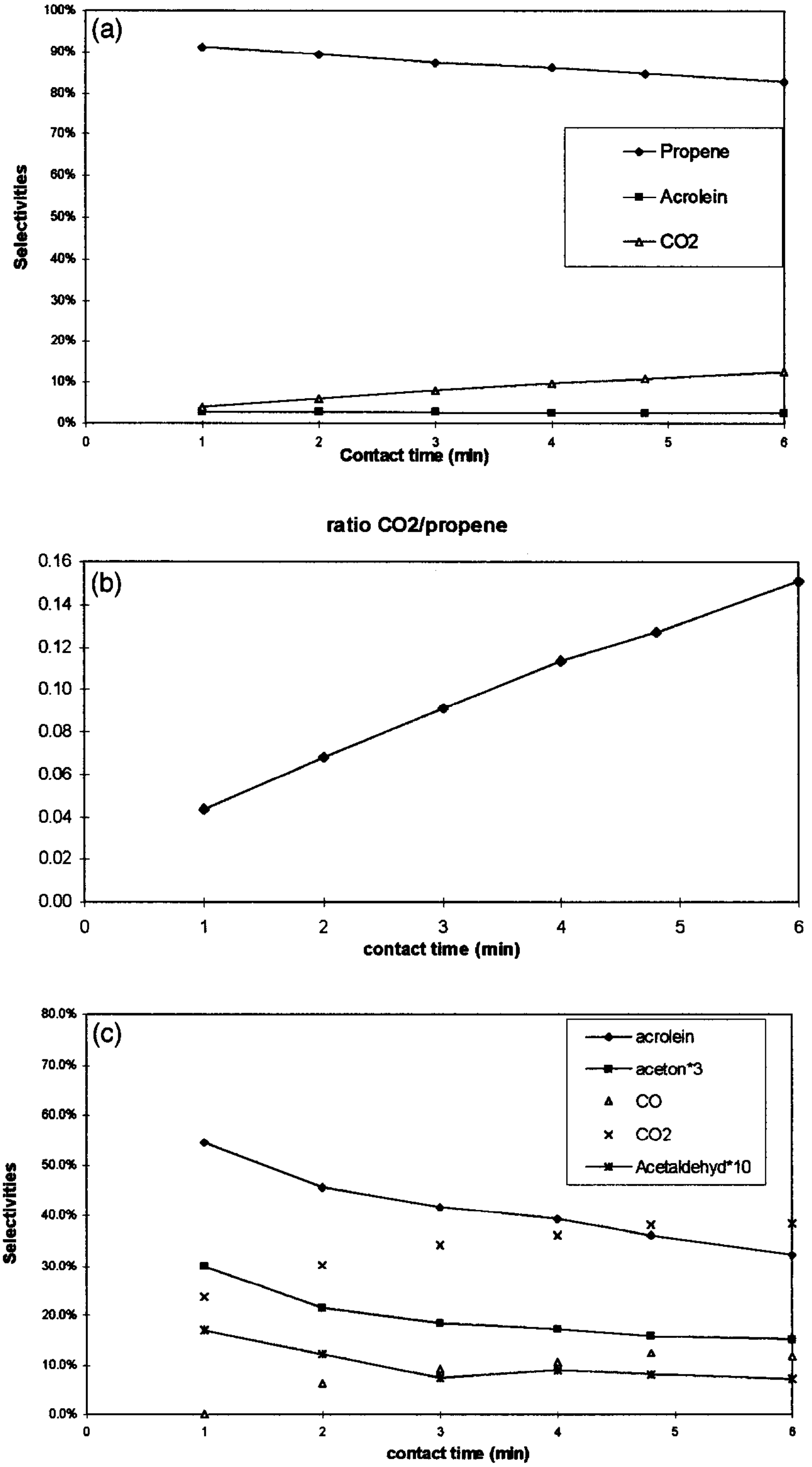


Fig. 1. (a) and (b) Kinetic study of propane oxidation on $CdV_2P_2O_{10}$(o). (c) Kinetic study of propene oxidation on $CdV_2P_2O_{10}$(o).

to 23%. The main product is acrolein (20–25%), the other being acetone, acetic acid, and acetaldehyde. Balance is CO_x.

Under different reaction conditions, it was shown that the propene partial oxidation over the same catalysts is also a structure sensitive reaction [7]. The conditions used in the present study enhance secondary reactions and do not allow the different catalysts to be differentiated enough from each other, and, in addition, when a high temperature is used, $T = 411–460°C$, diffusion phenomena seem to occur ($E_a = 5$ kcal/mol).

The observed propene conversions (20–25%) and oxygenate selectivities (20–56%) are quite low (Table 1b). The $AV_2P_2O_{10}$ catalysts thus activate moderately, explaining the good propene selectivities obtained (Table 1a) in the ODHR of propane, even at the highest temperature considered (Table 1a).

4. Kinetic study of propane and propene selective oxidation

Kinetic studies using the method of variation of the selectivities as a function of the contact time were performed at 400°C for the $CdV_2P_2O_{10}$(o) catalyst. When propane is in the feed gas (conversion < 2%), the observed selectivity at zero contact time (Fig. 1a and Fig. 1b) seems to indicate that CO_2 is partly directly produced from propane. Calculations based on the results given in Table 1a and Table 1b assuming that propene is the intermediate to oxygenated products and that the rate law of propene oxidation is the same whatever the reactant atmosphere, confirm the kinetic conclusions. Fig. 1a also shows that acrolein and propene are probably formed directly from propane but, both by independent ways. In the case of propene selective oxidation (Fig. 1c), it can be seen that the oxygenates are primary products whereas the CO_x stem from them via secondary reactions.

5. Conclusions

The $AV_2P_2O_{10}$ compounds are quite good in the ODHR of propane, with a good selectivity in propene. Structure–activity relationships have been analyzed in terms of the nature of the active sites and of the geometric and electronic effects induced by the inserted cations. In addition, propane and propene partial oxidation results were analysed, and the involved reaction paths were discussed.

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