Structural Effects on Propane Mild Oxidation from Comparative Performances of Molybdenum and Vanadium Phosphate Model Catalysts

G. Costentin,*,† L. Savary,† J. C. Lavalley,† M. M. Borel,‡ and A. Grandin‡

Laboratoire de Catalyse et Spectrochimie and Laboratoire CRISMAT, ISMRA,
6 Bd Maréchal Juin 14050, Caen Cedex, France

Received March 26, 1997. Revised Manuscript Received October 2, 1997⊗

Thirty well-defined catalysts AMPO (A = alkaline, alkaline earth metal, Cd, Pb, Ag; M = Mo, V) with different compositions and structures were tested for propane mild oxidation in the same conditions ($C_3H_8/O_2/N_2$ = 60/20/20, W/F = 3.5 g h L^{-1} at 450 °C). Comparisons of their catalytic performances allowed us to conclude that if sodium should be left out from catalytic formulations, cadmium and silver are quite promising cations. The best performances are obtained with a lattice involving polynuclear limited size units (two, three, or four transition metal atoms). This configuration makes easier electronic exchanges occurring during the reaction.

Introduction

Despite the importance of the challenge of the mild oxidation reaction of propane, the performances of the different improved catalysts tested up to now are still quite low. These problems are relative to the high activation energy value of the C−H bond of the propane molecule in comparison with the low stability of the mild oxidation products. One possible way to improve the catalysts formulations is to methodically study the structure sensitivity of this reaction. The aim of this work was to evaluate the influence of many well-defined structural parameters on the catalytic performances. This kind of study should help us to define new performant catalysts.

The transition metal phosphates isolated in the past few years in the CRISMAT laboratory (Caen, France) exhibit mixed frameworks MPO (M = Mo, V, Nb, W, Fe) which are built up from the linkage of PO_4 tetrahedra with, most of the time, MO_6 octahedra. These frameworks delimit cavities or tunnels where cations are inserted, ensuring cohesion and electroneutrality of the whole 3D system. One of the main characteristics of these phosphates concerns their ability to stabilize transition metals at a low oxidation state, even with mixed valencies, which implies the simultaneous presence of two different oxidation states for one metal inside the same lattice. That kind of structural property makes them good candidates as model catalysts for the mild oxidation reactions, and in particular for propane oxidation. In this paper, we will focus on the Mo and V containing catalysts, these two transition elements being the most promising according to literature.[1]

Comparison of the catalytic performances of the well-crystallized compounds whose structures are well-known[2−25] and which could therefore be used as model catalysts allows us to evaluate the influence of some structural parameters, as the nature of the inserted cation or the transition metal, their oxidation state, their structural arrangements, on the activity and

---

[†] Laboratoire de Catalyse et Spectrochimie.

[‡] Laboratoire CRISMAT.

[⊗] Abstract published in *Advance ACS Abstracts,* December 1, 1997.

(1) Kim, Y. C.; Ueda, W.; Moro-Oka, Y. *Chem. Lett.* **1989**, 531.

(2) Masse, R.; Averbuch-Pouchot, M. T.; Durif, A. *J. Solid. State Chem.* **1985**, *58*, 157.

(3) Kierkegaard, P.; Holmen, S. *Ark. Kemi* **1964**, *23*, 213.

(4) Costentin, G.; Leclaire, A.; Borel, M. M.; Grandin, A.; Raveau, B. *J. Solid State Chem.* **1990**, *89*, 83.

(5) Guesdon, A.; Borel, M. M.; Grandin, A.; Leclaire, A.; Raveau, B. *J. Solid. State Chem.* **1993**, *108*, 46.

(6) Costentin, G.; Leclaire, A.; Borel, M. M.; Grandin, A.; Raveau, B. *Z. Kristallogr.* **1992**, *201*, 53.

(7) Costentin, G.; Borel, M. M.; Grandin, A.; Leclaire, A., Raveau, B. *J. Solid State Chem.* **1990**, *89*, 83.

(8) Costentin, G.; Borel, M. M.; Grandin, A.; Leclaire, A.; Raveau, B. *J. Solid State Chem.* **1991**, *95*, 168.

(9) Guesdon, A.; Leclaire, A.; Borel M. M.; Raveau, B. *J. Solid. State Chem.*, submitted.

(10) Borel, M. M.; Guesdon, A.; Leclaire, A.; Grandin, A.; Raveau, B. *Z. Allg. Anorg. Chem.* **1994**, 620.

(11) Borel, M. M.; Leclaire, A.; Guesdon, A.; Grandin, A.; Raveau, B. *J. Solid State Chem.* **1994**, *112*, 15.

(12) Borel, M. M.; Chardon, J.; Leclaire, A.; Grandin, A.; Raveau, B. *J. Solid. State Chem.* **1994**, *112*, 317.

(13) Lii, K. H.; Johnston, D. C.; Goshorn, D. P.; Haushalter, R. C. *J. Solid. State Chem.* **1987**, *71*, 131.

(14) Benhamada, L.; Grandin, A.; Borel, M. M.; Leclaire, A.; Raveau, B. *C. R. Acad. Sci.* **1992**, *t314*, Ser. II, 585**.**

(15) Lii, K. H.; Chueh, B. R.; Kang, H. Y.; Wang, S. L. *J. Solid. State Chem.* **1992**, *99*, 72.

(16) Leclaire, A.; Chardon, J.; Grandin, A.; Borel, MM.; Raveau, B. *Eur J Solid State Inorg. Chem.* **1993**, *30*, 461.

(17) Leclaire, A.; Grandin, A.; Chardon, J.; Borel, MM.; Raveau, B. *Eur J Solid State Inorg. Chem.* **1993**, *30*, 393.

(18) Grandin, A.; Chardon, J.; Borel, MM.; Leclaire, A.; Raveau, B. *J. Solid. State Chem.* **1992**, *99*, 297.

(19) Grandin, A.; Chardon, J.; Borel, MM.; Leclaire, A.; Raveau, B. *Acta Crystallogr.* **1992**, *CA48*, 1913.

(20) Benhamada, L.; Grandin, A., Borel, M. M.; Leclaire, A.; Raveau, B. *J. Solid. State Chem.* **1992**, *101*, 154.

(21) Leclaire, A.; Chardon, J.; Grandin, A.; Borel, M. M.; Raveau, B. *J. Solid. State Chem.* **1994**, *108*, 291.

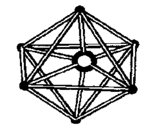
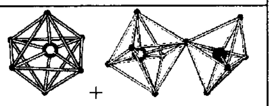
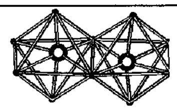
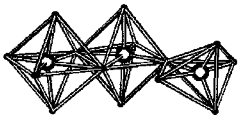
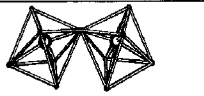
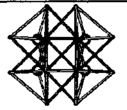
(22) Hwu, S. Y.; Willis, E. D. *J. Solid. State Chem.* **1991**, *93*, 69.

(23) Leclaire, A.; Chardon, J.; Borel, M. M.; Grandin, A.; Raveau, B. *Z. Anorg. Allg. Chem.* **1992**, *617*, 127.

(24) Wang, S.; Hwu, S. J. *J. Solid. State Chem.* **1991**, *90*, 31.

(25) Boudin, S.; Grandin, A.; Borel, M. M.; Raveau, B. *Acta Crystallogr.* **1995**, *C50*, 796.

Table 1. List of the Tested Compounds and Their Structural Pecularities

Compound	Cation	Mild oxidation state of transition metal	organization of the MO_6 or MO_5 polyhedra	
$BaMo_2P_2O_{12}$ (<u>2</u>)	Ba	6	$Mo^{VI}O_6$ isolated	
$AgMoPO_6$ (<u>3</u>)	Ag	6	«	
$\xi NaMo_2P_3O_{13}$ (<u>4</u>)	Na	5	$Mo^{V}O_6$ isolated	
$CsMoP_2O_8$ (<u>5</u>)	Cs	5	«	
$Mo_2P_4O_{15}$ (<u>6</u>)	-	-		
$BaMo_2P_4O_{16}$ (<u>7</u>)	Ba	5	«	
$NaMo_3P_3O_{16}$ (<u>8</u>)	Na	5.33	$Mo^{V}O_6$ isolated + $\nearrow Mo^{V}O_6$ Mo_2O_{10} $\searrow Mo^{VI}O_5$	
$CdMoPO_6$ (<u>9</u>)	Cd	5	$Mo^{V}{}_2O_{10}$	
$SrMo_3P_2O_{14}$ (<u>10</u>)	Sr	5.33	$\nearrow MoO_6$ $\nearrow Mo^{V}{}_2O_{10}$ $\searrow MoO_6$ Mo_3O_{14} $\searrow Mo^{VI}O_5$	
$AgMo_3P_2O_{14}$ (<u>10</u>)	Ag	5.66	$\nearrow Mo^{V}O_6$ $\nearrow Mo_2O_{10}$ $\searrow Mo^{VI}O_6$ Mo_3O_{14} $\searrow Mo^{VI}O_5$	
$Rb_3Mo_4P_4O_{22}$ (<u>11</u>)	Rb	5.25 (stat)	$\nearrow Mo^{5.25}O_6$ Mo_2O_{11} $\searrow Mo^{5.25}O_6$	
$BaMo_4P_2O_{16}$ (<u>12</u>)	Ba	5	$Mo^{V}{}_4O_{16} \longrightarrow 4\ MoO_6$	

selectivity in mild oxidation products. Our approach of this problem consists of a screening, that is to say the tested phases, are chosen in relation with their relative structural properties. Indeed, despite the great diversity of the compounds which is illustrated by the great number of original frameworks isolated,[2–25] a close comparison of them shows that there are many common features, analyzed in term of structural filiation.[26,27] Starting with the knowledge of several frameworks issued of the structural determinations performed at the CRISMAT laboratory, a classification of these materials as a function of their common features or their differences could be performed. The influence of the different structural parameters on the catalytic properties could thus be estimated.

Experimental Section

Preparation of the Catalysts. The preparation methods of the various compounds were already described in the literature.[2–25] Almost all the compounds that have been studied in this paper involve transition metal atoms in a reduced oxidation state (Table 1). Two steps were thus necessary to prepare such materials as was already described elsewhere.[28] First, MoO_3 or V_2O_5 were mixed with $(NH_4)_2HPO_4$ and A_xCO_3 (A = inserted cation) in an agate mortar in the adequate ratio to obtain intermediate compounds involving transition metal species with VI or V valency for Mo and V, respectively. The various mixtures were heated at about 673

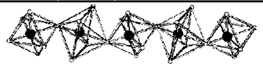
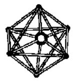
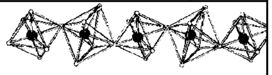
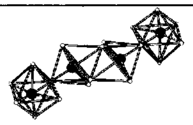
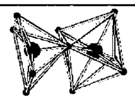
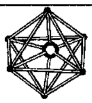
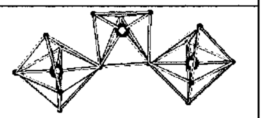
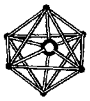
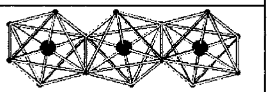
---

(26) Guesdon, A. Thèse Universitéde Caen, France, 1996.

(27) Costentin, G.; Borel, M. M.; Grandin, A.; Leclaire, A.; Raveau, B. *Inorg. Chem.* **1993**, *13*, 77.

(28) Savary, L.; Costentin, G.; Guesdon, A.; Studer, F.; Maugé, F.; El Fallah, J.; Lavalley, J. C. *J. Catal.* **1997**, *169*, 287.

Table 1 (Continued)

$AgMo_5P_8O_{33}$ (<u>13</u>)	Ag	5	$(Mo^{V}O_3)_\infty$ + $Mo^{V}O_6$ isolated	 + 
$NaMo_5P_8O_{33}$	Na	5		
$Ag_{0.5}Na_{0.5}Mo_5P_8O_{33}$	Ag/Na	5		
$NaVPO_5$ (<u>14</u>)	Na	4	$(V^{IV}O_3)_\infty$	
$CaV_2P_2O_{10}$(<u>15</u>)	Ca	4	«	
$CdV_2P_2O_{10}$ (o) (<u>16</u>)	Cd	4	«	
$CdV_2P_2O_{10}$ (m)(<u>17</u>)	Cd	4	$V^{IV}_4O_{20} \nearrow V_2O_{10}$ $V^{IV}_4O_{20} \searrow 2\ VO_6$	
$BaV_2P_2O_{10}$ (<u>18</u>)	Ba	4	$V^{IV}_2O_{10} \nearrow VO_6$ $V^{IV}_2O_{10} \searrow VO_5$	
$PbV_2P_2O_{10}$ (<u>19</u>)	Pb	4		
$Na_2VP_2O_8$ (<u>20</u>)	Na	4	$V^{IV}O_6$ isolated	
$Pb_2V_3P_4O_{17}$ (<u>21</u>)	Pb	3.33	$V_3O_{15} \nearrow 2\ V^{III}O_6$ $V_3O_{15} \searrow V^{IV}O_5$	
$PbV_2P_4O_{14}$(<u>22</u>)	Pb	3	$V^{III}O_6$ isolated	
$CaV_2P_4O_{14}$ (<u>22</u>)	Ca	3	«	
$CdV_2P_4O_{14}$ (<u>22</u>)	Cd	3	«	
$BaV_2P_4O_{14}$ (<u>23</u>)	Ba	3	«	
$BaMo_2P_4O_{14}$ (<u>23</u>)	Ba	3	$Mo^{III}O_6$ isolated	
$BaTi_2P_4O_{14}$ (<u>24</u>)	Ba	3	$Ti^{III}O_6$ isolated	
$CaV_2P_2O_9$ (<u>25</u>)	Ca	3	$(V^{III}_2O_4)_\infty$	

K in air, in a platinum crucible, for about 3 h in order to eliminate CO_2, NH_3, and H_2O. In a second step, when it was required, the finely ground products were mixed with an appropriate amount of metal molybdenum or vanadium to allow the reduction of the transition metal to final values (Table 1). The mixtures were heated in evacuated silica tubes for 6 h at different temperatures according to the nature of the prepared phase.

XRD Characterizations. X-ray diffraction patterns of the prepared samples were indexed following the crystallographic symmetries and parameters deduced from the single-crystal studies.[2-25] These characterizations ensured that samples were single phased and very well crystallized. These properties therefore implied very low specific areas for all samples (<1 m^2/g).

No X-ray powder diffraction pattern modification was detected after catalytic tests.

Catalytic Tests. The feed was a mixture of $C_3H_8-O_2$ diluted with N_2, with a molar composition of $C_3H_8/O_2/N_2 = 60/20/20$. The total flow rate was 8 mL/min to realize a W/F contact time of 3.5 g h L^{-1}. Activity was measured by varying temperature from 350 to 450 °C. It was checked that, in those conditions, there is no homogeneous step contribution to the reported results. The temperature of the catalysts bed was maintained within ±1 °C of the required value, controlled by a thermocouple located close to the wall of the quartz tube. The analytic procedure was previously described.[28]

Results

Among the thirty tested compounds (Table 1), the catalytic performances in propane mild oxidation are quite different, but propane conversion is enough for half of them to allow comparisons (Table 2). The conversion range is also close enough, so that the selectivities in the several formed products could be compared: the highest propane conversion is 12% at 450 °C for the $SrMo_3P_2O_{14}$[10] compound. The major products formed are propene, acrolein, and carbon oxides. In a few cases, acetaldehyde and acetic acid are also detected. The selectivities in propene and acrolein are in some cases very high, up to 80% in propene and to 9% in acrolein for the $AgMo_5P_8O_{33}$[13] and $CdV_2P_4O_{14}$[22] catalysts, respectively. The best yields in propene are obtained for the $AgMo_3P_2O_{14}$[10] and $CdMoPO_6$[9] compounds: at 450 °C, 7% of propane conversion, 70% of propene selectivity and 6% and 4% of acrolein selectiv-

Table 2. Catalytic Performances of Several Compounds in Propane Mild Oxidation ($C_3H_8/O_2/N_2 = 60/20/20$, W/F = 3.5 g h L^{-1}, $T = 400-450$ °C)

compound	temp (°C)	conv C_3H_8 (%)	Sel C_3H_6 (%)	Sel C_3H_4O (%)	Sel CO_2 (%)	Sel CO (%)
$CdMoPO_6$ (**9**)	400	3	88	3	8	0
	450	6.5	71	4	10	14
$SrMo_3P_2O_{14}$ (**10**)	400	5	42	2	8	41
	450	12	35	2	16	43
$AgMo_3P_2O_{14}$ (**10**)	400	3	82	4	1	6
	450	7	70	6	10	8
$BaMo_4P_2O_{16}$ (**12**)	400	1	0	0	100	0
	450	1.5	21	0	79	0
$AgMo_5P_8O_{33}$ (**13**)	400	1	85	5	10	0
	450	3.5	81	7	12	0
$Ag_{0.5}Na_{0.5}Mo_5P_8O_{33}$	400	0				
	450	1	85	5	4	0
$CaV_2P_2O_{10}$ (**15**)	400	3.5	75	2	8	17
	450	6.5	61	2.5	18	19
$CdV_2P_2O_{10}$ (o) (**16**)	400	3.5	37	6	42	13
	450	6.5	42	4	36	18
$CdV_2P_2O_{10}$ (m) (**17**)	400	4	74	2	24	0
	450	8.5	55	2	19	24
$BaV_2P_2O_{10}$ (**18**)	400	3	73	1.5	25	0
	450	7.5	59	1.5	39	0
$PbV_2P_2O_{10}$ (**19**)	400	5	0	0	100	0
	450	6	0	0	100	0
$Pb_2V_3P_4O_{17}$ (**21**)	400	1	59	1	39	0
	450	2.5	70	3	25	0
$PbV_2P_4O_{14}$ (**22**)	400	1	0	0	100	0
	450	2	7	0	93	0
$CdV_2P_4O_{14}$ (**22**)	400	1	39	2	58	0
	450	2	62	9	19	8
$CaV_2P_2O_9$ (**25**)	400	4.5	66	2	25	4
	450	9	57	2	23	16

ity, respectively. Half of the tested phases are not able to activate the propane molecule in the experimental conditions used: $BaMo_2P_2O_{12}$,[2] $AgMoPO_6$,[3] ξ-$NaMo_2P_3O_{13}$,[4] $CsMoP_2O_8$,[5] $Mo_2P_4O_{15}$,[6] $BaMo_2P_4O_{16}$,[7] $NaMo_3P_3O_{16}$,[8] $Rb_3Mo_4P_4O_{22}$,[11] $NaMo_5P_8O_{33}$,[13] $NaVPO_5$,[14] $Na_2VP_2O_8$,[20] $CaV_2P_4O_{14}$,[22] $BaV_2P_4O_{14}$,[23] $BaMo_2P_4O_{14}$,[23] and $BaTi_2P_4O_{14}$.[24] All the results underline the structure sensitivity of the reaction.

Discussion

Correlations between catalytic performances and structural properties will be performed considering that the structural species present at the surface of the catalyst ensue from the catalyst bulk structure.

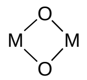
The connection modes of the transition atoms are reported in Table 1. A large variety of atomic arrangements are involved, allowing us to evaluate the effect of this parameter. It is quite clear that none of the solids containing isolated octahedra is active in propane oxidation, if we consider that the activity of $PbV_2P_4O_{14}$[22] and $CdV_2P_4O_{14}$,[22] though not null, is quite low (Table 2). So whatever the other particularities of these compounds (the nature of the inserted cation and the transition metal, its oxidation state, etc.), this isolated organization of transition metal atoms thus appears to inhibit the reaction.

Another factor which is important is the nature of the A cation inserted inside the MPO frameworks, which makes the cohesion of the 3-D edifice: its charge ensures the electroneutality of the structure, and its size is adapted to the cavity in which it is inserted. It is clear that among the five sodium-containing compounds that have been tested, none of them is active in propane oxidation. It therefore appears that Na^+ cations have a negative influence on the catalytic activity. Alkaline cations are known as poison in this kind of reaction due to the basicity they induce,[29,30] but others alkaline cations should be tested to check this hypothesis.

These two structural properties, isolated octahedra and the presence of sodium, lead to inactive compounds. Let us now methodically evaluate the influence of the several structural parameters on the catalytic performances of the other phases.

Role of Phosphorus Atoms. The role of phosphorus in the catalytic oxidation reaction has already been discussed by Monceaux et al.[31] In fact, if phosphorus does not seem to be directly involved in the reaction, its positive influence is clearly established if we compare the performances of MPO systems to those of simple oxides.[32] From the point of view of solid chemistry, phosphorus allows the stabilization of transition metals in unusual oxidation states. This point, as well as the acidic character of POH entities, could explain the benefit of phosphorus presence for oxidation reactions. Comparison of catalytic performances and PMO structures shows that no correlation can be established between the catalytic activity and either the metal/phosphorus ratio (in atoms number) or the nature of phosphorus groupments (PO_4, P_2O_7, P_4O_{14}).

Influence of the Organization of the Host Lattice. First, let us examine compounds containing Mo or V atoms which are built up with infinite MO_6 chains (M = Mo, V). The case of $CaV_2P_2O_9$[25] excepted, those compounds, $AMo_5P_8O_{33}$ (A = Ag, $Na_{0.5}Ag_{0.5}$),[13] $CaV_2P_2O_{10}$,[15] and $CdV_2P_2O_{10}$(o)[16], exhibit $(MO_3)_\infty$ infinite chains with MoO_6 or VO_6 octahedra linked by one apex (Table 1). In fact, this kind of chain is made of alternative short and long bonds M=O···M. The $CaV_2P_2O_9$[25] compound contains rutile chains (octahedra sharing one edge with therefore the presence of



double bridges). Most of these catalysts present quite good catalytic performances. The less active of them ($AMo_5P_8O_{33}$ (A = Ag, $Ag_{0.5}Na_{0.5}$)[13] contains also isolated octahedra and/or Na^+ cation, whose pernicious influence was already underlined.

The other catalysts involve finite polynuclear units. They are made of two, three, or four polyhedra. If one considers the nuclearity of such units, it was impossible to correlate this parameter to the catalytic results. The best performances are obtained with $AgMo_3P_2O_{14}$[10] and $CdMoPO_6$,[9] which contain respectively Mo_3O_{15} and Mo_2O_{10} units. $CdV_2P_2O_{10}$(m)[17] and $BaV_2P_2O_{10}$,[18] with respectively V_4O_{20} and V_2O_{10} units, also lead to quite good activities and selectivities.

---

(29) Busca, G.; Centi, G.; Trifiro, F.; Lorenzelli, V. *J. Phys. Chem.* **1986**, *90*, 1937.

(30) Grabowski, R.; Grzybowska, B.; Samson, K.; Slolzinski, J.; Stoch, J.; Wcislo, K. *Appl. Catal., A* **1995**, *125*, 129.

(31) Monceaux, L.; Courtine, P. *Eur. J. Solid State Chem.* **1991**, *28*, 233.

(32) Ai, M. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 3490.

(33) Corma, A.; Lopez Nieto, J. M. and Parades, N. *Appl. Catal A* **1993**, *97*, 159.

In fact, if we compare $CdV_2P_2O_{10}$(o)[16] and -(m),[17] with respectively infinite and limited size units, the first configuration seems to be less favorable than the second one, from the activity point of view, but even more, from propene selectivity's. This is in agreement Corma[33] V···O═V bridge, which are involved in infinite chains might enhance propene degradation, whereas the double bridge and/or free vanadyl bond site, which are involved in a finite unit, lead to an increase in alkene selectivity. This has to be compared to the fact that the propene selectivity decreases with the increasing size of the Mo_2O_{10}, V_4O_{20}, and $(VO_3)_\infty$ units, for the $CdMoPO_6$,[9] $CdV_2P_2O_{10}$(m),[17] and $CdV_2P_2O_{10}$(o)[16] catalysts, respectively. For Michalakos et al.[34] isolated sites are believed to give high selectivities. These results are also in agreement with the importance of the notion of limited size units described by Millet et al.[35] in other kinds of oxidation reactions. We could then consider that the presence of phosphorus in the MPO framework would indirectly improve catalytic results by limiting the size of transition metal clusters. This permits therefore the isolation of transition metal atom clusters and finally prevents deeper oxidation reactions. This role for phosphorus was suggested by Centi,[36] who considers that the isolation of active sites concept is as a key aspect for this kind of oxidation reaction.

Influence of the Transition Metal Oxidation State. The transition metals concerned in this study are molybdenum and vanadium. One characteristic of these materials is to allow the stabilization of transition metals in various oxidation states: Mo^{VI}, Mo^{V}, Mo^{III}, V^{IV}, V^{III}, and even mixed valences such as Mo^{V}/Mo^{VI} and V^{IV}/V^{III}. The oxidation state of the transition metals are reported in Table 1. The following discussion takes into account the initial oxidation states in the fresh catalysts.

In the case of the presence of only one redox element, which is the case in almost all tested compounds, literature reports that the active equilibrated catalyst (which corresponds most of the time to biphasic catalysts) involves two valences (V^{IV}/V^{V}, Mo^{V}/Mo^{VI}).[37] The initial oxidation state value may make easier the establishment of such equilibrium, and it is therefore interesting to evaluate the influence of this parameter.

If one excepts the catalysts involving isolated octahedra or sodium as countercation (in particular, there is no example of Mo^{VI} phosphates without isolated octahedra) many are active in propane mild oxidation, whatever the valency of the transition metal. None of the solids involving at the same time V^{IV} species and a good activity in the oxidation reaction is built up from isolated octahedra. There is only one compound involving Mo^{V} or V^{III} without isolated octahedra: $CdMoPO_6$ and $CaV_2P_2O_9$, respectively. $CdMoPO_6$ is also one of the most active among all the tested compounds, and $CaV_2P_2O_9$ is also quite active.

Even if the V^{4+}/V^{5+} couple is often said to be concerned in the oxidation reaction,[37] it appears in the latter example that the presence of V^{3+} species inside the fresh catalyst could also lead to quite good performances in the propane ODH reaction. Nevertheless, if one compares the results obtained with this phase with those obtained with the $CaV_2P_2O_{10}$ catalyst which exhibits V^{IV} species,[15] it appears to be less selective in propene. According to Germain,[38] the selectivity is related to the oxidation state of the metal transition atom where the allylic intermediate species is adsorbed and therefore to the electronic density around this atom: the higher the electronic density on the active site, the more probable the breaking of the C−C−C bond is.

If one considers all the molybdenum and vanadium phosphates tested, the presence of a mixed valency does not seem to be essential to get good catalytic performances. Indeed, even if the bad results of $NaMo_3P_3O_{16}$ ($Mo^{5.33}$)[8] and $Rb_3Mo_4P_4O_{22}$ ($Mo^{5.25}$)[11] should be considered carefully because of the nature of the involved inserted cations, it is possible to observe catalytic results as good as those obtained with $AgMo_3P_2O_{14}$ ($Mo^{5.66}$)[10] with phases that do not present a mixed valency, such as $CdMoPO_6$,[9] for instance.

In conclusion, this study seems to indicate that the relative disposition of the octahedra in the structural units (such as isolated octahedra, for instance) is certainly a more important criterion than the initial oxidation state of the transition metal. Considering the hypothesis of the peculiar importance of such redox equilibrium establishment, the configuration involving isolated octahedra could prevent the electronic exchanges during the catalytic reaction.

Indeed, if the oxidation state of the transition metal is well-known before catalytic reaction, there is no proof that it is conserved during the reaction. In the case of $AgMo_3P_2O_{14}$,[10] XPS and X-ray absorption spectroscopy performed at the K edge of molybdenum have shown that the average oxidation state of molybdenum is diminished from 5.66 to 5.2 during the catalytic reaction.[28] Finally, the prime importance of the organization of the framework over the oxidation state initial value could be explained by the fact that the ability of the transition metal atoms to adapt their oxidation state to the studied reaction without any spectacular modification of the framework (no modification of the XRD patterns was observed after the catalytic test) is certainly greatly related to the number and relative positions of the octahedra inside the structural units. When phosphate groups completely isolate transition metal atoms from each other, such electronic exchange cannot occur.

Nature of the Inserted Cation. The nature of the cations is quite various: alkaline metals, alkaline earth metals, Ag^{+}, Cd^{2+}, and Pb^{2+}. In a few cases, different cations whose sizes are quite close can be localized in the same host lattice, leading to isotypic compounds. This particularity will allow us to evaluate the real influence of the nature of the inserted cation on the catalytic activity. It appears that the discussion should leave out the catalysts containing Cs, Rb, and Sr cations, because in each case, only one phase of each has been tested.

As far as Ca, Ba, Cd, Ag, or Pb inserted cations are concerned, results are quite various. The best performances are obtained with the Cd and Ag metal cation

---

(34) Michalakos, P. M.; Kung, M. C.; Jahan, J.; Kung, N. H. *J. Catal.* **1993**, *140*, 226.

(35) Millet, J. M.; Védrine, J. C. *Appl. Catal.* **1991**, *76*, 209.

(36) Centi, G. *Catal. Lett.* **1993**, *22*, 53.

(37) Forissier, M.; Foujols, D.; Modaressi, A.; Gleitzer, C. *Bull. Soc. Chim. Fr.*, **1985**, *3*, 410.

(38) Germain, J. E. *Intra Sci. Chem. Rep.* **1972**, *6*, 101.

containing catalysts, particularly with $CdV_2P_2O_{10}$(o),[16] $CdV_2P_2O_{10}$(m),[17] $CdMoPO_6$,[9] and $AgMo_3P_2O_{14}$[10] catalysts. The molybdenum-containing compounds lead to the best selectivities in mild oxidation products. One cadmium catalyst, $CdV_2P_4O_{14}$,[22] leads to worthwhile results, especially in terms of activity (2% at 450 °C), whereas its selectivity in mild oxidated products is quite good (71%). Opposite from the others, it involves isolated octahedra. Among the other Cd-containing compounds, we observe a decreasing propene selectivity with increasing size of the molybdenum or vanadium structural units (Table 1): Mo_2O_{10}, V_4O_{20}, and $(VO_3)_\infty$ units, for $CdMoPO_6$,[9] $CdV_2P_2O_{10}$(m),[17] and $CdV_2P_2O_{10}$(o),[16] respectively. As for silver, this cation is known to improve the performances of many catalytic systems in the oxidation reactions, particularly in the case of methanol oxidation.[39] Moreover, it has been reported that doping bismuth molybdates catalysts by silver atoms improves their catalytic performances in the propane oxidation reaction.[40] However, only two catalysts among the four that contain silver as inserted cation are active in this reaction. The $AgMoPO_6$[3] compound is totally inactive, but it contains $Mo^{VI}O_6$ isolated octahedra. The $(Mo_5P_8O_{33})_\infty$ lattice, which contains both $Mo^{V}O_6$ isolated octahedra and $(Mo^{V}O_3)_\infty$ files,[13] is less active than the $AgMo_3P_2O_{14}$ catalyst, whose structure contains $Mo^{5.66}{}_3O_{15}$ units.[10] The influence of silver cation in the $AgMo_3P_2O_{14}$,[10] $AMo_5P_8O_{33}$,[13] and $AgMoPO_6$[3] catalysts appears thus particularly complex. Analysis of this problem was related in detail: [28] it was concluded that the position of the silver cation inside the framework and, more precisely, its ability to move, seemed to be essential.

Then, among isostructural systems, it clearly appears that the nature of the inserted cation influences the orientation of the reaction and thus the selectivities of the mild oxidation products. If one excepts the case of $AMo_3P_2O_{14}$ (A = Ag, Sr)[10] compounds, which is complicated because of the different electronic charge of the cations, Ag^+ and Sr^{2+}, the nature of the inserted cation does not really modify the propane conversion, but the selectivities are more influenced by this parameter, specially when an alkaline earth metal (Ca, Ba)[15,18] is substituted by cadmium or lead.[16,19] These modifications could be due to the induced electronic perturbations on other atoms. The study of the $AV_2P_2O_{10}$ series[41] has shown that the nature of the cation influences the metal−oxygen bond polarity, which modifies the electronic density on the neighboring active site (vanadium atom). This results for instance in an increase of acrolein selectivity when the metal−oxygen bond covalent character increases (the electronic density around vanadium is thus diminished), this observation being in agreement with Germain's results.[38]

Conclusion

Though it is difficult to well separate the effects of the different factors such as the organization of the host lattice, the transition metal oxidation state, and the nature of the inserted cation, it clearly appears that structures containing isolated octahedra and Na^+ as inserted cation must be discarded of catalytic formulation for propane oxidation. As far as metal transition (Mo, V) oxidation states are concerned, the ability of the lattice to relax the valencies modifications certainly occurring during the catalytic reaction is certainly a more important property than the presence of an initial mixed valency. So, VO_6 or MoO_6 octahedra linked by the edges or the apexes would make easier the electronic exchanges involved during the catalytic reaction. However, that kind of polyhedral linkage should exist in a limited size unit to prevent deeper oxidation reactions.

Acknowledgment. The authors are grateful to Rhône-Poulenc for financial support.

CM970169K

---

(39) Pestryakov, A. M.; Davydov, A. A. *Appl Catal., A, Gen*. **1994**, *120*, 7.

(40) Kim, Y.; Ueda, W.; Moro-Oka, Y. *Appl Catal*. **1991**, *70*, 175.

(41) Savary, L.; Costentin, G.; Bettahar, M. M.; Grandin, A.; Gubelmann-Bonneau, M.; Lavalley, J. C. *Catal. Today* **1996**, *32*, 305.