ARANAY

Structure-sensitivity study of partial propene oxidation over AV₂P₂O₁₀ vanadium phosphate compounds

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The activity and selectivity of five $AV_2P_2O_{10}$ compounds have been examined with respect to the mild oxidation of propene at different temperatures. These materials with orthorhombic symmetry (A=Ca, Cd) or monoclinic symmetry (A=Ba, Pb, Cd) have been prepared as well crystallized samples in an evacuated silica tube. Their crystalline structure, followed by X-ray diffraction (XRD), was unchanged after the catalytic reaction and their structural properties made them ideal model catalysts to study structure-sensitivity effects. Orthorhombic compounds were more active than monoclinic ones. Catalytic results were discussed, taking into account the nature of the inserted cations, the distortion of the framework and the organization of the lattice polyhedra.

Several authors have established that oxides containing cations in stabilized lower-valence oxidation states enhance partial oxidation activity. VPO systems have often been studied for alkane partial oxidation and in particular $(VO)_2P_2O_7$ catalyst led to very good results in the conversion of butane to maleic anhydride.¹⁻¹³ As far as propylene oxidation is concerned, high activity and selectivity to acrolein have been obtained with Mo-based catalysts^{14–21} especially with multicomponent catalysts such as Mo-Co-Fe-Bi-K-O.²²

We report here a study on five original VPO catalysts, which are very different model materials than the systems previously described in the literature.¹⁻¹³ Indeed, vanadium phosphates with the generic formula $AV_2P_2O_{10}$, A = Ca, Cd, Ba, Pb, exhibit original crystalline structures which have been characterized by X-ray single crystal diffraction by Raveau and co-workers²³⁻²⁶ and Lii *et al.*²⁷ In addition to the interest in evaluating new materials as oxidation catalysts, the investigation of the studied series allows the real influence of different structural criteria on mild oxidation activity and selectivity to be determined. The $AV_2P_2O_{10}$ materials were indeed particularly adapted to such an investigation for several reasons related to their structural homogeneity: the solid-solid preparation, obtained from precursors taken in stoichiometric proportions and characterized by XRD, allowed pure polycrystalline samples to be synthesized. Moreover, all the investigated componds exhibit the same generic formula: AV₂P₂O₁₀ and the vanadium species involve the same low oxidation state, IV. Among the phases studied, some are isostructural (A = Ba, Pb for the monoclinic form and A = Ca, Cd for the orthorhombic form), one is not (A = Cd, monoclinic form). It will thus be possible to throw some light on the term 'structure sensitivity', distinguishing, for instance, the effects of substitution of the inserted cations from those related to the geometry of the first coordination sphere of the vanadium atoms. This approach should help us to describe the better atomic organization for allylic oxidation. We report here the first results obtained for five samples for propene selective oxidation a structure-sensitive reaction. Other investigations have also been undertaken on the selective oxidation of propane.28

Experimental

Preparation of catalysts

Synthesis of AV₂P₂O₁₀ products²³⁻²⁷ was performed in two steps. First, (NH₄)₂HPO₄, V₂O₅ and, according to the nature of the insertion cation and to the symmetry form, $Cd(CH_3COO)_2$ (monoclinic form),²⁵ CdO (orthorhombic form),²⁶ CaCO₃, BaCO₃ or PbO were mixed in an agate mortar in the appropriate molar ratio to obtain the $AV_{1.6}^{V}P_{2}O_{10}$ composition. The mixtures were heated at ca. 380 °C in air, in a platinum crucible, for ca. 3 h in order to eliminate CO₂, NH₃ and H₂O. A higher temperature may be required in the presence of particularly stable carbonates such as CaCO₃. In the second step, the obtained products were ground and mixed with an appropriate amount of metallic vanadium to allow reduction of V^{V} to V^{IV} . The mixtures were then placed in an evacuated silica ampoule. Suitable thermal treatments led to single-phase polycrystalline products. Except for CdV₂P₂O₁₀ (monoclinic form),²⁵ where the synthesis temperature is 930 °C, all the tubes were heated at 700 °C for ca. 6 h and guenched at room temperature. XRD patterns of all samples were indexed in the crystalline cells deduced from the single crystal studied. All samples present very low surface areas ($\leq 1 \text{ m}^2 \text{ g}^{-1}$).

Catalytic tests

Reaction procedure. The catalytic tests were carried out in a fixed-bed flow Pyrex microreactor (U tube, id 5 mm), under atmospheric pressure, in the temperature range 300-430 °C. The catalyst loading was 0.5 g of granules in the size range 0.16–0.3 mm. To minimize possible homogeneous reactions, the pre- and post-catalytic volume was reduced as far as possible, filling the lower and upper parts of the catalytic bed with quartz powder. It was also checked, from the results obtained using a reactor filled with quartz powder instead of catalyst, that there was no significant catalytic contribution of the glass walls of the reactor and that the homogeneous reaction could be neglected. The temperature of the catalyst bed was maintained within ± 1 °C of the required value and controlled by a thermocouple sited against the wall of the Pyrex tube. In each case, the catalyst was heated in air to 430 °C, this

J. Chem. Soc., Faraday Trans., 1996, 92(8), 1423–1428 1423

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temperature was held for 3 h, first in air for 1 h, then in the stream of reactants for 2 h. After this pretreatment, the catalyst was cooled to 300 °C, the temperature was then gradually raised to 430 °C; the catalytic activity analyses were successively performed at 45 min intervals. The feed was a mixture of $C_3H_6-O_2$ diluted with N_2 , with a molar composition of $C_3H_6:O_2:N_2 = 13:22:65$. The total flow rate was 60 ml min⁻¹ to realize a W/F contact time of 23.9 g h mol⁻¹.

Analyses. The reactor inlet and outlet gases were analysed on-line by gas chromatography. The tube connecting the reactor to the chromatographs was heated at 180 °C in order to avoid any condensation of reaction products. The analyses were performed on-line by means of two chromatographs in series: a Hewlett Packard 5890 gas chromatograph equipped with two detectors in parallel [a flame-ionization detector (FID) and a thermal conductivity detector (TCD)], and a VARIAN chromatograph equipped with a thermal conductivity detector (TCD). The gases entering or leaving the reactor passed through a sampling system involving two gas valves: a ten-way valve which fed the reactants or effluent gases to the two parallel detectors of the HP chromatograph and a six-way valve, situated at the exit of the ten-way valve, which fed the gases to the third detector (Varian). The injection valves were actuated automatically by means of an HP 3396 integrator.

Separation of organic oxygenated compounds was performed on a CPSIL column (50 m, id 0.32 mm). A suitable separation of O_2 , N_2 , CO and CO_2 was achieved by using the two TCD detectors: O_2 , N_2 and CO were separated on a molecular sieve 5A column (4 m, id 2.2 mm) connected to the HP TCD detector; (air+CO), CO₂ and propene were analysed by means of two packed columns in series: an HAYESEP Q (3 m, id 2.2 mm, T = 80 °C) and a HAYESEP DB (2 m, id 2.2 mm, T = 80 °C) connected to the VARIAN TCD detector. Each analysis lasted *ca.* 45 min, and a temperature programme was required to analyse the products separated on the HP chromatograph: the temperature was maintained at 40 °C for 30 min, then raised to 80 °C at a rate of 40 °C min⁻¹.

In the following discussion, conversions and selectivities are defined as follows:

Conversion for propene

 $= \frac{\text{moles of propene converted to products}}{\text{moles of propene initially present}}$

Conversion for oxygen

$$= \frac{\text{moles of oxygen converted to products}}{\text{moles of oxygen initially present}}$$

Selectivity to product X

$$= \frac{\text{moles of X product formed}}{\text{moles of propene converted to products}}$$
$$\times \frac{\text{number of carbon atoms in X product}}{3}$$

The carbon balance obtained was very close to 1.

The activity measurements were performed several times for each catalyst and for each temperature. Their reproducibility allows us to consider the results, even those obtained at low conversion, as reliable.

Results

Catalysis

Conversion variations were achieved by varying the inlet temperature between 350 and 430 °C. The major organic product was acrolein. Acetone, acetaldehyde and acetic acid were also formed as minor products. The propene conversion remains quite low for the five samples. At low temperature, conversions are very low and the corresponding selectivities cannot therefore be precisely calculated. The increase in conversion with temperature is more pronounced in the case of compounds with orthorhombic symmetry: their catalytic activity is about twice that of the monoclinic compounds at 430 °C. No deactivation was observed with time on stream up to 24 h. Table 1 summarizes the main results in terms of C_3H_6 and O_2 conversions and selectivities which were obtained on the five samples at 430 °C.

The selectivity for acrolein ranges from 18 to 41% at 430 °C, the less selective compound being $CaV_2P_2O_{10}$ (18%), whereas the isotypic $CdV_2P_2O_{10}$ (orthorhombic form) leads to 32% selectivity.

As far as CO_x are concerned, CO, which appears at 400 °C, seems to be a high-temperature product. The orthorhombic catalysts give more total oxidation than monoclinic ones at high temperature (*ca.* 70% *cf.* 60%). The behaviour of $PbV_2P_2O_{10}$ is quite different since it essentially produces CO_2 , whereas CO is only formed in low quantity at 430 °C.

The minor products (2-15%), acetone acetaldehyde and acetic acid, tend to diminish with increasing temperature. Acetic acid is only formed when A = Cd, Ca and when the temperature is higher than 400 °C.

Structural characterization

XRD. Analysis of samples, after reaction, shows that the solids are not significantly modified during the mild oxidation reaction since the samples exhibit the same XRD patterns and surface areas before and after the catalytic test. All the compounds initially present the same reduced oxidation state V^{IV} for vanadium species, and, as the compounds are pretreated in the same conditions, the eventual change in this oxidation state of some vanadium atoms would probably occur in the same way for all of them. Nevertheless, other characterization techniques X-ray absorption near-edge spectroscopy (XANES), extended X-ray absorption fine structure (EXAFS) and especially surface techniques such as X-ray photoelectron spectroscopy (XPS) will be performed to verify that no finer modifications of these materials occur during the catalytic test.

Structural analysis. Comparison and analysis of many results reported in the literature on reduced vanadium phosphates²⁹ allowed us to establish some general properties of vanadium(IV) phosphates: their structural diversity is related to the ability of the vanadium(IV) to adopt either a square-pyramidal or an octahedral coordination. The VO₆ octahedron presents three kinds of V-O bonds: the four equatorial V-O bonds are *ca.* 2 Å long, and vanadium(IV) presents an abnormally short V-O bond of *ca.* 1.6 Å. Opposite to this vanadyl ion, there is a long V-O bond (*ca.* 2.3 Å): the vanadium atom is off-centred inside its octahedron. This particularity leads to a (5 + 1) pseudo-octahedral coordination.

Among the vanadium(IV) phosphates, those involving the same generic formula $AV_2P_2O_{10}$ perfectly illustrate this continuous variation in correlation with the size of the inserted ion. The $[V_2P_2O_{10}]_{\infty}$ frameworks are thus built up from PO₄ tetrahedra, VO₆ octahedra and/or VO₅ square pyramids.

The $AV_2P_2O_{10}$ structural properties have been more finely analysed: our purpose was to examine not only their common structural features, but also their differences. The main results are summarized in Table 2.

First, two kinds of structural series should be considered according to the symmetry type of the several frameworks.

Monoclinic symmetry. The compounds with A = Ba, Pb and Cd are characterized by a continuous distortion of the $[V_2P_2O_{10}]_{\infty}$ monoclinic host lattice. Indeed, the $[V_2P_2O_{10}]_{\infty}$ monoclinic framework exhibits an amazing flexibility which allows various coordinations of the inserted ion to be

Table 1	Catalytic result	s for propene mild	oxidation at 430 °C
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	conversion (%)		selectivity (%)					
sample	C ₃ H ₆	O ₂	acrolein	acetone	acetaldehyde	acetic acid	CO ₂	СО
monoclinic								
$\mathbf{A} = \mathbf{B}\mathbf{a}$	4 ± 0.5	8	35 ± 2	1	1	0	32 + 2	31 + 2
A = Pb	3 ± 0.4	7	41 ± 3	1	1	0	48 ± 3	9 + 0.5
$\mathbf{A} = \mathbf{C}\mathbf{d}$	5 ± 0.6	11	32 ± 2	1	1	2	32 ± 2	32 ± 2
orthorhombic								
A.= Cd	8 ± 0.6	20	32 ± 2	2	1	5	25 ± 2	35 ± 2
A = Ca	9 ± 0.6	16	18 ± 1	2	1	4	19 ± 1	56 ± 3

adopted. Therefore, we shall consider the variation of the framework with decreasing size of the inserted cation.

The $BaV_2P_2O_{10}^{23}$ host lattice consists of corner-sharing VO₅ square pyramids, VO₆ octahedra and single PO₄ tetrahedra and delimits tunnels with an elliptic section (Fig. 1). The barium ions are located in the elliptic tunnels. One of the two



Fig. 1 Projection along [100] of the structure of $BaV_2P_2O_{10}$

long V—O distances of the two independent vanadium atoms is indeed so long [3.47(2) Å], that the coordination of this vanadium atom can be considered as square pyramidal. Each VO₅ pyramid shares its apical oxygen, corresponding to the short V—O bond, with the VO₆ octahedron, building a V₂O₁₀ unit (Fig. 2). As a result, the V—O—V bond is nonlinear and asymmetric: the oxygen of this bridge is strongly bonded to the pyramidal vanadium [1.603(2) Å] and weakly bonded to the octahedral vanadium [2.379(2) Å]. Opposite this long V—O bond, there is a second short V—O bond [1.611(2) Å] corresponding to the free apex of the octahedron.

The host lattice of the $PbV_2P_2O_{10}^{24}$ compound is very similar to that of barium. The main difference is in the size and shape of the tunnel, in agreement with Pb^{II} being smaller than Ba^{II} and the steric effect of the $6s^2$ lone pair.

Distortion is achieved for the monoclinic form of $CdV_2P_2O_{10}$,²⁵ changing the coordination of the pyramidal vanadium atoms into octahedral [the long V—O bond becomes 2.294(2) Å]: two facing VO₅ pyramids corresponding to the barium phosphate are brought closer together, in such a way that the oxygen atoms of pyramidal basal planes



 Table 2
 Structural relationships and surroundings of vanadium atoms

	monoclinic	symmetry	orthorhombic symmetry
nature of the cation	Ba Pb	Cd	Cd Ca
structural relationships	isostructural		isostructural
	continuous distortion		
nature of the V _n unit	V_2O_{10} unit	V_4O_{20} unit	$[VO_3]_{\infty}$ chain
size of the V,	2 ŽV	4V	2 33400
number of vanadyl bonds formed by vanadium atom	1	1	1
oxygen atom linkage	V=O	V=O	
	V···O=V	V···O=V	V···O=V
	V-O-P	voov	V-O-P
		V-O-P	
nature and repetition	50% linked V=O	50% linked V=O	100% linked V=O
of the vanadyl bonds	50% free V=O	50% free V=O	

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become a common apical apex for the two VO₆ octahedra in the cadmium phase; two V_2O_{10} units corresponding to the lead and barium structures are transformed into a V_4O_{20} unit in this cadmium phase (Fig. 3). Note that, in this last unit, the two centre octahedra are sharing one edge. This distortion leads to the elliptic tunnel being transformed into two smaller tunnels in which the cadmium ions are located (Fig. 4).

In conclusion, we can consider that the studied monoclinic compounds belong to two groups involving quite similar monoclinic symmetry: $BaV_2P_2O_{10}$ and $PbV_2P_2O_{10}$, considered as isotypic compounds, and $CdV_2P_2O_{10}$, whose framework is derived from that of the previous compounds by a continuous distortion.





Fig. 5 Projection along [001] of the orthorhombic $AV_2P_2O_{10}$ structure, A = Cd, Ca



Orthorhombic symmetry. The second structural series concerns two isotypic compounds involving an orthorhombic symmetry framework: A = Cd or $Ca.^{26,27}$ This framework is built up with corner-sharing VO₆ octahedra and PO₄ tetrahedra and forms intersecting tunnels in which the Cd^{2+} or Ca^{2+} ions are located (Fig. 5). The VO₆ octahedra are linked to each other in such a way that they form infinite $[VO_3]_{\infty}$ chains (Fig. 6). As the vanadium atom is situated off-centre inside the octahedron, the $[VO_3]_{\infty}$ chains have alternating short and long V—O bonds of 1.604(6) and 2.085(6) Å, respectively, for the cadmium compound and of 1.597(8) and 2.123(8) Å for the calcium compound. The cadmium and calcium ions have nearly the same surroundings.

Vanadium bonding in the various frameworks. In the following paragraphs, we shall denote the vanadyl bond (>1.6 Å) as V=O to distinguish it from the V-O bond (>2 Å) and from the V...O bond (2.3 Å), even if, evidently, it does not correspond to a real double bond.

Each vanadium species in all the compounds exhibits one V=O bond, but two kinds of vanadyl bonds can be distinguished: the 'linked' vanadyl bond, *i.e.* $V=O\cdots V$, and the 'free' vanadyl ion, V=O, whose oxygen atom is not linked covalently to another vanadium atom or to a phosphorus atom (this oxygen sometimes participates in the stabilization of one inserted cation by an ionic bond).

If we only consider the first coordination sphere of the vanadium atoms, several kinds of oxygen sites exist: V-O-P, $V=O\cdots V$, V=O and the double bridge



The distribution of such atomic arrangements in the different frameworks is reported in Table 2.

The main feature of the orthorhombic framework compared with monoclinic framework is the absence of any octahedral free apex of the vanadyl ion. Note that the absence of such species in the orthorhombic framework leads to infinite vanadium units V_{∞} , whereas its existence in the monoclinic frameworks results in smaller units: V_2 and V_4 , respectively, for Ba, Pb and Cd compounds. Moreover, the number of the linked vanadyl bonds in the monoclinic series is only half that in the orthorhombic series.

Note that, among the several phases, the double bridge



which is often evoked in the activity of $(VO)_2P_2O_7$ compound, only exists in the $CdV_2P_2O_{10}$ monoclinic compound.

Discussion

As seen in the Results section, the conversion of propene with various compounds is quite low below $430 \,^{\circ}$ C: the several active sites in the different compounds do not seem to be sufficiently differentiated in these conditions, as expected from the very narrow structural differences between the various compounds. Moreover, reaction paths can change with temperature. Reasonable interpretations, in terms of structure-activity correlations, should essentially be performed with results obtained at higher temperature.

The substitution of one inserted cation in the mixed framework by another, even with an approximately similar size, can induce some distortions of the framework. The problem is then to determine whether the modifications of the catalytic activity are related to the chemical nature of the cation (this would indicate an intrinsic effect of the nature of the cation), or to the distortions of the framework (indirect effect of the chemical nature of the inserted cation).

In addition to these two factors, we will also consider in a more refined manner, the effect of the organization of the polyhedra which are building up the host lattice.

Nature of the inserted cation

Only isotypic compounds will be considered to evaluate this criterion (see Table 2). As far as the orthorhombic isotypic compounds $CdV_2P_2O_{10}$ and $CaV_2P_2O_{10}$, are concerned, they exhibit nearly the same catalytic activities. Nevertheless, the selectivity to acrolein of the cadmium phase is higher than that of the calcium phase (32 and 18%, respectively, at 430 °C); the balance corresponds to carbon oxides.

Calcium and cadmium ions have the same ionic radii and the same surroundings. Nevertheless, their electronic structures are different: $Ca^{2+} - O$ bonds are ionic whereas $Cd^{2+} - O$ bonds exhibit a relatively strong covalent character. Moreover, Cd^{2+} ion is a redox ion whereas Ca^{2+} is not, the two cations can therefore be distinguished by the different effects they induce on the vanadium atoms of their second coordination sphere. It can be seen that cadmium influences the redox character of vanadium atoms in such a way that the selectivity to acrolein is greatly increased as compared with the calcium-containing compound.

Considering the case of barium and lead in the monoclinic framework, it should be noted, at $430 \,^{\circ}$ C, that the lead compound is slightly more selective to acrolein than the barium compound (41% and 35%, respectively) for a similar catalytic activity and this is also in agreement with the higher covalent character of lead than barium. Nevertheless, as seen in the 'Structural properties analysis' section, there is a continuous

distortion of the monoclinic framework with variation in the size of the inserted cation. It is thus difficult to separate the intrinsic effect of the nature of the cation from the geometric effects that the size of the cation induces in the framework. This particular case perfectly illustrates how important it is to control finely the slight structural differences in order to prevent drawing any misleading conclusions.

Distortions of the framework induced by cationic substitution in the monoclinic framework

At 430 °C, the yields in acrolein of the three monoclinic compounds (A = Cd, Ba, Pb) do not follow the distortion order: the classification of the ionic radii which generate the framework distortions is $r(Cd^{2+}) < r(Pb^{2+}) < r(Ba^{2+})$, whereas the yields (y) of acrolein at 430 °C are such as $Y(Pb^{2+}) = 1.23\% < Y(Ba^{2+}) = 1.4\% < Y(Cd^{2+}) = 1.6\%$. In fact, what we observe here is only the resulting effect of two parameters since examination of the distortion effect always involves structures with a different inserted cation. The results simply indicate that the structural effect inherent to the framework distortion seems to be opposite to that previously described, producing, in this case, an inversion of the selectivity order between lead and barium.

In conclusion, we can note that if the inserted cations certainly do not directly involve active sites, they can influence their strength by modifying the redox character of vanadium atoms in their vicinity^{30.31} or acidity properties³² and can therefore change selectivity values.

Organization of the host lattice polyhedra

The distortion effects do not influence the activity so much. It is thus possible to gather the results obtained on monoclinic compounds in one group and those relative to orthorhombic compounds in another, and to compare the results. It appears that the activity of orthorhombic catalysts is higher than that of monoclinic, notably at 430 °C. Therefore, from the point of view of the activity, it seems that the effect of the structure type is more pronounced than that of the nature of the cation.

As the reaction mechanisms are probably the same for the two sets of oxides, this leads us to take into account the different types of active sites which could occur in the redox mechanism for each structure. Since the surface area of all the samples as very low and considered to be approximately the same, and since we have no information about the morphology of the samples, catalytic properties have to be correlated to the bulk structures. In fact, a crystal structure is a result of the field acting between all the atoms: it accounts not only for the arrangement of the different atoms in the cell, but also for the oxygen-metal bond lengths and strengths. An important factor is certainly the coordination of the vanadium atoms, we will therefore try to correlate the catalytic results with the type of V—O bond (Table 2) counted per formula unit in arbitrary units.

V=O bonds are expected to act as active lattice oxygen:³³ this short covalent bond probably acts as an electron reservoir. We specified previously (Table 2) that two kinds of vanadyl bonds should be considered. Note that, on one hand, the number of the 'free' vanadyl bonds is doubled on going from the orthorhombic to the monoclinic series and, on the other hand, the catalytic activity of the orthorhombic series is higher than that of the monoclinic series, at least at 430 °C. These observations are thus consistent with a correlation between the catalytic activity for partial propene oxidation and the existence of the linked vanadyl ions in the materials.

Some authors have discussed whether an M=O bond (M = transition metal) is involved in the selectivitydetermining step^{34,35} of the reaction, or whether it is a bridging single-bonded site (M=O-M).^{15,36} In our case, considering the different $AV_2P_2O_{10}$ mixed frameworks, the latter oxygen atom is always in the form of $V=O\cdots V$ with two asymmetric bonds and belongs to a linked vanadyl group whose importance has been emphasized previously.

Interpretation of the selectivity results seems to be less straightforward. Large V_n units are obtained via V-O-Vbonds, such metal-O-metal bonds being generally claimed in the literature to promote total oxidation.^{33,28} In fact, comparison of the results in Tables 1 and 2 shows that a decrease in the size of the V_n units increases the proportion of acrolein among products of the mild oxidation. It seems that, at high temperature, too large V_n units result in a reoxidation of some of the products from the mild oxidation. Nevertheless, as far as the vanadyl bonds are concerned, we can also note that their presence corresponds to an increase in the ratio acrolein/ total mild oxidation products formed. As previously seen, this structural effect has also to be related to the decreasing size of the V_n vanadium atoms units. It is therefore difficult to distinguish between these two structural effects and to know whether that kind of vanadyl bond is definitely implied in the route leading selectively to acrolein.

The double bridge



only exists in the $CdV_2P_2O_{10}$ monoclinic compound. This kind of linkage is met in the well known $(VO)_2P_2O_7$ catalyst. Comparison of results with those relative to the two other monoclinic compounds, where this double bridge is absent, indicates that the bridge does not seem to be particularly involved in the selectivity-determining step, at least for the series of compounds studied.

Conclusion

We have studied new catalytic systems involving five compounds which are at the same time very similar but also sufficiently different from a crystalline point of view, to realize a fine structure-sensitivity study.

The experimental results on the activity and selectivity to acrolein for the five investigated catalysts throw some light, at least, on the degree of validity of the few criteria formulated in the introduction: we have shown that the chemical nature of the inserted cation (electronic structure), the distortion resulting from the different sizes of the inserted cations inside one type of mixed framework, the organization of the polyhedra of vanadium atoms and, finally, the nature of the V-O bonds, are all factors which influence the catalytic results. A clear conclusion is that the selective mild oxidation of propene is a structure-sensitive reaction. However, the catalytic reaction is a surface reaction process. More information on the surface properties of such materials is needed. However, we can consider that the differences observed in the catalytic properties are related to the general properties of the bulk structure of the solid. Preliminary results obtained on propane oxidation confirm²⁸ that this reaction is also a structuresensitive reaction.

The authors acknowledge with thanks the helpful discussions they had with Prof. B. Raveau, CRISMAT.

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Paper 5/03334I; Received 24th May, 1995