Effect of Zinc Incorporation on the Structure of the Catalyst Precursor $(VO)_2H_4P_2O_9$

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The incorporation of zinc into the layered catalyst precursor $(VO)_2H_4P_2O_9$ is found to result in intercalation with change in the structure of the parent compound in an aqueous medium whereas in an organic medium the zinc appears to substitute into the lattice inducing only a slight perturbation in the structure.

Phosphorus–vanadium oxides used as catalysts for the selective oxidation of butane to maleic anhydride have been the subject of intensive research recently.[1] Although the nature of the active sites, the mechanism of the reaction *etc.* remain controversial, it is clear that the active phase of the catalyst is the pyrophosphate $(VO)_2P_2O_7$ which is obtained from an orthophosphate precursor $(VO)_2H_4P_2O_9$ through a topotactic transformation. In other words, the structural order–disorder and morphology of the precursor phase are maintained during the transformation to the pyrophosphate and it is therefore possible to control the structural and morphological characteristics of the active phase by controlling the nature of the precursor phase. The vanadyl hydrogen orthophosphate precursor has an interesting layer structure[2] which should make it amenable to intercalation. In this context, the reported[3] improvement in the performance of the catalyst on zinc incorporation appeared interesting and led us to study the effect of zinc addition on the structure of the catalyst precursor $(VO)_2H_4P_2O_9$. We report herein the changes in the structure of the orthophosphate that are observed on the incorporation of varying amounts of zinc. The medium in which the preparation is carried out was found to have a marked influence on the structure.

In the preparation[4] of the orthophosphate in an aqueous medium involving reduction of V_2O_5, mixed with varying amounts $ZnCl_2$ (in the atomic ratio P : V : Zn = 1 : 1 : 0.00, 1 : 1 : 0.01, 1 : 1 : 0.05, 1 : 1 : 0.1, 1 : 1 : 0.2) with hydroxylamine hydrochloride, followed by the addition of H_3PO_4, it can be seen from the X-ray powder diffraction (XRD) pattern (Fig. 1) that samples *A* and *B* containing 0 and 0.03% of zinc respectively give a pattern typical[5] of $(VO)_2H_4P_2O_9$. However, with the incorporation of 0.12% zinc (sample *C*) the XRD pattern changes completely with the intensity of one of the lines being strongly enhanced. Samples *D* (0.16% Zn) and *E* (0.41% Zn) have a similar pattern with the intensity and *d* spacing of the strong line increasing slightly with increasing

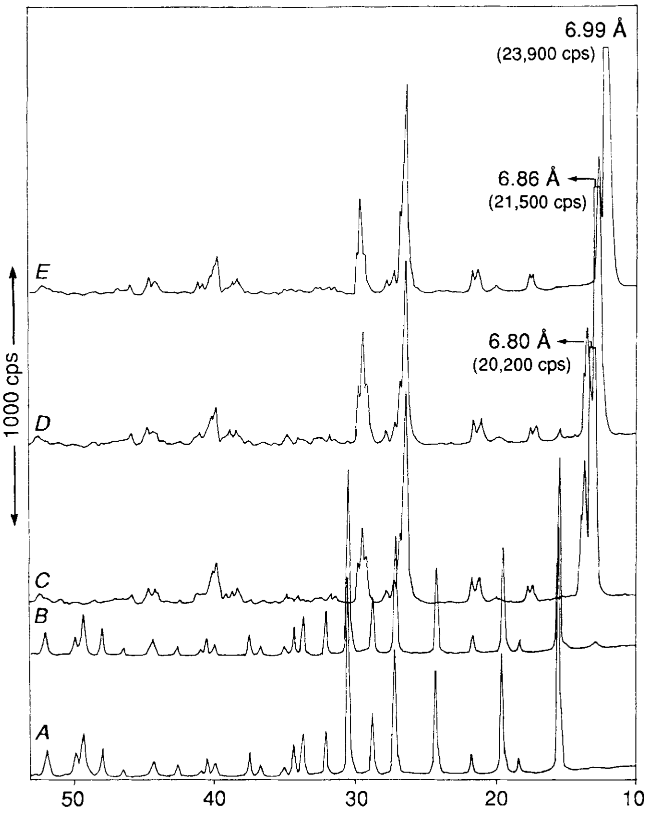

Fig. 1 XRD patterns of samples prepared in an aqueous medium with zinc contents of (*A*) 0.0%; (*B*) 0.03%; (*C*) 0.12%; (*D*) 0.16%; (*E*) 0.41%

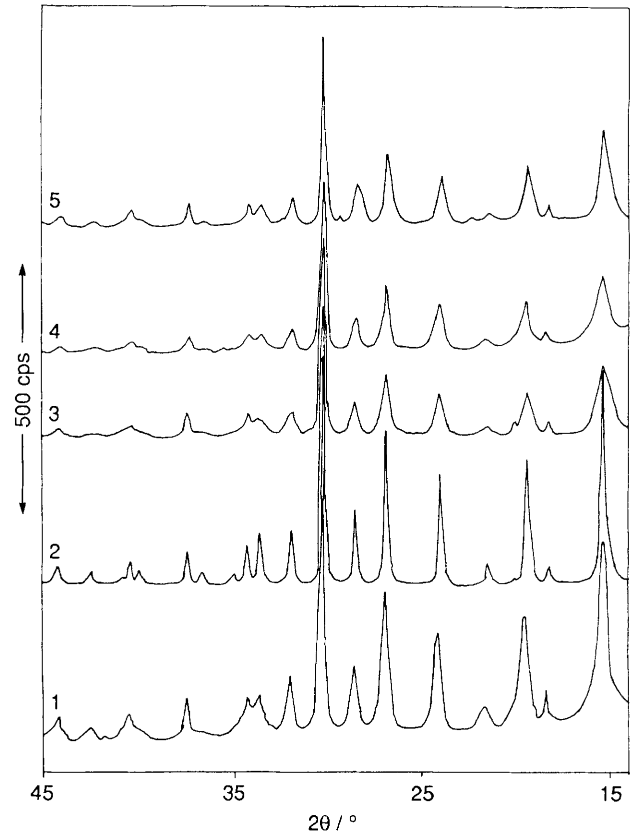

Fig. 2 XRD patterns of samples prepared in an organic medium with zinc contents of (1) 0.0%; (2) 0.11%; (3) 0.42%; (4) 0.68%; (5) 1.02%

zinc content. The XRD patterns of samples *C–E* do not correspond with that of any of the other reported phases of the V–P–O system.[6] However, it would be reasonable to assume that these compounds still retain a layer structure, in which case the intense line should correspond to reflection from the (001) plane, and the increase of the *c* axis spacing from 5.74 Å in the case of the unmodified precursor to 6.99 Å (sample *E*) suggests that the zinc is incorporated in the interlayer region and contributes to ordering primarily along the (001) plane.

Electron microscopic and particle size distribution studies show that compounds *A* and *B* consist of platelets which are agglomerated and have a wider distribution in particle size. On the other hand, sample *C–E* consist of well separated plates with a narrower particle size distribution. The binding energy of 1022.6 eV for the $2p_{3/2}$ state of zinc in the XPS spectrum indicates that it is present in the +2 state. At the same time there is evidence in the XPS spectrum for the presence of both V^{4+} and V^{5+} in samples *C–E*. This was further confirmed by the determination[4] of the average oxidation state of vanadium which showed that samples *A* and *B* have an average oxidation state very close to +4 whereas the corresponding values for samples *C–E* are in the region 4.55–4.57. Intercalation of metal ions into the layered vanadyl phosphate, $VOPO_4$, leading to change in the basal spacing, but with retention of the structure of the host lattice, is known.[7] Also, in these cases, the extent of metal ion intercalated is related to the amount of V^{5+} reduced to V^{4+}. However, in the present case the average oxidation state of 4.55–4.57 found for vanadium samples *C–E* is independent of the amount of zinc and the extent of reduction of vanadium is far greater than the amount of zinc incorporated. It would appear therefore that the introduction of just 0.12% zinc into the interlayer of $(VO)_2H_4P_2O_9$ expands the basal spacing and induces the structure of the host lattice to change to a new mixed-valent vanadyl phosphate. This kind of behaviour of layered compounds, to the best of our knowledge, has not been observed before. The fact that chloride ions themselves are not responsible for inducing the structural changes is evident from the observation that these effects are not seen in the absence of added zinc (as $ZnCl_2$) although $NH_2OH{\cdot}HCl$, the reducing agent used, is itself a good source of chloride ions. Also the same effects were observed when zinc acetate was used instead of zinc chloride.

On the other hand, when the precursors are prepared[5] in an organic medium by reduction of V_2O_5 and varying amounts of $ZnCl_2$ (in the same ratios as in the aqueous preparations) with benzyl alcohol in isobutyl alcohol (or just isobutyl alcohol itself), followed by the addition of phosphoric acid, although the same $(VO)_2H_4P_2O_9$ phase is obtained, the incorporation of even up to 1.02% of zinc does not affect the crystal structure of the precursor phase (Fig. 2) except for a general broadening of all the lines in the XRD pattern for samples 3–5. Also, no expansion in the basal spacing is observed indicating that the zinc is not incorporated in the interlayer region. This is in sharp contrast to the samples prepared in an aqueous medium. Electron microscopic studies show that all the samples had a rosette structure, which became more open with increasing zinc content of the samples. The average oxidation state of vanadium in all the samples was determined to be close to +4.0 and this was also evident from the XPS spectrum. The identical *d* values of samples 1–5 along with the general broadening of the lines in the XRD pattern and the increasing openness of the rosette morphology of the samples with increasing zinc content seem to indicate that the zinc substitutes randomly into the lattice causing a slight perturbation in the structure. If the added zinc were to form a separate phase, these effects would not have been observed. Also, the ionic radius of Zn^{2+} (0.74 Å) is identical to that of V^{3+} [which is also believed[5] to be present in small amounts in

$(VO)_2H_4P_2O_9$] and close to that of V^{4+} (0.63 Å). Consequently, substitution of up to 1.02% of Zn^{2+} for some of the V^{3+} or V^{4+} sites in the $(VO)_2H_4P_2O_9$ framework is unlikely to cause a lattice expansion but may introduce a slight disorder in the structure leading to the observed general broadening of the XRD lines on zinc incorporation. Such heteroatom substitution in the vanadyl phosphates has not been reported before and assumes significance when viewed in the light of reports[8] on the modification of the acidity of zeolites and aluminophosphate molecular sieves through substitution of various metal ions into the molecular framework. The complex 14-electron oxidation of butane to maleic anhydride, involving the abstraction of eight hydrogen atoms and the insertion of three oxygen atoms, is believed[1] to require the cooperative action of both acidic and lattice oxygen sites.

It is evident therefore that the addition of zinc has a profound effect on the structure of the $(VO)_2H_4P_2O_9$ phase with the nature and extent of zinc incorporation being strongly dependent on the preparation conditions. The diverse nature of the incorporation of zinc into the same parent compound, in different media for preparation, represents a novel aspect of the structural chemistry of layered compounds. At the same time, the highly selective ordering of the zinc ions along a particular plane observed in the preparations in an aqueous medium raises the interesting possibility of making novel catalysts by similarly incorporating other catalytically active metals, in an ordered fashion, into the vanadyl phosphate layer. Finally the present findings are expected to have an important bearing on the catalytic activity for selective butane oxidation of the active phase topotactically produced from the Zn-modified $(VO)_2H_4P_2O_9$ precursors.

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