

METAL PHOSPHATES: NEW VISTAS FOR CATALYSED OXIDATIONS WITH HYDROGEN PEROXIDE

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INTRODUCTION

Crystalline zirconium phosphates are potentially interesting as catalysts, since certain forms possess regular layer structures within which are strongly acidic sites which may undergo ion exchange with a range of metal cations. The ion exchange properties of zirconium phosphates were recognised in the 1950's^{1,2,3}; however, the initial preparations were amorphous gels of variable composition and it was not until 1964⁴ that zirconium phosphate was isolated in its crystalline form. Following on from this, other Group IV phosphates were then made in their crystalline forms. The phosphates have the general formula $M(HPO_4)_2 \cdot 2H_2O$ and possess a layer structure (Figure 1).

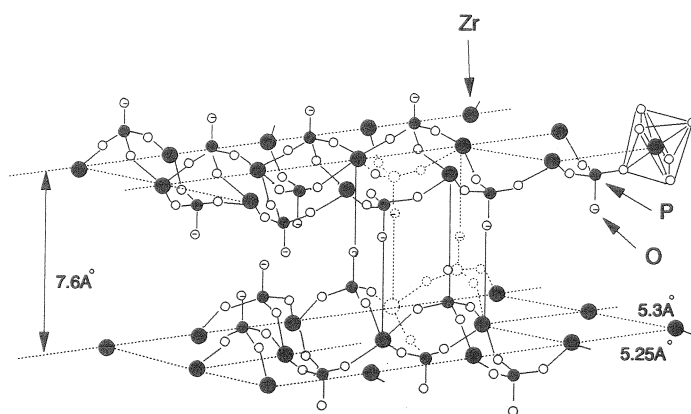


Figure 1 - Idealised Structure of α -Zirconium Phosphate

These materials can be considered as strong inorganic solid acids and much of the catalytic activity so far observed in the literature has been attributed to their acidic nature. This acidity is attributed to the Brønsted acidity of the hydroxyl groups in the interlayers and to the Lewis acidity of the metal centre.

Hydrogen peroxide is particularly suitable to catalytic activation. Under neutral conditions at ambient temperature it is not very reactive but it may be converted 'in-situ' to a wide range of active species which will perform specific oxidations. It may also be used to re-oxidise other active oxidants within a process giving an overall catalytic effect. Other peroxygen reagents such as percarboxylic acids are generally more reactive than hydrogen peroxide. Some examples of how hydrogen peroxide is activated for use in chemical synthesis are given in Figure 2.

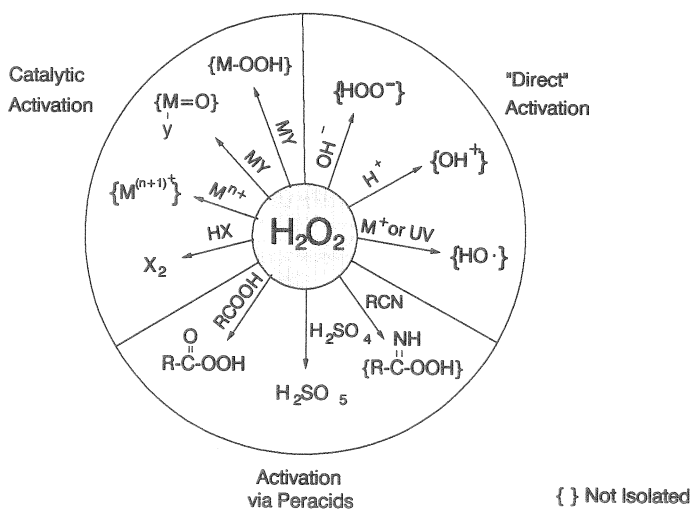


Figure 2 - Activation of H₂O₂

The simplest means of activation of H₂O₂ are by so-called direct methods. These produce anionic, cationic and radical species which carry out the oxidation. In general terms, these species are not particularly useful in synthetic reactions as they are often relatively non-specific.

The main synthetically useful ways of activating H₂O₂ are by conversion to peracids or by catalytic activation⁵. While peracids are good reagents with improved environmental properties compared with many traditional oxidants, the direct use of H₂O₂ is much more attractive. This can be achieved by the use of a catalyst to activate the oxidant. Many metals, especially amongst the transition series, can be converted to peroxy or oxo metal species, or take part in a redox couple. In general terms, catalytic systems have at least as wide a scope of reactivity as peracids and are being increasingly used in industry. Most systems are based on homogeneous catalysts, though recent research effort is focused towards finding a good heterogeneous catalyst. This would provide a 'zero-effluent' option, the only by-product of H₂O₂ oxidation being water. Tetravalent metal phosphates, being highly insoluble and having strongly acidic sites, were therefore candidates for study as H₂O₂ catalysts.

HYDROXYLATION

The hydroxylation of phenol by H_2O_2 is known to be catalysed by strong acids. This is a high capacity industrial process. Rhone Poulenc, Enichem and Ube produce catechol (CAT) and hydroquinone (HQ) from phenol by catalytic hydrogen peroxide processes (Figure 3).

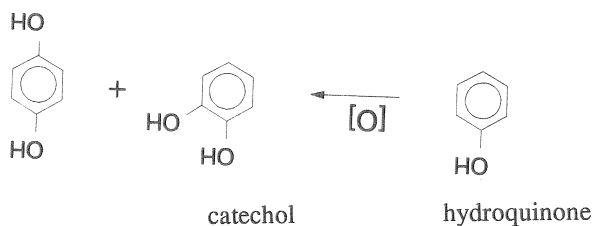


Figure 3 - Phenol Hydroxylation

Acid catalysts⁶, transition metal redox catalysts⁷, and titanium zeolites⁸ are all known to be effective for phenol hydroxylation. Acid catalysis proceeds by an ionic mechanism involving an intermediate hydroxonium ion ($H_3O_2^+$) whereas some transition metal ions promote the formation of hydroxyl radicals to effect substitution. However the introduction of a second hydroxyl substituent onto the aromatic nucleus tends to activate the molecule towards further reaction and this leads to the formation of unwanted, tarry by-products. The commercial solution is to use very low mole ratios of hydrogen peroxide to phenol and to recycle the unreacted phenol, ie. operate at low conversion. Some typical commercial methods are given in Table 1.

Table 1. Commercial Routes to Catechol and Hydroquinone

Catalyst	% Phenol Conversion	Selectivity dihydroxy	Ratio CAT:HQ
$H_3PO_4/HClO_4$ (Rhone Poulenc)	5	90	1.5:1
TS-1 (Enichem)	25	90	1:1
Ketone/acid (Ube)	<5	90	1.5:1

Early Experiments

Crystalline zirconium phosphate was prepared by the method described by Clearfield and Thakur⁹. Thermal activation was carried out at 100, 200, 300, 400°C. A portion of the amorphous material used to make the crystalline zirconium phosphates was retained for evaluation. Catalysts were characterised using titrimetric methods to measure acidity and x-ray diffraction to examine crystallinity. Thermogravimetric analysis (TGA) was used to determine phase changes on heat treatment.

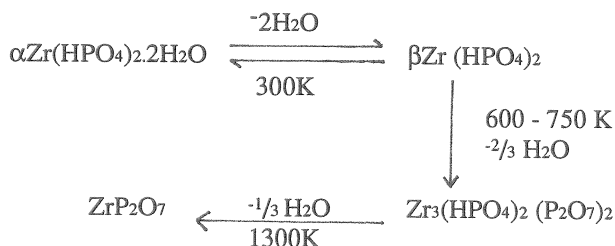
The titrimetric results were as follows: The amorphous material would not give an end point, but the crystalline samples dried at 100°C were found to be the most acidic, acidity decreasing with heat treatment (Table 2).

Table 2 - Acidity of Zirconium Phosphates

Activation temperature	meq NaOH/g	
Amorphous	100°C	no end point
Crystalline	100°C	8.65
	200°C	3.72
	300°C	2.93
	400°C	1.32

From our TGA experiments it appears that two moles of water, presumably of crystallisation, are displaced up to 200°C. Between 200 and 500°C a gradual change is seen with rapid loss of water seen between 500 and 600°C. There is a further gradual loss between 600 and 900°C.

Segaura et al¹⁰ have postulated the following scheme:



X-ray diffraction analysis of the catalyst samples would tend to show that a chemical change takes place about 100°C. The crystalline sample has a very distinct diffraction pattern (Figure 4). However the sample heated to 400°C is pure zirconium pyrophosphate (Figure 5). At intermediate temperatures the samples are shown to be mixtures of zirconium phosphate and pyrophosphate. This contradicts Segaura's findings.

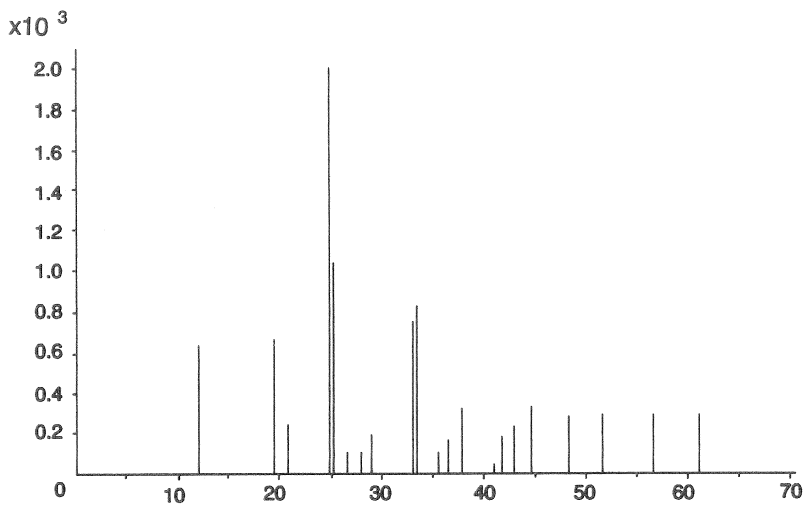


Figure 4 - XRD Analysis of Zirconium Phosphate Heated to 100°C

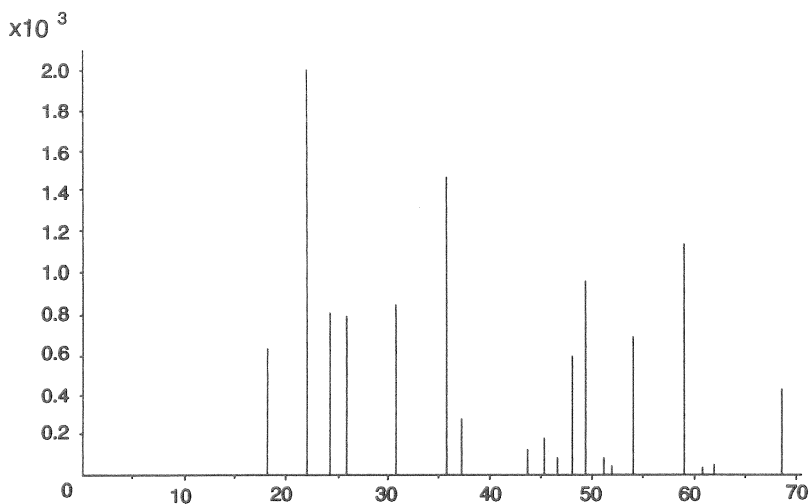


Figure 5 - XRD analysis of zirconium phosphate heated to 400°C

Five catalysts were assessed for activity in phenol hydroxylation. These were amorphous zirconium phosphate and the four crystalline samples heated at 100, 200, 300 and 400°C. The best catalyst in terms of conversion of phenol to catechol and hydroquinone was the crystalline sample heated at 100°C. This gave typically >90% selectivity to dihydroxybenzenes at 12% conversion of phenol and 2:1 mole ratio of phenol to H₂O₂¹¹. Reactivity decreased with high activation temperatures.

Other phenols and phenol ethers were examined to assess the breadth of activity of this catalyst. Anisole was selected as an electron rich aromatic system though less so than phenol. A cleaner reaction at lower conversion was expected. Under similar conditions employed for phenol hydroxylation, a 20% conversion of anisole was measured with selectivity to 4-methoxy phenol of 15% and to guaiacol of 42%. 1-naphthol was also assessed. No conversion was seen, presumably due to the bulky nature of the molecule. These findings are consistent with a mechanism involving an electrophilic oxidant species.

Mechanistic Studies

Zirconium phosphate was examined for activity in a range of solvents. Initial experiments were attempted in methanol, which may be used with the Enichem catalyst TS-1, but no reaction was observed. Acetonitrile was also tried but without success. Acetic acid was chosen as the next solvent for study, as a water miscible solvent, also the possibility of generating in-situ peracetic acid was considered feasible. This proved to be the best solvent.

Assuming a peracid to be the oxidising species, then propionic acid as solvent should show some activity. This was found to be the case. (Table 3).

Table 3 - Effect of Solvent

Solvent	% Phenol conversion	Selectivity dihydroxy	Ratio CAT:HQ
Acetic acid	26	59	1.4:1
Propionic acid	32	27	2.5:1

Conditions: Sn(IV), 35% H₂O₂, 5 hrs, 60°C, H₂O₂ : phenol 1:2

Phenol hydroxylation was then attempted with peracetic acid in the absence of a metal phosphate catalyst. Overoxidation of the substrate was observed, the major product being muconic acid. The phosphates were also found to be ineffective as catalysts for peracetic acid formations (from acetic acid and H₂O₂ alone). It was concluded that the mechanism was not a straight forward peracid oxidation.

A characteristic of the phenol hydroxylation reaction was that there was a lag between the disappearance of substrate and the appearance of products (Figure 6). No intermediates were observed. This led us to believe that the substrate was being absorbed into the interlayers and oxidation taking place there.

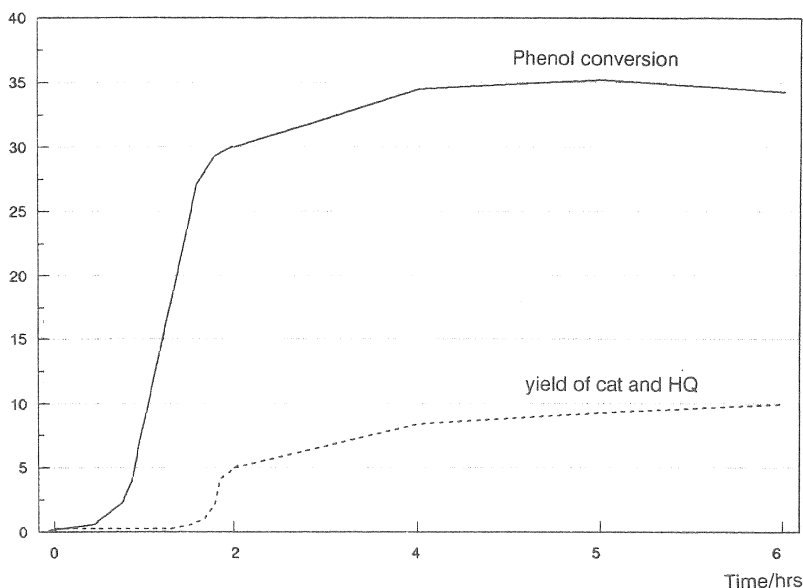


Figure 6 - Relationship of Phenol Conversion to Catechol and Hydroquinone Formulation

A further experiment was done to look at oxidant concentration in the solid and in solution (Table 4). It was found that, even after thorough washing, the peracetic acid formed was very much concentrated in the solid. This would explain why zirconium phosphate inhibits the formation of free peracetic acid, as it suggests that peracid is formed but held in the interlayers. The selectivity to dihydroxy products may then be attributed to adsorption selectivity. This is our current understanding of the mechanism.

Table 4 - Oxidant Concentration in the Solid and in Solution

Oxidant	g/kg oxidant in solid	g/kg oxidant in solution	Ratio
H ₂ O ₂	3.5	340	~1:100
PAA	15.5	99	~1:6

Conditions: Zr@amorphous, 6 hrs, 70% H₂O₂, nt, AcOH

Catalyst Synthesis Improvement

The existing method for preparing crystalline zirconium phosphate is firstly to precipitate the amorphous form from a mixture of phosphonic acid and zirconyl chloride and secondly to reflux the amorphous form in 12M phosphoric acid for several days after washing the amorphous form free of chloride. This gives the α -form. Not only is this a time consuming process, but the amorphous form is difficult to filter. We aimed to develop a one step process to the crystalline material by using crystal habit modifiers.

The rationale for this was as follows: Zirconium phosphate is able to exist in different forms. Since each crystallises differently, the initial disposition on the surface of the Zr^{4+}

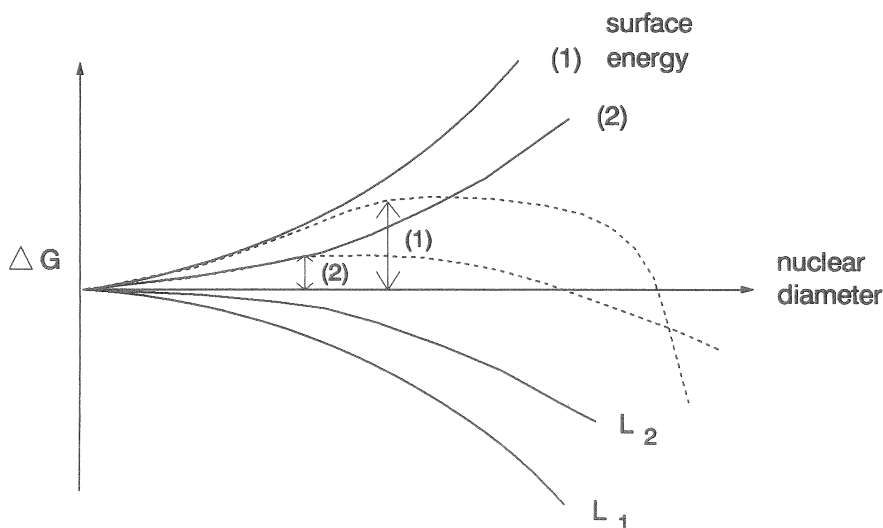


Figure 7 - Energy Diagram for Two Crystals

and HPO_4^{2-} ions is important. Kinetic control of the surface determines the form of the crystal obtained. Crystallisation almost invariably occurs on surfaces (of vessels, dust etc). If two crystals are considered in an energy diagram (Figure 7), the lattice L_1 is more stable than the lattice L_2 , therefore L_1 is more insoluble than L_2 . However since L_2 has a poorer lattice structure, water can still hydrate the surface and hydration leads to a more stable surface. Also (2) has a lower activation energy than (1) and a more stable nucleus, but as the crystals grow (1) becomes more stable than (2).

The above observations obey the Gay-Lussac Law which states that a compound that crystallises from a highly super-saturated solution first is the most soluble (from a saturated solution first it is the least soluble). In the above case, amorphous (2) is more soluble than (1). By choice of crystal habit modifier, it is possible to preferentially precipitate one form of the phosphate.

The addition of crystal habit modifiers to the original phosphoric acid/zirconyl chloride solution gave catalysts which were mainly crystalline in less than one hour but still had some amorphous character (Figure 8).

Nonetheless these materials were found to be effective phenol hydroxylation catalysts (Table 5) showing similar conversions and selectivities to a crystalline zirconium phosphate heated at 100°C.

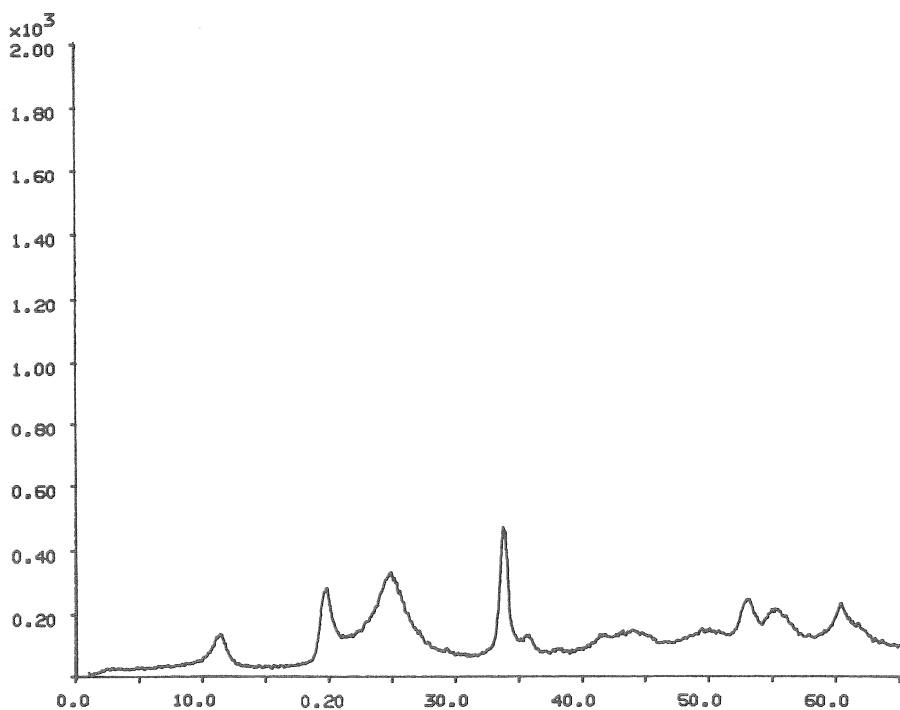


Figure 8 - X-ray Diffraction Pattern of Zirconium Phosphate Seeded with Cetyl Pyridinium Chloride (Zr@CPC)

Table 5 - Phenol Hydroxylation Using Zirconium Phosphates Made with Crystal Habit Modifiers

Crystal Habit Modifier	% Phenol Conversion	Selectivity Dihydroxy	Ratio CAT:HQ
Cetyl pyridinium chloride	38	64	1.9:1
ALIQUAT 336	39	53	1.7:1
ETHYLAN CD919	43	49	1.6:1
None*	48	48	1.6:1

* 5 hrs

Conditions: Zr@AcOH solvent, 90°C, 6hrs, H₂O₂:phenol 1:1

Catalyst Recycle

An experiment was conducted to demonstrate that the zirconium phosphate catalyst was indeed working in a heterogeneous manner. After one recycle using Zr (P) CPC, no significant reduction in catalytic activity was observed (Table 6).

Table 6 - Effect of Catalyst Recycle on Phenol Hydroxylation

Experiment No.	% Phenol conversion	Selectivity dihydroxy	Ratio CAT:HQ
1	32	53	1.5:1
2	35	47	1.5:1

Conditions: 50% H₂O₂, AcOH solvent, 80°C, 4 hrs

Selectivity to dihydroxy products and the ratio of catecol to hydroquinone formed was also maintained.

ALTERNATIVE PHOSPHATES

Our studies extended to look at other tetravalent metal phosphates. The results for those which were active phenol hydroxylation catalysts are given in Table 7¹².

Table 7 - Tetravalent Metal Phosphates as Phenol Hydroxylation Catalysts

Phosphate	% Phenol conversion	Selectivity dihydroxy	Ratio CAT:HQ
Zr	12	90	1.6:1
Sn	17	80	1.5:1
Ce	17	95	2.0:1
Ti	29	7	3.9:1

Conditions: H₂O₂ 35-50%, AcOH solvent, 60-90°C, 6 hrs, H₂O₂:phenol 1:2

Other tetravalent metal species were examined and found to have no activity. These were vanadyl (VO₄⁺), molybdenum, and mixed zirconium tungsten phosphates.

A comparison of the amorphous and crystalline forms of zirconium and tin phosphates was also made (Table 8). It is apparent that the crystalline forms show greater selectivity to the dihydroxy products. This is consistent with the oxidation largely taking place in the interlayers (which, of course, are not present to great extent in the amorphous form).

Table 8 - A Comparison of the Amorphous and Crystalline Forms of Zirconium and Tin Phosphates

Phosphate	% Phenol conversion	Selectivity dihydroxy	Ratio CAT:HQ
Zr amorphous ^a	34	56	0.9:1
Zr crystalline ^a	33	97	1.4:1
Sn crystalline ^b	26	59	1.4:1
Sn amorphous ^c	34	25	2.3:1

Conditions: 35% H₂O₂ , AcOH solvent, 5 hrs

a: 90°C, H₂O₂:phenol 1:1, b:100°C, H₂O₂:phenol 1:2, c: 60°C, H₂O₂:phenol 1:2

CONCLUSIONS

1. Both amorphous and crystalline zirconium, tin and cerium phosphates are active catalysts for phenol hydroxylation.
2. The activity shown is in line with the acidity of the metal centre.
3. Crystalline phosphates exhibit greater activity and selectivity than their amorphous counterparts in phenol hydroxylation.
4. Interlayer peracetic acid is implicated as the oxidising species.

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