Study of catalyst selectivity in the oxidation of phenol

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The selectivity of γ-crystalline zirconium phosphate, amorphous zirconium phenylphosphonate, amorphous zirconium molybdenum phosphate and microporous crystalline aluminium methylphosphonate was evaluated in oxidation reactions of phenol. The different selectivities are correlated to the properties and structure of each compound.

KEY WORDS: phosphonates; tetravalent metal phosphates; selectivity; oxidation reactions.

1. Introduction

The oxidation of phenol is a very important reaction from the industrial point of view, since it produces hydroquinone and catechol, important starting materials in the production of fine chemicals for use in agrochemicals, pharmaceuticals, flavors and aromatic essences. This reaction can also result in the formation of *cis,cis*-muconic acid or β-substituted muconic acids if derivatives of phenol are involved in the oxidation.

So far, most of the methods available for the production of catechol, hydroquinone and muconic acids are not selective or give low yields. These results justify a detailed investigation of the potential catalysts to be used in the selective oxidation of phenol.

Porous materials have been used successfully as shape-selective catalysts, adsorbents, molecular sieves, sensor materials and ion exchangers. An ultimate goal in the syntheses of these compounds is the control of size, shape, hydrophilic or hydrophobic character of micropores, better acidity and better thermal stability [1–7]. Within this group of compounds, microporous aluminophosphates (ALPOs) adopt a great variety of structures, depending on the synthesis conditions. A new family of microporous aluminophosphonates has been prepared, by substituting the phosphate groups in the microporous aluminophosphates by methylphosphonate groups, producing novel open frameworks. In 1995, the synthesis and crystal structure of the first microporous inorganic–organic composite, aluminium methylphosphonate (AlMepO-β), was reported [2].

Metal (IV) phosphates and phosphonates are also interesting as potential selective catalysts, since they possess good ion-exchange properties and are extremely resistant to extremes of temperature and radiation. So far, the catalytic activity reported in the literature for phosphates has been attributed to the Brönsted acidity of the hydroxyl groups in the interlayers and to the Lewis acidity of the metal center [8–12]. Owing to the layered nature of these materials, it is possible to pillar them with organic spacer groups, leading to pillared and non-pillared organophosphates or phosphonates [8,13–15]. The preparation of mixed metal phosphates and metal arsenate, antimonate and bismuthate analogues have also been described [16].

In the present work, we compare the selectivities of γ-crystalline zirconium phosphate (γ-ZrPC), amorphous zirconium phenylphosphonate (ZrPhPA), amorphous zirconium molybdenum phosphate (ZrMoPA) and microporous crystalline aluminium methylphosphonate (AlMepO-β) when used in oxidation reactions of phenol. These phosphates and phosphonates have different characteristics and properties, which are correlated to the differences in selectivity.

2. Experimental

2.1. Characterization of phosphonates, phosphates and reaction products

For known phosphonates and phosphates, sufficient spectroscopic data was obtained for their identification. Crystalline samples were analyzed by powder X-ray diffraction (XRD) spectroscopy. Amorphous zirconium phenylphosphonate and amorphous zirconium molybdenum phosphate was also identified by solid-state ^{31}P MAS NMR.

High-pressure liquid chromatography (HPLC) analysis has been performed on a Varian 2000 chromatograph with a Hypersil ODS column (25 cm × 5 μm). Infrared spectra were recorded on a Perkin-Elmer 1720-X infrared Fourier-transform spectrometer, liquid compounds as films and solids as KBr disks. A Hewlett Packard 8452A diode array spectrometer was used to record ultraviolet/visible (UV/VIS) spectra.

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Mass spectra were obtained on a VG 7070E spectrometer using electron ionization at 70 eV. ^1H nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AMX300 (300 MHZ). Solid-state ^{31}P MAS NMR spectra were measured on a Bruker MSL 400P spectrometer. Chemical shifts were quoted in ppm from 85% phosphoric acid. A Gallenkamp melting point apparatus was used to determine melting points. Powder XRD data was collected on an X'Pert MPD Philips diffractometer (Cu Kα X-radiation) with a curved graphite monochromator, a fix receiving slit of 0.5°, and a flat-plate sample holder, in a Bragg–Brentano para-focusing optics configuration. Intensity data was collected by the step-counting method (step 0.05° and time 1 s) in the range 2θ3–50°.

2.2. Synthesis of metal (IV)phosphates and phosphonates

γ-Crystalline zirconium phosphate [17] and microporous crystalline aluminium methylphosphonate [2] were prepared as previously described in the literature. Amorphous zirconium phenylphosphonate and amorphous zirconium molybdenum phosphate were prepared as described below.

2.2.1. *Amorphous zirconium phenylphosphonate* [16]

A solution of zirconyl chloride (3.8 g, 11.46 mmol) in water (30 mL) was slowly added to an aqueous solution of phenylphosphonic acid (3.0 g, 19 mmol) at room temperature and with stirring. A white suspension formed immediately and, after filtration, the resulting solid was air-dried for 24 h and subsequently dried further at 65 °C in vacuum for 72 h. Yield: 4.04 g; ^{31}P MAS NMR (solid state) $\delta = -4.87$ ppm (main peak); board peak between 13.00 and -8.00 ppm centered at 2.13 ppm.

2.2.2. *Amorphous zirconium molybdenum phosphate* [16]

Zirconyl chloride (4.56 g, 13.86 mmol) in water (100 mL) was added slowly to a solution of sodium molybdate dihydrate (3.83 g, 15.68 mmol) and di-sodium hydrogen phosphate (3.14 g, 17.10 mmol) in water (200 mL). Immediately, a white gel was formed and warmed to 80 °C with stirring for 4 h. After cooling the mixture, the precipitate was filtered off and washed with distilled water until pH = 6 of the filtrate. The final white solid was dried at 80 °C in vacuum for 12 h. Yield: 4.497 g; ^{31}P MAS NMR (solid state) $\delta = -12.29$ and -14.97 ppm.

2.3. *Preparation of cis,cis-muconic acid* [21]

By use of a teflon-coated stirrer, phenol (5.00 g, 0.0532 mol), glacial acetic acid (20.0 g) and basic ferric acetate (0.0104 g, 0.0544×10^{-3} mol) were reacted in a glass-stoppered 125-mL flask. After the ferric acetate had dissolved, a mixture of 10.5 g of acetic acid and 30.5 g of aqueous peracetic acid solution (40% w/w, 12.2 g, 0.161 mol AcOOH) was added over a period of 5 min. Colorless *cis,cis*-muconic acid precipitated from the solution as the reaction proceeded. After stirring at 25 °C for 5 days, the mixture was cooled to about 10 °C and the product filtered off, washed with cold water (1 mL) and air-dried to give *cis,cis*-muconic acid, m.p. 194–195.5 °C (from methanol; lit., 194–195 °C) [18]; λ_{max} (0.1 M NaOH) 251 nm (ε 15 600), 258 nm (ε 17 000) and 264 nm (ε 15 300); ν_{max} 1250, 830 cm^{-1}; MS, *m/z* 142 (29%) $[M]^+$, 124 (54%), 97 (100%), 79 (27%) and 69 (27%).

2.4. *Preparation of cis,trans-muconic acid* [18]

cis,cis-Muconic acid (2.00 g), produced as described above, was boiled during 1 h with just sufficient distilled water to effect solution. When the filtrate was cooled, small prismatic needles of *cis,trans*-muconic acid separated, m.p. 188–189.5 °C (lit., 190–191 °C) [18]; λ_{max} (0.1 M NaOH) 251 nm (ε 23 400), 259 nm (ε 25 600) and 265 nm (ε 23 400); ν_{max} 890, 750 cm^{-1}.

2.5. Oxidation of phenol in the presence of different phosphate and phosphonates

Because of the many potential variables in these systems, the oxidation of phenol was optimized by use of the Simplex method [19]. We have used the optimum reaction conditions for the best yields of hydroquinone and catechol, determined in our previous study [21]: temperature (60 °C), reaction time (6 h), concentration of H_2O_2 (35% w/w) and amount of H_2O_2 oxidant (0.5 mol to each mol of phenol). These define the standard conditions, used in all subsequent oxidations with other metal phosphates and phosphonates.

To study the effect of tetravalent metal phosphates and phosphonates on the rate of oxidation and the product range, phenol (0.94 g, 0.01 mol) was dissolved in glacial acetic acid (5 mL) with the phosphate/phosphonate added (0.05 g) and heated to 60 °C. An aqueous hydrogen peroxide solution (35% w/w, 0.5 g, 5 mmol) was slowly added via a peristaltic pump. The reaction mixture was maintained at this temperature for a total of 6 h. The formation of hydroquinone, catechol, *cis,cis*-muconic and *cis,trans*-muconic acids was quantified by HPLC and the results are listed in table 1. *cis,cis*-Muconic acid and the *cis,trans* isomer were identified by comparison with authentic specimens, prepared as described above.

2.6. Oxidation of phenol in the absence of phosphate/phosphonate

In a typical reaction, phenol (0.94 g, 0.01 mol) was dissolved in glacial acetic acid (5 mL) and heated to 60 °C. An aqueous hydrogen peroxide solution (35% w/w, 0.5 g, 5 mmol) was added slowly via a peristaltic

Table 1
Distribution of products from oxidation of phenol in the presence of different tetravalent metal phosphates and phosphonates

	γ-ZrPC (%)	ZrPhPA (%)	ZrMoPA (%)	AlMepO-β (%)	No phosphonate/phosphate (%)
Selectivity of hydroquinone	29.6	—	—	—	12.1
Selectivity of catechol	31.3	13.8	—	—	32.4
Selectivity of *cis,cis*-muconic acid	—	9.3	7.3	12.7	—
Selectivity of *it cis,trans*-muconic acid	—	—	6.8	—	—
Phenol conversion (w/w)	18.3	18.1	23.4	14.2	20.7

Note: Reaction conditions were all similar and are described in the experimental section. In all cases, acetic acid was used as solvent. Remaining products are non-identified tars.

pump over a period of about 30 min. The reaction mixture was maintained at this temperature for a total of 6 h and then analyzed by HPLC, which revealed a selectivity of 12.1 and 32.4% for hydroquinone and catechol, respectively, as shown in table 1. In this table, selectivity is the percentage of each formed product relatively to the converted phenol.

3. Results and discussion

The work described in this contribution analyzes and correlates the selectivities obtained on the oxidation of phenol, considering several metal phosphates and phosphonates with different characteristics and properties. Our studies started by examining the oxidation of phenol in the absence and presence of metal phosphates and phosphonates, with aqueous H_2O_2 as oxidant, in a range of solvents. In acetonitrile, methanol or *tert*-butyl alcohol, no significant oxidation occurred. However, in glacial acetic acid, the oxidation proceeded to give different products (see table 1). These results confirm the conclusion of our previous studies that peroxyacetic acid is formed and must be the major phenol oxidant. It was also found that the peroxyacetic acid quantified in the absence and presence of some metal (IV) phosphates is approximately the same [20]. These results, together with the results of table 1, show that some tetravalent metal phosphates have a selectivity effect (the true role of the phosphates), which influences the nature of the oxidation products obtained from the reaction of oxidant with phenol, but have no catalytic effect on the formation of peroxyacetic acid (the true oxidant).

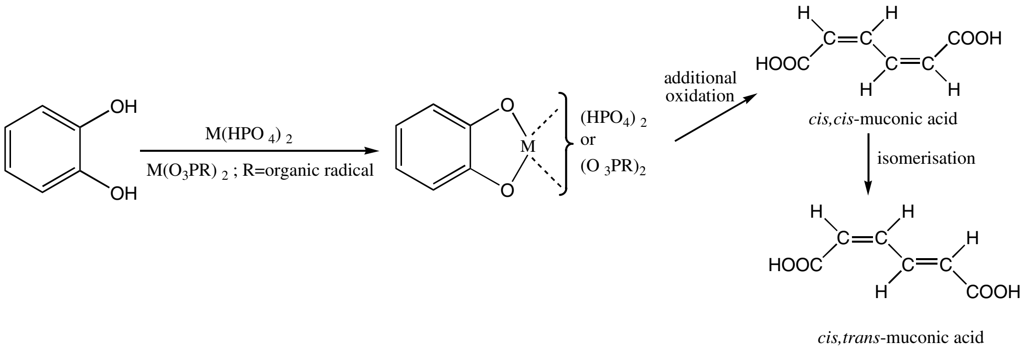
Additional studies with α-ZrPA, performed to further clarify the phosphate role, suggested that H_2O_2 penetrated the phosphate structure where it was possibly held by hydrogen bonding. Then any effect of the phosphates on oxidation of phenol with H_2O_2 can occur by affecting selectivity towards product formation in their pores and not by catalyzing effects. The differences in phenol conversion in the presence of different phosphates could arise from different mechanisms of trapping and removing peroxyacetic acid from the reaction products, owing to their heterogeneous lamellar nature. Consequently, the differences between various phosphates/phosphonates are much more in selectivity, rather than in conversion of phenol. The latter can be lower in the presence of phosphate/phosphonate compared to the reaction without phosphate, depending on the mechanism inside the phosphate/phosphonate. In some cases, the shape effect can lead to a better selectivity but also to a lower phenol conversion (AlMepO-β). The selectivity properties of this compound are discussed later on in this contribution.

Table 1 compares the results obtained for the phosphates and phosphonates considered in this study. Since the aim of our study is the selectivity aspect of the various compounds, we have used the optimum reaction conditions found in a previous study [21], but did not adjust the conditions to optimum for each catalyst separately. Owing to the different characteristics and properties of the catalysts studied here, this optimization will likely result in better yields, and will be carried out in the second stage of our investigations, once the most promising compounds are identified by the present selectivity studies.

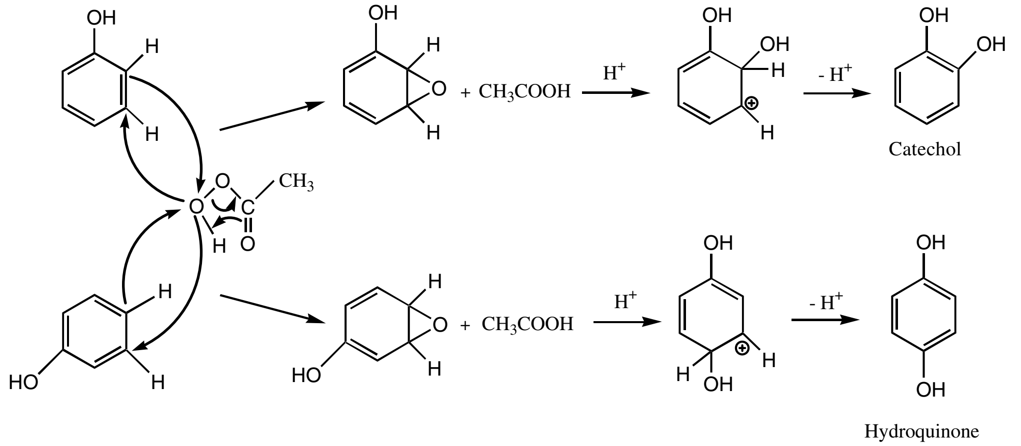
3.1. Oxidation of phenol

In the first stage, the oxidation reaction of phenol may produce hydroquinone and catechol, which can be followed by oxidative aromatic ring cleavage of catechol to give *cis,cis*-muconic acid (scheme 1). This product may or may not be isomerized to *cis,trans*-muconic acid. Owing to the formation of peroxyacetic acid in our systems, it is likely that the reactions follow an "ionic" mechanism (scheme 2).

Table 1 shows that, in the absence of a metal phosphate or phosphonate, there is a 20.7% conversion of phenol to products, of which 12% is hydroquinone and 32% is catechol. When γ-ZrPC is added to the reaction media, the overall conversion remained approximately the same, but the selectivity towards hydroquinone increased considerably. Since, as explained above, the phosphates/phosphonates seem to affect selectivity through a mechanism of product formation in their pores, the increased selectivity can be analyzed in terms of the structure of γ-ZrPC. The γ-layer is constituted by two ideal planes containing the



Scheme 1.



Scheme 2.

zirconium atoms bonded by tetrahedral PO_4 and H_2PO_4 groups. The PO_4 group shares all four oxygens with four zirconium atoms, while the H_2PO_4 shares two oxygens with two different zirconium atoms and points the remaining two OH groups towards the interlayer region. The adjacent layers are linked through hydrogen bonds involving the water molecules and the $P(OH)_2$ groups. Regarding these characteristics, the γ-layer results in a more compact and rigid structure. This property together with a interlayer distance of 12.3 Å could justify the increased selectivity of 29.6% towards hydroquinone relatively to the 12.1% for the reaction with no phosphonate/phosphate.

In the presence of ZrPhPA, the reaction was selective regarding the formation of catechol, compared to the γ-ZrPC case, but *cis,cis*-muconic acid was also formed. The structure of ZrPhPA may play a decisive role in the formation of catechol and *cis,cis*-muconic acid. In fact, the interlayer distance of ZrPhPA increases to 14.7 Å, compared to the value of 12.3 Å in the γ-crystalline zirconium phosphate, because of the introduction of phenyl groups [8]. The presence of phenyl groups and the larger distance between the interlayers may be responsible for the exclusive formation of catechol and the posterior conversion of some percentage into *cis,cis*-muconic acid.

3.2. *Exclusive formation of muconic acids*

Remarkably, for ZrMoPA and AlMepO-β, only muconic acids were formed (table 1). Using the best selectivity criterion, the microporous aluminium methylphosphonate is the most interesting material, since it results in the exclusive formation of *cis,cis*-muconic acid.

In the case of the mixed phosphate ZrMoPA, some phosphorous atoms were substituted with molybdenum. Only *cis,cis*-muconic acid and *cis,trans*-muconic acid were formed. In a previous work [20], the oxidation reaction of phenol was carried out with ZrWPA (in the acidic and the basic form). Also, with this mixed phosphate only *cis,cis*-muconic and *cis,trans*-muconic acids were produced, although with rather different selectivities, specially for the basic form. In both cases (ZrMoPA and ZrWPA), the formation of a complex between the catechol and the molybdenum (or the tungsten) is possible, with the conversion of catechol into *cis,cis*-muconic acid, which is later inverted into *cis,trans*-muconic acid. For the latter transformation, it is known that *cis,cis*-muconic acid is quantitatively inverted to *cis,trans*-muconic acid in boiling water. Indeed, as described above in the experimental section, this method was used in our work to produce *cis,trans*-muconic acid, for product identification purposes [18].

In relation to AlMepO-β, the compound showing the best selectivity regarding the exclusive formation of *cis,cis*-muconic acid, we note that the framework composition is $Al_2(CH_3PO_3)_3$ and that the solid possesses unidimensional channels formed from intertwined fused four-ring chains. The channel walls in the AlMepO-β were modified relatively to the ALPO, by the introduction of methylphosphonate groups directly attached to the phosphorus atoms, producing open frameworks. The channel-type arrangement of AlMepO-β contains six crystallographically independent CH_3PO_3 tetrahedra, which share oxygen atoms at their corners with three adjacent Al atoms. Among the four independent Al atoms, three are four-coordinate and the fourth is six-coordinate, all of which are bound by phosphonates [1,3]. The unidimensional channels in the structure and the acidity of aluminium atoms may confer a better selectivity to the AlMepO-β. The transformations observed may take place on the surface of the AlMepO-β where the aluminium atoms may have a decisive role in the formation of an aluminium–catechol complex and the quick formation of *cis,cis*-muconic acid.

The proposed formation of a metal–catechol complex was based on the studies of the oxidation of phenol to *cis,cis*-muconic acid by peroxyacetic acid in the presence of catalytic quantities of Cu(II) and Fe(III) [22]. The first step would involve hydroxylation of phenol to give a mixture of catechol and hydroquinone and is independent of metal. It was considered that catechol, in the presence of Fe (III) or Cu (II) acetate, forms a complex with the metal that is rapidly and cleanly oxidized to *cis,cis*-muconic acid. One possible mechanism for the proposed oxidation of the metal–catechol complex could involve a concerted electron transfer from the ligand through the metal to coordinated peroxyacetic acid molecules.

Following the results mentioned above, we could postulate the probable reaction mechanism shown in scheme 1. From our proposal, the formation of a complex between phenol and the metal of the phosphate or phosphonate being studied is possible. This complex could result in the formation of the corresponding *o*-benzoquinone with additional oxidation to *cis,cis*-muconic acid.

4. Conclusions

The results presented in this contribution agree with our earlier studies, which indicate that peroxyacetic acid is presumably the effective phenol oxidant, rather than H_2O_2 itself. Furthermore, we conclude that some phosphonates and metal(IV) phosphates do influence decisively selectivity towards oxidation products, but do not act as catalysts in the formation of peroxyacetic acid.

Given the role of peroxyacetic acid in the systems studied in this contribution, we may assume that the reaction with γ-ZrPC follows an "ionic" mechanism, with the formation of hydroquinone and catechol. In the presence of ZrPhPA, the reaction is selective relatively to the formation of catechol, but *cis,cis*-muconic acid was also formed. The selectivity is rather different for ZrMoPA and AlMepO-β, since here only muconic acids are formed.

The different selectivities regarding the oxidation products can be correlated to the catalyst properties and structure. The results with ZrMoPA suggest a mechanism involving the formation of a molybdenum–catechol complex, which is oxidized to *cis,cis*-muconic acid. This product is then inverted into *cis,trans*-muconic acid. The characteristics of the structure and the acidity of aluminium atoms may confer a better selectivity to AlMepO-β, with the specific formation of an aluminium–catechol complex that is immediately oxidized to *cis,cis*-muconic acid.

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References

[1] J. Rocha, Z. Lin, C. Fernandez and J.P. Amoureux, J. Chem. Soc., Chem. Commun. (1996) 2513.

[2] K. Maeda, J. Akimoto, Y. Kiyozumi and F. Mizukami, J. Chem. Soc., Chem. Commun. (1995) 1033.

[3] K. Maeda, J. Akimoto, Y. Kiyozumi and F. Mizukami, Angew. Chem., Int. Ed. Engl. 34(11) (1995) 1199.

[4] K. Maeda, Y. Kiyozumi and F. Mizukami, Angew. Chem., Int. Ed. Engl. 33(22) (1994) 2335.

[5] A. Clearfield, Chem. Mater. 10 (1998) 2801.

[6] J. Rocha, P. Brandão, A. Phillippou and M.W. Anderson, Chem. Commun. (1998) 2687.

[7] J. Rocha, P. Brandão, Z. Lin, A. Kharlamov and M.W. Anderson, Chem. Commun. (1996) 669.

[8] G. Alberti, M. Casciola, U. Costantino and R. Vivani, Adv. Mater. 8(4) (1996) 291.

[9] G. Alberti, Acc. Chem. Res. 11 (1978) 163.

[10] A. Clearfield, Mater. Chem. Phys. 35 (1993) 257.

[11] J. Wang, A. Clearfield and G.-Z. Peng, Mater. Chem. Phys. 35 (1993) 208.

[12] A. Johnstone, P.J. Middleton, R.C. Wasson, R.A.W. Johnstone, P.J.C. Pires and G.O. Rocha, in *Activation of Dioxygen And Homogeneous Catalytic Oxidation*, D.H.R. Barton *et al.*, (eds) (Plenum Press, New York, 1993) p. 45.

[13] M.E. Thompson, Chem. Mater. 6 (1994) 1168.

[14] G. Alberti, S.M. Mascarós and R. Vivani, Mater. Chem. Phys. 35 (1993) 187.

[15] G. Cao, H.-G. Hong and T.E. Mallouk, Acc. Chem. Res. 25 (1992) 420.

[16] P.J.C. Pires, Ph.D.Thesis (University of Liverpool, Liverpool, 1995).

[17] R.H. Blessing, A. Clearfield and J.A. Stynes, J. Inorg. Nucl. Chem. 30 (1968) 2249.

[18] J.A. Elvidge, R.P. Linstead, P. Sims and B.A. Orkin, J. Chem. Soc. (1950) 2235.

[19] S.N. Deming and S.L. Morgan, Anal. Chem. 45(3) (1973) 278.

[20] G.M.S.R.O. Rocha, R.A.W. Johnstone, B.F. Hemmings, P.J.C. Pires and J. Philip Sankey, J. Mol. Catal., A: Chem. 186(1-2) (2002) 127.

[21] G.M.S.R.O. Rocha, R.A.W. Johnstone and M.G.P.M.S. Neves, J. Mol. Catal., A: Chem. 186(1-2) (2002) 127.

[22] J.A. Pandell, J. Org. Chem. 41 (1976) 3992.