

Hydrogenation of alkenes over palladium and platinum metals supported on a variety of metal(IV) phosphates

Robert A.W. Johnstone*, Jun-Yao Liu, Ling Lu, David Whittaker

Department of Chemistry, University of Liverpool, Liverpool L69 3BX, UK

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Abstract

Platinum(0) and palladium(0) catalysts have been prepared by first exchanging the acidic protons in a variety of metal(IV) phosphates with platinum or palladium ions followed by their reduction to metal. The resulting supported catalysts were examined for their effectiveness in the hydrogenation of 1-octene, 1-, 3-, 4-methylcyclohexenes and cyclododecene. Rates of reduction and stereoselectivity were compared with a standard commercial palladium-on-charcoal catalyst and were found to vary widely by a factor of about 500, depending on the support used. Data are reported as relative rates of reduction. Steric effects due to substrate/support interaction played a major role in selectivity to hydrogenation.

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1. Introduction

Amorphous polymeric metal(IV) phosphates have been known for some time. Unlike the crystalline varieties, they have irregular structures and somewhat variable elemental composition, depending on the method of preparation [1]. X-ray analysis suggests that the amorphous materials consist of microcrystalline domains arranged randomly. Zirconium phosphate was the first of these inorganic polymers to be crystallized [2]; it was shown to have a lamellar structure [3,4] with the layers comprising zirconium atoms lying in a plane and bridged by phosphate groups located alternately above and below this plane. Other tetravalent metal phosphates crystallize similarly so that the topography of the planes differs

with the metal, while retaining some similarities. In addition to the variations possible in the four-valent metal, it has been shown that organophosphonates can be prepared from almost any phosphonic acid, organophosphonic acid or mono-organophosphate [5]. The wide variety of topographies available can be enhanced further by formation of solid solutions of different metal(IV) phosphates and of solutions incorporating metal(III) and metal(V) phosphates [6,7].

Amorphous metal phosphates are valuable catalysts and behave as solid acids. They have greater surface areas than the crystalline forms and hence greater specific catalytic activities. Such phosphates and phosphonates are particularly valuable in areas in which stability to high temperatures and high acidity are required [8]. It is also possible to make use of their ion exchange capacities to deposit other metal ions such as platinum or palladium onto their surfaces and then to reduce the metal ions to the zero-valent state,

* Corresponding author. Tel.: +44-151-794-3502;
fax: +44-151-794-3588.
E-mail address: rj05@liv.ac.uk (R.A.W. Johnstone).

giving a product [9,10] which is active in catalysing hydrogenations [11]. Although some experiments on these supported catalysts have been reported, they involve only one metal(IV) phosphate as support and no attempts have been made to study the effects of gross changes in the topography of the catalyst support on the course of reduction.

Therefore, in the present work, a wide range of metal phosphate catalyst supports has been examined for their effects on the course of hydrogenation. Such a preliminary study is inevitably somewhat empirical since detailed topographic studies of amorphous metal phosphates have not been carried out. Nevertheless, by examining the results of hydrogenation of pairs of compounds, it is possible to show that different metal phosphates can have significant effects on relative rates of reduction of the pairs of substrates.

The catalysts used in this work consisted of platinum or palladium deposited on a variety of metal(IV) phosphates. The Pt and Pd metals were deposited using published procedures [9] and the resulting catalysts were investigated for their effects on the relative hydrogenation rates of a small range of alkenes (1-octene, 1-, 3-, 4-methylcyclohexenes and cyclododecene), selected for their stereochemical variation in ease of access to the double bond to be reduced. Additionally, a commercial palladium-on-charcoal catalyst was chosen as a standard against which to assess changes in selectivity in the metal phosphate supported catalysts being studied.

2. Experimental

The alkenes and the corresponding alkanes are all known compounds, for which commercial samples were obtained (Aldrich) and used as such. Palladium-on-charcoal catalyst (5% w/w) was used as received (Engelhardt). Analyses of the progress of reaction were carried out on a Dani 3800 gas chromatograph with flame ionisation detector and either an SE30 or an FFAP capillary column (0.3 mm × 25 m). GC/MS data were recorded on a Fisons gas-liquid chromatograph, using a similar column to that for the analytical work. Surface areas were measured on a Micromeritics ASAP 2000 instrument, using nitrogen absorption.

2.1. Hydrogenation of alkenes

2.1.1. Reduction of 4-methylcyclohexene with platinumized or palladized metal(IV) phosphate catalysts

Catalyst (0.06 g), 4-methylcyclohexene (0.025 g), dodecane (0.022 g) and ethanol (5 ml) were placed in a 25 ml flask. After flushing out the air with hydrogen, the mixture was stirred at room temperature and pressure under hydrogen. The progress of reaction was monitored by removing samples through a rubber septum at intervals and analysing them by GC. The amount of unreacted alkene was calculated from peak areas, using dodecane as internal standard. At the end of reaction, the products were analysed by GC and by GC/MS. Other alkenes were hydrogenated similarly.

2.1.2. Calculation of rates of hydrogenation

The raw experimental data for yields of individual products was difficult to compare but the rate of disappearance of alkene was obtainable from its variation in concentration with time. Since the reactions at all times involve excess of hydrogen, they were treated as *pseudo* first order and the logarithm of alkene concentration was plotted against time. These plots were generally linear and enabled relative rate data to be extracted easily by comparison of the slopes of the graph plots. The rate of hydrogenation of 1-octene over Pd/C (5% w/w) was taken as a standard and its measured rate was arbitrarily assigned a value of 100 (units of per time).

It should be emphasised that these reported relative rates cannot be regarded as true rate constants. The rate at which hydrogen is adsorbed or diffuses to the surface of the catalyst may be significant but, because all reaction conditions remained the same throughout the series of experiments except for changes in the type of catalyst, the comparison of rates reported here is a valid procedure.

Data for the hydrogenation of 4-methylcyclohexene over palladized amorphous zirconium phosphate are given in Table 1. Hydrogenation of 1-octene over Pd/C gave a similar plot but hydrogenation over palladized metal(IV) phosphates gave different effects. Thus, hydrogenation of 1-octene over palladized pellicular zirconium phosphate gave the rate data shown in Table 2. In this last case, the hydrogenation had clearly ceased when only 27% complete. Analysis of the products showed that the 1-octene had rearranged to isomeric

Table 1
Hydrogenation of 4-methylcyclohexene over Pd⁰ZrPA^a

Time (min)	4-Methylcyclohexene remaining (A; %)	log ₁₀ (A)
0	100	2.000
5	60	1.778
10	50	1.703
15	36	1.559
20	22	1.346
30	9	0.949

^a 4-Methylcyclohexene (24 mg) in ethanol (5 ml). See Section 2 for other details.

octenes, which were not reduced to octanes, unlike the initial 1-octene. The log plot was curved and so the rate of hydrogenation of 1-octene was taken from the initial slope of the graph. This result is somewhat less accurate than the results obtained in those cases where isomerization was not observed.

2.1.3. Preparation of catalysts

In the following sections, the various phosphates are referred to by such descriptions as ZrPC (zirconium phosphate, crystalline) and ZrPA (zirconium phosphate, amorphous). Synthesis of amorphous zirconium phosphate ZrPA [11], titanium phosphate TiPA [7], tin phosphate SnPA [11] and pellicular zirconium phosphate ZrPpel [12] have been described elsewhere. Crystalline zirconium phosphate ZrPC was prepared by the published method [1]. Crystalline phosphates were further specified by descriptions such as ZrPC (11:126), denoting that the sample had been refluxed in 11 M phosphoric acid for 126 h.

Table 2
Hydrogenation of 1-octene over ZrPApel^a

Time (min)	1-Octene remaining (B; %)	log ₁₀ (B)
0	100	2.000
20	86	1.935
40	75	1.913
60	73	1.875
80	73	1.863
600	73	1.863
1400	73	1.863

^a 1-Octene (25 mg) in ethanol (5 ml). See Section 2 for other details of the standard conditions.

2.1.4. Amorphous yttrium phosphate [YPA]

An aqueous solution of yttrium chloride (YCl₃·6H₂O; 9.1 g) in water (75 ml) was added slowly to an aqueous solution of trisodium phosphate (9.84 g) in water (120 ml) with rapid stirring at room temperature [6]. After 60 min, the resulting gelatinous precipitate was washed with water several times. Each time, the gel was stirred in fresh water and allowed to stand for some time. The supernatant liquid was decanted off until it reached pH 7. Finally, the gel was dried gently at 110 °C under a vacuum of about 20 mm Hg.

2.1.5. Amorphous zirconium/yttrium phosphate (Zr/YPA)

A mixture of amorphous zirconium phosphate (3 g) and amorphous yttrium phosphate (3 g) was added to phosphoric acid (12 M; 400 ml) and the whole was refluxed until all of the phosphates had dissolved (6 h). The solution was diluted to 3 l with water and then neutralised by addition of solid sodium carbonate. The mixture was allowed to stand and the excess of liquid was decanted off. The residual precipitate was washed with water by decantation until the pH of the supernatant had dropped to 7. The residue was washed with distilled water and air-dried at 80 °C for 16 h [6].

2.1.6. Amorphous zirconium/titanium phosphate (Zr/TiPA)

A mixture of amorphous zirconium phosphate (2 g) and amorphous titanium phosphate (2 g) was added to phosphoric acid (14 M; 400 ml) and the whole was refluxed until the phosphates had dissolved (480 h) [6]. After cooling it to room temperature, the resulting clear solution was diluted with distilled water to 3 l, after which it was neutralised to pH 7 by addition of solid sodium carbonate. The product was worked up as for Zr/YPA.

2.1.7. Amorphous zirconium phenylphosphonate, ZrPhPA and amorphous titanium phenylphosphonate, TiPhPA

These were prepared by the general method for metal(IV) phenylphosphonates [13].

2.1.8. Platinized metal(IV) phosphates

These were prepared following a published procedure [9]. Sufficient catalyst was prepared in one batch to study all of the alkenes, thus ensuring that all results

Table 3
Relative rates of hydrogenation of alkenes^{a,b}

Catalyst ^c	1-Octene ^d	4-Methylcyclohexene	3-Methylcyclohexene	1-Methylcyclohexene	<i>cis</i> -Cyclododecene
Pd/C (5% w/w)	100	151			8.1
PdZrPA	40	125			7.9
PdTiPA	344	2.3			6.0
PdSnPA	260	8.1			3.0
PdZrPpel	8.5	7.9			0.2
PdZr/TiPA	6.8	1.5	0	0	0
PdTiPhPA	62	11.9	2.1	0	0
PtZrPA	0	0	0	0	0
PtZrP (11:126)	0	0	0	0	0
PtZr/TiPA	182	24	5.4	4.7	0
PtZr/YPA	23	3.2	0	0	0
PtZrPhPA	0	0	0	0	0
PtTiPhPA	0	0	0	0	0

^a Reactions were carried out at room temperature and atmospheric pressure. Detailed conditions are given in Section 2.

^b These are relative pseudo first-order rates of hydrogenation, compared with the rate of hydrogenation of 1-octene over Pd/C (5% w/w) set arbitrarily to 100.

^c See text for designations.

^d The rate of initial reaction was used because the substrate rearranged during the hydrogenation.

obtained for any one catalyst were comparable and that there could be no variations due to variations in batches of catalyst. In a typical reaction, a solution of PtCl₂ (1 g) in aqueous HCl (1 M; 2 l) was treated with aqueous ammonia (14%; approximately 350 ml) until pH 4.8–5.4. At this stage ZrPA (3 g) was added and the mixture was stirred at room temperature for 24 h to enable exchange to take place. The resulting solid was filtered off, washed with distilled water (50 ml) and dried at 50 °C to give Pt²⁺/ZrPA. This material was spread through a copper tube and heated to 400 °C in a stream of hydrogen for 14 h to give Pt⁰/ZrPA as a light grey solid.

Crystalline zirconium phosphate ZrPC (11:126) was platinumized similarly to give Pt⁰/ZrPC (11:126). The remaining phosphates were platinumized slightly differently in that exchange with Pt(NH₃)_nCl₂ was driven further to completion by refluxing it with the phosphate for 8 h instead of stirring them together for 24 h at room temperature. The platinumized phosphates are listed in Table 3.

2.1.9. Palladized metal(IV) phosphates

The above procedure for platination was followed except that PdCl₂ (1 g) was used in place of PtCl₂. Exchange was carried out exactly as above for 24 h at room temperature or 8 h under reflux for the corre-

sponding phosphates. The palladized phosphates (e.g. Pd⁰/ZrPA) are listed in Table 3.

3. Results and discussion

Catalysts may be prepared by coating a pre-prepared support with the catalytic metal salt before its reduction or by mixing catalytic metal salts in with the preparation of the support material. In the present work, only the first method was used so as not to disturb the structure of the support material, for which there are published data. The second method could well be expected to change the structure and topography of a metal phosphate support as well as making much of the catalytic metal inaccessible and, for these reasons, this form of preparation was not used.

Relative rates of hydrogenation of 1-octene (**1**), 4-methylcyclohexene (**2**), 3-methylcyclohexene (**3**), 1-methylcyclohexene (**4**) and *cis*-cyclododecene (**5**) are listed in Table 3. Attempted hydrogenation of α - or β -pinene for 24 h under the standard conditions given above showed no evidence for the formation of any reduced products. Comparison of rates of reduction amongst the various catalysts are not valid since topographies and metal coatings probably varied from catalyst to catalyst. However, as only one

batch of each catalyst was used throughout the work, comparison of rates of hydrogenation of the different alkenes on the same catalyst are perfectly valid. Thus, any observed rate variations can be discussed in the context of any one catalyst but no attempt has been made to compare such rates for any one alkene between the different catalysts.

Over the Pd/C catalyst, 4-methylcyclohexene, with its *cis*-disubstituted double bond, was reduced most rapidly. 1-Octene, with a singly substituted double bond was hydrogenated at only two-thirds of the rate of that for 4-methylcyclohexene. Since steric effects would be expected to dictate a reversal of the order, the greater electron density in the disubstituted bond may lead to the faster rate. Cyclododecene, also with a disubstituted double bond was very much slower to hydrogenate, as might be expected for steric reasons, the double bond being shielded by the folded ring system. When all of the catalysts listed in Table 3 are examined for this order of reactivity of the three alkenes towards hydrogenation, it is found that the cyclododecene is always the slowest, sometimes showing no detectable hydrogenation. The amorphous palladized catalysts gave rates of hydrogenation of cyclododecene, which were similar but the platinumized catalysts afforded no reduction. However, the order of reduction of 4-methylcyclohexene and 1-octene showed a remarkable variation amongst the catalysts. The results for Pd/C have been discussed above, where it was suggested that electronic and not steric factors played a large part in determining which alkene was reduced fastest. Palladized amorphous zirconium phosphate was almost as active as Pd/C and revealed the same order of ease of reduction for 1-octene and 4-methylcyclohexene as Pd/C but palladized amorphous titanium phosphate, with a somewhat smaller specific surface area, gave a remarkable reversal of this order, the 1-octene being reduced some 3.5 times faster than for Pd/C and the 4-methylcyclohexene some 70 times slower than for Pd/C (see Table 4). Palladized amorphous tin phosphate gave a similar result.

For palladized pellicular zirconium phosphate and platinumized crystalline zirconium phosphate, the specific surface areas of the support are very low and therefore, the amount of palladium or platinum deposited on the surface must be low. Only the palladized catalyst showed significant activity and this was some

Table 4
Surface areas of the various metal(IV) phosphates

Metal phosphate ^a	Surface area (m ² g ⁻¹) ^b
ZrPA	271
TiPA	110 ^c
ZrPpel	1.4
ZrP (11:126)	8.7 ^c
Zr/TiPA	338.0 ^d
Zr/YPA	338.2 ^d
ZrPhPA	196

^a See text for designations.

^b Measured by the BET method.

^c Taken from [15].

^d Taken from [16].

12 times worse than the best catalysts. In addition, there was much reduced selectivity. This suggests that many of the palladium (or platinum) sites on the amorphous catalyst surfaces are placed in sterically somewhat hindered positions, whereas the crystalline varieties of support have only crystal surfaces, which are not expected to have any marked steric effects.

The steric effects in the substrate would be expected to show up in the series of methylcyclohexenes, which were chosen so as to move the methyl group nearer and nearer to the double bond to be hydrogenated. Over palladized titanium phenylphosphonate and platinumized titanium phosphate, reduction of 4-methylcyclohexene was slower than reduction of 1-octene, an inverse of the order found for Pd/C catalyst. However, the 3- and 2-methylcyclohexenes were reduced much more slowly or not at all for some catalysts. It seems clear that increasing proximity of the methyl group to the double bond hinders the rate of hydrogenation through steric effects.

Steric effects are also shown to be important in the behaviour of 1-octene during hydrogenation. Its rate of hydrogenation over all of the catalysts was initially pseudo first order but, before it could be completely converted to octane, the reaction ceased. Gas chromatographic analysis of aliquots from the reaction mixture revealed that the slowing down of hydrogenation coincided with formation of other octenes. Migration of double bonds can occur as a result of acid catalysis but it can also result from metal catalysis, particularly with platinum [14]. The rearrangement of 1-octene to isomers leads to disubstituted

double bonds, which would be expected to hydrogenate at a different rate from the initial singly substituted double bond. However, the *cis*-double bond in 4-methylcyclohexene is easily reduced by most of the catalysts and, therefore, the observed effect is probably steric. With a terminal double bond, 1-octene can approach sites on the amorphous supports which are somewhat sterically hindered. When migration of the double bond has occurred to give more highly substituted bonds, approach to the catalyst site becomes more restricted and the rate of hydrogenation diminishes.

Overall, some of the palladized or platinized phosphate catalysts were as efficient or more so than was the commercial Pd/C but others were inferior, sometimes greatly so. There is a general correlation with steric effects in the substrate but the electronegativities of the metals in the phosphates (Zr, 1.2; Ti, 1.3; Sn, 1.7) do not correlate with relative rates. Neither of these factors could have any bearing on the significant and unpredictable variations in the order of reactivities of the two alkenes, 1-octene and 4-methylcyclohexene. The most likely cause of the effects is a variation in their interaction with the catalyst surface. Although the reason for the observed variation remains obscure, the effects are valuable empirically for indicating how selectivity in hydrogenation of alkenes might be improved in comparison with many “standard” catalysts. Because the reactions proceed rapidly, it could be argued that rates of diffusion of hydrogen to the catalyst surface would affect results. Since it is difficult to understand by this argument why rates of hydrogenation of individual alkenes should reverse with change of catalyst, it is concluded that any effects of variations due to diffusion control of relative rates must be very small.

4. Conclusion

The results demonstrate a substantial variation in relative rates of hydrogenation of 1-octene and 4-methylcyclohexene over a series of platinized and

palladized metal(IV) phosphates, some of which were more effective than standard Pd/C catalyst. The variation may correlate with surface topography but does not appear to correlate with the electronegativity of the metal in the metal phosphate.

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References

- [1] A. Clearfield, J.A. Stynes, *J. Inorg. Nucl. Chem.* 26 (1964) 117.
- [2] A. Clearfield, G.D. Smith, *Inorg. Chem.* 8 (1969) 431.
- [3] J.M. Troup, A. Clearfield, *Inorg. Chem.* 16 (1977) 3311.
- [4] G. Alberti, M. Casciola, U. Constantino, G. Levi, G.J. Riccardi, *J. Inorg. Nucl. Chem.* 40 (1978) 1113.
- [5] A. Clearfield, T.N. Frianeza, *J. Inorg. Nucl. Chem.* 40 (1978) 1925;
G. Bagnasco, P. Ciambelli, A. Frezza, P. Galli, A. La Ginestra, M. Turco, *Appl. Catal.* 68 (1991) 55.
- [6] L.F. Hodson, D. Whittaker, *J. Chem. Soc. Chem. Commun.* (1996) 2131.
- [7] G. Alberti, P. Cardini-Galli, J. Costanin, E. Torracca, *J. Inorg. Nucl. Chem.* 29 (1967) 571.
- [8] Y. Onoue, Y. Mizutani, S. Akiyama, Y. Izumi, Y. Watanabe, *Chem. Tech.* 7 (1977) 36.
- [9] Y. Watanabe, Y. Matsumura, Y. Izumi, Y. Mizutani, *Bull. Soc. Chem. Jpn.* 47 (1974) 2922.
- [10] Y. Onoue, Y. Mizutani, S. Akiyama, Y. Izumi, Y. Watanabe, *J. Catal.* 40 (1975) 76.
- [11] C.B. Amphlet, L.A. McDonald, M.J. Redman, *J. Inorg. Nucl. Chem.* 6 (1958) 220.
- [12] G. Alberti, M. Casciola, U. Constantino, *J. Colloid Interf. Sci.* 107 (1985) 256.
- [13] G. Alberti, U. Constantino, S. Alluli, N. Tomassini, *J. Inorg. Nucl. Chem.* 40 (1978) 1113.
- [14] A. La Ginestra, P. Patrono, M.L. Berardelli, P. Galli, C. Ferragina, M.A. Massucci, *J. Catal.* 103 (1987) 346.
- [15] M.C. Cruz Costa, Ph.D. Thesis, Faculty of Science, University of Liverpool, 1991.
- [16] L.F. Hodson, Ph.D. Thesis, Faculty of Science, University of Liverpool, 1996.