High surface area Pd, Pt and Ni ion-exchanged Zr, Ti and Sn(IV) phosphates and their application to selective heterogeneous catalytic hydrogenation of alkenes

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Abstract

Amorphous acidic metal(IV) phosphates of zirconium, titanium and tin have been prepared and hydrogen-exchanged for bivalent Pd, Pt and Ni. These bivalent metals were returned to the zero valent state by reducing them with either hydrogen at 400 °C or with sodium tetrahydroborate at room temperature. The resulting Pd^0, Pt^0 and Ni^0 phosphates were investigated as selective catalysts for heterogeneous hydrogenation of alkenes in solution at normal temperatures and pressures and, for Ni, also in the vapour phase. Quantitative studies on rates of hydrogenation are discussed. The usual methods for preparing metal(IV) phosphates give either crystalline or amorphous solids having low specific surfaces areas. A method has been developed, by which metal(IV) phosphates having large surface areas (lsa) may be prepared easily. These lsa supports take up large amounts of transition metal cations by simple exchange. The enhanced incorporation of Pd, Pt or Ni and increases in surface areas of the phosphate supports have provided some active, selective catalysts. Pd/Ti phosphates were the most active and compared well with commercial Pd on carbon. Ni/Ti phosphate is a very selective catalyst for vapour phase hydrogenation of alkenes and, at slightly higher temperatures, it is an efficient hydrocarbon cracking catalyst.
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1. Introduction

It is only relatively recently that serious attention has been paid to the diverse properties of metal(IV) phosphates [1], particularly for catalysis of organic reactions. The earliest investigations were in the nuclear industry and were prompted by their excellent ion-exchange capacity coupled with their stability to extremes of radiation, temperature and pH. The structures of various crystalline and isomorphous forms of metal(IV) phosphates [2], of which Zr has been by far the best studied, are well known [3]. Other phosphates include those of Ti, Sn, Hf and W [3,4]. Because of an abundance of acid sites, metal(IV) phosphates have been used in acid-catalysed reactions [5].

Exchanging protons for transition metal ions (Scheme 1; reaction 1) increases the catalytic range of the simpler metal(IV) phosphates but efficient exchange requires adequate spatial access to the protons. In crystalline forms of metal(IV) phosphates most of the acidic protons lie within the crystal structure and are not readily accessible. Better exchange can be achieved by opening up the layered structure in crystals [2,6] or by using amorphous forms. During the course of this present work, a simple method was developed to provide amorphous phosphates having much larger surface areas (lsa; about 100–200 m^2 g^{-1}) than either crystalline materials (about 1–2 m^2 g^{-1}) or previously described amorphous forms (about 10 m^2 g^{-1}). The lsa materials allow exchange of Pd^{2+}, Pt^{2+} and Ni^{2+} to the extent of 2–8% (w/w), similar to the usual content found in commercial catalysts supported on carbon.

Reduction of transition metal ions to metal can be effected with H$_2$ gas at 400 °C but this process causes a reduction in surface area and loss of acidity due to conversion of adjacent phosphate groups into pyrophosphate (Scheme 1, reaction 2a).
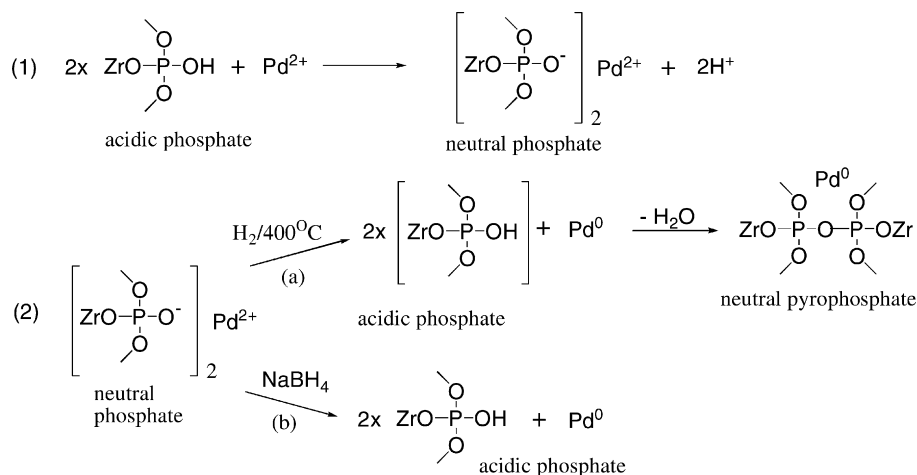
Scheme 1.

Much of the exchanged metal becomes inaccessible inside pyrophosphate "cages". However, reduction of many metal ions to the zero valent state is readily effected with NaBH$_4$ at room temperature [7]. Advantageously, with this method of reduction, phosphate acidity is retained without significant change in surface area (Scheme 1, reaction 2b). Thus, reduction of Pd^{2+}, Pt^{2+} or Ni^{2+}-exchanged lsa metal(IV) phosphates of Zr, Ti and Sn with NaBH$_4$, gave 9 new catalyst types, which were studied for their effectiveness towards hydrogenation of alkenes in the liquid phase and, for Ni, also in the vapour phase. With improved content and dispersion of transition metal and large surface areas, the solids compared favourably in activity with commercial Pd/C catalysts. Variations in catalytic activity were found, which might be expected because of electronic changes in the transition metal (Pd, Pt, Ni) coupled with changes in the central tetravalent metal (Ti, Sn, Zr) and possibly because of steric effects caused by the topography of the lsa phosphates.

2. Experimental

All chemicals were obtained from commercial sources and were checked for purity before use (GC, MS, ^{1}H NMR). Products from hydrogenation experiments were checked for identity by comparison with authentic specimens.

2.1. Metal(IV) phosphates

Zr [8], Sn [9], and Ti [10] phosphates were prepared as amorphous variations by two different methods [11,12] and in crystalline form.

2.1.1. Amorphous metal(IV) phosphates

Method 1: In a typical procedure, phosphoric acid (23.3 g) in water (470 mL) was added quickly to a rapidly stirred solution of zirconyl chloride (22.5 g) in water (140 mL) at room temperature. After centrifugation and removal of the supernatant liquor, the resulting gel was stirred with distilled water (4 × 400 mL), the gel being separated each time by centrifugation until the

supernatant liquid reached pH 4. The final gel (G) was dried overnight at 100 °C to give ordinary amorphous zirconium phosphate, ZrPA (17.4 g).

Method 2 (large surface area, lsa): The water-washed gel (G) was stirred for 15 min for each of five times with ethanol (5 × 300 mL). Finally, the suspension was centrifuged to remove most of the excess of solvent and the damp residue was spread out on a glass plate and dried under vacuum (100 °C/0.5 mmHg) for 30 min to give ZrPA/lsa (16.7 g). Similarly, amorphous titanium (TiPA, TiPA/lsa) and tin (SnPA, SnPA/lsa) phosphate were prepared [11,12].

2.1.2. Crystalline metal(IV) phosphates

In a typical procedure, the amorphous gel (G; 2 g) was dispersed into a solution of phosphoric acid (8 M, 100 mL) and the mixture was heated under reflux for 144 h. The resulting crystalline zirconium phosphate (ZrP) was filtered off, washed with water until the filtrate reached pH 4 and then dried overnight at 100 °C (1.92 g). Similarly, crystalline TiP and SnP were prepared.

2.1.3. Metal^{2+}-metal(IV) phosphates

Palladium: To a solution of PdCl$_2$ (1 g) in HCl (1 M, 1 L) was added an aqueous solution of ammonia (14%, w/w; ca. 350 mL) so that 4.8 < pH < 5.4 was attained. Into an aliquot of this PdCl$_2$ solution (100 mL) was dispersed amorphous ZrPA/lsa (1 g) with gentle stirring for 24 h at room temperature. The resulting H$^+$-exchanged solid (Pd^{2+}-ZrPA/lsa) was filtered off, washed with distilled water (100 mL) and dried overnight at 80 °C.

Platinum: PtCl$_2$ (1g) was dissolved in aqueous ammonia (14%, w/w, about 500 mL) and amorphous ZrP/lsa (1 g) was dispersed with stirring into a portion (100 mL) of this solution at room temperature. After 24 h, the resulting suspension was filtered off, washed with distilled water (100 mL) and dried overnight at 80 °C to give a dark solid (Pt^{2+}-ZrPA/lsa).

Nickel: Amorphous ZrPA/lsa (1 g) was dispersed into an aqueous solution of n-butylamine (0.1 M, 280 mL) and then stirred at room temperature for 24 h. The resulting suspension was filtered off, added to a solution of nickel acetate (0.1 M;

100 mL) and again stirred for 24 h at room temperature. Filtration gave a residue of Ni^{2+}-ZrPA/lsa, which was washed with water and dried overnight at 100 °C.

Similar Pd^{2+}, Pt^{2+} and Ni^{2+}-exchanged materials were prepared from TiPA/lsa and SnPA/lsa.

2.1.4. Metal[0]-metal(IV) phosphates

Method 1: The above ion-exchanged phosphates were reduced to the zero valent state by heating them at 400 °C in a slow stream of H_2 for 24 h. For example, Pt^{2+}-ZrPA gave Pt^0-ZrPA. Similarly, Pd^0 catalysts were prepared from ZrPA and TiPA but not from SnPA, in which Sn^{4+} is reduced to Sn^0 under these conditions.

Method 2: Pd^{2+}, Pt^{2+} and Ni^{2+}-exchanged Zr, Ti and Sn phosphates/lsa were reduced to the zero valent state by stirring them with a solution of $NaBH_4$. For example, a suspension of Pd^{2+}-SnPA/lsa (1 g) in ethanol (10 mL) was stirred with a solution of $NaBH_4$ (160 mg) in ethanol (10 mL) for 24 h at room temperature. The suspension was filtered and the residue was washed with ethanol (50 mL) and water (10 mL) and dried overnight at 50 °C. For Ni-exchanged materials, there has been debate about the nature of the 'Ni' produced by this method in that it may be partly or wholly a metal rich form of nickel boride, Ni_2B, in which isolated boron atoms are surrounded by Ni atoms [7,13,14a,15a]. For convenience of discussion in the present work, nickel formed this way is simply designated as Ni^0.

2.2. Structures of the amorphous phosphates

Several methods were used to provide an insight into the structures of the lsa phosphates in relation to the known lamellar arrangement of the corresponding crystalline metal(IV) phosphates [3,9,16]. Surface areas were measured on a Quantasorb Multipoint BET instrument with N_2 as sorbent gas. Infrared spectra of samples as KBr discs were obtained with a Perkin-Elmer 1720-X Fourier transform spectrometer in the range $4000–400\,cm^{-1}$. For atomic absorption spectroscopy, samples were dried overnight at 80 °C and measured for Pd, Pt and Ni content (metal/support, $mg\,g^{-1}$). Thermogravimetric analysis was kindly carried out by Interox Ltd., Warrington, UK. Samples were first dried at 80 °C overnight to remove adventitious water and then analysed by heating them in the range $20–1000\,°C$ at $10\,°C\,min^{-1}$ under a flush of N_2 of $80\,mL\,min^{-1}$ (automatic recording of percentage weight loss). X-ray powder diffraction spectra were measured on a Phillips PW 1710 X-ray diffractometer at 0–80° diffraction angles (2θ). For solid state ^{31}P NMR spectroscopy, samples were measured as crystalline or amorphous powders on a Bruker MSL 400P (9.4 T) instrument set for magic angle spinning, with and without cross-polarisation for detection of hydrogen bonding from water or POH groups. Isotropic chemical shifts (ppm) were measured against concentrated H_3PO_4 ($\delta = 0$) [17].

2.3. Analysis of products of reduction of alkenes

Gas chromatographic analyses were obtained with a Dani 3800 HRPTV gas chromatograph using a high resolution 30 m × 0.32 mm capillary column wall-coated with SE-30 liquid phase of 0.25 mm thickness. For quantification, a known amount of an internal standard (toluene) was added at the start to all reaction mixtures, from which small aliquots were withdrawn at intervals. The GC apparatus was pre-calibrated by using solutions of known concentrations of the substances to be monitored together with a known quantity of toluene. When accurate rate data were required, analyses were duplicated or triplicated to give mean values. Gas chromatography/mass spectrometry was used to confirm identities of products of hydrogenation by use of a Fisons Trio 3000 GC–MS, operating under EI conditions at 70 V and by comparison of mass spectra and retention times with those of authentic specimens.

2.4. Reduction of alkenes

The Pd^0, Pt^0 and Ni^0 versions of the crystalline and amorphous Zr, Ti, and Sn phosphates were examined for their ability to catalyse the reduction of a selected range of alkenes with H_2. The resulting activities and selectivities were compared with those of samples of Pd/C (5 or 10%, w/w) catalyst taken from single manufactured batches (kindly supplied by Johnson-Matthey).

2.4.1. Liquid phase hydrogenation at atmospheric pressure

In a typical experiment, Pd^0-TiZrPA/lsa (0.06 g) was placed in a flask and a vacuum was applied to remove air. A solution of 1-octene (40 μL) and toluene (30 μL; internal standard) in ethanol (5 mL) was added and the mixture was stirred gently at room temperature. After filling the flask with H_2 at atmospheric pressure, the progress of reduction was monitored by taking small samples of the liquid phase at intervals for analysis by GC or GC–MS.

2.4.2. Liquid phase hydrogenation under pressure

In a model experiment, Pt^0-ZrPA/lsa (0.08 g), toluene (30 μL), and cyclohexene (40 μL) were stirred at 60 °C in a high pressure vessel (50 mL) filled with H_2 at 5 atmospheres. Small aliquots were withdrawn at regular intervals and analysed by GC or GC–MS.

2.4.3. Hydrogenation of alkenes with Ni-TiPA/lsa in the gas phase

A stream of H_2 was bubbled through the alkene (pre-heated to 120–180 °C), the vapour of which was swept by the gas stream through a heated glass tube containing the catalyst sprinkled on glass wool. Two temperature regimes were used, one with the catalyst held at 200 °C and the other at 140 °C. Products of reaction were collected in glass U-tubes cooled to −60 °C and were analysed by GC–MS.

3. Results and discussion

3.1. Metal(IV) phosphates

Easily made and cheap amorphous metal(IV) phosphates provide many possibilities for large structural changes to be made

Table 1
Surface areas of some metal(IV) phosphates

Phosphate	Surface area ($m^2 g^{-1}$)
ZrPA	7[a]
ZrPA/lsa	259[b]
Pd-ZrPA/lsa	65[b]
TiPA/lsa	121[b]
Pd-TiPA/lsa	68[b]
SnPA	9[a]
Pd-SnPA	1[c]

[a] Typical value for an amorphous material made directly from aqueous gel.
[b] Amorphous material made from ethanolic gel.
[c] Collapse of open structure on reducing Pd^{2+} to Pd^0 at 400 °C in H_2.

in the form and properties of a catalyst support. The range can be vastly extended by using organic phosphinates and phosphates as interlamellar pillars in place of or together with inorganic phosphate [5,18]. One of the most important properties of metal(IV) phosphates lies in their multiplicity of protonic sites [19], which can be exchanged for other cations [20].

3.1.1. Large surface area amorphous metal(IV) phosphates

Phosphates used in the present study were made in crystalline form (ZrP, TiP, SnP) and as large surface area amorphous solids (ZrPA/lsa, TiPA/lsa, SnPA/lsa). Some specific surface areas are listed (Table 1). Crystalline varieties were used mostly as structural standards, with which to compare the amorphous forms. Generally, amorphous metal(IV) phosphates are prepared as gels in an aqueous medium and are dried by evaporating entrained water by heat or freeze drying. Incipient cavities form as the gels solidify but, as evaporation continues, the fragile cavity walls collapse because of the high surface tension of water, resulting in materials having surface areas not much larger than the crystalline forms. To obtain larger surface areas, water needs to be displaced from the gels by a water-miscible solvent of lower surface tension. In this present work, ethanol proved to be suitable and gave amorphous solids having much larger surface areas (lsa) than those made by evaporation of water. For example, ZrPA formed from an aqueous gel had a surface area of only 7 $m^2 g^{-1}$ but ZrPA/lsa made by the ethanol process had a surface area of 259 $m^2 g^{-1}$. On exchange with $PtCl_2$, ZrPA isolated from an aqueous solvent took up only about 8 $mg g^{-1}$ of Pt^{2+} but ethanol-derived ZrPA/lsa exchanged 85 $mg g^{-1}$ (8.5%, w/w; Table 2).

3.1.2. Spectra of metal(IV) phosphates

Table 2
Transition metal uptake ($mg g^{-1}$) by metal(IV) phosphates[a]

Phosphate	Pd	Ni	Pt
ZrPA	7	–	8
ZrPA/lsa	18	51	85
TiPA	14	–	–
TiPA/lsa	24	69	85
SnPA/lsa	21	63	84

[a] Samples dried at 80 °C before analysis.

3.1.2.1. X-ray diffraction.
The XRD spectra of crystalline phosphates exhibited several sharp reflections. The smallest angle reflection (2θ) is ascribed to interlayer spacing [21], which was 7.46, 7.58 and 6.70 Å for α-ZrP, TiP and SnP, respectively. XRD spectra of lsa phosphates showed very broad peaks but the maxima of the more intense were centred on the narrow peaks observed in spectra of the crystalline forms. The results suggest that there is still a degree of crystallinity in the amorphous materials and that they probably consist of short sections of ordered crystalline layers (microcrystallites) arranged almost randomly.

3.1.2.2. Infrared.
Infrared spectra of the crystalline and lsa metal(IV) phosphates are all similar and are dominated by a few broad bands, mainly at 3600–2700 cm^{-1} due to O–H stretch from H_2O and phosphate and to P–O stretch (1060 cm^{-1}). There were only small differences between the IR spectra of crystalline ZrP and its metal-exchanged form Pd^0-ZrP indicating that Pd atoms must be present in the main ZrP structure without there being formal covalent bonding to phosphate.

3.1.2.3. Thermogravimetric analysis.
On heating any of the phosphates up to about 200 °C, interstitial water H-bonded to phosphate (POH) is driven off. At about 400 °C more water is driven off as –OH groups condense to form pyrophosphate ($2 \times$ [P-OH] → [P-O-P] + H_2O). These changes were accompanied by a large decrease in the intensity of the O-H stretch band near 3500 cm^{-1}. From 600 to 1000 °C, there was no significant further weight loss. The weight changes due to water loss at about 200 and 400 °C are sharply defined in crystalline phosphates but occur over greater temperature ranges in amorphous materials.

3.1.2.4. ^{31}P NMR (mas).
^{31}P-Solid state (magic angle) NMR spectroscopy provided greater detail about the arrangement of phosphate groups in both crystalline and amorphous metal(IV) phosphates. Data for ZrP are discussed in detail here while similar data for TiP and SnP are only compared with ZrP. "Connectivity" (Q^n, $n = 0$–4) for solid phosphates has been used as a means of distinguishing the arrangement of bonds between phosphate groups and the tetravalent metals to which they are attached. Thus, 4 bonds from phosphate to a metal centre is four-fold connectivity Q^4, three bonds is Q^3 and so on to Q^0 [22]. Connectivities are associated with a spread of ^{31}P chemical shifts of about 10–15 ppm. The ^{31}P NMR spectrum of crystalline α-ZrP consisted of two peaks at −19.5, −21.3 ppm (δ) from the internal standard (H_3PO_4). The first peak is only slightly smaller than the second but, on cross-polarization, the peak at −19.5 ppm becomes much bigger than the other. Since cross-polarization enhances the signal from phosphate groups, which are H-bonded to water, it is clear that crystalline α-ZrP must be Q^3 connected to Zr with half of the phosphate groups H-bonded to interstitial water. The observation is entirely in keeping with the published XRD analysis of its structure [23]. Similar shifts and behaviour on cross-polarization were found for TiP (−18.6, −18.9 ppm) and SnP (−11.2, −12.0 ppm), demonstrating that all three phosphates have very similar structures. There is a linear correlation of

mean ^{31}P chemical shift (Δ) and electronegativities (X) of Zr, Ti and Sn, Δ (ppm) = 16.9X − 41.4), in keeping with a single structural type and isomorphous changes at the metal centres. Samples of zirconium phosphate were also examined by ^{31}P NMR spectroscopy, after drying them at 150 or 530 °C. At the lower temperature, thermogravimetric analysis indicates the loss of almost all interstitial water and this anhydrous state is reflected in the ^{31}P NMR spectrum. The Q^3 peak at −19.5 ppm (phosphate H-bonded to H_2O) almost disappears and the remaining peak at −21.3 ppm is substantially unaffected by cross-polarization, in keeping with the absence of H-bonding from P–OH groups to water. A small new peak appears as a shoulder near −30 ppm. After heating ZrP at 530 °C, the Q^3 signal at −21.3 ppm almost disappeared and was largely replaced by a new band at −33 ppm due to the formation of pyrophosphate.

The above chemical shift changes in crystalline phosphates are valuable indicators of structural variations in their amorphous forms. Deconvolution of the broad peaks in the ^{31}P NMR spectrum of ZrP/lsa dried at 150 °C revealed five components. The main peak at −21 ppm, which corresponds to the dominant Q^3 signal in crystalline ZrP is unchanged on cross-polarization. The broadness of the peak (3.5 ppm at half-height) is consistent with a fairly random orientation of microcrystallites, in each of which the Q^3 units ($\equiv$P–OH) retain their crystal orientation with respect to each other. Other smaller peaks occur at −26, −19, −13 and −7 ppm. These large shifts away from the Q^3 signal, suggest they are caused by other connectivities, viz., a substantial proportion of phosphate groups must have Q^4, Q^2 and Q^1 connectivities in the amorphous state. A reasonable conclusion would be that the microcrystallites indicated by XRD spectra have sides and edges possessing phosphate groups with more or fewer PO– linkages to Zr. The increased proportion of such sites would afford better exchange with Pd, Pt or Ni ions than is possible in crystalline ZrP, in which the majority of $\equiv$P–OH sites reside in the interiors of close-packed crystals. As shown (Table 2), a characteristic of the lsa amorphous phosphates is their much greater capacity for ion exchange in comparison with crystalline forms.

3.1.3. Reduction of Pd^{2+}, Pt^{2+} and Ni^{2+} to the metallic state

The final step of reducing the exchanged ions to their zero valent states was initially effected by heating ion-exchanged amorphous phosphates in a stream of H_2 at 400 °C. This high temperature treatment inevitably leads to elimination of water and loss of acidity as phosphate groups are transformed into pyrophosphate. Surface area measurements showed that, with this method of reduction, the original large surface area was reduced considerably and Pd^0 sites appear to become trapped in pyrophosphate 'cages'. Even worse, reduction of tin phosphate at 400 °C produced a large weight loss and a total collapse in surface area as Sn^{4+} was converted to Sn^0 (Table 1).

Loss of acidity and surface area during reduction with H_2 at 400 °C (Scheme 1; reaction 1) was avoided by using $NaBH_4$ as the reducing agent at room temperature (Scheme 1; reaction 2) [7]. Although there is some uncertainty about the nature of
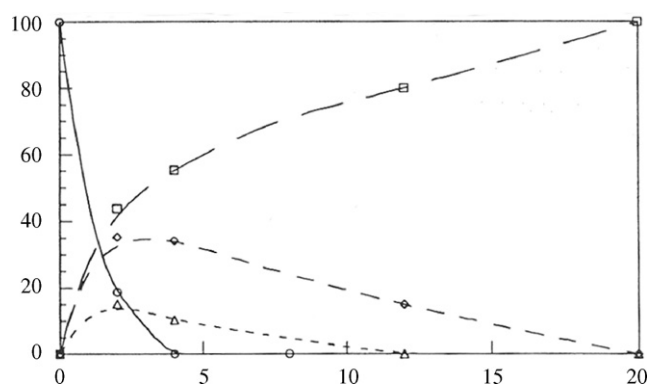
Fig. 1. Percentage conversion (y-axis) of 1-octene ($\bigcirc$) with H_2 into octane ($\square$), *trans*-2-octene ($\lozenge$) and *cis*-2-octene ($\triangle$), using Pd^0-TiPA/lsa as catalyst in ethanol at 20 °C; x-axis is time (min); (Section 3.2.1).

the nickel produced by hydride reduction, the method is particularly advantageous for Ni^{2+}-exchanged phosphates because finely divided Ni^0 oxidises in air and its formation at 400 °C in H_2 gives a product that rapidly reverts to Ni^{2+}. However, for vapour phase experiments, Ni^{2+}ZrPA/lsa was reduced to Ni^0 with H_2 in the alkene reactor vessel immediately prior to its use as a catalyst for hydrogenation.

3.2. Hydrogenation of alkenes

3.2.1. With Pd^0-metal(IV) phosphates

Initial experiments on hydrogenation of 1-octene showed that Pd^0 catalysts made from large surface area phosphate supports were catalytically very active and selective. A solution of 1-octene in ethanol stirred with Pd^0-TiPA/lsa under H_2 at 1 atm leads to complete disappearance of the terminal alkene in 4 min and gives octane but only in 55% yield. At the same time as some 1-octene is hydrogenated to octane, the remainder is isomerized to a mixture of *cis*-2-octene (10%) and *trans*-2-octene (35%). Fig. 1 shows that the rate of disappearance of 1-octene is classically exponential and can be interpreted as pseudo first order or in terms of the proportion of catalyst sites covered with reactant [24–26]. The 2-octenes appear in bursts alongside the burst of formation of octane. Immediately after the 1-octene has disappeared, the rate of formation of octane becomes less and constant (steady state [27]) over the next 15 min until a 100% yield is attained. This steady state rate of formation of octane is matched by similar constant rates of disappearance of the 2-octenes as they are hydrogenated (Fig. 1). The rates of hydrogenation of the *trans*- and *cis*-2-octene are almost identical and are much less than the rate for direct reduction of 1-octene to octane. Assuming rates of reaction at catalytic sites can be represented as pseudo-first order with rate = k[substrate], where k is a complex experimental rate constant [24–26], then the graphs up to 4 min in Fig. 1 can be analysed to give the rate constants shown in Table 3. Thus, the rates of appearance of octane, *trans*-2-octene and *cis*-2-octene gave respective rate constants of k_1, k_2, k_3 and the rate of disappearance of 1-octene gave k_4. As expected of three concomitant pseudo-first order reactions from a single substrate, $k_4 \approx k_1 + k_2 + k_3$. After total consumption of 1-octene, steady-state conditions are assumed for the long linear

Table 3
Rate constants for hydrogenation of 1-octene solutions with H_2 and Pd^0/Pt^0-metal(IV) phosphates as catalysts at 20 °C[a]

Phosphate	k_1	k_2	k_3	k_4	k_1'	k_2'	k_3'
Pd^0-TiPA/lsa	0.0060	0.0050	0.0020	0.0140	0.00043	0.00040	0.00025
Pd^0-ZrPA/lsa	0.0035	0.0015	0.0011	0.0066	0.00001	0.00001	0.000005
Pd^0-SnPA/lsa	0.0018	0.0010	0.0004	0.0032	0.00005	0.00005	0.00005
Pt^0-ZrPA/lsa	0.0005			0.0005	0.00005		

[a] See Scheme 2 for designation of rate constants, k. All k are in s^{-1} and relate to the fraction (f) of material converted at any time t ($0 \leq f \leq 1$). In all experiments, the initial molar concentration of 1-octene in ethanol was 0.052 mol l^{-1} ($f = 1$). For $k_1 - k_4$, the kinetics were interpreted as first order and the units are dimensionless. For $k_1' - k_3'$, the above values need to be multiplied by the initial concentration of 1-octene to convert them to mol L^{-1} s^{-1} [23].

sections representing formation of octane from *cis*- and *trans*-2-octene so that the corresponding rate constants are given by the slopes for formation of octane (k_1') and disappearance of *trans*-2-octene (k_2') and *cis*-2-octene (k_3'). All the above rate constants for hydrogenation of 1-octene with Pd^0-TiPA/lsa, together with the corresponding ones for Pd^0-SnPA/lsa and Pd^0-ZrPA/lsa, are listed in Table 3 [27].

By using combined pseudo-first order and steady-state rate equations with the experimentally derived rate constants of Table 3, the graphs shown in Fig. 1 are reproduced accurately. Kinetic implications are discussed later (Section 4).

As experimental verification, the rate of hydrogenation of an authentic sample of *trans*-2-octene over Pd^0-TiPA/lsa was measured directly. After a small initial burst that produced some octane and about 11% of *cis*-2-octene, the rate of formation of octane became constant at 5×10^{-4} s^{-1} [27]. This rate is close to that observed for the steady state rate reduction of 1-octene with the same catalyst (Table 3; Pd^0-TiPA/lsa; k_1'). There was no further double bond migration along the octyl chain. To verify this lack of isomerization, attempts were made to hydrogenate authentic specimens of *trans*-3- and *cis*/*trans*-4-octene. No octane was formed and no isomerization could be detected over periods of 3–4 h. These results show that Pd^0-TiPA/lsa is a good catalyst for hydrogenation of terminal *n*-alkenes but is poor for other C=C bonds.

Isomerization of alkenes over Pd^{2+} and Pd^0 catalysts is well documented [28–30] and is believed to proceed either through a hydride addition/elimination reaction or via a π-complex. In the latter, the allylic hydrogen that is removed must be sterically accessible and lie on the same side of the molecule as the entering hydrogen. Except when particularly stable double bonds can be formed, isomerization may be expected to continue almost randomly, particularly at elevated temperatures.

The selectivity exhibited by Pd^0-TiPA/lsa could be either electronic in origin or could be due to topographical (steric) features of the catalyst support. As a simple extension to the molecular size and shape of 1-octene, hydrogenation of the bigger analogue, 1-decene, was studied. Overall, the results were identical to those seen with 1-octene except that the reaction was slightly slower. There was an initial 10 min burst of formation of decane (62%) with concomitant isomerization to *cis*-(14%) and *trans*-2-decene (23%) and then a second steady state stage occurred as the 2-decenes were slowly hydrogenated to decane. This second stage hydrogenation was much slower than for 1-octene with a rate constant of 3×10^{-5} s^{-1} compared with 43×10^{-5} s^{-1}. Again, no isomers other than *cis*/*trans*-2-decene

were formed. Clearly, the terminal alkene could still reach Pd sites almost as easily as 1-octene and, like the 2-octenes, 2-decenes were reduced with greater difficulty.

Because acidic phosphates are known to cause isomerization of alkenes by a proton addition/release mechanism [31], it was necessary to verify that the protonic sites in Pd^0-TiPA/lsa and its analogues were not the primary cause of the double bond shifts observed during hydrogenation. When the above hydrogenation experiments were repeated in the absence of H_2 and even extended for several hours, there was no isomerization in either 1-octene or 1-decene. Because there is isomerization and reduction in the presence of H_2 and neither occurs in its absence, simple acid catalysis can be eliminated as a cause of the observed isomerization, at least at room temperatures.

Scheme 2 demonstrates that two separate complexes are needed to explain the observations. Apart from the possibility of shape selectivity in the support or unusual electronic effects in the catalyst/substrate intermediate, there seems no reason for complex 1 to form complex 2 and then for the latter not to form similar π-complexes by migration along the octyl chain. Other than terminal alkenes, double bonds along an alkyl chain such as those in *trans*- and *cis*-2-, 3- and 4-octenes are each connected to two hydrogen atoms and two alkyl groups and have very similar thermochemical energies. This aspect to selectivity towards isomerization was studied further by hydrogenation of cyclic alkenes (see below).

When the catalyst was changed to the zirconium analogue, Pd^0-ZrPA/lsa, two changes were immediately apparent. First, the rate of disappearance of 1-octene was significantly less than with Pd^0-TiPA/lsa, requiring about 20 min instead of only 4 to complete of the first stage (Table 3; k_4 values). Secondly,
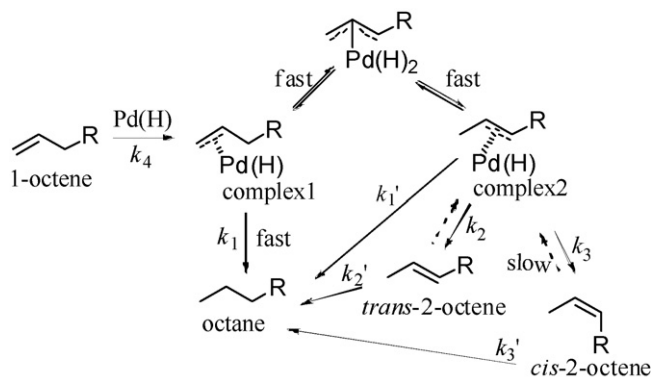
Scheme 2.

isomerization was still observed but when reduction of 1-octene was complete, there was no hydrogenation of 2-octenes. This makes Pd^0-ZrPA/lsa more selective than Pd^0-TiPA/lsa and also demonstrates that back isomerization from 2- to 1-octene cannot be energetically favourable. The increased selectivity of Pd^0-ZrPA/lsa was confirmed by its failure to hydrogenate authentic samples of 2-, 3- or 4-octene. Apart from some initial isomerization, the catalyst is remarkably selective in its ability to reduce only terminal alkenes.

On changing the catalyst to the tin analogue, Pd^0-SnPA/lsa, the rates of hydrogenation and isomerization fell below those observed with Pd^0-ZrPA/lsa and Pd^0-TiPA/lsa. Again, initial bursts of formation of octane, *trans*-2-octene and *cis*-2-octene were followed by further reduction of the 2-octenes (Table 3). For the three Pd^0 catalysts supported on Ti, Zr and Sn phosphates, rates of hydrogenation and isomerization vary with the tetravalent metal in the order Ti > Zr > Sn and their electronegativities change in the order Sn > Ti ≈ Zr. The rates appear to be consistent with an electronic effect of the tetravalent metals on Pd.

The effect of substrate size on catalyst activity was examined further by varying the alkene to be hydrogenated. Cyclohexene has a disubstituted *cis* double bond, the ends of which are held back by the small ring itself and the *trans* version cannot be isolated under normal conditions. Its molar volume ($M_v = 101$ mL) is significantly less than that of 1-octene ($M_v = 157$ mL). Migration of the *cis*-double bond around the ring of cyclohexene is not observable in the present experiments because, in the absence of isotopic labelling, bond migration would only reproduce starting material. However, such unobserved bond movement might be expected to have an effect on rates of hydrogenation.

Hydrogenation of cyclohexene with the most active catalyst, Pd^0-TiPA/lsa, produced a short burst of fairly rapid reduction to cyclohexane ($k_1 = 6 \times 10^{-4}$ s^{-1}) but still about 10 times slower than that for initial conversion of 1-octene into octane. After the burst, the steady state rate (k_1') was 7×10^{-5} s^{-1}. Small rates of reaction with porous solids can be caused by interference with diffusion as substrate molecules try to move towards a catalyst site through narrow channels. However, the metal(IV) phosphates have relatively large average pore diameters of about 10 nm and they are stirred during reaction. The observed rates are much greater than those usually associated with diffusion controlled reactions [32–34]. Therefore, the slower steady state rate of hydrogenation of cyclohexene compared with 1-octene does not appear to be related to its size (smaller than 1-octene) nor to the sizes of any pores in the catalyst support.

The apparent absence of significant steric effects was examined by hydrogenating the larger cyclooctene ($M_v = 130$ mL) and cyclododecene ($M_v = 195$ mL). Each produced a very small burst phase and the subsequent steady state rates of hydrogenation (k_1') were, respectively, 4×10^{-5} and 2×10^{-5} s^{-1}, which are only slightly less than that for cyclohexene. Molecular size does not appear to be a controlling factor in differentiating these rates of hydrogenation.

To determine whether or not unobserved movement of the double bond around the cyclohexene ring might mask its true rate of reduction, 4-methylcyclohexene having a methyl
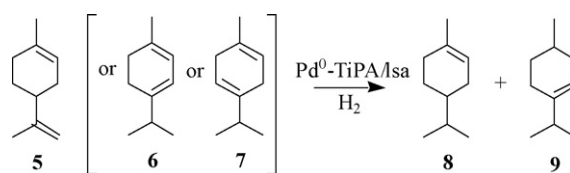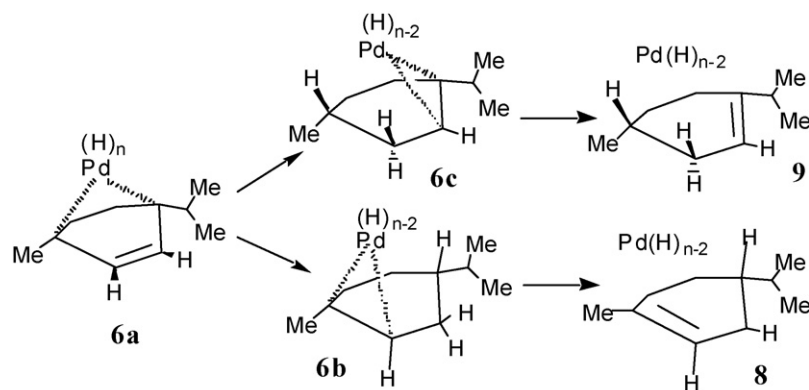

Scheme 3.

group remote from the double bond was hydrogenated. Reduction to 1-methylcyclohexane proceeded at a steady state rate (8×10^{-5} s^{-1}), which is almost the same as that for cyclohexene. No double bond isomers of 4-methylcyclohexene were formed. Similarly, attempted hydrogenation of 1-methylcyclohexene gave no double bond isomers and no reduction to 1-methylcyclohexane occurred. Thus, rates of hydrogenation for cyclohexene and 4-methylcyclohexene were similar to those found with *trans*- and *cis*-2-octene and *cis/trans*-2-decene and, like the latter, there was no movement of the double bond around the structure.

Reaction of Pd, Pt or Ni with alkenes gives $^2\eta$ or π-allyl complexes but these metals also form $^4\eta$ compounds with conjugated and non-conjugated dienes, in which both double bonds are simultaneously bonded to one metal atom [14b]. In the $^4\eta$ complexes, it is known that hydrogenation of just one of these bonds then becomes relatively easy [29a]. To discover whether or not double bond migration could be induced in cyclohexadienes as against lack of it in cyclohexenes, limonene **5**, α-terpinene **6**, and γ-terpinene **7** (Scheme 3) were hydrogenated with Pd^0-ZrPA/lsa. With limonene, the 2,2′ disubstituted double bond in the propenyl side-chain was reduced to propyl at a faster rate ($k_4 = 1 \times 10^{-4}$ s^{-1}) than the 1,2-substituted bonds in 2-alkenes but slower than the singly substituted double bond in 1-octene.

After hydrogenation ceased, the expected 1-methyl-4-isopropylcyclohexene **8** (Scheme 3) had been formed in 75% yield but its isomer, 1-isopropyl-4-methylcyclohexene **9** was also present in 25% yield. As with 1-methylcyclohexene, the trisubstituted double bond in the ring of limonene was not hydrogenated but it was partly shifted from the 1- to the 3-position. Thus, although there was no conjugated diene in limonene and the side-chain was rapidly reduced, there was also some ring isomerization. This behaviour is consistent with earlier findings that dienes can be isomerized and selectively reduced on complexation to various transition metal salts [30,35].

The next hydrogenations were carried out with α- and γ-terpinene **6**, **7**, in which both double bonds are in the ring and the side chain is already in the reduced state. Both dienes **6**, **7** gave the same products **8**, **9** as those obtained from limonene (Scheme 3).

The conjugated diene in α-terpinene can form a $^4\eta$ complex with Pd and was rapidly reduced to a mixture of the two monoenes **8**, **9** in 56 and 44% yield respectively. The simultaneous burst in formation of the two monoenes ($k_1 = 6.3 \times 10^{-4}$ and 3.2×10^{-4} s^{-1}) carried reaction to completion in less than 40 min and indicated that they were formed from the same initial Pd complex **6a** (Scheme 4). Complexation of the diene to Pd(H)$_n$ is followed by H-transfer to give $^2\eta$ complexes **6b**, **6c** which are unstable and dissociate to give the products **8**, **9**. No

Scheme 4.

further reduction or isomerization was observed during the next 5 h.

For the non-conjugated diene in γ-terpinene, formation of a $^4\eta$ complex is more difficult. Hydrogenation and isomerization to products **8,9** was not complete even after nearly 6 h ($k_1 = 5.6 \times 10^{-5}$ and $5.1 \times 10^{-5}\,\mathrm{s^{-1}}$), at which stage the monoenes had been formed in 48 and 40% yields respectively. The large difference in rates for α- and γ-terpinene but formation of the same products in similar yields suggests that, for γ-terpinene there is first a slow isomerization to α-terpinene followed by faster reduction of one of the bonds. Similar isomerization of $^4\eta$ diene complexes has been observed when sterols were reacted with $Fe(CO)_5$ or $RhCl_3$ [35].

The above observations show that, for 1-alkenes, reduction is always accompanied by isomerization of the double bond to the 2-position but there is no further isomerization. No bond migration is observed in cyclohexenes. Random isomerization in any of the alkenes is not observed. For the most active catalyst (Pd⁰-TiPA/lsa), rates of hydrogenation of 1-alkenes are comparable to those of normal 5% Pd/C catalysts but, except for 2-octenes, which hydrogenate very slowly, rates of reduction of other types of double bond are zero. In this sense, the phosphate supported catalysts are similar in activity to Pd/C with regard to terminal alkenes but are much more selective towards hydrogenation of other types of alkene. Less active or 'poisoned' Pd/C catalysts have been prepared to discriminate between double bond types [15b,36]. It is known that increasing alkyl substitution in an alkene lowers the stability of $^2\eta$ and $^4\eta$ complexes with transition metals and that *trans* double bonds form less stable complexes than do *cis* bonds [14b]. The results with Pd phosphate catalysts are entirely consistent with changes in stability of catalyst/alkene complexes. Selectivity towards hydrogenation of terminal alkenes suggests that the electronic activity of the Pd has been modified by the support in such a way that it can form complexes with terminal alkenes but hardly or not at all with more highly substituted alkenes. As discussed above, steric effects on rates of hydrogenation due to the amorphous nature of the phosphate supports do not appear to be important. The importance of stable complex formation to Pd being the over-riding factor in determining the rate of hydrogenation of alkenes is confirmed by the experiments with cyclohexenes, limonene and α- and γ-terpinene. Simple cyclohexenes can only form $^2\eta$

complexes to Pd and only hydrogenation of *cis*-disubstituted double bonds is observed and there is no isomerization. In contrast, dienes limonene, α- and γ-terpinene can form stronger complexes to Pd and so that both hydrogenation of trisubstituted double bonds and isomerization is observed. Significantly, after one of the diene double bonds has been hydrogenated and only a $^2\eta$ complexation is possible, no further hydrogenation or isomerization takes place. Therefore, it is probable that the phosphate support modifies the electronegativity of Pd in such a way that complex formation to 1-alkenes and cyclic dienes is marginally favourable and becomes less so for other types of alkene. The sensitivity to stable complexation results in the observed selectivity in the catalysts. In this sense, these catalysts are similar to the intentionally 'poisoned' catalysts used to improve selectivity of Pd on carbon catalysts [15b,36]. These kinetic aspects are discussed below (Section 4).

3.2.2. With Pt⁰ metal(IV) phosphates

Pt⁰-ZrPA/lsa was less active than Pd⁰-ZrPA/lsa even though the proportion of Pt to support ($85\,\mathrm{mg\,g^{-1}}$) was much greater than that of Pd ($18\,\mathrm{mg\,g^{-1}}$). The selectivity towards reduction of terminal alkenes remained and, typically for Pt catalysts [29,30,35], double bond migration was not observed at room temperatures. Thus, 1-octene was hydrogenated to octane in 4 h at room temperature and 1 atm pressure of H_2 but revealed no formation of isomers (see Table 3 for rate constants). Cyclohexene, 1- and 4-methylcyclohexene and cyclooctene were all hydrogenated at similar low rates. For example, cyclooctene gave only 25% of cyclooctane after 10 h. At 60 °C and 5 atmospheres pressure of H_2, all hydrogenations became faster but products of isomerization of double bonds began to be significant. Because of their low activity even at elevated temperatures and hydrogen pressure, these Pt catalysts were not examined further. Some typical results are shown in Table 4.

3.2.3. With Ni⁰ metal(IV) phosphates

In attempted heterogeneous liquid phase reactions at atmospheric pressure or greater and at room temperature or higher, Ni⁰-ZrPA/lsa and Ni⁰-TiPA/lsa were only modest catalysts for reduction of alkenes with H_2 but the Ti phosphate was significantly better than its Zr analogue. For example, using Ni⁰-TiPA/lsa, 1-octene could be reduced to octane in 90% yield

Table 4
Hydrogenation of alkenes with Pt^0-ZrPA/lsa at 60 °C and 5 atmospheres pressure for 2 h

Alkene	Yield of alkane (%)
1-Octene	69
trans-2-Octene	82
trans-4-Octene	0
1-Decene	48
Cyclohexene	86
1-Methylcyclohexene	17
4-Methylcyclohexene	29
Cyclooctene	44

Table 5
Hydrogenation of alkenes with H$_2$ in the vapour phase using Ni^0-TiPA/lsa[a] as catalyst at atmospheric pressure

Alkene	Reaction temperature (°C)	Yield of alkane (%)[b]
1-Octene	145	>99
trans-2-Octene	145	1
trans-4-Octene	145	0
1-Decene	190	98
Cyclohexene	100	16
4-Methylcyclohexene	120	2
1-Methylcyclohexene	130	0
Cyclooctene	165	1

[a] Prepared by reduction of Ni^{2+}-TiPA/lsa with H$_2$ in situ at 400 °C.
[b] GC–MS analysis of condensate from heated reactor.

after 2 h at 60 °C in the liquid phase. Under these more forcing conditions, cyclohexene, 4-methylcyclohexene, *trans*-2-octene, cyclooctene and 1-decene were all reduced to the corresponding alkane in poor to modest yields ranging from 21 to 78% after 2 h. For liquid phase work at room temperatures, these results did not compare favourably with the analogous Pd or Pt phosphate catalysts but selectivity appeared to be different and there was no isomerization. Therefore, it was decided to examine the vapour phase hydrogenation of alkenes with Ni^0-TiPA/lsa, in which the nickel was definitely Ni^0 and not a mixture of nickel borides.

A slow stream of hydrogen was passed through a heated (400 °C) silica tube containing Ni^{2+}-TiPA/lsa sprinkled on glass wool for 8 h to produce Ni^0-TiPA/lsa, which was used in situ. The reactor tube was cooled to about 200 °C. The hydrogen flow was then bubbled through an alkene maintained at about 20 °C below its boiling point, the mixed vapours and gas being immediately passed over the catalyst. Products of reaction were trapped in U-tubes at −60 °C. Initially, the catalyst was maintained at 50–80 °C above the boiling point of the alkene to be reduced. For example, 1-octene vapour and H$_2$ were passed over the catalyst at 200 °C. At this temperature, there was a very poor recovery of product, indicating that non-condensable gases had been formed. In addition, the liquid that was recovered contained no 1-octene and very little octane but it did contain a wide range of other alkanes and alkenes of lower molecular mass. Analysis of the products by GC–MS showed that extensive cracking of the hydrocarbon had occurred to give a complex mixture of straight and branched chain alkanes and alkenes. Although this was not the desired hydrogenation, the efficiency of the Ni^0-TiPA as a cracking catalyst was remarkably good at such a relatively low temperature.

Assuming that the reactor temperature had been too high, it was reduced to about 150 °C, at which temperature no cracking was observed and recovery of products was good. The catalyst revealed remarkable selectivity towards hydrogenation of terminal alkenes (Table 5). 1-Octene and 1-decene were reduced to the corresponding alkanes in almost 100% yield but *cis*- and *trans*-2-octene, *trans*-4-octene, 1- and 4-methylcyclohexene were almost unchanged; cyclohexene was reduced only to the extent of 17%. No optimisation of these results was attempted but the selectivity indicates that the Ni catalyst prepared in situ was much more selective towards hydrogenation of terminal alkenes than the catalyst made by reduction of Ni^{2+}-TiPA/lsa with NaBH$_4$. There was no double bond isomerization. The slow

reduction of cyclohexene indicates some reactivity towards a *cis*-double bond but the very small yields of octane from *trans*-2- and 4-octene show the catalyst has excellent selectivity. There exists a possibility for development of Ni^0-TiPA/lsa as a cheap selective catalyst for vapour phase hydrogenation of terminal alkenes or, at slightly higher temperatures, as an excellent hydrocarbon cracking catalyst.

4. Kinetics

All of the reductions were characterised by an initial burst phase of product(s) followed by a steady state to completion. This form of kinetics can be related to complex formation with enzymes [25,26]. The basic equation for kinetic interpretation of enzyme catalysis is, $r = k[E_0][S]/(K_m + [S])$, where r = rate of reaction, $[E_0]$ is the amount of enzyme, $[S]$ is the concentration of substrate and K_m is the stability constant for complexation of substrate to enzyme. For present purposes, this equation is transformed to $r = k[C][\text{alkene}]/(K + [\text{alkene}])$, where C is the heterogeneous catalyst. For $K \gg [\text{alkene}]$, the rate becomes $r = k'$ $[C][\text{alkene}]$, where $k' = k/K$ and, because the amount of heterogeneous catalyst is constant, this becomes a pseudo first order reaction [25]. In contrast, if complexation is weak with $K \ll [\text{alkene}]$ then $r = k'[C]$, viz., the rate is constant (steady state). The reaction of 1-octene with Pd^0-TiPA/lsa and H$_2$ produces a rapid exponential burst of formation of octane (k_1), *trans*-2-octene (k_2) and *cis*-2-octene (k_3) and this may be ascribed to good complexation of the terminal alkene to the Pd catalyst. The rate of disappearance of 1-octene (k_4) is similarly exponential and $k_4 = k_1 + k_2 + k_3$ [27]. Further production of octane through hydrogenation of the *cis*- and *trans*-2-octene is much slower and follows a "zero" order, corresponding to weak complexation of 2-octene to the Pd catalyst ($K \ll [\text{alkene}]$). The result is confirmed by direct hydrogenation of *trans*-2-octene, which proceeds almost entirely through a steady state or zero rate process (k_1') having a rate constant identical to that found in the 1-octene experiments. Since all reactions were carried out under almost identical conditions of amounts, temperature and pressure, the observed variations in Pd, Pt and Ni catalysts at room temperature are all ascribable to changes in the complexation constant (K) between each metal and any one alkene. The complexation constant for *cis*- or *trans*-3- and 4-octene must be even smaller

again because no significant hydrogenation was observed over periods of several hours. The selectivity of these catalysts appears to be directly related to modifications to the complexation constant K brought about by the type of phosphate support used (Ti, Zr, Sn). Since $^2\eta$-alkene complexes to metal atoms is the result of σ-donation to the metal and π-back donation to the alkene, any changes to this balance will be reflected in the values for the complexation constant K. Therefore, it seems likely that the observed variations in hydrogenation rates may be attributed to effects of the metal phosphates on electron densities in the valence orbitals of the Pd, Pt and Ni (or Ni_2B) metals. For Ni in the gas phase, the highly selective results and lack of isomerization suggest that the phosphate supports provide a very sensitive control over the ability of the metal to form $^2\eta$ complexes.

5. Conclusions

All hydrogenation described here proceeded through an initial burst phase, in which isomerization may occur particularly with Pd and a subsequent steady state phase, in which hydrogenation of the initial alkene or its isomers continues to completion. Rates of reaction are steady state, often after an initial burst phase (burst kinetics). Rates of reaction appear to be related to the electronegativity of the 4-valent metal in the phosphate support and to the degree of substitution in the double bond. Hydrogenation of trisubstituted bonds occurred only when they were associated with another double bond as part of a 4η complex. When isomerization did occur, it was not random. There appeared to be little or no relationship of rates of hydrogenation with either molecular size or with the topography of the support. The major conclusion is that alkenes only form reasonably strong $^2\eta$ complexes with terminal alkenes and $^4\eta$ complexes with conjugated dienes. The strength of the complexes varies with the nature of the 4-valent metal in the catalyst support, giving scope for development of even more selective hydrogenation catalysts.

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[27] For convenience, rate data were interpreted as mole fractions (f; $0 \leq f \leq 1$), viz., as percentage yield at any time t divided by 100. Disappearance or formation through first order kinetics [k_1, k_2, k_3, k_4) has no effect on absolute k values by using f. The rate constants are related through the expression, $k_4 = k_1 + k_2 + k_3$. For steady state kinetics, values listed in Table 3 [k'_1, k'_2, k'_3] need to be multiplied by the initial concentration of alkene ($0.052 \, \mathrm{mol \, l^{-1}}$) to obtain the more usual molar values of k ($\mathrm{mol \, l^{-1} \, s^{-1}}$). Since all initial concentrations were the same, this change does not affect the interpretation of the results.

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[32] With these small rate constants, the possibility of diffusion controlled reactions becomes feasible. However, rate constants for such reactions are generally in the range of 10^{-9}–$10^{-10} \, \mathrm{s^{-1}}$ [33,34], considerably smaller than the values found here. For Zeolites having controlled pore diameters, it has been found that, at pore sizes of about 10 nm Knudsen flow must be considered, in which interaction with the pore walls slows the diffusion process. For the pore sizes in the metal(IV) phosphates/las, present surface area measurements gave a mean pore diameter of 10 nm, which is at the level that Knudsen diffusion can be expected to reduce normal rates of molecular diffusion to about 10^{-7}–$10^{-9} \, \mathrm{s^{-1}}$. Even these values are about 100 to 1000 times less than the rates observed in the present work. It is therefore assumed that the small rates of reaction reported here are inherent in the process and have little if any cause from restricted access to Pd sites.

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