

## Studies on some hydrogenation reactions using Pd (II) and Ru(III) supported catalyst

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Amorphous and crystalline phases of zirconium(IV) phosphate of the class of tetravalent metal acid (tma) salt have been synthesized by sol-gel method. These materials have been characterized for elemental analysis (ICP-AES), thermal analysis (TGA), X-ray analysis, surface area (BET method) and FTIR spectroscopy. Chemical resistivity of these materials has been accessed in acids, bases and organic solvent media. Exchangeable protons, contained in structural hydroxyl groups, indicate good potential for tma salts to be investigated as supports in heterogenised homogeneous catalysis. Pd(II) and Ru(III) has been exchanged onto amorphous and crystalline zirconium phosphate by ion exchange technique and catalytic activity investigated in some hydrogenation reactions.

**Keywords:** Heterogenised homogeneous catalysis, Hydrogenation, Palladium supported catalyst, Ruthenium supported catalyst

### Introduction

Catalytic hydrogenation reactions are of widespread use in food, drug and cosmetic industries<sup>1</sup>. Use of transition metal catalysts in selective hydrogenation of organic compounds is extensively reported<sup>2,3</sup>. However, such catalysts are easily poisoned by sulfur compounds, normally present in hydrocarbon streams<sup>4,5</sup>. Transition metal complexes are reported excellent hydrogenation catalysts, both homogeneous and heterogeneous<sup>6-9</sup>. Heterogenised homogeneous catalysis is gaining increasing importance over traditional homogeneous and heterogeneous catalysis. Major advantage of heterogenised homogeneous catalysis is unique microenvironment created for reactants within the support, improved catalyst stability within matrix<sup>10</sup>, increased selectivity for intramolecular reactions<sup>11</sup>, enhanced regioselectivity due to steric hindrance<sup>12</sup> and superior activity of some supported chiral catalysts due to site cooperation<sup>13</sup>.

Ru, Pd, Pt and Rh, supported onto organic (polymeric) and inorganic supports have been studied for various hydrogenation reactions<sup>14-17</sup>. However, polymeric supports and metal oxide supports pose problems due to poor heat transfer ability and leaching respectively.

Ion exchangers prove to be superior supports in heterogenised homogeneous catalysis. Tetravalent metal acid (TMA) salts are cation exchangers possessing structural hydroxyl groups, H of structural –OH being exchangeable sites. TMA salts possess excellent thermal and chemical resistivity and have good potential for application as supports in heterogenised homogeneous catalysis<sup>18-20</sup>.

In present study, zirconium phosphate (ZrP) has been synthesized as ZrPA (amorphous) and ZrPC (crystalline) by sol gel method and characterized for elemental analysis (ICP-AES), thermal analysis (TGA), X-ray analysis and FTIR spectroscopy. Chemical resistivity has been accessed in acids, bases and organic solvent media. Pd(II) and Ru(III) have been anchored onto ZrPA and ZrPC by ion exchange method to yield PdZrPA & PdZrPC and RuZrPA & RuZrPC respectively. Materials were explored for catalytic hydrogenation of 1-octene and cyclohexanone.

### Materials and Methods

#### Preparation of Amorphous Zr(IV) Phosphate (ZrPA)

Amorphous Zr(IV) phosphate has been prepared by mixing aqueous solutions of 0.1 M  $ZrOCl_2 \cdot 8H_2O$  (100 ml) and 0.2 M sodium dihydrogen phosphate (100 ml) at pH 1-2, dropwise and with continuous stirring at 70°C. Gelatinous precipitates obtained was digested for 1 h at 70°C, filtered, washed with conductivity water till removal

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of chloride ions, followed by drying at room temperature. Material was sieved (30-60 mesh) and finally converted to acid form by treating material (5g) with 1M HNO<sub>3</sub> (50 ml) for 30 min, with occasional shaking. Sample was then separated from acid by decantation and washed with conductivity water for removal of adhering acid. Acid treatment was repeated at least five times. After final washing, material was dried at room temperature, and used for all studies.

#### Preparation of Crystalline Zr(IV) Phosphate (ZrPC)

Crystalline material was prepared by HF method<sup>21</sup>. To a 0.2 M solution of ZrOCl<sub>2</sub>·8H<sub>2</sub>O, containing HF and Zr (molar ratio F/Zr = 5.2) was added to 46 ml o-phosphoric acid (85%). It was heated on a water bath (70-75°C) for 5-6 days. Distilled water was added periodically to keep volume constant. Microcrystals obtained were filtered from the system, washed thoroughly with deionised water and dried at room temperature.

#### Preparation of RuZrPA and RuZrPC

RuZrPA and RuZrPC were prepared by equilibrating aqueous RuCl<sub>3</sub> solution (0.1% wt/vol, 100 ml) with ZrPA or ZrPC (2 g) as the case may be, with continuous stirring at 50°C for 100 h. Solid was separated by filtration and washed with conductivity water for removal of adhering ions and dried at room temperature.

#### Preparation of PdZrPA and PdZrPC

PdZrPA and PdZrPC were prepared by equilibrating aqueous PdCl<sub>2</sub> solution (0.1% wt/vol, 100 ml) with ZrPA or ZrPC (2 g) as the case may be, with continuous stirring at 50°C for 100 h. Solid was separated by filtration and washed with conductivity water for removal of adhering ions and dried at room temperature.

#### Instrumentation

Samples were analyzed for Zr, P, Pd and Ru content by ICP-AES. X-ray diffractogram (2θ = 5-80°C) was obtained on X-ray diffractometer (Rigaku Dmax 2200) with Cu-Kα radiation and nickel filter. FTIR spectra were recorded using KBr wafer on a Bomem MB series. Thermal analysis (TGA) was carried out on a Shimadzu thermal analyzer at a heating rate of 10°C/min. Surface area measurement of supports were carried out by BET multipoint method using a Micromeritics Gemini 2220 series surface area analyzer. Chemical resistivity in various media (acids, bases and organic solvents) was studied by taking 500 mg of particular M(IV) phosphate in 50 ml of particular medium and allowing to stand for

24 h. Change in color, nature and weight was observed. Further, to confirm stability/solubility of exchanger in particular media, supernatant liquid was checked qualitatively for respective elements of the exchanger.

#### Catalytic Reactions

Hydrogenation reactions were carried out by varying amounts of catalyst and substrate, hydrogen (H<sub>2</sub>) pressure, reaction time and stirring speed and these parameters optimized. All reactions were carried out in an autoclave (500 ml) with a PID controller at 25°C. Catalyst was initially allowed to swell in methanol for 15 min. To this, 10 mmol substrate was added and reactor was sealed. H<sub>2</sub> pressure in the reactor was varied (100-300 psi) and contents were stirred for specific time intervals. H<sub>2</sub> remaining in the system was released and product obtained analyzed by GC. Blank experiments were also performed to see if support itself facilitates any hydrogenation. Further, to check leaching of metal from supports, after reaction, catalyst was separated from reaction mixture and again same reaction mixture was charged to reactor, and hydrogenation was carried out. After 4 h, sample was withdrawn and analyzed by GC.

## Results and Discussion

### Characterization

ZrPA was obtained as white hard granules, while ZrPC as fine white powder. Elemental analysis performed by ICP-AES shows Zr: P in ZrPA and ZrPC to be 1:2. Pd was found to be: PdZrPA, 1.62; and PdZrPC, 1.31%. Ru was found to be: RuZrPA, 1.92; and RuZrPC, 1.41%. Absence of any sharp peaks in X-ray diffractogram for ZrPA (Fig. 1) indicates amorphous nature of material. In case of ZrPC (Fig. 2), sharp peaks (2θ=11.2,25.1) were obtained confirming crystalline nature. FTIR spectra of both ZrPA and ZrPC (Figs 3 & 4) exhibit a broad band (~3400cm<sup>-1</sup>), attributed to asymmetric and symmetric –OH stretches. A sharp medium band (1635cm<sup>-1</sup>) is attributed to aquo (H–O–H) bending, a band (~1035cm<sup>-1</sup>) is attributed to P=O stretching, and a medium intensity band (1400cm<sup>-1</sup>) is attributed to ν(POH)<sup>22</sup>.

TGA of ZrPA (Fig. 5) indicates two weight loss regions: i) ~13% up to 180°C is attributed to loss of moisture/hydrated water; ii) ~6% for temperature range 250-500°C is attributed to condensation of structural hydroxyl groups. TGA of ZrPC (Fig. 6) also indicates two weight loss regions: i) ~1.04% up to 180°C is attributed to loss of moisture/hydrated water; and ii) ~9.7% up to 800°C is attributed to condensation of structural hydroxyl groups.

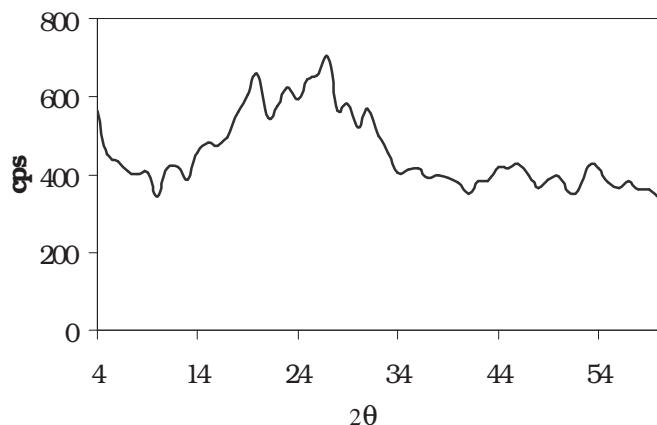


Fig. 1—XRD of ZrPA

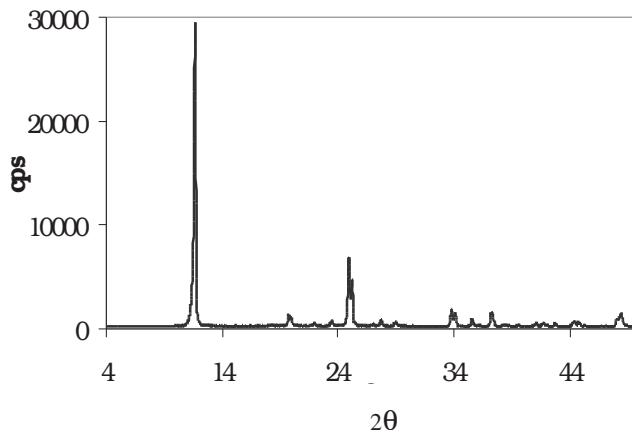


Fig. 2—XRD of ZrPC

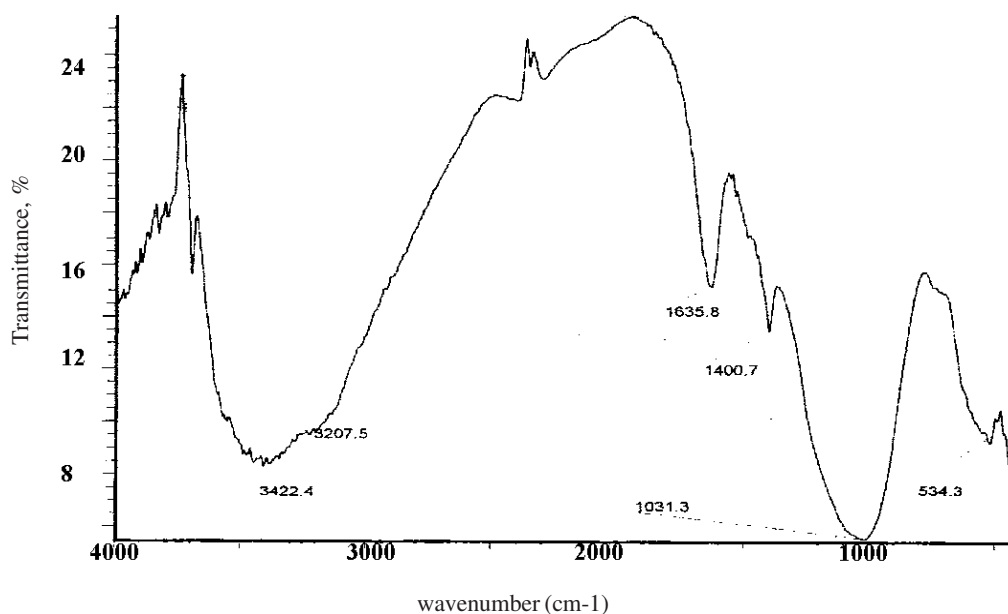


Fig. 3—FTIR of ZrPA

Surface areas of supports were found to be: ZrPA, 282.17; ZrPC, 2.722; RuZrPA, 190.18; PdZrPA, 184.27; RuZrPC, 2.52; and PdZrPC, 2.48 m<sup>2</sup>/g. Metal exchanged phases exhibit lower surface area compared to parent materials, probably due to pore blocking in the structure by incorporation of larger ions in place of replaceable  $\text{H}^+$  ions. Based on ICP-AES and TGA data, ZrPA and ZrPC has been formulated as  $\text{Zr}(\text{HPO}_4)_2 \cdot 2.5\text{H}_2\text{O}$  and  $\text{Zr}(\text{HPO}_4)_2 \cdot 0.75\text{H}_2\text{O}$  using Alberti and Torracca formula<sup>23</sup>. ZrPA and ZrPC are found to be stable in acid medium [maximum tolerable limits being ( $\text{H}_2\text{SO}_4 \sim 36\text{ N}$ ,  $\text{HNO}_3 \sim 16\text{ N}$  and  $\text{HCl} \sim 10\text{ N}$ )] and also stable in organic solvent media (ethanol, benzene, acetone, acetic acid etc.), but not so stable in base medium, [maximum tolerable limits being (5 N in NaOH and KOH)].

#### Catalytic Reactions

No hydrogenation of substrates in absence of either catalyst or  $\text{H}_2$ , confirms that both catalyst and  $\text{H}_2$  are essential for hydrogenation reactions. Upon hydrogenation, 1-octene gives n-octane, whereas cyclohexanone gives cyclohexanol. Higher yields, obtained using RuZrPA in case of hydrogenation of 1-octene (Table 1), may be due to higher loading of Ru and ability of Ru to facilitate reactions at relatively milder operating conditions as compared to Pd. Yields are directly dependent on catalyst amount, substrate concentration, amount of hydrogen present ( $p\text{H}_2$ ) and stirring speed, in the system. Increase in yields with increasing amounts of catalyst and decreasing amounts of substrate, could be attributed to higher catalyst to

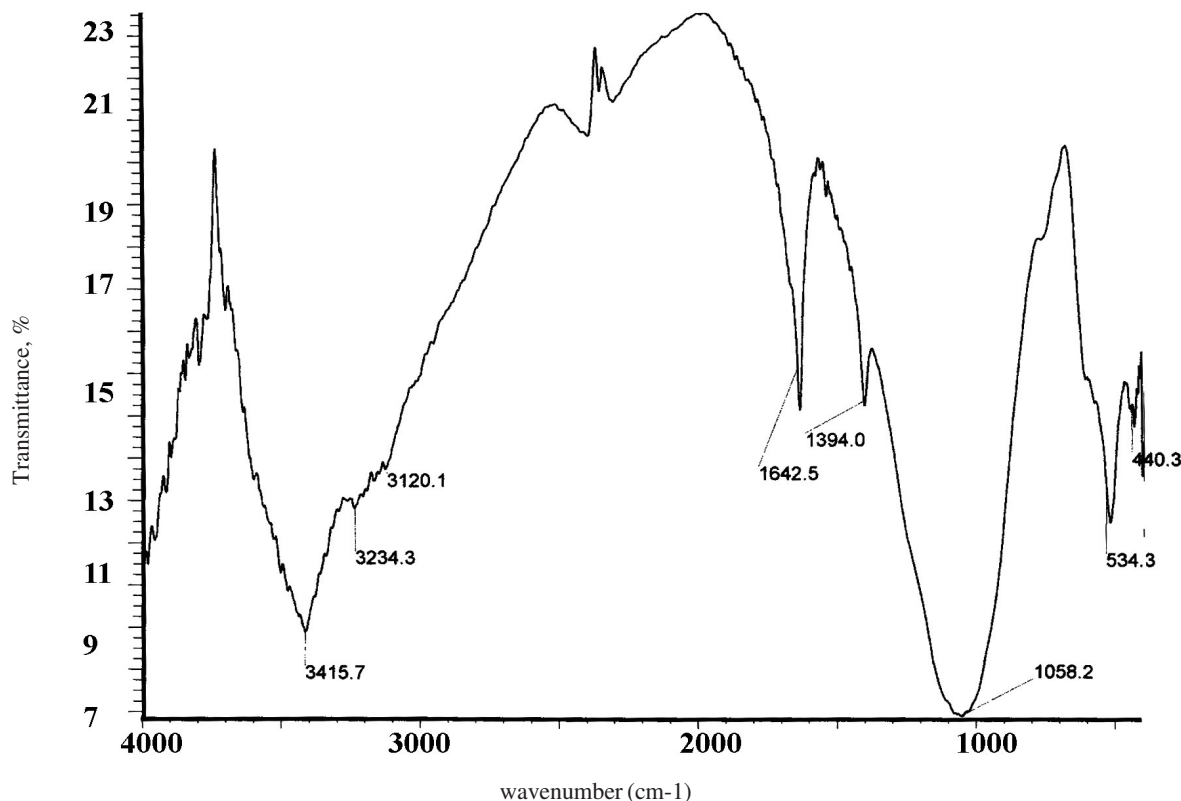


Fig. 4—FTIR of ZrPC

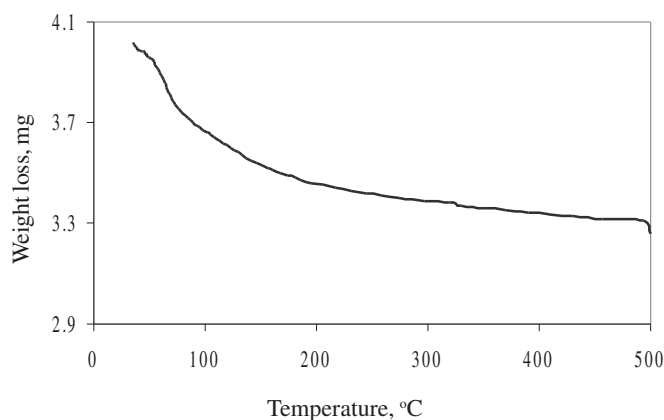


Fig. 5—TGA of ZrPA

substrate ratio. On increasing pressure, yield increases, may be attributed to a concentrated  $H_2$  environment resulting in greater  $H_2$  adsorption by catalyst. Higher yields due to increased stirring may be attributed to greater dissolution of  $H_2$  into the system and hence more availability for reaction. Low yields are obtained using RuZrPC and PdZrPC in 1-octene hydrogenation, may be attributed to very low surface area of support, which in turn does not allow a monolayer dispersion of active

component (Ru or Pd) onto support as well as a very low metal loading. Also, amount of Ru and Pd loading obtained onto supports are less than those obtained in case of amorphous supports.

Under reduction of cyclohexanone using Ru and Pd supported systems (catalyst, 0.1 g; cyclohexanone, 10 mmol; stirring, 100 rpm;  $pH_2$ , 200 psi; and time, 4 h), cyclohexanol yield was found as follows: PdZrPA, 46.20; PdZrPC, 33.14; RuZrPA, 1; and RuZrPC, 1%. In case of hydrogenation of cyclohexanone, yields are higher with PdZrPA. Ru based systems are better catalysts when carbonyl group is in vicinity of a conjugated or isolated double bond<sup>24</sup>. In order to hydrogenate double bond in a Ru supported system, basicity of the system has to be increased for better interaction between carbonyl function and catalytic system<sup>24</sup>. Using a Ru based system, for preferential hydrogenation of C=O to occur, a promoter such as Ga, Ti, alkali metals etc<sup>25</sup>. is essential. Acidic support used in present work may be contributing factor, affecting reactivity of C=O group in case of both RuZrPA and RuZrPC. Cyclohexanone conversion does not go beyond 1% for both RuZrPA and RuZrPC, may be attributed to very high activation energy required to break

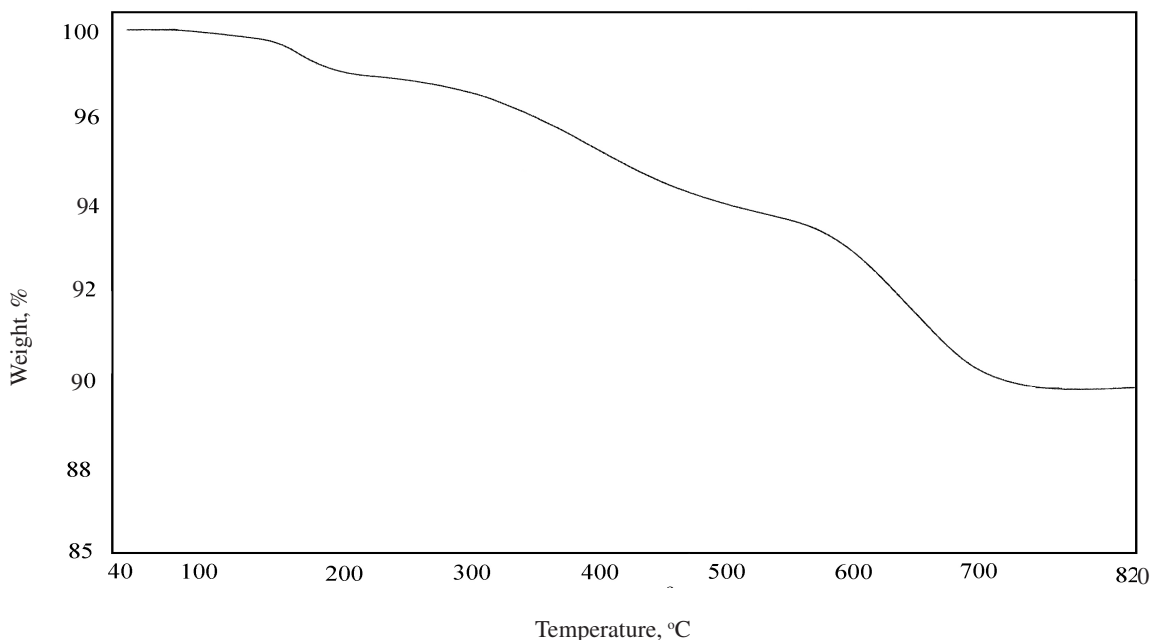
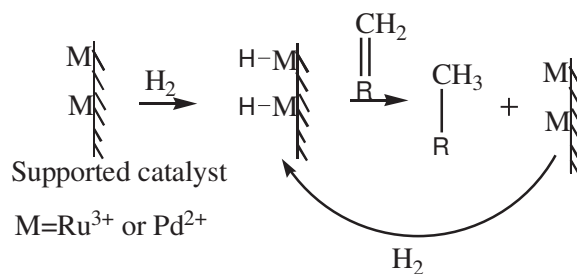


Fig. 6—TGA of ZrPC

Table 1—Reduction of 1-octene using ruthenium supported catalyst at different reaction conditions

Parameters	Catalyst g	1-octene mmol	Stirring rpm	pH <sub>2</sub> psi	Time h	Octane yield %	
						RuZrPA	PdZrPA
RuZrPA & PdZrPA						RuZrPA	PdZrPA
Catalyst concentration	0.05	10	100	200	4	8.1	6.9
	0.1	10	100	200	4	19.9	23.7
Substrate concentration	0.1	5	100	200	4	36.8	15
	0.1	10	100	200	4	28.8	10.3
Stirring speed	0.1	10	0	200	4	23.9	11.5
	0.1	10	200	200	4	59.7	41.7
pH <sub>2</sub>	0.1	10	100	100	4	14.1	6.1
	0.1	10	100	300	4	31	20.2
RuZrPC & PdZrPC						RuZrPC	PdZrPC
	0.1	10	100	200	4	3.2	3.0

C=O bond present in cyclic ring system (without any conjugated double bond). Comparable yields are obtained for PdZrPA and PdZrPC, attributed to almost same amount of loading of Pd metal. Further, conversions were found to be unaltered after separation of catalyst from reaction mixture, indicating that catalysis is heterogeneous and there is no leaching of the metal. Hydrogenation reaction probably follows a free radical pathway<sup>26</sup> (Scheme 1).



Scheme 1—Mechanism for hydrogenation using metal exchanged ZrPA and ZrPC

## Conclusions

ZrPA and ZrPC have potential as supports in hydrogenation of 1-octene and cyclohexanone.

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