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Hydrogenation and Oxidation Reactions Involving Ruthenium Supported Catalysts

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The present study involves synthesis and characterization of M(IV) phosphates and tungstates which are inorganic cation exchangers of the class of tetravalent metal acid (tma) salts possessing structural hydroxyl groups, the H of the structural –OH being the cation exchange sites, which indicates good potential for application as supports in heterogenized homogeneous catalysis. Ru(III) has been exchanged onto these materials by an ion exchange technique and catalytic activity investigated for oxidation of benzyl alcohol and styrene. Further, Ru(III) has been reduced to Ru(0) and catalytic activity has been explored for hydrogenation of 1-octene, nitro benzene, and cyclohexanone.

1. Introduction

Catalytic selective oxidation and hydrogenation reactions are of fundamental importance in synthetic organic chemistry. Hydrogenolysis is a chemical reaction whereby a carbon–carbon or carbon–heteroatom single bond is cleaved or undergoes “lysis” by hydrogen.¹ The heteroatom may vary, but it is usually oxygen, nitrogen, or sulfur. A related reaction is hydrogenation, where hydrogen is added to the molecule, without cleaving bonds. Usually hydrogenolysis is conducted catalytically using hydrogen gas. The use of supported and unsupported transition metal catalysts in the selective hydrogenation of organic compounds is reported.^{2,3} In recent years, significant advances have been observed in the development of active and selective catalysts for liquid phase oxidation of organic compounds involving the use of homogeneous^{4,5} and heterogeneous catalysts.⁶ The development of environmentally benign synthesis has evoked a renewed interest in developing solid supported systems and considerable attention focused toward the choice of environmentally benign oxidants from the viewpoint of improving reaction atom efficiencies.^{4,7–9} The factors that influence the choice of oxidant include the active oxygen content, availability, selectivity, and nature of the waste produced.

Ruthenium catalyzed reactions are both mild as well as versatile. Ruthenium supported onto polyoxometallates, zirconia, and polystyrene have been studied for various hydrogenation and oxidation reactions.^{10–12} However, polymeric supports and metal oxide supports pose problems due to poor heat transfer ability and leaching, respectively. The ion exchange method of catalyst immobilization is simple, when compared to the procedures for the attachment of complexes to the polymers, besides the active species being firmly held to the supports. Due to these advantages, ion exchangers prove to be superior supports in heterogenized homogeneous catalysis.

Tetravalent metal acid (TMA) salts are cation exchangers possessing structural hydroxyl groups, the H of the structural –OH being the exchangeable sites. TMA salts possess excellent thermal and chemical resistivity (as compared to the organic polymeric supports). TMA salts thus indicate good potential for application as supports in heterogenized homogeneous catalysis. Literature survey reveals the use of TMA salts as supports in heterogenized homogeneous catalysis using Rh and

Pd complexes.^{13–15} We have earlier reported the study of some oxidation reactions using Ru(III) supported onto TMA salts.¹⁶

In the present endeavor, TMA salts, the M(IV) phosphates and tungstates [M(IV) = Zr, Ti, Sn] abbreviated as ZrP, TiP, SnP and ZrW, TiW, SnW have been synthesized by a sol–gel method. The synthesized materials have been characterized for elemental analysis (ICP-AES), thermal analysis (TGA), X-ray analysis, Fourier transform infrared (FTIR) spectroscopy, surface area (BET method), surface acidity (NH₃ TPD), and Na⁺ ion exchange capacity by the column method. Ru(III) has been anchored onto these materials by an ion exchange method to give Ru(III)ZrP, Ru(III)TiP, Ru(III)SnP, Ru(III)ZrW, Ru(III)TiW, and Ru(III)SnW. The materials have been explored for catalytic oxidation of benzyl alcohol and styrene. Further, Ru(III) has been reduced to Ru(0) and catalytic activity explored for hydrogenation of 1-octene, nitrobenzene, and cyclohexanone.

2. Experimental Section

2.1. Synthesis of M(IV) Phosphates and Tungstates. M(IV) phosphates and tungstates were prepared by the sol–gel method. An aqueous solution (0.2 M, 100 mL) of sodium dihydrogen phosphate or sodium tungstate was added dropwise to an aqueous solution (0.1 M, 100 mL) of zirconium oxy chloride or titanium tetrachloride or stannic tetrachloride with continuous stirring, maintaining the resultant solution temperature at 70 °C and pH ~ 2. A gel was formed, and the solution along with the gel was further stirred for 1 h. The gel was filtered, washed with conductivity water until free of chloride ions, and dried at room temperature. A 5 g portion of this material was taken and treated with 50 mL, 1 M HNO₃ for 30 min with occasional shaking. The sample was then separated from acid by decantation and treated with conductivity water for removal of adhering acid. This process (acid treatment) was repeated at least five times. After final washing, the material was dried at room temperature.

2.2. Preparation of Ru(III) and Ru Supported Materials. A 2 g portion of M(IV) phosphates and tungstates obtained in 2.1 was equilibrated with RuCl₃ solution (0.01–0.05 wt %/vol., 100 mL) with continuous stirring at 50 °C for 48 h to give Ru(III)ZrP, Ru(III)TiP, Ru(III)SnP, Ru(III)ZrW, Ru(III)TiW, and Ru(III)SnW. The solid was separated by filtration and washed with conductivity water for removal of adhering ions and dried at room temperature (step 1). These materials have

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Table 1. Characterization of Catalysts

catalyst	ZrP	TiP	SnP	ZrW	TiW	SnW
	Ru(III)ZrP	Ru(III)TiP	Ru(III)SnP	Ru(III)ZrW	Ru(III)TiW	Ru(III)SnW
	RuZrP	RuTiP	RuSnP	RuZrW	RuTiW	RuSnW
elemental analysis (M:P/W)	1:2	1:2	1:2	1:2	1:2	1:2
surface area (m ² /g)	81.9	75.45	98.55	73.11	107.75	87.33
	69.2	55.22	72.52	46.21	89.45	59.20
	71.1	51.32	73.44	44.53	85.70	55.12
surface acidity (mmoles)	2.34	0.59	1.81	0.64	0.89	0.77
XRD	amorphous	amorphous	amorphous	amorphous	amorphous	amorphous
IEC (mequiv/g)	3.09	2.77	2.96	1.32	1.95	1.52

been used for catalytic oxidation. The Ru(III) supported materials obtained in step 1 were reduced to Ru(0) by treating with hydrogen in a 500 mL autoclave at 200 °C for 1 h to give RuZrP, RuTiP, RuSnP and RuZrW, RuTiW, RuSnW. These materials were used for catalytic hydrogenation.

2.3. Characterization. Elemental analysis (Zr, Ti, Sn, P, W) was carried out using ICP-AES (Labtam, 8440 Plasmalab), while ruthenium was analyzed by atomic absorption spectroscopy. Thermogravimetric analysis of the materials was performed on a Shimadzu DT-30 thermal analyzer at a heating rate of 10 °C/min. FTIR spectra of the sample were performed using KBr wafer on a Bomem M.B. series with an Epson Hi 80 printer/plotter. X-ray diffractograms ($2\theta = 5-90^\circ$) were obtained on X-ray diffractometer (Rigaku-Dmax-30) with Cu-K α radiation and a Nickel filter. The surface area measurement (BET method) was carried out on a Micromeritics Gemini 2120 at -196°C using nitrogen adsorption isotherms. Surface acidity was determined on Chemisorb 2720, by a temperature programmed desorption of ammonia. Ammonia was chemisorbed at 120 °C and then desorption was carried out up to 700 °C at a heating rate of 10 °C/min. In order to determine the reduction temperature of Ru(III) to Ru(0), temperature programmed reduction of the supported catalyst was carried out on Chemisorb 2720 using 10% H₂ + N₂ up to 700 °C.

2.4. Catalytic Reactions. **2.4.1. Hydrogenation.** Reactions were carried out in a 500 mL autoclave with a proportional–integral–derivative (PID) controller. The catalysts were initially allowed to swell in 80 mL methanol for 15 min, after which 10 mmol of the substrate (1-octene, nitrobenzene, or cyclohexanone) was added and the reactor was sealed. Hydrogen pressure in the reactor was varied in the range 100–300 psi, and the contents were stirred at 150/1000 rpm for specific time intervals. Samples were withdrawn from the sampling valve of the autoclave and analyzed by GC. The hydrogen remaining in the system was released, and the product obtained was analyzed by GC. For GC analysis, a capillary column was used with a detector temperature at 200 °C, injector temperature at 180 °C and oven temperature at 50 °C for 2 min initially and then ramped up to 200 °C at a rate of 20 °C/min. The column flow for carrier was kept at 1 mL/min. Calibration plots were drawn by plotting area percent values against concentration for mixtures of authentic reactant and product samples of known composition. Percent yield values were calculated using these calibration plots. Hydrogenation reactions were carried out by varying several parameters such as the amount of catalyst, metal loading on catalyst, amount of substrate, hydrogen pressure, stirring speed (rpm), reaction time, temperature, etc., and these parameters were optimized. Blank experiments were also performed to see if the support itself facilitates any hydrogenation. Further, to check leaching of metal from supports during reaction, the catalyst was separated from reaction mixture and the reaction mixture was charged to the reactor for hydrogenation. After 4 h, the sample was withdrawn and analyzed by GC. The catalyst was regenerated by refluxing the used catalyst in ethanol followed by drying at room temperature.

2.4.2. Oxidation. In a typical reaction setup, 0.15 g catalyst along with 10 mmol of the substrate and 15 mmol of *t*-BHP(oxidant) were taken in a 50 mL three-necked round-bottom flask equipped with a condenser. The reaction mixture was stirred in an oil bath with magnetic stirrer for 3 h. TBHP plays a dual role of oxidant as well as solvent media. When H₂O₂ was used as oxidant, acetonitrile was used as solvent media. For comparison, blank experiments (using supports without Ru as catalysts) were also performed to see if the support itself facilitates any oxidation. Further, to check leaching of metal from supports, after reaction, the catalyst was separated from reaction mixture and again the same reaction mixture was charged to the reactor, for oxidation. After 4 h, sample was withdrawn and analyzed by GC. The conditions used for GC analysis were the same as mentioned earlier in the case of hydrogenation. The catalyst was regenerated by refluxing the used catalyst in ethanol followed by drying at room temperature.

3. Results and Discussion

3.1. Characterization of M(IV) Phosphates and Tungstates. Data on catalyst characterization has been presented in Table 1. The ratio of M(IV) to P or W is 1:2 in all materials. The Na⁺ exchange capacity of the material was found to be in the range of $\sim 1.5-3.0$ mequiv/g (Table 1). The absence of sharp peaks in X-ray diffractogram reveals the amorphous nature of the samples. The BET surface area ranges from 75 to 105 m²/g. The NH₃ temperature-programmed desorption (TPD) patterns have been presented in Figures 1 and 2. The area under the curve indicates the amount of NH₃ desorbed and hence the number of surface acid sites. In general, M(IV) phosphates exhibit higher surface acidity compared to M(IV) tungstates. Among M(IV) tungstates, TiW exhibits highest surface acidity with a desorption peak at $\sim 435^\circ\text{C}$, indicating the presence of

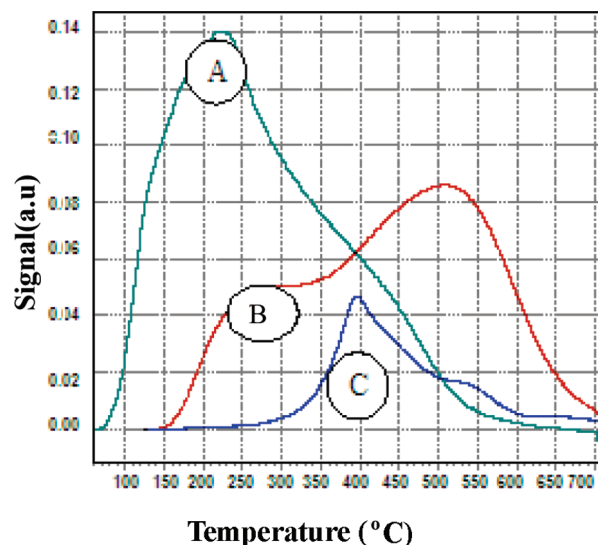


Figure 1. NH₃ TPD patterns of ZrP, SnP, and TiP (A = ZrP, B = SnP, C = TiP).

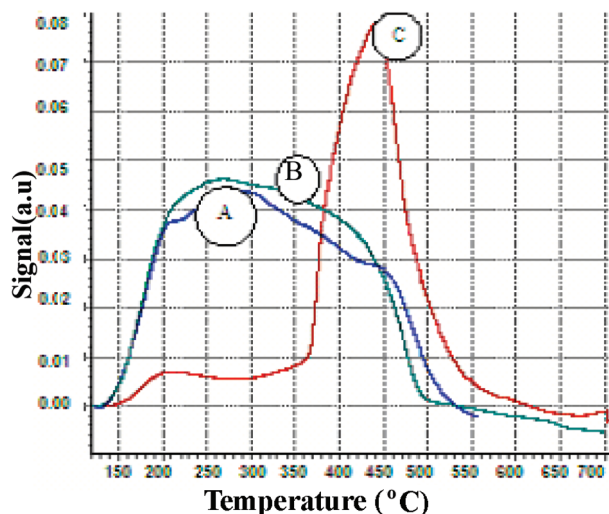


Figure 2. NH_3 TPD patterns of ZrW, TiW, and SnW (A = ZrW, B = SnW, C = TiW).

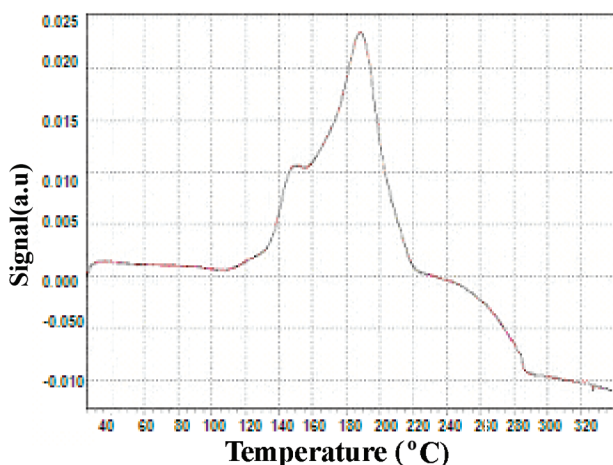


Figure 3. TPR pattern of Ru(III)ZrP.

strong acid sites. The FTIR spectra show broad bands in the region $\sim 3400\text{ cm}^{-1}$ attributed to asymmetric and symmetric —OH stretching. A medium band around $\sim 1620\text{ cm}^{-1}$ is attributed to aquo H—O—H bending. This indicates the presence of structural hydroxyl protons in these materials. For M(IV) phosphates, a band in the region $\sim 1035\text{ cm}^{-1}$ is attributed to the presence of P=O stretching. A medium intensity band at $\sim 1400\text{ cm}^{-1}$ is attributed to the presence of $\delta(\text{POH})$. TGA indicates $\sim 15\%$ weight loss in the temperature range of $100\text{--}180^\circ\text{C}$ corresponding to the loss of water molecules, after which a gradual weight loss is observed until 600°C . This may be due to the condensation of structural hydroxyl groups.

3.1.2. Characterization of Ru Supported Catalysts. Ru(III) loaded onto M(IV) phosphates and tungstates is found to be in the range $0.5\text{--}2.5\text{ wt } \%$ BET surface area of Ru(III) and Ru supported catalysts is found to be in the range $45\text{--}80\text{ m}^2/\text{g}$ (Table 1). The reduction in the BET surface area after metal loading could be attributed to pore blockage due to the higher size of the Ru(III) cation.

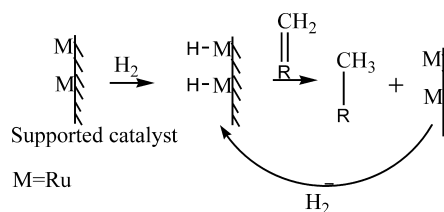
The TPR pattern of Ru(III)ZrP is presented in Figure 3 as an example, which indicates reduction temperature of Ru(III) at 190°C , and beyond this temperature, no peak is observed indicating that all Ru(III) sites are reduced to Ru(0). For all the Ru(III) supported M(IV) phosphates and tungstates, the reduction temperature is found to be in the range $190\text{--}200^\circ\text{C}$.

Table 2. Optimization of Reaction Conditions for 1-Octene to Octane Conversion Using RuTiP^a

catalyst [amount (g)]	A	B	C	conversion (%)	TON
metal loading					
0.5% RuTiP (0.15)	200	3	100	25.2	1.88
1% RuTiP (0.15)	200	3	100	29.6	2.21
1.5% RuTiP (0.15)	200	3	100	35.1	2.62
2% RuTiP (0.15)	200	3	100	42.3	3.16
2.5% RuTiP (0.15)	200	3	100	49.2	3.67
time					
2.5% RuTiP (0.15)	200	0.5	100	15	1.12
2.5% RuTiP (0.15)	200	1	100	23.2	1.73
2.5% RuTiP (0.15)	200	1.5	100	30.1	2.25
2.5% RuTiP (0.15)	200	2	100	38.2	2.85
2.5% RuTiP (0.15)	200	2.5	100	43.1	3.22
2.5% RuTiP (0.15)	200	3	100	49.2	3.67
2.5% RuTiP (0.15)	200	4	100	49.3	3.68
catalyst amount					
2.5% RuTiP (0.05)	200	3	100	17.5	3.92
2.5% RuTiP (0.10)	200	3	100	30.6	3.43
2.5% RuTiP (0.15)	200	3	100	49.2	3.67
temperature					
2.5% RuTiP (0.15)	200	3	60	32.1	2.40
2.5% RuTiP (0.15)	200	3	75	38.4	2.87
2.5% RuTiP (0.15)	200	3	85	42.9	3.20
2.5% RuTiP (0.15)	200	3	100	49.2	3.67
pressure					
2.5% RuTiP (0.15)	100	3	100	31.8	2.37
2.5% RuTiP (0.15)	150	3	100	39.2	2.93
2.5% RuTiP (0.15)	200	3	100	49.2	3.67
stirring speed (rpm)					
2.5% RuTiP (0.15)	200	3	100	49.2	3.67
2.5% RuTiP ^b (0.15)	200	3	100	85.6	6.39

^a A = pressure (psi), B = reaction time (h), C = reaction temperature ($^\circ\text{C}$), stirring speed = 150 rpm. ^b Stirring speed 1000 rpm.

Scheme 1. Probable Mechanism for Hydrogenation Using Ru Supported M(IV) Phosphates and Tungstates



3.2. Catalytic Reactions. 3.2.1. Hydrogenation. 1-Octene, nitrobenzene, and cyclohexanone selectively gave octane, aniline, and cyclohexanol, respectively. The catalytic activity/turnover number (TON) increases with Ru loading, probably due to the increase in the number of Ru active sites. Equilibrium is reached within 3 h, and no further catalytic activity is observed. Catalytic activity increases with temperature; however, the temperature is kept at an optimum of 100°C (Table 2). The pressure has been optimized at 200 psi. The activity increases with catalyst amount (Table 2), since the number of active sites per gram of substrate increases. Catalyst amount is optimized at 0.15 g. It is observed that stirring speed has a marked effect on catalytic activity. The hydrogenation reaction probably follows a free radical pathway as presented in Scheme 1, which has also been proposed by other workers.¹⁷ Product yield increased from 49.2% to 85.6% (Table 2), when stirring speed was increased from 150 to 1000 rpm (with the same reaction time). This may be attributed to greater miscibility/higher collision of hydrogen molecules with the catalyst surface,

Table 3. Catalytic Hydrogenation Using Ru Supported M(IV) Phosphates and Tungstates at Optimized Conditions^a

substrate	catalyst [amount (g)]	conversion(%)	TON
1-octene	2.5% RuZrP (0.15)	83.9	6.27
	2.5% RuTiP (0.15)	85.6	6.39
	2.5% RuSnP (0.15)	83.5	6.23
	2.5% Ru ZrW (0.15)	67.9	5.07
	2.5% Ru TiW (0.15)	73.1	5.47
nitrobenzene	2.5% Ru SnW (0.15)	69.6	5.20
	2.5% RuZrP (0.15)	71.3	5.84
	2.5% RuTiP (0.15)	76.9	6.31
	2.5% RuSnP (0.15)	71.9	5.90
	2.5% RuZrW (0.15)	59.2	4.86
cyclohexanone	2.5% RuTiW (0.15)	64.4	5.27
	2.5% RuSnW (0.15)	60.9	4.99
	2.5% RuZrP (0.15)	4.7	0.33
	2.5% RuTiP (0.15)	5.6	0.39
	2.5% RuSnP (0.15)	5.2	0.31
	2.5% RuZrW (0.15)	3.8	0.27
	2.5% RuTiW (0.15)	4.9	0.34
	2.5% RuSnW (0.15)	4.1	0.29

^a Pressure = 200 psi, reaction time = 3 h, reaction temperature = 100 °C, stirring speed = 1000 rpm.

Table 4. Catalytic Hydrogenation Using Regenerated RuTiP^a

substrate	catalyst [amount (g)]	conversion (%)	TON
1-octene	2.5% RuTiP (0.15)	82.2	6.1
nitrobenzene	2.5% RuTiP (0.15)	73.1	6.0
cyclohexanone	2.5% RuTiP (0.15)	5.3	0.4

^a Pressure = 200 psi, reaction time = 3 h, reaction temperature = 100 °C, stirring speed = 1000 rpm.

resulting in a higher number of free radical hydrogen species which in turn results in higher conversion of reactant molecules.

The catalytic activity for all the materials is found to be in the range 75–85% for 1-octene, 65–75% for nitrobenzene, and 4–6% for cyclohexanone (Table 3). Catalytic activity/TON is maximum for 1-octene followed by nitrobenzene and then cyclohexanone. Cyclohexanone conversion does not go beyond 6% for all the catalysts (Table 3). This may be attributed to the structure of the substrate. Very high activation energy required

to break C=O bond present in cyclic ring system (without any conjugated double bond) could be a reason for this. Almost similar catalytic activity/TON for all the materials may be attributed to almost similar surface area of the supports (Table 1).

Lashdafa et al.¹⁸ have reported the effect of surface acidity of supports on catalytic activity of Ru supported β zeolites and observed that Ru crystallite size decreases with higher surface acidity which leads to better catalytic activity. This seems to be applicable to porous crystalline materials with well-ordered structures. In the present work, not much variation in catalytic activity is observed among the various Ru(III) supports, which could be attributed to ruthenium being well and similarly dispersed in all the catalysts. The amorphous nature of supports indicates less chances of existence of isolated Ru crystallites and hence contribution to catalytic activity.

3.2.2. Oxidation. Both benzyl alcohol and styrene selectively gave benzaldehyde. The oxidants used are TBHP (17.8% active oxygen) and 50% H₂O₂.

Catalytic activity/TON increases with increase in temperature up to 80 °C (Table 5). Beyond this temperature, catalytic activity does not increase. Higher temperature probably leads to decomposition and loss of active oxygen from the oxidant resulting in a decrease in conversion. TBHP acts as an oxidant as well as solvent media. Catalytic activity is higher when TBHP is used in excess molar ratio to substrate (Table 5), probably due to greater miscibility of oxidant and substrate. Conversion is less when H₂O₂ is used as oxidant (Table 5). Since acetonitrile is employed as solvent, the number of active sites per gram of substrate decreases and hence conversion is less. Conversion is more in the case of tBHP (17.8% active oxygen) which has a low active oxygen content compared to H₂O₂ (47.0% active oxygen). Excellent selectivity toward benzaldehyde formation in case of benzyl alcohol using tBHP could probably be due to the mild nature of the catalyst as well as controlled availability/release of active oxygen.

A higher yield of benzaldehyde is obtained when benzyl alcohol is used as substrate compared to styrene (Table 5). This could be attributed to the oxidative cleavage that has to occur in case of styrene. In the case of benzyl alcohol, a conjugated system facilitates the oxidation process. A negative charge on

Table 5. Catalytic Oxidation Using Ru(III) Supported M(IV) Phosphates and Tungstates^a

substrate (mmol)	catalyst [amount (g)]	oxidant (mmol)	temperature (°C)	conversion (%)	TON
benzyl alcohol (10)	2.5% Ru(III)TiP (0.15)	TBHP (10)	25	12.0	0.86
	2.5% Ru(III) TiP (0.15)	TBHP (10)	80	33.0	2.38
	2.5% Ru(III) TiP (0.15)	TBHP (10)	100	30.0	2.16
	2.5% Ru(III) TiP (0.15)	H ₂ O ₂ (10)	80	5.0	0.36
	2.5% Ru(III) TiP (0.15)	TBHP (15)	80	49.0	3.53
	2.5% Ru(III) TiP (0.20)	TBHP (15)	80	56.8	4.09
	2.5% Ru(III) TiP ^b (0.20)	TBHP (15)	80	56.8	4.10
	2.5% Ru(III) ZrP (0.20)	TBHP (15)	80	51.0	3.67
	2.5% Ru(III)SnP (0.20)	TBHP (15)	80	52.4	3.77
	2.5% Ru(III)TiW (0.20)	TBHP (15)	80	49.2	3.54
	2.5% Ru(III)SnW (0.20)	TBHP (15)	80	48.2	3.47
	2.5% Ru(III) ZrW (0.20)	TBHP (15)	80	46.1	3.32
	2.5% Ru(III) TiP (0.20)	TBHP (15)	80	35.0	2.43
	2.5% Ru(III) ZrP (0.20)	TBHP (15)	80	33.1	2.29
	2.5% Ru(III)SnP (0.20)	TBHP (15)	80	32.1	2.23
styrene (10)	2.5% Ru(III)TiW (0.20)	TBHP (15)	80	31.0	2.15
	2.5% Ru(III)SnW (0.20)	TBHP (15)	80	29.4	2.04
	2.5% Ru(III) ZrW (0.20)	TBHP (15)	80	27.1	1.88

^a Reaction time 3 h. ^b Reaction time 4 h.

Table 6. Catalytic Oxidation using Regenerated Ru(III)TiP

substrate (mmol)	catalyst [amount (g)]	oxidant (mmol)	temperature (°C)	conversion (%)	TON
benzyl alcohol (10)	2.5% Ru(III) TiP (0.20)	TBHP (15)	80	53.4	3.84
styrene (10)	2.5% Ru(III) TiP (0.20)	TBHP (15)	80	33.6	2.33

the CH_2O^- is distributed over the benzene ring conjugation. In the present reaction, use of solvent is eliminated as TBHP serves both as oxidant and solvent.

3.2.3. Regeneration and Leaching Studies. For both hydrogenation and oxidation, the regenerated catalyst exhibit similar efficiency (Tables 4 and 6). The activity of the regenerated catalyst was reduced by ~5% probably due to the reacting molecules getting adsorbed on the surface of the catalyst. Also the reaction mixture shows no further conversion on removing the catalyst from the system, indicating that ruthenium is not leaching from supports.

4. Conclusion

The above study reveals the potential use of M(IV) phosphates and tungstates as supports for selective catalytic oxidation using Ru(III) and selective catalytic hydrogenation using Ru(0). The potential use is further enhanced as Ru(III) or Ru(0) does not leach out during reaction.

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