CHAPTER 6

RUTHENIUM SUPPORTED CATALYSTS FOR OXIDATION AND HYDROGENATION

6.1 INTRODUCTION

Hetrogenising homogeneous catalysts is a trend towards dissolving the traditional barriers between homogeneous and heterogeneous catalysis. The notable superiority in these kinds of materials is in single site reaction i.e. specificity, high selectivity and tenability and their built in ease of separation of products from reactants, durability, stability and easy handling. This has already been described in detail in Chapter 1, section 1.5.

Transition metal catalyzed oxidation reactions have been extensively studied [1-4]. Among the transition metals, ruthenium and its complexes are extremely versatile oxidation catalysts, both homogeneous and heterogeneous for a wide range of organic substrates [5-9]. Moreover, conditions for the ruthenium catalyzed reactions are very mild [10], mainly because of the fact that ruthenium exhibits a wide range of oxidation states [11], with a facile interconversion of these, from one oxidation state to another. The availability of these oxidation states and the various co-ordination numbers for complex formation, is a useful feature of the chemistry of ruthenium. Ruthenium catalytic systems reported so far seem to offer a low energy reaction pathway for the reactants leading to a fairly large turnover number of the product [12]. These reactions are also known to proceed with high selectivity and specificity of the required product, without the final destruction of the catalyst. A variety of solvents can be used and depending on the oxidant, a wide range of pH can be tolerated. Early workers [13] used ruthenium tetroxide as an oxidant. However, it is less convenient to use and is less selective. Soon focus was shifted to the use of catalytic amount of ruthenium in oxidation reactions.

6.2 SELECTIVE CATALYTIC OXIDATION

Oxidation reactions are of fundamental importance in synthetic organic chemistry, catalytic selective oxidation [14-16] being a useful method for the preparation of a range of valuable compounds. These compounds are used as intermediates and finished products in numerous sectors of the chemical industry including pharmaceuticals and polymers. 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 [15,17] and heterogeneous [18] catalysts. The development of environmentally benign synthesis has evoked a renewed interest in developing solid supported systems and considerable attention focussed towards the choice of environmentally benign oxidants from the view point of improving reaction atom efficiencies [15, 19-21]. Conventionally used stoichiometric oxidants such as nitric acid, chromates etc.[1,20], though very effective, are toxic and environmentally hazardous.The factors that influence the choice of oxidant include, active oxygen content, cost, availability, selectivity and nature of the waste produced.

6.3 LITERATURE SURVEY IN THE CURRENT AREA OF STUDY

In recent times, catalysis by supported metal ions/complexes is an area of intense research mainly due to enhanced activity observed [22]. Ruthenium has been supported onto different supports like polyoxometallates, zirconia and polystyrene [23-25]. From our laboratory we have reported the study of some oxidation reactions using –Ru(III) supported onto tma salt (zirconium molybdate) [26]. In literature, a lot of reports are available indicating the use of ruthenium based catalytic systems [13-17]. Supported ruthenium catalysts are widely reported, conventional impregnation [27-30] and incipient wetness method being the prominent ones [31]. In some cases metallic ruthenium particles have been supported onto the support matrix by the reduction of a ruthenium compound. The effectiveness of the preparation, strongly depends on the course and the experimental arrangement of the reduction and/or calcination of the catalyst precursor, considering that chlorides and residual elements (also impurities) may drastically change the activity and selectivity of the final catalyst [32,33].

Khan and Rao observed that oxidation of 1-hexene to ketone 2-hexanone by molecular oxygen is catalysed by Ru(III) ion. The reaction shows a first order dependence in catalyst and substrate concentrations and one-half order dependence with respect to molecular oxygen concentration [7].

Takahashi et al studied the hydrogen transfer type oxidation of alcohols and found that primary alcohols were converted into aldehydes by hydrogen transfer reaction using methyl vinyl ketone and ruthenium catalyst under microwave irradiation [6].

Bifunctional titanium-mesoporous molecular sieves containing both acid and oxidizing catalytic sites have been investigated and found to be very active in epoxidation of bulky olefins and highly selective in diol formation [34].

Plucinski et al studied selective oxidation of benzyl alcohol catalysed by ruthenium oxide supported on alumina. High activity and selectivity were obtained even when working with reactant concentrations approaching industrial levels [35].

The polybenzimidazole(PBI) metal complexes have been investigated as potential catalysts in the oxidation of cyclohexene by *t*-butylhydroperoxide (TBHP). Ru(PBI) induces allylic oxidation and high conversion to cyclohexane-1,2-diol. This seems to occur by direct dioxygenation of cyclohexene and the reaction could be of synthetic utility under aerobic conditions [9].

Leitner et al [36] have reported activity of Ru/CeO_2 catalysts for ozonation of aqueous succinic acid solutions. The influence of ruthenium, the catalyst preparation mode (impregnation or exchange), support pretreatment, surface area and the final treatment of the catalyst (by calcination or reduction) has been examined. The best activity is observed for the catalysts prepared by impregnation.

Choque et al [37] have reported ruthenium supported on Ta_2O_5–ZrO_2 and Nb_2O_5–ZrO_2 as catalysts for the partial oxidation of methane. 2% Ru loaded catalysts were prepared using $RuCl_3$ and $RuNO(NO_3)_3$ as Ru precursors.

Mitsui et al [38] have reported support effect and the effect of reduction treatment on catalytic combustion of ethyl acetate, acetaldehyde, and toluene over various Ru supported catalysts prepared by impregnation method. Among the as-calcined catalysts tested, Ru/CeO_2 showed the highest activity for all tests regardless of the pre-treatment in hydrogen atmosphere. Further, it was observed that catalytic activity of Ru/SnO_2 was significantly degraded by the reduction treatment, whereas the activity of Ru/ZrO_2 and Ru/γ-Al_2O_3 was enhanced.

Mizuno et al [39] have reported selective aerobic oxidations of alcohols, diols, and amines over supported ruthenium hydroxide catalysts. A reaction mechanism involving ruthenium alkoxide formation/β-elimination has been proposed for the present catalytic oxidations.

In the present endeavour Ru(III) has been anchored onto M(IV) phosphates and tungstates by 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.

6.4 EXPERIMENTAL

Catalyst synthesis and Characterisation

Described in Chapter II, section 2.5.

Materials

Styrene, benzyl alcohol, tertiary butyl hydrogen peroxide (TBHP, 17.8% active oxygen), acetonitrile and Hydrogen peroxide(47.0% active oxygen) were obtained from Merck India.

Experimental Setup

In a typical reaction set up, 0.15 g catalyst along with 10mmol of styrene or benzyl alcohol and 15 mmol of TBHP were taken in a 50 mL three necked round bottomed flask equipped with a condenser. The reaction mixture was stirred in an oil bath with magnetic stirrer for 3h. TBHP plays a dual role of oxidant as well as solvent media. When H_2O_2 was used as oxidant, acetonitrile was used as solvent media. Reaction parameters mole ratio of reactants, temperature, time, catalyst amount has been optimized using Ru(III)TiP(Table 6.1). Using these optimized conditions, the activity of the other catalysts have been explored. After completion of reaction, the catalyst was separated by decantation and reaction mixture was distilled to obtain the product. For comparison, blank experiments 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 the same reaction mixture charged to reactor, for oxidation. After 4h, sample was withdrawn and analysed by GC. The catalyst was regenerated by refluxing in ethanol followed by drying.

6.5 RESULTS AND DISCUSSION

Both benzene and styrene selectively gave benzaldehyde. Catalytic activity/TON increases with increase in temperature upto 80°C. Beyond this temperature catalytic activity does not increase. Higher temperatures could also lead to decomposition and loss of active oxygen from the oxidant and conversion may decrease. TBHP acts as an oxidant as well as solvent media. Catalytic activity is higher when TBHP is used in excess molar ratio to substrate, probably due to greater miscibility of oxidant and substrate. Conversion is less when H_2O_2 is used as oxidant. Since acetonitrile is employed as solvent the number of active sites per g of substrate decreases and hence conversion is less. Excellent selectivity towards 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.

Higher yield of benzaldehyde is obtained when benzyl alcohol is used as substrate compared to styrene. This could be attributed to the oxidative cleavage that has to occur in case of styrene. In case of benzyl alcohol, a conjugated system facilitates the oxidation process. A negative charge on the CH_2O^- is distributed over the benzene ring conjugation. Further, use of solvent is eliminated as TBHP serves both as oxidant and solvent.

The reaction mixture shows no further conversion on removing the catalyst from the system, indicating that Ruthenium is not leaching from the support.The activity of the regenerated catalyst was reduced by ~5% probably due to the reacting molecules getting adsorbed on the surface of the catalyst.

Table 6.1 Catalytic Oxidation using Ru(III) supported M(IV)phosphates and Tungstates

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_2O_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*(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
Styrene(10)	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
	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

Reaction time 3h, *=reaction time 4h

6.6 SELECTIVE CATALYTIC HYDROGENATION

Reduction of organic functional groups can be categorized into (i) addition of hydrogen to unsaturated groups e.g.reduction of ketones to alcohols (hydrogenation)(ii) addition of hydrogen across single bonds leading to cleavage of functional groups (hydrogenolysis).

6.7 LITERATURE SURVEY IN THE CURRENT AREA OF STUDY:

The use of some supported transition metals as catalysts in the selective hydrogenation of organic compounds is reported in the literature [40,41]. A major limitation in the lifespan of such catalysts is the fact that these metals (Pt,Pd) are easily poisoned by sulfur compounds, normally present in hydrocarbon streams [42,43]. Transition metal complexes have proven to be excellent catalysts as they operate under mild conditions [44] for both homogeneous and heterogeneous hydrogenation reactions [45-47]. Considerable activity, selectivity and sulfur resistance levels are observed using these catalysts.

In recent times the applicability of Ru in some specific hydrogenation reactions has been extensively studied. Supported Ru catalysts have been used in case of o-xylene hydrogenation [48]. Ru supported on carbon system has been found to be most effective system for hydrogenation of D-glucose [49]. Heterogeneous bimetallic Ru-Sn catalysts system are found to be effective for the liquid-phase hydrogenation of C=O group in carboxylic acids. When Ru-Sn was supported on alumina, a stable catalyst exhibiting high activity, under mild conditions was observed in the flowing system [50]. The performance of bimetallic Ru-Sn catalysts for the liquid phase selective hydrogenation of oleic acid to unsaturated alcohols has been investigated [51]. Hydrogenation over metallic ruthenium catalysts leads primarily to the saturated stearic acid, which is then consecutively hydrogenated to the saturated stearyl alcohol. The titania-supported metallic ruthenium catalyst exhibits greater activity than the alumina-supported catalyst, prepared via sol–gel method for the hydrogenation of oleic acid to the saturated stearyl alcohol [51].

Lashdaf et al [52] have studied hydrogenation of cinnamaldehyde using Ru supported β zeolites. The behaviour of ruthenium was studied in relation to the acidity of β zeolite. The acidity of the β zeolite influenced the particle size of ruthenium. The catalyst with highest Bronsted acidity yielded the highest conversion of cinnamaldehyde.

Chatterji et al [53] have reported selective hydrogenation of cinnamaldehyde using a Ru–Pt bimetallic catalyst supported on MCM-48 in super critical carbon dioxide media. They observed that the reaction is completely selective to the unsaturated alcohol in supercritical carbon dioxide and the selectivity to the desired unsaturated alcohol is a function of pressure.

Blackmond et al [54] have reported hydrogenation of α,β-unsaturated aldehydes, cinnamaldehyde and 3-methylcrotonaldehyde over Ru, Pt, and Rh supported zeolites. The use of zeolite supports was compared with activated carbon for Ru, and the effect of changing the neutralizing cation in the Y zeolite was compared for all three metals. It was observed that the selectivity to the unsaturated alcohol can be influenced by both geometric and electronic effects, and the relative importance of these effects was dependent on the nature of the organic substrate.

Galvagno et al[55] have reported hydrogenation of cinnamaldehyde over Ru catalysts supported on activated carbon at 333 K and atmospheric pressure using ethanol as solvent. They have observed that the specific activity expressed per Ru surface atom remains constant with metal dispersion, indicating that the rate-determining step of the reaction is structure-insensitive. Further, selectivity to cinnamyl alcohol increases with Ru particle size, reaching a value of about 60% on the less dispersed samples.

Recent literature shows the use of Rh ions and complexes intercalated into zirconium and titanium phosphates as efficient catalysts for arene hydrogenation [56]. Reports [57-61] are also available regarding the investigation of the catalytic activity of metal-ions and/or their complexes intercalated into α- or γ-titanium or zirconium hydrogen phosphate. Tma salts containing Pd or Rh-ions, or their complexes have proved to be very efficient for the catalytic hydrodechlorination of poly-chlorobenzenes, that are converted to benzene under mild conditions [62].

In the present endeavour, Ru(III) supported on TMA salts has been reduced to Ru(0) to give RuZrP, RuTiP, RuSnP, RuZrW, RuTiW and RuSnW. The catalytic activity has been explored for hydrogenation of 1-octene, nitrobenzene and cyclohexanone.

6.8 EXPERIMENTAL

Catalyst synthesis and Characterisation

Described in Chapter II.

Materials

1-octene, cyclohexanone, nitrobenzene and methanol were obtained from Merck India.

Experimental setup

Reactions were carried out in a 500 ml autoclave with a PID controller. The catalysts were initially allowed to swell in 80 mL methanol for 15 minutes, after which 10 mmol of the substrate (1-octene, nitrobenzene or cyclohexanone) was added and the reactor sealed. Hydrogen pressure in the reactor was varied in the range 100 to 300 psi and the contents were stirred at 150 rpm for specific time intervals. The hydrogen remaining in the system was released and the product obtained analysed by GC. Hydrogenation reactions were carried out by varying several parameters such as amount of catalyst, metal loading on catalyst, amount of substrate, hydrogen pressure, reaction time, temperature etc. and these parameters optimized using RuTiP (Table 6.2). Using these optimized conditions the activity of the other catalysts have been explored (Table 6.3). After completion of reaction, the catalyst was separated by decantation and reaction mixture was distilled to obtain the product. 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 reaction mixture charged to reactor for hydrogenation. After 4h, sample was withdrawn and analysed by GC. The catalyst was regenerated by refluxing in ethanol followed by drying.

6.9 RESULTS AND DISCUSSION

1-octene, nitrobenzene and cyclohexanone selectively gave octane, aniline and cyclohexanol respectively. Catalytic activity/ turn over number (TON) increases with Ru loading, probably due to increase in 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. Pressure has been optimized at 200 psi. Activity increases with catalyst amount, since the number of active sites per g of substrate increases. Catalyst amount is optimized at 0.15 g.

Catalytic activity/TON is maximum for 1-octene followed by nitrobenzene and then cyclohexanone. Cyclohexanone conversion does not go beyond 1% for all the catalysts. 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. The catalytic activity for all the materials is found to be in the range 39-49% for 1-octene, 34-43% for nitrobenzene and 1% for cyclohexanone. Higher surface area of the supports give rise to better dispersion of Ru and better catalytic activity. However, in the present work the surface area values of the supports (75-105 m^2/g) do not differ much and hence difference in the catalytic activity/TON also is not very high.

Lashdaf et al [52] 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 amongst the various Ru(0) 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.

The reaction mixture shows no further conversion on removing the catalyst from the system, indicating that Ruthenium is not leaching from the support.The activity of the regenerated catalyst was reduced by ~5% probably due to the reacting molecules getting adsorbed on the surface of the catalyst.

Table 6.2 Optimisation of reaction conditions for 1-octene to octane conversion using RuTiP:

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
Temparature					
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

A=Pressure (psi), B=Reaction time(h), C=Reaction temperature(^{o}C)

Table 6.3 Catalytic hydrogenation using M(IV) phosphates and tungstates at optimized conditions

Substrate	**Catalyst**	**Conversion(%)**	**TON**
1-octene	2.5% RuZrP(0.15)	48.2	3.60
nitrobenzene	2.5% RuZrP(0.15)	41.0	3.36
cyclohexanone	2.5% RuZrP(0.15)	1.0	0.07
1-octene	2.5% RuTiP(0.15)	49.2	3.67
nitrobenzene	2.5% RuTiP(0.15)	42.8	3.51
cyclohexanone	2.5% RuTiP(0.15)	1.0	0.07
1-octene	2.5% RuSnP(0.15	48.0	3.58
nitrobenzene	2.5% RuSnP(0.15)	41.3	3.39
cyclohexanone	2.5% Ru SnP(0.15)	1.0	0.06
1-octene	2.5%Ru ZrW(0.15)	39.0	2.91
nitrobenzene	2.5%Ru ZrW(0.15)	34.0	2.79
cyclohexanone	2.5%Ru ZrW(0.15)	1.0	0.07
1-octene	2.5% Ru TiW(0.15)	42.0	3.14
nitrobenzene	2.5% Ru TiW(0.15)	37.0	3.03
cyclohexanone	2.5% Ru TiW(0.15)	1.0	0.07
1-octene	2.5%Ru SnW(0.15)	40.0	2.99
nitrobenzene	2.5%Ru SnW(0.15)	35.0	2.87
cyclohexanone	2.5%Ru SnW(0.15)	1.0	0.07

Pressure=200 psi, Reaction time=3h, Reaction temperature=100°C

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