Supported Ruthenium Catalysts for Oxidation of Benzyl Alcohol under Solvent-Free Conditions

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Summary: The investigation comprised an evaluation of the use of the catalyst, 1%Ru/TiO$_2$, to oxidize Phenylmethanol into benzenecarbaldehyde. nitrogen adsorption isotherms and transmittance electron microscope (TEM) were deployed to delineate the properties of the supported catalysts. The findings indicated a superior catalytic performance from 1%Ru/TiO$_2$ prepared using sol-immobilization method. No reaction was taken place with blank reaction or with undoped support. This was deemed to be a consequence of the dispersion and loading of Ru on the TiO$_2$.The reaction conditions, i.e., temperature, reaction time, nature of catalyst and activating quantity, were optimized to achieve superior reaction parameters. This process gave rise to a benzyl alcohol transformation rate of up to 10%; and selectivity of benzaldehyde was 98%.

Keywords: Oxidation, Benzyl alcohol, Ruthenium catalyst, Benzaldehyde, Sol-immobilization.

Introduction

Chemoselective oxidation is one of the most powerful processes in the field of organic chemistry. During this process, alcohols are converted into relevant aldehydes or ketones [1–3]. In recent times, new discoveries have led to the development of highly active heterogeneous catalytic systems, with supported metal nanoparticles being widely researched as potential catalysts. Thus, product aldehydes are very important intermediates for organic synthesis, as well as extremely useful components for fine chemicals. Nonetheless, It is important to note that two factors controls transformation, harsh condition of reaction and amount of oxidant must be stoichiometric [4–6].

The most common process used to commercially produce benzaldehyde (BzH) is the toluene oxidation and benzyl chloride hydrolysis. Benzaldehyde (BzH) is a significant chemical that serves as an intermediate in numerous organic compounds. Moreover, it is widely applied in the fields of pharmaceuticals, dyestuffs, perfumery, and agrochemical industries [2, 3]. The benzyl alcohol oxidation (BzOH) during the liquid phase is generally the most favored reactive and selective pathway for producing BzH that is free from chlorine. This is an environmentally friendly and cost-effective process [4]. In recent times, noble transition metals Ruthenium, Rhodium, Palladium, Silver, Platinum, Gold, and others have been increasingly applied as heterogeneous catalysts to produce ketons and

aldehydes from alcohols oxidation. [5-7]. Gold based catalyst show high catalytic activity and selectivity for producing benzaldehyde from benzyl alcohol oxidation at liquid phase in several investigations [8–11].

High toxicity, high cost, and harmful metal salt waste, represents the main disadvantages of traditional alcohol oxidation methods using permanganate and dichromate oxidants. Researchers have always been interested in searching for environmentally friendly oxidizing agents and methods, such as oxygen and hydrogen peroxide, to reduce chemical waste and dangerous resulting from such processes [9–15].

In one study, benzyl alcohol was oxidized aerobically. The oxygen flow rate was 10 mL/min in presence of 10 mol% of tert-butyl hydroperoxide in liquid phase using ruthenium nanoparticles as a catalyst. The alcohol conversion was 100% and 97% yield benzaldehyde were produced accompanied by Ru-DD3 (5%) at these conditions.[16]

Heterogeneous catalysts made from ruthenium nanoparticles have been found to be effective in supporting nonnatural zeolites and other synthesized inorganic materials. Nonetheless, other naturally porous materials with large surface areas (e.g., clay) can also be considered as alternative

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supports for heterogeneous catalysts in green organic transformations.

The results indicated that the catalytic system efficiently oxidized the non-activated alcohols to produce the relevant carbonyl compounds. Additionally, primary, and secondary allylic alcohols enabled the corresponding enals or enones to be produced without any intramolecular hydrogen transfer or geometrical isomerization of the double bonds. Meanwhile, the Ru/Al_2O_3 system was found to have high catalytic activity during the process of oxidating the activated and non-activated alcohols with just 1atm of O_2 .96% in all cases. The primary and secondary benzylic alcohols were all quantitatively transformed into the relevant benzaldehydes and ketones.

Other investigations have been conducted to examine the effectiveness of Ru catalysts (such as Ru/alumina [17] Ru-hydroxyapatite (HAP) [18] and Ru/Fe3O4, Ru/Ni(OH)2 [19]). These catalysts have been found to be well-distributed at active Ru sites. Nonetheless, they were found to have low catalytic proficiency (TOFs from 2 h−1 to 40 h−1) [19], whilst the solid supports are very simple immobilization materials at Ru active sites .

Furthermore, another study has revealed that ruthenium hydroxide is an effective support for zirconia catalysts during the alcohol oxidation process, with the oxidation of benzyl alcohol (BzOH) showing high TOF (BzOH) [20]. Yet, none of the existing studies has investigated atmospheric pressure as a source of oxygen under mild conditions in isolation. In the present study, the effectiveness of 1%Ru/TiO2 catalyst during the oxidation of benzyl alcohol (BzOH) under solvent-free conditions has been examined, with air being employed as the primary oxygen source. The results indicated that the benzaldehyde (BzH) had high activity and selectivity, even in the absence of high pressure/temperature or any type of oxidants.

Experimental

All the chemicals used in this study were obtained from commercial companies (Sigma Aldrich) and used as it is without any modification. For comparing purpose, the catalyst was prepared by two well-known methods: sol-immobilization method and wet-impregnation method. The amount of catalyst metal loaded on the support was represented as a weight percentage.

Sol immobilization method [21] was also used to synthesis 2 g of supported ruthenium catalyst as follows: The required mass of ruthenium chloride hydrate was mixed with 0.8 L of distilled water and stirred continuously by magnetic stirrer. A recently prepared 1 wt.% solution of polyvinyl alcohol (80% hydrolyzed, MW= 10000 g/mol) was added. The suspension was stirred for 16 minutes. 0.2 molar of recently obtained sodium borohydride solution was added ($Ru/NaBH_4$ molar ratio was 0.2), a dark brown sol was formed. Graphite or titanium oxide was added in some cases. sulphuric acid solution was added drop by drop with continuous stirring until the pH was adjusted to 2 and stirring was continued another 30 minutes. The supported catalyst was obtained by addition of 1.98 g of support and stirred for 2 hours. The resulted supported catalyst was filtered and thoroughly washed with enough amount of distilled water to remove the foreign ions (about 2 L) after that, the catalyst was dried at 110 °C until constant weight.

Wet-impregnation technique was used to obtain 2 g of supported metal catalyst as follows: the water percentage in ruthenium chloride was estimated by volatilization method then calculated amount of $RuCl_3 \cdot xH_2O$ was dissolved in suitable amount of distilled water, a specific amount of support was added, evaporation with continuous stirring at 80 ºC were conducted until a paste was obtained from the mixture. The paste was dried at 110 °C for 16 hours, then grinded and calcined at 300 °C for 3 hours, the heating rate of calcination was 20 ºC per minute.

The morphology of surface of the resulted supported catalysts was investigated out using an EVO40VP model Carl Zeiss scanning electron microscope. The sample (0.2 g) was ground before sprinkled over a carbon disc stuck onto an aluminum stub and the excess sample were tapped off the disc prior to attaching to the sample holder. The entire SEM column was pumped to attain a good vacuum placed at a working distance between 8-10 mm. The electron gun emits an electron beam within a voltage range of 5-25 kV at an I-probe current of 1000 pA (1.0 nA), the generated secondary electron was utilized for topographic analysis. The particle size distribution (PSD) of all samples was determined from bright field TEM micrographs.

The benzyl alcohol oxidation was used as a model to measure the catalytic activity of the synthesized supported catalysts. 0.12 g of dried supported catalyst was added to 10 mL of benzyl alcohol (96.632 m mol) and refluxed at 110 °C in 50 mL conical flask equipped with helical condenser on hotplate and magnetic stirrer for 4 hours (different

times was used for some reaction to study the effect of time). The remaining unreacted benzyl alcohol and the oxidation products were quantitatively determined by using GC-2010 plus, Gas Chromatograph from Shimadzu Corporation equipped with AOC-20i Auto injector. RESTEK Rtx-5 column was used (Film Thickness 0.25 um, Column Length 30 m, Inner Diameter 0.25 mm ID). The carrier gas was He and the detector was Flame Ionization Detector (FID).

The following equation (1) was used to calculate the conversion factor as a percentage.

$$\text{Conversion factor (\%)} = \frac{\sum P_i}{(\sum P_i + \sum R_i)} \times 100 \quad (1)$$

where

P_i: the concentration of the product I, R_i: the concentration of the reactant i

The following equation (2) was used to calculate the selectivity for each product as a percentage.

$$\text{Selectivity (\%) of product i} = \frac{P_i}{\sum P_i} \times 100 \quad (2)$$

The following equation (3) was used to calculate the yield percentage for each product.

$$\text{Yield (\%) of product i} = \frac{\text{Selectivity (\%) of product i} \times \text{Conversion factor}}{100} \quad (3)$$

Results and Discussion

Catalyst Performance Evaluation of Benzyl Alcohol Liquid-Phase Oxidation Reaction

Achieving green chemistry requirements, our catalytic reaction was performed under most safe conditions, where oxygen air at atmospheric pressure was used as oxidant and without solvents. In this research, benzaldehyde comprised the main reaction product, together with minute quantities of toluene and benzoic acid. The results of the catalytic oxidation experiments are shown in Fig. 1.
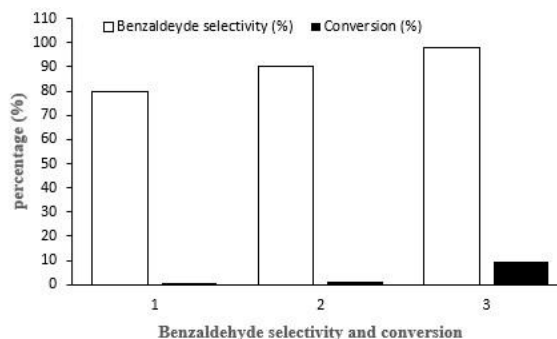

Fig. 1: Oxidation of benzyl alcohol. 1: absence of support or catalysts, 2: support only, 3: Ru catalyst on supports, Reaction conditions: 0.1g catalyst, benzyl alcohol (96.632 mmol, 10 mL), 110ºC, atmospheric pressure air, 3 hour, 800rpm. 1: blank reaction, 2: TiO$_2$ as catalyst, 3: 1%Ru/TiO$_2$ as a catalyst.

The reaction that was performed in the absence of supported Ru catalysts, i.e. blank or support only, the conversion of benzyl alcohol is very low. This implies that the support defect site did not act as active centers of the catalyst. The addition of the Ru catalyst to the supports exhibited a marked catalytic impact on the selective oxidation of benzyl alcohol reaction.

Effect of different supports

The performance of a catalyst is often affected by the support properties, which may exhibit a notable impact on both reaction conversion rates and selectivity, as reported in previous studies in relation to oxidation reactions [22]. The preparation of several Ru catalysts on a range of oxide and graphite supports was carried out; these were then investigated with respect to the oxidation of benzyl alcohol. When contrasted against the undoped supports, 1%Ru/support catalysts' surface area diminished, potentially implying Ru impregnation within the pores of the supporting material as shown in Table-1.

Table-1: The oxidation of benzyl alcohol using different supports.

Catalyst	BET	Conversion (%)	Selectivity (%)		
			Benzaldehyde	**Toluene**	**Others**
Blank	-	0.5	80	8	10
Graphite (G)	11	0.5	90	9	-
1%Ru/G*	8	3	90	8	-
1%Ru/G	8	4.8	93	3	1
SiO$_2$	125	0.8	91	5	4
1%Ru/SiO$_2$	119	2.7	96	3	1
TiO$_2$	53	1.3	90	1	-
1%Ru/TiO$_2$	46	10	98	-	-

Reaction conditions: 0.12g catalyst, benzyl alcohol (96.632 mmol, 10 mL), 110ºC, atmospheric pressure air, 3hour, 800rpm. *: Prepared with wet-impregnation method.

Initial testing was conducted on bare supports. However, there was no conversion acceleration detected with respect to the blank test (Table-1). This implies that the supports' (TiO_2, SiO_2 and graphite) defect sites did not act as active centers of catalysis. The addition of the Ru catalyst to the supports exhibited a marked catalytic impact on the selective benzyl alcohol oxidation reaction as shown in Table 1, However, the highest catalytic activity was exhibited by a Ru catalyst in conjunction with a TiO_2 support, conversion, and benzaldehyde selectivity of 10% and 98%, respectively, were attained. Potentially, TiO_2 and additional reducible supports have the capacity to diffuse onto the Ru, and thus have a notable influence on the performance of the catalyst, a situation termed strong metal support interaction [23]. Previous research has additionally determined that TiO_2 is an opposite substance for oxidation reactions and engages with the metal positively during its support role [24, 25]. Thus, additional experiments encompassed use of this compound

Effect of reaction temperature

Identification of reaction condition at equilibrium (i.e., no reaction takes place) in absence of catalyst must be done. We found that no oxidation reaction occurs in range of temperature conditions investigated in absence of catalyst. In other words, in absence of catalyst no benzyl alcohol oxidized before temperature reaches 140 °C. But as soon as temperature became 140 °C, reaction spontaneity started and resulted in 0.5% benzyl alcohol conversion and 70% selectivity for benzaldehyde. It must be noted that, to avoid benzyl alcohol autoxidation, the reaction temperature must be kept less than 140 °C. In the presence of 1%Ru/TiO_2, different reaction temperatures have been found, with increasing the reaction temperature more than 110 °C conversion of benzyl alcohol largely increased, however, the selectivity for benzaldehyde significantly decreased as shown in Table-2. Particularly, the conversion of benzyl alcohol was only 3% at 85 °C because reaction kinetics is thermally affected [26]. Therefore, the benzyl alcohol conversions favor high temperature, increase in conversion was recorded from 3% to 11% as a result of temperature raises from 85 °C to 125 °C.

Nevertheless, increasing temperature lowers benzaldehyde selectivity. The benzaldehyde at lower temperature was the only detected product, and then its selectivity decreased from 99% at 85 °C to 90% at 125 °C. Therefore, and because of the contradiction between the conversion ratio of benzyl alcohol and the selectivity of benzaldehyde with increasing temperature, 110 °C was chosen as the optimum temperature condition to obtain the best results.

Time online study

The differences in benzyl alcohol conversion rates and selectivity for each product are presented in Table-3; the data were assessed with respect to the reaction time for the various products. As indicated in Table-3, the benzyl alcohol conversion increase from 5.4% to 13.6% as the reaction time increase from 1h to 8h, which refers to occurrence of consecutive oxidation reaction of benzyl alcohol. Initially, a relatively poor degree of benzyl alcohol transformation was sustained, yielding predominantly benzaldehyde. As the reaction progressed, there was a rise in benzaldehyde yield caused by the accelerated reaction rate as shown in Table-3. After 4 hours of reaction time, the synthesis rate of benzaldehyde started to diminish; This may be because of that benzaldehyde produced by the reaction continues to oxidize to form small amount of toluene and benzoic acid, resulting in a decrease in selectivity.

Effect of preparation method

Catalyst performance is highly dependent on the preparation method (Table 4). 1% Ru/TiO_2 catalyst was generated using both sol-immobilization and wet-impregnation techniques. When the two techniques were compared, increased catalytic activity with respect to oxidation of benzyl alcohol (10% versus 5%) and benzaldehyde selectivity (98% versus 93%) was seen with the catalyst produced via sol-immobilization rather than with the wet-impregnation method. Therefore, sol-immobilization method resulted in Ru/TiO_2 catalyst of greater catalytic activity in comparison to wet-impregnation techniques.

Table-2: Effect of reaction temperature on oxidation of benzyl alcohol.

Catalyst	T (ºC)	Conversion (%)	Selectivity (%)		
			Benzaldehyde	Toluene	Others
Blank	110	0.5	80	8	10
TiO$_2$	110	1.3	90	5	2
1%Ru/TiO$_2$	85	3	99	-	-
	90	4.8	98	-	1
	100	7.8	98	2	-
	110	10	98	1	1
	120	10.6	94	1	-
	125	11	90	8	-

Reaction conditions: 0.12 g catalyst, benzyl alcohol (96.632 mmol, 10 mL), atmospheric pressure air, 3hour, 800rpm.

Table-3: Effect of reaction time on oxidation of benzyl alcohol.

Catalyst	Reaction time (hour)	Conversion (%)	Selectivity (%)		
			Benzaldehyde	Toluene	Others
Blank	3	0.5	80	8	10
TiO$_2$	3	1.3	90	5	2
1%Ru/TiO$_2$	1	5.4	96	-	-
	2	7.8	97	-	1
	3	10	98	2	-
	4	11	98	1	1
	6	12	96	1	-
	8	13.6	93	7	-

Reaction conditions: 0.1g 1%Ru/TiO$_2$ catalyst, benzyl alcohol (96.632 mmol, 10 mL), atmospheric pressure air,110°C, 800rpm.

Table-4: The effect of preparation method on oxidation of benzyl alcohol.

Method of preparation	Conversion (%)	Selectivity (%)		
		Benzaldehyde	Toluene	Others
Sol-immobilization	10	98	-	1.3
Wet-impregnation	5	93	3.2	2

Reaction conditions: 0.12g 1%Ru/TiO$_2$ catalyst, benzyl alcohol (96.632 mmol, 10 mL), 110°C, atmospheric pressure air, 3hour, 800rpm.

Table-5: Effect of catalyst mass on oxidation of benzyl alcohol.

Catalyst	Mass (g)	Conversion (%)	Selectivity (%)		
			Benzaldehyde	Toluene	Others
Blank	0.12	0.5	80	8	10
TiO$_2$	0.12	1.3	90	5	2
1%Ru/TiO$_2$	0.04	1.4	94	2	-
	0.06	2.6	94	5	1
	0.08	4.6	98	2	-
	0.1	7.2	98	-	1
	0.12	10	98	1	-
	0.2	9	93	3	4
	0.3	7	85	5	7.4

Reaction conditions: 0.12g catalyst, benzyl alcohol (96.632 mmol, 10 mL), 110°C, atmospheric pressure air, 3hour, 800rpm.
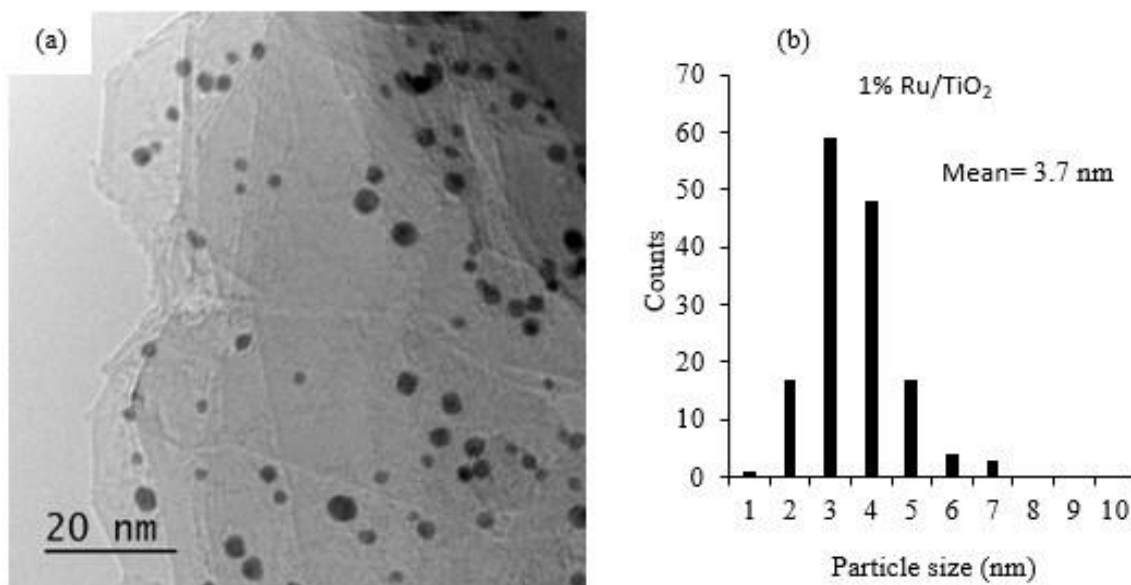

Fig. 2: (a) Transmission electron microscopy (TEM) and (b) Particle size distribution (PSD) for 1% Ru/TiO$_2$ prepared by sol-immobilization method. Counts: represent repetition number of specified diameter particles.

Thus, the best performance of 1%Ru/TiO₂ was attained using sol-immobilization preparation method. This catalyst underwent assessment using TEM; the analysis data, together with those from distribution of particle size (PSD), as shown in Fig. 2. PSD demonstrated that 1%Ru/TiO₂ was comprised of tiny particles, most 3-4 nm in dimension with a diameter spectrum of 1-7 nm. The lower the particle dimensions the better the distribution of Ru, which may explain the superior performance of this catalyst. 1%Ru/TiO₂ catalyst synthesized by wet-impregnation exhibited particle dimensions between 7 and 12 nm (Fig 3). This may diminish the spread of RU, and therefore give rise to diminished catalytic activity.

Table-6: Catalyst reusability study for benzyl alcohol oxidation.

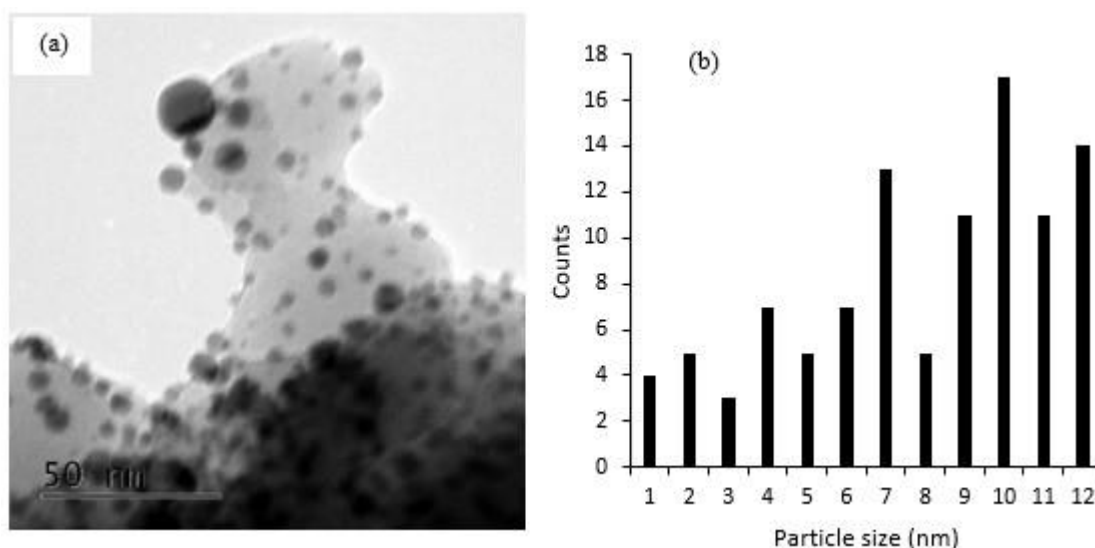| Washing conditions	Conversion (%)	BzH selectivity (%)
Newly used catalyst	10	98
Unwashed reused catalyst	5	76
Reused catalyst after washed by acetone	7.5	90

Effect of catalyst mass

Fig. 3: (a) Transmission electron microscopy (TEM) and (b) Particle size distribution (PSD) for 1% Ru/TiO2 prepared by wet-impregnation method. Counts: represent repetition number of specified diameter particles.

The prevalence of active site on the catalyst surface also exerted a notable effect on the catalyst's influence on selective oxidation of benzyl alcohol. This impact is illustrated in Table-5. With rising catalyst quantity, the catalytic reaction speed is increased markedly as it is influenced by the active site on the catalyst. The catalytic reaction rate is affected by the catalytic active site. It was worth noting that the benzyl alcohol conversion responses linearly to catalyst mass until certain point. Restrictions associated with the latter dictate that once 0.04 g catalyst is utilized, only a small part of the benzyl alcohol can be subject to the catalyzed reaction (2.6% conversion), thus causing a reduced conversion rate. Further increase in the 1%Ru/TiO₂ mass result to increase the conversion and benzaldehyde selectivity as shown in Table-5. When the catalyst exceeds 0.12 g, however, failed to impact the conversion rate of benzyl alcohol per se, rate did not show any significant differences, but new oxidation products were formed, e.g., benzoic acid. Full deliberation is required in relation to this catalytic amount 0.12 g.

Reusability and stability of ruthenium catalysts

An excessive quantity of 1%Ru/TiO₂ catalyst prepared using the sol-immobilisation technique was added to the previously described reaction to establish its recycling capacity. After the reaction was terminated, the catalyst was filtered, rinsed with acetone, oven dried at 110 °C for 16 hours. The requisite quantity (0.1g of 1%Ru/TiO₂) for a further

typical reaction was then separated for repeated use. The parameters of performance from the de novo and recycled catalyst are presented in Table-6. Benzyl alcohol conversion was 10% and benzaldehyde selectivity, 98%, with the former sample. The recycled catalyst demonstrated diminished capacity; reutilisation was unsuccessful after drying and without prior washing. This reduced level of activity may reflect its deactivation by the adsorbed reaction products.

When judged against the catalyst that did not undergo cleansing, the reused catalyst which was rinsed in acetone demonstrated greater activity, with a 7.5% benzyl alcohol conversion and 90% benzaldehyde selectivity. Nevertheless, when compared with the fresh catalytic material, the reutilised and rinsed catalyst displayed poor parameters of performance, a potential outcome of carbon inhibition of the active site. It can additionally be appreciated that the harvest of the catalyst following an acetone rinse is greater than that procured in the absence of the rinsing phase.

Reaction conditions: 1% Ru/TiO_2 (0.12 g), benzyl alcohol (96.632 mmol, 10 mL), 110 °C, atmospheric pressure air, reaction time 4 h, rate of stirring 800 rpm.

One of the major difficulties in applications of heterogeneous catalysts is the leaching of the active sites of the catalyst in solution. Fortunately, one of the most significant results of our work is that ruthenium was not detected as indicated by inductive couple plasma (ICP) analysis.

Conclusion

Ruthenium catalyst supported on titanium oxide was synthesized by two different route, sol immobilization and wet impregnation. The synthesized supported catalyst was characterized by SEM and PSD. The catalytic activity was evaluated by oxidation of benzoic acid to benzaldehyde and sol immobilization technique resulted in supported Ru catalyst with higher catalytic activity than wet impregnation method. Among the different supports examined, TiO_2 show the best catalytic activity. The optimum reaction temperature with respect to best results of benzyl alcohol conversion and benzaldehyde selectivity was 110 °C. Studying reaction time indicate that oxidation of benzyl alcohol occurs within the consecutive reaction. The catalytic activity increases by increasing the amount of catalyst used until 1% Ru/TiO_2 mass after that there was no effect. The Ru/TiO_2 catalyst could be reused after rinsed with

acetone and dried even though with less catalytic activity than new one.

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