

## Synthesis, Characterization and Catalytic Activity of Pd Supported Zirconia for the Oxidation of Benzyl Alcohol in Liquid Phase Solvent Free Conditions

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**Summary:** Selective oxidation of benzyl alcohol was carried out using molecular oxygen under mild conditions at high turnover frequency [TOF] over palladium supported on zirconia. Zirconia was synthesized by co-precipitation of zirconyl chloride with dilute ammonia solution. Palladium supported zirconia was synthesized by incipient wet impregnation method. The high surface area of zirconia was responsible for the better dispersion of palladium metal over the support which improved the accessibility of the relatively large molecules to the active sites, leading to an improved catalytic performance for alcohol oxidation. The catalyst was characterized by different physical and analytical techniques. The catalyst was found to be active and selective towards the formation of benzaldehyde. The TOF was found to be > 6000/hour, which was amongst the highest reported in literature. Langmuir-Hinshelwood kinetic model was found to be applicable to the solvent free oxidation of benzyl alcohol oxidation.

**Key words:** Alcohols; Fine Chemicals; Oxidation; Kinetics; Catalysis; Turn over Frequency.

### Introduction

The use of molecular oxygen combined with a heterogeneous catalytic system has effectively been acknowledged as an attractive green technique for the synthesis of a number of fine chemicals in different industries [1-4]. Stoichiometric oxidants like chromates and di-chromates have been used for the production of active oxygen, vital for the oxidation of organic compounds. These oxidants however produce large amount of wastes and often show poor product efficiency, making them less environment and economy friendly [5, 6]. In this regard, homogeneous catalysts have shown promising oxidation potential in liquid phase, resulting in high product yields [7, 8]. However homogeneous catalyst systems are potentially disadvantageous in the regard that the homogeneous catalysts are associated with the problem of separation and reusability. Therefore, attention has been shifted to develop heterogeneous catalyst system, which can be used with equal significance in both batch reactor systems as well as fixed bed reactor systems [9, 10]. A diverse group of heterogeneous catalyst has been introduced in the last few years, based on multi component metal oxides, vanadia and platinum/platinum oxide based metals deposited on different supports [11-16]. In fact platinum based catalysts are the most promising ones currently used on commercial basis [17]. However the drawback associated with the use platinum based catalyst is often poor selectivity and deactivation of the used catalyst [18]. Palladium based catalyst have

shown better activity and selectivity as compared to platinum based catalyst. Recent studies have shown the activity of Pd based catalyst for the aerobic oxidation of alcohols and other polys [19-21]. In our previous studies we have shown activity of zirconia as effective catalyst for the oxidation of benzyl alcohol and toluene [22] and also Pt/Zirconia [23, 24] for the efficient oxidation of alcohols. In this study our aim to examine the oxidation of benzyl alcohol under milder conditions of temperature and pressure using a simple three necked round bottom flask as our bath reactor and molecular oxygen as oxidant. Pd/ Zirconia have been investigated as heterogeneous recyclable catalyst. We are using the oxidation of benzyl alcohol as model reaction and intend to use the catalyst for a broad range of alcohols as demonstrated in the literature elsewhere [25].

### Experimental

#### Materials

All the materials supplied were used as supplied without any further purification. ZrOCl<sub>2</sub>·8H<sub>2</sub>O [Merck, 8917], NH<sub>4</sub>OH [BDH, 27140], AgNO<sub>3</sub> [Merck, 1512], PdCl<sub>2</sub> [Alfa Aesar, 1103], benzyl alcohol [Merck, 9626], benzaldehyde [Scharlu, BE0160], *n*-heptane [Merck, 4379], toluene [BDH, 10284], and *n*-octane [BDH, 29407] were used as received.

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H<sub>2</sub> [99.999%], Nitrogen and oxygen gas cylinders were supplied by BOC Pakistan Ltd. and were further purified by passing through traps [C.R.S. Inc. 202268] to remove traces of water and oil. Traces of oxygen in the nitrogen gas were removed by using specific oxygen traps [C.R.S. Inc. 202223].

#### *Synthesis of Zirconium Oxide Support*

Zirconium oxide was synthesized by adding drop wise addition of 100 cm<sup>3</sup> ammonia solution to 0.4 M solution of ZrOCl<sub>2</sub> under continuous stirring until the pH of the solution reached to ~10. The white dense precipitate of hydrated zirconia was left to age for 24 hours without stirring. The solid was filtered in folds of standard filter paper and was thoroughly washed with triply distilled water so as the Cl<sup>-</sup> test with silver nitrate solution was negative. The resultant zirconium oxide powder was dried at room temperature for 24 hours and then in a drying oven for 24 hours. Then the powder was calcined at 700 °C for three hours with a ramp rate of 5 ° rise per minute [26].

#### *Pd Impregnation on Zirconia Powder*

The zirconia powder was impregnated using an aqueous solution of palladium nitrate solution containing palladium metal required to make a loading equal to 0.1 wt % using the incipient wetness impregnation technique. The catalyst was dried at room temperature for 24 hours and then at 105 °C for 24 hours. Before each activity the catalyst was calcined again at 500 °C and activated in hydrogen flow at 280 °C [26].

#### *Characterization*

The surface area [SA] and pore diameter of the catalyst were obtained using nitrogen adsorption isotherms using Quanta Chrome Nova 1200 apparatus. Prior to adsorption the catalyst powder was degassed in vacuum at 200 °C for 2 hours. The crystal structure of the catalyst was determined using a JEOL [JDX-3532] Japan instrument using filtered Cu-K $\alpha$  radiation [ $\lambda$  = 0.15406 nm], the machine was operated on 40 kV and 40 mA current. Diffraction patterns were recorded between 10°–70° with a resolution of 0.05 ° [20]. Prior to the test, samples were dried at 373 K overnight. The grain size of the catalyst was determined using Analysette 22 Compact, [Fritsch-Germany] particle size analyzer. Wet method of analysis was applied for the determination of the grain size of the as synthesized powder. IR Prestige 21, Shimadzu Japan instrument

was used to determine the IR spectra of the dried and annealed catalyst powder in the wave number range of 450-4000 cm<sup>-1</sup> for studying the functional chemical groups. For each analysis the samples were pressed in KBr pallets before recording IR activity.

#### *Activity Measurement*

Oxidation experiments of benzyl alcohol in solvent free conditions were carried out in Pyrex three necked round bottom flask batch reactor at four different temperatures i.e. 343-373 K. In a typical run 10 ml benzyl alcohol equivalent to 97 m.moles and 0.2 grams of catalyst was taken in the reactor. The reactor was equipped with a heater, a digital thermometer and a magnetic stirrer. Molecular oxygen was used as oxidant. The stirrer was set at 950 rpm. Afterwards the batch reactor was swiftly mounted on to the preheated base, to the reaction temperature. The condenser temperature was maintained at 281 K so that the substrate molecules remain intact. Oxygen was passed through the reaction mixture at 60 ml/min. After regular intervals of time samples were withdrawn from the reaction mixture. The samples were filtered immediately and analyzed using a gas chromatograph equipped with an FID [Elite-5 capillary column] detector. Benzaldehyde and benzoic acid were detected as the reaction products. The oxygen partial pressure was altered by mixing molecular nitrogen with oxygen gas. The oxygen partial pressure was calculated by the following formula

$$O_2 \text{ [Partial Pressure]} = [O_2 \text{ [ml/min]} / O_2 \text{ [ml/min]} + N_2 \text{ [ml/min]}] \times 101.2 \text{ kPa}$$

## **Results and Discussions**

#### *Characterization*

The XRD patterns of the calcined powder shows that the zirconia powder was mainly in monoclinic phase [27, 28] showing visible and sharp peaks at 2 $\theta$  angles equal to 28.1° and 31.38° respectively as shown in Fig. 1. A small peak at 2 $\theta$  angles equal to 46.8° corresponds to metallic Pd [29]. There seems no evident palladium peak which may be due to very low palladium loading on the support material. Furthermore, there seems no visible difference between the unused [a], used in the presence of molecular oxygen [b] and the catalyst used in nitrogen atmosphere [c], which suggests that the monoclinic phase and morphology of the catalyst is well retained while being used in the reaction conditions. The retention of the crystal structure of the catalyst also suggests the heterogeneous behavior

of the catalyst. Surface area and pore size analysis of the powder was examined using a still volumetric machine at 77K. The BET surface area of the powder was calculated using the nitrogen adsorption-desorption isotherm. The BET surface area of the uncalcined catalyst powder was found to be 350 m<sup>2</sup>/gram before calcination; however the surface area of the catalyst drastically decreased to 12.4 m<sup>2</sup>/gram. The adsorption-desorption isotherm [not shown] of the calcined catalyst corresponds to type II according to the IUPAC classification [26, 30,31]. This type of isotherm is characteristic of solids having aggregates of particles with non-uniform size and shape. The particle size of the calcined catalyst was found to be in the range of 3- 10 micro meters. The IR spectra of Pd supported zirconia is shown in Fig. 2, the bands corresponding to wave numbers 3300-3600 cm<sup>-1</sup> and 1565 cm<sup>-1</sup> can be assigned to the stretching and bending vibrations of the bound water and coordinated water respectively. Another visible band can be seen at 466 cm<sup>-1</sup>, this band is related to the vibrational stretching of Zr-O bond in ZrO<sub>2</sub> [32, 33]. There seems no noticeable difference between the [a] unused [b] used in oxygen and [c] used in nitrogen atmosphere, which suggests that the both the substrate and the product molecules are well removed from the surface of the catalyst.

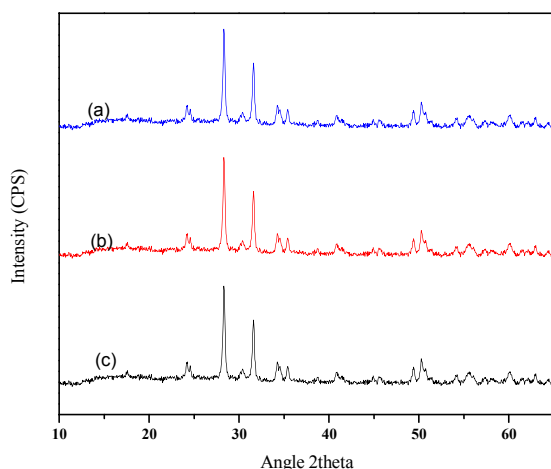


Fig. 1: XRD Patterns of (a) Fresh, (b) Used in oxygen atmosphere (c) Used in nitrogen atmosphere.

#### Catalytic Activity

0.1% Pd supported ZrO<sub>2</sub> was employed as heterogeneous catalyst for oxidation of benzyl alcohol in solvent free condition at various temperatures and oxygen partial pressures. It was observed that 0.1% Pd/ZrO<sub>2</sub> can be employed as an efficient catalyst for aerobic oxidation of benzyl

alcohol. It was noted that there was no conversion of benzyl alcohol after one hour employing only ZrO<sub>2</sub> as catalyst, while about 13% conversion was achieved with 0.1% Pd/ZrO<sub>2</sub> catalyst. It was evident from the subsequent experimental data that benzaldehyde was the more selective product [>70%] along with the formation of benzoic acid. The reaction mechanism was proposed to be consecutive in nature for the formation of benzoic acid. It was proposed that at condenser temperature small amount of water is produced which subsequently reacts with benzaldehyde in the presence of molecular oxygen to form benzoic acid. Although the conversion of benzyl alcohol and TOF increases with temperature, the selectivity towards benzaldehyde and benzoic acid remain almost constant. These results are given in Table-1.

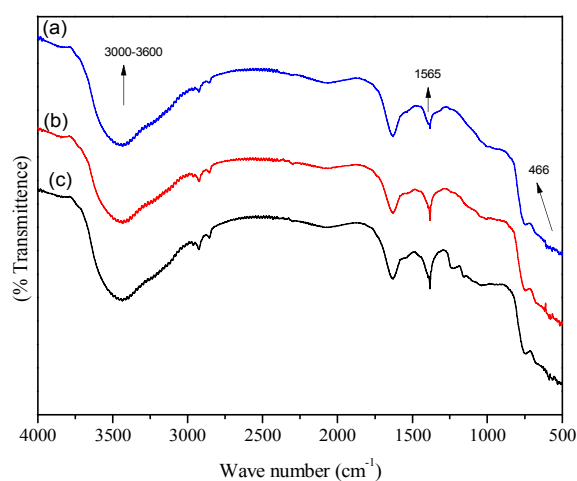


Fig. 2: IR Spectra of (a) Fresh, (b) Used in oxygen atmosphere (c) Used in nitrogen atmosphere.

Table-1: Effect of temperature on Pd/ZrO<sub>2</sub> catalyzed oxidation of benzyl alcohol in solvent free conditions for 1 hour

Temperature (K)	Conversion (%)	Selectivity (%)		TOF*
		BzH	BzOOH	
343	3.15	77.7	22.2	1612
353	3.61	78.1	21.9	1847
363	5.29	78.1	21.9	2707
373	13.1	78.1	21.9	6699

TOF= Moles of benzyl alcohol converted per mole of Pd per hour

#### Time Profile

The oxidation of benzyl alcohol as a function of time was investigated at different temperatures at atmospheric pressure of oxygen. The results shown in Fig. 3[a] illustrates that there is almost a linear increase in conversion of benzyl alcohol with time. Fig. 3[b] shows the conversion of benzyl alcohol and selectivity of benzaldehyde and

benzoic acid with TOF at 373 K. Conversion of benzyl alcohol increases with time while selectivity to benzaldehyde and benzoic acid remain the same. In this investigation it is observed that selectivity towards benzaldehyde and benzoic acid doesn't change either with temperature or time.

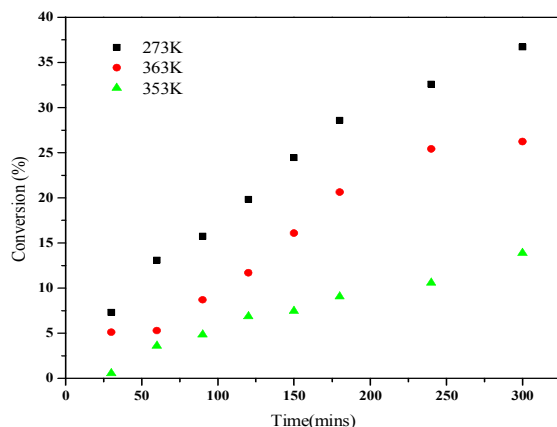


Fig. 3: (a): Time profile data at different temperatures.

(Reaction Conditions: Substrate 97 m,mol, Oxygen 1atm)

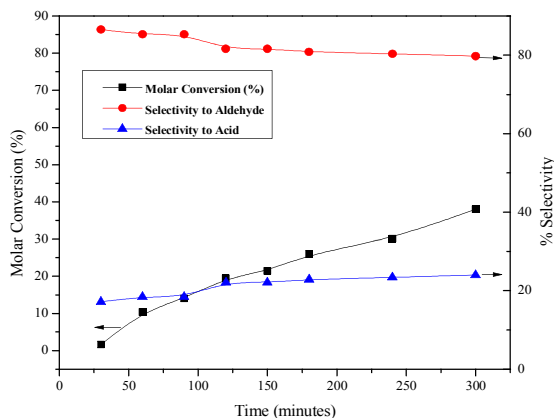


Fig. 3: (b): Time Profile Date at 373K and 1 atm oxygen pressure (Selectivity to products)

#### Influence of Catalyst Weight

The influence of catalyst load was scrutinized in the domain of 30-230 mg 373 K and atmospheric pressure of oxygen. The stirring speed of the reaction mixture was maintained 900-950 rpm [maximum speed] for 60 minutes. It was observed that the conversion of alcohol increases with increasing load of the catalyst however it become constant above 150 mg, the conversion/gram-minute decreases with the increase of catalyst load up to 150 mg and then increases and at higher load the

conversion of alcohol becomes constant as shown in Fig. 4. Transport limitation of the alcohol to the surface of the catalyst was found to be active below a catalyst load of 200 mg which becomes eliminated at or above 200 mg loading. This indicates the kinetically control regime, hence 200 mg was chosen as optimal catalyst loading for oxidation of benzyl alcohol in solvent free condition.

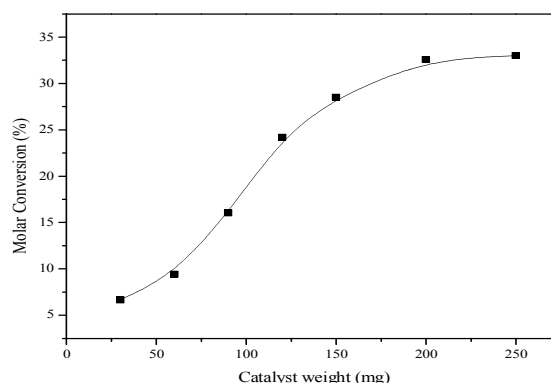


Fig. 4: Effect of Catalyst loading on the conversion of Alcohol.

#### Effect of Agitation

Oxidation of benzyl alcohol over Pd/ZrO<sub>2</sub> is a classic slurry three phase reaction consisting of a liquid [benzyl alcohol], a gas [oxygen] and solid reactant [Pd/ZrO<sub>2</sub>] as catalyst. In the batch reactor, the reaction mixture was agitated strongly in order to distribute the solid catalyst homogeneously throughout the substrate molecules. To investigate the true kinetics of a multiple phase reaction, the mass transfer effect must be eliminated.

If the reaction rate is changing with the speed of agitation, then the mass transfer limitations are said to exist. However if the rate of the reaction becomes independent of the agitation speed, the reaction is said to be free from mass transfer limitation. In order to observe the effect of the speed of agitation on the rate of oxidation of benzyl alcohol, experiments were carried out at different stirring speeds in the range of 150–950 rpm at 373 K for one hour [Fig. 5]. It was observed that with an increase of stirring speed from 150-650 rpm, the conversion/rate of benzyl alcohol goes on increasing, indicating the existence of mass transfer regime, however above 650 rpm the rate of reaction does not change with speed of agitation, which indicates the absence of any mass transfer limitations. As this was our area of interest hence all the subsequent reactions were carried out at 950 rpm [maximum speed].

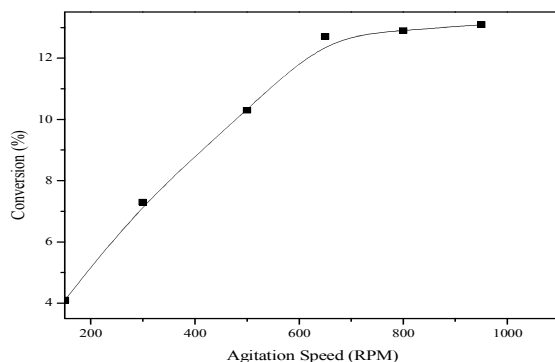


Fig. 5: Effect of agitation speed on oxidation of alcohol at 373 K.

#### Re-Use of Catalyst

A good industrial catalyst is one which can be recycled and used over longer periods of time. The reuse of the catalyst not only minimizes the cost of production but it also helps in maintaining the environmental sector. To investigate possible reusability of the catalyst, catalyst was separated from reaction mixture and was washed with ethanol and distilled water. It was then dried at 373 K for 12 hours. The catalyst performance was checked with the washed catalyst, the results showed that the catalyst performance was found to be same as fresh catalyst. In second experiment we did not wash the catalyst and checked its catalytic performance towards the oxidation of benzyl alcohol under the same conditions, it was found that the performance of the catalyst was reduced by about 5 percent with each subsequent use. The results are shown in Fig. 6 [a and b] respectively.

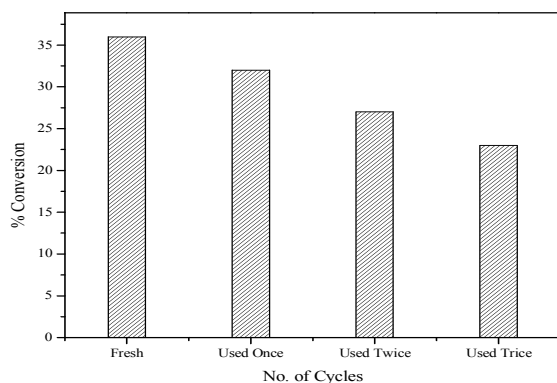


Fig. 6: (a): Reuse of the catalyst without any post treatment.

#### Comparison of Oxidation Reaction in Solvents and Solvent Free Conditions

In order to compare the oxidation potential of our catalyst, the oxidation of benzyl alcohol was

carried out in the presence as well as in the absence of different organic solvents like *n*-heptane, *n*-octane as well as water. The reaction was found to be 100% selective towards the formation of benzaldehyde in the organic solvents i.e. *n*-heptane and *n*-octane. The reaction was 100% selective towards benzoic acid formation in aqueous medium. The reaction in the presence of *n*-heptane was faster than *n*-octane. In aqueous medium the reaction was complete in 30 minutes. In case of solvent free condition there was formation of benzoic acid as well. The reason could be the complete removal of water in case of organic solvents but in case of solvent free conditions the complete removal of water is not possible, therefore the water produced may react with benzaldehyde to form benzoic acid. Under reaction conditions at 60 ml/minute oxygen flow and the condenser temperature at 281K, ~ 0.02 and ~97 m.moles of water is produced in presence and absence of solvent respectively. At condenser temperature 23.3 m.moles of water can vaporize in 300 minutes. Therefore we suggest that all the water gets vaporized in the presence of organic solvents. However, 97-23.3= 73.7 m.moles of water is still present inside the reaction mixture which could react with the benzaldehyde to form benzoic acid. The results are summarized in Table-2.

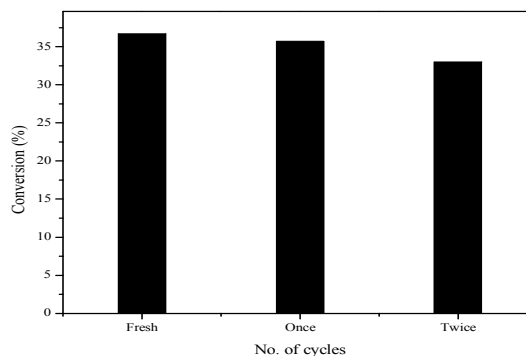


Fig. 6: (b): Reuse of the catalyst after washing with water and ethanol.

Table-2: Pd/ZrO<sub>2</sub> catalyzed oxidation of benzyl alcohol in absence and presence of solvents for 5 hours at 373 and 353 K respectively

Temperature (K)	Conversion (%)	Selectivity (%)		TOF*
		BzH	BzOOH	
<b>In absence of solvent at 373 K</b>				
343	10.3	74.8	24.9	1758
353	13.9	75.8	24.0	2372
363	26.4	73.5	25.9	4506
373	36.2	71.7	29.7	6178
<b>In presence of solvent at 353 K</b>				
<i>n</i> -heptane	40.8	100	-----	37
<i>n</i> -octane	98.3	100	-----	87

TOF= Moles of benzyl alcohol converted per mole of Pd per hour

### Oxygen Partial Pressure

The oxidation of benzyl alcohol was carried out at different partial pressure of oxygen ranging from 0.0 to 101 kPa. The reactions were conducted at 373 K and 10ml [0.097 m.moles] benzyl alcohol, 200 mg of catalyst was used as catalyst in all the reactions.

Fig. 7 shows the variation of benzyl alcohol oxidation as function of time at different partial pressures of oxygen. With increase in partial pressure of oxygen, the conversion of the substrate increases linearly.

### Leaching of the Catalyst

The leaching of the catalyst is an obstacle to the heterogeneous nature of the catalyst. To know whether the catalyst is leaching into the reaction mixture, hot filtration method was employed. The reaction was carried out according to the standard procedure i.e. Reaction temperature 100 °C, Oxygen flow 60 ml/min, and catalyst loading 0.2 grams. The reaction was carried out for 30 minutes and then the catalyst was filtered off swiftly. The reaction was again carried from the same point without the catalyst. The reaction carried out before filtration shown normal activity but after filtration no products formation occurred. This suggested that the catalyst remained intact and was not leaching into the reaction mixture.

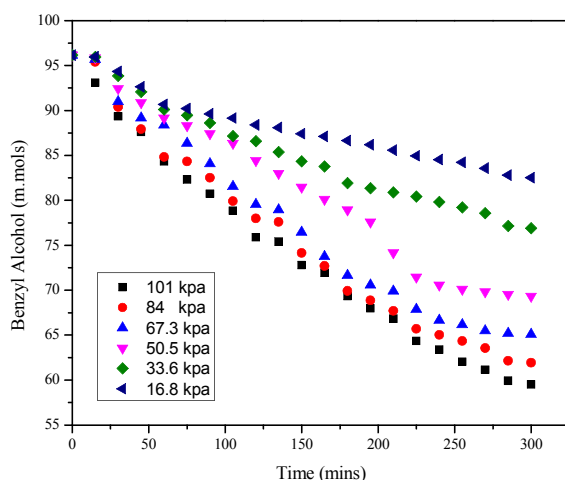


Fig. 7: Effect of oxygen partial pressure (33-101 kpa) at 373K.

### Kinetic Analysis

Langmuir-Hinshelwood kinetic model was used to explain the solvent free oxidation of benzyl

alcohol by Pd/ZrO<sub>2</sub>. It was assumed that the reaction is taking place at the catalyst surface. According to this model, the gas and the substrate molecules approach the catalyst surface in then and gets adsorbed there. In second step both the reactants react on the surface of the catalyst and generate products. Finally the product molecule desorbs from the solid surface [34, 35]. Langmuir Hinshelwood model describes that the rate of a chemical reaction is proportioned to the surface covered by the reacting molecules,  $\theta$

$$\text{Rate} = k\theta_{BzOH}\theta_{O_2} \quad [2]$$

Where  $k_r$ , represents the rate constant,  $\theta_{BzOH}$  as surface covered by benzyl alcohol and  $\theta_{O_2}$  represents surface covered by molecular oxygen.

Due to the negligible change in the concentration of substrate molecules, the concentration of benzyl alcohol is taken as equal to 1 at all stages of the reaction. Hence, equation 2 modifies as

$$\text{Rate} = k'\theta_{O_2} \quad [3]$$

At constant partial pressure of oxygen equation no.3 can be written as

$$\text{Rate} = k'' \quad [4]$$

Equation 4 represents a typical pseudo zero order reaction and on integration transforms as

$$(BzOH)_t = -k''t \quad [5]$$

were  $[BzOH]_t$  represents concentration of benzyl alcohol left after reaction time "t". It is evident from Fig. 8, that under these reaction conditions the rate constant k depends upon the partial pressure of oxygen [also evident from equation 3 and 4]. When equation [5] was employed to the time profile data for the oxidation of benzyl alcohol at different partial pressures of molecular oxygen, it resulted in straight lines. The slopes of the lines gave the values of  $k''$ .

Considering that  $k'' = k'\theta_{O_2}$  [equation 3 and 4], and if the Langmuir adsorption isotherm is applicable for the adsorption of oxygen then:

$$\theta_{O_2} = \frac{K_{O_2} p_{O_2}}{1 + K_{O_2} p_{O_2}} \quad [6]$$

where  $K_{O_2}$  represents the adsorption equilibrium constant for oxygen and  $p_{O_2}$  partial pressure of oxygen. Hence equation [6] for  $\theta_{O_2}$  becomes

$$k'' = \frac{k'K_{O_2}p_{O_2}}{1 + K_{O_2}p_{O_2}} \quad [7]$$

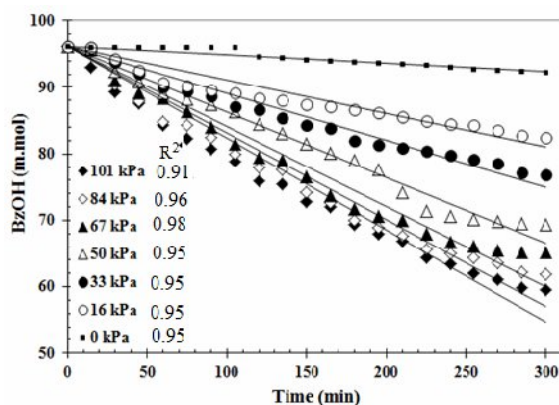


Fig. 8: Application of equation 5 to time profile data for oxidation of benzyl alcohol at various partial pressure of oxygen.

By applying equation [7] to the time profile data at different partial pressure of oxygen by non-linear least square approach using the software curve expert 3.1 resulted in excellent agreement between experimental and theoretical values of  $k''$  as shown in Fig. 9. The values of rate coefficient  $k'$  and adsorption equilibrium " $K$ " obtained by non-linear least square fit are 0.236 m.mol /min. and 0.0144/kPa respectively, with correlation coefficient [ $R^2$ ] of 0.9932. It can be summarized that the rate of oxidation of benzyl alcohol in the liquid phase solvent free conditions is:

$$Rate = k\theta_{BzOH} \frac{K_{O_2}p_{O_2}}{1 + K_{O_2}p_{O_2}} \quad [8]$$

As  $\theta_{BzOH}$  in solvent free conditions is constant or equal to 1 and thus this equation is reduced to:

$$Rate = k' \frac{K_{O_2}p_{O_2}}{1 + K_{O_2}p_{O_2}} \quad [9]$$

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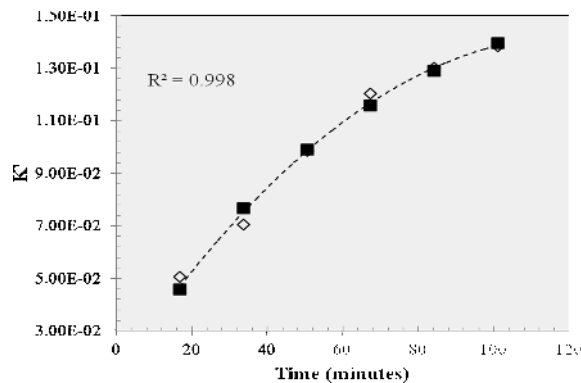


Fig. 9: Agreement of calculated and experimental values of  $K$  (Filled squares represents experimental values of  $K$ , Open squares represent calculated values of  $K$ ).

## Conclusions

0.1 % Pd/ZrO<sub>2</sub> has demonstrated its efficiency for the oxidation of benzyl alcohol in solvent free condition in batch reactor. Thus palladium supported on zirconia can be considered as effective catalyst for oxidation of benzyl alcohol, having turnover frequency [TOF] of > 6000/hr at 373 K. Catalyst was heterogeneous in nature and was highly stable under reaction conditions. Variation in temperature and partial pressure of oxygen has great effects the oxidation of benzyl alcohol. The oxidation of benzyl alcohol catalyzed by Pd/ZrO<sub>2</sub> in present case is taking place in kinetic controlled region, where Langmuir-Hinshelwood type of mechanism is operative. According to this mechanism reaction proceed in two steps. In first step both the reactants i.e. benzyl alcohol and oxygen are adsorbed at the surface of catalyst, while in second step the adsorbed reactants react and give the final products. Adsorption of both reactants was taking place according to Langmuir adsorption isotherm. It shows that the adsorption sites for were homogeneous in nature. The overall kinetic expression can be concluded as

$$Rate = k\theta_{BzOH} \frac{K_{O_2}p_{O_2}}{1 + K_{O_2}p_{O_2}}$$

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