Kinetics of oxidation of benzyl alcohol by molecular oxygen using manganese oxide supported activated carbon with phase transfer catalyst

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ABSTRACT

Kinetics of the selective oxidation of benzyl alcohol using molecular oxygen and manganese oxide supported activated carbon in presence of tetrabutylammonium bromide as phase transfer catalyst in toluene was studied at room temperature. Scanning electron microscopic imaging and X-ray diffraction analysis of the catalytic surface supported the aggregation of highly dispersed MnO_x crystalline nanoclusters (a mixture of Mn_2O_3 and MnO) on activated carbon surface. In these highly dispersed manganese oxide species, the coexistence of Mn^{2+} and Mn^{3+} were postulated to be the active sites in aerobic oxidation of benzyl alcohol with molecular oxygen. The presence of phase transfer catalyst found to increase the rate of oxidation considerably. The increased rate of oxidation of benzyl alcohol with molecular oxygen in presence of phase transfer catalyst is may be due to more and easier interaction of the reactants due to the closer proximity of oxygen and alcohol with the manganese species present on the catalyst surface and this reduces the interfacial surface tension. The use of phase transfer catalyst also ensured the smooth progress of the reaction at ambient conditions with high yield.

KEY WORDS: Aerobic oxidation, benzyl alcohol, manganese oxide supported activated carbon, molecular, oxygen, kinetics, phase transfer catalyst.

1. INTRODUCTION

Selective oxidation of alcohols to corresponding aldehydes has been a subject of intense research as these transformations have high significance in laboratory as well as in commercial synthesis (Lenoir, 2006, Matsumoto, 2008 and Fan, 2009). Benzaldehyde is one of the most desirable important precursor and intermediate in pharmaceuticals and fine organics (Amamoto, 2005; Pina, 2008). Selective oxidation of alcohols to corresponding aldehydes with environmentally benign inexpensive oxidants, such as molecular oxygen, hypochlorite and other oxidants has attracted great attention from both economic and environmental points of view (Pillai, 2004; Zhan, 2004; Mallat, 2004; Bijudas, 2004, 2014, 2015). There are reports on oxidation of benzyl alcohol to benzaldehyde with molecular oxygen, where addition of supporting materials, promoters and visible light irradiation have been used to improve the efficiency of the catalytic systems (Sigman, 2006; Arends, 2004). Studies on catalytic oxidation using precious metals or metal based compounds as catalysts, such as Au (Choudhary, 2010; Chen, 2011), Pd (Hai, 2011; Yasu-eda, 2010), Ru (Yu, 2009; Yamada, 2007) and Pt (Mallat, 1994; Perez, 2012) have been reported for selective oxidation of benzyl alcohol. But these catalysts are costly and less available and so it is desirable to investigate and develop inexpensive catalysts consist of 3d transition metals because those metals offer environmentally benign and cost effective alternative to noble metal catalysts. Among transition metals, manganese exhibits high catalytic activity for oxidation of benzyl alcohol to Benzaldehyde. Highly dispersed manganese oxide supported on activated carbon and alumina showed high efficiency for the aerobic oxidation of benzyl alcohol using molecular oxygen (Tang, 2009). This paper reports the studies on the characterization and structural identification of the catalyst surface. The role of efficient phase transfer catalysts (PT catalysts) like tetraalkylammonium salts in the kinetics of such air-liquid-solid phase oxidation is of great significance in environmental as well as theoretical points of view. Since there is dearth of information about such studies, we report the study of the kinetics and mechanism of the oxidation of benzyl alcohol using molecular oxygen with manganese oxide supported activated carbon in presence of PT catalyst.

2. EXPERIMENTAL

2.1. Materials: Manganese nitrate (2.0 mol dm^{-3}) solution was prepared by mixing equal volumes of 2.0 mol dm^{-3} solution of manganese sulphate and barium nitrate (Merck Millipore, India) after removing the precipitated barium sulphate. High purity activated carbon was prepared by washing with 2.0 mol dm^{-3} HNO_3 and deionised water. After washing and drying, manganese oxide was deposited on activated carbon using aqueous solution of manganese nitrate by conventional wet impregnation method. 25 mL of manganese nitrate solution was taken in a

beaker containing 2 g activated carbon. The mixture was stirred vigorously for about 3 hours and allowed to stand for 24 hours under ambient conditions. The manganese oxide impregnated activated carbon was obtained by heating at 350 K to evaporate water and incubated at 635 K for 6 hours. The catalyst samples were analysed by X ray diffraction analysis and by scanning electron microscope. Benzyl alcohol and toluene (Merck Millipore, India) were used after purification by distillation. A small Oxycare unit was used as the source of molecular oxygen. A standard gas burette was used for kinetic investigation. Tetra butyl ammonium bromide (Merck KGaA, Germany) was used as PT catalyst.

2.2. Methods: The oxidation of benzyl alcohol using manganese oxide impregnated activated carbon was carried out in a gas burette connected to around bottom flask. The reaction system consists of 4 g MnO_x loaded activated carbon, benzyl alcohol (0.5 mol. dm^{-3}) and 0.4 g TBAB (0.025 mol. dm^{-3}) in 40 mL toluene. Oxygen gas was bubbled to the round bottom flask using a gas burette for about one hour. After one hour the solid catalyst was filtered off and the remaining solution is extracted with ether three times. The collected ether layer was extracted with 2% aqueous sodium carbonate three times. The aqueous layer and ether layer were separated. The aqueous layer on acidification with dilute acid did not give any precipitate and rules out the formation of benzoic acid. The ether layer was treated with saturated sodium bisulphite solution. The white crystalline product-bisulphite adduct was filtered off and it was treated with dilute HCl solution to get the product. The product is treated with 2, 4-dinitrophenylhydrazine and is recrystallized from ethanol. The pure 2, 4-dinitrophenylhydrazone of the product is analyzed by melting point determination, UV-Visible and infrared spectral techniques.

2.3. Kinetic investigation: Benzyl alcohol (0.25 mol. dm^{-3}) and 0.4 g TBAB (0.025 mol. dm^{-3}) in 40 mL toluene was taken in a 250 mL round bottom flask. 2 g MnO_x loaded activated carbon was added to it and a gas burette is connected to it. Oxygen gas was allowed to flow into the system after sufficient evacuation of the reacting system by connecting the gas burette to a vacuum pump. Volume of oxygen used was monitored at 5 minute intervals and was noted as V_t, which corresponds to the amount of benzyl alcohol reacted at each time interval. Oxygen was allowed to flow for about one hour and noted all the readings. Total volume of gas used up is given by V_∞ and it corresponds to the total amount of benzyl alcohol reacted or oxidised completely to benzaldehyde. The concentration of benzaldehyde is proportional to V_∞, total volume of oxygen used. The concentration of benzyl alcohol at a time 't' was given by ($V_\infty - V_t$). Thus the rate constant for the first order reaction is given by $k = 2.303/t \times \log [V_\infty / (V_\infty - V_t)]$. A graph is plotted between t against $\log [V_\infty / (V_\infty - V_t)]$ and from the slope of the graph (k/2.303), k can be calculated.

3. RESULTS AND DISCUSSION

Benzyl alcohol on oxidation gave benzaldehyde as the product with high yield (>90%). Benzaldehyde was obtained as the product in the form of 2, 4-dinitrophenylhydrazone and no traces of benzoic acid was detected. The recrystallized sample of the product was characterized by its melting point and by various spectrophotometric techniques. The melting point of the product obtained on the oxidation of benzyl alcohol was found to be 237 ± 2 °C and the reported value is 239 °C. This gives an idea that the obtained product will be the 2, 4-dinitrophenylhydrazone of benzaldehyde. This was further confirmed by IR and UV-Visible spectral analysis of the obtained product. Infrared and UV-Visible spectra of obtained product were compared with that of 2, 4-dinitrophenylhydrazone of pure benzaldehyde for further confirmation. This method is found to be highly selective since no traces of acid is formed and the product, benzaldehyde is obtained with high yield. Characterization of both bare activated carbon and manganese activated carbon was carried out by SEM and XRD analyses.

3.1. SEM analysis: The SEM analysis was carried out by JEOL JSM 6390(Japan) and the SEM images of bare activated carbon and manganese impregnated carbon after calcination at 635 K are given in Figure 1 and in Figure 2. The SEM results show the presence of Mn_3O_4 (MnO_x) adsorbed on activated carbon and is reported elsewhere (Bukharkina et al., 2004).

3.2. XRD analysis: The XRD analysis of bare activated carbon and manganese impregnated activated carbon was carried out by X'Pert PROPANalytical, Netherlands and is given in figure 3 and 4. The results show that the Mn_3O_4 was highly dispersed over the activated carbon surface.[23] The weak peaks obtained in the XRD pattern in figure 4 indicate the formation of MnOx nanoclusters (a mixture of Mn_3O_4 and MnO) with diameter below the detectable limit of X-ray diffractometer. The XRD analysis supports the presence of body centered nanocubic clusters of manganese oxide.

3.3. Kinetic studies: Kinetic studies of the oxidation of benzyl alcohol was carried out at 303 K and Table 1 gives the volume of oxygen consumed by the reaction system in each time interval without the use of PT catalyst at room temperature and Table 2 gives the rate constant at various time intervals.Mean value of rate constant is found to be 101.2×10^{-3} min^{-1}.A graph is plotted between t against log $(V_\infty - Vt) + 1$and the value of rate constant obtained from the slope is 92.2×10^{-3}min^{-1}. Kinetic studies of the oxidation of benzyl alcohol were repeated by adding tetrabutylammonium bromide as PT catalyst and the volume of oxygen consumed is given in Table 3 and the rate constant at various time intervals is given in Table 4. Mean value of the rate constant is found to be 159×10^{-3} min^{-1}and a graph is plotted between t against log $(V_\infty - Vt)$. The value of rate constant obtained from the slope is 138.2×10^{-3}min^{-1}.

Based on the above results the mechanism of oxidation of benzyl alcohol to benzaldehyde over manganese oxide supported activated carbon by molecular oxygen was found to be a non - chain free radical mechanism as reported (Bukharkina, 2004).The reaction mixture induces the polymerization of added acrylonitrile. Manganese oxide supported on carbon is the catalyst used in this oxidation, in which the co-existence of manganesein Mn(II) and Mn(III) states over the active sites of the support. The reduction potential created due to the co-existence of Mn (II) and Mn(III) in the same support provides the driving force for the oxidation. It is already reported the effect of concentration of loaded manganese on the catalyst surface (Tang, 2009). Accordingly the benzyl alcohol conversion increases with the increase in the percentage weight of manganese loaded on the catalyst surface and reaches a maximum limiting value corresponding to a weight of 10%, indicating its first order dependence on the oxidation. The increased rate of oxidation of benzyl alcohol with molecular oxygen in presence of PT catalysts is found to be due to much closer interaction of oxygen and the alcohol molecule with the manganese species present on the catalyst surface, probably brought about by the reduction in the interfacial surface tension and thereby reducing the surface of separation between liquid and catalyst surface (Makosza, 1997).
Reaction Scheme is given as

$$PhCH_2OH + O_2 \xrightarrow[\text{TBAB/Toluene}]{Mn_2O_3/Carbon} PhCHO + Mn_2O_3 + H_2O_2$$
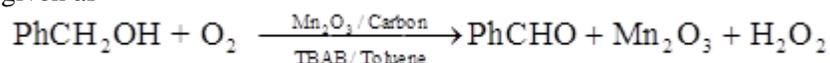
Scheme.1.Oxidation of benzyl alcohol

The mechanism can be proposed as

$$Mn^{3+} + PhCH_2OH \rightarrow Ph\overset{\cdot}{C}.HOH + Mn^{2+} + \ H+$$

$$Ph\overset{\cdot}{C}HOH + O_2 \xrightarrow{Fast} PhCO\overset{\cdot}{O}HOH$$

$$PhCO\overset{\cdot}{O}HOH + Mn^{2+} + H^+ \xrightarrow{Fast} PhCHO + Mn^{3+} + H_2O_2$$
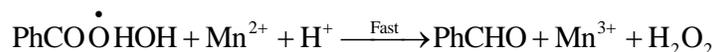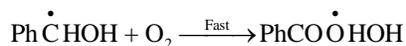
Scheme 2, Mechanism of the oxidation of benzyl alcohol.

The oxidation of benzyl alcohol proceeds by a non-chain free radical mechanism at the low concentration of Mn^{3+} and the rate limiting step is an electron abstraction by metal oxide complex.[24]

$$\frac{d[PhCH_2OH]}{dt} = k[Mn_2O_3][PhCH_2OH]$$

The equation is in agreement with the observation that the reaction is first order in alcohol concentration and also dependent on manganese oxide concentration loaded on carbon.

Table.1.Volume of oxygen consumed at various time intervals

Time in minutes	5	10	15	20	25	30	35	40
Volume of oxygen used(mL)	6	10	12	13.1	13.7	14.2	14.7	15.1

V_∞ - Total volume of oxygen used up and it corresponds to the total amount of
benzylalcohol oxidized =15.1 mL.

Table 2. Rate constant at various time intervals

Time in minute	5	10	15	20	25	30	35
$\log(V_\infty - Vt) + 1$	1.959	1.707	1.491	1.30	1.146	0.955	0.603
$k \times 10^{-3}$ (min^{-1})	101.3	108.5	105.5	101	95	94	103.7

Table.3.Volume of oxygen consumed at various time intervals

Time in minutes	5	10	15	20	25	30	35	40
Volume of O_2 used (mL)	10.3	13.8	15.1	15.7	16.2	16.4	16.5	16.6

V_∞ is found to be 16.6mL

Table.4.Rate constant at various time intervals

Time in minutes	5	10	15	20	25	30	35
$\log(V_\infty - Vt) + 1$	1.799	1.44	1.176	0.903	0.602	0.301	0
$k \times 10^{-3}$(min^{-1})	193.7	177.9	160.3	145	149	147	146
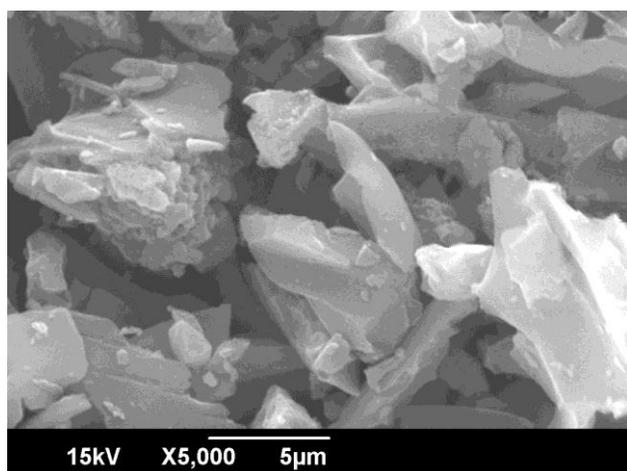
Figure.1.SEM image of bare carbon
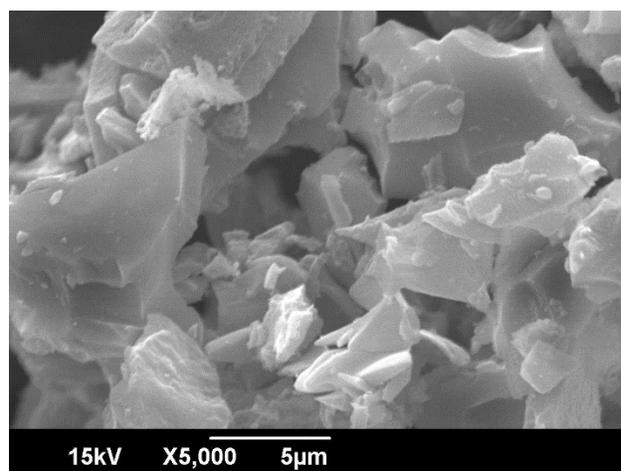
Figure.2.SEM image of manganese activated carbon
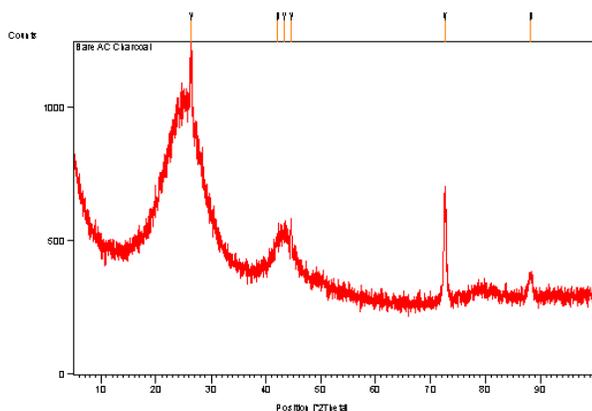
Figure.3.XRD Pattern of bare activated carbon
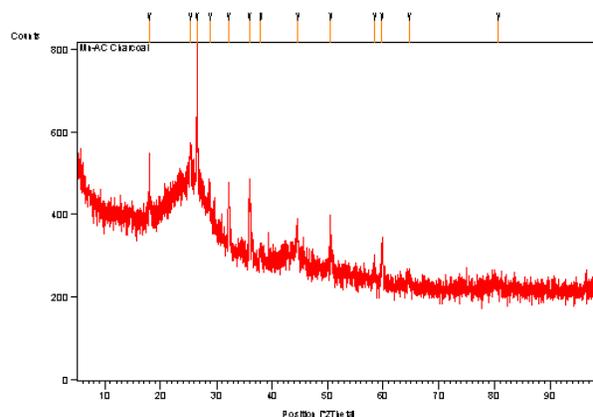
Figure.4.XRD Pattern of manganese Activated carbon

4. CONCLUSION

The activated carbon supported manganese oxide catalyst prepared by wet impregnation method was found to exhibit excellent catalytic activity and selectivity for the oxidation of benzyl alcohol to benzaldehyde. SEM imaging and XRD analysis of the catalytic surface supported the aggregation of high dispersed MnO_x crystalline nanoclusters (a mixture of Mn_2O_3 and MnO) on activated carbon surface. In these highly dispersed manganese oxide species, the co-existence of Mn^{2+} and Mn^{3+} were postulated to be the active sites in aerobic oxidation of benzyl alcohol with molecular oxygen. Kinetic studies have shown that the oxidation of benzyl alcohol under catalytic condition follows first order kinetics. The use of PT catalyst is found to increase the rate of reaction to almost twice that of without PT catalyst. The increased rate of oxidation of benzyl alcohol with molecular oxygen in presence of PT catalyst is may be due to more and easier interaction and the more closer proximity of oxygen and the alcohol molecule with the manganese species present on the catalyst surface, brought about by the reduction in the interfacial surface tension and thereby reducing the surface of separation between liquid and catalyst surface.

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