Kinetics of Lab Prepared Manganese Oxide Catalyzed Oxidation of Benzyl Alcohol in the Liquid Phase

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Received 4 September 2014; revised 16 January 2015; accepted 30 March 2015

DOI 10.1002/kin.20922

ABSTRACT: The oxidation of benzyl alcohol in the liquid phase was studied over manganese oxide catalyst using molecular oxygen as an oxidant. Manganese oxide was prepared by a mechanochemical process in solid state and was characterized by chemical and physical techniques. The catalytic performance of manganese oxide was explored by carrying out the oxidation of benzyl alcohol at 323–373 K temperature and 34–101 kPa partial pressure of oxygen. Benzaldehyde and benzoic acid were identified as the reaction products. Typical batch reactor kinetic data were obtained and fitted to the Langmuir–Hinshelwood, Eley–Rideal, and Mars–van Krevelene models of heterogeneously catalyzed reactions. The Langmuir–Hinshelwood model was found to give a better fit. Adsorption of benzyl alcohol at the surface of the catalyst followed the Langmuir adsorption isotherm. The heat of adsorption for benzyl alcohol was determined as –18.14 kJ mol^{-1}. The adsorption of oxygen followed the Temkin adsorption isotherm. The maximum heat of adsorption for oxygen was –31.12 kJ mol^{-1}. The value of activation energy was 71.18 kJ mol^{-1}, which was apparently free from the influence of the heat of adsorption of both benzyl alcohol and oxygen. © 2015 Wiley Periodicals, Inc. Int J Chem Kinet 47: 447–460, 2015

INTRODUCTION

The oxidation of organic compounds in the liquid phase is one of the most important and widely used reactions in laboratory-scale organic synthesis as well as in large-scale chemical industrial processes [1,2].

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Many processes with different reagents and methods are available for the oxidation of organic compounds. Stoichiometric oxidants such as peroxides or high oxidation state metal compounds such as permanganate and dichromate are frequently used reagents for oxidation purposes. But these reagents are expensive, toxic, and produce large amount of wastes and hence separation and disposal of the waste increases the number of steps [3,4]. When these oxidation reactions are scaled to tons instead of grams, the use of these stoichiometric oxidants is not an attractive option. For these kinds of oxidation reactions, an alternative and environment friendly oxidant is desirable. An ideal oxidant for any large-scale oxidation reaction is the one which has low price, high quality (purity), nontoxic, and easy availability. Molecular oxygen is the one which qualify this criterion [5]. It is easily available as it is present in air, and the only by-product produced from it is water. There are a few points, however, which make the use of molecular oxygen challenging: first, although molecular oxygen has a high oxidation potential, it is not very reactive toward organic molecules and second the reactions where molecular oxygen is present are often radical reactions, which are hard to control. To make an efficient use of molecular oxygen as an oxidant, an appropriate catalyst is needed, which can activate the oxygen molecules for an appropriate reaction. Both homogeneous and heterogeneous catalysts can be used for these transformations. However, with homogeneous catalytic reactions both the reactants and catalysts are present in one phase and from an engineering viewpoint, a major disadvantage of this arises from the difficulty in separating the products from the catalyst, which increases the number of steps [6–9]. Therefore, the use of heterogeneous systems would be superior to homogeneous counterparts due to the easier separation of products and catalysts and reuse of catalysts. Metal oxides and supported metal oxides have been proposed as effective heterogeneous catalysts for the oxidation of organic compounds. In many cases, alumina- and zirconia-supported metal oxides of precious metals such as Pt and Pd have shown high activity for the oxidation of organic compounds. From the economical point of view, using oxides of non-precious transition metals like manganese (Mn), as heterogeneous catalysts for the oxidation of organic compounds, using clean oxidants such as molecular oxygen is of great importance [10–13]. Many synthetic routes can be applied for the preparation of Mn-based catalysts such as pulsed laser deposition, sol–gel route, reduction-oxidation route, gel hydrothermal oxidation, homogeneous precipitation, staged oxidation process, cobalt salt decomposition, and mechanochemical process. The later one is a novel one for large-scale synthesis, in which manganese oxide can be obtained in the solid-state displacement chemical reaction, either during milling or heat treatment. This mechanochemical process for the synthesis of manganese oxide is suitable for the large-scale synthesis due its simplicity and low cost. In this work, the synthesis of the Mn catalyst, which is much cheaper as compared to precious metal catalysts, by the mechanochemical process and its use as a catalyst for the oxidation of benzyl alcohol in the liquid phase has been investigated.

EXPERIMENTAL

Preparation of Catalyst

For the preparation of catalyst, the method of Li et al. [10] was modified [11]. Solid manganese chloride and potassium permanganate were first ground at a 2:3 mol ratio in an agitated mortar at room temperature for 30 min and then heated for several hours and ground again. After grinding, the reaction mixture was kept at 373 K for 24 h to complete the reaction. The resultant solid was washed with distilled water to remove the untreated precursor materials. After washing, it was dried at 383 K for 24 h. The resultant black powder was designated as the unreduced manganese oxide catalyst. A portion of this sample was reduced at 573 K under the flow of molecular hydrogen at a flow rate of 100 mL min^{-1}, for 2 h. The resulted powder was designated as a reduced manganese oxide catalyst.

Characterization

The prepared catalyst was characterized by the determination of oxygen content, surface area, particle size, XRD, FTIR, and SEM analyses as described earlier [11].

Oxidation Protocol

The liquid-phase oxidation of benzyl alcohol was carried out in a magnetically stirred round-bottom Pyrex glass three-necked batch reactor of 50 mL capacity, provided with a reflux condenser and mercury thermometer. Reaction temperature was maintained by using a hot plate. For a typical reaction run, the reactor was charged with 2 mmol benzyl alcohol and 1.6 mmol methyl benzoate as an internal standard, in 10 mL of *n*-octane as a solvent. After getting the required temperature (363 K), 0.1 g of catalyst was added to the reactor. The flow of oxygen was kept at a flow rate of 60 mL min^{-1}, while stirring the reaction mixture continuously at the agitation speed of 800 rpm. Moisture was removed from oxygen by passing it through a moisture adsorbent. This drying of oxygen is necessary because it affects the selectivity of the reaction products. We have noted that if molecular oxygen is not dried before entering to the reactor, formation of benzoic acid in addition to benzaldehyde can be observed even at the beginning of the reaction. In case of dry conditions only, benzaldehyde was detected as the reaction product at the start of reaction. Before entering to the reactor, molecular oxygen was saturated with a solvent by passing it through the saturator containing a solvent at condenser temperature. This saturation of oxygen with the solvent minimizes the loss of solvent with flow of oxygen from the reaction mixture. The catalyst was separated from the reaction mixture with Whatman glass microfiber filter No. 1825 055 using glass syringes. Analysis of the reaction mixture was carried out by a UV–vis spectrophotometer (Shimadzu UV-160A; Tokyo, Japan) and GC (Clarus 500; Perkin Elmer, USA) equipped with a Flame ionization detector (FID).

RESULTS AND DISCUSSION

Comparison of Reduced and Unreduced Manganese Oxide as Catalyst

For comparison of catalytic activity of reduced and unreduced manganese oxide, separate experiments were carried out at 363 K by taking 2 mmol benzyl alcohol in 10 mL *n*-octane using reduced and unreduced manganese oxides as catalysts. About 98% and 50% conversion of benzyl alcohol was achieved at a batch time of 2 h using reduced and unreduced manganese oxide as catalysts, respectively. As reduced manganese oxide was more active catalyst, therefore it was used as a catalyst in all subsequent experiments.

Manganese Oxide as a Catalyst or Oxidant

As manganese oxide can be used as stoichiometric oxidants for the oxidation of alcohols, therefore it should be confirmed that whether the manganese oxide in the present investigation acts as a stoichiometric oxidant or as a catalyst. For this purpose, separate reactions with 2 mmol benzyl alcohol were carried out under the flow of molecular nitrogen and oxygen. Traces of oxygen in nitrogen gas were removed by using specific oxygen traps (C. R. S. Inc.; 202223). The results revealed that conversion of benzyl alcohol under the flow of molecular nitrogen was less (31.5% of 2 mmol) as compared to the conversion under the flow of molecular oxygen (82.3% of 2 mmol) in 1 h at 363 K. The low conversion of benzyl alcohol in the presence of nitrogen could be due to the oxygen from the lattice taking part in the reaction; however, this reduction of manganese oxide could be limited to a few surface layers as there is no difference in the XRD pattern of the unused and used catalysts as described earlier [11].

In another experiment, the amount of benzyl alcohol was doubled, almost same conversion of benzyl alcohol was achieved under flow of oxygen in 2 h as was in 1 h. These results strongly indicated that the present manganese oxide acts as a catalyst for the oxidation reaction between benzyl alcohol and molecular oxygen. Furthermore, evidence for the catalytic role of the manganese oxide was obtained by the dependence of benzyl alcohol conversion on the partial pressure of oxygen. The conversion of benzyl alcohol was reduced from 82.3% to 53% when the partial pressure of oxygen was reduced from 101 to 34 kPa. Finally, the used catalyst was washed, dried, and reused for the oxidation of benzyl alcohol under the flow of molecular oxygen. It was observed that the used catalyst has same catalytic performance as a fresh catalyst. From these observations, it could be concluded that manganese oxide in the present case acts as a catalyst rather than a stoichiometric oxidant.

Effect of Mass Transfer

The oxidation of benzyl alcohol using manganese oxide as a catalyst in the present case is a typical slurry-phase reaction having one liquid reactant (benzyl alcohol), a gaseous reactant (oxygen), and a solid catalyst (manganese oxide). True kinetics of any multiphase reaction is likely to be masked by the effect of mass transfer. Hence, before investigating any oxidation kinetics, it is needed to eliminate any mass transfer limitation that might exist. The effect of mass transfer limitation may either be external or internal mass transfer limitation. The effect of external mass transfer on the rate of reaction can be investigated by studying the effect of speed of agitation on the rate of reaction (conversion). The dependence of the rate (conversion) of the reaction on speed of agitation shows the existence of mass transfer limitation. To investigate the effect of speed of agitation on the oxidation reaction, conversion of benzyl alcohol at various speeds of agitation in the range of 50–900 rpm at 363 K for 20 min was studied. The effect of agitation on conversion is shown in Fig. 1, which shows that initial conversion of benzyl alcohol increases with increasing agitation speed, showing a mass transfer regime from 50 to 450 rpm. The later part of the graph shows that the increase in agitation speed above 500 rpm has no effect on the conversion, indicating that the oxidation of benzyl alcohol is most

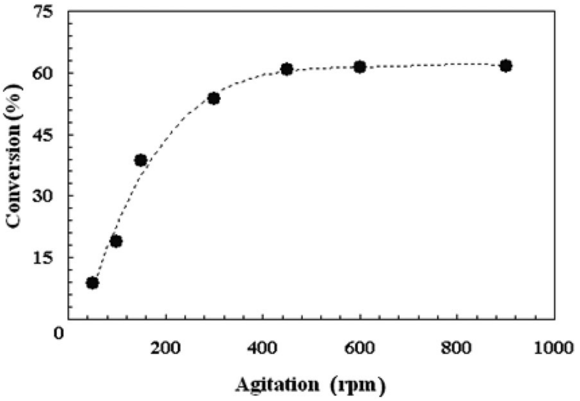

Figure 1 Effect of mass transfer on the oxidation of benzyl alcohol. Reaction conditions: BzOH 2 mmol/10 mL solvent, catalyst 100 mg, temperature 363 K, pressure of oxygen 101 kPa, time 20 min.

probably free from the external mass transfer limitations, i.e. the reaction has taken place in a kinetically controlled regime. This is the region of our interest, and all the subsequent experiments were performed at 800 rpm. A Polytetrafluoroethylene (PTFE) coated stirrer bar was used for stirring.

For the internal mass transfer limitations, the Thiele modulus (ϕ) can be used, which provides a convenient nondimensional measure of the importance of internal diffusion on the rate of reaction (conversion). If the Thiele modulus for a reaction is less than 1, it is considered that the said reaction is free from internal mass transfer limitations [4]. The Thiele modulus can be calculated by the following expression:

$$\phi = L\sqrt{\frac{k}{D}} \tag{1}$$

where L is the length of pore (in meters) of the bulk catalyst, D is the coefficient of diffusion of benzyl alcohol, and k is the initial rate for benzyl alcohol disappearance. Taking the length of the pore (L) equal to the maximum particle size (50 μm), the initial rate (k) 4.55×10^{-3} min^{-1}, and the diffusion coefficient (D) for benzyl alcohol as 2.8×10^{-9} m^2 s^{-1} [4], the Thiele modulus (ϕ) is 0.06, which is much less than 1. The small value of the Thiele modulus indicates that the rate of reaction is not limited by internal diffusion. Thus on the basis of the effect of agitation on the rate of reaction (conversion) and the Thiele modulus, we can confidently assume that in the present conditions the oxidation of benzyl alcohol catalyzed by manganese oxide is a kinetically controlled reaction.

Time Profile Investigation

The time course study of manganese oxide catalyzed oxidation of benzyl alcohol was monitored periodically. This investigation was carried out by suspending 0.1 g catalyst in 10 mL *n*-octane, 2 mmol benzyl alcohol, 1.6 mmol methyl benzoate, and passing oxygen through the reaction mixture with a flow rate of 60 mL min^{-1} at 1 atm pressure. It was observed that only benzaldehyde was detected as the reaction product in beginning of the reaction. Once the benzyl alcohol was almost completely converted (~98%) to benzaldehyde, then formation of benzoic acid started (Fig. 2a). The effect of reaction temperature on the progress of the oxidation of benzyl alcohol was studied in the temperature range of 323–363 K. Conversion of benzyl alcohol increased from 39.4% to 95.6% in 120 min with an increase in temperature from 323 to 363 K for 0.1 g of manganese oxide and 2 mmol benzyl alcohol in 10 mL solvent. Time profile investigation at various temperatures is shown in Fig. 2. In all experiments, reaction conditions were kept the same except temperature.

Kinetics Analysis

The rates of heterogeneous catalytic reactions are complex, because adsorption of the reacting species on the surface of the catalyst, reactions between the adsorbed species and desorption of the products take place simultaneously. Basically, the catalytic reactions are described with surface concentrations; however, the effect of surface concentrations on rates of reactions can be eliminated by using simplifying assumptions, such as quasi-equilibrium and quasi–steady-state hypotheses [14]. The kinetics of the oxidation of benzyl alcohol in the present case can be expressed as the power rate law,

$$\text{Rate} = k'[\text{BzOH}]^m[\text{O}_2]^n \tag{2}$$

where k is the rate constant and m and n are the reaction orders with respect to benzyl alcohol and oxygen, respectively. This representation has limited utility for mechanistic elucidation; however, it can be used to obtain a preliminary dependency of the rate of the reaction on the concentration of benzyl alcohol and oxygen. At constant partial pressure of oxygen, the rate expression becomes as

$$\text{Rate} = k'[\text{BzOH}]^m \tag{3}$$

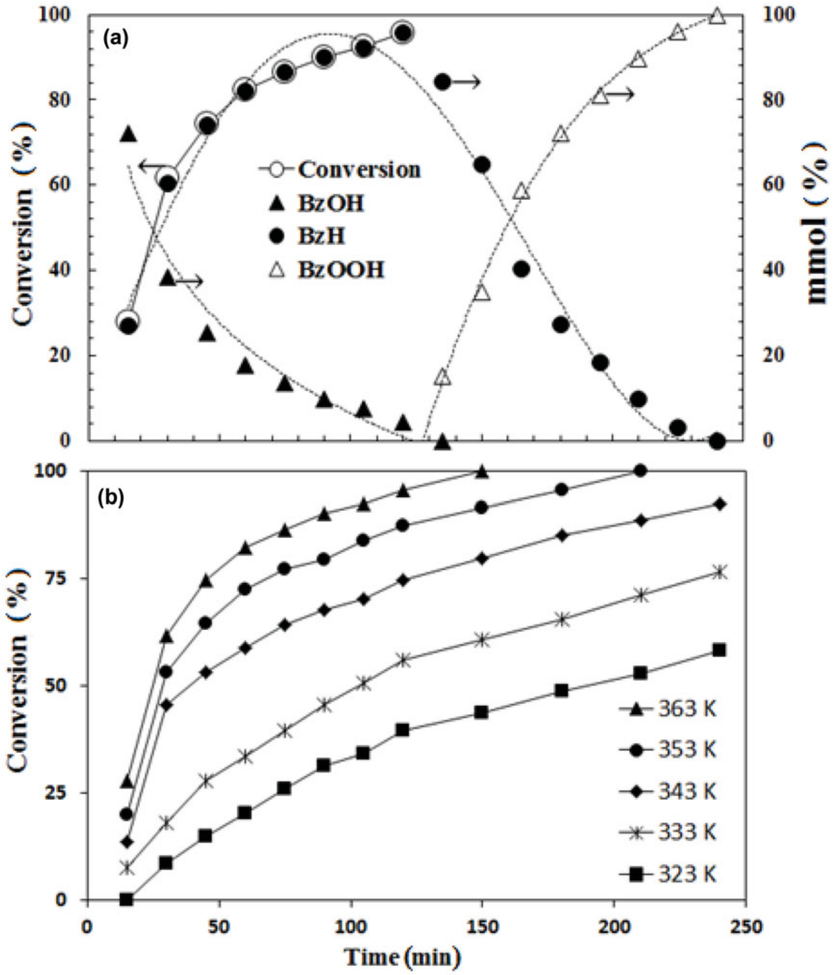

Figure 2 Time profile for the oxidation of benzyl alcohol (a) at 363 K, (b) at different temperatures. Reaction conditions: BzOH 2 mmol/10 mL *n*-octane, catalyst 100 mg, agitation 800 rpm, pressure of oxygen 101 kPa.

where

$$k' = k[O_2]^n \tag{4}$$

Equation (3) can be integrated to the following equation:

$$-\ln(1 - X) = k't \tag{5}$$

where X is conversion of benzyl alcohol at batch time t. Equation (5) was applied to time profile data for the oxidation of benzyl alcohol at various temperatures as given in Fig. 3. The linearity of plots indicates the first-order dependence of the oxidation rate on the concentration of benzyl alcohol. The values of the rate constants (k') were calculated from the slopes of the graphs and are listed in Table I. However, such representation has limited utility. Hence, we have followed the approach of fitting experimental data to one of the three possible mechanisms of heterogeneous catalysis [2,15–18]:

i. The Langmuir–Hinshelwood mechanism,
ii. The Mars–van Krevelen mechanism,
iii. The Eley–Rideal mechanism.

According to Langmuir–Hinshelwood mechanism, the reaction proceeds in two steps. In the first step, the reactants adsorb on the surface of the catalyst followed by a reaction between adsorbed reactants to form products in the second step. For manganese oxide catalyzed oxidation of benzyl alcohol with molecular oxygen, the rate expression can be written as

$$\text{Rate} = k_r \theta_{\text{BzOH}} \theta_{O_2} \tag{6}$$

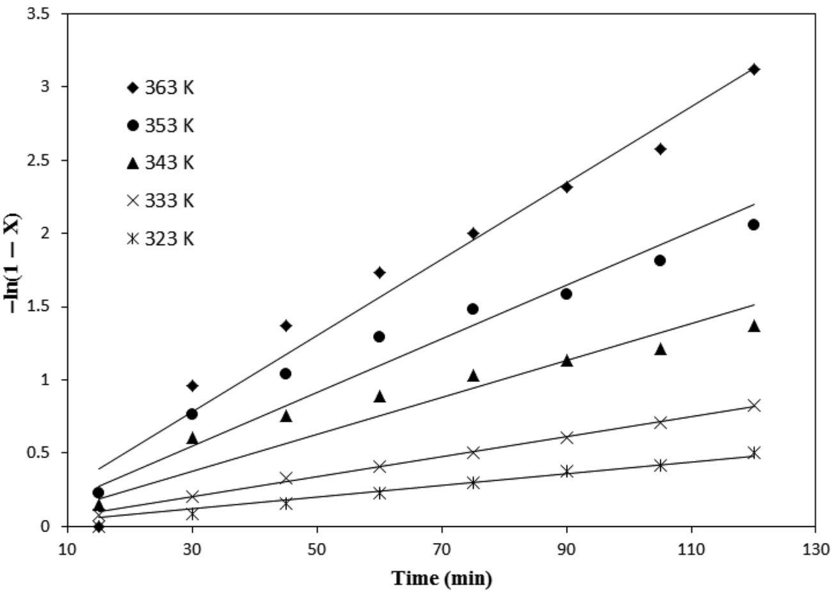

Figure 3 Application of the first-order kinetic expression to time profile data at different temperatures from Fig 2.

Table I First-Order Rate Constants Determined from Fig. 3

T (K)	k' (min^{-1})	R^2
323	0.0102	0.9709
333	0.0191	0.9974
343	0.0385	0.8269
353	0.0760	0.9288
363	0.1483	0.9580

where θ_{BzOH} and $\theta_{\mathrm{O_2}}$ represents surface covered by benzyl alcohol and molecular oxygen, respectively.

Adsorption of benzyl alcohol and oxygen on the surface of catalyst may take place either according to Langmuir, Temkin, or Freundlich adsorption isotherm. The Langmuir adsorption isotherm may be either competitive or noncompetitive. For competitive adsorption, the rate expression can be written as

$$\mathrm{Rate} = k_r \frac{K_{\mathrm{BzOH}}[\mathrm{BzOH}]K_{\mathrm{O_2}}[\mathrm{O_2}]_g^n}{(1 + K_{\mathrm{BzOH}}[\mathrm{BzOH}] + K_{\mathrm{O_2}}[\mathrm{O_2}]_g^n + K_{\mathrm{P}}[\mathrm{P}])^2} \tag{7}$$

where K_{BzOH}, $K_{\mathrm{O_2}}$, and K_{P} represent adsorption coefficient for benzyl alcohol, oxygen, and products, respectively. The value of n can be 1 or 0.5 for molecular or dissociative adsorption of oxygen, respectively.

Adsorption/desorption processes in the above steps are fast enough to be assumed at equilibrium. This assumption helps to simplify the above expression as

$$\mathrm{Rate} = k_r \frac{K_{\mathrm{BzOH}}[\mathrm{BzOH}]K_{\mathrm{O_2}}[\mathrm{O_2}]_g^n}{(1 + K_{\mathrm{BzOH}}[\mathrm{BzOH}] + K_{\mathrm{O_2}}[\mathrm{O_2}]_g^n)^2} \tag{8}$$

At constant partial pressure of oxygen, the rate expression can be written as

$$\mathrm{Rate} = \frac{ab[\mathrm{BzOH}]}{(c + b[\mathrm{BzOH}])^2} \tag{9}$$

where a, b, and c are k_r $K_{\mathrm{O2}}[\mathrm{O_2}]$, K_{BzOH}, and $1 + K_{\mathrm{O2}}[\mathrm{O_2}]$, respectively.

Similarly, at the constant concentration of benzyl alcohol, the rate expression is

$$\mathrm{Rate} = \frac{ab[\mathrm{O_2}]}{(c + b[\mathrm{O_2}])^2} \tag{10}$$

In case of noncompetitive adsorption of benzyl alcohol and oxygen, the rate expression can be written as

$$\mathrm{Rate} = k_r \frac{K_{\mathrm{BzOH}}[\mathrm{BzOH}]K_{\mathrm{O_2}}[\mathrm{O_2}]_g^n}{(1 + K_{\mathrm{BzOH}}[\mathrm{BzOH}])(1 + K_{\mathrm{O_2}}[\mathrm{O_2}])} \tag{11}$$

Equation (11) can be simplified by keeping the concentration of benzyl alcohol or oxygen constant. At constant partial pressure of oxygen, Eq. (11) can be transformed to Eq. (12)

$$\text{Rate} = \frac{ab[\text{BzOH}]}{1 + b[\text{BzOH}]} \quad (12)$$

Similarly at the constant concentration of benzyl alcohol, Eq. (11) can be transformed to Eq. (13):

$$\text{Rate} = \frac{ab[\text{O}_2]}{1 + b[\text{O}_2]} \quad (13)$$

Considering the Temkin adsorption isotherm, the rate expression becomes

$$\text{Rate} = k_r(K_1 \ln K_2[\text{BzOH}])(\bar{K}_1 \ln \bar{K}_2[\text{O}_2]) \quad (14)$$

where K_1 and K_2 are constants related to heat of adsorption, which decreases linearly with surface coverage in this case.

For the constant concentration of oxygen and benzyl alcohol, Eq. (14) can be simplified to Eqs. (15) and (16), respectively:

$$\text{Rate} = \bar{k}_r(K_1 \ln K_2[\text{BzOH}]) \quad (15)$$

$$\text{Rate} = \bar{k}_r(\bar{K}_1 \ln \bar{K}_2[\text{O}_2]) \quad (16)$$

A plot of ln[BzOH] or ln[O_2] against the rate gives a straight line.

Similarly, considering the Freundlich adsorption isotherm, the rate expression becomes

$$\text{Rate} = k_r K_{\text{BzOH}}[\text{BzOH}]^{1/n} K_{\text{O}_2}[\text{O}_2]^{1/n} \quad (17)$$

where K_{BzOH} and K_{O2} are the adsorption coefficient for benzyl alcohol and oxygen, respectively, and n (>1) is a constant.

This equation can be simplified by keeping oxygen/benzyl alcohol constant and lumping together all the constants as below.

$$\text{Rate} = \bar{k}_r\ K_{\text{BzOH}}[\text{BzOH}]^{1/n} \quad (18)$$

$$\text{Rate} = \bar{k}_r\ K_{\text{O}_2}[\text{O}_2]^{1/n} \quad (19)$$

A plot of ln[BzOH] or ln[O_2] against ln rate gives a straight line.

Like the Langmuir-Hinshelwood mechanism, the Mars–van Krevelen mechanism also comprises two steps. In the first step, the lattice oxygen of the catalyst oxidizes the substrate molecule and hence produces a partially reduced catalyst. In the second step, the reduced catalyst is reoxidized by molecular oxygen. The rate equation for the Mars–van Krevelen mechanism can be given by the following expression:

$$\text{Rate} = \frac{k_1[\text{BzOH}]k_2[\text{O}_2]_g^n}{\beta k_1[\text{BzOH}] + k_2[\text{O}_2]_g^n} \quad (20)$$

In this equation, k_1 and k_2 represent the rate constant for the oxidation of benzyl alcohol and reoxidation of the partially reduced catalyst, respectively. β is the stoichiometric coefficient for oxygen, which is considered as 0.5. The above expression can be simplified by considering oxygen or benzyl alcohol constant as discussed in the Langmuir–Hinshelwood mechanism. For the constant oxygen and benzyl alcohol rate can be expressed by expressions (21) and (22), respectively:

$$\text{Rate} = \frac{a[\text{BzOH}]}{b + c[\text{BzOH}]} \quad (21)$$

$$\text{Rate} = \frac{a[\text{O}_2]}{b + c[\text{O}_2]} \quad (22)$$

According to the Eley–Rideal mechanism, the gaseous reactant get adsorbed on the surface of the catalyst while the second reacts with the adsorbed reactant from the fluid phase. In the present case, oxygen is adsorbed at the surface while benzyl alcohol remains in the fluid phase.

The rate expression for the Eley–Rideal mechanism can be given by Eq. (23)

$$\text{Rate} = k_r\theta_{\text{O}_2}[\text{BzOH}] \quad (23)$$

Considering the Langmuir adsorption isotherm, we get

$$\text{Rate} = k_r \frac{K_{\text{O}_2}[\text{O}_2]_g^n}{1 + K_{\text{O}_2}[\text{O}_2]_g^n}[\text{BzOH}] \quad (24)$$

At the constant partial pressure of oxygen, the above equation can be transformed as

$$\text{Rate} = a[\text{BzOH}] \quad (25)$$

Similarly in case of the constant concentration of benzyl alcohol, Eq. (25) can be transformed to Eq. (26):

$$\text{Rate} = \frac{a[\text{O}_2]}{1 + b[\text{O}_2]} \quad (26)$$

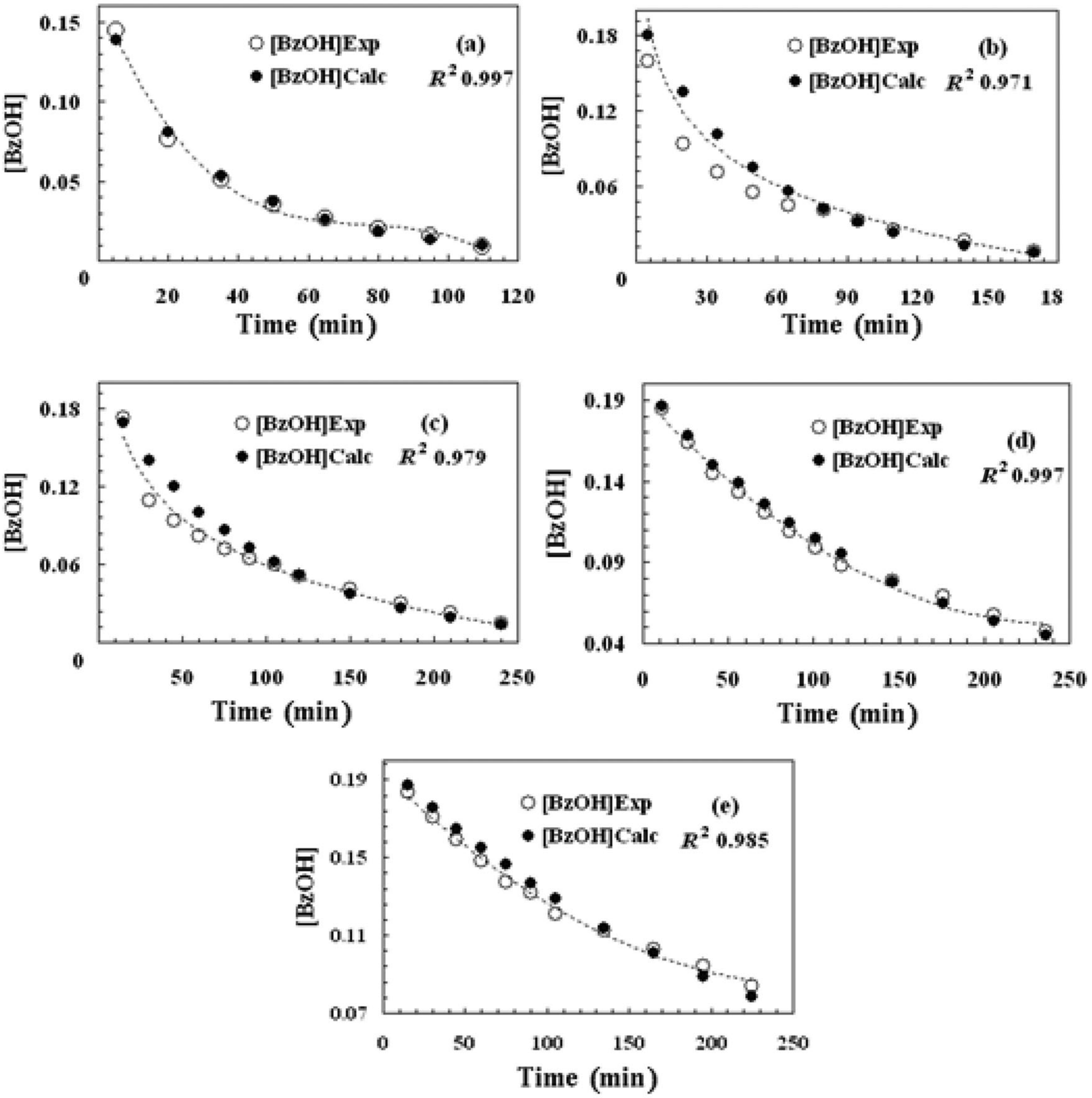

Figure 4 Applicability of noncompetitive Langmuir–Hinshelwood model (Eq. (12)) to time profile data by nonlinear least-square analysis at 101 kPa pressure of oxygen and various temperatures: (a) 363 K, (b) 353 K, (c) 343 K, (d) 333 K, and (e) 323 K.

The time profile data at various temperatures in the range of 323–263 K at 101 kPa partial pressure of oxygen from Fig. 2 was subjected to kinetic analysis using a nonlinear regression analysis according to the above models, using Curve Expert 1.3 software.

Equation (12) fitted best to the data at constant partial pressure of oxygen (101 kPa) and different temperatures. This equation was applied to time profile data in an integral form (Eq. (27)) as given in Fig. 4.

$$t = (b * (0.2 - x) * (4 + b * (0.2 - x)) + 2 * \ln(0.2/x))/(2 * a * b) \qquad (27)$$

The values of noncompetitive Langmuir–Hinshelwood constants were determined using Curve Expert 1.3 software and are listed in Table II.

Effect of Partial Pressure of Oxygen

The effect of the partial pressure of oxygen on the oxidation of benzyl alcohol was investigated in the range of 34–101 kPa with a constant initial 0.2 M benzyl alcohol concentration at various temperatures in the range of 323–363 K. For the determination of various partial pressure of oxygen, nitrogen was admixed with oxygen having the total flow rate of

Table II Kinetic Constants Determined by Nonlinear Least-Square Analysis According to Langmuir–Hinshelwood, Noncompetitive Model (Eq. (12)) at the Constant Oxygen Partial Pressure of 101 kPa

T (K)	$a = \frac{k_r K_{O_2} p_{O_2}}{1+K_{O_2} p_{O_2}} = k_r'$ (mol L^{-1} min^{-1})	$b = K_{BzOH}$, (L mol^{-1})	R^2
323	0.0102	0.4271	0.998
333	0.0191	0.3529	0.997
343	0.0385	0.2979	0.999
353	0.0760	0.2615	0.999
363	0.1483	0.2237	0.997

60 mL min^{-1} as described earlier [4,11,16,17]. It was found that with the increase in partial pressure of oxygen conversion of benzyl alcohol increases as shown in Fig. 5. The time profile data at various partial pressures of oxygen from Fig. 5 was subjected to kinetic analysis according to Langmuir–Hinshelwood, Mars–van Krevelen, and Eley–Rideal mechanism as discussed earlier. The Langmuir–Hinshelwood mechanism was applicable where adsorption of benzyl alcohol at the surface of catalyst takes place according to the noncompetitive Langmuir adsorption isotherm, from which rate coefficients and adsorption coefficient of benzyl alcohol were determined (Table III). It is evident from Table III that the values of k_r' depends upon the oxygen partial pressure and temperature as well. Using the Arrhenius equation by plotting ln (k_r') versus 1/T at various oxygen partial pressures (Fig. 6) gives the apparent activation energies (Table IV), which are free from the effect of the heat of adsorption of benzyl alcohol (ΔH_{BzOH}). The apparent activation energies depend on the partial pressure of oxygen.

At constant partial pressure of oxygen, Eq. (6) can also be written as

$$\text{Rate} = k_r'\theta_{BzOH} \tag{28}$$

From the comparison of Eqs. (6) and (28), it is obvious that

$$k_r' = k_r\theta_{O_2} \tag{29}$$

This is the reason that the apparent activation energies (E_{ap}) increase with the increase in the oxygen partial pressure (Table IV). Considering that the apparent activation energy is

$$E_{ap} = E_t + \Delta H_{ad} \tag{30}$$

where E_t and ΔH_{ad} represents the true activation energy and heat of adsorption, respectively. Since the adsorption is exothermic in nature in this case, therefore the apparent activation energy is less than the true activation energy by the amount of the heat of adsorption. Obviously, it can be concluded that the heat of adsorption of oxygen decreases with an increase in the partial pressure of oxygen, a situation that arises due to the nonhomogeneous nature of the oxygen adsorption sites. It was proved that the Langmuir adsorption isotherm for oxygen adsorption was not successful. Similarly, the Freundlich isotherm was also not applicable to the data. The Temkin adsorption isotherm was applicable to the data. Insertion of the Temkin adsorption isotherm in Eq. (29) for θ_{O_2}, gives

$$k_r' = k_r K_1 \ln(K_2 p_{O_2}) \tag{31}$$

which could be changed to

$$k_r' = a \ln(b p_{O_2}) \tag{32}$$

Values of a and b were determined by applying Eq. (32) to the data by nonlinear least-square fit analysis using Curve Expert 1.3. Values of a, b, and regression coefficient are listed in Table V. It shows that the Temkin Isotherm is the best fit for oxygen adsorption in this case. Furthermore, recalculation of the k_r' values using the constants a and b from Table V shows excellent agreement with the k_r' values in Table V, as given in Fig. 7. By using the values obtained from the Temkin isotherm the apparently true activation energy (free from the heat of adsorption of both benzyl alcohol as well as the heat of adsorption of oxygen) can be calculated. It can be seen that the constant a in Eq. (32) is

$$a = k_r K_1 \tag{33}$$

Considering that $K_1 = \frac{RT}{\alpha\Delta H_0}$, where as ΔH_0 is the maximum value of the heat of adsorption obtained at the lowest surface coverage, i.e. as $\theta \to 0$ and α is the proportionality constant used for estimating the decrease in the heat of adsorption with surface coverage. Therefore, dividing the value of a by the temperature T will give

$$\frac{a}{T} = k_r \frac{R}{\alpha\Delta H_0} \tag{34}$$

A plot of ln($\frac{a}{T}$) versus 1/T will give the apparently true activation energy, free from the heat of adsorption of both oxygen and benzyl alcohol as given in Fig. 8, giving the $E_t = 71.8$ kJ mol^{-1}, which is almost equal to

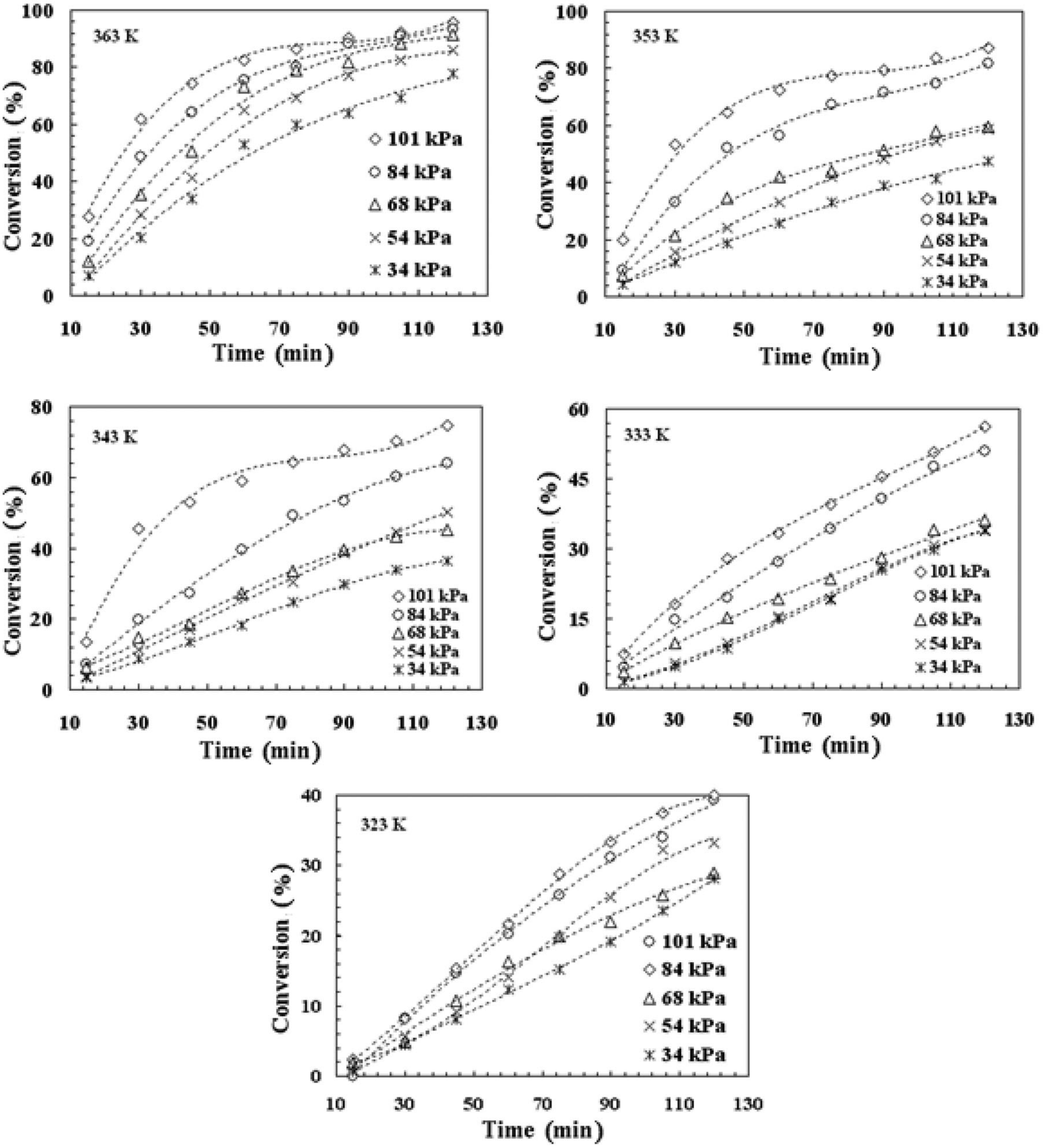

Figure 5 Time profile data for oxidation of benzyl alcohol at various temperatures and partial pressure of oxygen. Reaction conditions: BzOH 2 mmol/10 mL *n*-octane, catalyst 100 mg, agitation 800 rpm.

the value obtained previously for the vapor-phase dehydrogenation of cyclohexanol to cyclohexanone catalyzed by Y_2O_3/ZrO_2, using the Temkin isotherm [19].

On the other hand, the constant b in Eq. (32) is $b = b'e^{\frac{\Delta H_0}{RT}}$, where b' is a constant. If b' is independent of temperature then a plot of ln(b) versus I/T would give the value of ΔH_0. However, a plot of ln(b) versus 1/T (Van't Hoff equation) shows that the value at 363 K has a large deviation as given in Fig. 9a. It is probably due to the fact that b' has some contribution from the entropy of adsorption, which has more pronounced effect at the highest temperature.

A reasonably good straight line ($R^2 = 0.923$) is obtained for the other four temperatures (323, 333, 343, and 353 K) giving a value of –31.12 kJ mol^{-1} for the heat of adsorption (ΔH_0) of oxygen (Fig. 9a). Similarly for the determination of heat of adsorption of benzyl alcohol, Van't Hoff equation was applied to

Table III Kinetic Parameter for Oxidation of Benzyl Alcohol at Various Temperatures and Partial Pressure of Oxygen Calculated According to the Langmuir–Hinshelwood Noncompetitive Kinetic Model

	323 K		333 K		343 K		353 K		363 K	
pO_2 (kPa)	k_r (mol L^{-1} min^{-1})	K_{BzOH} (L mol^{-1})	k_r (mol L^{-1} min^{-1})	K_{BzOH} (L mol^{-1})	k_r (mol L^{-1} min^{-1})	K_{BzOH} (L mol^{-1})	k_r (mol L^{-1} min^{-1})	K_{BzOH} (L mol^{-1})	k_r (mol L^{-1} min^{-1})	K_{BzOH} (L mol^{-1})
34	0.00591	0.453	0.00890	0.390	0.0142	0.279	0.0205	0.268	0.0611	0.224
51	0.00742	0.480	0.0101	0.345	0.0197	0.291	0.0340	0.245	0.0882	0.212
68	0.00810	0.398	0.0128	0.308	0.0245	0.224	0.0443	0.187	0.108	0.223
84	0.00940	0.500	0.0182	0.335	0.0311	0.284	0.0605	0.240	0.136	0.192
101	0.01030	0.427	0.0192	0.353	0.0385	0.298	0.0766	0.261	0.148	0.224

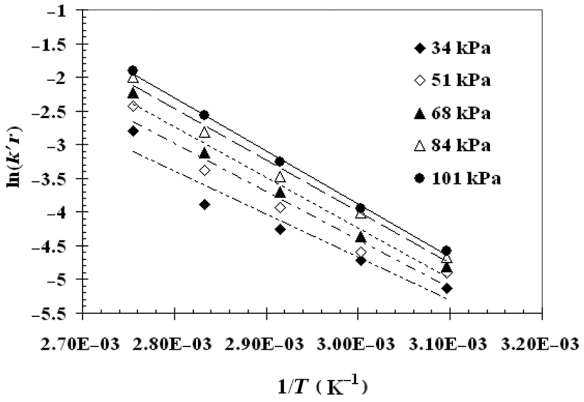

Figure 6 Application of Arrhenius equation to the data from Table III.

Table IV Apparent Activation Energies Calculated from Fig. 6

pO_2 (kPa)	Ea_{ap} (kJ mol^{-1})
34	52.51
51	60.30
68	63.07
84	64.50
101	65.41

Table V Constants Determined by Applying the Temkin Isotherm by Nonlinear Least-Square Method of Analysis

T (K)	$a = k_r K_1$ (mol L^{-1} min^{-1})	$b = K_2$	R^2
323	0.004	0.115	0.951
333	0.010	0.061	0.941
343	0.022	0.052	0.971
353	0.050	0.041	0.973
363	*0.082*	*0.060*	*0.992*

Note that bothK_1 and K_2 are unitless quantities.

the adsorption constant of benzyl alcohol at various temperatures as in Table III as given in Fig. 9b (in this figure average values of K_{BzOH} at various partial pressures of oxygen were used). Heat of adsorption of benzyl alcohol (ΔH_0) was –18.14 kJ mol^{-1}. Gibbs free energy (ΔG) and entropy (ΔS) of adsorption for benzyl alcohol were –35.36 kJ mol^{-1} and 58.45 J mol^{-1}, respectively. Now considering that $E_t = E_{ap} - \Delta H_{ad}$, where ΔH_{ad} is the heat of adsorption. Using the values of apparent true activation energy ($E_t = 71.81$ kJ mol^{-1}) and apparent activation energies (E_{ap}) from Table IV, the heat of adsorption at various oxygen partial pressures was calculated as given in Table VI. According to the Temkin isotherm, heat of adsorption

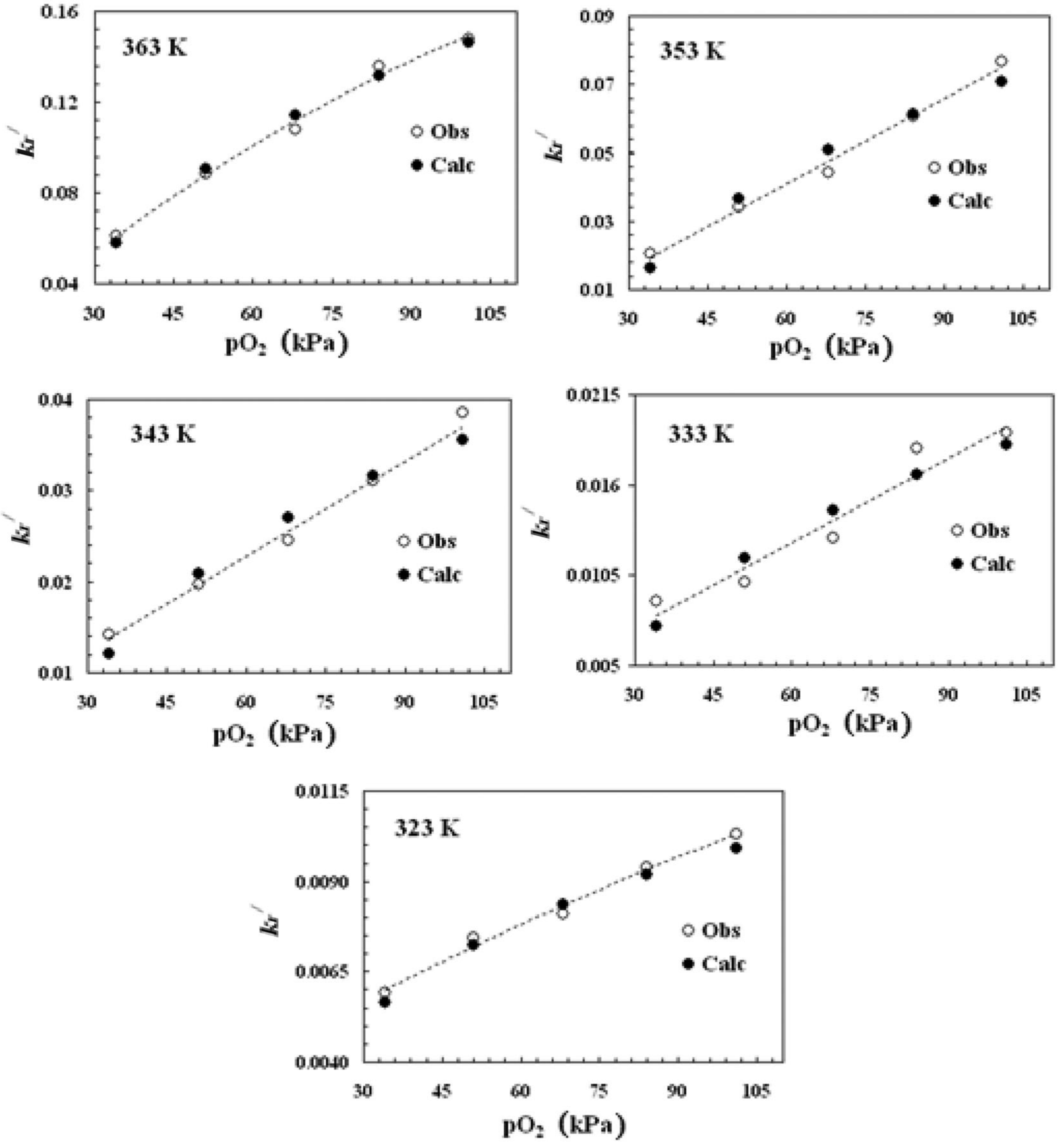

Figure 7 Comparison of the apparent rate constant $k_r{}'$ from Table V (observed) with those calculated by using the Temkin isotherm (the constant was obtained by nonlinear least-square fitting).

(ΔH_{ad}) is decreased linearly with surface coverage (θ) according to

$$\Delta H_{ad} = \Delta H_{\circ}\,(1 - \alpha\theta) \tag{35}$$

However, considering that according to the Temkin isotherm

$$\theta = A + B\ln(p) \tag{36}$$

Therefore, a plot of ΔH_{ad} versus ln(p) must be linear with a negative slope. Figure 10 shows that the plot of ΔH_{ad} versus ln(p) is linear with a negative slope. It shows that the Temkin isotherm in this case is applicable. However, in this case we are unable to calculate the value of ΔH_0 and/or α from the intercept and slope as the constants A and B in Eq. (36) becomes more complicated when these are inserted in Eq. (35). It is also important to remember that the Temkin isotherm is applicable only in the middle range of surface coverage ($\theta \sim 0.3$–0.6); therefore, deviation in the lower and upper regions of surface coverage is expected. Furthermore, the apparently true activation energy ($E_t = 71.81$ kJ mol^{-1}) is free from the effect of heat of

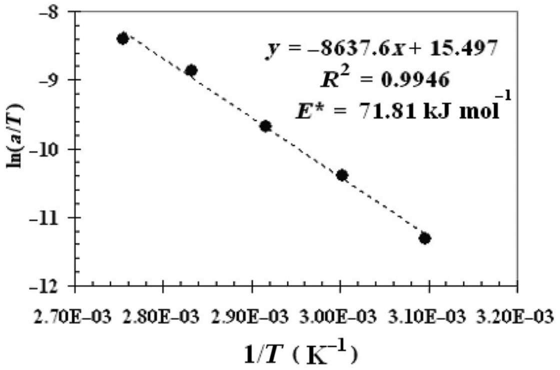

Figure 8 Determination of apparently true activation energy, free from the heat of adsorption of both oxygen and benzyl alcohol.

adsorption of benzyl alcohol and oxygen only. The effect from the heat of adsorption of the solvent and other products (i.e., benzaldehyde, benzoic acid, and water) could not be ignored.

The Final Kinetic Equation

From these analyses, it is evident that the following kinetic equation (Eq. (37)) is the best fit as evident from Tables II and V:

$$\text{Rate} = k_r \left(\frac{K_{\text{BzOH}}[\text{BzOH}]}{1 + K_{\text{BzOH}}[\text{BzOH}]} \right) (K_1 \ln(K_2 p_{\text{O}_2})) \tag{37}$$

This is based upon the Langmuir–Hinshelwood mechanism, where the adsorption of benzyl alcohol takes place according to the Langmuir adsorption isotherm whereas adsorption of oxygen follows the Temkin adsorption isotherm.

Considering that the heat of adsorption of benzyl alcohol (ΔH_0 ~ –18 kJ.mol^{-1}) is low; therefore, the adsorption is relatively weak. In this case, Eq. (37) can

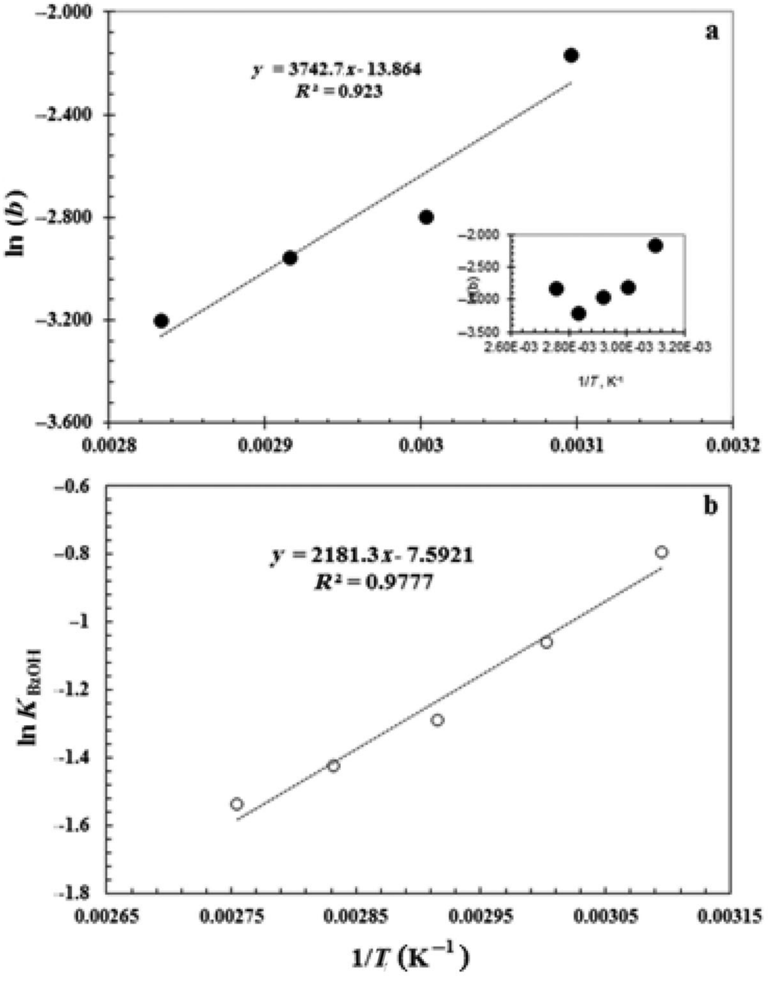

Figure 9 Van't Hoff plot for the determination of heat of adsorption of (a) oxygen and (b) benzyl alcohol.

Table VI Activation Energies and Heat of Adsorption of Oxygen at Various Partial Pressure of Oxygen

pO_2 (kPa)	E_a, (kJ mol^{-1})	ΔH_{ad} (kJ mol^{-1})
34	53.28	18.53
51	59.72	12.09
68	62.33	9.48
84	63.64	8.17
101	65.38	6.43

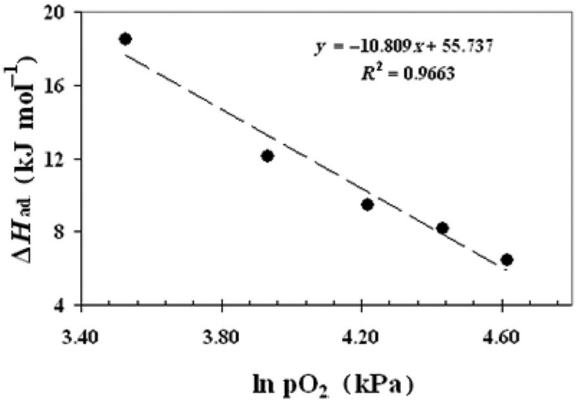

Figure 10 Heat of adsorption ΔH_{adb} versus ln(pO_2).

be modified to Eq. (38):

$$\text{Rate} = k_r(K_{\mathrm{BzOH}}[\mathrm{BzOH}])(K_1 \ln(K_2 p_{\mathrm{O_2}})) \quad (38)$$

as the K_{BzOH}[BzOH] term in the denominator could be ignored in comparison to 1.

CONCLUSIONS

The oxidation of benzyl alcohol catalyzed by manganese oxide in the present case is purely taken place in a kinetically controlled region, where Langmuir–Hinshelwood type of mechanism is operative. According to this mechanism, the reaction proceed in two steps. In first step, both the reactants, i.e. benzyl alcohol and oxygen, are adsorbed at the surface of catalyst, whereas in second step the adsorbed reactants react and give the final products. Adsorption of benzyl alcohol and oxygen has taken place according to the noncompetitive Langmuir adsorption isotherm and Temkin adsorption isotherm, respectively. It shows that the adsorption sites for benzyl alcohol are homogeneous in nature ($\Delta H_{\mathrm{BzOH}}{}^{`} = -18.14$ kJ mol^{-1}). The adsorption sites for oxygen are heterogeneous in nature, whereas the heat of adsorption varies with surface coverage by oxygen. The maximum value for ΔH_{O2} is –31.12 kJ mol^{-1} at $\theta \to 0$.

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