Catalytic Oxidation Kinetics of Vapor Phase BTX over Pt/γ-Al₂O₃

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(Received January 12, 1999; Accepted June 29, 1999)

Abstract: The objective of this study was to depict the kinetic behavior of the platinum catalyst for the deep oxidation of BTX. The oxidation kinetics of BTX were studied on a 0.5% Pt/γ-Al₂O₃ catalyst at temperature ranging from 200 to 350 °C and the inlet concentration ranging from 133 to 333 ppmv. An approach based on the two-stage redox model was used to analysis the results. The conversions of BTX were increased as the inlet concentration was decreased and the reaction temperature was increased. The maximum deep conversion of benzene, toluene and m-xylene were 95.81%, 72.20% and 65.70% at 350 °C, respectively. A simple multicomponent model based on two-stage redox rate model made reasonably good predictions of conversion over the range of parameters studied. The kinetic parameters of multicomponent model were independently evaluated from the single compound oxidation experiments. Toluene and m-xylene conversion was inhibited by benzene. The reaction model reveals that there is a competition between the two reactants for the oxidized catalyst. Benzene competes more effectively for the oxidized site and is thus oxidized more rapidly.

Keywords: catalytic oxidation kinetics, BTX, 0.5% Pt/γ-Al₂O₃ catalyst, two-stage redox rate model

1. Introduction

Recently catalytic oxidation of volatile organic compounds (VOCs) has been widely used to control gas emissions [1-2]. Catalytic oxidations operate at a lower temperature as compared to the thermal oxidations - typically about 300–500 °C. From an industrial perspective, two different types of heterogeneous catalytic oxidation processes may be recognized; (i) partial oxidation for manufacturing of commercially significant products (e.g. benzene to maleic anhydride, and toluene to benzoic acid, benzaldehyde and phenol) [3-4] and (ii) deep (or complete) oxidation of low concentration organic contaminants (VOCs) in air (e.g. air purification, industrial emission control, and automotive exhaust catalysis).

In spite of its widespread applications, the kinetics of deep oxidation of mixtures of VOCs is still not fully understood, mainly because the rate depends on catalyst composition and preparation, which changes from user to user. Pyatnitskii and Skorbilina [5] utilized the Mars-van Krevelen redox mechanism for oxidation of aromatics over a V₂O₅ catalyst, and competition for adsorbed oxygen to be responsible for the mutual reduction in the reaction rate. Recently, the same model was adopted by Ganwal and coworkers [6] for a n-hexane-benzene mixture over platinum.

This study describes experiments and analysis aimed at elucidating the mixture effect in the deep catalytic oxidation of two selected BTX. Pure component experiments were performed to obtain kinetic rate parameter, which were then used in a rate expression for the mixture kinetics. The oxidation of BTX was studied on a 0.5% Pt/γ-Al₂O₃ catalyst at
temperature ranging from 200 to 350 °C. An approach based on the two-stage redox model was used to analyse the results.

2. Catalytic Oxidation Kinetics

A general theory on the mechanism of the heterogeneous catalytic oxidation of low molecular weight vapors at trace concentrations in air was not developed. But many researchers proposed that the mechanism of complete catalytic oxidation depends on the type of catalyst used. The oxygen concentration in the gas phase is essentially constant, and overall rate will usually be a function of the benzene, toluene and xylenes (BTX) concentration only. The oxidation of hydrocarbon was generally assumed to occur via a surface redox cycle known as the two-stage redox rate model (Mars-Van Krevelen). A schematic expression of the two-stage redox rate model for BTX oxidation may be described by the following stepwise scheme [6-8].

\[ \text{BTX} + \text{oxidized catalyst} \xrightarrow{k_1} \text{reduced catalyst} + \text{products} \]

\[ \text{O}_2 + \text{reduced catalyst} \xrightarrow{k_a} \text{oxidized catalyst} \]

In this mechanism, the above steps are assumed to be first-order in the respective gaseous species. Thus, if \( \theta \) is the fraction of oxidized catalyst at any time, then,

\[ r_1 = k_1 C_{\text{BTX}} \theta \]

\[ r_{O_2} = k_a C_{O_2} (1 - \theta) \]

from Equation (3)–(4), eliminating \( \theta \),

\[ r_{O_2} = k_a C_{O_2} \left(1 - \frac{r_1}{k_1 C_{\text{BTX}}} \right) \]

\[ k_1 C_{\text{BTX}}(\nu_1 r_1) = k_{0_2} k_1 C_{O_2} C_{\text{BTX}} - k_{0_2} C_{O_2} r_1 \]

\[ r = \frac{k_a k_1 C_{O_2} C_{\text{BTX}}}{k_a C_{O_2} + \nu_1 k_1 C_{\text{BTX}}} \]

where \( \nu_1 \) is the stoichiometric coefficient of oxygen in the overall reaction (\( \nu_1 = 15/2 \), 9, and 21/2 for complete oxidation of BTX, respectively). \( C_{O_2} \) is oxygen concentration [mol %], and \( C_{\text{BTX}} \) is BTX concentration.

3. Experimental

3.1. Chemicals and Catalyst

Benzene, toluene and m-xyylene (special grade) were obtained from Duksan Pure Chemical Co. The 0.5% Pt/\( \gamma \)-Al\(_2\)O\(_3\) catalyst used in this study was obtained from Engelhard Corporation. The catalyst had a nominal BET surface area of 86.4 m\(^2\)/g. The spherical catalyst particles were crushed and particles with diameters in the range of 100 to 200 \( \mu \)m were used in the reaction. Before the catalyst was placed into the reactor, it was preheated by calcining in air. In the precalcining procedure, the oven temperature was increased from ambient to 450 °C at a rate of 2 °C per minute and held at 450 °C for 16 h.

3.2. Catalytic Oxidation and Apparatus

The schematic representation of the experimental assembly is presented in Figure 1. BTX gas-phase oxidation was carried out in a fixed bed tubular reactor consisting of 10 cm long stainless steel tube (0.6 cm I.D.) packed with 1 g of 0.5% Pt/\( \gamma \)-Al\(_2\)O\(_3\) catalyst, which diluted by 7 g of 60/80 mesh glass bead. The catalyst was positioned at the center of the reactor using an inert support. The preheater (L: 5 cm, I.D.: 0.6 cm) and the fixed-bed reactor were placed in the same convection oven that temperature can be controlled. Operating temperature was in the range of 200 to 350 °C. The feed stream was composed of the contaminated air containing 133–333 ppmv BTX. Benzene-toluene and benzene-xyylene binary mixture concentration was varied in the range of 133–333 ppmv. The flow rate of the streams of air was controlled by mass flowmeter (Sierra 902C-PS). It was observed that the external mass-transfer effect was absent when the gas-phase velocity was over 0.118 cm/sec. Thus, the BTX oxidation experiments were carried out at a superficial feed gas velocity of 0.147 m/sec to avoid mass transfer effect. The average space velocity was 5300 hr\(^{-1}\), giving an average

Figure 1. Catalytic oxidation apparatus of gaseous VOCs.
residence time of about 0.68 sec. The outlet product compositions of the tubular reactor were analyzed by GC/MSD (HP 5890/HP 5972, HP). The column temperature was increased from 70 to 200 °C at rate of 5 °C/min and detector temperature was maintained 250 °C. Analysis was performed under the following conditions; column, a HP-5MS (30 m length×0.25 mm I.D., Hewlett-Packard Co.); split ratio, 1:100; a carrier gas, helium.

4. Results and Discussion

4.1. Catalytic Activity and Deactivation

In our preliminary studies, we observed that although there was significant catalytic activity at temperatures as low as 127 °C, the catalyst was deactivated rapidly at reaction temperature of 150⁻200 °C. The platinum on the catalyst surface formed a yellow-colored compound. We considered that the deactivation was due to product inhibitions (water reacting with Pt). Catalyst deactivation was measured at the lowest operating temperature for each oxidation reaction before running the experiments for kinetic studies. Figure 2 shows a time on stream analysis for benzene oxidation at 200 °C, and toluene and m-xylene oxidation at 250 °C with an inlet concentration of 200 ppmv. The absence of significant catalytic deactivation at these temperature is consistent with the results reported by other researchers who studied the gas phase oxidation of organic compounds over Pt/Al2O3 catalyst [9-11].

4.2. Identification of Intermediates

Many intermediates can be produced by the oxidation of BTX, depending on the reaction conditions. However, there were no by-products detected from off-line samples. The analytical results of the reactor effluent indicated that BTX were completely oxidized.

4.3. Catalytic Oxidation Kinetics of Pure BTX

Figure 3 presents the conversion of BTX versus inlet concentration in the range of 133⁻350 ppmv at constant temperature. The deep conversions of BTX were increased as the the reaction temperature was increased. Also, the deep conversions were varied inversely with the inlet concentration of BTX.

For plug flow reactor under steady state as this apparatus, the integration formula for a first-order and zero-order reaction can be represented by Equations (8) and (9).

First order : $X = 1 - \exp(-kt)$  \hspace{1cm} (8)

Zero order : $X = \frac{kr}{C_{\text{BTX}}}$  \hspace{1cm} (9)

where $t$ is space time and $C_{\text{BTX}}$ is inlet concentration of BTX. Equation (8) suggests that the conversion is independent of the inlet concentration for a first-
order reaction whereas Equation (9) suggests a reverse relationship between conversion and inlet concentration. Therefore, the catalytic oxidation mechanism of this study was zero-order reaction at all temperature in terms of kinetics. Maximum conversions of benzene, toluene, and m-xylene were 95.81%, 72.20% and 65.70% at 350 °C, 133 ppmv, respectively. Toluene and m-xylene have lower conversion than benzene. In the oxidation of toluene and m-xylene, e.g., it is known from kinetics investigation that the rate-determining step is a hydrogen abstraction from the methyl group.

Since the oxygen concentration would always be much larger than the BTX reactant concentration, the concentration of oxygen considered as constant. Therefore, the integration of Equation (7) in a plug flow tubular reactor results in the form [8]

$$\ln(1-X) = -\left[\frac{k_1 X}{k_a c_{O_2} \times 10^6}\right] X^C_{BHX} + k_1 \tau$$  (10)

where $X$ is the complete conversion of BTX, $C^C_{BHX}$ is inlet concentrations of BTX, $\tau$ is space time. Rate constants, $k_0$ and $k_1$ can be calculated by plotting $-\ln(1-X)$ and $X^C_{BHX}$.

Figure 4 shows that $-\ln(1-X)$ versus $X^C_{BHX}$ of two-stage redox rate model. The linearity of these plots resulted from the stepwise mechanism, assumed for BTX deep oxidation on the catalyst. Then, the rate constants ($k_0$ and $k_1$) were obtained from the relationship between $-\ln(1-X)$ and $X^C_{BHX}$. Activation energy for the deep oxidation of BTX was represented in Table 1, and the activation energy was calculated numerically by Arrhenius equation.

$$k = k_0 \exp\left[-\frac{E}{RT}\right]$$  (11)

where $R$ is gas constant (8.314 J/mol.K).

### 4.4. Binary Mixture Oxidation Kinetics

Figures 5 and 6 show the conversion data for benzene-toluene and benzene-m-xylene mixture as a function of temperature. As shown in the figure, the conversion of toluene and m-xylene are significantly inhibited in the binary mixture. The conversion of benzene appears to be less affected than that of toluene and m-xylene. Toluene and m-xylene conversion was inhibited by benzene. The inhibition can be explained on basis of competition for the oxidized portion of the catalyst.

The rate data as a function of temperature and concentration are shown in Figure 7 for BTX. BTX exhibits close-to-zero-order behavior at all temperatures tested. The zero-order behavior of BTX clearly demonstrates rate inhibition in the mixture.

For the oxidation of a mixture of BTX, the following may be postulated [6,12-13],

$$\text{BTX}_1 + \text{oxidized catalyst} \xrightarrow{k_{11}} \text{[reduced catalyst]}_1 + \text{products}$$  (12)

$$\text{O}_2 + [\text{reduced catalyst}]_1 \xrightarrow{k_{02}} \text{oxidized catalyst}$$  (13)

$$\text{BTX}_2 + \text{oxidized catalyst} \xrightarrow{k_{12}} [\text{reduced catalyst}]_2 + \text{products}$$  (14)

$$\text{O}_2 + [\text{reduced catalyst}]_2 \xrightarrow{k_{02}} \text{oxidized catalyst}$$  (15)
If at any instant \( \theta_1 \) and \( \theta_2 \) are fractions of the catalyst surface occupied by \( \text{[reduced catalyst]}_1 \) and \( \text{[reduced catalyst]}_2 \), respectively, then the following balances may be written,

\[
\begin{align*}
  r_1 &= k_1 C_{\text{BTX}} (1 - \theta_1 - \theta_2) = \gamma_1 k_{al} C_{O_1} \theta_1 \quad (16) \\
  r_2 &= k_2 C_{\text{BTX}} (1 - \theta_1 - \theta_2) = \gamma_2 k_{al} C_{O_2} \theta_2 \quad (17)
\end{align*}
\]

\( \theta_1 \) and \( \theta_2 \) may be evaluated from Equations (16), (17) substituted in the righthand sides of these equations to yield the respective rate equations for oxidation in a binary mixture,

\[
\begin{align*}
  r_1 &= \frac{k_{al} k_1 C_{O_1} C_{\text{BTX}}}{k_{al} C_{O_1} + \gamma_1 k_1 C_{\text{BTX}} + \sum_{i=1}^{n} \left( \frac{k_{al}}{k_{al}} \right) \gamma_i k_i C_{\text{BTX}}_i} \quad (18) \\
  r_2 &= \frac{k_{al} k_2 C_{O_2} C_{\text{BTX}}}{k_{al} C_{O_2} + \gamma_2 k_2 C_{\text{BTX}} + \sum_{i=1}^{n} \left( \frac{k_{al}}{k_{al}} \right) \gamma_i k_i C_{\text{BTX}}_i} \quad (19)
\end{align*}
\]

A general rate form for deep oxidation of \( i \)th component in an \( n \)-component mixture may be easily inferred from Equations (18) and (19),

\[
r_i = \frac{k_{al} k_i C_{O_i} C_{\text{BTX}}}{k_{al} C_{O_i} + \sum_{j=1}^{n} \left( \frac{k_{al}}{k_{al}} \right) \gamma_j k_j C_{\text{BTX}}_j}
\]

Using single component rate data (Table 1), Equation (20) may be used to predict the conversion of each BTX component in mixture. The tubular reactor has been used in our experiments, the rate of reaction changes along the reactor since concentration change along the reactor. Thus differential component balances (assuming plug flow) have been set up as follows for \( n \)-component mixture

\[
\frac{dX_i}{dw} = \frac{r_i}{v \omega C_{\text{BTX}}^i}, \quad i = 1, 2, \ldots, n
\]

with inlet boundary condition, \( f_i(0) = 0, \quad i = 1, 2, \ldots, n \), where \( X_i \) is the predicted conversion of species \( i \) and \( \omega \) is the catalyst weight.

A fourth-order Runge-Kutta method has been used to solve these equations and to evaluate conversions of benzene, toluene and \( m \)-xylene in their binary.

Figure 6. Effect of mixture on conversion of benzene and \( m \)-xylene.
Figure 7. Differential reaction rate for BTX oxidation.

Figure 8. Parity plot comparing the experimentally measured conversion of benzene and toluene.

Figure 9. Parity plot comparing the experimentally measured conversion of benzene and m-xylene.

The model evaluations for the binary mixture are compared to the actual experimental results in Figures 8 and 9.

Figures 8 and 9 provide a parity plot for experimental conversion versus model predictions for the mixture experiment. It can be observed that the mixture model overpredicts the conversion of toluene and m-xylene but underpredicts the conversion of benzene. The reaction model reveals that there is a competition between the two reactants for the oxidized catalyst. Benzene competes more effectively for the oxidized site and is thus oxidized more rapidly.

5. Conclusions

The oxidation of BTX was studied on a 0.5% Pt/γ-Al₂O₃ catalyst at temperature ranging from 200 to 350 °C. An approach based on the two-stage redox rate model was used to explain the results. The conversions of BTX were increased as the reaction temperature was increased. Also, the BTX conversions varied inversely with the inlet concentration. The maximum deep conversion of benzene, toluene and m-xylene were 95.81%, 72.20% and 65.70% at 350 °C, respectively.

The behavior of BTX mixtures in catalytic oxidation cannot be foreseen simply by knowing the single compound kinetic data. Deep conversions of toluene and m-xylene were inhibited by benzene. The inhibition can be explained on basis of competition for the oxidized portion of the catalyst.

Acknowledgement

The authors wish to acknowledge the financial support of the Korea Research Foundation made in the program year of 1998.
Nomenclature

\( C_{O_i} \): oxygen concentration [mol%]
\( C_{BTX} \): BTX concentration [mol/cm\(^3\)]
\( C_{BTX}^{in} \): inlet concentrations of BTX [mol/cm\(^3\)]
\( k_i \): surface reduction rate constant for species i [cm\(^3\)/g \cdot sec]
\( k_{ra} \): surface reoxidation rate constant for species i [cm\(^3\)/g \cdot sec]
\( R \): gas constant (8.314 J/mol \cdot K)
\( r_i \): rate of oxidation of species i [mol/g \cdot sec]
\( w \): catalyst weight [g]
\( X \): deep conversion of BTX
\( X_{sp} \): predicted conversion for species i

Greek
\( \theta \): the fraction of oxidized catalyst at any time
\( \nu_i \): the stoichiometric coefficient of oxygen in the overall reaction
\( \tau \): the space time [sec]

References