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Catalytic Vapor-Phase Oxidation of Toluene to Benzaldehyde

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The vapor-phase air oxidation of toluene to benzaldehyde over a V_2O_5 catalyst was investigated in an isothermal integral flow reactor at atmospheric pressure between 350 and 480 °C. The effects of several variables, the feed ratio of oxygen to toluene, the reaction temperature, and the reciprocal of the space velocity, on the conversion and selectivity to benzaldehyde were determined. Nine different mechanisms were postulated and the rate expression $r_T = (K_1 K_2 \gamma_T^2) / (K_1 \gamma_T^2 + K_2)$ fit the data best.

1. Introduction

The purpose of this study was to investigate the effects of several variables, the oxygen to toluene feed ratio, the reaction temperature, and reciprocal of the space velocity (W/F) on the conversion of toluene and on the selectivity for benzaldehyde, (S), over a V_2O_5 catalyst and to find a suitable rate equation for the reaction.

Various catalysts have been tried in order to obtain high conversion and selectivity for the production of benzaldehyde from toluene in the vapor phase.

Popova and Kabakova (1964) obtained the highest yields of benzaldehyde (of the order of 100-150 g/h) in the oxidation of toluene on copper catalysts doped with molybdenum and tungsten oxides on silit between 350 and 450 °C. Admixture of V_2O_5 , Bi_2O_3 , PbO , P_2O_5 , ZnO , and Ag_2O to this catalyst didn't improve the yield. Kinetic study showed that reaction was zero order with respect to the hydrocarbon (at concentrations from 5% to 30%) and first order with respect to oxygen (at concentrations from 5% to 25%).

Trimm and Irshad (1970) have investigated the oxidation of unsubstituted and substituted toluenes over molybdenum trioxide. Molybdenum trioxide was found to be selective but to be a rather inactive catalyst for the oxidation of toluenes. The catalyst was much more selective than bismuth molybdate. Kinetic studies showed that the reaction was controlled by the rate of the reduction of the catalyst, and the initial rate was first order in toluene and was independent of the concentration of oxygen.

Papadatos and Shelstad (1973) used cobalt-metal oxide (NiO , CuO , ZnO) catalysts for the oxidation of toluene. Wirtz et al. (1975) studied the reaction on WO_3-MoO_3 catalysts. Van Der Wiele (1975) and Van Den Berg (1975) studied the oxidation of toluene by air over a silica-supported Bi-Mo-P-O catalyst (commercial Ketjen A catalyst, atomic ratio Bi/Mo/P/Pi approximately 2.25:0.2:14) and over pure bismuth molybdate at temperatures between 450 and 550 °C. Kinetic measurements indicated that a Mars-Van Krevelen mechanism fit the experimental data. Kumar Ray and Mukherjee (1983) studied the catalytic vapor-phase oxidation of toluene to benzaldehyde over a series of catalysts in a fixed bed reactor at 300-400 °C. The highest activity and selectivity for conversion of toluene to benzaldehyde were obtained with $V_2O_5-K_2S-$

O_4-SiO_2 catalyst. The selectivity with this catalyst was 89.2%, and the conversion per pass to benzaldehyde was 20.8 mol % at 350 °C with practically no other side product. The composition of catalyst was 12.1% V_2O_5 , 6.1% MoO_3 , and 81.8% SiO_2 . Also it was seen that the addition of K_2SO_4 changed the activity of the catalyst. K_2SO_4 was incorporated in the catalyst by two different procedures: coprecipitation and addition as solution. The incorporation of K_2SO_4 to the catalyst by coprecipitation rendered the catalyst more active. It was significant that the presence of K_2SO_4 at high concentration only (up to 30-35%) rendered the catalyst more active. At lower concentrations, the activity was found to be poor.

Kumar Ray and Mukherjee have also investigated the effects of air space velocity and feed rate on the conversion of toluene to benzaldehyde in the presence of a catalyst composed of 10.4% V_2O_5 , 34.6% K_2SO_4 , and 55.0% SiO_2 . It was found that the maximum conversion to benzaldehyde occurred at 350 °C with an air space velocity of 500 $L^{-1} h^{-1}$ and a feed rate of 43 $g L^{-1} h^{-1}$. The maximum yield of benzaldehyde obtained was 20.8 mol % per pass.

Madhok (1983) investigated the selective oxidation of toluene to benzaldehyde over SnO_2-MoO_3 catalyst at temperatures between 350 and 650 °C. An increase in temperature from 350 to 450 °C increased the percentage of benzaldehyde from 6.2% to 19.8%. Thus, selective oxidation was favored at 450 °C. A further increase in temperature from 450 to 650 °C decreased the total conversion and conversion to benzaldehyde. All the SnO_2-MnO_3 catalyst samples obtained by heating at different temperatures showed first-order kinetics for the oxidation of toluene.

Gasior et al. (1983) have studied the oxidation of toluene on catalysts prepared by deposition of a vanadia phase on AN or RT titania (AN is the anatase form of TiO_2 ; RT is the rutile form of TiO_2) at conditions where no solid-state reactions between V_2O_5 and TiO_2 took place; i.e., titania merely played the role of a support. Their results at a reaction temperature of 330 °C showed that the selectivities toward partial oxidation products were higher for AN-containing samples, whereas those toward total combustion products showed higher values for RT-containing catalysts.

2. Experimental Section

2.1. Catalyst Preparation. Four catalysts were prepared for the selectivity studies.

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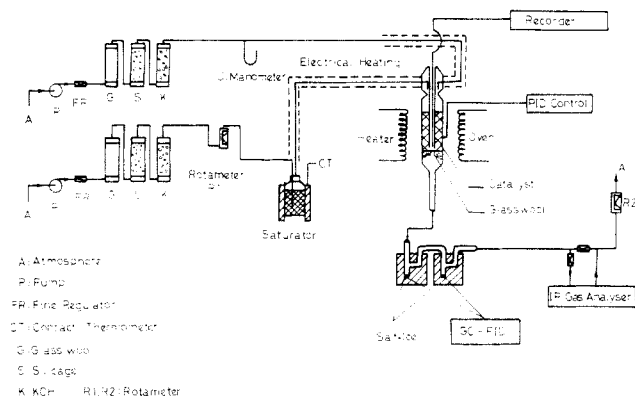


Figure 1. Experimental setup.

The first catalyst was prepared by the method of Trimm and Irshad (1970). Pumice stone was used as the carrier in this catalyst, and its composition was 20.0% V_2O_5 and 80.0% pumice stone.

The second catalyst was prepared by the method of Kumar Ray and Mukherjee (1983). Silica gel was prepared in the first instance from sodium silicate solution by the addition of 10% H_2SO_4 until it attained pH 5.5–6.0. The gel thus prepared was washed free of Na_2SO_4 and was dissolved in KOH solution when potassium silicate was formed. The potassium silicate solution was diluted to a pH of 5.5–6.0 by addition of dilute H_2SO_4 . After filtration, the precipitated silica gel was dried. An appropriate amount of ammonium *m*-vanadate was reduced by oxalic acid in warm water until the solution turned blue. To this solution, an appropriate amount of silica gel (containing K_2SO_4) was added and well mixed. The solution was evaporated and the catalyst was dried at 100 °C and activated at 450 °C for 4 h. The composition of the catalyst was 10.4% V_2O_5 , 34.6% K_2SO_4 , and 55.0% SiO_2 by weight.

The third catalyst had a composition that was the same as that of catalyst 2. Commercial silica gel was only used as carrier, K_2SO_4 (Riedel, De Haen) was added to this silica gel, and the catalyst was prepared similarly.

The fourth catalyst had a composition that was also the same as that of catalyst 2. Kieselguhr (Camag, Switzerland) was used as the carrier, and K_2SO_4 was added to kieselguhr. The catalyst was prepared similarly.

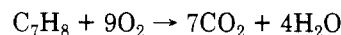
The results of the selectivity screening test showed that catalyst 2 was the most selective one (Akpolat, 1988). So, this catalyst was used, determined by a Fisher sorptometer using the one-point BET technique, and found to be 148.50 m^2/g . The particle size of the catalyst was about 1 mm.

2.2. Experimental Setup. A tubular reactor was employed in the experiments. The setup is given in Figure 1. The air stream, used for oxidation, was metered by a U manometer, after passing through a series of driers, and was fed to the reactor, passing through a heated piping. Toluene was kept in a saturator located in a constant-temperature bath. Air was used as the hydrocarbon carrier and passed through a series of driers and metered with a rotamer. In some experiments, the flow rate of toluene fed to the reactor couldn't be maintained constant because of the fluctuations in the flow rate of the carrier gas. This insufficient experimental accuracy caused the scatter in those data. The hydrocarbon stream from the saturator was fed to the reactor through a Pyrex tube that was kept over 120 °C in order to prevent toluene condensation. The reactor was a tubular reactor, operating in integral mode, 10 mm in diameter, made of Pyrex glass. The reactor was located in an electrical oven and heated by radiation. An Fe-constantan thermoelement was located in the middle of the catalyst bed to measure the temperature of the

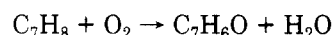
catalyst, and the temperature was recorded continuously during the experiment and was kept constant. The product stream from the reactor passed through two cold traps connected in series. The cold traps were kept in salt-ice mixtures.

The liquid-phase components in the product stream were trapped in the cold traps, and then the stream was passed through a Leybold-Heraeus IR gas analyzer for CO_2 determination. The products cooled in the traps were dissolved in acetone and analyzed by gas chromatography on a column packed with SE-30. The exit from IR gas analyzer was vented to the atmosphere.

The CO_2 formed comes from complete oxidation of toluene, and the amount of toluene used in the complete oxidation can be determined by use of the reaction



The amount of toluene fed to the reactor was known. The amounts of unreacted toluene and benzaldehyde obtained in the partial oxidation reaction were determined by subtracting the amount of toluene used in the complete oxidation from the amount fed to the reactor. By use of the equation of partial oxidation reaction



and the results of the GC analysis, the amounts of unreacted toluene and benzaldehyde produced were calculated separately. The amount of oxygen in the exit stream was calculated by using the reaction equations and the amount of O_2 fed to the reactor. The reaction rate was determined using the conversion, X_T , versus space time, W/F_{T_0} , data. The X_T versus W/F_{T_0} curves were differentiated numerically to get the rate.

An experimental run took 6–8 h, and no important catalyst deactivation was noted. By use of standard procedures (Smith, 1970), it was shown that both external and internal diffusion do not influence the reaction rate. External diffusion effects were calculated using the generalized J_D factor, and it was found that $(C_b - C_s)/C_b \approx 10^{-8}$, so it was assumed that $C_b \approx C_s$. To calculate the internal diffusion effects, the generalized Thiele modulus based on the reaction rate was determined. The effective diffusivity was estimated by use of a pore size of 100 Å for silica gels employing the procedure based on the average pore volume, density of the catalyst, and surface area. The generalized Thiele modulus was found to be of the order 0.5, and hence, the effectiveness factor was assumed to be unity.

3. Results and Discussion

Experimental data were obtained by means of the isothermal fixed bed reactor given in Figure 1. The effects of various variables, the oxygen to toluene feed ratio, the reaction temperature, and the reciprocal of the space velocity (W/F_{T_0}) on the conversion of toluene and on the selectivity for benzaldehyde (*S*) were investigated. While the conversion, X_T , was defined as the moles of toluene reacted per hour to the moles of toluene fed per hour, the selectivity, *S*, was referred to as the ratio of moles of benzaldehyde produced per hour to the moles of toluene reacted per hour.

3.1. Effect of Oxygen/Toluene Feed Ratio. Figure 2 shows the effect of feed ratios on the conversion of toluene and selectivity for the oxidation of toluene to benzaldehyde at 430 °C for a W/F_{T_0} ratio of 90.91. During the runs, though the rate of toluene charged into the reactor was maintained constant, different feed ratios, oxygen/toluene ratio, were obtained by adjusting the air flow

Table I. Kinetic Models Employed for the Experimental Data^a at 430 °C

no.	model (two-step redox)	rate expression	K_1	K_2	C^*
1	first order with respect to toluene and oxygen	$r_T = \frac{K_1 K_2 y_T y_O}{K_1 y_T + K_2 y_O}$	11.75	0.0274	0.72
2	one-half order with respect to toluene and oxygen	$r_T = \frac{K_1 K_2 y_T^{1/2} y_O^{1/2}}{K_1 y_T^{1/2} + K_2 y_O^{1/2}}$	0.37	0.0136	0.37
3	one-half order, toluene; first order, oxygen	$r_T = \frac{K_1 K_2 y_T^{1/2} y_O}{K_1 y_T^{1/2} + K_2 y_O}$	0.37	0.0306	0.37
4	with oxygen dissociation	$r_T = \frac{K_1 K_2 y_T y_O^{1/2}}{K_1 y_T + K_2 y_O^{1/2}}$	11.43	0.0121	0.70
5	first order, toluene; zero order, oxygen	$r_T = \frac{K_1 K_2 y_T}{K_1 y_T + K_2}$	11.19	0.0056	0.71
6	one-half order, toluene; zero order, oxygen	$r_T = \frac{K_1 K_2 y_T^{1/2}}{K_1 y_T^{1/2} + K_2}$	0.36	0.0062	0.36
7	zero order, toluene; first order, oxygen	$r_T = \frac{K_1 K_2 y_O}{K_1 + K_2 y_O}$	3.99×10^{-4}	N*	0.23
8	second order, toluene; zero order, oxygen	$r_T = \frac{K_1 K_2 y_T^2}{K_1 y_T^2 + K_2}$	4347.91	0.0056	0.89
9	adsorbed toluene and oxygen (surface reaction)	$r_T = \frac{K_s K_T y_T}{1 + K_T y_T + K_B y_B} \frac{K_O y_O}{1 + K_O y_O}$	N*	N*	N*

^a C^* = correlation coefficient. N* = negative.

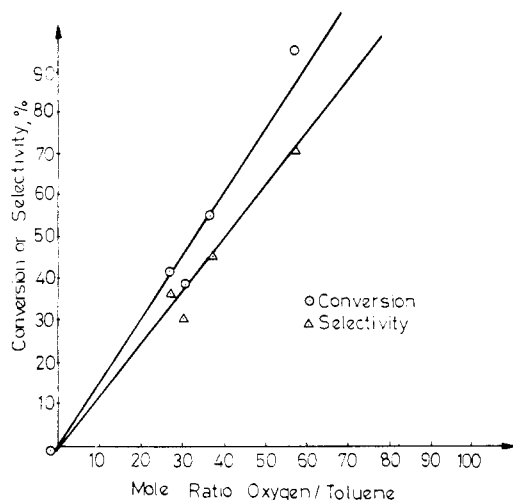


Figure 2. Effect of feed ratio, O_2/C_7H_8 , on the conversion and selectivity.

rate, for an average flow rate of toluene. The conversion and selectivity for benzaldehyde increased linearly with increasing oxygen/toluene ratios, but at a given oxygen/toluene ratio, the selectivity is always smaller than the conversion.

3.2. Effect of Temperature. Figure 3 shows the effect of temperature on the conversion and selectivity in the temperature range 350–480 °C, at a W/F_{T_0} ratio of 90.81 for an average value of 0.46% toluene in air. An increase in the reaction temperature from 350 to 460 °C provides a continuous increase in the conversion. After a maximum conversion at 460 °C, a decrease in the conversion was observed with increasing temperature.

The selectivity to benzaldehyde increases with temperature up to 430 °C; after a maximum at 430 °C, the selectivity decreases with increasing temperature. In this work, it wasn't searched why the conversion or selectivity decreased with increasing temperature. The mechanism of the reaction or rate-controlling step may be changed.

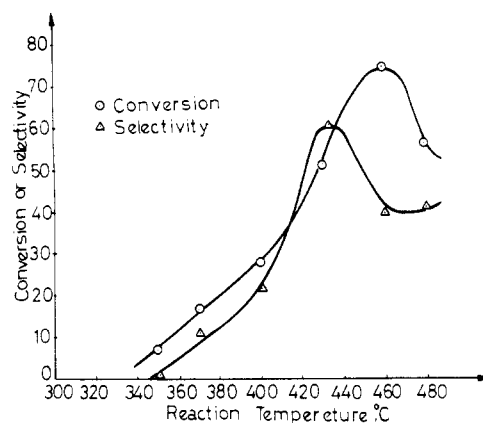


Figure 3. Effect of temperature on the conversion and selectivity.

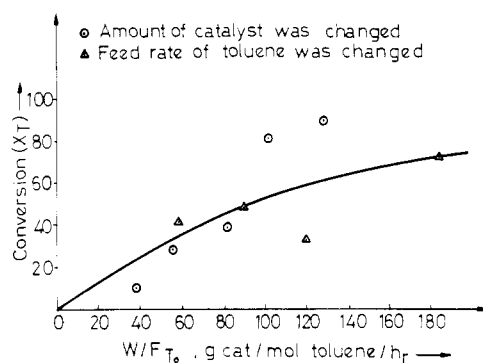


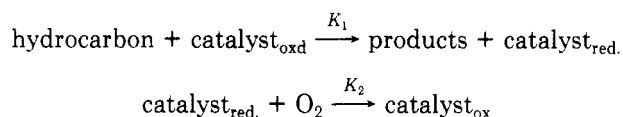
Figure 4. Effect of the reciprocal of the space velocity on conversion.

But this investigation is out of the scope of this study.

3.3. Effect of W/F_{T_0} Ratios. Figure 4 shows the effect of the reciprocal of the space velocity (W/F_{T_0}) on the conversion and selectivity of benzaldehyde. During the runs, the reciprocal of the space velocity was varied by changing the amount of catalyst for an average flow rate of toluene or by changing the feed rate of toluene at 430

°C. It was seen that the conversion increased rapidly with increasing values of W/F_{T_0} .

3.4. Modeling of the Toluene Oxidation. Most catalytic oxidation reactions proceed by a two-step redox mechanism. Especially in oxidation over V_2O_5 catalyst, this mechanism is usually proposed (Subramanian and Murthy, 1972, 1974; Van Der Wiele and Van Den Berg, 1975), keeping in mind that a two-step redox mechanism was proposed for this reaction as well. According to this mechanism, the first step is the adsorption on hydrocarbon on the catalyst surface and its reaction with the oxygen atom of the catalyst to yield the products and the reduced catalyst; the second step is the oxidation of the reduced catalyst by oxygen:



The generalized form of this type rate expression can be written as

$$\frac{1}{r_T} = \frac{1}{K_2 y_O^\beta} + \frac{1}{K_1 y_T^\alpha} \quad (1)$$

or

$$r_T = \frac{K_1 K_2 y_T^\alpha y_O^\beta}{K_1 y_T^\alpha + K_2 y_O^\beta} \quad (2)$$

Equation 2 was tried for different values of α and β to determine a suitable reaction mechanism. These models are summarized in Table I. Model 9, which was a surface reaction between adsorbed toluene and oxygen, has been used by Mann and Ko (1973) for the oxidation of 2-methylpropene over bismuth molybdate catalyst. With that in mind, this mechanism was also tried. The rate constants for each model were determined at 430 °C by least-squares techniques, and correlation coefficients of the equations were calculated. The rate expression that gave the best fit was retained, and the others were discarded. Table I clearly indicates that model 8 fits the data best and explains the partial oxidation of toluene over the catalyst used. The rate constants K_1 and K_2 were evaluated at 430 °C to be 4347.91 and 5.58×10^{-3} , respectively. But, because of the lack of experimental data at different temperatures, the activation energies for K_1 and K_2 couldn't be calculated. Since $K_2 \ll K_1$, the rate-controlling step for the reaction is the oxidation of the reduced catalyst as found by Trimm and Irshad (1970) and also by Van Der Wiele and Van Den Berg (1975).

4. Conclusions

The catalytic air oxidation of toluene over a V_2O_5 catalyst has been investigated between 350 and 480 °C, and the effects of several variables, the feed ratio of oxygen to toluene, the reaction temperature, and the reciprocal of the space velocity on the conversion and selectivity to benzaldehyde, were determined. The highest selectivity of about 60% was obtained at 430 °C for a 0.46% toluene in air mixture and a W/F_{T_0} of 90.91. The rate equation

$$r_T = (K_1 K_2 y_T^2) / (K_1 y_T^2 + K_2)$$

fit the experimental data best.

Nomenclature

C_b = concentration of the gas in the bulk
 C_s = concentration of the gas on the catalyst surface
 $\text{catalyst}_{\text{ox}}$ = concentration of the oxidized catalyst
 $\text{catalyst}_{\text{red.}}$ = concentration of the reduced catalyst
 F_{T_0} = flow rate of the feed, mol/h
 K_1 = rate constant for toluene oxidation
 K_2 = rate constant for catalyst oxidation
 K_B = thermodynamic equilibrium constant of benzaldehyde
 K_O = thermodynamic equilibrium constant of oxygen
 K_s = equilibrium constant for the surface reaction
 K_T = thermodynamic equilibrium constant of toluene
 r_T = reaction rate, mol of toluene/(g of catalyst h)
 y_B = benzaldehyde concentration, mole fraction
 y_O = oxygen concentration, mole fraction
 y_T = toluene concentration, mole fraction
 W = amount of catalyst, g
 X_T = conversion

Greek Symbols

α = reaction order with respect to toluene
 β = reaction order with respect to oxygen

Registry No. V_2O_5 , 1314-62-1; toluene, 108-88-3; benzaldehyde, 100-52-7.

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