Journal of Environmental Sciences (China), Vol. 2, No. 2, pp 41-50, 1990 ISSN 1001-0742

Steady-state kinetics and osillation phenomena for complete oxidation of benzene over Pt/Al_2O_3 catalyst*

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(Received February 24, 1989)

Abstract—The steady-state kinetics for complete oxidation of benzene over Pt/Al_2O_3 has been investigated by the external recycling reactor. The kinetics equation was described by the L-H model of adsorption of benzene and oxygen with the inhibition of carbon dioxide. The parameters of the kinetics model were estimated by the method of orthogonal design. The heats of adsorption of benzene, oxygen and carbon dioxide were determined by the method of gas-adsorption chromatography. The details of oscillations of complete oxidation of benzene were investigated.

Keywords: steady-state kinetics; complete oxidation; benzene; Pt/Al_2O_3.

INTRODUCTION

Catalytic combustion is one of the effective processes for removing pollutants in air (Prasad, 1984; Pfefferle, 1987). The kinetic research is necessary for use in reactor design and process controling. Although the empirical kinetic equations of L-H model for the complete oxidation of benzene were given by different authors (Dryakhlov, 1981; Stasevich, 1985; Pyatnitskii, 1985; Shaprinskaya, 1986), the inhibition of carbon dioxide in the above mentioned equations had not been considered. Oscillatory behavior was observed for the complete oxidation of benzene (Dryakhlov, 1981; Stasevich, 1982; Stasevich, 1985). In the present article we report the L-H kinetic equation of complete oxidation of benzene with inhibition of carbon dioxide. In order to prove the kinetic model, the heats of adsorption of benzene, oxygen and carbon dioxide are determined by the method of gas-adsorption chromatography. The details of oscillations of complete oxidation of benzene over Pt/Al_2O_3 catalyst are investigated.

EXPERIMENTAL

The platinum was only supported on the external surface or the mouths of catalyst pores for the sake of strong interaction of platinum with Al_2O_3, if the catalyst was prepared by the ordinary impregnating method. In this paper the catalyst was prepared by the method of competing adsorption. Al_2O_3 was impregnated with 0.1mol/L latic acid for 8h and dried

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*Supported by the National Sciences Fundation of China.

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at 130°C. Then the latter was impregnated with the chloro-platinic acid, dried at 130°C and calcined at 500°C for 2h. At last the catalyst was reduced by hydrogen. The catalyst contained 0.01wt.% Pt on Al_2O_3.

A laboratory-scale gradientless reactor based on external recycle of reactants has been used to measure the kinetic data. Since the recycle ratio is greater than 25, therefore perfect mixing can be achieved in the recycle reactor (Berty, 1974). The absence of external transport limitations was checked by the variation of the recycle rates of reactants. Internal diffusion limitations were avoided by using catalyst particles of diameter between 0.45 and 0.60mm.

Gaseous product CO_2 was analyzed by a gas chromatography with the mixtures of ophthalic dibutyl ester and β, β'-oxy-dipropionitril at 20°C. 6201 carrier had been used for chromatographic column. The O_2, CO and N_2 were analyzed by another gas chromatography with 5Å molecular sieve and activated carbon. The carrier gas was hydrogen. Materials above mentioned were analyzed by the thermal conductivity detector.

Since the complete oxidation of benzene is a highly exothermal reaction, therefore the water vapor, with partial pressure of 66.7 kPa, was fed into the mixtures of reactants for transfer the reaction heat. During the experiments the temperatures of the catalyst remained constant. The kinetic data were shown in Table 1. In which P_B, P_O, P_{CO} are the partial pressures of benzene, oxygen and carbon dioxide respectively. $r_{(exp.)}$ and $r_{(calc.)}$ are the reaction rates determined by experiments and calculated by Eq. (2) correspondingly.

Table 1 The kinetic data for complete oxidation of benzene over Pt/Al_2O_3 catalyst

Temperature, °C	P_O, kPa	P_B, KPa	P_{CO}, kPa	$r_{(exp.)}$, 10^3mol/ml. h	$r_{(calc.)}$, 10^3mol/ml. h
	12.2	2.59	1.12	3.66	3.50
	12.2	3.07	0.888	2.89	3.01
	12.2	3.67	0.722	2.35	2.56
	11.5	4.24	0.577	1.98	2.11
	11.9	5.01	0.589	1.92	1.87
	11.7	5.67	0.636	2.07	1.64
320	4.65	4.41	0.227	0.739	0.829
	6.28	4.40	0.271	0.883	1.12
	7.55	4.61	0.320	1.06	1.29
	9.44	4.59	0.426	1.39	1.61
	11.4	4.81	0.494	1.61	1.86
	12.3	4.78	0.631	2.06	2.02
	14.0	4.98	0.808	2.63	2.20
	15.1	4.98	0.760	2.48	2.38
	17.7	5.20	0.820	2.67	2.67
	19.9	5.17	0.977	3.18	3.01
	12.5	1.88	1.51	6.06	7.02
340	12.1	2.23	1.30	5.21	5.91
	10.8	3.52	0.775	3.20	3.56
	10.2	4.20	0.804	3.22	3.28

Table 1 (continued)

	10.7	5.68	0.592	2.37	2.27
	10.6	7.69	0.498	2.00	1.69
	11.3	9.92	0.495	1.99	1.41
	3.25	4.40	0.250	1.01	0.381
	6.10	4.38	0.410	1.64	1.65
	10.8	4.20	0.761	3.12	3.03
	12.5	4.78	0.677	2.71	3.11
	13.0	4.98	0.791	3.17	3.11
	14.7	4.94	1.00	4.02	3.53
	15.2	4.95	0.971	3.89	3.65
	17.1	5.13	1.21	4.86	3.96
	18.9	5.09	1.48	5.94	4.30
	12.7	1.97	2.00	10.4	9.88
	12.9	2.30	1.69	8.80	8.88
	11.5	2.66	1.45	7.52	7.04
	12.2	3.12	1.25	6.54	6.52
	12.0	3.69	1.09	5.70	5.54
	11.5	4.26	0.898	4.68	4.67
360	11.8	5.03	0.936	4.88	4.12
	11.9	5.71	0.816	4.24	3.70
	11.2	7.72	0.644	3.36	2.63
	5.20	4.38	0.403	2.10	2.08
	7.87	4.62	0.580	3.02	2.98
	8.17	4.62	0.548	2.86	3.10

Table 1 (continued)

	10.1	4.61	0.740	3.86	3.83
	11.6	4.82	0.800	4.18	4.21
	12.8	4.81	0.881	4.59	4.65
	14.7	5.03	0.998	5.20	5.12
	16.1	5.02	1.11	5.78	5.61
	19.1	5.19	1.69	8.78	6.43
	10.5	1.81	1.96	12.9	12.3
	11.7	2.18	1.59	10.4	11.9
	11.2	2.50	1.65	10.8	10.2
	11.8	2.99	1.42	9.28	9.29
	11.8	3.58	1.20	7.83	7.98
	11.4	4.16	1.05	6.83	6.77
	11.0	4.96	0.899	5.87	5.59
	10.7	5.65	0.744	4.87	4.83
	12.0	7.67	0.634	4.14	4.08
380	11.7	9.92	0.490	3.21	3.12
	6.05	4.48	0.424	2.77	3.39
	7.45	4.57	0.457	3.60	4.09
	9.07	4.55	0.712	4.65	4.99
	10.4	4.74	0.879	5.74	5.50
	11.8	4.71	1.04	6.82	6.27
	12.9	4.89	1.30	8.50	6.61
	13.9	4.90	1.25	8.14	7.11
	16.7	4.85	1.58	10.3	8.59
	18.8	5.10	1.41	9.23	9.24

Table 1 (continued)

	10.4	1.85	1.70	16.2	16.4
	10.2	2.11	2.00	18.9	14.6
	9.64	2.53	1.47	14.0	12.0
	9.67	3.01	1.25	11.9	10.5
	9.48	3.61	1.03	9.78	8.88
	10.0	4.19	0.870	8.27	8.25
	9.49	4.97	0.842	8.01	6.74
400	9.54	5.65	0.738	7.02	6.05
	9.42	7.67	0.624	5.34	4.52
	7.46	4.57	0.554	5.27	5.73
	7.91	4.77	0.708	6.73	5.84
	8.06	4.56	0.652	6.20	6.19
	9.18	5.00	0.691	6.57	6.49
	10.7	4.78	0.764	7.27	7.87
	10.7	4.99	0.787	7.48	7.57
	13.6	5.16	1.00	9.56	9.31
	15.8	5.15	1.18	10.1	10.8

RESULTS AND DISCUSSION

The kinetic equation of complete oxidation of benzene on Pt/Al_2O_3 catalyst.

The effects of partial pressures of benzene, oxygen and CO_2 on the rates of reaction were shown in Table 1. The Langmuir-Hinshelwood equation of adsorption of benzene and oxygen with the inhibition of carbon dioxide was chosen to represent the progress of the reaction. The kinetic equation was

$$r = \frac{K b_B b_{O_2} P_B P_{O_2}}{(1 + b_B P_B + b_{O_2} P_{O_2} + b_{CO_2} + b_{CO_2} P_{CO_2})^2} \tag{1}$$

where K is rate constant; b_B, b_{O_2}, b_{CO_2} are the adsorption coefficients of benzene, oxygen and CO_2 respectively. According to the Arrhenius and Clausius-Clapeyron equations, from Eq.

(1) we obtained

$$r = \frac{K_0 \exp(-E/RT) b_{0_B} \exp(Q_B/RT) b_{0_{O_2}} \exp(Q_{O_2}/RT) P_B P_{O_2}}{[1 + b_{0_B} \exp(Q_B/RT) P_B + b_{0_{O_2}} \exp(Q_{O_2}/RT) P_{O_2} + b_{0_{CO_2}} \exp(Q_{CO_2}/RT) P_{CO_2}]^2} \quad (2)$$

where K_o is the frequency factor of Arrhenius'Law; E is the activation energy of reaction; Q_B, Q_{O_2}, Q_{CO_2} are the heats of adsorption of benzene, oxygen and carbon dioxide correspondingly; $b_{O_B}, b_{O_{CO_2}}, b_{O_{O_2}}$ are the pre-exponential factors of Clausius-Clapeyron'equation; R is gas constant; T is absolute temperature. Eq. (2) is consisted of 8 kinetic parameters, which were estimated by the method of orthogonal design (Yu, 1986). The method is based on the combination of the least square method with orthogonal design for parameters of Eq. (2). The parameters chosen were based on the least sum of residual error of the orthogonal design. The values of parameters estimated by the above mentioned method were reported.

$$K = K_0 \exp(-E/RT) = 3.28 \times 10^5 \exp(-55000/RT)(\text{mol/ml.h}),$$
$$b_B = b_{O_B} \exp(Q_B/RT) = 7.71 \times 10^{-3} \exp(34500/RT)(\text{kP}_a{}^{-1}),$$
$$b_{O_2} = b_{O_{O_2}} \exp(Q_{O_2}/RT) = 1.00 \times 10^{-4} \exp(24700/RT)(\text{kP}_a{}^{-1}),$$
$$b_{CO_2} = b_{o_{CO_2}} \exp(Q_{CO_2}/RT) = 1.34 \times 10^{-5} \exp(43800/RT)(\text{kP}_a{}^{-1}).$$

The average of relative error of reaction rates, which were calculated by the Eq. (2) with above estimated parameters, was 9.09% from 85 sets of experiments in Table 1.

Determination of heats of adsorption of benzene, oxygen and carbon dioxide

For proving the kinetic model and the values of adsorption coefficients in Eq. (2), the heats of adsorption of benzene, oxygen and CO_2 have been determined by the method of gas-adsorption chromatography (Hall, 1985). The carrier gas was nitrogen.

According to Hall, Heaton and Rosseinsky (Hall, 1985), the heat of adsorption of i component was determined by the following equation

$$\ln V_g = Q_i/RT + S_i/R \quad (3)$$
$$(\text{i} = \text{benzene, oxygen, or } CO_2)$$

Where V_g is the specific adjusted retention volume of i component; Q_i, S_i are the heat and entropy of adsorption of i component respectively. V_g was determined by the equation

$$V_g = F_N (t_i - t_{He})/W \quad (4)$$

Where F_N is flow rate of carrier gas, N_2, which is 20ml/min; t_i, t_{He} are the retention times of i component and He respectively; W is the weight of catalyst, which is 1.08g. The experimental data of the heats of adsorption of benzene, oxygen and CO_2 were shown in Fig. 1, 2, 3, correspondingly. The determined values of heats of benzene, oxygen and CO_2 were 34.3kJ/mol, 25.8kJ/mol, 44.8kJ/mol correspondingly. They coincided with the values estimated by the

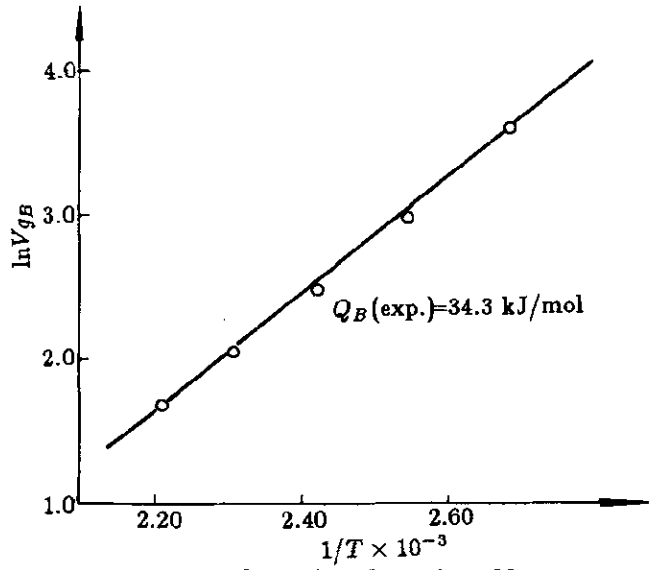

Fig. 1 Temperature dependency for adsorption of benzene according to Clausius-Clapeyron equation

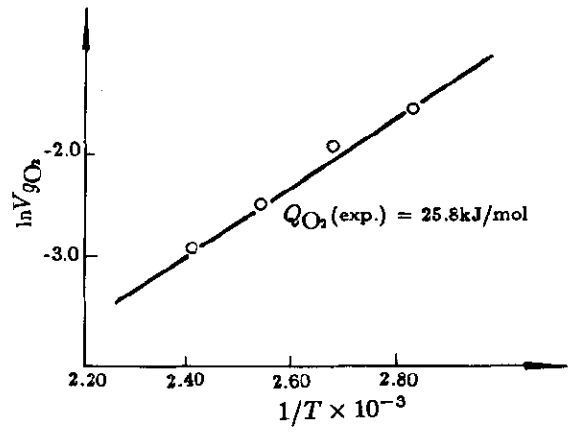

Fig. 2 Temperature dependency for adsorption of oxygen, according to Clausius-Clapeyron equation

method of orthogonal design, which were 34.5 kJ/mol, 24.7kJ/mol and 43.8kJ/mol correspondingly.

Oscillations for complete oxidation of benzene

Oscillatory behavior in heterogeneous catalytic systems attracted considerable attention in recent years and has inspired comprehensive reviews of the subject (Sheintuch, 1977; Slin'ko, 1978; Rozon, 1986). Though the oscillations for complete oxidation of benzene were observed (Dryakhlov, 1981; stasevich, 1982; stasevich, 1985), it had not been investigated in details.

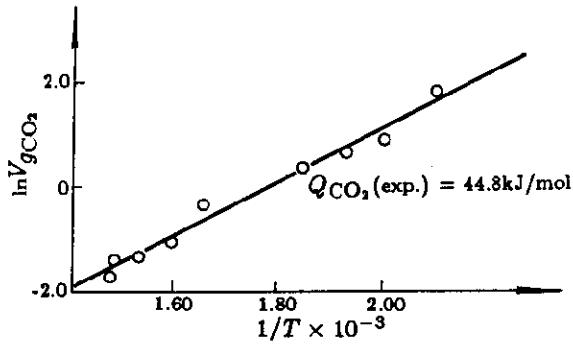

Fig. 3 Temperature dependency for adsorption of carbon dioxide according to Clausius-Clapeyron equation

When the amounts of catalyst and feed fates of reactants were greater than 3 times of the amounts used in the steady-state kinetics, the oscillations of temperatures were observed. Oscillatory behavior for complete oxidation of benzene was studied with the external recycling reactor, by means of it the reaction rates were obtained approximately. The oscillatory data were listed in Table 2 and illustrated in Figure 4.

Table 2 Oscillatory data for complete oxidation of benzene over Pt/Al_2O_3.

(Wt. of catalyst 0.197g., temperature 400°C, feed rates of benzene and water vapor were 214 and 6000ml/h respectively)

Feed rates, ml/h		C,	P_{O_2}	P_B	P_{CO_2},	$\tilde{r}$,	$\tilde{\Delta}t$,
O_2	N_2	%	kPa	kPa	kPa	10^3mol/ml.h	°C
1000	1786	58.3	4.68	0.991	8.32	21.1	8
1200	1586	47.3	7.23	1.25	6.35	17.9	12
1400*	1386	43.7	10.8	1.34	6.24	16.6	16
1600	1186	79.3	8.18	0.492	11.3	32.0	18
1800	986	86.3	9.50	0.325	12.3	32.7	13
2150	636	90.7	9.43	0.221	12.9	34.4	20

In Table 2 C is percent conversion of reaction, $\tilde{r}$ is reaction rate measured by external

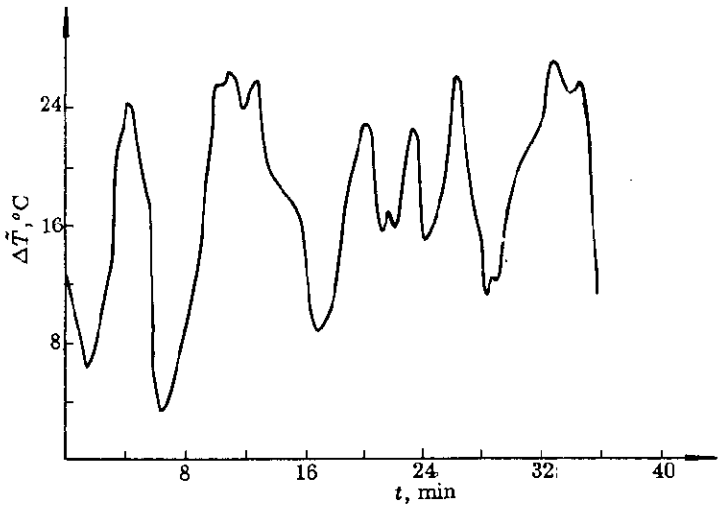

Fig. 4 Temperature oscillations for complete oxidation of benzene over Pt/Al_2O_3 (The condition of temperature oscillations was shown in Table 2)

recycling reactor approximately, $\tilde{\Delta}t$ is approximate amplitudes of temperature oscillations.

Table 2 showed that the amplitudes of temperature oscillations, reaction rates and percent conversion of reaction increased approximately with the rise of feed rates of oxygen. These observations suggested that the reason of temperature oscillations is the inhibition of transfer of reaction heat.

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