

THE BURNING RATE OF COKE DEPOSITED ON ZEOLITE CATALYST

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Burning rate of coke deposited on zeolite catalyst is evaluated under conditions of chemical reaction control and compared with experimental data reported previously by other investigators. The rate equation obtained in this paper is first order with respect to both coke concentration and oxygen partial pressure. Its activation energy is 26.2 kcal/g-mol, slightly lower than those of other works. Burning rate is approximately independent of the source of coke, but is affected by a certain kind of cation in zeolite.

Introduction

In catalytic reactors, fouling of catalyst activity occurs by the deposition of coke on the surface of catalyst. Regeneration of activity is achieved by burning off the coke with air. The burning of coke is a noncatalytic gas-solid reaction between coke on the catalyst and oxygen in the feed gas, accompanied by a large amount of reaction heat. To express the burning kinetics using various catalysts⁴, several models have been proposed, e.g. surface reaction model^{8,11} and homogeneous model. The present study is carried out on zeolite catalyst, which has been used as an industrial catalyst recently in place of silica-alumina catalyst. Zeolite catalyst has micropores of smaller diameter than does silica-alumina catalyst, and has metallic cation in its crystalline structure. Some effect of these characteristics on burning rate may be expected, but has not been reported yet. In this paper, the burning rate was determined and the effects of the source of coke and cation on the rate constant are discussed.

1. Experimental

1.1 Experimental apparatus and method

Reaction was carried out in a fixed bed reactor. In Fig. 1, the flow diagram of experimental apparatus is shown.

The reactor used was a stainless steel tube of 1.0 cm I.D., heated by an electric furnace which was controlled within $\pm 1^\circ\text{C}$.

1) Formation of coke Toluene and *o*-xylene were used as a source of coke formation. Also cumene,

n-hexane, cyclohexene and methylcyclohexane were used for comparison. These feeds were passed through the reactor packed with zeolite catalyst under the following conditions: concentration of reactants diluted by hydrogen was from 10 to 20 mol %; reaction temperature from 500 to 550°C; *W/F* from 0.20 to 2.60 g-cat·hr/g-mol. The concentration of coke produced was controlled with varying reaction time and kept below 0.08 g-coke/g-cat. to lower the temperature rise accompanying burning.

2) Burning of coke After the reactor was set at a given temperature, gas mixture of oxygen and nitrogen was controlled at appropriate flow rate, preheated and fed into the reactor.

The reactor temperature was varied from 400 to 570°C, oxygen concentration from 6 to 22 mol % and feed rate from 100 to 700 ml/min. Distribution of temperature during the reaction was measured by moving a chromel-alumel thermocouple in the thermowell inserted in the catalyst bed. Consumption of

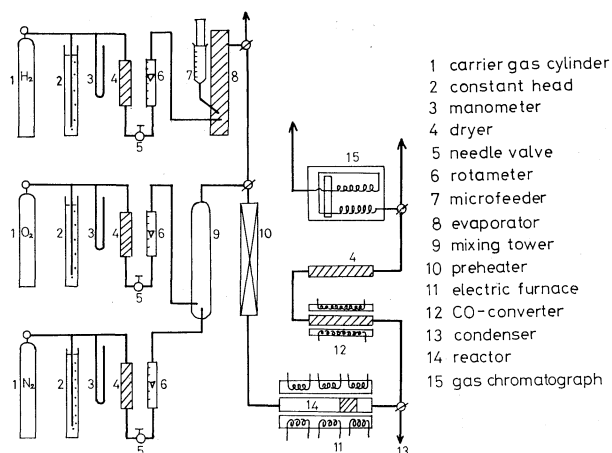


Fig. 1 Experimental apparatus

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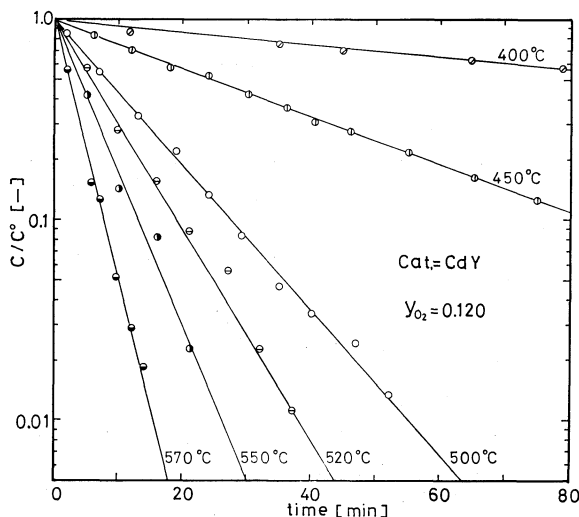


Fig. 2 Fit of experimental results to first-order rate expression

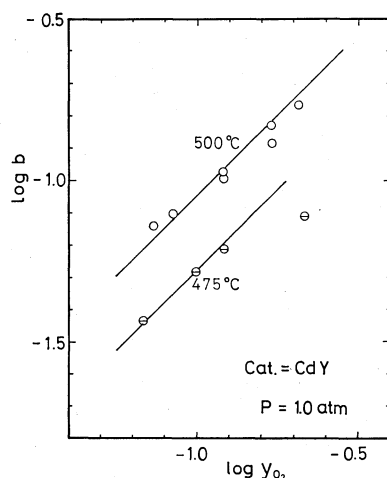


Fig. 3 Dependence of b on y_{O_2}

Table 1 Variation of b with C^0 and F_{air}

Run No.	T [°K]	$10^2 \times C^0$ [g/g-cat]	F_{air} [ml/min]	$10^2 \times b$ [1/min]
116	773	3.69	205	10.2
117	773	2.63	205	10.7
123-1	773	4.35	295	9.78
124	773	2.36	158	10.5
221	773	3.35	620	11.9
301	723	1.97	693	2.85
302	723	6.50	225	2.45
727	723	7.80	192	2.83

oxygen in this reaction was low and the temperature profile along the bed was nearly uniform. Therefore, experimental data obtained in this study could be analyzed on the basis of an isothermal differential reactor. Pressure drop across the bed was so small that total pressure was considered to be atmospheric.

1. 2 Catalysts

Zeolite catalyst CdY was prepared by exchanging Na^+ in Y type Molecular Sieve (SK-40) of Linde Co.

for Cd^{2+} using aqueous solution of $CdCl_2^{2)}$. The same procedure was used for the preparation of other zeolite catalysts. The levels of ion exchange for these catalysts were CdY (65%); MgY (58%); AlY (83%); CrY (83%); CoY (67%); CuY (83%). About 1 gr. of catalyst having 0.59~0.84 mm diameter was diluted with 3 gr. of silica having the same diameter to obtain isothermal experimental conditions.

1. 3 Analysis of exit gas

The reaction products were water, carbon monoxide and carbon dioxide. Among them, water was absorbed with phosphorous pentoxide and carbon monoxide was oxidized to carbon dioxide over CuO catalyst, then total content of carbon dioxide was measured. The exit gas was analyzed by gas chromatography using a single column⁷⁾ composed of silica gel and Molecular Sieve 5A column. Carbon dioxide was analyzed by the former, and oxygen and nitrogen by the latter.

1. 4 Elementary analysis of coke

The sample for the elementary analysis of coke was preheated thoroughly in nitrogen stream before the analysis to remove absorbed water. Carbon dioxide produced was absorbed in soda asbestos, water in anhydrous magnesium perchlorate. CH ratio was calculated from these results.

2. Experimental Results and Discussion

2. 1 Determination of the rate equation for coke combustion

The burning rate of coke is expressed as follows^{3,8)}:

$$-(dC/dt) = k p_{O_2}^\alpha C^\beta \quad (1)$$

Constants α and β in Eq. (1) are affected by the properties of catalysts and reaction conditions.

1) Dependence on coke concentration The burning rate of deposited coke was evaluated from the variation of carbon content in catalyst. Initial coke concentration and the fraction of original coke remaining on catalyst were evaluated from the following equations⁸⁾, using measured mole fraction of carbon dioxide y_{CO_2} in exit gas.

$$C^0 = (12 \cdot F_{air} / 22400 \cdot W) \int_0^\infty y_{CO_2} dt \quad (2)$$

$$C/C^0 = \left(\int_t^\infty y_{CO_2} dt \right) / \left(\int_0^\infty y_{CO_2} dt \right) \quad (3)$$

In Eq. (2), it was assumed that coke concentration was nearly equal to carbon concentration. Integral of y_{CO_2} in Eqs. (2) and (3) was calculated using a suitable function of y_{CO_2} of time t which satisfied the experimental data well. In Fig. 2, the logarithm of C/C_0 is plotted against t , and the linear relation was obtained up to high conversion. The slope of this straight

line, expressed as b , corresponds to $kp\delta_2^\alpha$ in Eq. (1). b , as shown in Table 1, didn't vary with initial coke concentration C^0 . From these results, it was found that reaction rate was first order with respect to coke concentration, namely, $\beta=1$. Furthermore, it was shown from the results in Table 1 that b was not influenced by the flow rate of burning gas, that is, the resistance of film diffusion was negligibly small under this experimental condition.

2) Dependence on oxygen partial pressure In Fig. 3, the relation of b and oxygen mole fraction y_{O_2} is shown at 475°C and 500°C and total pressure of nearly 1 atm. The slope of straight line in Fig. 3 was almost 1.0 and α in Eq. (1) was 1.0. These results, $\alpha=\beta=1$, were the same as that published by Hughes³⁾, Weisz¹²⁾ and Tone⁹⁾, although catalysts and the reaction conditions of coke formation used in their experiments were different from this study.

3) Dependence on temperature The dependence of the rate constant on temperature was studied. The Arrhenius plot of k for the burning of the coke formed with toluene is shown in Fig. 4, which gave a nearly straight line over the range of 400 to 570°C.

From this, the frequency factor and the activation energy were calculated and substituted into Eq. (1), which gave the following rate equation.

$$-(dC/dt) = 1.80 \times 10^7 [\exp(-26200/RT)] P y_{O_2} C \quad (4)$$

From the Arrhenius plot of k obtained with various particle sizes, as shown in Fig. 4, it was found that the resistance of intra-particle diffusion was small in the particles used in this study. Although the activation energy of 26.2 kcal/g-mol is slightly lower than the values reported by other investigators^{1,5,9,12)} as shown in Fig. 4, it is considerably higher than the activation energy under mass transfer controlling. It was concluded from these results that Eq. (4) represented the burning rate of deposited coke under the reaction rate controlling.

2. 2 Effect of the source of coke on burning rate

It has been reported by several investigators that coke formation is a complex reaction and that the structure of coke varies with the kinds of reactants and the reaction conditions. The following compounds were used to examine the effect of the source on the burning rate of coke; *o*-xylene and cumene as aromatic compound; cyclohexene and methylcyclohexane as alicyclic compound; *n*-hexane as aliphatic compound. The composition of coke obtained in these experiments was between $CH_{0.37}$ and $CH_{0.46}$. As shown in Fig. 5, the Arrhenius plots of the data for these sources agreed well with that for toluene source.

Consequently, the burning rate was not influenced by the source of coke. Weisz and Goodwin obtained the same results in an experiment using silica-alumina

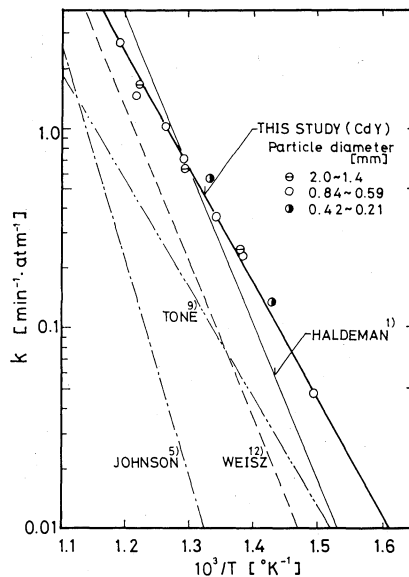


Fig. 4 Arrhenius plots of experimental results and several other works

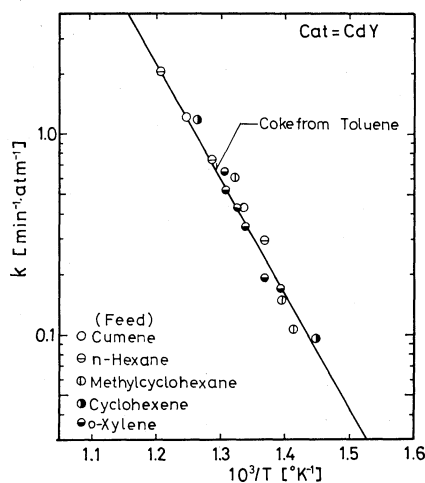


Fig. 5 Effect of the source of coke on rate constant

catalyst¹²⁾.

2. 3 Effect of the cation in zeolite on burning rate

In general, the combustion of coke is treated as a noncatalytic gas-solid reaction^{1,4)}. However, the existence of catalytic effect has been reported for a certain kind of catalyst. For example, the reaction rate on catalyst containing transition metal oxide was accelerated remarkably¹²⁾.

And transition metal cation exchanged zeolite is known as oxidation catalyst for various organic compounds⁹⁾. From these investigations, a catalytic effect of the cation in zeolite was expected. Fig. 6 shows the experimental results for alkaline-earth metal cation exchanged zeolite (MgY and AlY) and transition metal cation exchanged zeolite (CrY, CoY and CuY). For MgY, almost the same rate constant as that for CdY was obtained. For AlY, CrY

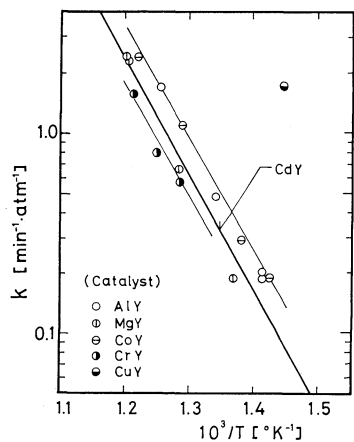


Fig. 6 Arrhenius plots of k for various zeolite catalysts

and CoY, the activation energy was not so different from that for CdY although the frequency factor changed 1.5 times (AlY and CoY) and 0.75 times (CrY). Comparing these results, large catalytic effect of CuY was observed. The rate constant k for CuY evaluated at 420°C was about 14 times that for CdY, which was obtained from the straight line in Fig. 6. Consequently, it was found that the cation in zeolite catalyst affected the burning rate of coke.

Conclusion

The combustion of the coke was studied on zeolite catalyst, and the following results were obtained.

- 1) The rate equation was first order with respect to the coke concentration and the oxygen partial pressure, and the activation energy was 26.2 kcal/g-mol.
- 2) Burning rate was approximately independent of the source of coke, but was affected by a certain kind of cation in zeolite.

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Nomenclature

b	= $k \cdot p_{O_2}^\alpha$	[1/min]
C	= coke concentration	[g-coke/g-cat]
C^0	= initial coke concentration	[g-coke/g-cat]
F	= flow rate of reactant for coke formation	[g-mol/hr]
F_{air}	= flow rate of gas for coke burning	[ml/min]
k	= rate constant of coke burning	[1/min·atm]
P	= total pressure	[atm]
p_{O_2}	= oxygen partial pressure	[atm]
R	= gas constant	[cal/g-mol·°K]
T	= absolute temperature	[°K]
t	= reaction time	[min]
y_i	= mole fraction of the i th component	[—]
W	= weight of catalyst	[g]
α	= order of burning rate with respect to oxygen partial pressure	
β	= order of burning rate with respect to coke concentration	

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