

## REGENERATION KINETICS OF COKED SILICA-ALUMINA CATALYST

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### INTRODUCTION

The regeneration of coked catalysts by means of a gas stream containing a few per cent of oxygen is a well established process. The main problem is to limit the temperature rise caused by the exothermic combustion of the deposited coke so as to prevent sintering of the catalyst. Coke contains appreciable amounts of hydrogen as well as carbon and its composition may be represented as  $\text{CH}_n$ , where  $n$  usually lies between about 0.2 to 1.5.

Earlier studies (1,2,3) considered coke to be composed of carbon only and neglected the hydrogen component. Haldeman and Botty (4), however, studied the deposition and subsequent oxidation of the coke and suggested that the hydrogen-rich part of the coke is attacked preferentially in the first stages of reaction. Following this Massoth (5), proposed a double reaction model with the hydrogen reacting at a retracting interface leaving a carbon rich residue for subsequent oxidation. This concept was extended by Ramachandran et al (6) who were able to predict temperature rises in catalyst particles for the early stages of combustion for varying values of  $n$  in  $\text{CH}_n$ . Hashimoto et al (7) proposed a multiple reaction model based on separate oxidations of hydrogen and carbon in the coke from which rate constants for either reaction could be obtained.

The aim of the present work is to obtain kinetic constants for both the hydrogen and carbon components of the coke as well as determining the variation of the oxidation products  $\text{CO}$ ,  $\text{CO}_2$  and  $\text{H}_2\text{O}$  with temperature.

### EXPERIMENTAL

Materials. The catalyst employed was a commercial silica-13% alumina bead catalyst, crushed and sieved to give 80-100 mesh particles. The catalyst surface area was  $328 \text{ m}^2/\text{g}$ , with a total pore volume of  $0.3 \times 10^{-3} \text{ m}^3/\text{kg}$  and an average pore radius of 2 nm.

Xylene, which was used for coking the catalyst was of standard laboratory grade (low sulphur). Gases employed were obtained from cylinders and dried with silica gel; any traces of carbon dioxide were removed by soda-lime.

Apparatus. Both coking and the subsequent regeneration were carried out in a stainless steel reactor operating under differential conditions. Xylene was vaporised in a heated tube and mixed with preheated nitrogen as carrier before entering the reactor in order to coke the catalyst. The preheater used to heat the nitrogen also served to preheat the oxygen/nitrogen gas mixtures during the regeneration experiments. The stainless steel reactor was heated by a resistance furnace controlled to  $\pm 1^\circ\text{C}$  and the catalyst bed was contained by a stainless steel gauze supported on a 5 mm bore stainless steel tube which contained two thermocouples, the junctions of which were placed within the catalyst bed.

The product gas was analysed for  $\text{CO}$ ,  $\text{CO}_2$  and water vapour. Infra-red analysers were used for analysing the former, while water vapour was determined using a recording dewpoint meter. The range of the dew point meter was from 0-1000 ppm water vapour, which covered the range of interest.

Procedure. The catalyst in the reactor was brought up to a temperature of 400°C and was then coked for an appropriate time using a xylene flow of  $2 \times 10^{-5}$  kg/s and a nitrogen flow of  $5 \times 10^{-6}$  m<sup>3</sup>/s. After coking, the xylene flow was stopped and the reactor heated to the temperature required for regeneration in the nitrogen stream. Approximately 7% of coke was deposited on the catalyst in all the experiments to ensure that measurable amounts of combustion products were obtained. The required oxygen/nitrogen mixture at the appropriate flow rate was then substituted when a steady temperature had been obtained. Water vapour, CO and CO<sub>2</sub> were monitored continuously during the regeneration and after sufficient time had elapsed the final traces of coke were removed by changing the gas mixture to air and raising the reactor temperature to 580°C.

### RESULTS AND DISCUSSION

Preliminary experiments in which the total gas flow rate was varied from 3 to  $10 \times 10^{-6}$  m<sup>3</sup>/s gave only small random variations in rate, indicating that external mass transfer resistances were negligible. Similarly variation of the average catalyst particle size from 20 to 100 mesh showed only slight random variations in the rate constant and therefore intraparticle diffusion could be neglected with the 100 mesh particles used in this work.

An example of the results obtained in a typical regeneration run is shown in Fig. 1. Cumulative amounts of CO<sub>2</sub>, CO and H<sub>2</sub>O released were obtained by measuring the areas under the appropriate curves. Both CO<sub>2</sub> and CO were observed to be present as products in all experiments, the amount of CO<sub>2</sub> always being greater than CO. Water vapour arises from the oxidation of hydrogen in the coke and decays more rapidly than the oxides of carbon. A plot of the mole fractions of elemental carbon and hydrogen in the coke which are converted are plotted against time in Fig. 2., and it can be seen that removal of hydrogen is much more rapid than carbon, in agreement with the results of Massoth<sup>5</sup>. All experiments were conducted at 1.05 bars.

Kinetics of carbon oxidation. Because the carbon constituent of the coke reacts more slowly than the hydrogen constituent, two separate and parallel gas-solid reactions were considered. The overall order of reaction in oxygen (to yield both CO and CO<sub>2</sub> products) was determined by varying the partial pressure of oxygen in the nitrogen stream from .06 to .2 bar. The oxidation rate was measured at each partial pressure value and a log-log plot (Fig. 3) of the oxidation rate against partial pressure of oxygen for two levels of coke conversion gave slopes of 1.05 ( $X_c = 0$ ) and 0.953 ( $X_c = 0.5$ ). These are sufficiently close to unity to regard the reaction in oxygen as being first order, in agreement with most previous work<sup>1,2</sup>. The order of reaction in oxygen for individual production of CO<sub>2</sub> and CO was also found to be unity.

The order of reaction with respect to deposited carbon was determined by fitting the experimental data to standard kinetic expressions. The data were found to give a best fit to a first order dependency in carbon. Therefore, the rate equation for the reaction may be written as

$$-\frac{dC_c}{dt} = k_c C_{Ag} C_c \quad (1)$$

where  $C_{Ag}$  is the gas phase concentration of oxygen,  $C_c$  is the concentration of carbon and  $k_c$  is the overall second order rate constant for the reaction of carbon. Since the oxygen is in excess, its concentration will be only very slightly diminished in a differential reactor, so that the concentration  $C_{Ag}$  may be considered as constant and lumped with the rate constant. Therefore eqn. (1) may be written as a pseudo first order reaction

$$-\frac{dC_C}{dt} = (k_C C_{A_g}) \quad (2)$$

Integrating

$$-\ln(1 - X_C) = (k_C C_{A_g}) t \quad (4)$$

and a plot of  $-\ln(1 - X_C)$  against time should be a straight line with a negative slope equal to  $k_C C_{A_g}$ . Plots for experimental data at various temperatures and a constant oxygen partial pressure of 0.21 bar are given in Fig. 4 and good straight line fits for the data were obtained. Thus the reaction is first order in the concentration of deposited carbon.

The temperature dependence of the carbon oxidation was determined using first order kinetic expressions with respect to both carbon and oxygen. An Arrhenius plot of the data gave a value of  $151,640 \pm 9900$  kJ/kmol for the activation energy. This compares with values of 156,000 kJ/kmol obtained by Hughes & Shettigar (2) and 156,200 kJ/kmol obtained by Hashimoto et al (7) from their analysis of a model based on experimental measurements after all the hydrogen in the coke has been consumed. The comparable value of the activation energy observed in this work plus the absence of any discernable curvature in the Arrhenius plot confirms that the kinetic results were obtained under conditions of chemical control.

The overall rate constant for the oxidation of carbon may therefore be written as

$$k_C = \frac{1.914 \times 10^8}{C_{A_g}} \exp \left[ \frac{151,640 \pm 9900}{RT} \right]$$

Kinetics of hydrogen oxidation. The order of reaction in oxygen was determined by varying the partial pressure of this gas in the nitrogen stream from 0.07 to 0.21 bar. A log-log plot of the hydrogen oxidation rate against oxygen partial pressure for two values of the fraction hydrogen conversion is shown in fig. 5. The slopes of the lines were close to unity (0.93 at  $X_H = 0$ , 0.98 at  $X_H = 0.5$ ) confirming the first order kinetic behaviour for oxygen.

An integral method of analysis of the data was attempted in order to determine the order of reaction with respect to the hydrogen component of the coke. No correlation was found over the complete range of experimental points for zero order, first order or second order kinetics. Only when the first 10 minutes of reaction were considered, was a reasonable fit obtained to any of these integral rate expressions.

It appeared therefore that the reaction was not kinetically elementary and could not be

satisfactorily represented by any of the simple rate expressions produced by the integral method of analysis. The differential method of analysing the data was therefore adopted to obtain an empirical order of reaction for the hydrogen in the coke. The order of reaction in hydrogen, at different temperatures in the range 430°C to 550°C were found by plotting the rates ( $-dC_H/dt$ ) against the corresponding hydrogen concentration values ( $C_H$ ) on a log-log scale (Fig. 6). The slope of the lines represents the order of reaction in hydrogen at different temperatures. The orders obtained varied from 1.57 to 1.86 and showed no trend with respect to temperature. This result indicates that the apparent kinetics of the hydrogen oxidation reaction is more complex than that of carbon.

The temperature dependence of the hydrogen oxidation was obtained by first obtaining values of the rate constant at each temperature from the intercepts of the lines in Fig. 6. An Arrhenius plot gave an activation energy for the hydrogen oxidation of  $97,800 \pm 8000$  kJ/kmol, a value significantly less than that for carbon oxidation, and confirming the easier removal of hydrogen from the coke.

The lower value of the activation energy for hydrogen oxidation in the coke has been confirmed by the results of Hashimoto et al<sup>7</sup>. However, they found the hydrogen activation energy to be 140,300 kJ/kmol compared with their value for carbon oxidation of 156,200 kJ/kmol, and thus the effect of early hydrogen oxidation would be less pronounced than that obtained from our results.

It is of some interest to compare the variation of the  $CO/CO_2$  and the  $H/C$  ratios with temperature. Some results given in Table 1 for an oxygen partial pressure of 0.21 bars and a gas flow rate of  $6.0 \times 10^{-4}$  m<sup>3</sup>/min. It can be seen that the  $CO/CO_2$  ratio increases with temperature from 0.31 at 430°C to 0.50 at 550°C. This is in general agreement with previous investigations. The hydrogen to carbon ratio, however, changes only slightly decreasing from 0.55 at 430°C to 0.49 at 550°C. This indicates that the hydrogen content is important at all effective regeneration temperatures and must be considered in all regeneration procedures.

The final expression obtained for the rate constant for the oxidation of the hydrogen in the coke in the present work was

$$k_H = 3.56 \times 10^5 \exp \left[ \frac{96,140 \pm 8,000}{RT} \right]$$

#### CONCLUSIONS

The kinetics of both carbon and oxidation of coke deposited on a silica-alumina catalyst from

xylene vapour have been investigated. The effects of oxygen partial pressure, temperature and gas velocity have been evaluated. The reaction products consisted of carbon dioxide, carbon monoxide, water vapour and unreacted regeneration gas. It was observed that the carbon associated with the coke reacted more slowly than the hydrogen fraction in the coke. Hence the water vapour arising from the hydrogen oxidation decays more rapidly than the carbon oxides concentrations. Consequently two separate and parallel gas-solid reactions have to be considered. Both carbon monoxide and carbon dioxide are primary products of carbon oxidation and were observed to form throughout the range of oxidation conditions. Carbon dioxide was also the major product but the CO/CO<sub>2</sub> ratio increased with reaction temperature. First order dependency on oxygen concentration was observed for both carbon and hydrogen. The order of reaction with respect to the carbon in the coke was unity but the order in hydrogen was not elementary indicating a complex mechanism. The activation energy for hydrogen was much less than that for carbon, confirming the initial nature of hydrogen oxidation.

#### References

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**TABLE 1. EFFECT OF TEMPERATURE ON PRODUCT COMPOSITIONS**

Partial pressure of oxygen =  $0.21 \times 10^5 \text{ N/m}^2$

Gas flow rate =  $6.0 \times 10^{-4} \text{ m}^3/\text{Min}$

Coke weight 1%	Weight of the sample (g)	TEMP. °C	CO CO <sub>2</sub>	H C
7.2	0.301	430	0.31	0.55
7.2	0.370	460	0.33	0.56
7.2	0.310	490	0.38	0.55
7.6	0.350	520	0.45	0.49
7.6	0.340	550	0.50	0.49

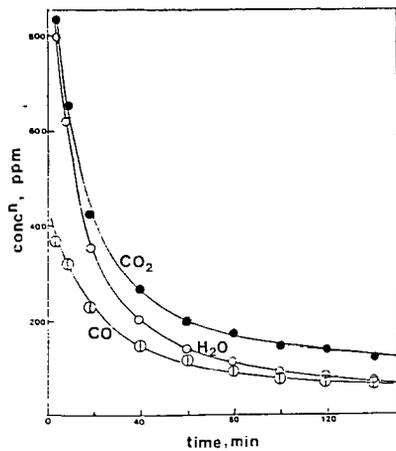


Fig. 1. Typical oxidation product concentrations as a function of time.

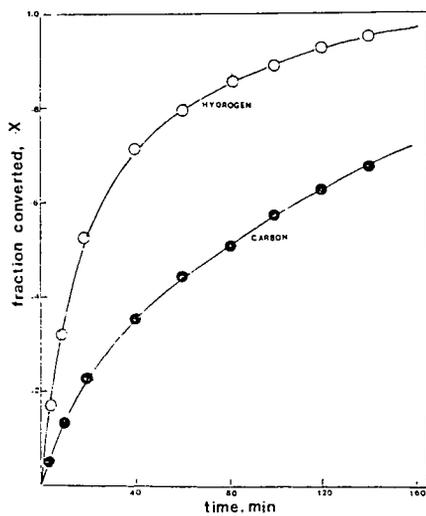


Fig. 2. Carbon and hydrogen conversions (data as for Fig. 1).

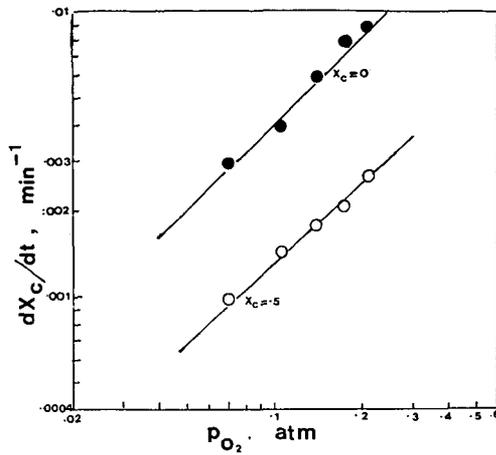


Fig. 3. Effect of oxygen partial pressure on carbon burning rate.

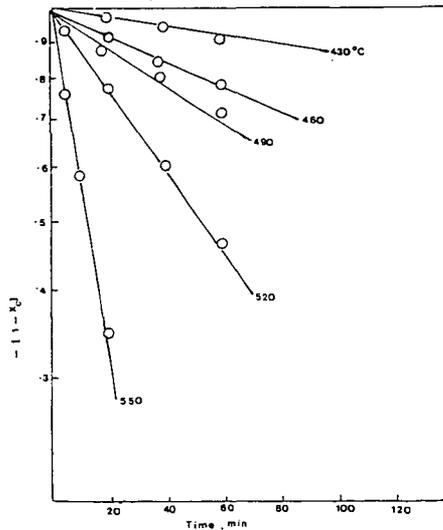


Fig. 4. First order correlation for carbon oxidation.

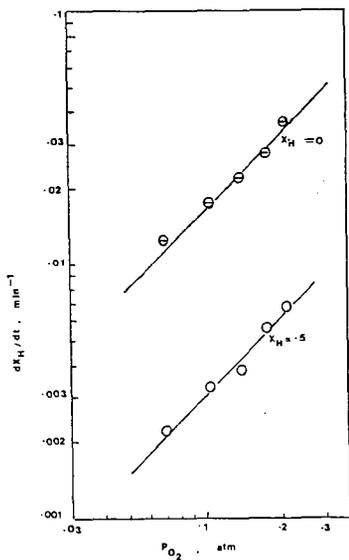


Fig. 5. Effect of oxygen partial pressure on hydrogen burning rate.

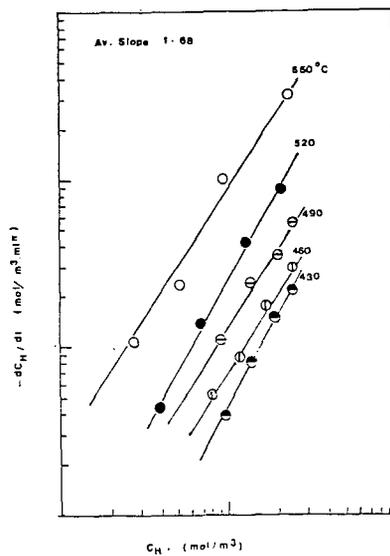


Fig. 6. Differential analysis plot for hydrogen oxidation.