CATALYSIS OF WATER VAPOUR GASIFICATION OF COKE BY IRON

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Introduction

Gasification of carbonaceous materials like coal or coke with pure water vapour offers a possibility for producing clean fuel gases, synthesis or reduction gases.
As reaction rate is rather small the use of catalysts becomes of interest. Alkali metals and earth alkali metals are known as being potential catalysts (G. WOYKE, 1975). Among the transition metals iron has shown to be very effective (D.McKEE, 1974), provided that is exists in reduced metallic state under reaction conditions. It was chosen for this study, because iron-sulfate or -chloride are available in waste acids of chemical industry. The coke used was a calcined, needle-like petroleum coke of low ash (o,o3 wt-%) and low sulfur (o,46 wt-%).

Experimental

The coke particles, one to two mm in diameter, were vacuum impregnated with iron-sulfate solutions of different concentrations and then vacuum dried at $50^{\circ}C$. Iron-sulfate was present as tetrahydrate. Iron concentrations were in the range 0,05 up to 1,8 wt-%. Electron microprobe analysis showed homogeneous distribution of iron on the walls of the pores.

The reaction was studied in a fixed bed reactor at temperatures between 890 and $1000^{\circ}C$ using N_2/H_2O-gas mixtures and one bar total pressure. Besides temperature and partial pressure the influence of time, feed rate, bed depth and catalyst concentration on coke and water vapour conversion were investigated. Coke conversion was in the range up to 50% and water vapour conversion up to 100%.

Results

In the following, some selected results will be given in order to demonstrate the extent and the limits of iron catalysis. The rate of coke gasification was measured under various conditions up to 50% and found to be constant, i.e. independent of burn-off. Fig. 1 shows the corresponding constant water vapour conversion. Fig. 2 gives the BET-surface increasing linearly with time. Variations of water vapour partial pressure and feed rate had the most dramatic effect on gasification rate, as shown in fig.3 and 4, respectively. Stationary water vapour conversion decreases with increasing partial pressure and increasing feed rate in two distinct ranges with different intensity. In any case the rate of the catalized reaction is higher than that with pure coke.

Fig. 5 shows the reaction rate for various catalyst concentrations. Maximum rates are already obtained with low iron concentrations. Temperature dependence is finally given in Fig. 6 by an ARRHENIUS plot. The starting temperature of catalysis is around $900^{\circ}C$. The apparent activation energy for the catalyzed reaction varies between 10 and 20 kcal/mol as compared to 43 kcal/mol for the uncatalyzed coke gasification.

Discussion

Gasification rates,which are constant and independent of burn-off, although BET-surface increases strongly , seem to be surprising. De facto, it can be suggested, that the reaction only occurs at carbon surfaces covered with catalyst. Electron microprobe analysis showing agglomeration of iron with burn-off and combined with the observation, that increasing catalyst concentrations beyond o,5% don't accelerate the reaction, confirm this suggestion.

The two ranges found with increasing water vapour pressure and feed rate show that the reaction is well catalyzed by metallic iron and less catalyzed by iron oxide.

The temperature range in which catalysis starts coincides with the transition of α -iron to ß-iron at $910^{\circ}C$. It can be the supposed that the higher carbon solubility of ß-iron is of influence on the catalysis by iron.

Literature

G. WOYKE, "Zur katalytischen Wasserdampf-vergasung von Kohle bei hohen Drücken", Diss. Universität Erlangen, 1975
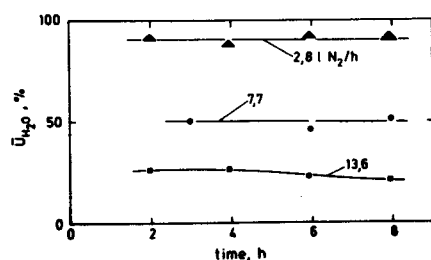
D. McKEE, Carbon 12 (1974), 453

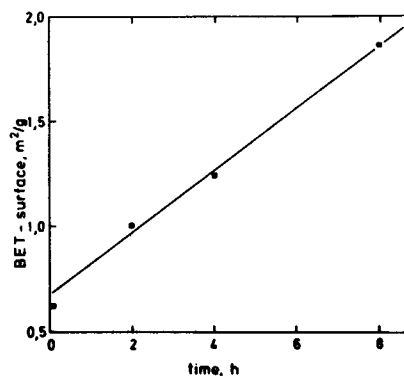Fig.1-Water vapour conversion with time at 935°C; catalyst concentration 1,8 wt-%; $p_{H_2O} = 0,055$ bar

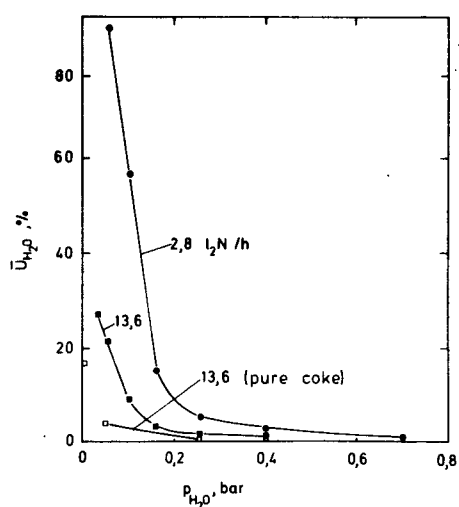Fig.2-BET-surface with reaction time at 935°C; catalyst concentration 1,8 wt-%; $p_{H_2O} = 0,055$ bar

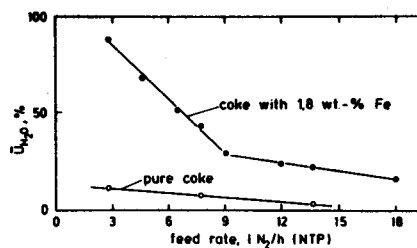Fig.3-Water vapour conversion with partial pressure at 935°C; catalyst concentration 0 and 1,8 wt-%

Fig.4-Water vapour conversion with feed rate at 935°C; catalyst concentration 0 and 1,8 wt-% $p_{H_2O} = 0,055$ bar
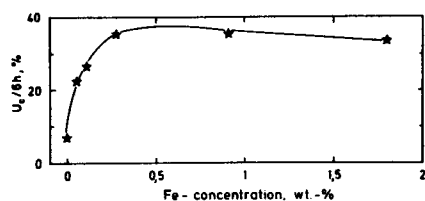

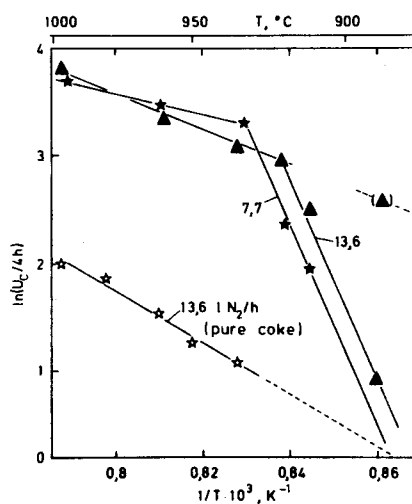Fig.5-Coke conversion with catalyst concentration at 935°C; $p_{H_2O} = 0,055$ bar

Fig.6-Arrhenius-plot, catalyst concentration 0 and 1,8 wt-%; $p_{H_2O} = 0,055$ bar

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