

Kinetics of Carbon Formation Over Iron Foils from CO and CO/He Mixtures

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Abstract

The kinetics of carbon and CO_2 formation from CO and CO diluted with He has been studied experimentally on iron foils. Studies were performed using a tubular flow microbalance reactor, at atmospheric pressure, operating in the range of 250 to 450°C and 3 to 100% CO. The dependence of the rate on the CO partial pressure follows a zero order kinetics in the range studied. The activation energy for carbon formation is 31 Kcal/gmol. These results are consistent with a reaction mechanism in which a rapid CO adsorption and dissociation step is followed by a slower, rate determining carbon formation step.

Introduction

Catalytic carbon formation from gases containing CO is an important reaction from an academic and industrial point of view. Carbon monoxide can decompose over different metals to originate an active type of carbon. This is thought to be a possible path for methanation and Fischer-Tropsch reactions. Also, the carbon deposited from CO can deactivate and disintegrate catalyst particles, and plug reactor tubes. In order to avoid these problems, knowledge of the factors affecting carbon formation is essential.

Studies performed in the 400 to 700°C temperature range show that carbon deposits over Fe catalysts in the form of filaments, whose crystallinity depends on the temperature of formation¹⁻³. Most of the filaments contain an active metal nuclei of about the same diameter as the filament where they are. The active catalyst site for the Boudouart reaction has been claimed to be either an Fe oxide⁴ or an Fe carbide⁵.

Experimental

All kinetic experiments were performed in the thermogravimetric flow system described previously⁶. The catalyst samples were suspended from the balance and reduced

in hydrogen at 450°C for 10 to 12 hours. After flushing with He, reactants were admitted to the reactor and weight changes of the sample were continuously recorded. Gas composition of reactants and products was analyzed by gas chromatography. Metal surface areas were determined by measuring the conversion of the ethylene hydrogenation reaction, previously calibrated with known metal surface areas, at pre-established conditions.

Poly-crystalline iron foils were obtained from Johnson Matthey Chemicals Company. Foils were provided in the form of 10x10 cm sheets, 0.1 mm thick and a purity of 99.99%. Foils of geometric areas from 1 to 10 cm² were cut from the original sheets.

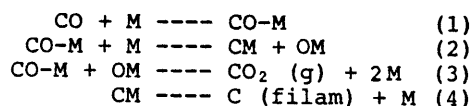
Results

The CO decomposition over iron foils was characterized by constant rates of carbon deposition for long periods of time (3 to 4 days). Induction periods for foils were in the order of 20 to 30 hours. The effect of temperature, CO partial pressure and flow-rate was studied for iron foils of different geometric areas. The rate of carbon formation was proportional to the geometric area of the foils. The order of reaction with respect to CO partial pressure was near zero. The activation energy for

the rate of carbon and carbon dioxide formation was 31 Kcal/gmol. Carbon filaments were observed on the foil, allowing for the reaction to proceed at a constant rate. The fragility of the filaments permitted only a limited growth. Deactivation of the catalytic performance of the foils was not observed.

Discussion

The partial pressure of CO has no effect on the rates of carbon and CO₂ formation. This can be described by a surface mechanism in which the CO adsorption and dis-association on the catalytic surface is fast (and reaches equilibrium) and the filament growing step is rate limiting. The following sequence of reactions can be proposed:



Reactions (1) to (3) can be considered to be in quasi-equilibrium, being the filament growth the rate determining step. Assuming that CO adsorbs strongly on the metal sites, the reaction will be zero order with respect to CO. The overall reaction rate will be given by reaction (4) above.

The formation rate of the filament has been related to the diffusion of carbon carbon through a metal crystallite⁶. The diffusion cleans the surface, so that the reaction can continue. From our experiments, the rate of reaction is:

$$r = k \exp (31,500/RT) \text{ (mg C/cm}^2 \text{ min)}$$

The activation energy for the diffusion

of carbon on iron has been reported in the range 18 to 34 Kcal/gmole. Since the activation energy observed experimentally is within this range, the above mechanism is a plausible explanation of the experimental results.

Conclusions

1. Carbon formation on an iron catalyst goes through an induction period prior to carbon filament growth when iron foils are treated with CO and CO/He mixtures.

2. The rate of carbon deposition can be approximated by a zero order kinetic equation with respect to CO in the range of partial pressures studied. The rate of carbon formation is limited by the growth of the filaments.

References

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