Catalysis Letters 45 (1997) 215–219

The carburization kinetics of iron-based Fischer–Tropsch synthesis catalysts

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Received 7 November 1996; accepted 18 March 1997

The carburization kinetics of iron supported by silica gel was studied in Fischer–Tropsch synthesis. The effect of several variables (content of K and Cu promoters and partial pressure of CO and H_2) on the rate of carburization was examined. It was found that the maximum of carburization rate coincides with a minimum of the hydrocarbons production rate.

Keywords: iron/silica, Fischer–Tropsch, in situ magnetisation, kinetics of the carburization, promoters

1. Introduction

The influence of carbide phases on the performance of iron-based Fischer–Tropsch (FT) synthesis catalysts has been recognized for a long time. Characterisation techniques such as Mössbauer spectroscopy (MES) [1], X-ray diffraction (XRD) [2], and temperature-programmed gravimetry [3] have been used to study changes in the bulk phase of iron catalysts. However, although many authors have given semi-quantitative descriptions of the carburization during the synthesis, no satisfactory theoretical model for this process has been proposed yet.

In this in situ study magnetisation measurements were made to investigate the kinetics of the carburization in the case of iron supported by silica gel. In particular, the effects of several variables (content of K and Cu promoters and partial pressure of CO and H_2) on the rate of carburization were examined.

2. Experimental

2.1. Materials

Catalysts were prepared by impregnation of silica gel (surface area 340 m^2/g, average pore diameter 14 nm) with aqueous solution of $Fe(NO_3)_3$. After impregnation the samples were dried in air at 373 K for 7 h followed by calcination in air at 773 K for 6 h. K and Cu promoters were added by a second impregnation of the calcined samples with aqueous solutions of K_2CO_3 or $Cu(NO_3)_2$. Iron content was found to be 13 wt% in all cases, while potassium and copper loading was about 2 wt%.

Catalysts were reduced in the microreactor of a magnetometer by hydrogen at 723 K for 1 h and cooled in hydrogen flow to the temperature of experiment. CO of 99.99% purity and H_2 of 99.999% purity were used. Gases were fed into the reactor through a deoxidation unit and a molecular sieve trap. Carbon monoxide was additionally purified in an active carbon column installed before the reactor to avoid contamination by iron carbonyls.

2.2. Measurements of carburization degree

There are many reasons to consider the magnetic method as one of the most well-suited methods for studies of carburization processes in iron-containing catalysts, for it allows exclusion of the influence of a forming surface carbon layer from the consideration.

The vibrational magnetometer [4] has been designed exclusively for the studies of chemical transformations of ferromagnetic phases. The magnetometer has a relatively high sensitivity allowing the study of samples with magnetic susceptibility about $\chi = 10^{-5}$ mol^{-1}. The design of the magnetometer allows recording of the curves of sample magnetisation during programmed heating or under isothermal conditions as time–magnetisation or/and temperature–magnetisation plots. The temperature is maintained within ±0.3 K range.

The magnetometer is fitted with a continuous-flow quartz microreactor; the latter is equipped with a built-in Pt–PtRh thermocouple. A catalyst sample (about 10^{-2} g) is placed between two porous quartz membranes, permeable to gases and fixed inside the reactor. The reactor is connected rigidly to the vibrator by a non-magnetic rod. Vibrator frequency, adjusted by an oscillator, was 33 Hz. Field intensity in the gap of an electromagnet was 6.3 kOe. Data handling was carried out using an on-line computer. Special programs, allowing the representation of experimental data directly as time–conversion plots, have been written. The degree of iron conversion to carbides is defined as

$$\alpha(t) = \frac{J_0^T - J_c^T(t)}{J_0^T - J_c^T(\infty)}, \tag{1}$$

where J_0^T denotes the magnetisation of a sample before carburization, $J_c^T(t)$ the magnetisation at time t, $J_c^T(\infty)$ the magnetisation at the end of carburization, and T the temperature. It is easy to show that the thus defined degree of iron conversion does not depend on the composition of the forming carbide mixture, and the latter has not been analyzed in our experiments.

Table 1
Characterisation of the catalysts

N	Catalyst	Fe content [a] (wt%)	S_{Fe} (m^2/g)	d_{chem} [b] (nm)	$d_{X\text{-ray}}$ [c] (nm)	ε, 10^6
1	Fe/SiO_2	11 ± 0.1	6 ± 0.5	15 ± 2	15 ± 1	3.4 ± 0.1
2	$K/Fe/SiO_2$	10 ± 0.1	2 ± 0.2	40 ± 5	18 ± 1	3.4 ± 0.1
3	$Cu/Fe/SiO_2$	12 ± 0.1	8 ± 1	11 ± 1	13 ± 0.5	4 ± 0.1

[a] Content of Fe^0 is determined by magnetic method after reduction.

[b] d_{chem} is determined from surface area S_{Fe} and iron content as $d_{chem} = wt\%Fe^0 \times 76.2/S_{Fe}$.

[c] $d_{X\text{-ray}}$ is determined from X-ray data.

2.3. Measurements of catalytic activity in CO/H_2 synthesis

Catalytic experiments were performed at 1 atm, 473–543 K. The gas flow rate was 70 cm^3/min in all experiments. The reaction mixture at the outlet of the reactor was detected by a flame ionisation detector in order to provide satisfactory detection in short time intervals. Thus, the overall yield of hydrocarbons was measured. Since CO conversion to hydrocarbons did not exceed 1% in these experiments and methane was the main reaction product, the flame ionisation detector was calibrated on methane. It was satisfactory for our main goal, the investigation of carburization.

2.4. Iron surface area measurements

The experiment involving temperature-programmed desorption (TPD) was performed with the same apparatus and previously used procedures [5]. Samples of the catalysts were reduced by hydrogen at 723 K for 1 h and cooled to room temperature in H_2. After that, hydrogen was switched to argon flowing at the rate 20 cm^3/min, and samples were heated at 0.3 K/s. A thermal conductivity detector was used for hydrogen desorption studies. The surface area of iron (S_{Fe}, m^2/g) was deduced from TPD spectra [5]. Metal crystallite size calculations were based on the assumption that iron is present as spherical particles of uniform size.

2.5. X-ray diffraction

X-ray diffraction studies were conducted on a DRON X-ray diffractometer. The source of radiation was Co K_α. Analysis of the line broadening was based on Fourier analysis of diffraction profiles [6]. Average crystallite size and strain effects were also calculated by this method.

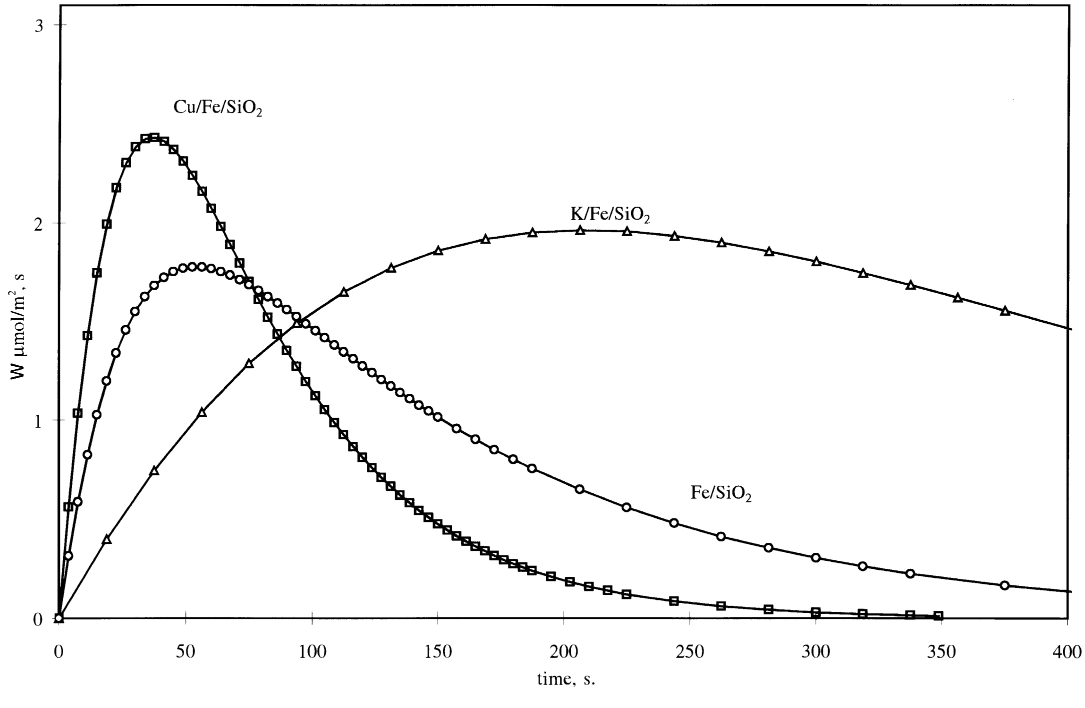

Figure 1. Time dependence of carbide formation rate for Fe/SiO_2, $K/Fe/SiO_2$, and $Cu/Fe/SiO_2$.

3. Results and discussion

Composition, iron content after reduction, iron surface area, average crystallite size (obtained from chemisorption and X-ray data) and strain effects (ε) for each catalyst are given in table 1.

It has been noted previously [7] that the presence of potassium decreases hydrogen adsorption. A comparison between d_{chem} and $d_{\text{X-ray}}$ allows suggesting the decoration of iron particles by K_2SiO_3 takes place. In the presence of K the extent of reduction decreases in comparison with that for unpromoted Fe/SiO_2. If Cu is used as promoter, the increase in the degree of reduction is observed along with the increase of the strain effects.

Figure 1 illustrates the changes in the rate of carbide formation for these catalysts. The rate of carburization is defined as

$$W = \frac{n}{S}\frac{\mathrm{d}\alpha}{\mathrm{d}t}, \qquad (2)$$

where n is the concentration of α-Fe (μmol/g); S is the surface area of iron (m^2/g), and α is the iron conversion to carbides. It is obvious that promotion has an effect on both the maximum of carburization rate (W_m) and the time spot of this maximum (τ).

The analysis of kinetic data has been made in the framework of the topochemical model [8]. It is supposed that carbide nuclei growth is the rate determining step.

In a previous investigation [9] we have shown that the kinetics of carburization can be described by the equation:

$$W = k_0 z_0 (1 - \exp\{-k_2 t\})(1 - \alpha), \qquad (3)$$

where k_0 is the constant of the nuclei growth rate, k_2 is the constant of the nucleation rate, and z_0 is the quantity of the nucleation centers.

The rate of nucleation is defined as the number of stable carbide domains formed at a time unit on a surface unit of the iron particle. The surface defects of the iron particles (dislocations or/and impurities) serve as the nucleation centers.

It seems likely that the rate of nuclei growth is determined by the concentration of defects in the bulk of the iron particles. The constants ($k_1 = k_0 z_0$ and k_2) can be found by using standard non-linear regression procedures [10].

The presence of potassium causes the decrease of k_2 resulting in the increase of τ, as seen from figure 1. At the same time k_1 and W_m remain unchanged. In contrast, the presence of Cu leads to the increase of k_2 as well as k_1 and W_m. It means that potassium affects the process of nucleation, but does not affect the carbide nuclei growth. In the presence of copper both the rate of nucleation and the rate of nuclei growth increase.

It has been shown by Jung and Thomson [2] that the composition of the synthesis gas affects the total carburization rate. Iron particles carburized at a much slower rate when the ratio of H_2/CO was higher.

Figure 2 shows the effect of CO partial pressure (P_{CO}) on the constant of the nuclei growth rate. It can be seen that the constant k_1 does not depend on P_{CO}. Similarly, k_1 is independent of P_{H_2}. These observations lead to the suggestion that the nuclei growth rate constant is independent of both CO and H_2 pressure, which proves the validity of our theoretical model. Because the

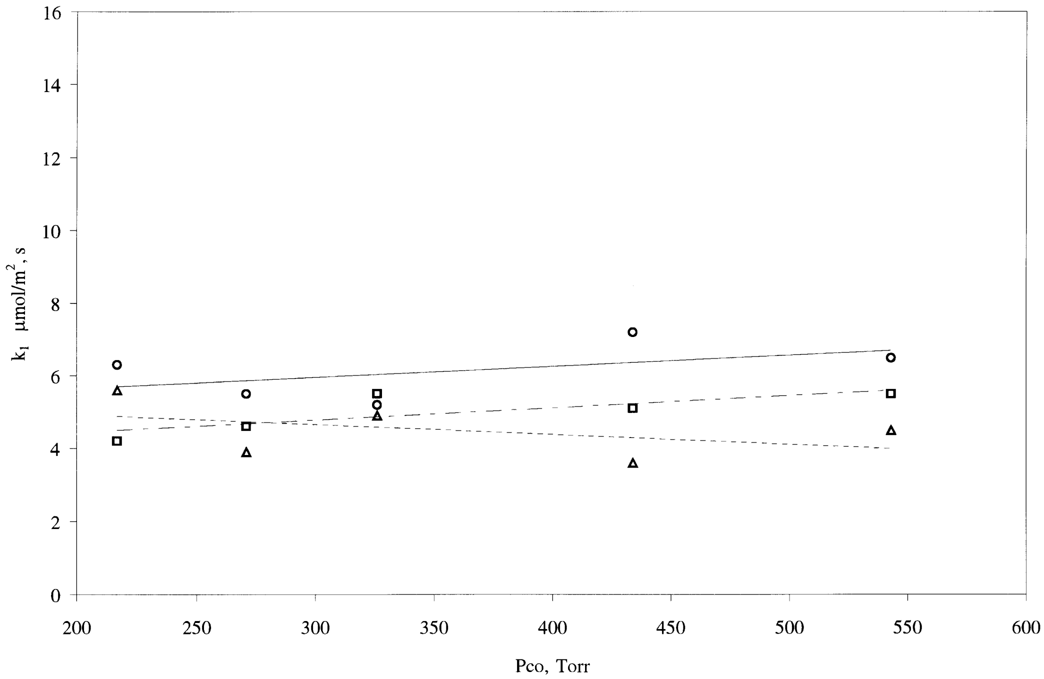

Figure 2. The effect of CO partial pressure (P_{CO}) on the nuclei growth rate constant.

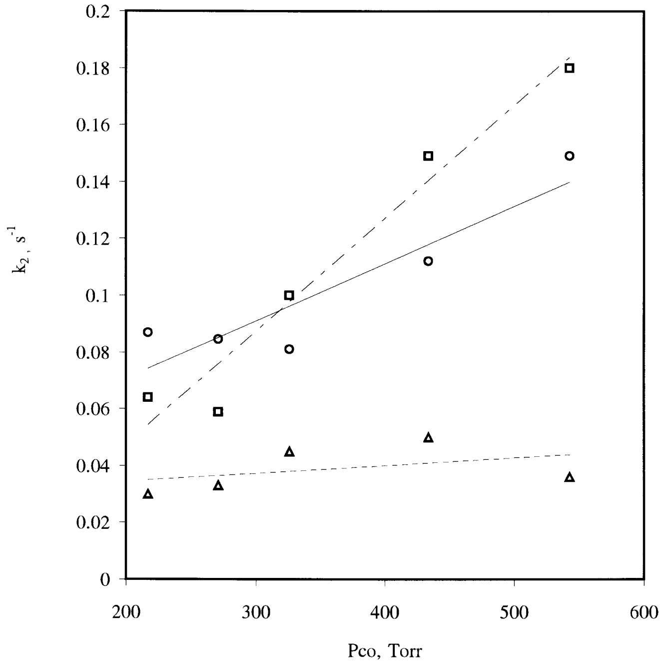

Figure 3. The effect of CO partial pressure (P_{CO}) on the nucleation rate constant.

nuclei growth takes place in the bulk catalyst, the partial pressures of reactants should not affect the nuclei growth rate.

However, P_{H_2} and P_{CO} do influence the nucleation rate constant. Such dependencies are illustrated by figures 3 and 4. The nucleation rate constant for Fe/SiO_2 and Cu/Fe/SiO_2 increases with the increase of P_{CO} (figure 3), and decreases with the increase of P_{H_2} (figure 4). On the other hand, the nucleation rate constant of K/Fe/SiO_2 is unaffected by the partial pressures of CO and H_2 within the experimental error.

We suppose that in the case of Fe/SiO_2 and Cu/Fe/SiO_2 competitive adsorption of CO and H_2 on iron takes place, as indicated by the decrease of the nucleation rate constant with the increase of P_{H_2}.

As the authors [11,12] have shown previously, promo-

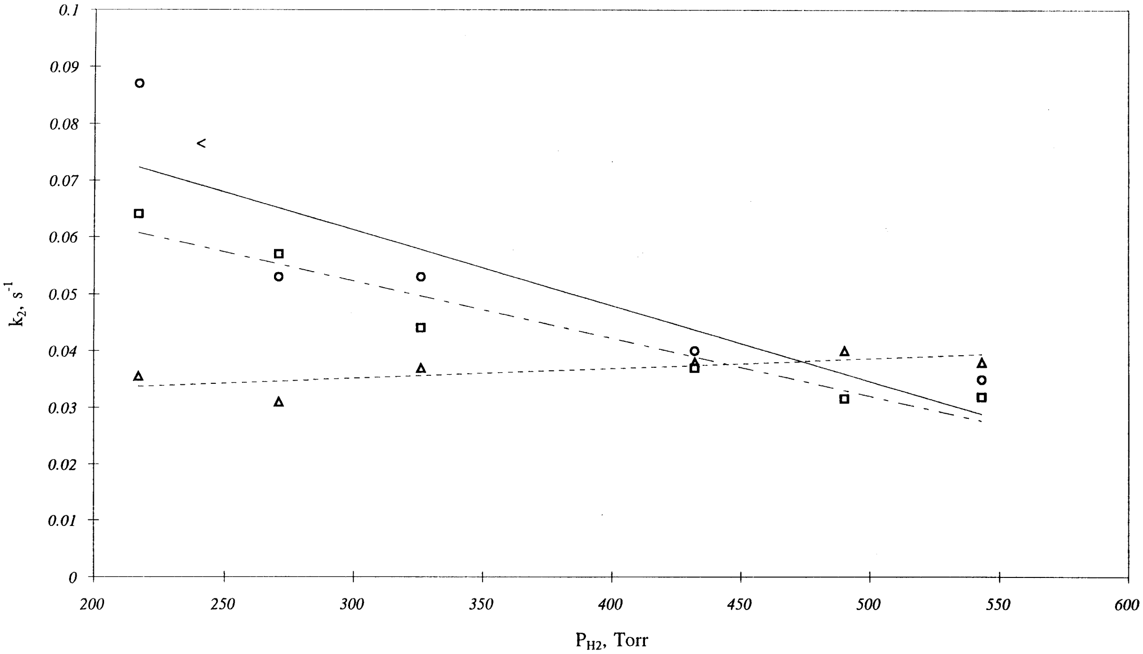

Figure 4. The effect of H_2 partial pressure (P_{H_2}) on the nucleation rate constant.

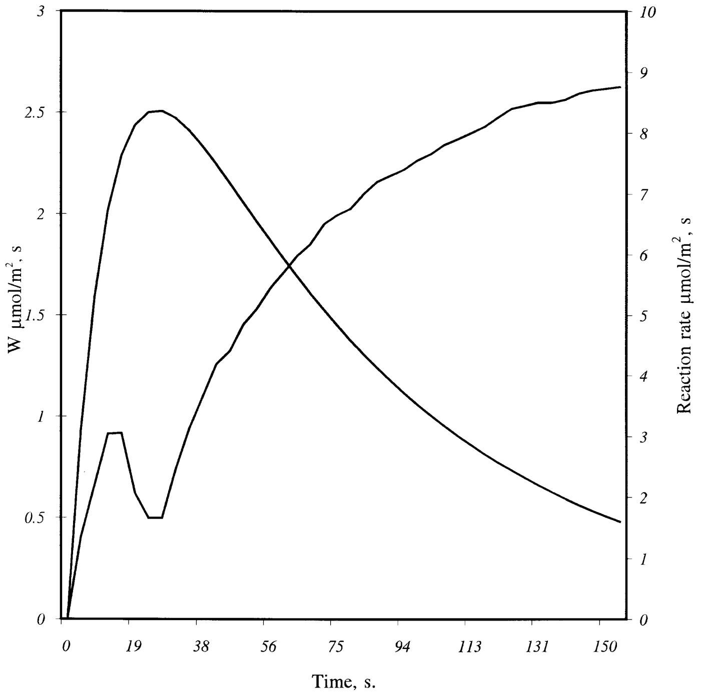

Figure 5. The time dependence of the carburization rate and catalytic activity of the reduced Fe/SiO_2 catalyst.

tion of transition metals by alkali metal oxides inhibits the adsorption of H_2 and reduces the mobility of adsorbed hydrogen. It causes the decrease of the nucleation rate because the removal of surface oxygen is a necessary condition of nucleation. Furthermore, it is known that in the absence of H_2 the carburization rate is substantially smaller [3].

Since conversion of CO was, as a rule, about 1% or less, our microreactor can be regarded as a differential reactor in which heat and mass transfer effects are negligible. Because of the low conversion, only hydrocarbons up to C_2 were produced in measurable amounts. In order to relate the catalytic activity to the changes in the bulk catalyst, only the formation rate of the total amount of hydrocarbons was used as a measure of the catalytic activity.

A typical curve of catalytic activity of reduced Fe/SiO_2 catalyst is shown in figure 5 along with the time dependence of the carburization rate. During the first 30 s of reaction the hydrocarbons formation rate increases from zero to a maximum, then decreases to a minimum at $t = 28$ s. Similar observations were made by Bianchi et al. [13].

It can be seen that the maximum of the carburization rate coincides with a minimum of the hydrocarbons production rate.

We have observed that any changes in the conditions of FT synthesis that caused time shifts of the carburization rate maximum also led to corresponding time shifts of the catalytic activity minimum. From this fact we can conclude that the kinetics of the carburization is connected with the catalytic activity in FT synthesis. It seems that some surface intermediate serves as the one and only source of carbides and hydrocarbons.

Acknowledgement

The author wishes to thank Dr. G.P. Murav'eva for X-ray diffraction studies, Professor V.V. Lunin for his support of this work and I.N. Zavalishin for assistance.

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