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Kinetic investigations of CO disproportionation on Fe catalyst

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On the surface of a Fe catalyst carbon monoxide disproportionates into C (carbon black) and CO_2. Kinetic parameters of this reaction (reaction rate constant, order, and occupancy of catalyst surface) were established in the range of temperatures 430–490 °C. At the beginning of the process in all cases an induction period was observed. Under definite conditions the process develops with oscillating dynamics. Induction period and oscillations indicate an autocatalytical nature of the process. The distribution of the Fe catalyst in the profile of the reaction zone (in the bulk of carbon black and on the surface of small crystals) was investigated.

KEY WORDS: carbon monoxide; Fe catalyst; disproportionation; autocatalysis; oscillations; carbon black

1. Introduction

Disproportionation of CO on a Fe catalyst (known as Boudouard's reaction) is widely used for the production of graphitized carbon black (CB). This reaction occurs as solid state synthesis on the surface of a solid state catalyst. Synthesis conditions allow control of size, shape, electrical conductivity, and other parameters of small CB crystals in the bulk [1]. Boudouard's reaction is very sensitive to external conditions, such as temperature, reagents purity and concentrations, surface state of the catalyst, etc. In literature it is possible to find some models explaining the mechanism of CO disproportionation on the catalyst surface [2]. Nevertheless, ideas explaining the oscillations of the process as well as the transformations of the Fe catalyst in Boudouard's reaction are scarce.

2. Experimental

Graphitized CB was synthesized from its CO precursor using finely dispersed carbonyl Fe as a catalyst. The experimental arrangement for synthesis of the graphitized CB and investigation of the reaction kinetics is shown in figure 1. Reaction occurs in tube 1 (12 mm in diameter) on the Fe catalyst placed in ceramic boat pan 2 (dimensions 3 × 8 × 19 mm). In the reaction zone the constant temperature is maintained using thermoisolated tube furnace 3 which is linked up to thermoregulating device 4 via platinum–platinorhodium thermocouple 5. Carbon monoxide is produced in flask 6 from formic acid:

$$\mathrm{HCOOH} \xrightarrow{H_2SO_4} \mathrm{CO}\uparrow + \mathrm{H_2O}\uparrow \qquad (1)$$

Formic acid is dropped from separatory funnel 7 into hot sulphuric acid warmed by heater 8. Steam produced in the reaction is condensed in reflux condenser 9 and directed into calibrated volumetric tube 10. The carbon monoxide stream is purified by bubbling through KOH solution 11. The gas stream after reaction is analysed using flow conductometric cell 12 with dropping 0.1 mol/l NH_3 solution 13. The CO_2 amount produced in Boudouard's reaction is registered by recorder 14.

The conductometric cel was calibrated in the range of different dropping rates for NH_3 solution. The indicator reaction causing difference in electric conductivity was

$$\mathrm{CO_{2(aq)}} + 2\mathrm{NH_{3(aq)}} + \mathrm{H_2O} \rightarrow \mathrm{CO^{2-}_{3(aq)}} + 2\mathrm{NH^{+}_{4(aq)}} \qquad (2)$$

Calibration curves for the conductometric cell are presented in figure 2. CO flow rate was regulated maintaining a constant formic acid dropping rate. The amount of carbon monoxide produced at every current moment was determined from the volume of H_2O condensed in the volumetric flask.

During Boudouard's reaction synthesized CB together with Fe catalyst is accumulated in the reaction zone. Distribution of the Fe catalyst in the profile of that zone (figure 3) was investigated. For that purpose two sorts of analyses were carried out: determination of Fe in the bulk of CB and on the surface of small CB crystals. Determination in the bulk was carried out by means of a gravimetric method after burning of analyte [3]. Fe on the surface was determined using a photometric method with *o*-phenanthroline [4]. The sample

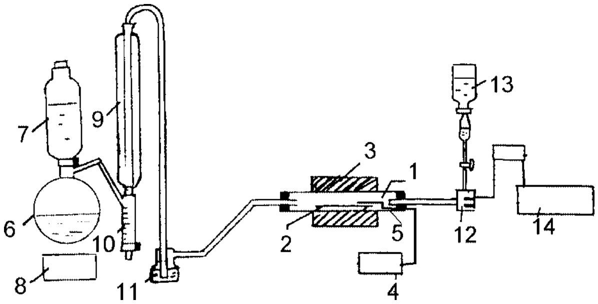

Figure 1. Experimental arrangement for synthesis of the graphitized CB and investigation of reaction kinetics.

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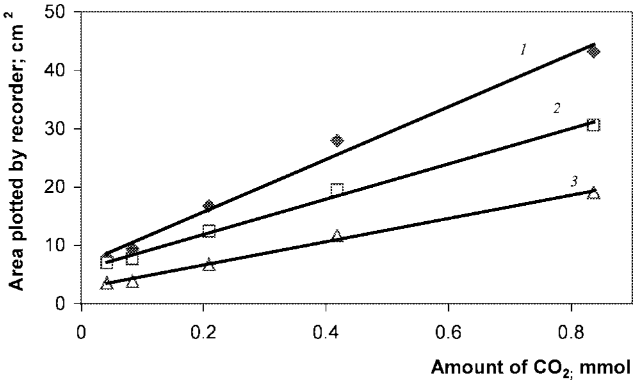

Figure 2. Calibration curves for determination of CO_2 at different dropping rates of NH_3 solution: (1) 20, (2) 30, and (3) 40 drops/min.

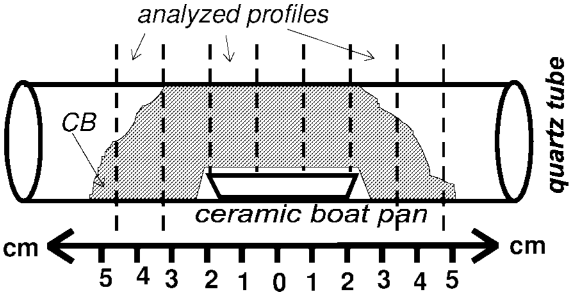

Figure 3. Investigation of Fe distribution in the reaction zone.

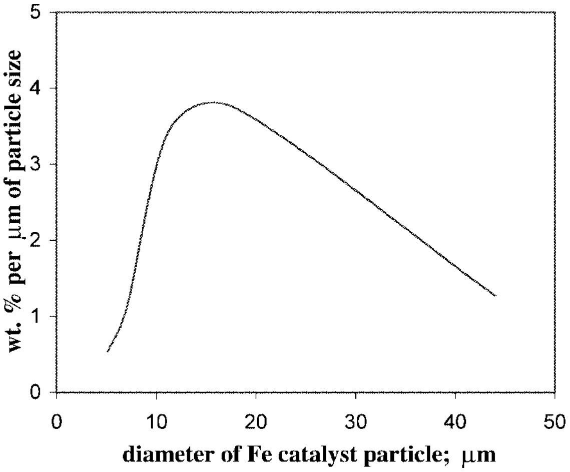

Figure 4. Particle size distribution of Fe catalyst.

for analysis was prepared by treating 10 min with 12 ml of 5% HCl solution (dissolving Fe from the surface of small crystals of CB) and separation of solid phase by means of filtration.

Particle size of the Fe catalyst was determined by means of sedimentation analysis [5]. Results obtained in particle size distribution are shown in figure 4.

3. Results and discussion

3.1. Kinetic parameters of Boudouard's reaction

Determined kinetic parameters of the reaction (reaction rate constant, order, and occupancy of catalyst surface) are presented in table 1. In figure 5 is shown the reaction rate change in the process of Boudouard's reaction. Reaction rate (v) in the flow was determined as:

$$v = -\frac{\mathrm{d}c}{\mathrm{d}t} = -\frac{u(C_0 - C)}{V}, \tag{3}$$

where V is reaction volume, C_0 the initial concentration, C the current concentration, u the CO flow rate. In figure 5 one can see three distinctive periods: induction, increasing of reaction rate and constant reaction rate period. Kinetic curves are dependent on CO flow rate.

Table 1
Kinetic parameters of Boudouard's reaction.

Temperature (°C)	Amount of Fe catalyst (g)	Reaction order	Reaction rate constant, k (s^{-1})	Occupancy of catalyst surface, $\theta \times 10^{-5}$ (mol/m^2)
490	0.1	0.9740	0.259	0.21
490	0.3	0.9990	0.090	1.58
490	1.0	0.9977	0.330	2.85
460	1.0	0.9981	0.098	4.26
430	1.0	0.9992	0.091	3.22

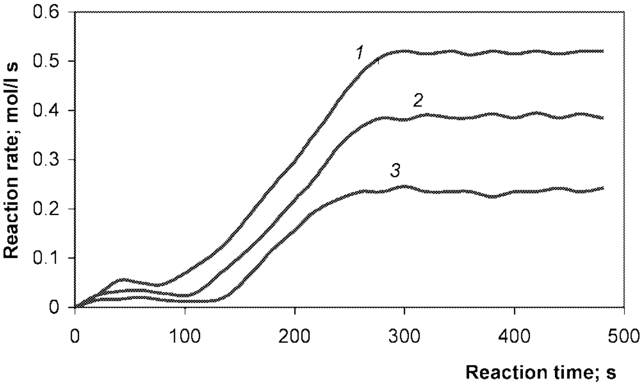

Figure 5. Reaction rate change in the process of Boudouard's reaction. CO flow rates: (1) 0.362, (2) 0.317, and (3) 0.253 l/s.

Reaction rate in the heterogeneous process is determined by the reaction rate on the surface of the catalyst from one side and the flow of the reagent into the reaction zone from the other side. In our case CO flow rate was maintained constant, consequently, reaction rate in our case was conditioned by diffusion kinetics. The proper reaction rate was considered as a process rate on the catalyst surface, v_S,

$$v_S = \frac{vV_C}{\mathrm{d}S}, \tag{4}$$

where V_C is the volume of the catalyst and dS the catalyst surface area per length of the reaction zone.

The reaction order (n) in our conditions was established equal to 1, independent of the temperature and amount of the catalyst (in the range 0.1–1.0 g). This parameter was determined plotting initial reaction rate vs. CO flow rate. Obtained results agree with those found in literature [6]. At 430–460 °C, k is slightly dependent on temperature. Rising temperature up to 490 °C increases slope $\lg k$ vs. $1/T$. Those data indicate a change in the mechanism of the process.

Occupancy of the catalyst surface with reacting CO molecules (θ) was determined according to

$$v_S = k\theta^n. \tag{5}$$

Results are shown in table 1. There we see that the occupancy of catalyst surface is nearly independent of the temperature. At the same time dependence of this parameter on the amount of catalyst is observed as more significant. This fact can be explained considering that the process occurs in the kinetic zone where adsorption is of little influence on the general development. Hence, the temperature should not have significant influence over the reaction, since this parameter for the most part has effect on adsorption. The limiting stage in those conditions is determined by the chemical nature of the reaction. A directly proportional connection with amount of Fe catalyst means greater dS in the reaction zone. Consequently, we have more active centers where Boudouard's reaction occurs. The obtained results correlate with those presented in literature [7].

3.2. Distribution of catalyst in the bulk of carbon black

Being an active mediator, a catalyst is subjected to conversions during the reaction [2]. Assumptions about the role of the catalyst could be done after analysis of the Fe distribution in the profile of CB synthesized in the reaction zone (see experimental part). Distribution of the catalyst is presented in figures 6 and 7. Series of syntheses were carried out at constant temperatures and amount of Fe in the reaction zone.

In some cases (in presence of small amount of the catalyst and at lower temperatures) total concentration of Fe ($C_{\mathrm{Fe/total}}$) is distributed more or less evenly in the profile of the reaction zone. Increasing amount of Fe catalyst leads to uneven distribution. Higher temperatures set the same effect. In both cases we can see a maximum of total amount of Fe in the profile. Thus we can draw a conclusion about the transport of the catalyst from the center to remote zones during the reaction time. Uneven distribution of Fe particles is expressed more clearly at greater amount of the catalyst and higher temperatures. The concentration of Fe on the surface of small CB crystals in the profile ($C_{\mathrm{Fe/surf}}$) constantly decreases going from the center of the reaction zone. This effect is more evident at greater amount of the catalyst and at higher temperatures, as well. We see that in the process small crystals of Fe are covered with CB layers. Receding from the center of the reaction zone these layers grow thicker. In a distance of 4 cm from the reaction center $C_{\mathrm{Fe/surf}}$ do not differ in all cases. In the center of the reaction zone nearly all the catalyst remains not encapsulated, especially when reaction occurs in presence of a greater deal of Fe. Assumptions about this situation could be found guessing that a definite part of the catalyst crystals have no active centers and cannot take part in the reaction. Thus, they cannot be transported in the process, remaining not encapsulated in the center of the tube. For corroboration of this assumption could be taken ratios of $C_{\mathrm{Fe/surf}}$ in the center of the reaction tube at different initial amounts of Fe catalyst (32% : 13% : 4% ≈ 1 g : 0.3 g : 0.1 g).

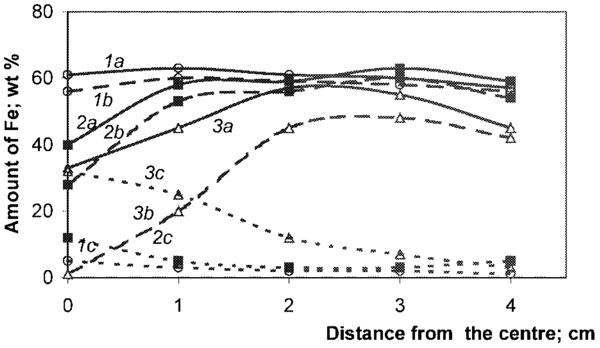

Figure 6. Distribution of Fe catalyst in profiles of the reaction zone. Total mass of the catalyst used: (1) 0.1, (2) 0.3, and (3) 1.0 g. Fe analysed: a – total, b – in the bulk of CB, and c – on the surface of small CB crystals.

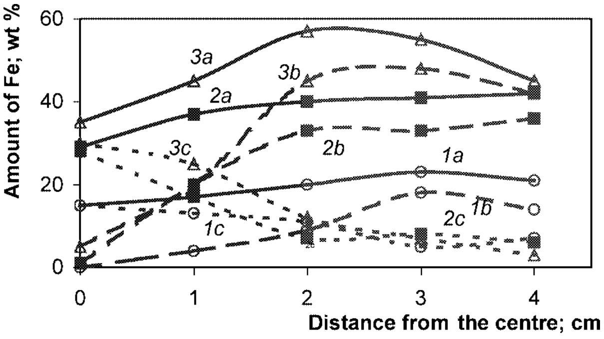

Figure 7. Distribution of Fe catalyst in profiles of the reaction zone. Temperature of the reaction: (1) 430, (2) 460, and (3) 490 °C. Fe analysed: a – total, b – in the bulk of CB, and c – on the surface of small CB crystals.

When reaction occurs on 0.1 g of Fe, CB is densely saturated with the catalyst. The process in this case occurs languidly and the obtained amount of CB is considerably less.

3.3. Oscillations in the process

We did mention above some facts implying an autocatalytical nature of Boudouard's reaction: induction periods in kinetic curves and uneven Fe distribution in the profile of the reaction zone. It is known that under definite conditions occurrence of autocatalytical reactions can be oscillating. So, it stands to reason that the same dynamics should be expected in the case of Boudouard's reaction. Actually, oscillations were observed in our system (figure 8). At the initial period the reaction develops in a traditional way: induction, increasing of the reaction rate, and constant reaction rate periods. After that at a certain moment a period of oscillations is observed. Approximately, after 2.5–3 h from the beginning of the reaction the oscillation disappears. The CO flow rate for the reaction with oscillating dynamics was 0.176 l/s, amount of Fe catalyst 1 g, reaction temperature 460 °C. In figure 8 we see that oscillations are born with small period and amplitude; during the time these grow longer and higher. Oscillation waves are asymmetric: the CO_2 concentration increases sharply and decreases slowly. Originating and ex-

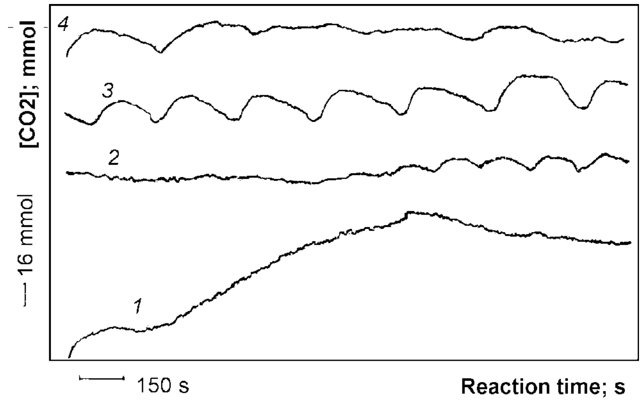

Figure 8. Boudouard's reaction with oscillating dynamics: (1) initial stage (induction, reaction rate increase and constant rate periods), (2) development of oscillations, (3) oscillating process, and (4) disappearance of oscillations.

tinction of oscillations is related with the state of the catalyst in the reaction tube. At a certain moment, when the oscillations begin, the surfaces of small catalyst particles are covered with synthesized CB layer. The average thickness of this layer at the initial moment of oscillations is 4.42 μm; that at the end of oscillations amounts to 11.4 μm. Oscillations are conditioned by diffusion of gaseous CO and CO_2 through the layer of that thickness.

Some authors pointed on CO_2 playing the role of autocatalyst in Boudouard's reaction [2]. They emphasize the model proposed by Baker et al. [8] and existence of partial equilibrium at both metal–carbon and metal–gas interfaces of each metal particle. Several authors investigated the formation of graphite from gaseous phase [9]. They found formation of special defects during this reaction. These defects are additional C atoms distorting the hexagonal arrangement and stitching up graphite planes. It was established that activation energy in the process of graphite formation is less for defects in comparison with atoms in the graphite plane. Thus, it is credible that these defects take place in the process of oscillating dynamics.

4. Conclusions

Reaction of CO disproportionation into graphitized carbon black and carbon dioxide on the surface of a Fe catalyst (known as Boudouard's reaction) was investigated. Kinetic parameters of the reaction (in the range of temperatures 430–490 °C) were established; they correlate with those found in literature. During Boudouard's reaction synthesized carbon black together with the Fe catalyst is accumulated in the reaction zone. Distribution of the catalyst in the profile of that zone was investigated. For that purpose two sorts of analyses were carried out: determination of Fe in the bulk synthesized mass and on the surface of small carbon black crystals. From results of these analyses a conclusion about the transport of catalyst from the center to remote zones during the reaction was drawn. An uneven distribution of Fe particles is expressed more clearly at greater amount of the catalyst and higher temperatures. Under definite conditions observed Boudouard's reaction developed with oscillating dynamics: oscillations are born with small period and amplitude; during the time these grow longer and higher. Observed oscillating dynamics, uneven Fe distribution and induction period indicate an autocatalytical nature of Boudouard's reaction. Some models found in literature and explaining the mechanism of autocatalysis in the process of CO disproportionation are compared.

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