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Fluidization of the active component of catalysts in catalytic formation of carbon assisted by iron and nickel carbides

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A simple thermodynamic analysis evidences that ultrafine iron and nickel particles, assisting many carbon creating catalytic reactions, should fluidize in the course of such reactions, even if the reactions occur at sufficiently low or moderate temperatures. The main driving force of this fluidization is a sufficient oversaturation of the metal particles with carbon thus resulting in formation of metastable carbides with extremely low melting temperatures. The possibility of this fluidization allows explanation of some well-known phenomena of catalytic chemistry of carbon, like, e.g., rapid diffusion of carbon atoms through catalytically active metal particles, a tendency to unification of the sizes of the catalytically active metal particles in the course of catalytic processes, as well as formation of filamentous carbon of the "fish bones" structure.

Keywords: fluidization; carbon; carbides; iron; nickel

1. Introduction

Nickel, iron and some other transition metals are known to play an important role in the formation of carbon deposits on the surface of catalysts during conversion or decomposition of hydrocarbons at sufficiently low or moderate temperatures. In this process, carbon is often deposited as graphite filaments with a diameter of ca. 10–40 nm via a so-called carbide cycle assisted by the above metals in the ultradisperse (ca. 10 nm in size) state, which locate on the basal face of the growing carbon filament (see, e.g., refs. [1– 5]). Carbon, depositing on the open catalyst surface during the catalytic process involving hydrocarbons, is assumed to react with metals, thus producing active metal carbides. Then it diffuses through the thus produced active particles and accumulates in an orderly fashion on the basal face of a growing carbon filament [1– 5]. Unfortunately, the physicochemical nature of the driving force for the rapid carbon diffusion through the above catalytically active particles, determining also the size of growing filaments, has not been completely elucidated yet. The simplest way to explain carbon transfer through the carbide particles is to assume the particles to be in a fluid state during the catalytic process [1,2,4]. Nevertheless, the known assumptions on the fluidization of the active components during the above processes [4,6] are still not well accepted by the scientific community, since the process temperatures are rather low (550–900°C, as a rule) in comparison with the melting temperatures of the corresponding metal carbides.

Recently, a topochemical exothermic conversion of amorphous carbon to graphite scales ($d \approx 20$–40 nm) was observed in situ with electron microscopy, the particles of iron carbide ($d \approx 20$–40 nm) serving as the catalyst [7]. A direct observation has shown these particles to be fluid or fluid-like during the catalytic process. It is of importance, that the lowest temperature of the particle fluidization was measured to be close to 920 K. This is considerably lower than the melting point of either eutectic mixture Fe–C (4.3 mass% of C) or pure iron and iron carbide Fe_3C (1420, 1819 and 1920 K, respectively). The reason for the carbide fluidization at so low a temperature was not considered.

Earlier, the quickly moving nickel particles were observed at 920 K in a thin (50 nm) layer of amorphous carbon on glass carbon [8]. Here, the nickel particles were also found to leave a trace consisting of recrystallized carbon. The phenomenon was ascribed to the formation of metastable eutectics well known for carbon solutions in various metals [9].

The analysis presented below and based on some simple thermodynamic considerations shows that fluidization of carbides at "abnormally" low temperatures during active carbon producing catalytic reactions should be a rather typical phenomenon. This phenomenon explains as well some features of the growth of carbon filaments and their particular size.

2. Melting of ultradisperse iron particles oversaturated with carbon: a thermodynamic analysis

Our analysis concerns ultradisperse iron carbide particles of a definite size, possessing a particular fluidization temperature as determined in ref. [7].

At high temperatures, carbon is known to dissolve well in iron. Under these conditions, when no individual but thermodynamically unstable carbides (Fe_3C, cementit, or rarely Fe_2C, chalipid) have crystallized yet, behavior of carbon solutions in iron follows well the thermodynamic rules for ideal solutions in liquid iron [9]. Indeed, from the fundamentals of thermodynamics, the melting point T of an ideal solution should obey the relation:

$$\ln(1-x) = -\frac{\Delta H_\mathrm{m}}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right), \tag{1}$$

where x is the mole content of the dissolved component while ΔH_m and T_0 are the enthalpy and melting point of the pure solvent (for iron $\Delta H_\mathrm{m} = 13.8$ kJ/mol and $T_0 = 1810$ K [10]), R is the universal gas constant. Introducing the known molar carbon content of the eutectics of the carbon–iron mixture to eq. (1) (4.3 mass% of C corresponds to $x = 0.173$), we obtain a theoretical melting point for this solution:

$$T = T_0\Delta H_\mathrm{m}/[\Delta H_\mathrm{m} - RT_0\ln(1-x)] \approx 1500\ \mathrm{K}.$$

This temperature is quite close to the really observed melting temperature 1420 K, being, however, a little bit higher. Thus, we can use the ideal formula (1) for further estimations of melting temperatures and carbon concentrations in the melts, taking into account that existing nonidealities should diminish a little the calculated temperatures and corresponding concentrations.

Note, that all equilibria of carbon–iron solutions described in the ordinary reference books relate as a rule to the conditions, when thermodynamically stable graphite is the main carbon phase being in equilibrium with the melt. At the same time, contacts of iron with carbon phases more saturated with energy than graphite, e.g., with amorphous carbon or active carbon, just formed on the catalyst surface after hydrocarbons decomposition, should increase the concentration of dissolved carbon [9]. The chemical potential μ of, e.g., amorphous carbon exceeds that of graphite by $\Delta\mu = \Delta H^0 - T\Delta S^0$, where ΔH^0 is the difference in standard enthalpies of amorphous and graphite carbon formation and equal to 15.2 kJ/g-atom [11], ΔS^0 is the difference of the corresponding standard formation entropies. The entropy of amorphous carbon is indeed higher than that of graphite, however, ΔS^0 seems not to exceed the entropy difference of diamond and graphite formation ($S^0_\mathrm{f,diamond} - S^0_\mathrm{f,graphite} \approx 3.37$ J/mol K) due to a large similarity in the structure of the nearest environment of carbon atoms in graphite and amorphous carbon. Thus, at temperatures near to 1000 K the chemical potential of amorphous carbon should exceed that of the massive graphite by not less than 11.8 kJ/mol. Consequently, at $T \approx 1000$ K the content of carbon in its saturated solution in iron at equilibrium with amorphous carbon should exceed that at the equilibrium with the bulk graphite by a factor of $\exp(\Delta\mu/RT) \approx 4$. Assuming that the eutectic point corresponds to the latter case, we can conclude, that the content of carbon in its saturated solution in iron at its contact with amorphous carbon should correspond to $x \geqslant 0.69$.

Thus, one can expect that formation of carbon in a catalytic reaction can lead to an oversaturation of iron particles with carbon thus producing iron–carbon particles resembling carbides by their composition but with the melting point lower than that of the eutectics. A simple calculation with the idealized formula (1) shows, that to attain the melting point of 920 K observed in ref. [7], one should have a 0.59 molar content of carbon in the melt or somewhat lower, when taking into account a temperature deviation from that ideal for the eutectics. (More sophisticated approaches to the calculation of the melting temperatures of the metastable eutectics of carbon–metal solutions are suggested in ref. [9].) This value with a good accuracy (!) corresponds to the composition of carbide particles FeC detected after finishing the topochemical process observed in ref. [7].

There is also another factor decreasing the melting temperature of highly disperse carbides of carbon solutions in iron. This phenomenon is well known for disperse materials and is provided by the surface tension energy σ. Simple thermodynamic calculations show (see, e.g., ref. [12]), that the melting point T_r of the solid phase dispersed in balls of radius r is related with T_0 of the bulk phase by the formula:

$$T_r = T_0\exp\left(-\frac{2\sigma V_\mathrm{m}}{r\Delta H_\mathrm{m}}\right), \tag{2}$$

where V_m is the molar volume of the melting phase and ΔH_m is the enthalpy of its melting. Unfortunately, the correct figures for σ and ΔH_m values for highly carbon-saturated ion carbides at temperatures below 1000°C are not well known. Estimating σ with regard to the typical values for the low-saturated iron carbides at T above 1200°C ($\sigma \approx 1.0$–1.7 J/m^2 [13,14]) and $\Delta H_\mathrm{m} \approx 15$ kJ/mol (see ref. [9]), and taking into account that molar volumes of carbides Fe_3C, Fe_2C and FeC are 23.3, ca. 17.7 and 11 cm^3, respectively, for carbide particles with $r \approx 10$ nm, one can estimate the exponential factor in (2) as 0.73–0.59, 0.79–0.67, and 0.86–0.78, respectively. For the similar particles of pure iron one obtains ca. 0.57–0.38. Obviously, the mentioned phenomenon provides an extra decrease of the melting temperature (by more than 100–300 K) for the highly dispersed iron carbides [#1].

Provided for this factor, the case of the easily melting carbide discussed in ref. [7] brings the composition of a liquid carbide with the melting temperature at 920 K even nearer to the solution with a 0.5 molar content of dissolved carbon.

Note also numerous pieces of evidence that during coke formation the smallest metal particles are under-

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[#1] In refs. [4,6], when supposing a fluidization of the active components of the catalysts, this size-dependent decrease of the melting points was considered to be a main driving force for the fluidization. Unfortunately, the decrease of the melting temperature of *pure* metals rather than that of *metal carbides* was considered in the cited papers.

going the coking in a less extent than the larger ones, the latter being covered by a thin carbon layer not penetrating into the particle and thus inhibiting it.

3. Reasons for melting the carbide particles at the catalytic reaction and factors controlling the size of graphite crystals formed

In the course of a carbon-producing catalytic reaction, carbon accumulates continuously. This signifies a progressive increase of the carbon concentration in a catalytically active particle in the case of continuously dissolving carbon in this particle. Obviously, such an increase of concentration cannot go on forever. At a steady state, the carbon supply to the particle bulk is reimbursed by its removal or deposition in the form of its most stable phase, i.e. graphite. It is of importance, that the conversion cycle "active carbon–graphite" is exothermic. So, at the steady state, even when the catalyzed reaction appears to be endothermic as a whole (e.g., formation of carbon in pyrolysis of hydrocarbons), heat evolves intensively on the active site of the catalyst. This provides a considerable local overheating of the reaction site (by hundreds of degrees) in comparison to the temperature of the environment or support of the site [15]. This local overheating depends on the rate of the energy-producing reaction and, in principle, can be large enough to melt the ultradisperse iron particle oversaturated with carbon.

One can assume that without an external heat supply to the system, a stable steady state of the active site is provided by: (1) a necessity to fulfill the conditions of a heat balance of the site and (2) a condition of a steady state flow of carbon.

Apparently, carbon should escape from the molten carbon-saturated active particles via crystallization into graphite particles. The thermodynamics predicts the minimal size of a nucleus required for this purpose and thus the size of the graphite particles forming.

Indeed, according to the Gibbs–Freindlich–Ostwald law for ideal bulk solutions [16], at a given temperature T the solubility of crystals is a function of their size r:

$$x(r) = x_0 \exp\left(\frac{2\sigma' V'_\mathrm{m}}{rRT}\right), \tag{3}$$

where x_0 is the limit solubility of a macroscopic phase, σ' is the surface tension at the solution–crystal interface, V'_m is the crystal molar volume. Assuming for simplicity that in our case the limit solubility of the macroscopic phase corresponds to an eutectics with $x_0 = 0.173$ and that the temperature of our system corresponds to the melting point of iron oversaturated with carbon of concentration x (eq. (1)), one can obtain a certain correlation using eqs. (1) and (3). This correlation allows estimation of the size of graphite particles forming, when the temperature of the catalyst site retains value T:

$$1 - x_0 \exp\left(\frac{2\sigma' V'_\mathrm{m}}{rRT}\right) = \exp\left[-\frac{\Delta H_\mathrm{m}}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right]$$

or

$$r = \frac{2\sigma' V'_\mathrm{m}}{RT} \Big/ \ln\left\{\left\{1 - \exp\left[-\frac{\Delta H_\mathrm{m}}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right]\right\}\frac{1}{x_0}\right\}. \tag{4}$$

Here, we do not consider the effects provided by the dispersity of the active particle. In principle, the role of a nucleus for the graphite particle formation can be played by either the disperse carbon-oversaturated iron particle itself or the surface of its contact with graphite. In both cases the value of r calculated from (4) should correspond or be close to the size of the catalyst particle. The catalyst particle size either depends on the size of the particle precursor (see, e.g., refs. [1–8]) or forms upon the catalyst adaptation to temperature T and sometimes is larger, the larger is the temperature of the process [4,6].

In the case when r is fixed independently, correlation (4) allows estimation of the temperature T of the steady process. For this purpose one should know the true local overheating of the active site. This requires additional data on the steady state rate of the catalytic carbon formation under particular conditions (see ref. [15]).

Note, that the size of graphite particles determined by formula (4) should correspond to the size of the basal face of the particle, since the latter is the place of the melt contact with the nucleus of the graphite crystal. The true figures for σ' are not known. However, from the TEM patterns presented in ref. [7] one can see, that the carbide melt does not wet carbon. Thus, σ' is likely to be somewhat higher than σ for the carbide melts estimated as $\geqslant 1.0$–1.7 J/m^2 (see ref. [9] as well). So, for providing the respective estimate of r by formula (4) for $T = 920$ K (adjusted in ref. [7]) one can use $V_\mathrm{m} = 5.3$ cm^3 and $\sigma' \approx 2$ J/m^2 which gives $2r \approx 5$ nm. Since our estimate is quite approximate, it agrees well with the direct observation of graphite scales with $2r \approx 20$ nm (as well as the molten carbide particles of the same size). Note, that the contribution of the logarithmic cofactor in (4) and thus arbitrary x_0 do not affect the order of the r value.

One can estimate as well the size of the basal particle faces of the graphite, responsible for the filament carbon growth at the hydrocarbon pyrolysis on nickel particles [1,8]. Indeed, nickel has its melting temperature and enthalpy close to those of iron (1728 K and 17.5 kJ/mol, respectively) and produces at least one crystalline carbide Ni_3C. Note, that the melting point of highly disperse nickel particles oversaturated with carbon can be even lower than that of iron particles at the same carbon concentration, since ΔH_m of nickel is noticeably higher and T_0 is lower, than those of iron. This is quite probably the reason for a higher catalytic activity of nickel in comparison to iron and thus for a lower temperature at the catalytic hydrocarbon pyrolysis producing filamentous carbon.

Note, that, similarly as in the macroscopic systems, the crystallization of carbon from the ultradisperse carbon-oversaturated particles of Fe and Ni does not occur under the pure stationary mode. Indeed, one can expect, that, after the active particle appears to be saturated with carbon, the graphite scale starts to crystallize in an explosive manner consuming more and more carbon dissolved in the active catalyst particle. This is quite reasonable, since a slow kinetics of steady state carbon accumulation in solution (melt) somewhat contradicts the fast unsteady crystallization on a graphite nucleus. Since the size of the active particle in the "adapted" catalyst responsible for the filamentous carbon formation is close to that of the graphite basal face, we can conclude, that the thickness of graphite scales, deposited at each act of such crystallization, should correspond to the particular carbon amount accumulated inside the active site. The latter corresponds also to the oversaturation of the active particle at the maximal temperature of its overheating and thus should correspond typically to tenths parts of the metal mole (atomic) content in the active catalyst particle. Thus, the thickness of the graphite scales at each crystallization act should compose ca. 10% of the basal face which determines the starting conditions of the crystallization. So, under some conditions the filamentous carbon can resemble fish bones. Such a phenomenon is indeed well known for many filamentous carbons (see ref. [17]).

4. Conclusions

The above analysis, even though it is based on rather simple thermodynamic concepts, evidences that the pumping of active metal particles with carbon in the course of catalytic reactions yielding active carbon can produce oversaturated (with respect to the equilibrium "graphite–solution of carbon in the metal") carbon solutions in the catalytically active metals. Such oversaturated and highly disperse solutions can have abnormally low melting point and fluidize at the temperatures of the corresponding catalytic reaction. This fluidization is likely of key importance for the catalytic reactions yielding the graphitized carbon among other products. Indeed, in this case the cycle "primary thermodynamically active carbon–oversaturated carbon solution in the metal–graphite particle crystallization" becomes easy to perform without deactivation of the metal particles and produces large amount of graphitized carbon.

Note, that for highly dispersed iron and nickel one can expect, that introduction of not only carbon but other components as well (e.g., copper [18]) can result in oversaturated and thus easy melting solutions.

One can expect also, that the melting of the active components in the course of carbon-producing catalytic reactions occurs not only in the case of iron and nickel but also in the case of other catalytically active carbide-forming compounds. For example, the metal-consisting particles looking like the fluidized ones and formed at growth of carbon filaments or the particles location on the surface of amorphous carbon were registered in systems containing cobalt, chromium and titanium [2,9,19].

In ref. [20] kinetics of a molybdenum wire carbonization by means of methane catalytic pyrolysis at 1450–2200°C was found to be limited by the carbon diffusion. The calculated diffusion coefficient appears to be abnormally large for a solid and ranges from 1×10^{-7} cm^2/s (1450°C) to (5–6)$\times 10^{-6}$ cm^2/s (2200°C). Similar abnormally high carbon diffusion coefficients at the catalytic carbonization are known for iron as well [21]. Note, that the above carbon diffusion coefficients are probably more close to the typical coefficients of fluidized rather than of solid systems, since the latter exhibit diffusion coefficients ranging from 10^{-9} to 10^{-12} cm^2/s.

Note also that the discussed phenomenon can be even more general and concerns not only carbon-producing reactions but also catalytic reactions of some other types when the product of the reaction appears firstly in the thermodynamically nonstable state and then crystallizes.

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