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 ≈ 20–40 nm) was observed in situ with electron microscopy, the particles of iron carbide (d ≈ 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 Fe3C (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 (Fe3C, cemen-
melting temperature 1420 K, being, however, a little bit 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 \( \mu \) of, e.g., amorphous carbon exceeds that of graphite by \( \Delta \mu = \Delta H^p - T \Delta S^p \), where \( \Delta H^p \) is the difference in standard enthalpies of amorphous and graphite carbon formation and equal to 15.2 kJ/g-atom [11], \( \Delta S^p \) is the difference of the corresponding standard formation entropies. The entropy of amorphous carbon is indeed higher than that of graphite, however, \( \Delta S^p \) seems not to exceed the entropy difference of diamond and graphite formation (\( S^p_{\text{diamond}} - S^p_{\text{graphite}} \approx 3.37 \text{ J/mol K} \)) 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 \( T \approx 1000 \text{ K} \) 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 \( x \geq 0.69 \).

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 \( \sigma \). 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:

\[
T_r = T_0 \exp \left( -\frac{2 \sigma V_m}{r \Delta H_m} \right),
\]

where \( V_m \) is the molar volume of the melting phase and \( \Delta H_m \) is the enthalpy of its melting. Unfortunately, the correct figures for \( \sigma \) and \( \Delta H_m \) values for highly carbon-saturated iron carbides at temperatures below 1000°C are not well known. Estimating \( \sigma \) with regard to the typical values for the low-saturated iron carbides at \( T \) above 1200°C (\( \sigma \approx 1.0-1.7 \text{ J/m}^2 \) [13,14]) and \( \Delta H_m \approx 15 \text{ kJ/mol} \) (see ref. [9]), and taking into account that molar volumes of carbides Fe2C, Fe3C and FeC are 23.3, ca. 17.7 and 11 cm\(^3\), respectively, for carbide particles with \( r \approx 10 \text{ nm} \), 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-

\#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.