## Thermodynamics and Kinetics of Carbon Deposition from Mixtures of Hydrogen and Carbon Tetrachloride

A. V. Elyutin and M. V. Vorob'eva

State Research Institute for the Rare-Metals Industry, Bol'shoi Tolmachevskii per. 5, Moscow, 109017 Russia e-mail: vorobjeva@yandex.ru

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**Abstract**—The thermodynamics and kinetics of pyrolytic carbon deposition via hydrogen reduction of  $CCl_4$  were studied. Thermodynamic analysis of the C–Cl–H system was used to determine the compositions of the gas and condensed phases at  $CCl_4 : H_2 = 1 : 4$  to 1 : 90, temperatures from 700 to 1400 K, and a pressure of  $10^5$  Pa. The reactions leading to the formation of solid carbon in the H<sub>2</sub>–CCl<sub>4</sub> system were considered, and the deposition parameters were optimized in terms of carbon yield.

Heterogeneous processes for hydrogen reduction of volatile chlorides find practical application in various fields and open up new possibilities for producing highpurity coatings. The deposition of carbon layers via hydrogen reduction of carbon tetrachloride at relatively low temperatures and high rates is a promising technique for the preparation of new carbon materials. Understanding the thermodynamics and kinetics of carbon deposition from mixtures of hydrogen and carbon tetrachloride is crucial for the ability to optimize the deposition conditions and improve the properties of the coatings. To optimize the deposition temperature and gas-phase composition in terms of carbon yield, we carried out the thermodynamic evaluation of the C-Cl-H system. Data on the gas-phase equilibria in the C-Cl-H system are not available in the literature.

Since the presence of chlorine or another halogen in the gas phase makes it possible to enhance the deposition rate and improve the structural perfection of the deposit, we used carbon tetrachloride,  $CCl_4$ , as the carbon precursor. Thermal dissociation of CCl<sub>4</sub>, pure or mixed with an inert carrier gas, yields molecular chlorine (above 700 K), atomic chlorine (above 1600 K), and carbon. In any case, the reaction involves the formation of carbon in the gas phase. Therefore, the process should be run at a reduced pressure or an elevated partial pressure of the carrier gas in order to reduce the CCl<sub>4</sub> vapor pressure. Since inert carrier gases are incapable of fully preventing the presence of chlorine, we used hydrogen, which reduces CCl<sub>4</sub>, thereby preventing the formation of carbon in the gas phase. The reduction process can be represented by the following overall reaction scheme:

$$\operatorname{CCl}_4(g) + 2\operatorname{H}_2(g) = \operatorname{C} + 4\operatorname{HCl}(g).$$

It seems unlikely that the hydrogen reduction of  $CCl_4$  to carbon proceeds in only one step. A literature search,

using the ASTD system, revealed that carbon forms a large number of compounds with chlorine:

$$\begin{aligned} 2\text{CCl}_4(g) + \text{H}_2(g) &= 2\text{CCl}_3(g) + 2\text{HCl}(g), \\ \text{CCl}_4(g) + \text{H}_2(g) &= \text{CCl}_2(g) + 2\text{HCl}(g), \\ 2\text{CCl}_2(g) + \text{H}_2(g) &= 2\text{CCl}(g) + 2\text{HCl}(g), \\ \text{CCl}_4(g) + 2\text{H}_2(g) &= \text{CH}_2\text{Cl}_2(g) + 2\text{HCl}(g). \end{aligned}$$

Consequently, it would be expected that the hydrogen reduction of CCl<sub>4</sub> yields a wide variety of vapor species. The possible reactions can be identified using the principle of maximum entropy. There are several computer programs for assessing the composition of the gas or condensed phase, in particular ASTRA (B.G. Trusov et al., Bauman State Technical University, Moscow) and WORK (V.V. Nechaev et al., State Research Institute for the Rare-Metals Industry, Moscow). The algorithm of these programs relies on the principle of maximum entropy in a system at thermodynamic equilibrium. Clearly, a real thermodynamic system is at least slightly displaced from and tends to equilibrium. In view of this, we treat thermodynamic parameters as characterizing separate regions at local thermodynamic equilibrium [1].

To find a constrained extremum in the entropy of a thermodynamic system, we used the Lagrange method of multipliers [2]. In the thermodynamic evaluation of the C–Cl–H system, we used the ASTRA program. The compositions of the gas and condensed phases were determined for  $CCl_4 : H_2 = 1 : 4$  to 1 : 90, temperatures from 700 to 1400 K, and a pressure of  $10^5$  Pa. The condensed phase was found to consist of carbon only, independent of the  $CCl_4 : 2$  ratio. The presence of hydrogen notably reduces the reaction yield in terms of carbon. At a pressure of  $10^5$  Pa, the highest yield of solid carbon is expected at temperatures above 1100 K.



**Fig. 1.** Equilibrium composition in the C–Cl–H system as a function of temperature at an  $H_2$ : CCl<sub>4</sub> molar ratio of 9 : 1; (*1*)  $H_2$ , (*2*) CH<sub>3</sub>Cl, (*3*) CH<sub>3</sub>, (*4*) Cl<sub>2</sub>, (*5*) HCl, (*6*) H, (*7*) C<sub>2</sub>H<sub>2</sub>, (*8*) C<sub>2</sub>H<sub>3</sub>, (*9*) CH<sub>4</sub>, (*10*) C<sub>2</sub>H<sub>4</sub>, (*11*) C(solid), (*12*) CH<sub>2</sub>Cl, (*13*) C<sub>2</sub>H<sub>6</sub>, (*14*) Cl, (*15*) C<sub>2</sub>H<sub>3</sub>Cl, (*16*) C<sub>2</sub>HCl.

The calculation results for  $CCl_4 : H_2 = 1 : 9$  are displayed in Fig. 1. The reaction is likely to proceed in several steps, via consecutive substitution of hydrogen for chlorine, as evidenced by the presence of  $CH_3Cl$  throughout the temperature range studied. Above 1200 K, we observe the formation of  $C_2H_2Cl$ . With increasing temperature, the  $CH_4$  concentration decreases slightly owing to  $CH_4$  dehydrogenation. The presence of excess hydrogen in the reaction mixture inhibits  $CH_4$  decomposition. The  $CH_4$  concentration is higher by 4 to 5 orders of magnitude than the concentrations of intermediate hydrocarbons ( $C_2H_4$ ,  $C_2H_6$ , and  $C_2H_2$ ) and radicals.

These results suggest that condensed carbon is thermodynamically stable only above 1300 K; at lower temperatures, only hydrocarbons are stable. However, in real systems, carbon exits in a stable state at low temperatures, down to room temperature. In view of this, to take into account the nonequilibrium state of the system due to the presence of condensed carbon, we calculated a pseudoequilibrium composition of the gas phase over

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**Fig. 2.** Pseudoequilibrium composition in the C–Cl–H system as a function of temperature at an  $H_2$  : CCl<sub>4</sub> molar ratio of 9 : 1; (*I*)  $H_2$ , (2)  $C_2H_4$ , (3)  $C_2H_3Cl$ , (4)  $C_2HCl$ , (5) HCl, (6) Cl, (7)  $C_2H_5$ , (8) CH<sub>2</sub>Cl<sub>2</sub>, (9) CH<sub>4</sub>, (*10*) CH<sub>3</sub>, (*11*)  $C_2H_3$ , (*12*)  $C_2H$ , (*13*)  $C_2H_6$ , (*14*)  $C_2H_2$ , (*15*) CH<sub>2</sub>Cl, (*16*) CH<sub>3</sub>Cl, (*17*) H, (*18*) C(solid), (*19*)  $C_2HCl$ , (*20*)  $C_2H_2Cl_2$ .

the entire temperature range of interest. The results for  $CCl_4$ :  $H_2 = 1 : 9$  are shown in Fig. 2.

The data displayed in Figs. 1 and 2 for the C–Cl–H system and earlier data for similar systems suggest that the process under consideration has a homogeneous–heterogeneous character. There is no predominant reaction, and carbon deposition is due to a number of parallel and consecutive reactions. According to our calculations, thermal decomposition of  $CCl_4$  in argon carrier gas yields appreciable amounts of atomic and molecular chlorine and lower carbon chlorides. On the surface, carbon is probably transported in the form of lower carbon chlorides. In the presence of hydrogen, some of the chlorine atoms may be replaced by hydrogen, but the mechanism of carbon transport (in the form of lower carbon chlorides) remains unchanged.

Thus, there are two possible mechanisms of carbon deposition in the  $H_2$ -CCl<sub>4</sub> system. One of them involves steplike decomposition of carbon tetrachloride and formation of intermediate hydrocarbons, consecutive dehydrogenation of the intermediate hydrocarbons,



**Fig. 3.** Arrhenius plots of the deposition rate at  $CCl_4 : H_2 = (1) 1 : 9, (2) 1 : 12, and (3) 1 : 13.$ 



**Fig. 4.** Deposition rate as a function of total gas flow rate at (1) 1423, (2) 1533, and (3) 1623 K.

and direct decomposition of the hydrocarbons. The other mechanism involves consecutive detachment of chlorine atoms from CCl<sub>4</sub> to give compounds such as CCl<sub>3</sub> and CCl<sub>2</sub>, and the transport of carbon to the substrate in the form of lower carbon chlorides. According to the thermodynamic calculation results, the optimal conditions for carbon deposition from H<sub>2</sub> + CCl<sub>4</sub> mixtures are T = 1100-1400 K and CCl<sub>4</sub> : H<sub>2</sub> = 1 : 4 to 1 : 50. To identify the rate-limiting process and examine its effect on the morphology and structure of the deposits, we investigated the kinetics of carbon deposition.

The deposition rate was measured between 1100 and 1400 K at  $CCl_4$  :  $H_2 = 1 : 9$  to 1 : 13, a pressure of  $10^5$  Pa, and a total flow rate of 240 m<sup>3</sup>/h. The Arrhenius plots of the deposition rate (Fig. 3) show a maximum. Below 1300 K, the deposition rate varies exponentially with inverse temperature, suggesting that the process is kinetically limited (by the reaction rate). Since the process involves a number of parallel reactions, it cannot be described by a single rate equation. The activation energy determined from the slope of the Arrhenius plots is 220 kJ/mol. According to earlier results, this value is typical of kinetically limited heterogeneous reactions in chemical vapor deposition processes. In the range 1300-1573 K, the deposition rate decreases with increasing temperature, which cannot be accounted for by diffusional limitations in the gas phase. The likely reason is homogeneous carbon formation in the gas phase, as supported by the observed formation of carbon black. This effect can be eliminated by cooling the reactor wall.

The deposition rate of carbon depends strongly on the  $CCl_4 : H_2$  ratio. The best results were obtained at  $CCl_4 : H_2 = 1 : 9$ . The plots of the deposition rate versus total gas flow rate are displayed in Fig. 4. These data, obtained at constant temperature and  $CCl_4$  concentration, lead us to conclude that the process is kinetically limited: the flow rate has little or no effect on the deposition rate, which decreases slightly only at very high flow rates. This can be accounted for by the substantial decrease in the  $CCl_4$  concentration at the substantial surface, and the accelerated rate of the reaction with the deposited carbon, which reduces the deposition rate.

Thus, the present thermodynamic calculations and kinetic studies of the hydrogen reduction of carbon tetrachloride allowed us to optimize the process parameters: T = 1523-1573 K, CCl<sub>4</sub> : H<sub>2</sub> = 1 : 9, and total gas flow rate of 400–450 m<sup>3</sup>/h. Under these conditions, we obtained high-quality pyrolytic carbon layers (10<sup>-3</sup> to 10<sup>-4</sup> wt % impurities, density of 2.19 g/cm<sup>3</sup>, interlayer spacing of 3.45 Å, average crystallite diameter of 51 Å) on graphite substrates at a deposition rate of up to 200 µm/h, which is about 30 times higher than the rate of carbon deposition via conventional vacuum pyrolysis of hydrocarbons [3].

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