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Nickel Oxide Reduction under Nonisothermal Conditions

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Abstract—The interaction of nickel(II) oxide with carbon, polyethylene, and polystyrene in the temperature range 20–1000°C has been investigated by thermal analysis. The interaction of NiO with carbon and polyethylene under these conditions results in complete nickel reduction. In the case of polystyrene, because of its low decomposition temperature, the reduction process is incomplete. As compared to reduction with polyethylene, reduction with carbon takes place at a much higher temperature (750 versus 370°C) and requires a higher activation energy (68 ± 3 versus 41 ± 1 kcal/mol).

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The reduction of nickel oxide with various reagents has been reported in sufficient detail [1–6]. Hydrogen [1–3] and carbon monoxide [4] have been employed as gaseous reductants. The best known solid reductant is carbon [5, 6]. Other possible solid reductants are organic compounds containing at least two reducing elements (C and H), which are called combined reductants. Such compounds are now used in the reduction of metal oxide powders in the solid-phase combustion regime [7], which is based on self-propagating high-temperature synthesis [8].

Earlier, we carried out a DTA study of the kinetics of copper(II) oxide reduction with polystyrene [9], a combined reductant, and demonstrated that this reaction is exothermic.

Many exothermic and endothermic reactions and physical transformations are accompanied by weight changes, which can be precisely estimated by thermogravimetry (TG) [10, 11].

Here, we report a DTA study of nickel oxide reduction with carbon and combined reductants, including some kinetic parameters of these reactions.

EXPERIMENTAL

Thermal analysis was carried out using an MOM Q-1500 instrument (Hungary) connected to a PC to facilitate data recording and processing. This instrument allows the sample to be linearly heated up to 1000°C at a rate of V = 2.5–20 K/min. This technique makes it possible to monitor physicochemical transformations accompanied by heat absorption or evolution (DTA) and to record sample weight changes (TG) and the rate of the weight changes (DTG).

The starting chemicals were nickel(II) oxide powder (reagent grade, USSR specifications TU 6-09-4125-80), carbon (lampblack with a specific surface area of 36 m^2/g, P-803 brand), polyethylene (PND-277 brand, USSR state standard GOST 16338-85), and polystyrene (PES-1 brand, USSR state standard GOST 20282-74) with a mean particle size no larger than 10 μm.

The reduction of nickel oxide with carbon, polyethylene (PE), and polystyrene (PS) was studied under conditions of linear heating in an inert atmosphere (helium or nitrogen).

The initial compositions of reaction mixtures were adjusted to the following stoichiometries:[1]

$$2NiO + C = 2Ni + CO_2, \quad (I)$$

$$6NiO + (1/n)(C_2H_4)_n = 6Ni + 2CO_2 + 2H_2O, \quad (II)$$

$$20NiO + (1/n)(C_8H_8)_n = 20Ni + 8CO_2 + 4H_2O. \quad (III)$$

Samples of weight m = 100 or 200 mg, prepared by mixing the initial powders, were placed into crucibles and were heated at a preset rate to the preset temperature. In separate experiments, we studied the thermal behaviors of PE and PS under the same conditions and recorded the corresponding thermoanalytical curves.

RESULTS AND DISCUSSION

System NiO–C

Thermoanalytical data for the 2NiO + C mixture are presented in Fig. 1. The DTA curve indicates an endotherm between 750 and 920°C. (The onset and end temperatures of thermal events were determined from T curves.)

According to the overall chemical equation (I), the complete reduction of nickel oxide with carbon must cause a weight loss of 27.2%. This was actually

[1] These reaction schemes were validated by our studies.

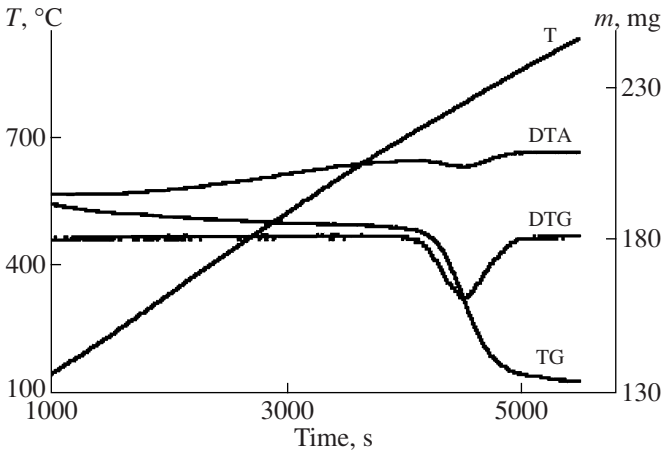

Fig. 1. Thermoanalytical data for the mixture 2NiO + C (V = 10 K/min, m = 200 mg).

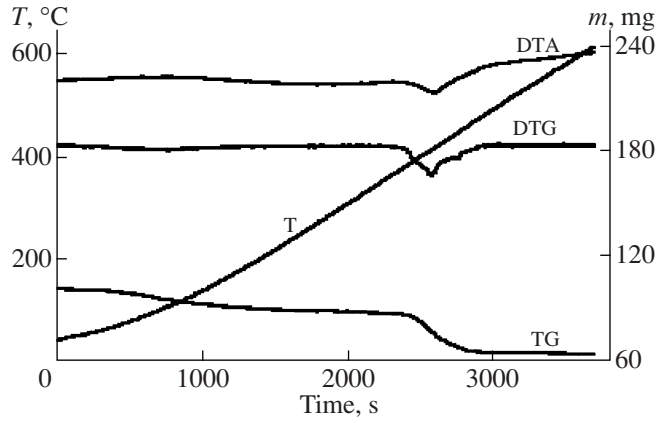

Fig. 2. Thermoanalytical data for the stoichiometric mixture NiO + PE (V = 10 K/min, m = 100 mg).

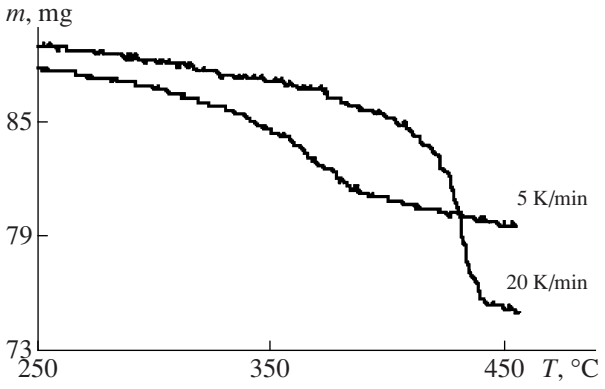

Fig. 3. Thermogravimetric data for the stoichiometric mixture NiO + PS (m = 100 mg).

observed in our experiments (see the TG curve). If part or all of the carbon had been oxidized into CO instead of CO_2, the weight loss would have been smaller. For example, if the reaction had proceeded according to the equation 2NiO + C = NiO + Ni + CO, the weight loss would have been as small as 17.3% and half the nickel oxide would have remained unreduced.

System NiO–PE

It is clear from the thermoanalytical curves of the stoichiometric NiO–PE mixture (Fig. 2) that endothermic reduction in this system begins at a lower temperature (~370°C) than the same process in the NiO–C system. At a heating rate of 10 K/min, the process in the NiO–PE system is over at 480°C and results in the complete reduction of the nickel oxide. This is confirmed by the 26% weight loss (TG curve), which indicates that all of the nickel oxide is reduced according to reaction (II). The weight of the residue (74% of the initial weight) is precisely equal to the elemental nickel content of the starting mixture. If the process had yielded CO, the weight loss would have been only 19.3%.

System NiO–PS

Figure 3 shows the TG curves recorded for the NiO + PS mixture. At a heating rate of 5 K/min, the weight loss is as small as 6.5% (6.5 mg); at a heating rate of 20 K/min, the weight loss is 12%. Note that the theoretical weight loss for reaction (III) is 26.5% and the weight loss corresponding to the decomposition of PS and the removal of the gaseous pyrolysis products without nickel oxide reduction is precisely 6.5%. Therefore, the 12% weight loss observed at the heating rate of 20 K/min (Fig. 3) is evidence that NiO reduction in this system is incomplete. The weight loss observed at a lower heating rate (5 K/min) is equal to the amount of PS in the starting mixture (6.5%). Therefore, under these conditions, all of the PS decomposes and leaves the reaction mixture without reacting with NiO.

These results can be explained by the fact that the decomposition temperature of PS is lower than that of PE (Fig. 4). The TG and DTG curves in Fig. 4 indicate that PS decomposition at a heating rate of 10 K/min begins at 340, 100°C below the PE decomposition temperature.

However, at a higher heating rate of 20 K/min, PS decomposition begins at a higher temperature of 360°C, which is closer to the NiO reduction onset temperature. Therefore, there is good reason to believe that, in this case, part of the reactive PS decomposition products [12] has insufficient time to leave the reaction mixture and is involved in NiO reduction. At heating rates of 30 K/min and above (which are unattainable with the setup used in this study), the reduction of NiO with PS would likely be complete.

The above findings suggest that, as the heating rate is increased, the NiO reduction onset temperature rises. For example, increasing the heating rate from 5 to 20 K/min in the NiO–C system (Fig. 5) shifts the onset temperature of the reaction by 70°C. This trend is also indicated by the TG curves for the NiO–PE system

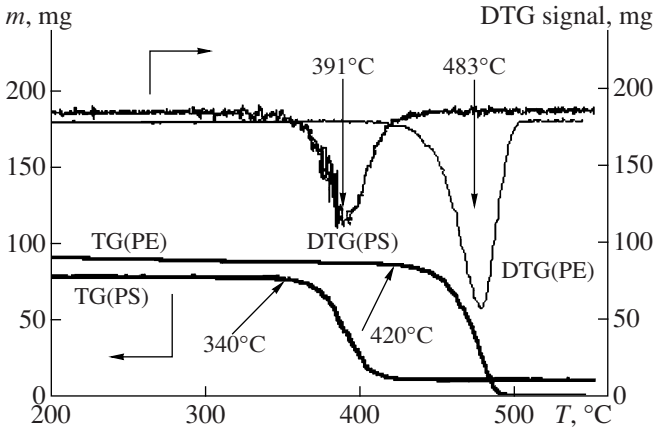

Fig. 4. PS and PE decomposition curves (V = 10 K/min, m = 100 mg).

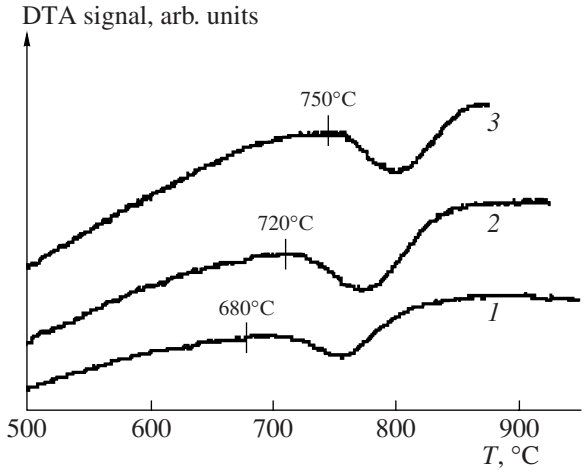

Fig. 5. Shift of the reaction (I) temperature range caused by an increasing heating rate: V = (*1*) 5, (*2*) 10, and (*3*) 20 K/min.

(Fig. 6): as the heating rate is increased, the onset temperature of NiO reduction shifts from 365 to 400°C.

As was note above, similar thermal decomposition behaviors are shown by pure combined reductants. Therefore, NiO reduction under the action of a combined reductant in a linear heating regime is possible owing to the fact that both the decomposition temperature of the reductant and the NiO reduction temperature increase as the heating rate is raised. We observed a similar effect for copper oxide reduction [9]. It is important that whether or not an increase in the heating rate brings about NiO reduction by a given combined reductant depends strongly on the relative shift of the decomposition and reduction temperature regions. If the decomposition onset temperature increases by a larger value than the reduction onset temperature and, as a consequence, the decomposition and reduction temperature ranges overlap, the reduction process will be possible.

Kinetic Calculations

Various approaches are used to calculate the effective activation energy for nonisothermal conditions. The best known approaches are those suggested by Kissinger [13] and Ozawa [14–16]. These are based on the Arrhenius equation corrected for the nonisothermicity of the reaction in such a way that the temperature is a function of time.

In particular, the shift of T_{max} in the DTA curve to higher temperatures as a result of an increase in the heating rate is described by the following equation, set up by Kissinger [13]:

$$\ln\left(\frac{V}{(T_{max}^{DTA})^2}\right) = \ln A - \frac{E}{R}\left(\frac{1}{T_{max}^{DTA}}\right), \qquad (1)$$

where V is the heating rate (K/min), T_{max}^{DTA} is the temperature corresponding to the maximum advance of the DTA curve, A is a constant, E is the effective activation energy of the process, and R is the universal gas constant.

The Ozawa equation [14] evaluates the effect of the heating rate on the temperature at which a given conversion (α) is reached:

$$\ln\left(\frac{V}{(T_{\alpha}^{DTG})^2}\right) = \ln A - \frac{E}{R}\left(\frac{1}{T_{\alpha}^{DTG}}\right), \qquad (2)$$

where T_{α}^{DTG} is the temperature corresponding to the maximum advance of the DTG curve. This method allows the effective activation energy to be determined at any α.

Another modification of the Ozawa equation involves the temperature corresponding to the highest conversion rate (maximum advance of the DTG curve), T_{max}^{DTG} [15, 16]:

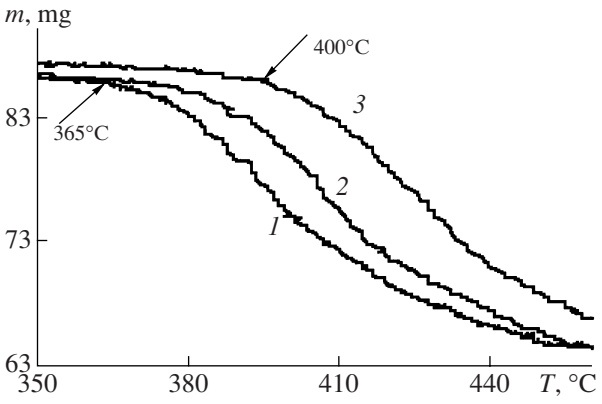

Fig. 6. Shift of the reaction (II) temperature range caused by an increasing heating rate: V = (*1*) 5, (*2*) 10, and (*3*) 20 K/min.

Temperatures corresponding to the maximum advance of the DTA curve for the decomposition of the reductants and for nickel oxide reduction at various heating rates and the effective activation energies of these processes

Substrate	T_{max}, °C			E, kcal/mol		
	V = 5 K/min	V = 10 K/min	V = 20 K/min	Eq. (1)	Eq. (3)	reference data
PE	473.6	497	509	43	38	38 [20] 53 [21] 57 [12]
PS	388	398	420	35	36.5	47 [12] 48 [21]
2NiO + C	758.5	771	800	66	71	75 [6]
6NiO + PE	401.5	416	436	41	43	–

$$\ln\left(\frac{V}{(T_{max}^{DTG})^2}\right) = \ln A - \frac{E}{R}\left(\frac{1}{T_{max}^{DTG}}\right). \quad (3)$$

As follows from experimental data, T_{max}^{DTG} corresponds to $\alpha = 0.5 \pm 0.02$.

Using Eqs. (1) and (3), we calculated the effective activation energies of nickel oxide reduction with carbon and PE. For reaction (I), E_I = 66 kcal/mol from the Kissinger equation and 71 kcal/mol from the Ozawa equation. For reaction (II), E_{II} = 41 kcal/mol from the Kissinger equation and 43 kcal/mol from the Ozawa equation. Hence, the mean effective activation energy of reaction (I) is 68 ± 3 kcal/mol and that of reaction (II) is 42 ± 1 kcal/mol.

The effective activation energies found using the two different equations are rather similar. Furthermore, the activation energy of nickel oxide reduction by carbon (reaction (I)) is comparable with the activation energy of the same reaction under isothermal conditions, 75 kcal/mol [6]. The Ozawa equation (2) was also used to calculate the activation energy of the reaction between NiO and PE at different conversion values: for α = 0.1–0.3, E_{II} = 36 ± 1 kcal/mol; for α = 0.7–0.9, E_{II} = 45 ± 1 kcal/mol.

A plausible explanation of the finding that the activation energy increases with increasing conversion is that the early stages of PE decomposition yield light fragments capable of reducing NiO at a lower temperature and with a lower activation energy (~36 kcal/mol) [12, 16–19]. As the light products are consumed, heavier intermediates build up in the system [12], whose reduction requires a higher activation energy (~45 kcal/mol).

Thus, it follows from our experimental data that, as compared to nickel oxide reduction with carbon, NiO reduction with PE takes place at lower temperatures (450 versus 850°C), and with a lower activation energy (42 ± 1 versus 68 ± 2 kcal/mol). This is a quite expected finding since PE decomposition yields active gaseous species, decreasing the activation energy of NiO reduction. By contrast, the NiO + C reaction is solid-phase. It takes place at high temperatures and requires a much higher activation energy. Note that the activation energies derived from thermoanalytical data using Eqs. (1)–(3) are effective values referring to the overall reduction process rather than to an individual elementary step.

The calculation of effective activation energies provides a means to find the most appropriate reductant (PE in this case) and makes it possible to make some assumptions as to the reaction mechanism.

The activation energies and T_{max} values characterizing nickel oxide reduction are listed in the table.

Polystyrene did not show the properties of a combined reductant under the conditions examined, even though it did so in its reaction with copper(II) oxide [9]. The cause of this distinction is that copper oxide is reducible at comparably low temperatures (310–350°C) close to the PS decomposition temperature (310–360°C). Note that the reduction of CuO with PS is an exothermic process and its activation energy is 29 ± 1 kcal/mol [9].

Thus, this study has demonstrated that, at heating rates of 5–20 K/min, both carbon and PE reduce nickel oxide and these processes are endothermic. The effective activation energies of NiO reduction with carbon and PE are 68 ± 3 and 42 ± 1 kcal/mol, respectively. Because PS decomposes at a comparatively low temperature, it can reduce nickel oxide only at high heating rates.

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