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Effect of the ZrO_2 Pore Structure on the Reduction of a Supported Cobalt Oxide in Catalysts for Fischer–Tropsch Synthesis[1]

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Abstract—Processes occurring in the preparation of the Co/ZrO_2 + 6% Y_2O_3 catalyst are studied by temperature-programmed reduction (TPR). The effects of the concentration of Co, the porosity of the support, and the calcination temperature on catalyst reduction were studied. As was shown by continuous magnetization measurements in the course of TPR, metallic cobalt appeared on the microporous support in two temperature ranges irrespective of the precalcination temperature and the concentration of supported cobalt. These factors affect the reduction rate but do not change the maximum temperatures of the corresponding peaks. It is suggested that the first maximum of the Co formation rate is due to the reduction of CoO particles on the surface of the support and within macropores, whereas the second maximum is due to the reduction of CoO particles located within support micropores. Only one temperature range of CoO reduction was found in the macroporous ZrO_2 + 6% Y_2O_3. This effect is likely due to mass transfer in support micropores.

INTRODUCTION

Supported cobalt catalysts are widely used in Fischer–Tropsch synthesis. Alumina and silica gel are usually used as supports [1], and titania is used more rarely [2]. A number of studies have been devoted to the modification of alumina [3] or silica [4] with zirconia additives to prepare more highly active and selective cobalt catalysts for Fischer–Tropsch synthesis. Studies of cobalt catalysts on pure zirconia are scanty [5], and they mostly concern catalytic activity rather than the preparation of catalysts. The interaction of cobalt oxides with zirconia and the effect of such factors as support texture, cobalt concentration, calcination temperature, calcination time, and reduction conditions on this process are little known. However, this knowledge is very important for the preparation of highly dispersed catalysts [6]. Zirconia with a surface area of 20–30 m^2/g was mainly used to prepare Co/ZrO_2 catalysts [6, 7]; therefore, catalysts with a large surface area in terms of cobalt cannot be obtained. This work is devoted to a study of the reduction of cobalt oxides in the $Co/ZrO_2 + 6\%Y_2O_3$ catalyst by temperature-programmed reduction (TPR).

EXPERIMENTAL

To prepare catalysts, ZrO_2 stabilized by $6\%Y_2O_3$ with a specific surface area of 200 m^2/g, a pore volume of 0.16 cm^3/g, and an average pore size smaller than 5 nm was used as a support (catalysts of series A). The hydrothermally treated $ZrO_2 + 6\%Y_2O_3$ support with a specific surface area of 90 m^2/g, a pore volume of 0.25 cm^3/g, and an average pore size of 15 nm was also used (catalysts of series B).

Cobalt was supported by impregnation with a solution of $Co(NO_3)_2 \cdot 6H_2O$. After impregnation, the samples were dried in air at 80°C for 6 h. The catalysts with Co concentrations of 5, 10, and 15 wt % were prepared. The specific volumes of the cobalt oxide Co_3O_4 formed after calcination were 0.04, 0.08, and 0.12 cm^3/g, respectively, and these values are much lower than the pore volume of the support.

Gases used in the work were purified on a nickel–chromium catalyst, zeolite 5 Å, and alumina according to a standard procedure. Additional purification was performed on a column with MnO/Al_2O_3. In the TPR experiments, a gas mixture of 5% H_2 + Ar was used. The catalyst samples were calcined immediately before the experiments in an argon flow at a specified temperature for 1 h.

The TPR experiments were performed in a microreactor, which served simultaneously as a cell of a vibration magnetometer. The magnetization of a sample was continuously monitored during the reduction. A change in the hydrogen concentration at the reactor outlet was measured using a thermal-conductivity detector. The TPR parameters (flow rate, heating rate, and catalyst weight) were chosen to fulfill the inequality

$$\frac{\beta S}{fC} < 20,$$

where β is the heating rate, K/s; S is the amount of the reduced oxide, mol; f is the flow rate, ml/s; and C is the

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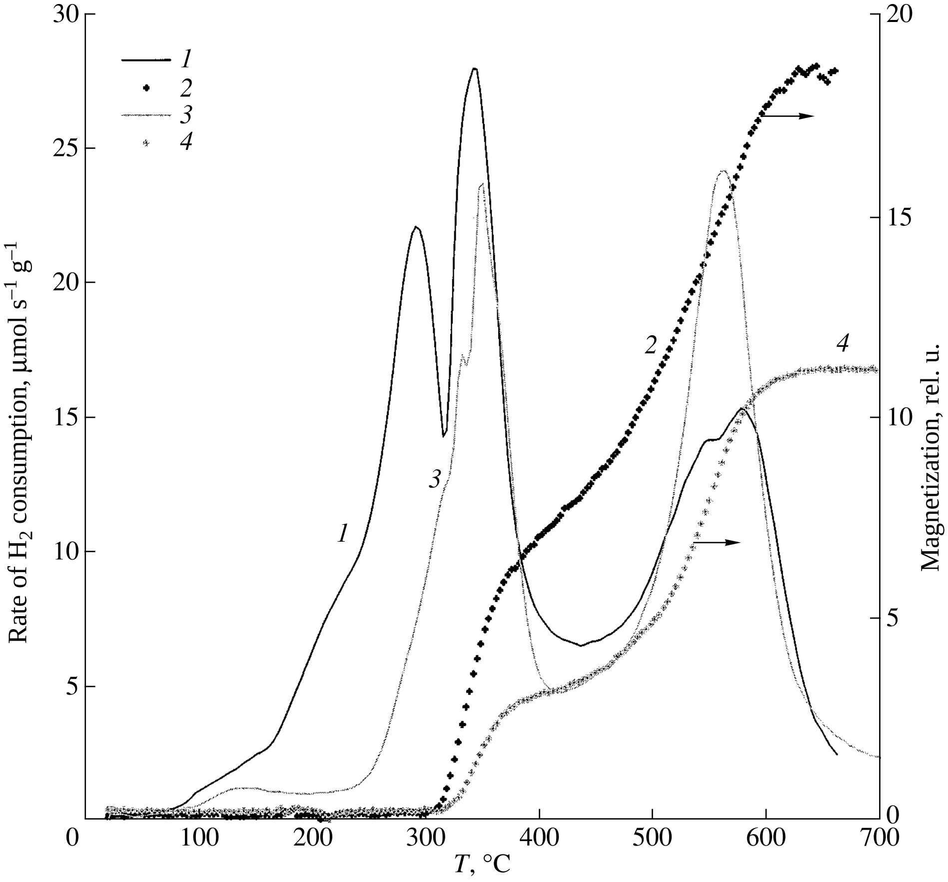

Fig. 1. (*1*, *3*) TPR spectra and (*2*, *4*) magnetization as a function of temperature during TPR for the catalyst 15% Co/ZrO_2 + 6% Y_2O_3 (A). T_{cal} = (*1*, *2*) 300 and (*2*, *4*) 600°C; t_{cal} is 0.5 h.

hydrogen concentration in the gas mixture at the reactor inlet.

As shown in [8], the fulfillment of the above inequality was responsible for the best peak resolution in the TPR spectrum. As a rule, the heating rate was 0.2 K/s at a reducing gas-flow rate of 30 ml/min and a catalyst weight of 0.02 g. The thermal-conductivity detector was calibrated against NiO.

The amount of Co metal in the reduced catalysts was determined by two independent methods: (1) by Co oxidation with oxygen pulses at 300°C (small Co particles in supported catalysts are known to be oxidized to Co_3O_4 [9]) accompanied by the measurement of the amount of consumed oxygen and (2) by the measurement of saturation magnetization. Both methods gave consistent results. Before the oxidation, as well as before magnetization measurements, the catalyst was exposed to an Ar flow to remove adsorbed H_2.

RESULTS AND DISCUSSION

It was found previously [10] that the continuous measurement of magnetization in the course of TPR provides additional information on the reactions that occur during reduction. As only metallic Co is ferromagnetic in the Co_3O_4–CoO–Co system and the Curie temperature of Co is 1115°C, an increase in sample magnetization during TPR is indicative of the appearance of metallic Co in the catalyst.

Figure 1 presents the TPR spectra of the catalyst 15% Co/ZrO_2 + 6% Y_2O_3 (A) calcined at 300 and 600°C for 0.5 h before reduction. The temperature dependence of the magnetization of the catalysts in the course of TPR is also shown in Fig. 1. The TPR spectrum of the catalyst 10% Co/ZrO_2 + 6% Y_2O_3 (A) is similar, and that of the catalyst 5% Co/ZrO_2 + 6% Y_2O_3 (A) consists of only one peak with T_{max} = 280°C.

As can be seen in Fig. 1, the TPR peak due to the reduction $Co_3O_4 \longrightarrow CoO$ precedes the appearance of magnetization in the system. The following peak in the spectrum is accompanied by an increase in magnetization growth; consequently, it corresponds to the $CoO \longrightarrow Co$ transition. The area of the first peak decreased with increasing calcination temperature. This peak disappeared from the spectrum of the sample calcined at 600°C. Most probably, this is due to a decrease in the stability of Co_3O_4 with increasing temperature and the transition of Co_3O_4 to CoO. Stacy *et al.*

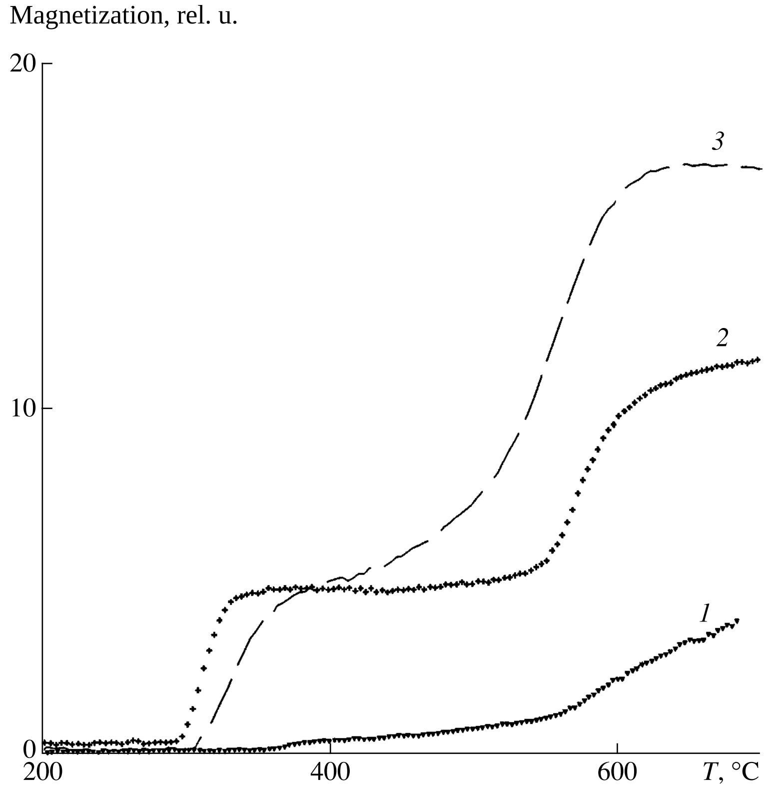

Fig. 2. Magnetization as a function of temperature in the course of TPR of the catalysts Co/ZrO_2 + 6% Y_2O_3 (A) with cobalt contents of (*1*) 5, (*2*) 10, and (*3*) 15%.

[11] found that this transition in an inert gas atmosphere occurred even at 350–400°C.

The third peak is observed in the TPR spectrum at $T > 500°C$. This peak is accompanied by an increase in magnetization; consequently, it corresponds to the appearance of an additional amount of metallic Co in the system. Under more severe calcination conditions, the degree of reduction substantially decreased and the intensity of the high-temperature peak increased.

The magnetization of the catalysts prepared with support (A) increased nonmonotonically, and two temperature ranges were detected, in which the rate of formation of metallic Co was higher. Both temperature ranges where the magnetization increased were most pronounced in the case of the sample containing 10 wt % Co.

Figure 2 presents the temperature dependence of magnetization during the TPR of catalysts A with various cobalt concentrations calcined at 300°C. Note that the magnetization of the sample containing 10% Co hardly increased at all in the temperature range 320–480°C; in other words, the reduction process was inhibited.

A significant change in the TPR spectrum was found on going to the catalysts based on support B. Figure 3 shows the TPR spectrum of catalyst B containing 10% Co. Its magnetization as a function of temperature during TPR is also presented in Fig. 3. The magnetization increased monotonically, and its decrease at $T >$ 600°C was due to the thermal disordering of magnetic moments as the temperature approached the Curie temperature of Co. The table summarizes the relative peak areas in the TPR spectra of catalysts A and B containing 10% Co precalcined at 300°C.

The first low-intensity peak at $T = 95$–$120°C$ is likely due to the interaction of hydrogen with superstoichiometric oxygen because it is known that the nonstoichiometric cobalt oxide CoO_{1+x} ($1.33 < x < 1.50$) with an insignificant excess of oxygen is formed upon the decomposition of cobalt nitrate [11].

The following reactions occur during the reduction of cobalt oxides:

$$Co_3O_4 + H_2 = 3CoO + H_2O, \qquad (I)$$

$$3CoO + 3H_2 = 3Co + 3H_2O. \qquad (II)$$

It follows from the stoichiometry of these reactions that the peak area corresponding to reaction (I) in the TPR spectrum should be 1/3 of the peak area corresponding to reaction (II).

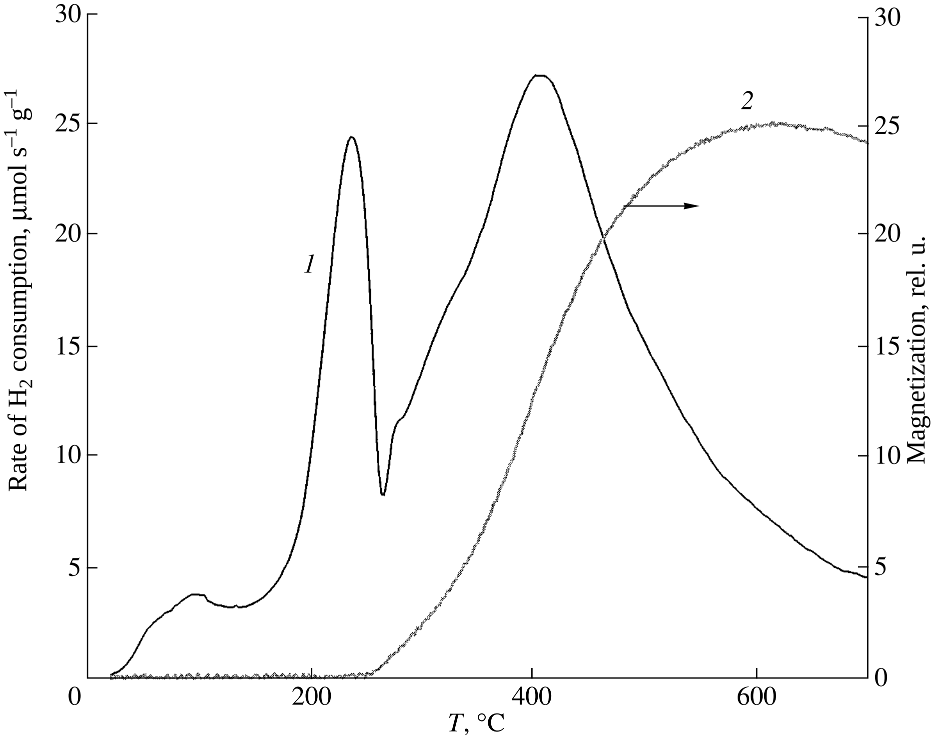

Fig. 3. (*1*) TPR spectra and (*2*) magnetization as a function of temperature in the course of TPR for the catalyst 10% Co/ZrO_2 + 6% Y_2O_3 (B).

As follows from the table, for catalyst A, the ratio between the sum of the areas of peaks nos. 3 and 4 and the area of the second peak is 3 : 1. At the first stage (peak no. 3), slightly less than half of the total CoO is reduced to metallic Co.

For catalyst B, this ratio is somewhat higher than 3. However, taking into account a baseline drift because of the reduction of surface hydroxyl groups, which are usually present on the surface of any support, the ratio is also close to 3. Thus, it follows from the ratio of peak areas in the TPR spectrum that reaction (I) occurs in the same temperature range (227–235°C) over both catalysts, whereas two peaks correspond to reaction (II). The degree of reduction was 80 ± 5% in both cases.

The experimental data suggest that reaction (II) occurs over catalyst A in two stages, while over catalyst B with relatively wide pores this reaction occurs in a single temperature range.

To clarify the reasons for the two-stage reduction of CoO over the microporous support, we performed a series of experiments on temperature-programmed oxidation (TPO). A mixture of 1% O_2 + He and a thermal-conductivity detector were used for TPO. The magnetization of the test sample was continuously measured in the course of TPO.

Figure 4 presents the TPO spectrum for sample A reduced at T = 300°C after preliminary calcination at the same temperature and the magnetization as a function of temperature in the course of TPO.

Figure 5 shows similar plots for the sample of catalyst A reduced at T = 650°C. As follows from Fig. 5, the oxidation of this sample occurred in two stages and the oxidation rate at the first stage was twice as high as that at the second stage. The peak of oxygen consumption of the sample reduced at 300°C (Fig. 4) corresponds to the temperature of the second peak in Fig. 5. As the oxidation rate depends on the metal particle size (as demonstrated in Appendix), one can suggest that, after reduction at 300°C, the catalyst contains mainly coarse Co particles, which are oxidized slowly. In the catalyst reduced at 650°C, small particles are present along with coarse particles, and the former are responsible for the first peak in the TPO spectrum (Fig. 5).

Parameters of the TPR spectra of catalysts A and B

Peak number	Catalyst A		Catalyst B	
	T_{max}, °C	peak area, %	T_{max}, °C	peak area, %
1	120	12	95	4
2	235	22	227	22
3	287	30	–	0
4	544	36	406	74

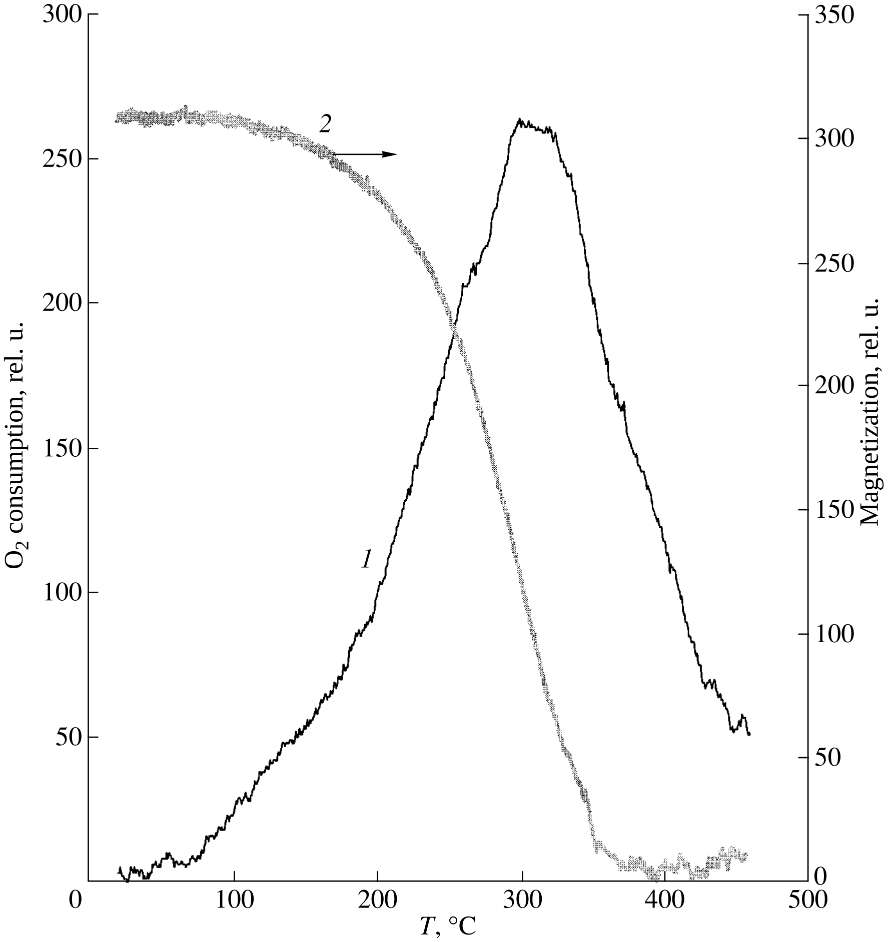

Fig. 4. (*1*) TPO spectrum and (*2*) magnetization as a function of temperature in the course of oxidation for the catalyst 10% Co/ZrO_2 + 6% Y_2O_3 (A); T_{red} = 300°C, T_{cal} = 300°C.

On the basis of the above experimental data, we can propose a mechanism for Co_3O_4 reduction on microporous and macroporous supports. After impregnation, drying, and calcination, the test catalyst was a system consisting of a porous support whose pores were totally or partially filled with Co_3O_4. At calcination temperatures above 500°C, the surface and pores of the support were partially filled with CoO.

During reduction, the reaction front moves from the surface of support granules to the pores. As the pores become narrower, the mass transfer of water formed upon reduction to the external surface of the granule can become a rate-determining process. It should also be taken into account that TPR is a nonisothermal process; therefore, the reduction rate continuously increases. As the activation energy of diffusion is always lower than that of a topochemical reaction, then beginning some time or other, diffusion in pores becomes the slowest process; that is, the process proceeds in an internal-diffusion region. The temperature of transition from a kinetic to an internal-diffusion region depends, other conditions being equal, on the average pore radius of the support, because Knudsen diffusion occurs in narrow pores and the Knudsen diffusion coefficient is proportional to the pore radius. In the Co_3O_4/ZrO_2 system, a decrease in the average pore radius from 15 to 5 nm leads to a fall in the temperature of transition from a kinetic to an internal-diffusion region falls in the temperature range in which the TPR spectrum is measured. As a result, an additional peak appears in the TPR spectrum. A similar situation has been theoretically considered in [12], and the internal-diffusion retardation was shown to have a substantial effect on the shapes of the TPR and TPD spectra. It can also lead to the appearance of an additional peak in the spectrum.

Note that the pore structure of the support does not affect the position of the first TPR peak spectrum due to the reduction of Co_3O_4 to CoO. A similar situation was observed previously [13, 14] in a TPR study of Co/SiO_2 catalysts containing silica gels with different porosity.

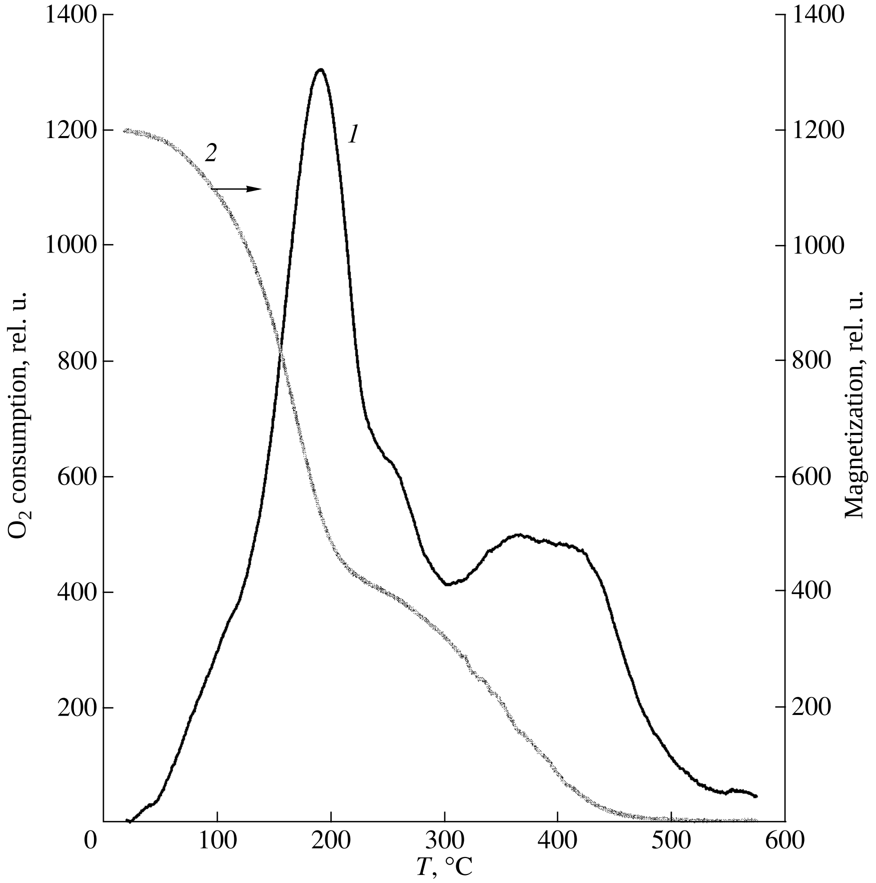

Fig. 5. (*1*) TPO spectrum and (*2*) magnetization as a function of temperature in the course of oxidation for the catalyst 10% Co/ZrO_2 + 6% Y_2O_3 (A); T_{red} = 650°C; T_{cal} = 300°C.

APPENDIX

In the oxidation of metal particles under nonisothermal conditions in a temperature range from 290 to 473 K (the temperature region in which thin oxide films are formed), the monotonic continuous growth of an oxide film occurs, which formally obeys an equation for a contracting sphere. This equation can be written as follows:

$d\alpha/dt = \frac{k}{r}3(1 - \alpha)^{2/3}$ or, taking into account $k = k_0\exp\left(-\frac{E}{RT}\right)$,

$$d\alpha/dt = \frac{k_0}{r}\exp\{-E/RT\}3(1-\alpha)^{2/3},$$

where α is the degree of conversion and k is the rate constant of migration of the reaction interface, cm/s. Taking into account the linear increase in temperature $T = \beta t$, the rate equation can be rewritten as

$$d\alpha/dt = \frac{k_0}{r}\exp\{-E/R\beta t\}3(1-\alpha)^{2/3}. \quad (1)$$

Equation (1) is the analytical description of the TPO spectrum for metal particles with radius r. By differentiating Eq. (1) with respect to t, we can find the condition for extremum, which gives the following condition for the time taken to reach a rate maximum:

$$t_{max} = \left(\frac{r(1-\alpha_{max})^{1/2}3E}{2k_0R\beta}\right)^{1/2}, \quad (2)$$

where α_{max} is the degree of conversion corresponding to the rate maximum. It follows from Eq. (2) that the time taken to reach a rate maximum or the temperature of a maximum rate is proportional to the square root of the average particle radius.

Assume that the test system has a bimodal particle-size distribution. Then, evidently, the TPO spectrum exhibits two peaks corresponding to the average particle radii r_1 and r_2. In this case, small particles are oxidized at lower temperatures, which is the required result.

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