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CATALYTIC REACTION MECHANISMS

Size Distribution of Cobalt Particles in Catalysts for the Fischer-Tropsch Synthesis

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Abstract—The effect of the size distribution of metal particles on the process kinetics was studied for the oxidation and reduction of cobalt nanoparticles (6–10 nm) in the Co/SiO_2, Co/Al_2O_3, and Co/ZrO_2 systems in both isothermic and temperature-programmed regimes in the temperature range from 280 to 500 K. The average size of the cobalt particles was estimated by measurements of the coercive force and residual magnetization using a vibration magnetometer. It was found that the average particle size increases upon cobalt oxidation and decreases upon cobalt reduction due to changes in the fraction of nonsuperparamagnetic particles with sizes of at least 6.5 nm.

INTRODUCTION

Reduction of oxides and oxidation of small metal particles in metal-supported catalysts is of interest from both practical and theoretical viewpoints. It is important for practice to know how the conditions of reduction and subsequent passivation of the catalysts affect the size distribution of metal particles. In addition, a metal, which is an active component of the catalyst, is often oxidized during the catalyst operation. Both factors require elucidation of the features of the reduction and oxidation of small metal particles.

From the theoretical viewpoint, the reduction and oxidation of metal nanoparticles are convenient for the study of the size factors in topochemical reactions.

Many research papers were devoted to the thermal oxidation of bulk metals (for the comprehensive review, see [1]). Nevertheless, only a few papers on the oxidation of small metal particles are known [2–4]. Comparatively high temperatures (>300°C) were mostly used, that is, oxidation occurs in the “Wagner region” and is controlled by diffusion in the oxide layer. As a rule, large particles with micron sizes were studied.

This work is aimed at the study of the effect of the particle size distribution on the kinetics of the reduction and oxidation of cobalt nanoparticles. The Co/SiO_2, Co/Al_2O_3, and Co/ZrO_2 catalysts for the Fischer–Tropsch synthesis with particle sizes of at most 20 nm were used. Previously, we studied these catalysts in the Fischer–Tropsch synthesis [5].

EXPERIMENTAL

Catalysts were prepared by the conventional impregnation of a support with a solution of cobalt nitrate with a specified concentration. Aluminum oxide with a specific surface area of $S = 200$ m^2/g, silica gel with $S = 340$ m^2/g, and zirconia with $S = 200$ m^2/g were used as supports. After impregnation, the catalysts were dried in an air flow at 80°C for 4 h and then calcined at 500°C for 6 h. The Co_3O_4/Al_2O_3, Co_3O_4/SiO_2, and Co/ZrO_2 systems with a cobalt concentration of 10 wt % were prepared according to this procedure. The catalysts were reduced in a hydrogen flow immediately before a run. A cell of a vibration magnetometer, which permitted us to monitor the magnetization of the sample under investigation, served as a reactor. The magnetometer was calibrated with respect to the cobalt metal sample of special purity before each experiment. The magnetization was assumed to be proportional to the weight of metal cobalt. The reduction was performed at 600°C up to the constant magnetization corresponding to the degree of reduction from 70% (support Al_2O_3) to 90% (support ZrO_2). To study the effect of the degree of reduction on the size of the cobalt particles, the reduction was carried out in the isothermic or temperature-programmed (TPR) regimes up to the specified degree of reduction. After reduction, the catalysts were cooled to 7°C in a flow of Ar of special purity. Oxidation was performed with a mixture of 1%O_2 + He in both isothermic and temperature-programmed (TPO) regimes. The oxidation rate was determined by numeral differentiation of the plot of the oxidized cobalt fraction vs. time (for isothermic oxidation) or temperature (for TPO). The heating rate in all nonisothermic experiments was 1°C/min. The sample weight was 30 mg. Before oxidation in the temperature-programmed regime, the sample under study was oxidized until the constant magnetization at 20°C. As can be seen in Fig. 1, the oxide layer is formed upon such pretreatment in 60 s and then does not markedly increase.

During oxidation, the magnetization decreases from the initial value J_0 corresponding to the reduced cobalt to the value $J(t)$ in the moment t. It is obvious that J_0 is proportional to r^3, where r is the average radius of cobalt particles. It is seen that the thickness of the oxide

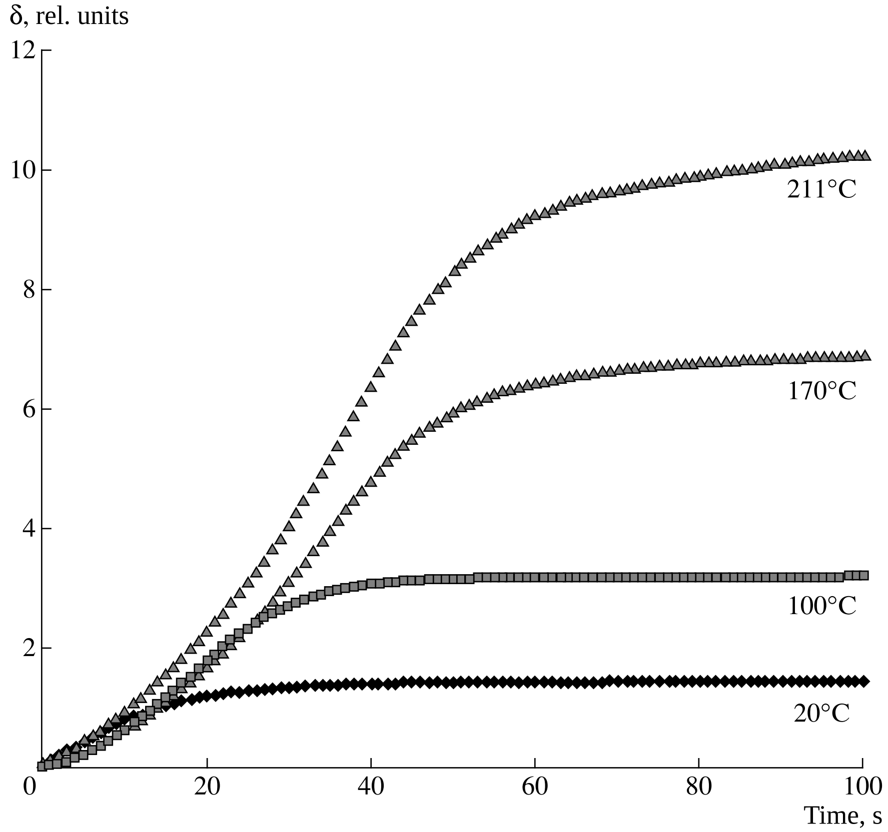

Fig. 1. Thickness of the oxide layer (δ) on the surface of cobalt particles in the 10 wt % Co/Al_2O_3 system vs. time of oxidation at different temperatures.

layer δ (in the case of oxidation) can be determined as follows:

$$\delta = r\left[1-\left(\frac{J(t)}{J_0}\right)^{1/3}\right]. \qquad (1)$$

It was shown by a special series of runs that the weight of the sample under study (from 10 to 50 mg) does not affect the temperature of the maximal oxidation rate during programmed heating with a rate of 0.5°C/s. This means that one can ignore mass- and heat-transfer processes in the catalyst layer during oxidation. Otherwise, the temperature of the maximal rate would depend on the thickness of the catalyst layer, that is, on the weight of the sample.

X-ray phase and X-ray diffraction analyses were carried out on a DRON-3M diffractometer with filtered cobalt K_α radiation. The average size of the coherent scattering regions (CSR) was estimated by the X-ray diffraction method based on the harmonic analysis of the profile of the diffraction maxima. To estimate the CSR of the Co_3O_4 phase under study, we monitored the diffraction maximum (110) with $d = 0.252$ nm. The diffraction patterns were recorded point-by-point at 0.01°C intervals and 10 s exposure. To take into account the instrumental line broadening, we used the α-Fe_2O_3 sample as a standard for which the diffraction maximum (110) with $d = 0.252$ nm was recorded. The standard sample was prepared by thermal decomposition of the More salt (800°C, 2 h) followed by pelleting the sample and its sintering at a temperature of 1250°C (5 h). Based on the physicochemical features of the powder samples, which are determined by the preparation conditions (comparatively low temperatures and dispersion of the sample in the matrix of the X-ray amorphous support), we assessed the value of the physical broadening of the X-ray bands to dispersion and evaluated the CSR size.

Freshly reduced catalyst samples were oxidized without control by exposure to air. Therefore, X-ray diffraction analysis of these samples gives a significant error because of burning the particles, which are lesser in size than the thickness of the oxide layer on the surface of the cobalt particles formed in an air atmosphere. To avoid this error, the samples were oxidized in a $1\%O_2$ + He flow by programmed heating up to 300°C before study on a diffractometer. Note that oxidation occurs under mild conditions (a low heating rate and a low oxygen concentration) in the temperature range in which the oxide film is not split. The oxidized catalyst samples are Co_3O_4/support systems. As the molar volume ratio of Co to Co_3O_4 is 0.75, the average size of

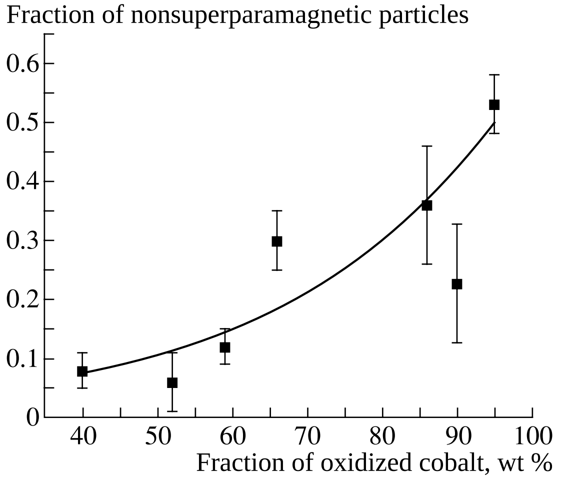

Fig. 2. Fraction of nonsuperparamagnetic particles vs. fraction of oxidized cobalt in the 10 wt % Co/Al_2O_3 system.

metal cobalt particles can be found from the average size of the Co_3O_4 particles.

It has been shown [6] that this method for estimating the average size allows one to avoid errors in the X-ray analysis of freshly reduced samples of cobalt catalysts. The X-ray diffraction analysis performed by us showed that the average size of the cobalt particles in all the systems studied is at most 15 nm.

RESULTS AND DISCUSSION

It is well known that when the thickness of oxide films formed is significant, the gradient of the electric field potential is very low and the mass transfer is only determined by the concentration gradient. Under these conditions, oxidation occurs according to the parabolic law, which follows from the Wagner theory [7]. When thin oxide films are formed, particularly under low temperatures, when the diffusion of ions is hampered, the gradient of the electric potential begins to play the main role. The kinetics of thin film formation under low temperatures is well described by the Cabrera–Mott theory [8]. This theory predicts the existence of a critical temperature below which the film achieves a limiting thickness of several nanometers and after that its fast growth stops. Below the critical temperature, there is the following relation between the temperature and the thickness of the oxide film δ:

$$\delta = \frac{Ueb}{(A - 39kT)}, \qquad (2)$$

where U is the electric field potential in the oxide layer, V; e is the electron charge; b is approximately equal to half the interplanar distance in the crystalline lattice of the oxide, nm; A is the work required for the transfer of the cationic vacancy from the surface to the bulk, J; and k is the Boltzmann constant. It follows from formula (2) that the limiting thickness only exists at temperatures lower than $A/39k$.

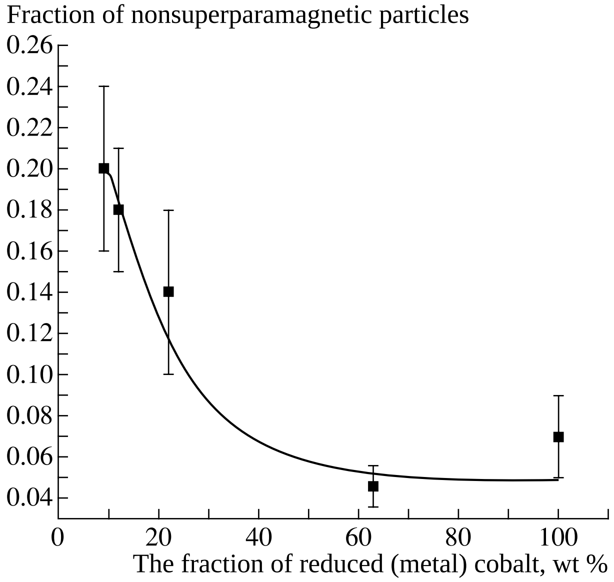

Fig. 3. Fraction of nonsuperparamagnetic particles vs. fraction of reduced cobalt in the 10 wt % Co/ZrO_2 system.

Figure 1 presents the thickness of the oxide layer as a function of time in the process of isothermic oxidation of cobalt particles in the 10 wt % Co/Al_2O_3 system at various temperatures.

As can be seen in Fig. 1, the growth of the oxide film stops after some thickness, which depends on the temperature. Such a process evolution qualitatively corresponds to the Cabrera–Mott model.

To determine the dimensional characteristics of the cobalt particles during reduction–oxidation processes, we used the dependence of the magnetic parameters on the sizes of cobalt particles. We assumed that the system under study consists of two kinds of particles. Particles whose sizes satisfy the condition of superparamagnetism belong to the first type, and particles whose sizes allow one to treat them as a single domain but are greater than the size corresponding to the upper limit of superparamagnetism belong to the second type.

The upper limit of the sizes of the superparamagnetic cobalt particles can be determined from the relation $KV = 25kT$, where K is the cobalt anisotropy constant, V is the volume of the cobalt particles, and T is the blockage temperature (in this case, $T = 7°C$; it is the temperature of measurements). The anisotropy constant was assumed to be 0.7 J/cm^3 [9]. The limiting size of the superparamagnetic cobalt particles estimated according to the above procedure is 6.4 nm. It is known [10] that under the condition that the system contains only single-domain particles, the fraction of the super-

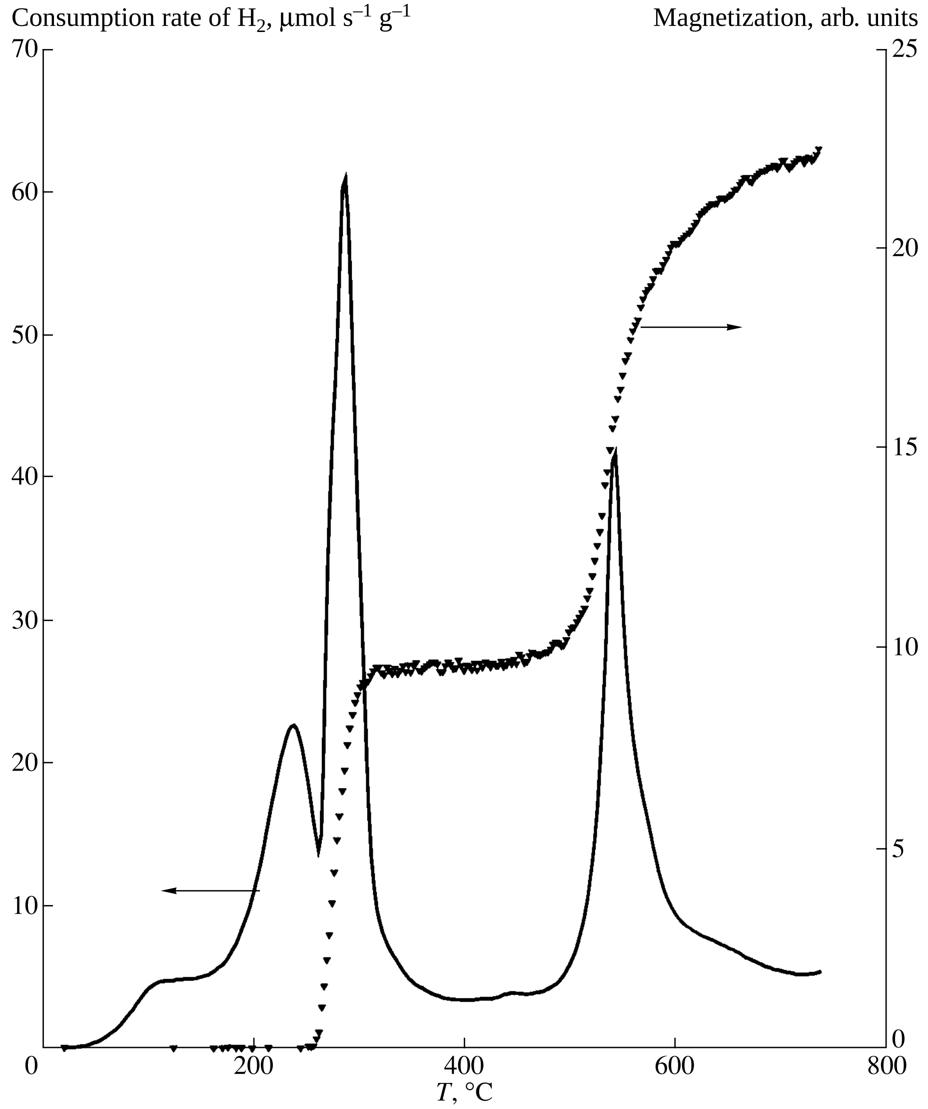

Fig. 4. Hydrogen consumption rate and magnetization vs. temperature for the Co/ZrO_2 system.

paramagnetic particles (γ) can be determined from the relation

$$\gamma = 1 - \frac{2J_r}{J_s}, \quad (3)$$

where J_s is the saturation magnetization and J_r is the residual magnetization. The critical diameter of the single-domain cobalt particles with uniaxial anisotropy is 20–25 nm [11]. According to XRD data, the average size of cobalt particles in the systems under study is 10–15 nm. Thus, in our case, Eq. (3) can be used to estimate the fraction of superparamagnetic cobalt particles. The saturation magnetization and residual magnetization were measured after interrupting the TPO process when the specified degree of oxidation was achieved. For this purpose, the flow of the oxidizing gas (O_2 + He mixture) was replaced by argon and the reactor was cooled to 7°C; then the J_s and J_r were measured.

The measurement of the residual magnetization in our systems showed that a decrease in the fraction of the superparamagnetic particles with an increase in the degree of oxidation was observed in all the cases. Figure 2 shows the fraction of nonsuperparamagnetic cobalt particles ($1 - \gamma$) vs. the degree of oxidation of the Co/Al_2O_3 catalyst. As can be seen in Fig. 2, the fraction of nonsuperparamagnetic particles grows with an increase in the fraction of oxidized cobalt and this is due to the predominant oxidation of small cobalt particles. A similar dependence was found for cobalt particles in the Co/SiO_2 and Co/ZrO_2 systems.

At first sight, the above dependence seems obvious, but this is not the case. To ascertain this, let us consider the expression for the average volume of acobalt particle

$$\bar{V} = \frac{4\pi\rho}{3}\left(\int_{r_{\min}}^{R} r^3 f(r)\mathrm{d}r\right) \Big/ \int_{r_{\min}}^{R} f(r)\mathrm{d}r, \quad (4)$$

where ρ is the density of metal cobalt, g/nm^3; $r_{\min}$ and R are the low and upper limits of the sizes of the cobalt particles in the system, respectively, nm; and $f(r)$ is the function of the size distribution of particles. After the formation of an oxide film with thickness δ on the particle surface during oxidation, the average particle volume $\bar{V}_\delta$ changes in such a way that

$$\overline{V_\delta} = \frac{4\pi\rho}{3}\left(\int_{\delta}^{R} (r-\delta)^3 f(r)\mathrm{d}r\right) \Big/ \int_{\delta}^{R} f(r)\mathrm{d}r. \quad (5)$$

By numeral integration for normal and lognormal distributions one can show that $\bar{V}_\delta < \bar{V}$. In other words, one should expect that during oxidation, the average particle size decreases rather than increases as it was found in experiments. In our opinion, this fact can be explained assuming that δ is the function of a particle size and is higher for the small particles than that for the large particles. The reasons for this fact and elucidating the connection between the thickness of the oxide layer and the particle size need a separate study and are beyond the scope of this work.

The opposite pattern is observed for the reduction process. Figure 3 presents the fraction of nonsuperparamagnetic particles vs. the degree of reduction for the Co/ZrO$_2$ system. Initially, larger particles are reduced. It is typical that when the fraction of the oxidized cobalt reaches ~40%, the fraction of nonsuperparamagnetic particles (whose sizes exceed 6.4 nm, according to our estimates) decreases. Figure 4 shows the reduction rate as a function of temperature for the Co/ZrO$_2$ system. As can be seen from Fig. 4, the magnetization increases in two temperature ranges. We showed earlier that this is due to the reduction of CoO particles with different sizes [12]. In the first temperature range (250–400°C), the larger particles are reduced, and the magnetization corresponding to the first reduction range is ~40% of the magnetization corresponding to the completion of the TPR process. Therefore, in the first reduction range, comparatively large CoO particles are reduced, so that the cobalt particles formed are not superparamagnetic.

In our opinion, the reduction of small particles is hampered for the following reasons. The mass transfer of H$_2$O formed upon CoO reduction prevents the formation of superparamagnetic cobalt particles located predominantly in the narrow pores of the support. Because of the high water partial pressure in the support pores, equilibrium in the reaction $CoO + H_2 = Co + H_2O$ shifts toward cobalt oxide and hydrogen, and higher temperature is also required for the metal formation. This is confirmed by the TPR experiment (Fig. 4). The authors of [13] share this point of view.

Hence, when CoO particles are reduced and cobalt is oxidized in the supported metal Fischer–Tropsch catalysts, the average particle size changes in such a way that the average size increases during metal oxidation and decreases during oxide reduction. It has been noted in the papers on the catalytic activity of supported cobalt catalysts that at high conversions, when the H$_2$O partial pressure is high, cobalt can be partially oxidized [14, 15]. It follows from our findings that oxidation results in an increase in the average size of cobalt particles and this, in turn, leads to a change in the selectivity of the synthesis. In particular, the high initial methanation activity is replaced by an increase in the fraction of heavier hydrocarbons in the reaction products [5]. We do not rule out that such a change in selectivity can be due to the predominant oxidation of small cobalt particles, which exhibit high methanation activity.

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