= CHEMICAL KINETICS AND CATALYSIS

Influence of the Method for Promoting the Co/MgAl₂O₄ Catalyst of Co Hydrogenation with Glucose on the Structural and Chemical Characteristics

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Abstract—The effect of *N*-layer-by-layer promotion (N = 0, 1, 5, 10 layers) of Co/MgAl₂O₄ catalysts (MgAl₂O₄ is aluminum-magnesium spinel with $S_{sp} = 23 \text{ m}^2/\text{g}$) with glucose on the textural and physicochemical properties of the catalyst was studied. For Co-supported catalysts, the dispersity of cobalt increased significantly after promotion of the MgAl₂O₄ support with glucose (N > 1). For cobalt catalysts prepared by impregnation of the support with both cobalt nitrate and glucose, the dispersity of cobalt did not change.

Keywords: Co-supported catalysts, aluminum-magnesium spinel, glucose, IR spectrometry, in situ magnetic method

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Cobalt catalysts (CCs) are widely used in the Fischer–Tropsch (FTS) synthesis due to their high activity and resistance to deactivation, as well as the low rate of the water shift reaction [1, 2]. Cobalt-containing catalysts on highly porous supports are used in selective production of C2–C4 alkenes, C5+ hydro-carbons, and liquid paraffins in CO hydrogenation (FTS), where metallic cobalt plays the role of an active site [1-3]. As is known, the catalysts of FTS should meet basic requirements such as high dispersity of cobalt, reducibility, and high specific surface area [4]. Low dispersity and nonuniform size distribution of cobalt particles often lead to underestimated catalytic activity and deactivation reaction rate.

The dispersity of cobalt can be increased by various methods. For example, the precursor is deposited on highly porous supports with a significant specific surface area, and the conditions of drying and calcination are varied [4, 5]. In this case, cobalt nitrate solutions are used, providing high solubility of the salt during impregnation and, as a consequence, high content of the precursor in the CC. Co-deposition of cobalt nitrates with chelating reagents is also used, which significantly reduces the particle size of metallic cobalt [6–8]. In [6], the H₂O ligand in the [Co(H₂O)₆ (NO₃)₂] complex was replaced with an organic ligand that forms a variety of chelating Co ions of the form [Co(ligand)(H₂O)_{6-x}]²⁺ by complexation. Chinese scientists studied the effect of coordination in the

Co(II)–glycine complex on the properties of the Co/SiO₂ catalyst [7]. It was noted that glycine is an effective chelating agent that improves the dispersity of cobalt and its activity in FTS at a molar ratio of glycine/Co²⁺ = 3 in the Co(3gly)/SiO₂ complex regardless of the preparation procedure. However, the Co(3gly)/SiO₂ complex prepared by the interaction of glycine with cobalt hydroxide is characterized by smaller and more homogeneous and stable cobalt nanoparticles than the complex prepared by the procedure in which glycine was mixed with a cobalt nitrate solution [7].

The effect of preliminary carbon coating on silica on the structure and characteristics of cobalt catalysts for the Fischer–Tropsch synthesis was studied in [9]. It was found that carbon coating of SiO₂ led to stabilization of fine cobalt oxide with partial reduction to metallic cobalt during heat treatment in an inert atmosphere. The size of cobalt oxide nanoparticles decreased from 10–15 nm to 5–6 nm as compared to the conventional Co/SiO₂ catalyst prepared without preliminary carbon coating. Calcination of the samples prepared using carbon coating in air resulted only in a partial increase to 7-8 nm, with uniform particle size distribution. High catalytic performance and finer cobalt particles were observed for cobalt catalysts with high carbon contents. The maximum activity in FTS was almost twice as high as that of reference catalysts without carbon coating; the catalysts showed high

selectivity to long-chain hydrocarbons and low methane selectivity.

Encapsulation of cobalt nanoparticles by carbon is considered to be the main reason for the low activity of catalysts containing a thin carbon layer. The removal of the carbon layer led to increased activity [10, 11].

In the present work, we studied the effect of layerby-layer promotion of the $Co/MgAl_2O_4$ catalyst with glucose as a carbon source on the textural and physicochemical properties of the catalyst.

EXPERIMENTAL

Preparation of Catalysts

The support of Co-containing catalysts promoted with glucose $C_6H_{12}O_6$ (GL) is stoichiometric aluminum-magnesium spinel MgAl₂O₄ (SASOL, Germany), brand Puralox MG 30 Spinel (hereinafter referred to as S) with $S_{sp} = 23 \text{ m}^2/\text{g}$ of the fraction with a particle size of <0.08 mm. The technical characteristics of this spinel were previously described in [12].

The supports were impregnated with an aqueous solution of Co(NO₃)₃·5H₂O for the catalyst to contain 15 wt % Co. The glucose content in the impregnating solution was determined based on the condition of N glucose monolayers (N=0, 1, 5, and 10) formed in the catalyst. The calculation was performed with allowance for the spherical shape of the glucose particle with a given average size $d_{av} = 0.7$ nm and specific surface area of spinel $S_{sp} = 23 \text{ m}^2/\text{g}$; the surface area of 1 mol of glucose was determined, and the amount (g) of glucose for N monolayers in the catalyst sample was calculated.

Two series of catalysts were prepared, which differed in the method of introducing glucose $C_6H_{12}O_6$ in the catalyst. In the first series, the spinel support was promoted with glucose; in the second, cobalt nitrate and glucose of given concentrations were co-deposited on spinel.

For the first series of Co-supported catalysts, the support was prepared as follows. MgAl₂O₄ spinel was initially impregnated with an aqueous glucose solution of a given concentration. The mixture was dried in a rotary evaporator for 4-5 h; then the dried samples were placed in a quartz reactor for glucose decomposition. The calcination was performed in a muffle furnace at 450°C in a temperature-programmed mode (heating rate $\beta = 7$ K/min) for 3 h in an atmosphere of an inert gas (nitrogen; gas-nitrogen flow rate, 10 mL/s). The supports prepared in this way were then impregnated with a $Co(NO_3)_3 \cdot 6H_2O$ solution based on 15 wt % Co followed by drying and calcination under the conditions described above. The catalysts of the first series were designated as Co/1GL&S, Co/5GL&S, and Co/10GL&S.

For the second series of catalysts, the MgAl₂O₄ support was impregnated with a mixture of aqueous solutions of Co(NO₃)₃·6H₂O and C₆H₁₂O₆ of a given concentration, dried in a rotary evaporator, and calcinated as described above. The catalysts of the second series were designated as Co&1GL/S, Co&5GL/S, and Co&10GL/S, respectively.

Before the analysis, all the samples were thoroughly ground to a powder state in an agate mortar, and fractions with particle sizes of <0.08 mm were selected.

Scanning Electron Microscopy (SEM)

Electron microscopy of the solid surface of the samples was performed on a JEOL JSM-6000 Neo-Scope scanning electron microscope with a built-in EX-230 X-ray analyzer equipped with a backscattered electron detector. Tungsten served as the cathode. The accelerating voltage was 15 kV. The images were obtained in a low vacuum mode. The micron amplification of the samples was 5000.

Low-Temperature Adsorption of Nitrogen

The structural properties of the supports and Cocontaining catalysts (total specific surface area, specific surface area of micropores, specific volume of micropores, and average pore size in the samples) were studied by low-temperature nitrogen adsorption on a Micrometrics ASAP 2010N absorbtometer. Before the experiments, the samples (0.2–0.3 g) were degassed in vacuum ($P \le 10$ Torr) at 300°C for 4 h. The measurements were performed at 77 K with an interval of 5 s.

IR Spectrometric Study

Diffuse reflectance infrared spectra (DR IR) were recorded on an EQUINOX 55/S IR Fourier spectrometer (Bruker). The powder fraction of the sample was placed in a quartz ampule with a CaF₂ window and calcinated at 400°C (for 1 h in air and 2 h under vacuum of no worse than 5×10^{-5} Torr). Gaseous CO was purified by passing it through a trap with liquid nitrogen and kept over calcinated zeolite for a long time. The differential spectra of adsorbed CO were obtained by subtracting the background spectrum from the experimental spectrum of the sample containing adsorbed CO, followed by baseline correction using the OPUS 6.0 program (Bruker). Digital subtraction of noise was performed to improve the spectrum quality.

In Situ Magnetometric Measurements

Magnetometry used in this work includes temperature-programmed reduction in hydrogen (TPR) with simultaneous measurement of magnetization (in situ) and magnetic granulometry (field dependences).

The samples were studied on an original vibrating magnetometer (laboratory unit) in the in situ mode to measure magnetization of the ferromagnetic components formed during the chemical reaction [13]. Cobalt has a significant magnetic moment, which just determines magnetization of the samples. When the temperature changes with time during the processes, magnetization (J) changes, which makes it possible to trace the dynamics of the reduction over time (dJ/dT).

The catalyst samples of 10-20 mg were reduced in an H₂ flow during heating to 500°C at a heating rate of 10 K/min in the measuring cell of a vibrating magnetometer. The cell of the vibrating magnetometer was a flow-through quartz microreactor with a volume of 0.3 cm³, which makes it possible to study topochemical transformations under in situ conditions [13]. The sample under study was rigidly fixed between two porous quartz membranes, and variation of magnetization was recorded continuously during heating at a frequency of 1 Hz. Before each experiment, the magnetometer was calibrated using a Co sample of special purity grade as a standard. After the desired temperature was reached, the catalyst was kept in an isothermal mode until magnetization became constant, indicating that the reduction ended. After the reduction, the samples were cooled in a flow of H₂ reducing gas at a rate of 10 K/min.

The magnetic characteristics of the systems were determined by granulometry. For the reduced catalysts, the magnetization J was measured as a function of the given magnetic field H or hysteresis loops, and the coercive force H_c was determined. The magnetic field H was varied from 0 to 8 kOe.

RESULTS AND DISCUSSION

Table 1 shows the structural characteristics of the obtained catalysts: specific surface area, average pore size, and specific micropore volume. The analysis showed that spinel promotion with glucose (the first series of CCs) leads to a significant increase in the specific surface area, from 14.3 to 104.0 m²/g, and in the micropore surface area from 8.9 to 66.5 m²/g, and, which is especially important, to a more than twofold decrease in the average particle size when 0–10 monolayers of glucose are formed on the support. For the samples obtained by co-deposition (second series of CCs), the structural parameters of CCs change insignificantly (Table 1).

Figure 1 presents micrographs of the samples. An analysis of the micrographs in Fig. 1 showed that all the samples have a meso- and microporous structure. According to Fig. 1a (1), 15%Co/S CC has a structure formed by round (grain) agglomerates with characteristic particle sizes of $1-3 \mu m$. For 15%Co/1GL&S (Fig. 1a (2)), flaky-lamellar structures are observed in a small proportion along with spherical (grain) shaped agglomerates, and the size of agglomerates is smaller,

 Table 1. Textural and structural characteristics of the samples obtained by low-temperature nitrogen adsorption

Sample	S _{BET} , m²/g	$S_{ m mcpore},$ m ² /g	$V_{\rm mcpore},$ cm ³ /g	D _{BET} , nm
S	14.8	7.1	0.003	7.5
1GL&S	19.2	1.3	0.00009	6.0
Co/S	14.3	8.9	0.0037	7.9
Co/1GL&S	14.1	7.1	0.003	9.8
Co/5GL&S	47.2	14.6	0.006	6.6
Co/10GL&S	104.0	66.5	0.030	3.6
Co&1GL/S	16.5	3.6	0.0015	8.5
Co&5GL/S	27.2	5.7	0.0022	8.4
Co&10GL/S	27.5	6.0	0.0024	7.2

within 0.7–2 μ m. As glucose is introduced in the CC, a mixture of round and lamellar agglomerates (15%Co/5GL&S) (Fig. 1a (3)) 1–3 μ m in size forms, and new columnar forms (needles) with a diameter of ~0.5 μ m and a length of 2 μ m are found. The structure of 15%Co/10GL&S (Fig. 1a (4)) is similar to that of 15%Co/5GL&S; however, the contribution of columnar structures is much higher, and the length of columns reaches 6 μ m. In addition, 15%Co/10GL&S contain regions with increased Co contents, which has a positive effect on the reduction of Co²⁺ ions.

The increased specific surface area of the 15%Co/5GL&S and 15%Co/10GL&S samples compared with unpromoted CC can be explained by the formation of new flaky and columnar structures.

An analysis of the second series of samples (Fig. 1b) showed that the 15%Co&1GL/S sample (Fig. 1b (1)) is characterized by dense agglomerates interspersed with fine agglomerates mainly of the flaky-lamellar type with characteristic sizes of $0.3-3 \mu m$. The structure of 15%Co&5GL/S (Fig. 1b (2)) is similar to that of 15%Co&1G/S; for 15%Co&5GL/S, however, round agglomerates of the same size are observed. The structure of 15%Co&10GL/S (Fig. 1 (3, 4)) is also formed by dense agglomerates, with a much smaller number of pores, and has a layered character. Thus, when CCs are prepared by co-deposition, the nature of the sample surface does not change significantly, which can be explained by the absence of columnar agglomerates.

Unfortunately, the CC samples containing 15 wt % Co absorb IR radiation very strongly, so it was impossible to record the spectra of these samples. To study the forms of CO adsorption on the surface of these systems, samples containing 3 wt % Co were prepared. Figures 2a and 2b show the spectra of carbon monoxide adsorbed at room temperature on the surface of the 3%Co/S and 3%Co/1GL/S samples. All the spectra are formed by a superposition of several absorption bands (ABs), which can be divided into three groups.



Fig. 1. Micrographs of the samples obtained by the SEM method: (a) (1) Co/S, (2) Co/1GL&S, (3) Co/5GL&S, (4) Co/10GL &S; (b) (1) Co&1GL/S; (2) Co&5GL/S; (3), (4) Co&10GL/S.



Fig. 2. Difference IR spectra of CO adsorbed at T_{room} on the surface of the samples: (a) 3%Co/S and (b) 3%Co/1GL&S. CO pressure: (1) 5, (2) 20, and (3) 50 Torr.

In Fig. 2a, the group of overlapping ABs 2135, 2152-2153, 2166, and 2180-2181 cm⁻¹ refers to the carbonyl complexes of Co²⁺ cations in different coordination environments [14]. The intense asymmetric band at 2070 cm⁻¹ belongs to the CO complexes with $Co^{\delta+}$ cations ($\delta < 1$). The asymmetry of this band indicates that it presents an unresolved superposition with lower frequency bands. Absorption in the range 1983–1995 cm^{-1} refers to the carbonyl complexes with Co^0 atoms. In the spectrum of CO adsorbed on the surface of the Co/1GL/S sample (Fig. 2b), the contribution of the absorption bands corresponding to the complexes with Co^{2+} (2165–2168, 2151–2155, and 2134–2137 cm⁻¹) is higher and exceeds in intensity the superposition of the 2070 and 2058 cm⁻¹ bands attributed to the CO complexes with Co^{δ^+} . In the low-frequency region of the spectrum, the 1980–1982, 2002–2008, and 2032– 2034 cm⁻¹ bands are observed; the 1980 cm⁻¹ band corresponds to the CO complexes with the Co⁰ cations. In this case, it is assumed that this frequency corresponds to the complexes with Co atoms on the surface of large particles, while the higher frequency band at 2002-2008 cm⁻¹ can be attributed to CO adsorption on isolated cobalt atoms [14]. The appearance of a band at 2032–2034 cm⁻¹ is possibly due to the presence of carbon in the catalyst and may correspond to CO adsorption on Co^{δ^+} in cobalt carbide. From the IR data it follows that the introduction of carbon in the catalyst leads to a significantly larger contribution to the spectrum of the complexes of Co^{2+} cations relative to the contribution of the complexes with Co^{δ^+} cations. In the presence of carbon, the reduction of Co^{2^+} cations is evidently hindered. In addition, the presence of the 2002–2008 cm⁻¹ band in the spectrum of the Co/1GL/S sample indicates the presence of isolated cobalt atoms, which is evidence for higher dispersity of cobalt particles.

Figures 3a and 3b show the difference IR spectra of carbonates formed during CO adsorption on the 3Co/S23 and 3Co/1GL&S catalysts at room temperature. It should be noted that carbonates remain unchanged on Co/S after the removal of CO as their decomposition requires high temperature. For Co/1GL/S23, a more intense spectrum is observed after the removal of CO, which indicates higher reactivity of the CC surface. In this case, the spectrum shape changes, which indicates the evolution of the surface carbonate-like structures with time even at room temperature. For Co/1GL/S23, there is greater contribution of symmetric (1435 cm⁻¹ absorption band) and monodentate carbonates with splitting of the ~65 cm⁻¹ doublet (1530 and 1415 cm⁻¹ bands): consequently, this sample has a greater number of more basic electron donor sites-coordinatively unsaturated oxygen anions.

If we consider the processes occurring during the preparation of the second series of CCs, then, possibly, H_2O in the $[Co(H_2O)_6(NO_3)_2]$ complex is replaced by an organic ligand that forms a variety of chelating Co ions $[Co(ligand)x(H_2O)_{6-x}]^{2+}$. The ligands are formed by complexation, which can sig-



Fig. 3. Difference IR spectra of carbonates formed during CO adsorption at T_{room} and pressures of: (1) 5, (2) 20, and (3) 50 Torr, and (4) after the removal of CO: (a) 3%Co/S and (b) 3%Co/1GL&S.

nificantly complicate the reduction of Co^{2+} to Co^{0} in the CC [6]. Importantly, the surface properties of Co are affected by the coordination of Co^{2+} and the molar ratio of Co^{2+} /glucose in the systems [7].

The use of in situ magnetometry makes it possible to trace the dynamics of processes involving ferromagnetic particles [15]. Figure 4 shows the time dependences of magnetization J during the reduction in H_2 in the TPR mode or the kinetic curves of the Co/S, Co/1GL&S, Co/5GL&S, and Co/10GL&S catalysts. As shown earlier, the reduction of Co oxides that do not possess magnetization in the TPR mode (0.5%H₂/Ar) corresponds to two reactions [16]:

$$Co_{3}O_{4} + H_{2} \Rightarrow 3CoO + H_{2}O,$$

$$3CoO + 3H_{2} \Rightarrow 3Co + H_{2}O.$$

Only the reduction of CoO \Rightarrow Co (300°C) is accompanied by an increase in magnetization to a constant value corresponding to complete (80–90%) reduction of catalyst. The XRD data showed that the samples contained both Co₃O₄ and CoO. As glucose is introduced, the peaks related to the CoO phase are detected (along with those of Co₃O₄), which promotes the reduction to metallic cobalt.

The kinetic curves of the reduction of cobalt oxides shown in Figs. 4 are monotonic, which is an essential condition of the monomodal size distribution of cobalt particles. It follows from the figure that the reduction rate of the samples increases in the sequence: Co/S < Co/1GL&S < Co/5GL&S <Co/10GL&S for the first series of the samples. That is, the presence of carbon significantly accelerates the reduction of cobalt oxides to metallic cobalt. For the second series, there was no effect of carbon on the reduction.

For the Co/S, Co/10GL&S, and Co&10GL/S samples reduced to 600°C, the dependences of magnetization J on the magnetic field H (field dependences) were measured (Fig. 5). It was shown that there was a hysteresis, indicating the presence of single-domain and multidomain Co particles in the systems. The absence of a hysteresis ($H_c = 0$) indicates that the system contains exclusively superparamagnetic particles. For cobalt, these are particles with a size of 7.6 nm or less.

For the Co/S and Co&10GL/S systems, the coercive force H_c coincides and the average size of cobalt particles is close enough. For Co&10GL/S, however, the hysteresis or H_c is significantly larger (by a factor of two) than for Co/10GL&S, which indicates the presence of much finer cobalt particles in the Co/10GL&S system.

Figure 6 presents the dependences of the coercive force H_c , calculated from the hysteresis loops, on the glucose content N. As follows from the graph, for the first series of CCs, H_c decreases when the glucose content increases, which indicates increased dispersity of cobalt in the presence of carbon. In contrast, for the second series of CCs, H_c increases with the glucose content, which is associated with an increase in the particle size of metallic cobalt in the presence of carbon (decrease in dispersity).

Thus, summarizing the results obtained by various physicochemical methods, it should be concluded that



Fig. 4. Dependences of magnetization J on the time t during the reduction in H_2 in the TPR mode or the kinetic curves: Co/S, Co/1GL&S, Co/5GL&S, and Co/10GL&S.



Fig. 5. Hysteresis loops for the catalysts Co/S, Co/10GL&S, and Co&10GL/S.

glucose introduction in aluminum-magnesium spinel is preferable to co-deposition as a method to prepare a more efficient Co-supported catalyst for CO hydrogenation. Promotion of spinel with glucose leads to a significant increase in the specific surface area due to the formation of new structures of flaky and columnar types. When glucose is deposited on the support, the dispersity of cobalt increases, which is confirmed by both magnetometry and IR spectroscopy data; for the codeposited systems, the particle size of metallic cobalt increases (dispersity decreases) with an increase in the glucose content.



Fig. 6. Dependences of the coercive force H_c on the glucose content N (N = 0, 1, 5, 10) for Co/S, Co/1GL&S, Co/5GL&S, and Co/10GL&S; Co&1GL/S, Co&5GL/S, and Co&10GL/S.

In the first series of samples, the presence of carbon significantly accelerates the reduction of cobalt oxides to metallic cobalt in a hydrogen flow. According to IR spectroscopy data, however, under weakly reductive conditions (conditions of thermal vacuum treatment) in the presence of carbon, the reduction of Co^{2+} cations on the surface is hindered. For the second series of samples, there was no effect of carbon on the reduction.

CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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