Features of a Three-Phase One-Step Synthesis of Alcohols from CO and H₂ in the Presence of Cu–Co-Containing Slurries

M. V. Chudakova^{a, *}, M. V. Kulikova^a, M. I. Ivantsov^a, G. N. Bondarenko^a, and A. L. Maximov^a

^aTopchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, Moscow, 119991 Russia *e-mail: chudakova@ips.ac.ru

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Abstract—Copper-containing catalytic slurries with different concentrations of active metal precursor solutions are synthesized by drop thermolysis in situ in the hydrocarbon medium of a slurry reactor. According to dynamic light scattering, the particle size of the catalytic slurry dispersion phase is 3-4.5 nm and it remains almost unchanged during the synthesis. Using FTIR spectroscopy it is shown that the structure of precursors of slurry active species depends on the concentration of solution, which may influence the phase composition of catalytically active fragments of the surface during the reduction and synthesis of alcohols. It is demonstrated that alcohols may be synthesized from CO and H₂ in the slurry reactor in the presence of the formed nanosized slurries. It is revealed that the composition of alcohol phase products differs significantly with target product selectivity being comparable: at a low concentration of precursor solution a marked amount of methanol is contained in the mixture (up to 66%), while an increase in the concentration of precursor solution causes a rise in the proportion of higher molecular weight alcohols to 88%.

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Alcohols have found an ever-increasing application in many industries as solvents, plasticizers, stabilizers, and flotation agents; they are the raw materials in the manufacture of surfactants, paint-and-vanish coatings, lubricants, detergents, and pharmaceuticals. Alcohol mixtures are used as motor fuel additives, which makes it possible not only to improve the octane number but also to increase the depth of burning fuels and to reduce the toxicity of waste gases [1].

The main method of producing alcohol mixtures is oxosynthesis, which involves preparation aldehydes with the number of carbon atoms one unit greater than that of the original olefin from alkenes and syngas $(CO + H_2)$ followed by the hydrogenation of aldehydes to alcohols. The disadvantages of the process are fairly robust synthesis conditions, low selectivity, and the need to use individual olefins as a feedstock. Therefore, the development of the one-step process for the synthesis of alcohols from syngas is currently an urgent problem.

Technologies in this field were developed by a number of companies, such as Saipem S.p.A. Italy), Eni S.p.A (Italy), Haldor Topsøe (Denmark), The Dow Chemical Company/Power Energy Fuels Inc. (United States), Lurgi (Germany), and IFP Energies nouvelles (France). However, the one-step synthesis of alcohols from syngas has not been implemented in industry up to now. These processes are commonly accomplished in fix-bed reactors under fairly severe conditions (P = 6-18 MPa, T = 260-430°C, W = 3000-15000 h⁻¹)^{1.1} Owing to a strong exothermicity of the reaction of syngas conversion to alcohols the implementation of catalysis in the dispersion medium providing the effective removal of heat from nanosized catalyst particles distributed in it is a topical issue. Catalytic transformations carried out under conditions of nanoheterogeneous catalysis are characterized by a number of benefits related to the structure of the catalytic system nanoparticles-medium (the absence of porous structure, size effect, accessibility of active particles) and high efficiency of hear transfer in the dispersion medium [2].

The major catalysts of alcohol synthesis are as follows:

(1) modified (mostly with alkali metals) catalysts of methanol synthesis (Zn–Cr, Zn–Cu). Note that a strict control over temperature and the presence of carbon dioxide in the feedstock are required [3, 4];

(2) molybdenum-based catalysts (MoS₂), for which a substantial performance drawback is the need to add H_2S to the feedstock in order to maintain the desired phase composition of the catalyst and, as a

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| - | | | | |
|----------|---|---|--|--|
| Sample | Concentration of Cu(NO ₃) ₂ , g/L | Concentration of Co(NO ₃) ₂ , g/L | | |
| Sample 1 | 53 | 19 | | |
| Sample 2 | 186 | 65 | | |

 Table 1. Concentrations of salts in precursor aqueous solutions during formation of catalytic slurries

consequence, the presence of sulfur-containing compounds in reaction products [5];

(3) modified Fischer–Tropsch catalysts (Co, Fe) show high selectivity for alcohols. They suffer from low stability, which may be considerably improved by selecting precursors and catalyst formation methods [6, 7].

Thus, the modified catalysts of methanol synthesis and Fischer–Tropsch synthesis are the most promising in the production of alcohol mixtures; Cu–Co catalysts are of particular interest among them because they combine properties of both types of catalytic systems.

Copper-containing catalysts for methanol synthesis in the slurry reactor were synthesized [8], and nanosized catalytic suspensions exhibited high activity in CO hydrogenation in situ in a medium of the slurry reactor were prepared [9]. This paper concerns the effect of active metal precursor concentration on the physicochemical and catalytic properties of Cu–Cocontaining nanosized slurries formed immediately in the medium of the slurry reactor.

EXPERIMENTAL

Catalytic systems were formed by the method of drop thermolysis, which consisted in a slow addition of the aqueous solution of copper and cobalt nitrates to the molten paraffin P-2 (a mixture of hydrocarbons $C_{16}-C_{32}$) under continuous stirring in an inert medium. The calculated amounts of $Cu(NO_3)_2 \cdot 3H_2O$ (Acros Organics, 99%) and $Co(NO_3)_2 \cdot 6H_2O$ (Acros Organics, 99%) were dissolved in distilled water to obtain solutions with different salt concentrations (Table 1). The weight ratio of Cu : Co was 3 : 1 at a total metal concentration of 20 wt %.

The particle size of the synthesized samples was determined by dynamic light scattering on a Malvern Zetasizer Nano ZS instrument. Sample preparation was conducted by dissolving 0.01 g of the average catalytic slurry sample in 10 mL of *n*-hexane containing 5 wt % surfactant (sodium dioctyl sulfosuccinate).

Catalytic tests were run on an autoclave-type unit equipped with a mechanical stirrer in the gas flow mode at a pressure of 5 MPa and a syngas space velocity (molar ratio of CO : $H_2 = 1 : 2$) of 10 L/h. The duration of the isothermal regime was 12 h. Sampling of the gas and liquid products was performed at each synthesis temperature. Prior to catalytic runs reductive activation in situ was performed under the following conditions: hydrogen, 20 L/h; pressure, 50 MPa; temperature, 350° C; and time, 1 h.

The feed syngas and the gaseous synthesis products were analyzed by gas-solid chromatography on a Kristallyuks-4000 chromatograph equipped with a thermal conductivity detector using helium as a carrier. CO and N₂ were separated under the isothermal regime at a temperature of 80°C using a 3 m × 3 mm column packed with CaA molecular sieves. CO₂ and hydrocarbons C₁–C₄ were separated using a Haye Sep R (3 m × 3 mm) packed column with temperature programmed heating from 80 to 200°C at a rate of 8°C/min.

A mixture of liquid hydrocarbons was analyzed by gas-liquid chromatography on a Kristallyuks-4000M chromatograph equipped with a flame ionization detector and a 50 m × 0.32 mm OV-351 capillary column. The flow rate of helium, hydrogen, and air was 30, 25, and 250 mL/min, respectively. The temperature programmed regime was as follows: 50°C (2 min), heating from 50 to 260°C at a rate of 6°C/min, heating from 260 to 270°C at a rate of 5°C/min, and holding at 270°C for 10 min. Oxygen-containing products contained in the aqueous phase were analyzed in the following chromatographic mode: the flow rate of helium, hydrogen, and air was 20, 25, and 250 mL/min, respectively. A 50 m \times 0.32 mm \times 0.50 µm HP-FFAP capillary column (nitroterephthalic acid-modified poly9ethylene glycol)) was used for analysis. The sample volume was 0.3 µL. The temperature programmed regime was as follows: 70°C (8 min), heating from 70 to 110°C at a rate of 10°C/min, heating from 110 to 220°C at a rate of 15°C/min, and holding at 220°C (10 min). Quantitative calculations were performed by the internal standard method using isobutyl alcohol as a standard.

The activity of catalytic systems was assessed from the value of CO conversion. The product selectivity was calculated as the ratio of the amount of carbon consumed in the formation of component to the total amount of carbon in the reacted CO.

Reflection IR spectra were measured on a HYPE-RION-2000 IR microscope coupled with a Bruker IFS-66 v/s FTIR spectrometer ($600-4000 \text{ cm}^{-1}$).

Magnetometry measurements were carried out in situ on a setup based on a vibrating magnetometer at room temperature [10]. The sample weight was 20 mg. Magnetic field strength was set by a GPR-30H10D dc source in the range from -0.6 to 0.6 T. Magnetic induction was measured with the aid of an RSh1-10 magnetic induction device. The vibration amplitude of the measuring cell in the vertical plane was maintained constant at a level of 0.5 mm at a frequency of 30 Hz. Signals were registered at a frequency of 1 Hz.



Fig. 1. Number-average dispersed phase particle size distribution for catalytic slurries. The samples are formed from solutions (g/L): (1) $Cu(NO_3)_2$ (53) + $Co(NO_3)_2$ (19), and (2) $Cu(NO_3)_2$ (186) + $Co(NO_3)_2$ (65).

RESULTS AND DISCUSSION

The introduction of precursor salts by drop thermolysis gives rise to stable nanosized slurries. Dynamic light scattering studies (Fig. 1) showed that the samples are characterized by the monomodal particle size distribution and the average particle size is 4.5 nm for the low-concentrated slurry (sample 1) and 3 nm for the high-concentrated slurry (sample 2). Note that the concentration of precursor solution insignificantly affects the average size of active-phase particles.

The structure of the catalytic systems was studied by IR spectrometry. Characteristic bands corresponding to the original metal nitrates (in 1285-1270 and 870-700 cm⁻¹ ranges) do not manifest themselves in the spectra of the test samples (Fig. 2), which indicates the full decomposition of the salts during formation of catalytic systems. However, the spectra of catalytic slurries show bands which may be assigned to the bridging nitro complexes of metals (1580, 1340, 815,

and 654 cm⁻¹) of type $M^+ O^-_{M}$. The intensity of

these bands is small, but it should be emphasized that they are stronger in the spectra of sample 1 than those in the spectra of sample 2. Nevertheless, compared with the spectrum of sample 1 the intensity of bands at 827, 1035, 1390, and 1690–50 cm⁻¹ and broad bands in the range of 3700–3300 cm⁻¹ in the spectra of sample 2 is higher. The latter bands may be attributed to the monodentate nitrate complexes of transition metals with several (1–4) water ligands of type $(L)_n M-O-N \bigcirc O$. Thus, it may be assumed that when slurries are formed in situ in the reaction medium of

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Fig. 2. IR spectra: (1) original paraffin, (2) sample 1 formed from the solution (g/L) of $Cu(NO_3)_2$ (53) + $Co(NO_3)_2$ (19), and (3) sample 2 formed from the solution (g/L) of $Cu(NO_3)_2$ (186) + $Co(NO_3)_2$ (65).

the slurry reactor the concentration of the precursor solution affects the structure of an active species precursor, which may influence the phase composition of catalytically active fragments of the surface during reduction and synthesis.

The Raman spectra of both samples (Fig. 3) exhibit bands G typical of the sp²-hybridized carbon atoms, that is, graphite-like structures, and bands D characteristic of the sp³-hybridized carbon atoms, that is, carbon atoms in the tetrahedral environment at the edges of graphite-like structures. In the longwave region of the spectra weak bands due to M–C and M–O bonds are seen. Note that bands in the range of 230–200 and 530–490 cm⁻¹ are commonly assigned to coordination bonds M–C in cene and pentacoordinated complexes and bands at 650– 500 cm⁻¹ are attributed to M–O bonds. The lower the wavenumber of these bands, the greater the contribution of neighboring multiple C=C or C=O bonds to the M–O bond.

An analysis of the intensities of Raman bands (Table 2) suggests that a decrease in the concentration of slurry precursor solution (sample 1) contributes to the formation of oxides. As follows from a broad absorption background covering the range from 500 to 1000 cm⁻¹, oxides in sample 1 have different structures. The spectra of the samples contain no graphene structures (at 2700 cm⁻¹) but graphite-like structures are detected. It is likely that during formation of the paraffin medium occurs under the influence of temperature and oxidizers (NO₂, O₂) evolved during the decomposition of precursor salts and the formed graphite-like structures are present in the dispersion medium and may be linked to nanosized particles.



Fig. 3. Raman spectra of slurry samples. The samples are formed from solutions (g/L) of salts: (1) Cu(NO₃)₂ (53) + Co(NO₃)₂ (19) and (2) Cu(NO₃)₂ (186) + Co(NO₃)₂ (65).

The slurries were studied by magnetometry in situ (Fig. 4). The studied catalytic slurry is composed of paraffin and copper and cobalt compounds. Paraffin and copper compounds (oxides, salts) possess diamagnetic properties, that is, demonstrate negative magnetization with magnetic field strengthening. During formation of the oxide phase cobalt will be characterized by a dependence inherent in paramagents; i.e., an increase in the magnetic field strength will cause an increase in the magnetization of the sample. Thus, a change in the type of magnetization dependence on the magnetic field strength enables one to make assumption regarding the feasible structure of the catalytic suspension.

The observed dependences of magnetization on the magnetic field strength are typical of compounds occurring in the diamagnetic state. The shape of the remagnetization curve measured for sample 2 is similar to that of the remagnetization curves obtained for the pure paraffin. This fact indicates that during the synthesis of slurries the diamagnetic system is formed, which may contain copper oxide nanoparticles, paraffin, and transition structures not decomposed to the oxide state, while cobalt most probably does not form oxide particles during formation of the catalytic system. Magnetization curves were obtained for the catalytic slurries after reduction and after catalytic testing (Fig. 5). It was found that upon reduction of the catalytic slurry in a medium of hydrogen and further catalytic runs in a medium of hydrogen-rich syngas (CO : $H_2 = 1:2$) the transition of Cu(II) to Cu(0) and Co(II) to Co(0) proceeds. As described above, copper and its compounds exhibit the diamagnetic behavior but during formation of metallic cobalt the ferromagnetic phase is formed from the paramagnetic one. This process is accompanied by a change in the magnetic behavior of the catalytic slurry which is fixed during magnetometric measurements.

The shape of magnetization dependences on the magnetic field strength measured for the catalytic slurries after reduction and after catalysis is typical of ferromagnets, namely, the hysteresis loop is fixed (Fig. 5). Thus, it may be stated that at the stage of activation and during the synthesis the reduction of cobalt (2+) to metallic cobalt occurs. A comparison of the magnetization of the standard cobalt sample (1 mg Co, 966 mV) and the magnetization of the test samples makes it possible to estimate the degree of reduction of cobalt; it is ~64% after reduction and ~100% after synthesis.

An examination of the values of the coercive force, which may implicitly be related to the size of particles, enables one to infer that a certain enlargement of cobalt-containing particles proceeds during the synthesis, as evidenced by dynamic light scattering. For example, it was found that the particle size of the dispersion phase of the catalytic slurry grows from 3 to 5 nm during the synthesis.

The catalytic activity of the formed composite materials was estimated during syngas conversion to alcohols in the temperature range of 230–330°C (Fig. 6). The samples are active throughout the studied temperature range; however, an increase in the precursor concentration leads to an increase in CO conversion from 66 to 84%. It is noteworthy that the selectivity for alcohols is low (Fig. 7).

Regardless of precursor solution concentration the modes of selectivity dependence on the synthesis temperature are the same. The maximum selectivity for oxygenates, which is attained at a synthesis temperature of 270–290°C, is not above 10–11%. However, despite a similar mode of the curves and comparable

| Sample | Intensity of bands | | | | | |
|----------|--------------------------|-------------------------------|-------------------------|-----------------------------|-----|------|
| | G | D (1382 cm ⁻¹) | М-С | | мо | G/D |
| | (1578 cm^{-1}) | | (523 cm^{-1}) | $(230-211 \text{ cm}^{-1})$ | M-O | |
| Sample 1 | 1080 | 811 | 307 | 112 | 412 | 1.33 |
| Sample 2 | 660 | 536 | 176 | 96 | 147 | 1.23 |

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Fig. 4. Remagnetization curves of catalytic Co–Cu-containing slurries before catalysis: (a) paraffin and (b) sample 2 formed from the solution of $Cu(NO_3)_2$ (186 g/L) and $Co(NO_3)_2$ (65 g/L) salts.

selectivity for alcohols, it should be emphasized that the concentration of precursor solution has a considerable effect on the composition of water—alcohol mixtures obtained in the presence of suspensions (Table 3).

In the presence of both samples oxygenates are formed in the temperature range of 270–330°C and the content of methanol in the alcohol phase grows with increasing temperature (Table 3). The concentration of precursor solution affects the distribution of oxygen-containing products in the alcohol phase with the target product selectivity being comparable. For example, at a low concentration of precursor solution a marked amount of methanol is contained in the mixture and an increase in the concentration of precursor solution leads to a noticeable rise in the proportion of higher molecular weight alcohols; their content is as high as 88%. Most likely, this result may be explained by different phase compositions of catalytically active fragments of the surface.

In the presence of sample 1 side products, such as methane and carbon dioxide, are formed more intensively; selectivity for these products attains 61 and



Fig. 5. Remagnetization curve of sample 2 formed from solutions of salts $Cu(NO_3)_2$ (186 g/L) and $Co(NO_3)_2$ (65 g/L): (1) after reduction (H₂, 20 L/h, 5 MPa, 350°C, 1 h) and (2) after catalytic tests (CO : H₂ = 1 : 2, 10 L/h, 5 MPa, 230–330°C).

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Fig. 6. Dependence of CO conversion on synthesis temperature in the presence of slurry samples. The samples are formed from the solutions of salts (g/L): (1) $Cu(NO_3)_2$ (53) + $Co(NO_3)_2$ (19), and (2) $Cu(NO_3)_2$ (186) + $Co(NO_3)_2$ (65).



Fig. 7. Dependence of selectivity for oxygenates on synthesis temperature in the presence of slurry samples. Samples are formed from solutions of salts (g/L): (1) $Cu(NO_3)_2$ (53) + $Co(NO_3)_2$ (19), and (2) $Cu(NO_3)_2$ (186) + $Co(NO_3)_2$ (65).

35%, respectively (Table 4). As the concentration of catalytic slurry precursor is increased (sample 2), CH_4 and CO_2 selectivity decreases to 48 and 22%, respectively. This difference in catalytic activities is probably associated with the ratio of phases for copper in different oxidation states and a distance between active sites on the surface of metal nanoparticles [11, 12].

Thus, when catalytic slurries are formed in situ in the medium of the slurry reactor particles with sizes of 3-4.5 nm are formed. The concentration of salts in the precursor solution influences the formation of transition complex systems: at a low concentration of active metal solutions bridging nitro complexes of metals are formed during the formation of slurries; at a high concentration, monodentate nitrate complexes of transition metals with several water ligands appear.

During the synthesis of catalytic slurries graphite-like structures are formed which result from destruction of the paraffin medium; for the sample prepared from a precursor solution with a low salt concentration their proportion is higher. During the synthesis of slurries the diamagnetic system composed of copper and cobalt oxide nanoparticles and paraffin is formed, and upon activation and synthesis cobalt (2+) is reduced to the metallic cobalt. The particles size of the dispersion phase of the catalytic slurry increases insignificantly, from 3.5 to 5 nm, during the synthesis. In the presence of the formed nanosized slurries alcohols are synthesized from CO and H₂ in the slurry reactor. The concentration of the active metal precursor considerably affects the catalytic activity of the slurries. It is worth noting that the compositions of alcohol phase products differ appreciably while the target product selectivity is comparable: at a low concentration of precursor solution the resulting mixture contains a large amount of methanol (up to 66%), while an increase in the concentration of precursor solution leads to a marked rise in the proportion of higher molecular weight alcohols (88%).

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| Sample | <i>T</i> , °C | Content, % | | | | | | |
|----------|---------------|----------------|----------------|----------------|----------------|----------------|----------------|-----------------|
| | | C ₁ | C ₂ | C ₃ | C ₄ | C ₅ | C ₆ | C ₂₊ |
| Sample 1 | 270 | 61.65 | 32.47 | 4.98 | 0.89 | 0.00 | 0.00 | 38.35 |
| | 290 | 64.73 | 29.72 | 4.34 | 1.22 | 0.00 | 0.00 | 35.27 |
| | 310 | 66.67 | 29.06 | 3.28 | 1.00 | 0.00 | 0.00 | 33.33 |
| | 330 | 63.65 | 33.13 | 2.55 | 0.67 | 0.00 | 0.00 | 36.35 |
| Sample 2 | 270 | 11.41 | 71.88 | 12.39 | 4.18 | 0.15 | 0.00 | 88.59 |
| | 290 | 24.55 | 58.68 | 11.47 | 4.96 | 0.35 | 0.00 | 75.45 |
| | 310 | 36.43 | 52.17 | 7.75 | 3.29 | 0.36 | 0.00 | 63.57 |
| | 330 | 30.77 | 61.63 | 4.79 | 2.69 | 0.13 | 0.00 | 69.23 |

Table 3. Distribution of products of the alcohol phase obtained in the presence of slurry samples. Samples are formed from solutions at salt concentrations (g/L): (1) Cu(NO₃)₂ (53) + Co(NO₃)₂ (19) and (2) Cu(NO₃)₂ (186) + Co(NO₃)₂ (65)

| Samula | T, ℃ | Selectivity, % | | | | | |
|----------|------|-----------------------|--------------------------------|-----------------|------|-----------------|--|
| Sample | | C ₁ | C ₂ -C ₄ | C ₅₊ | Oxy | CO ₂ | |
| Sample 1 | 230 | 1.7 | 3.1 | 60.1 | 0.0 | 35.0 | |
| Sample 2 | 250 | 31.9 | 9.6 | 54.8 | 0.0 | 3.7 | |
| | 270 | 52.3 | 8.6 | 27.3 | 9.2 | 2.6 | |
| | 290 | 54.9 | 5.1 | 26.3 | 8.7 | 4.9 | |
| | 310 | 59.9 | 3.9 | 17.4 | 4.3 | 14.4 | |
| | 330 | 60.9 | 4.5 | 10.5 | 1.8 | 22.4 | |
| | 230 | 19.1 | 3.1 | 75.7 | 0.0 | 2.1 | |
| | 250 | 22.2 | 29.5 | 47.4 | 0.0 | 0.9 | |
| | 270 | 29.3 | 32.2 | 22.9 | 10.6 | 5.0 | |
| | 290 | 31.8 | 28.6 | 18.6 | 10.1 | 10.9 | |
| | 310 | 37.2 | 35.8 | 6.5 | 5.3 | 15.2 | |
| | 330 | 47.6 | 11.3 | 14.9 | 0.5 | 25.6 | |

Table 4. Selectivity for the products of alcohol synthesis from CO and H₂ in the slurry reactor

A.L. Maximov, ORCID: http://orcid.org/0000-0001-9297-4950

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CONFLICT OF INTEREST

A.L. Maximov is the editor in chief of the journal Petroleum Chemistry. Other authors declare that there is no conflict of interest to be disclosed in this paper.

ADDITIONAL INFORMATION

M.V. Kulikova, ORCID: https://orcid.org/0000-0003-2235-8989

M.V. Chudakova, ORCID: https://orcid.org/0000-0001-9211-9970

M.I. Ivantsov, ORCID: https://orcid.org/0000-0002-1712-2341

G.N. Bondarenko, ORCID: https://orcid.org/0000-0002-6637-7594