Hydrogenation of CO₂ on the polymetallic catalysts prepared by self-propagating high-temperature synthesis*

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A new class of multifunctional polymetallic catalysts was developed, the precursors of which are complex multicomponent intermetallic compounds prepared by self-propagating high-temperature synthesis. The catalysts based on Co and Ni exhibit high activity in the hydrogenation of CO₂ to methane. The maximum yield of methane is observed at 250–350 °C with an almost complete conversion of CO₂ and 100% selectivity. Hydrocarbons C_1-C_4 , including unsaturated hydrocarbons (propylene and butadiene), were synthesized on the Co-Fe-La catalyst under a pressure to 2 MPa at 250–350 °C and the ratio CO₂ : H₂ = 1 : 1. The new class of catalysts is promising for the development of direct CO₂ hydrogenation to heavy (liquid) alkanes and unsaturated hydrocarbons.

Key words: hydrogenation of CO₂, hydrocarbons, polymetallic catalysts, self-propagating high-temperature synthesis.

Carbon dioxide is an important renewable raw materials for manufacturing valuable chemical semi-products and fuels. At present the most part of processed CO_2 is used in industry for the synthesis of urea and, in significantly smaller amounts, in manufacturing polycarbonates and light chemistry products by carboxylation reactions. Hydrogenation is the most promising process for the mass consumption of carbon dioxide with methanol or hydrocarbons as the predominant target products. Hydrogenation can afford the final products either immediately, or via the intermediate formation of carbon monoxide and subsequent processing of synthesis gas in such processes as the Fischer–Tropsch (FT) synthesis. In most of the works, the mentioned processes are considered as a method for the solution of ecological problems associated with CO_2 emissions to the atmosphere. Given a scale of CO₂ emissions the only possible way to solve this problem involves the mass production of cheap hydrogen without formation of carbon dioxide as a secondary product. However, hydrogen manufacturing, for example, by water electrolysis using environmentally friendly production of electric

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The studies of catalysts for CO₂ hydrogenation directly to hydrocarbons C_{1+} occupy an important position in literature. The mono- and bimetallic catalysts containing Ni, Co, and noble metals (Pd, Pt, Au), as well as a Ru and La, immobilized in various combinations on the oxide, ceramic, and organometallic supports were developed for methanation.^{1–8} In the presence of some catalysts, CO and methanol are also formed along with methane.^{1,2} Heavy hydrocarbons, including liquid hydrocarbons, predominate among the products obtained on the supported iron-containing catalysts, whereas methane is mainly synthesized on the cobalt catalysts.9,10 The bifunctional catalysts was described on which CO₂ was first reduced to CO and then liquid hydrocarbons were formed using the FT synthesis.¹¹ An appreciable yield of heavy (C₂₊) alcohols was observed on a series of the metalcontaining catalysts on both the oxide¹² and ceramic (Mo₂C)¹³ supports, and the yield increased with temperature parallel to an increase in the content of heavy hydrocarbons in the products.¹³

We have previously proposed the new class of polymetallic catalysts produced from complex multicomponent intermetallic compounds (aluminides), which are the

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products of self-propagating high-temperature synthesis (SHS).^{14–18} These catalysts are based on the metals of the iron group with additives of diverse promoters (Mn, Zr, V, Mo, Ce, La, and others). They demonstrated high activity and selectivity in the processes of deep oxidation of CO, hydrogen, and hydrocarbons; in the FT synthesis; and in the hydrodesulfurization of gasoil. Since examples of the successful use of the Co-, Ni-, and Fe-containing catalysts for CO₂ methanation are known, it seemed of interest to investigate the hydrogenation of carbon dioxide in the presence of cobalt-based catalysts earlier synthesized in our group for the FT reaction and include in the study nickel-, cobalt-, and iron-based systems prepared according to our procedure.

Experimental

For the preparation of intermetallic precursors of the polymetallic catalysts, a mixture of the calculated amounts of metal oxide powders with aluminum (charge) was placed into a graphite mold strewn inside with fractionated molten alumina and fired with a tungsten coil heated with electric current. The reaction proceeded in the combustion wave mode *via* the following scheme:

$$\Sigma M_x O_v + \alpha Al \longrightarrow [\Sigma M_u Al_v] + z Al_2 O_3.$$

The temperature of the process reached 2500-3000 °C, and the reaction products were in the bilayer liquid phase: lighter alumina was on the top, and the intermetallic alloy was on the bottom. The $[\Sigma M_{\mu}Al_{\nu}]$ alloy consisted of intermetallic compounds with higher and lower aluminum contents. The layers are readily separated after the liquid phase congealed, and the friable metallic ingot was broken to pieces and classified on sieves. The catalysts were prepared by leaching of the sampled fraction in an alkali (NaOH or KOH) solution followed by washing and stabilization with a solution of hydrogen peroxide. The process was described in more detail earlier (see, e.g., Ref. 17). The catalyst grains were dendrites of poorly leachable lower intermetallic compounds (as a rule, of a base metal) covered with the strongly disordered, partially amorphous, and nanostructured oxometallic active phase enriched in promoters. Thus, the catalysts always contain residual aluminum in an amount of about 10 wt.%. Further the composition of the catalyst is presented in wt.% based on the sum of active metals only minus aluminum. The fractions of 100-300 µm size were used in the physicochemical and catalytic studies of the synthesized catalysts. In the cases where the catalytic studies were carried out under pressure in a large reactor, the fractional composition of the catalyst ranged from 300 to 500 µm. The fraction of 50-100 µm was examined using X-ray diffraction. No preliminary treatment was carried out for the samples prior to the experiments.

The X-ray diffraction analysis (XRD) of the powdered samples was carried out on a DRON-3 X-ray diffractometer (Fe-K α radiation). The structure and elemental composition of the surface were studied by scanning electron microscopy (SEM) on a Zeiss Ultra plus instrument equipped with a JCXA-733 Superprobe X-ray spectral microanalyzer (JEOL, Japan).

The specific surface area of the samples was determined using the BET method by nitrogen on a Sorbi-M setup (Meta, Novosibirsk).

Hydrogenation under atmospheric pressure was carried out on a laboratory setup with a flow quartz reactor with the fixed catalyst bed (1 cm^3) at a gas hour space velocity (GHSV) of 12 000 h⁻¹. The gas mixture for all tested catalysts, except for the iron-containing sample, 4.1 vol.% CO₂, 16.4 vol.% H₂, and up to 100% helium. The following mixture was used for tests of the 85Co-10Fe-5La catalyst under atmospheric pressure: 6.0 vol.% CO₂, 24 vol.% H₂, and up to 100% helium. In both cases, the H₂ : CO₂ ratio was 4 : 1. The initial mixture and reaction products were examined on a 3700 computed chromatograph (Russia) with a thermal conductivity detector and two packed columns (zeolite 5A and Porapak Q) using helium as a carrier gas and on an Avtotest 02.03P gas analyzer (zero class of accuracy) (Russia).

The hydrogenation of CO₂ under a pressure of 1 and 2 MPa in the temperature range 250–350 °C was carried out on a flow setup with a stainless steel reactor with the fixed catalyst bed. The load of the catalyst was 4.6 cm³. A gas mixture of 50 vol.% CO₂ + 50 vol.% H₂ was used. The GHSV was 860 h⁻¹. The products were analyzed on a Khromos GKh-1000 gas chromatograph (Russia) equipped with four detectors (three thermal conductivity detectors and one flame-ionization detector), three packed columns, and one capillary column ValcoPiotVP-Alumina Na₂SO₄ (50 m×0.53 mm×10.0 µm) using argon and helium as carrier gases.

Results and Discussion

The Co-based catalysts developed previously for the FT process were used at the initial stage of the study. Their specific surface area ranged from 10 to 25 m² g⁻¹ depending on the chemical composition.^{15,17} According to the SEM data, the surface of these catalysts is formed by planar hexagonal nanostructures with a diameter of $1-2 \mu m$ and the thickness less than 100 nm, and their substructure consists of fragments <20–30 nm in size. The shape of these fragments depends on the chemical composition of the catalysts.

The 95Co-5Zr and 95Co-5La catalysts with high activity in the FT process were chosen for tests. Methane turned out to be the single product of CO₂ hydrogenation under atmospheric pressure. The temperature dependences of the conversion of CO₂ and yield of methane for these catalysts are presented in Fig. 1.

The maximum conversion of CO_2 and yield of methane for these catalysts are nearly the same (69 and 2.8 vol.%, respectively), whereas the 95Co—5La catalyst during the FT process showed increased activity and higher selectivity to liquid hydrocarbons, while the yield of methane turned out to be low.

The nickel-based catalysts were synthesized to increase the conversion of CO_2 , since they are characterized by excellent hydrogenation properties. In addition, cerium was included into the composition of these catalysts, be-



Fig. 1. Temperature dependences of the conversion of $CO_2(Y)$ and methane yield in hydrogenation on the 95Co-5Zr (a) and 95Co-5La (b) catalysts.

cause of all developed catalysts for the FT reaction only the cerium-containing system demonstrated a high activity combined with the maximum yield of methane. The catalysts 90Ni-5Co-5Ce ($S_{sp} = 3.6 \text{ m}^2 \text{ g}^{-1}$), 90Ni-5Mn-5Ce ($S_{sp} = 16.9 \text{ m}^2 \text{ g}^{-1}$), and 85Ni-5Co-5Mn-5Ce ($S_{sp} = 6.4 \text{ m}^2 \text{ g}^{-1}$) were studied. In all cases, the effect observed in our earlier study is evident: a manganese additive noticeably increases the specific surface area of the catalysts.

An enhanced yield of heavy hydrocarbons on the ironcontaining catalysts was repeatedly reported. Therefore, the iron-modified catalysts for the FT synthesis (95-x)Co-xFe-5La (x = 10, 30, and 50) were also developed. The first results on studying the 85Co-10Fe-5La catalyst are presented further.

All the four samples of the catalysts were studied by XRD. The results of analysis of the XRD patterns are presented in Table 1.

As follows from Table 1, only phases of nickel and nickel oxide are unambiguously identified in the nickelbased catalysts, whereas the formation of intermetallic compound Ni_{6.4}Mn_{0.806} can be assumed in 90Ni-5Mn-5Ce catalyst. No cerium-containing metallic or oxide phases were found. The presence of higher cobalt aluminide Co₄Al₁₃ in the 85Co-10Fe-5La catalyst is of inter-

Table 1. Phase composition of the 90Ni-5Co-5Ce,90Ni-5Mn-5Ce, 90Ni-5Co-5Mn-5Ce, and 85Co-10Fe-5La catalysts according to the XRD data*

Catalyst	Phases
90Ni-5Mn-5Ce	Ni, NiO _{cub} , Ni _{6.4} Mn _{0.806} ?
90Ni-5Co-5Ce	Ni, NiO _{cub}
90Ni-5Co-5Mn-5Ce	Ni, NiO _{cub}
85Co-10Fe-5La	CoCo ₂ O _{4 cub} , Co ₄ Al _{13 ort} ,
	$\text{Co}_7\text{Fe}_{3 \text{ cub}}, \text{CoAl}_{\text{cub}}$

* Indices "cub" and "ort" correspond to the cubic and orthorhombic phases, respectively.

est, since these intermetallic compounds are very actively destroyed during leaching. Possibly, the stability of this phase is related to the fine-layer structure of the catalyst grains (see further) impeding the penetration of an alkaline solution inside the grain. The metallic phase in this catalyst is also presented by intermetallic compound Co_7Fe_3 .

The SEM images and elemental composition of the grain surface of the 90Ni-5Mn-5Ce catalyst are presented in Fig. 2 and Table 2, respectively.

As can be seen in Fig. 2, individual regions (points 1, 2, and 5) covered by nanostructural aggregates with a significantly increased manganese content (see Table 2) are formed on the surface. Cerium is also nonuniformly distributed over the surface, and its concentration is appreciably lower than the average concentration in the sample (5 wt.%).

The surfaces of the 90Ni-5Co-5Ce and 90Ni-5Mn-5Ce catalysts are similar in morphology, but no nanostructured regions are observed on the surface of the cobalt system. The cobalt distribution in the surface layer is more uniform than that of manganese, and its content is close to the total volume concentration. The surface layer is impoverished in cerium as in the case of the 90Ni-5Mn-5Ce catalyst.

Unlike the previous catalysts, a high cerium concentration exceeding its average volume concentration is observed on the grain surface of the 85Ni-5Mn-5Co-5Cecatalyst. As in the case of the 90Ni-5Co-5Ce catalyst, cobalt shows a more uniform distribution, and its average content on the surface is ~5 wt.%. Manganese is concentrated on the regions with a fine nanostructure.

The surface morphology of the 85Co–10Fe–5La catalyst, as can be seen from Fig. 3, is distinguished by the fine-layer nanostructure of planar units, which is not characteristic of any earlier studied catalysts of the FT synthesis.

The results of test studies of the behavior of the nickelbased catalysts in hydrogenation of CO₂ are shown in Fig. 4.



Fig. 2. SEM images of the grain surface of the 90Ni-5Mn-5Ce catalyst.

Table 2. Content of elements (wt.%) in the points indicated in Fig. 2 according to the electron probe X-ray microanalysis data

Point No.	0	Al	Mn	Ni	Ce
1	24.80	3.44	22.28	48.16	1.32
2	34.68	2.72	29.62	32.06	0.92
3	26.86	6.40	1.70	65.03	_
4	19.97	4.95	_	75.09	_
5	28.16	4.86	37.04	29.94	_
6	22.82	9.45	1.44	64.31	1.98

Methane is the single hydrogenation product in all cases. The best results were obtained on the 85Ni-5Mn-5Co-5Ce catalyst on which the yield of methane and conversion of CO₂ are 4.0 vol.% and 97%, respectively. It remains unclear so far whether the high activity of the 85Ni-5Mn-5Co-5Ce catalyst is related to the increased cerium concentration on the surface. A peak-shaped pat-

terns of the temperature dependences of the CO_2 conversion and methane yield with a maximum at 250–300 °C (350 °C for the 95Co–5La catalyst, see Fig. 1, *b*) is also worth mentioning. These dependences are repeatedly observed for the studied catalysts in several consecutive experiments. The reversible deactivation of the catalysts at the temperatures higher than the point of maximum is observed. The nature of this phenomenon remains unclear.

An attempt to affect the composition of the products on similar catalysts by the variation of the H_2 : CO₂ ratio was unsuccessful. For example, a decrease in the ratio from 4 : 1 to 1 : 1 on the 85Ni-10Co-5Mo catalyst resulted in a simple decrease in the CO₂ conversion and methane yield by four times.

The sample of the iron-containing 85Co-10Fe-5La catalyst was first tested in the hydrogenation of CO_2 under atmospheric pressure. The results are presented in Fig. 5.

It can be seen that the conversion of CO_2 is lower than 50% under these conditions, the selectivity to methane is 100%, and the maxima on the curve of the temperature



Fig. 3. SEM images of the grain surface of the 85Co-10Fe-5La catalyst.



Fig. 4. Temperature dependences of the conversion of $CO_2(Y)$ and methane yield in hydrogenation on the 90Ni-5Mn-5Ce(a), 90Ni-5Co-5Ce(b), and 85Ni-5Mn-5Co-5Ce(c) catalysts.

dependences of the CO₂ conversion and methane yield fall onto the temperatures >300 °C. As a result, the activity of this catalyst under atmospheric pressure is fairly low, and no formation of heavy hydrocarbons is observed. Since the previously published data on the iron-containing catalysts were obtained in experiments at elevated pressures, we also tested this catalyst under pressures of 1 and 2 MPa (Fig. 6).



Fig. 5. Temperature dependences of the conversion of CO_2 (*Y*) and methane yield in hydrogenation on the 85Co-10Fe-5La catalyst.

As follows from Fig. 6, the conversion of CO_2 depends weakly on the pressure especially at high temperatures. The same is true the products of CO_2 hydrogenation on the 85Co-10Fe-5La catalyst. The typical compositions of the products at P = 1 MPa and T = 250 °C (based on reacted CO_2) are presented below.

Product	Content	Product	Content
	(vol.%)		(vol.%)
CO	0.1	Propylene	1.6
Methane	61.2	<i>n</i> -Butane	3.5
Ethane	16.5	Isobutane	0.3
Ethylene	0.1	Butadiene	0.8
Propane	15.9		

It can be seen that methane is the major product, but the fraction of heavier alkanes exceeds 35%, and the yields of ethane and propane are almost equal and their sum exceeds the yield of butanes by nearly an order of magnitude. Among the characteristics of unsaturated hydrocarbons, the very low concentration of ethylene inferior to those for propylene and butadiene is worth mentioning.



Fig. 6. Temperature dependences of the conversion of $CO_2(Y)$ in hydrogenation on the 85Co-10Fe-5La catalyst at a pressure of 1 (*I*) and 2 MPa (*2*).

To conclude, the polymetallic catalysts based on cobalt and nickel prepared by the SHS of intermetallic compounds are highly active in the methanation of CO₂ under mild conditions. The maximum conversion of CO₂ (97% for the 85Ni-5Mn-5Co-5Ce catalyst) and 100% selectivity to methane were achieved under atmospheric pressure at 250-350 °C. The catalysts with iron additives (95-x)Co-xFe-5La (x = 10, 30, and 50) with the nanostructured surface were synthesized from the most active catalyst of the FT synthesis to carry out the process at elevated pressure. A considerable (>35 vol.%) yield of the ethane-butane fraction with an appreciable content of unsaturated hydrocarbons (propylene and butadiene) was obtained on the 85Co-10Fe-5La catalyst at a pressure 1–2 MPa in the temperature range 250–350 °C. Ethylene was nearly absent.

Thus, the proposed class of the catalyst is promising for the development of the direct hydrogenation of CO_2 to heavy alkanes and unsaturated hydrocarbons.

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