lysts differ slightly. The maximum yields of liquid hydrocarbons at the same concentration of the metal oxide in the metallosilicate were equal to 129 g m⁻³ and 139 g m⁻³ for the samples with ZrO_2 and CoO, respectively. These data imply that the cobalt oxide incorporated into the support, along with the supported metal, is directly involved in the synthesis of hydrocarbons from CO and H₂.

The selectivity of the formation of liquid hydrocarbons exceeds 50 % for almost all the samples containing metallosilicates as a support, which is higher than the analogous value for the Co/SiO₂ catalysts (Table 2). Paraffins are the main products of the synthesis reaction on Co/metallosilicate catalysts, and their content in the catalysate is 90 %. The fraction of olefins in the liquid products is less than 12 %. This is typical³ of other Co catalysts of this type, too.

The isomerization activity of the catalysts studied depends on the nature of the metallosilicate used (Table 2). The smallest amount of isoparaffins formed on the catalysts containing Zn and Hf silicates and synthetic silica gel, while the largest amount of these products was obtained in the presence of the samples based on the Al and Co silicates. It is noteworthy that in the presence of all the Co/metallosilicate catalysts studied, hydrocarbons formed with a percentage of light paraffins from the gasoline fraction exceeding 50 %. Only the catalyst with synthetic silica gel as the support provides for the predominant synthesis of hydrocarbons of the diesel fraction (C_{11} - C_{18}). The lightest liquid products were obtained

on the Co/CoO \cdot SiO₂ catalyst (the C₅-C₁₀ fraction exceeded 90 %), while the samples based on Zr and Mg silicates permitted the synthesis of products containing more than 40 % hydrocarbons of the diesel fraction.

Thus, it is possible to influence the yield and composition of the liquid products of hydrocarbon synthesis by varying the composition of the support in the Co/metallosilicate catalyst. The catalyst based on $ZrO_2 \cdot SiO_2$ is promising for the preparation of the components of diesel fuel and the catalyst containing $CoO \cdot ZrO_2$ can be used for the preparation of light C_5-C_{10} paraffins.

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Reaction of CO₂ and H₂ in the presence of Co and Ni catalysts

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The activity and selectivity of 10 % Co/support and 10 % Ni/support catalysts (where the support is Al_2O_3 , SiO_2 , C) in the synthesis of hydrocarbons from CO_2 and H_2 were studied. The extent of conversion of the starting mixture and the yield of methane were shown to depend on the composition of the catalytic system. Cobalt catalysts with various types of carbons as supports are the most active. They permit the synthesis of methane in yields up to 70 % of the theoretical value.

Key words: carbon dioxide, hydrogenation, Co and Ni catalysts.

The involvement of a stable molecule of carbon dioxide in processes resulting in the synthesis of valuable

chemical compounds, e.g., hydrocarbons or alcohols, is of great practical and theoretical interest. The synthesis

Table 1. Influence of the composition of catalysts on their activity in the synthesis of hydrocarbons from CO_2 and H_2

Catalyst	Extent of conversion (%)			Yield of products relative to the original CO_2 (%)		
	(°C)	CO ₂	H ₂	CO ₂ +H	2 CH ₄	C ₂ H ₆
Ni/Al ₂ O ₃	380	38.4	70.2	59.3	38.1	
Ni/SiÕ ₂	420	40.0	78.3	63.2	38.9	0.5
Ni/C(AΓ-3)	320	50.1	97.2	82.6	49.6	0.5
Co/Al ₂ O ₃	250	59.5	93.1	83.5	59.0	0.5
Co/SiÕ ₂	360	41.5	74.0	60.4	39.5	-
Co/C(CKH-3)320	70.8	92.0	86.7	70.3	
Co/C(AHT-1)	360	72.6	92.6	88.1	72.0	
Co/C(AΓ-3)	380	44.1	82.4	71.0	44.1	

of hydrocarbons from CO₂ and H₂ is a promising method for utilizing carbon dioxide, which is abundant in exhaust gases from many chemical plants, particularly coal-chemical plants. Catalytic systems have been proposed for realization of this process.¹⁻³ However, the data presented are often difficult to compare due to different preparation methods, compositions, and conditions of testing of the catalysts.

This paper reports the results of a study of the effect of the nature of active component of the catalyst and the support on interaction of carbon dioxide with hydrogen.

Experimental

 γ -Al₂O₃ of type A-64, SiO₂ of the KSS N3 type, and activated carbon of the SKN-3, ANG-1 and AG-3 types were used as supports for preparing the catalysts. The supports were preliminarily calcined in a stream of air or in argon for 5 h at 450°C. The catalysts were prepared by impregnating the support with a solution of the corresponding metal nitrate. The samples were dried in a water bath and reduced in a stream of hydrogen for 5 h at 450°C. All the catalysts contained 10 mass. % Co (Ni).

The synthesis reaction was carried out in a KL-2 flow-type catalytic system equipped with a steel reactor having an internal diameter of 10 mm, into which 6 cm³ of the catalyst was loaded. The synthesis reaction was performed under the following conditions: P = 0.1 MPa, T = 200-450°C, CO_2 :H₂ = 1:3 (v/v), w = 100 h⁻¹.

The starting compounds and products were analyzed by chromatography according to a procedure described elsewhere.⁴

Results and Discussion

The total extent of conversion of carbon dioxide and hydrogen on the Co and Ni catalysts used was not less than 60 % (Table 1). The efficiency of these catalytic systems depends on the nature of metal and support used. In the presence of Co catalysts, the synthesis reaction proceeds at lower temperatures and the extent of conversion of the starting compounds exceeds that obtained with Ni on the same support.



Fig. 1. Temperature dependence of the yield of methane from CO_2 and H_2 in the presence of various catalysts: 1, Co/SiO_2 ; 2, Co/Al_2O_3 ; 3, Co/C(AG-3).

The main product of the synthesis reaction on both types of catalysts is CH₄, whose content in the emerging gases is determined by the composition of the catalytic system (Table 1). Thus, the Ni catalysts containing oxide supports exhibited similar activity: the overall extent of conversion of the original gas in their presence was equal to 60 %, and the methane content in the emerging gases was 38 %. The sample with a carbon support was more efficient: the total extent of conversion of the original gas mixture exceeded 80 % along with almost complete conversion of hydrogen. The concentration of CH_4 in the emerging gases was 1.3 times higher than for the Ni/Al₂O₃ and Ni/SiO₂ catalysts. The activity of the Ni catalysts with an AG-3 carbon support was a little higher than that of the Co samples: the optimal temperature for the synthesis reaction was found to be 320°C and 360°C, and the yield of CH_4 was 50 and 44 g m⁻³, respectively.

The extent of conversion of the original gas mixture on the Co catalysts exceeds 60 %, and it increases along the series $SiO_2 < Al_2O_3 < C$, reaching 84–88 %, and the concentration of \tilde{CH}_4 in the gases varies from 40 to 70 %. A comparison of the Co and Ni catalysts containing identical supports (except for the carbon ones) indicates that the former have higher selectivity with respect to methane formation (with the exception of the Co/SiO_2 catalyst). For example, the Co/C samples with a similar total extent of conversion of the original gas mixture are distinguished from the Ni/C by their higher extent of conversion of CO₂ and higher CH₄ content in the emerging gases. The different ratios between the starting compounds which reacted on the Co and Ni catalysts are probably due to the different mechanisms of the process on these catalysts.

Figure 1 presents plots of the temperature dependence of the yield of methane in the presence of Ni and Co catalysts. These plots are characterized by maxima, whose position is determined by the nature of the support used. Thus, the optimal temperature of the synthesis reaction for the set of Ni catalysts increases along the series $C < Al_2O_3 < SiO_2$. The yield of CH_4 varies in parallel, reaching 55–70 %, which amounts to 38–48 % of the theoretical value. Increases in the optimal temperature of the synthesis reaction for the set of cobalt catalysts are observed along the series $Al_2O_3 < C < SiO_2$, and increases in the product yield are observed along the series $SiO_2 < Al_2O_3 < C$. The yield of CH_4 under optimal conditions on the Co/C catalyst reached 105 g m⁻³, which amounts to 70 % of the theoretical value.

Coordinatively unsaturated compounds formed as a result of the interaction of the active phase with the support are normally present on the surface of Al_2O_3 catalysts.⁵ It seems reasonable to suppose that the formation of these compounds in the case of cobalt catalysts is responsible for the decrease in optimal temperature of the synthesis reaction. The incomplete reduction of Co, in contrast to Ni, and the presence of Co_3O_4 ,

CoO, and other oxide structures, including spinel species are probably of considerable importance.

Hence, methane can be synthesized from carbon dioxide and hydrogen in the presence of Co and Ni catalysts. The conversion of the original gas mixture and the yield of the products depend on the composition of the catalyst used. Those containing activated carbon as a support show higher activity in comparison with catalysts based on oxide supports.

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Activation of low-percentage Re—Al₂O₃ and Tc—Al₂O₃ catalysts for the dehydrogenation of paraffins

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The activity and selectivity of low-percentage (0.1-1 mass. %) Re-Al₂O₃ and Tc-Al₂O₃ catalysts in the dehydrogenation of *n*-dodecane is shown to increase in response to an increase in the temperature of their activation in hydrogen from 500°C to 900°C. The activities of such catalysts are comparable to those of analogous alumina-platinum systems, while the selectivity of the former catalysts in *n*-monoolefin production is higher than that of the latter.

Key words: dehydrogenation, n-dodecane, monoolefin, rhenium, technetium.

The treatment of a Tc-Al₂O₃ catalyst in hydrogen at temperatures above 500°C reduces its catalytic activity in the dehydrogenation of cyclohexane and alcohols.^{1,2} Re-Al₂O₃ catalysts are activated at $T < 700°C.^{3,4}$ However, as first reported in Ref.⁵, the treatment of lowpercentage Re-Al₂O₃ and Tc-Al₂O₃ catalysts in hydrogen at higher temperatures may significantly increase

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their catalytic activity and selectivity in the dehydrogenation of $C_6 - C_{16}$ *n*-paraffins.

In this work the influence of the activation temperature T_{act} on the efficiency of alumina—rhenium and alumina—technetium catalysts in the dehydrogenation of paraffins was studied in the example case of the conversion of *n*-dodecane.

Experimental

Catalysts containing 0.1-1 mass. % Re or Tc were prepared by impregnating γ -Al₂O₃ (specific surface 160 m² g⁻¹,

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