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Methane Reforming with Carbon Dioxide on Cobalt-Containing Catalysts

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Abstract—Cobalt- and iron-containing catalysts supported on MgO, ZrO_2, γ-, θ-, and α-Al_2O_3 were synthesized and studied in the CO_2 reforming of methane. The CoO/α-Al_2O_3 systems are the most active and stable. The dependence of the catalytic activity and the degree of reduction on the amount of supported CoO was studied. In the active catalysts, CoO is weakly bound to the support and can readily be reduced to metal cobalt. Coke formed in the course of the reaction does not affect the activity of the CoO/α-Al_2O_3 catalyst.

INTRODUCTION

Methane reforming with carbon dioxide to produce syngas

$$CH_4 + CO_2 = 2CO + 2H_2 \qquad \text{(I)}$$

is attracting considerable attention from researchers, which is evident from the growing number of recent publications. Carbon dioxide utilization as a product of vital functions becomes more and more topical, but this process is not yet at the stage of laboratory-scale research.

Reaction (I) is strongly endothermic. The thermodynamic analysis of equilibrium in reaction (I) taking into account the water-gas shift reaction

$$CO + H_2O = CO_2 + H_2 \qquad \text{(II)}$$

showed that the equilibrium conversion increases with an increase in temperature. At 800°C, the conversion of CH_4 and CO_2 to syngas is almost complete and the composition of syngas is close to CO : H_2 = 1 : 1. Methane reforming with carbon dioxide was first reported by Fischer and Tropsch [1]. Recent studies [2–7] devoted to this reaction and the steam reforming of methane

$$CH_4 + H_2O = CO + 3H_2 \qquad \text{(III)}$$

and the partial oxidation of methane by oxygen

$$CH_4 + 1/2O_2 = CO + 2H_2, \qquad \text{(IV)}$$

focused on supported Ni- and Pt-containing catalysts on which the conversion approached 100% at 700–800°C. Basic oxides (MgO, CaO, MnO, and ZrO_2) were used as catalyst supports. The authors of [2–7] determined that in the process of methane conversion on these catalysts, the deposition of carbon takes place, which is formed via the Boudouard reaction

$$2CO \longrightarrow C + CO_2 \qquad \text{(V)}$$

and via methane decomposition

$$CH_4 \longrightarrow C + 2H_2. \qquad \text{(VI)}$$

The role of carbon deposits on the catalyst surface in the process of methane reforming with carbon dioxide remains a debatable topic. According to [8–10], carbon deposition leads to a serious decrease in catalytic activity, whereas Goula *et al.* [11] assume that the activity is independent of the presence of coke. It has been found [11–14] that, in the course of the reaction, various carbon species are formed: amorphous carbon, graphite, and metal carbide.

According to [5–7], where nickel catalysts were studied, active and stable samples should contain both metal and oxide particles for the occurrence of redox reactions on their surface.

The main processes occurring in the catalysts both in the course of methane reforming with carbon dioxide can be described by the following equations:

$$M + CH_4 \longrightarrow M\text{–}C + 2H_2, \qquad \text{(VII)}$$

$$CO_2 + M\text{–}C \longrightarrow 2CO + M, \qquad \text{(VIII)}$$

$$M + CO_2 \longrightarrow M\text{–}O + CO, \qquad \text{(IX)}$$

$$M\text{–}O + M\text{–}C \longrightarrow 2M + CO. \qquad \text{(X)}$$

It was found in [15] that, on the NiO/Al_2O_3 sample, reactions (VII) and (VIII) occur much more rapidly than (IX) and (X) and determine the main route of reaction (I). Using local X-ray analysis of NiO/MgO and NiO–Cr_2O_3/MgO, it was shown [16] that the activity of these samples in reaction (I) is due to the presence of active nickel phase islands with a higher concentration of nickel than the background of the support surface. Note that the preliminary reduction of samples with hydrogen, which is necessary for their activation, leads to the growth of these islands.

Taking into account the importance of methane reforming with carbon dioxide, we started to search for new active and stable catalytic systems for this reaction. In this work we synthesized and studied catalytic systems containing VIII Group metals (Co and Fe) supported on various materials (MgO, ZrO_2, and Al_2O_3).

EXPERIMENTAL

Catalyst Preparation

Samples were prepared by impregnating support materials with cobalt and iron nitrate solutions with various concentrations. Upon impregnation, the samples were dried at 120°C. Then, the resulting powders were ground, heated at 350°C, and then ground again. Then, the resulting samples were calcined at 800°C in air for 4 h. Materials for support, MgO and ZrO_2, were of analytical purity grade. For the preparation of samples supported on Al_2O_3, several phases were used. The γ-Al_2O_3 with a high specific surface area (200–250 m^2/g), which was unstable at the reaction temperature, was initially taken. This was used to prepare the α-Al_2O_3 phase with a surface area higher than that of a commercial sample (6–8 m^2/g). γ-Al_2O_3 was converted into α-Al_2O_3 by calcination in air for a long time at the temperature ramping from 800 to 1150°C and controlling the phase composition by XRD. The XRD analysis of powder was carried out using a DRON-3M instrument with a filtered CuK_α radiation source. Phases were identified by comparing the interplane distances with those known from the literature. Phases obtained in the course of ramped-temperature calcination (α-, θ-, and γ-Al_2O_3) were used to prepare supported Co- and Fe-containing catalysts using the procedure described above.

Catalytic Activity Study

The activity of catalysts in methane reforming with CO_2 was studied using a flow-type setup. Reaction products were analyzed by chromatography. The products were separated using two columns packed with molecular sieves 13 Å NaX and Porapak QS. Thermal conductivity detectors were used. The experimental accuracy in determining the conversion was ±(0.1–0.2)%. The reactor was a quartz tube with a diameter of 3 mm. The catalyst loading was 50 mg, the contact time (τ) was varied from 0.2 to 0.027 s. The feed gas had the following composition: 43.13% CH_4, 52.5% CO_2, 4.08% N_2, and 0.38% O_2. Before catalytic tests, the catalysts were reduced in a flow of H_2 at 800°C for 30 min.

The specific surface areas of the samples were measured by the BET method using low-temperature argon adsorption.

Pulse Reduction of the Catalysts

Catalyst samples were reduced by pulses of pure hydrogen at 800°C. Each pulse was 1 ml. Argon was used as a carrier gas. The rate of argon was 20 ml/min. The catalyst loading was 50 mg (the height of the bed was 10–12 mm).

Temperature-Programmed Reduction

Initial and reduced samples were obtained by the method of temperature-programmed reduction (TPR). TPR was carried out in a flow of the gas mixture H_2/Ar at a rate of 100 ml/min. Thermal conductivity detector was used. The temperature ramp was 12°C/min in the temperature range 20–650°C. Before each experiment, a sample was calcined in a flow of air at 500°C for 1 h. The amount of absorbed hydrogen was determined from the areas of TPR peaks with an accuracy of ~10%. The reactor was charged with 0.25 g of a sample.

RESULTS

The samples of Co and Fe supported on MgO, Al_2O_3, and ZrO_2 (with the amount of metal ranging from 1 to 10 wt % per 1 g of the catalyst) were carried out at 700–800°C. Fe-containing catalysts were all inactive, no matter what support was used (Table 1). The conversion of methane (X_{CH_4}) at 800°C and a contact time of $\tau = 0.2$ was 9.5 and 12% for Fe/MgO and Fe/α-Al_2O_3, respectively. As can be seen from Table 1, the samples of Co supported on MgO were inactive either: X_{CH_4} was ~3% under the same conditions. The activity of Co supported on ZrO_2 was much higher: the initial conversion of methane on 6% CoO/ZrO_2 was 96%, but this catalyst was unstable; X_{CH_4} decreased in the course of the reaction and in 2 h of time-on-stream it became as low as 27.5% (Table 1). To stabilize the catalytic activity, we prepared samples containing additives of chromium and iron. A decrease in X_{CH_4} on the cobalt–chromium catalyst supported on ZrO_2 was not so pronounced after 2 h as in the case of the CoO/ZrO_2 sample: from 93.5 to 53% (Table 1). When iron oxide was added to the CoO/ZrO_2 sample, the initial activity of the catalyst became much lower: X_{CH_4} ~ 44% and the catalyst was also unstable.

It was possible to obtain the active and stable catalyst when cobalt oxide was supported on the α-Al_2O_3 surface. To obtain this sample, we prepared α-Al_2O_3 with a high specific surface area (~10 m_2/g). At intermediate stages of preparation, the phase composition of alumina was determined by XRD and its specific surface area was also determined. At each stage of alumina preparation, a portion of it was used to prepare 6 wt % CoO samples, and the catalytic properties of the samples were determined. The least active and stable was cobalt oxide supported on γ-Al_2O_3 (Table 2). The conversion of methane at 800°C and $\tau = 0.2$ s was at most 7%, and the sample rapidly lost its activity. When CoO was supported on θ-Al_2O_3, the value X_{CH_4} increased to 87% under the same conditions, but the catalyst was not stable. The most active and stable catalyst was cobalt oxide supported on α-Al_2O_3. The conversion of methane on this catalyst and the selectivity to H_2 and CO at 700–800°C and $\tau = 0.2–0.027$ s was at maximum. The CoO catalyst supported on α-Al_2O_3 and containing 5–10% of the θ-Al_2O_3 phase was less active at short contact times ($\tau = 0.027$ s) than CoO/α-Al_2O_3 (Table 2).

The dependence of the catalytic activity on the concentration of cobalt oxide was studied for two samples with different supports: CoO/α-Al_2O_3 and CoO/(α-Al_2O_3 + 5%θ-Al_2O_3). An increase in the concentration of cobalt oxide on the surface of α-Al_2O_3 with the 5% admixture of θ-Al_2O_3 affects in the most pronounced manner the activity of the catalyst at short contact times $\tau = 0.027$ s and low temperatures 700°C (Table 3). The conversion of methane in going from the samples containing 3% CoO to the samples containing 8% CoO increased from 28 to 65%, and the selectivities to H_2 and CO increased from 86 to 92% and from 77 to 89%, respectively. When a small amount of cobalt oxide (2–3%) is supported on α-Al_2O_3, the catalyst is inactive; the maximal activity is observed for the sample containing at least 6% CoO. A change in the activity of these catalysts depending on the amount of supported cobalt oxide is shown in Fig. 1.

To reach the maximum activity and selectivity to target products, it is necessary to reduce the catalysts for methane reforming with carbon dioxide at a high temperature (~800°C) in a flow of hydrogen before the reaction. Obviously, the reduction degree of supported oxides substantially affects the characteristic of these processes. Table 4 shows the results of pulse reduction of Fe- and Co-containing catalysts supported on various phases of Al_2O_3 by hydrogen. It is seen from this table that Co-containing (6 wt %) catalysts supported on γ-Al_2O_3 and θ-Al_2O_3 are characterized by a very low degree of reduction. This is possibly due to the strong interaction of cobalt oxide with γ-Al_2O_3 and θ-Al_2O_3 in the course of catalyst preparation, which results in the formation of a compound like $CoAl_2O_4$, which is irreducible under given conditions. It has been reported [17] that cobalt aluminates are hard to reduce. With an increase in the α-Al_2O_3 phase content of the support, the amount of absorbed hydrogen increases and reaches the maximum for the CoO/α-Al_2O_3 sample.

A change in the concentration of cobalt oxide from 2 to 8 wt % on the Al_2O_3 surface leads to an increase in the amount of H_2 absorbed in the course of reduction (Table 4). Note, however, that, when the same amount of CoO is supported on α-Al_2O_3 and α-Al_2O_3 containing 5% θ-Al_2O_3, catalysts are obtained for which the amount of H_2 necessary for reduction was different. Thus, for the reduction of the 4% CoO/α-Al_2O_3 and 6% CoO/α-Al_2O_3 samples, 4.7×10^{-4} and 6.25×10^{-4} mol H_2/(g Cat), respectively, is necessary, whereas for the samples 4% CoO/(α + 5%θ)-Al_2O_3 and 6% CoO/(α + 5%θ)-Al_2O_3 the reduction needs 1.78×10^{-4} and 2.98×10^{-4} mol H_2/(g Cat), respectively. Figure 2 shows the dependence of the degree of reduction of Co-containing catalysts on the amount of supported cobalt oxide. When CoO is supported on the α-Al_2O_3 or (α + 5%θ)-Al_2O_3 surface, the degree of reduction increases with an increase in the amount of CoO on the surface, but it is higher in the case α-Al_2O_3 for all CoO

Table 1. Conversion (*X*) of CH_4 and CO_2 and selectivity (*S*) to H_2 and CO on Co- and Fe-containing catalysts supported on MgO, ZrO_2, and Al_2O_3 ($\tau = 0.2$ s)

Catalyst	*T*, °C	Time, min	X_{CH_4}, %	X_{CO_2}, %	S_{H_2}, %	S_{CO}, %
6%F_2O_3/MgO	800	20	9.5	5.5	85	78
6%CoO/MgO	800	20	3	1.5	88	72
6%CoO/ZrO_2	800	5	96	87	93	88
		60	84	73	92	86.5
		120	27.5	18.5	89	79
3%Fe_2O_3–2%Cr_2O_3/ZrO_2	800	5	4	3.5	81	72
		65	4	3.5	81	72
6%CoO–2%Cr_2O_3/ZrO_2	800	5	93.5	84	89	80
		60	69	57	87	79.5
		120	53	40	85	76
6%CoO–2%Fe_2O_3/ZrO_2	800	5	44	35	89	80
		60	36	27	88	78
6%CoO/α-Al_2O_3	800	5	96.5	87	93	88
		60	96.5	87	93	88
6%Fe_2O_3/α-Al_2O_3	800	5	12	11	78	70
		30	8	1	58	37
6%CoO/α-Al_2O_3	800	>50 h	97.5	95	93	91.5

concentrations. Thus, we conclude that the α-Al_2O_3 surface is inert toward supported CoO, and the presence of a small amount of the θ-Al_2O_3 phase in the support may lead to partial CoO binding to form a poorly reducible compound like $CoAl_2O_4$.

In the reduction of the Fe-containing sample 6% Fe_2O_3/α-Al_2O_3, the amount of H_2 consumed was rather large, although this catalyst is inactive (see Tables 2 and 4). The activity of the samples probably depends mostly on the nature of a metal used for the catalyst preparation.

Analogous results were obtained in the TPR study of the Co-containing catalyst supported on various Al_2O_3 phases. Figures 3 and 4 show TPR spectra of these samples. The amount of the bulk CoO phase, corresponding to the TPR peak with T_{max} = 320–350°C is 0.05–0.46% or 0.8–5.8% per supported cobalt. Its concentration increases with a decrease in the surface area of the support. The main peak of hydrogen absorption is in the range 470–510°C and has a long tail in the high-temperature region, which is outside the scale of measurements. This fact suggests that the main portion of cobalt in the samples is at the state of interaction with the support. The degree of cobalt reduction in this peak increases from ~2.5 to ~66% with a change in the phase composition of the support when one switches from γ- to α-Al_2O_3. This points to the weakening of the interaction between Co^{2+} and Al_2O_3. Table 5 shows TPR maxima, the amount of hydrogen consumed and the degree of cobalt oxide reduction for various Co-containing catalysts. The reduction of the 6% CoO/γ-Al_2O_3 sample occurs in two temperature regions with T_{max} = 450°C and T_{max} > 600°C. The first peak points to the fact that the there is bulk oxide in the free state and that it is bound to the support. The second peak points to the strong interaction with the support possibly with the formation of the new bulk phase. The reduction of the 6% CoO/α-Al_2O_3 sample occurs in the same tempera-

Table 2. Conversion (*X*) of CH_4 and CO_2 and selectivity (*S*) to H_2 and CO on Co-containing catalysts supported on Al_2O_3 with various phase compositions and various specific surface areas (S_{sp})

Catalyst	τ, s	*T*, °C	*X*, %		*S*, %	
			CH_4	CO_2	H_2	CO
6% CoO/γ-Al_2O_3	0.2	800	After 5 min of reaction			
(S_{sp} = 126 m^2/g)			7	5.5	85	70
			After 15 min of reaction			
			2	1	58	45
6% CoO/θ-Al_2O_3	0.2	800	After 5 min of reaction			
(S_{sp} = 81 m^2/g)			87	85	87	76
			After 30 min of reaction			
			58	56	78	69
6% CoO/(α-Al_2O_3 + 10%θ-Al_2O_3)	0.2	800	96.5	93	93.5	92
(S_{sp} = 16 m^2/g)		750	89.5	86	94.5	94
		700	87	83.5	95	94.5
	0.027	800	90	86.5	89	76
		750	79	76	90.5	78.5
		700	58	55	92	80
6% CoO/(α-Al_2O_3 + 5%θ-Al_2O_3)	0.2	800	95	92.5	94.5	90.5
(S_{sp} = 14 m^2/g)		750	90	87	95	92
		700	87	83	96.5	94
	0.027	800	89	85.5	92	84
		750	78	74.5	92.5	88.5
		700	52	48	94	90
6% CoO/α-Al_2O_3	0.2	800	97.5	95	93	91.5
(S_{sp} = 7 m^2/g)		750	91	89	95	93
		700	86	83	97.5	94.5
	0.027	800	92.5	90	92	88
		750	83	79	87	81
		700	69	62.5	84	77

Table 3. Conversion (X) of CH_4 and CO_2 and selectivity (S) to H_2 and CO on the CoO/(α + 5%θ)-Al_2O_3 and CoO/α-Al_2O_3 catalysts

Catalyst	τ, s	T, °C	X, %		S, %	
			CH_4	CO_2	H_2	CO
3%CoO/(α + 5%θ)-Al_2O_3	0.2	800	92	89	92.5	86
		750	89	84.5	91	87.5
		700	80	77	92	87
	0.027	800	85	82	84	78
		750	56	52.5	82	75
		700	28	26	86	77
4%CoO/(α + 5%θ)-Al_2O_3	0.2	800	93	90	94	90
		750	89.5	86	92.5	91
		700	84	80.5	94	91
	0.027	800	88.5	84.5	83.5	75
		750	72	67.5	86	81
		700	50	48	89	80
6%CoO/(α + 5%θ)-Al_2O_3	0.2	800	95	92.5	94.5	92
		750	90	87	95	93
		700	87	83	96.5	93.5
	0.027	800	89	85.5	92	84
		750	78	74.5	88	82
		700	52	48	91	85
8%CoO/(α + 5%θ)-Al_2O_3	0.2	800	96	94.5	94	91
		750	91	89	95	92.5
		700	87.5	83	97.5	94
	0.027	800	90	86.5	89	86
		750	83	80.5	90.5	87
		700	65	62.5	92	89
2%CoO/α-Al_2O_3	0.2	800	8	3	60	35
4%CoO/α-Al_2O_3	0.2	800	94	92.5	92	90
		750	87	85	90	89
		700	61	66	91	87
	0.027	800	41	62	87	82
		750	15	21	85	73
		700	11	4	53	71
6%CoO/α-Al_2O_3	0.2	800	97.5	95	93	91.5
		750	91	89	95	93
		700	86	83	97.5	94.5
	0.027	800	92.5	90	92	88
		750	83	79	87	81
		700	69	62.5	84	77
8%CoO/α-Al_2O_3	0.2	800	97.5	95.5	93.5	92
		750	91	89	94.5	93
		700	85.5	83	97	95
	0.027	800	92	90.5	92.5	88.5
		750	83	79.5	86.5	82
		700	68.5	63	85	77.5

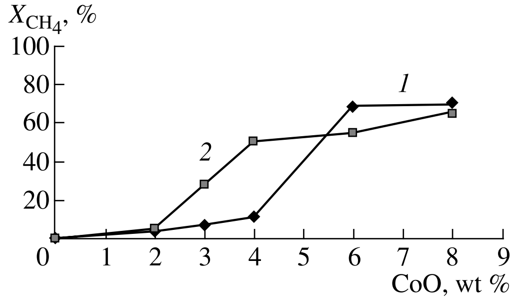

Fig. 1. Dependence of methane conversion (X_{CH_4}) on the concentration of CoO in the catalysts (*1*) CoO/α-Al_2O_3 and (*2*) CoO/(α + 5%θ)-Al_2O_3. (T = 700°C, τ = 0.027 s).

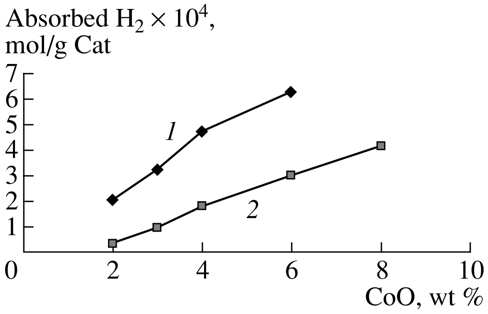

Fig. 2. Dependence of consumed hydrogen in the pulse reduction of the catalysts depending on the amount of CoO: (*1*) CoO/α-Al_2O_3 and (*2*) CoO/(α + 5%θ)-Al_2O_3.

ture range as the samples supported on Al_2O_3 consisting of a mixture of phases α + θ, but T_{max} shifts toward low temperatures.

A TPR study of the CoO/α-Al_2O_3 samples with various CoO concentrations (Fig. 4) showed that the values of T_{max} for the peaks change only slightly. For the 2% CoO sample the maximum is shifted toward low temperatures from 470 to 440°C. With a decrease in the concentration of cobalt in the sample, the degree of its reduction increases. Thus, for the 2% CoO/α-Al_2O_3 catalyst, the degree of reduction reaches 100%.

DISCUSSION

Experiments carried out in this work showed that Co/α-Al_2O_3 samples are the most active toward methane reforming with carbon dioxide of the synthesized Co- and Fe-containing catalyst supported on MgO, ZrO_2, and Al_2O_3. For these samples, almost complete conversion of methane and CO_2 is observed at 800°C and a contact time of 0.2 s. This corresponds to the thermodynamically possible conversion of these substances. Comparison of data obtained in the pulse reduction of Co-containing catalysts supported on Al_2O_3 with various phase compositions with hydrogen and TPR data for these samples (hydrogen flow) showed that these data coincide for the systems with the best catalytic properties. These are catalysts in which cobalt oxide weakly interacts with the surface in the course of supporting on alumina and exists on the surface mostly in the form of the bulk CoO phase. As follows from TPR data, the maximal amount of this CoO state is formed when cobalt oxide is supported on the α-Al_2O_3 or (α + 5%θ)-Al_2O_3 surface. After treatment with hydrogen, the CoO/α-Al_2O_3 catalyst shows the highest degree of reduction of CoO to metal cobalt.

According to the literature data [5–7], the main pathway of methane reforming with carbon dioxide is the dissociative adsorption of CH_4 on the reduced metal particles of supported catalysts with the formation of

Table 4. Reduction of Co- and Fe-containing catalysts supported on Al_2O_3 by hydrogen pulses

Active component (M)	Oxide (MO), wt %	Phase composition of support	S_{sp}, m^2/g	$[M]_{initial} \times 10^4$, mol/(g Cat)	Amount of consumed $H_2 \times 10^4$, mol/(g Cat)
Co	6	γ-Al_2O_3	140	8.00	0.46
Co	6	θ-Al_2O_3	82	8.00	0.20
Co	6	(α + 10%θ)-Al_2O_3	16	8.00	2.52
Co	6	(α + 5%θ)-Al_2O_3	14	8.00	2.98
Co	6	α-Al_2O_3	7	8.00	6.25
Co	3	(α + 5%θ)-Al_2O_3	9	4.00	0.94
Co	4	(α + 5%θ)-Al_2O_3	11	5.33	1.78
Co	6	(α + 5%θ)-Al_2O_3	14	8.00	2.98
Co	8	(α + 5%θ)-Al_2O_3	9	10.67	4.14
Co	2	α-Al_2O_3	6	2.67	2.03
Co	4	″	7	5.33	4.70
Co	6	″	7	8.00	6.25
Fe	6	″	6	8.43	3.45

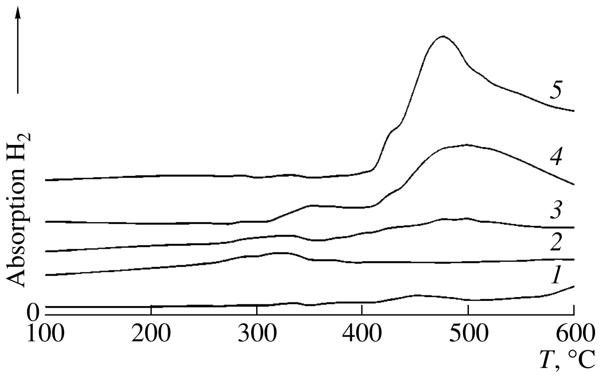

Fig. 3. TPR spectra of catalysts containing 6% CoO supported on (*1*) γ-Al_2O_3, (*2*) θ-Al_2O_3, (*3*) (α + 10%θ)-Al_2O_3, (*4*) (α + 5%θ)-Al_2O_3, and (*5*) α-Al_2O_3.

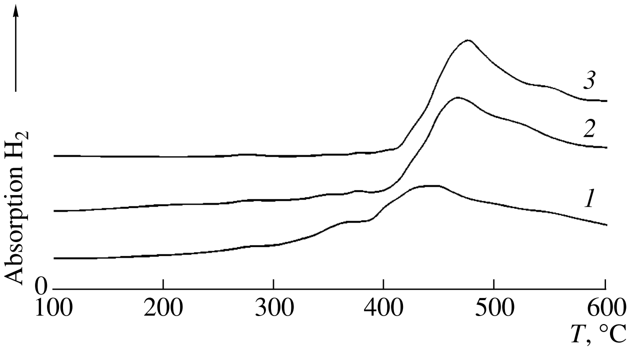

Fig. 4. TPR spectra of catalysts supported on α-Al_2O_3 containing CoO: (*1*) 2, (*2*) 4, and (*3*) 6%.

hydrogen and carbon and the further oxidation of carbon with carbon dioxide to form CO (reactions (VII and VIII)). It was shown in [18] that, methane reforming with carbon dioxide on the CoO/α-Al_2O_3 catalyst occurs according to Eqs. (VII) and (VIII). Only on the reduced sample containing the particles of metal cobalt, methane dissociates to form carbon and hydrogen. When CoO is supported on the γ- or θ-Al_2O_3 surface, CoO weakly bound to the support and capable of being reduced to metal Co is practically not formed. These systems are poorly active and unstable. The CoO/α-Al_2O_3 catalysts are characterized by high selectivity to syngas (H_2 + CO) and high stability under the condition of methane reforming with carbon dioxide. Thus, on the 6% CoO/α-Al_2O_3 sample, a decrease in X_{CH_4} at 800°C and a contact time of 0.2 s was at most 1.5% for 24 h of time-on-stream.

The stability of catalyst operation depends on the state of the surface under reaction conditions. As noted above [8–11], on Ni-containing catalysts for methane reforming with carbon dioxide, coke is formed in the course of the reaction, which may affect the activity of these samples. To estimate the amount of coke on the

Table 5. TPR of Co-containing catalysts

CoO, wt %	Support	T_{max}, °C	Amount of H_2 consumed × 10^4, mol/(g Cat)	Degree of reduction*, %	Overall degree of reduction, %	CoO_{bulk}**, wt %
6	γ-Al_2O_3	450	0.076	0.95		–
		>600	0.123	1.50	2.45	–
6	θ-Al_2O_3	320	0.071	0.88		0.05
6	(α + 10%θ)-Al_2O_3	320	0.042	0.52		0.03
		490	0.830	10.4	10.92	–
6	(α + 5%θ)-Al_2O_3	335	0.165	2.1	–	0.12
		490	3.000	37.5	39.6	–
8	(α + 5%θ)-Al_2O_3	320	0.614	5.8	–	0.46
		490	5.100	48.1	53.9	–
6	α-Al_2O_3	–	–	–	–	–
		470	5.300	66.3	66.3	–
4	α-Al_2O_3	–	–	–	–	–
		470	4.200	78.8	78.8	–
2	α-Al_2O_3	350	Σ = 2.8	Σ = 100	–	Traces
		400			100	–

*Relative to the amount of consumed cobalt.

**The concentration of the CoO phase not bound to the support; determined from the peak area with T_{max} = 320–335°C.

6% CoO/α-Al_2O_3 catalyst in the course of the reaction, we carried out the following experiments. A sample (50 mg) after 1-h operation at 800°C and a contact time of 0.2 s under conditions of CO_2 reforming of methane was treated with O_2 pulses (1 ml) at 750°C. Then, the amount of CO_2 formed was analyzed and the amount of reacted carbon was calculated. It was 9.7×10^{-2} (g C)/(g Cat). To compare this value with the corresponding amount of carbon for the known active catalysts for CO_2 reforming of methane, we synthesized nickel-containing samples supported on MgO: 6% NiO/MgO [5–7] and (6% NiO–2% Cr_2O_3)/MgO. The conversion of methane and CO_2 at 800°C and a contact time of 0.2 s on the former catalyst was 97 and 96%, respectively, and these characteristics for the latter catalyst were 96 and 95%. These catalysts were also stable in the process of CO_2 reforming of methane: the decrease in activity for the first hour (of 24 h) was 1–3%, after which activity remained practically constant.

In the pulse reoxidation by oxygen of 50 mg of nickel-containing samples operated for 1 h at 800°C (under the same conditions as 6% CoO/α-Al_2O_3), 3.8×10^{-4} (g C)/(g Cat) was removed from the 6% NiO/MgO surface and 5.8×10^{-4} (g C)/(g Cat) was removed from the (6% NiO–2% Cr_2O_3)/MgO surface. As can be seen from these experiments, the amount of carbon formed on the CoO/α-Al_2O_3 catalyst in the course of the reaction is much greater than on NiO/MgO and NiO–Cr_2O_3/MgO, but coke does not change the high catalytic activity of Co-containing catalysts. According to [18], metastable carbon formed on metal Co via the dissociative adsorption of methane (VII) intensively diffuses from Co atoms along the surface and forms a more stable phase of carbon, which is similar to nanotubes, freeing active sites of the catalyst. The higher acidity of the α-Al_2O_3 surface compared to MgO probably also favors these processes. In the case of catalysts supported on MgO, carbonates are formed intensively on the support surface in the course of methane reforming with carbon dioxide, which prevents coke formation.

Thus, we found that in the active CoO/α-Al_2O_3 catalysts, CoO is weakly bound with the support and readily reducible to metal Co. We also found that coke formed in the course of the reaction does not decrease the activity of such catalysts.

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