

Article

Bimetallic Co-Rh Systems as a Prospective Base for Design of CH₄ Reforming Catalysts to Produce Syngas with a Controllable Composition

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Abstract: Dry and bireforming (CO₂-H₂O) of methane are the most environmentally friendly routes involving two main greenhouse gases to produce syngas—an important building block for large-scale production of various commodity chemicals. The main drawback preventing their industrial application is the coke formation. Developing catalysts that do not favour or are resistant to coke formation is the only way to improve the catalyst stability. Designing an economically viable catalyst may be achieved by exploiting the synergic effects of combining noble (expensive but coke-resistant) and non-noble (cheap but prone to carbonisation) metals to form highly effective catalysts. This work deals with development of highly active and stable bimetallic Co-containing catalysts modified with small amount of Rh, 0.1–0.5 mass %. The catalysts were characterised by BET, XRD, TEM, SEM, XPS, and TPR-H₂ methods and tested in dry, bi-, and for comparison in steam reforming of methane. It was revealed that the bimetallic Co-Rh systems is much more effective than monometallic ones due to Co-Rh interaction accompanied with increasing dispersion and reducibility of Co. The extents of CH₄ and CO₂ conversion over the 5%Co-Rh/Al₂O₃ are varied within 85–99%. Syngas with variable H₂/CO = 0.9–3.9 was formed. No loss of activity was observed for 100 h of long-term stability test.

Keywords: syngas; dry reforming of methane; steam reforming of methane; bireforming of methane; bimetallic Co-Rh alumina supported catalysts



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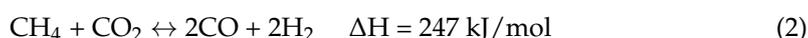
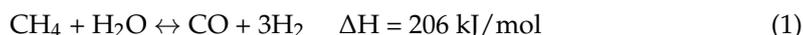
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1. Introduction

Syngas, a mixture of H₂ and CO in any ratios has been considered as a potential and promising sustainable energy from an economic and environmental point of view [1,2]. Syngas is an intermediate in the multi-tonnage production of fuels and chemicals and can be produced by three methane reforming processes, including steam (SRM, Equation (1)) or dry reforming (DRM, Equation (2)) and partial oxidation, collectively named in literature as oxyforming processes [3], or also by any combination of these reactions—bireforming (BRM), tri-reforming, autothermal reforming of methane.

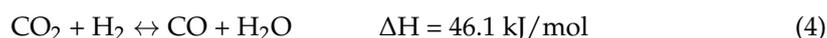
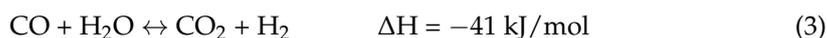


Among these methods for syngas production, the DRM [4,5] supplies a clean and cheap oxygen source derived from CO₂ [6]. Biogas mainly composed of carbon dioxide and methane is a cheap renewable source for DRM [7]. Also, some reservoirs of natural gas can contain comparable concentrations of CO₂ and methane, which makes the reaction more desirable for commercialization [8]. The main benefit of DRM is its potential to diminish

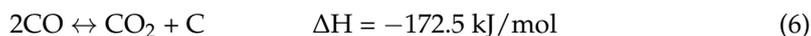
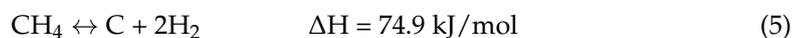
emissions of two greenhouse gases (CO_2 and CH_4), that is as a valorisation pathway of these gases. Dry reforming has currently attracted resurgent interest [1,9–11].

Steam methane reforming (SRM) is the most widely applied and still cost-effective method of industrial production of syngas and is regarded as one of the most efficient technologies for hydrogen production on a large-scale, which is not available as such in nature [12]. A primary feedstock for hydrogen production via SRM is natural gas, which can be replaced in future by its renewable counterpart—biogas [13–15].

The ratio of H_2/CO is of great importance for the subsequent application of syngas. The required H_2/CO ratio of syngas depending on the target processes can be achieved by the combined steam and dry reforming of methane so-called bireforming of methane (BRM). This is a feasible process to adjust the H_2/CO ratio of syngas with various feed ratios of $\text{H}_2\text{O}/\text{CO}_2$ [16]. Actually, the combination of steam reforming and dry reforming offers a more effective route for enhancing the H_2/CO ratio compared to increasing the temperature or the introduction of CH_4 [2,16]. The side reactions, which can affect H_2/CO ratio, are Water Gas Shift (WGSR, Equation (3)) and Reverse Water Gas Shift (RWGSR, Equation (4)) reactions. WGSR, which always occurs in the SRM process, leads to a higher hydrogen yield, but also gives a net CO_2 production (at least 3 kg per kg of CH_4 consumed) [14]. In opposite, RWGSR is responsible for decreasing of H_2/CO ratio and is essential only at lower temperatures in DRM.



The main drawback for all the methane reforming processes is the catalyst deactivation due to the surface coke formation as a result of methane decomposition (Equation (5)) and Boudouard's reaction (Equation (6)) [17] and thermal sintering of the active sites under high operation temperature [5].



In terms of catalysts reported to be efficient for the DRM and SRM reactions, one of the most commonly reported involves nickel either directly or supported. Nickel-based catalysts are widely studied due to their low price and comparable activity with noble metal catalysts. However, the key issue of the Ni-based catalyst is the carbon deposition.

Recently supported Co catalysts began to be actively investigated in the reforming of methane due to their low cost and availability on a larger scale [4,5,18–21]. It has been found that Co-based catalysts can be used as appropriate active metals with sufficient activity for the DRM reaction [5,22]. These catalysts have higher resistance to carbon deposition than Ni-based and can control the rate of carbon formation by oxidizing the surface carbon [19,20]. However, in addition to coke formation, the Co-based catalysts are prone to deactivation due to the oxidation of metallic Co, as well as the formation of inactive spinel structures, which lead to a reduction in the number of active sites [4,5,18,19,22].

From most of the previous research, transition metals of the VIII group except for the osmium, especially rhodium and ruthenium, are excellent reforming catalysts demonstrating both high catalytic activity and resistance to carbon formation and oxidation [21,23–27]. Unfortunately, there are strong constraints, such as the low reserves and high cost of these metals, preventing the industrial application of these metals as catalysts. Nevertheless, noble metals are good candidates to be used in a small amount to promote the catalyst's resistance to carbonization.

It has been reported that introducing a second metal component to catalyst system forming bimetallic alloy sites could also improve the anti-coking property of monometallic catalysts [28]. The addition of another metal to form bimetallic Co-based catalysts could be the crucial technique to develop the effective stable DRM catalyst. Thus, it has been reported

that the addition of an appropriate amount of Zn produced a noticeable improvement in the catalytic performance in DRM [5]. The enhanced stability of the Ru-promoted Co/ α -Al₂O₃ catalyst in DRM was observed by authors [29], which was caused due to facile removal of the deposited coke and suppression of metal oxidation. The authors concluded that the Ru promoter provided active sites during DRM, and structural stabilization of Co species [29]. In our previous works, the same effect of the second noble metal like Pt [30] and Pd [31] on the performance of Co-based catalysts in DRM and bireforming of methane were observed too. By authors [20] it has been found that the 10%Co/Al₂O₃ with additives of 0.1–0.5% Rh is more active in the CO₂ + CH₄ reaction than the monometallic Co/Al₂O₃. Besides DRM, the Co-Rh bimetallic catalysts may be applied in other processes, for example, they are also active in ethanol conversion [26,32].

The design of cost-effective, efficient, and robust (coking- and sintering-resistant) DRM catalysts is a grand challenge in the topic. Bimetallic catalysts, providing synergistic effects via metal-to-metal interactions seems to be an effective strategy for achieving these goals [9,11,28,33,34].

Since, among the vast number of synthesized and widely studied catalysts, only noble metals have a noticeable resistance to coke formation, it is advisable to add them to the catalyst composition. Their high cost can be offset by their long service life, in addition, precious metals can be removed from the spent catalyst for reuse. The appropriate pair of noble–nonnoble metals with possible synergetic effect should be chosen. Cobalt is a prospective candidate to be used as a nonnoble metal because studies of the CH₄ reforming on Co-containing catalysts are far less in number than those on Ni or noble metal catalysts.

On the basis of literature [13,20,23,26,35–38] and own studies [30,31,39], the bimetallic Co-Rh system was selected as a promising base for DRM catalysts. In contrast to the publication of the authors [20], in this work, the Co-Rh catalysts were studied with a lower amount of cobalt, 10 vs. 5 mass %, respectively while the amount of rhodium additive was the same—0.1–0.5 mass %. The synthesized catalysts were studied not only in the dry methane reforming reaction, but also in bireforming and steam methane reforming to elucidate their performance in presence of water with an aim to enhance hydrogen generation. In addition, the stability of the catalysts was investigated for 60–200 h. The effects of the reforming temperature, the amounts of the second metal—Rh, type of process, and steam amount on the conversion of initial reagents and yield and composition of syngas over the 5%Co-Rh/Al₂O₃ catalysts were investigated. To compare and elucidate the effect of Rh on Co, the data on monometallic Co/Al₂O₃ and Rh/Al₂O₃ studied by us earlier are also included.

2. Results and Discussion

2.1. Catalyst Characterisation

The BET surface areas of the fresh (before reaction, no any preliminary treatment) 5%Co-Rh/Al₂O₃ catalyst samples are varied within 144.5–156.5 m²/g depending on the Rh content (Table 1). After exploitation in methane reforming for 25–200 h, the specific surface areas of the spent catalyst were slightly decreased up to 126.8–147.6 m²/g.

Table 1. BET surface area of the 5%Co-Rh/Al₂O catalysts.

Catalyst	BET Surface Area, m ² /g		Duration of Testing, h
	Fresh	Spent	
5%Co-Rh(98:2)/Al ₂ O ₃	144.5	126.8	200
5%Co-Rh(95:5)/Al ₂ O ₃	156.5	147.6	60
5%Co-Rh(9:1)/Al ₂ O ₃	154.1	142.7	25

By X-ray analysis, no phases except γ -alumina were observed for all the Co-Rh-based catalysts including the fresh and spent samples. There are no reflexes related to metal phases. In Figure 1, almost the same XRD patterns are presented for the 5%Co-

Rh(98:2)/Al₂O₃ (Figure 1a) and γ -alumina (Figure 1b) used as a support. Reflexes—4.67, 2.85, 2.72, 2.43, 2.28, 1.99, 1.55, 1.38 (ASTM, 10-425) are characteristic for γ -alumina. A possible reason for this result is the highly dispersed and/or amorphous state of the metals in the catalysts.

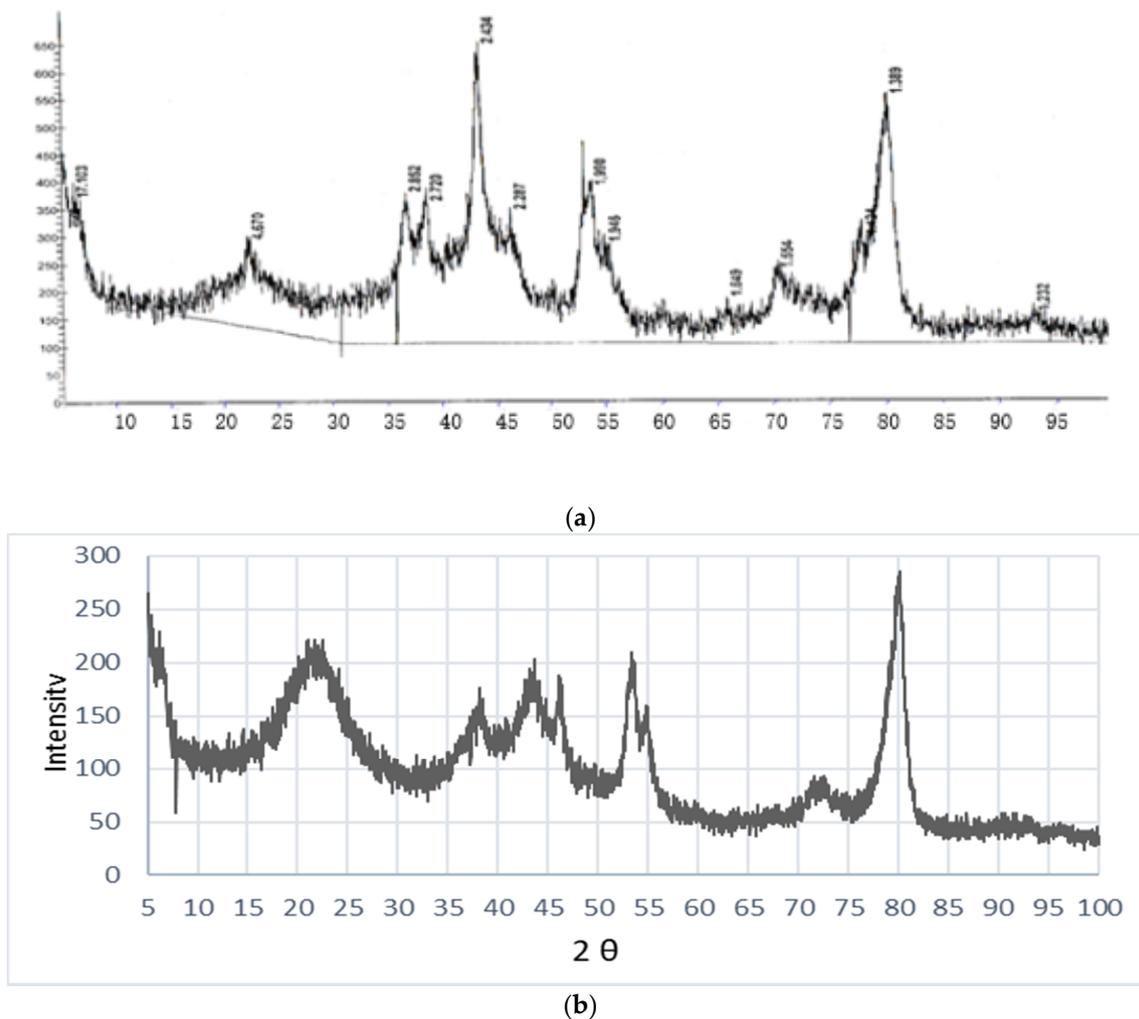


Figure 1. XRD pattern of the 5%Co-Rh(98:2)/Al₂O₃ (a) and γ -Al₂O₃ (b) used as a support.

The TEM study of a ‘fresh’ (preliminary reduced by H₂, 300 °C and then passivated in Ar flow) sample of the 5%Co-Rh(9:1)/Al₂O₃ catalyst showed the highly dispersed and uniformly distributed spherical particles with the average size of 1.5–2 nm, microdiffraction analysis of which revealed the existence of metallic states both of Rh⁰ and Co⁰ (Figure 2a).

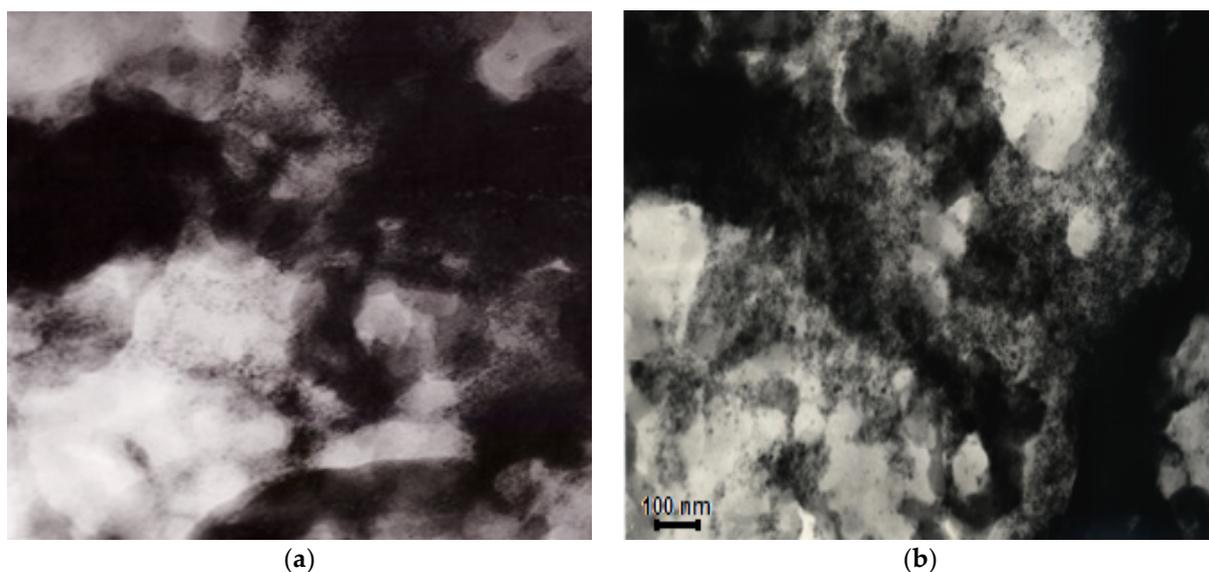


Figure 2. TEM patterns of 5%Co-Rh(95:5)/Al₂O₃ catalyst: (a) fresh and (b) used samples.

Rarely, the particles with a bigger size of 2.5 nm were observed. The last were presumably attributed to the oxidized state of metals; because microdiffraction was presented by small amounts of weak rings, their identification was difficult. The presence of metal oxides is not a surprise because the reduced and passivated sample has been undergone to air. It is notable that the reduced state of Co⁰ in the bimetallic catalyst was kept in an air environment. The Co⁰ state in a monometallic Co/Al₂O₃ catalysts with Co content of 2.5 and 5 mass % was not observed after passivation [31,39].

In a spent sample (after reaction and subsequent passivation by the Ar flow), the particles retained their spherical shape, but some of them increased in size varied within 1.5–3 nm (Figure 2b). Microdiffraction analysis showed the presence of Co⁰ and two oxidized states—RhO₂ (ASTM, 21-1315) and Rh₂O₃ (ASTM, 25-707). The presence of metallic state of Co in the catalyst used indicates that the Co was not oxidized in the reaction medium, which is a mixture of both oxidizing and reducing agents—CH₄, CO₂, H₂O, CO, and H₂. Besides, the metallic state of Co was kept even after air exposure when the catalyst was removed from the reactor. That is a result of Rh-Co interaction in the bimetallic catalyst.

No carbon species were observed over the bimetallic Co-Rh catalysts exploited in dry/bireforming of methane for 100–200 h. Whereas for monometallic catalysts used in DRM and studied for comparison, the monolayer carbon (ASTM, 26-1083) was unexpectedly observed for monometallic 2.5% Rh/Al₂O₃, while graphite formation was observed on the spent monometallic 2.5% Co/Al₂O₃. It is well known that the noble metal catalysts are more resistant to coking [27], while the Co and Ni-based ones are less stable [20]. On a basis of the TEM data, it may be concluded that the addition of Rh to Co leads to formation of sub-5 nm particles, which are more stable and resistant to carbonization than Co and even Rh alone.

By means of SEM of the 5%Co-Rh/Al₂O₃ catalyst, the loose amorphous structures covered the entire catalyst surface of both fresh samples, Co:Rh(95:5) and Co:Rh(9:1), were revealed (Figure 3a,c).

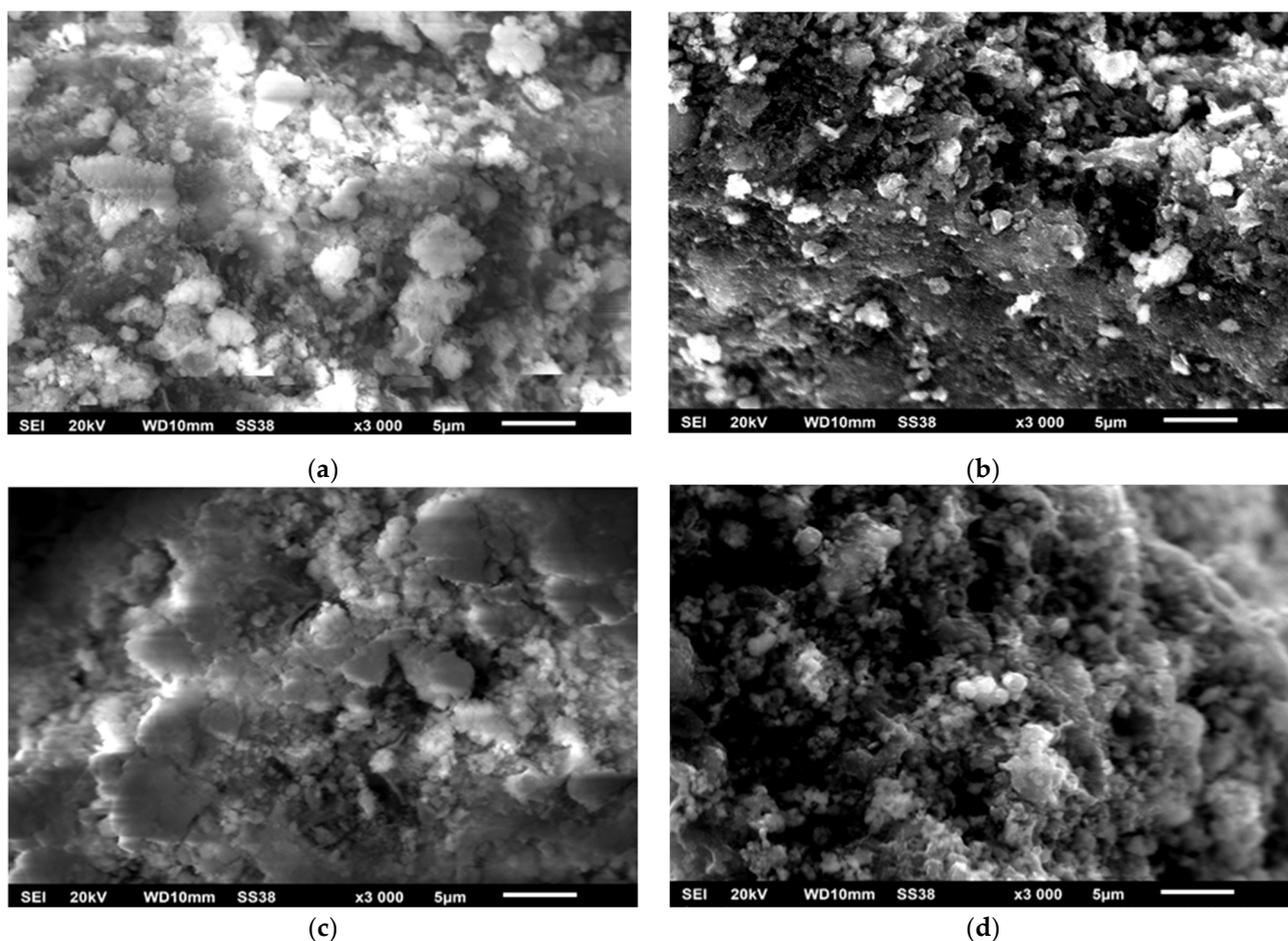


Figure 3. SEM patterns of (a) fresh and (b) used samples of 5%Co-Rh(95:5)/Al₂O₃ catalyst and (c) fresh and (d) used samples of 5%Co-Rh(9:1)/Al₂O₃ catalyst.

After reforming processes over the catalysts the amorphousness became less pronounced especially for the lower content of Rh—0.25 mass % (Figure 3b,d). This sample was continuously exploited for more than 60 h in the DRM and BRM at 700 °C. It is difficult to determine the contribution of each process in changing the catalyst morphology. Nevertheless, the catalyst did not lose its activity for all periods of operation.

According to the XPS data (Table 2) provided for the bimetallic 5%Co-Rh(1:1)/Al₂O₃ as well as for monometallic 2.5%Co/Al₂O₃ catalysts for comparison, both the metals are in oxidised states in the initial calcined samples (fresh). The XPS spectra of the calcined bimetallic Co-Rh catalyst are shown in Figure 4a,b.

Table 2. XPS data on binding energy for the components of 5%Co-Rh(1:1)/Al₂O₃ catalyst.

Element, Level	E _{bind} , eV
C 1s	284.4
O 1s	531.2
Al 2p	74.3
Co 2p	781.3
Rh 3d	308.9

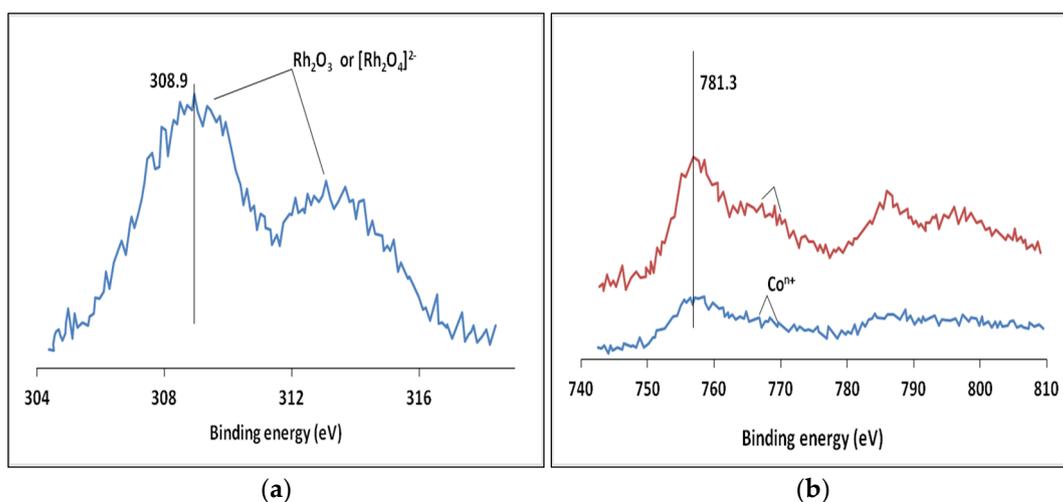


Figure 4. XPS spectra of (a) Rh 3d and (b) Co 2p levels for 2.5%Co/Al₂O₃ (1) and 5%Co-Rh(1:1)/Al₂O₃ (2) catalysts.

The binding energy (BE) of the Rh3d_{5/2} line is 308.9 eV. A comparison of the XPS data obtained (Table 2) with the reference data [40] shows that Rh exists in an oxidation state of 3⁺, which can correspond to rhodium oxide or CoRh₂O₄. As for Co, the binding energy of the Co2p_{3/2} line is 781.3 eV for both monometallic and bimetallic Co-Rh catalysts. This value is higher than for Co oxides (778.3–780.2 eV) and close to Co²⁺ in such compounds as CoRh₂O₄ (781.2 eV), CoAl₂O₄ (781.0 eV) or Co hydroxide (781.0 eV) according to the reference data [40]. By TEM data, no spinel and Co hydroxide were observed. A higher dispersed state of Co in both mono- and bimetallic catalysts and strong metal-support interaction can shift the BE to higher values by up to 1 eV. For these reasons it is possible to suppose that the BE at 781.3 eV can be assigned to Coⁿ⁺ either in CoO or Co₃O₄, which have the standard BE Co 2p_{3/2}—780.4 and 780.2 eV respectively [40]. TPR analysis described below indicates the existence of at least Co³⁺ state.

To elucidate the effect of Rh on Co reducibility, the bimetallic Co-Rh/Al₂O₃ catalysts have been studied by H₂-TPR. In Figure 5, the TPR profiles are presented for five catalyst compositions including monometallic ones.

There is one peak at 160 °C for monometallic Rh/Al₂O₃ catalyst corresponding to the reduction of Rh₂O₃ to Rh⁰. The oxidized states of Co in monometallic 2.5% Co/Al₂O₃ are reduced at higher temperatures and presented by two main peaks: at 386° and broad peak at 621 with a shoulder at 538 °C.

The addition of a noble metal, Rh, has a significant effect on the reducibility of cobalt supported on the alumina. The temperature of the reduction of Co oxides is significantly shifted to lower values. The shift is strengthened with an increase in Rh amount. Three peaks were observed for the bimetallic catalysts with various content of Rh. The first one at 160 °C is the same for all catalysts and attributed to the reduction of Rh³⁺, which presence was shown by XPS. The second and third peaks are assigned to the staged reduction of Co oxides via Co₃O₄→CoO→Co⁰ [20,28,39,41]. The positions of peaks are shifted to lower temperature from 386 °C to 258 → 227 → 210 °C, while the third peak assigned to the 2nd step of reduction, CoO→Co⁰, is shifted from 621 °C to 420 → 395 → 290 °C with an increase in Rh content: 0.25 → 0.5 → 2.5 mass% respectively. Thus, adding Rh to Co/Al₂O₃ catalyst promotes Co reduction and shifts its reduction temperature by 128–176° for Co₂O₃ and by 201–331° for CoO depending on Rh amount. The same effect of Rh on Co reducibility was reported in the literature [14,20].

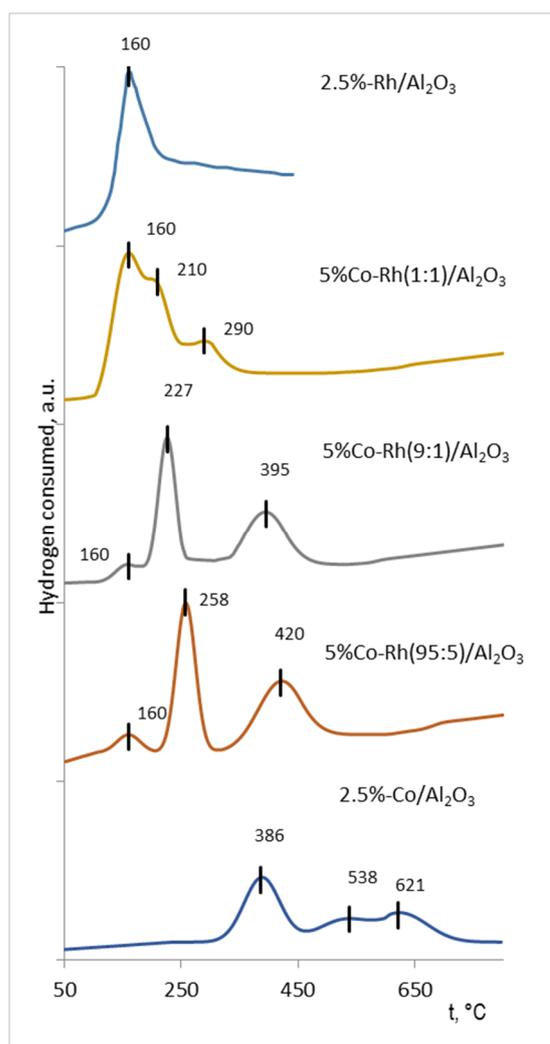


Figure 5. H₂-TPR profiles of the mono- and bimetallic Co-Rh/Al₂O₃ catalysts.

The reduced state of Co⁰ promoted by Rh is kept even in an air environment as was confirmed by TEM studies. This effect of Rh on Co is very important, because the methane reforming is activated by metallic Co and oxidation of metallic sites can cause the decrease in activity [6,20] and should be avoided. The data obtained correspond to the reported promotion effect of noble metals on Co. Thus, for the Co-Rh catalysts, Co⁰ was stated to be the active sites of the catalyst, and the presence of the optimum amount of rhodium led to highly dispersed active species [20]. Authors [32] concluded that the modification with Rh has at least two different roles in the Co-Rh catalytic system. First, the reduction of Co in H₂ is much more efficient in the presence of Rh due to the hydrogen spillover phenomena and Rh may also help to keep the cobalt in the metallic state. In addition, adding Rh to Co leads to higher dispersion state of metals and its stabilisation.

2.2. Catalyst Test

Due to the highly endothermic character of reforming reactions (Equations (1) and (2)), the temperature has the most significant effect on the dry reforming (DRM), steam reforming (SRM), and the combined DRM-SRM or bireforming of methane (BRM). The effect of temperature on the performance of the bimetallic Co-Rh supported catalysts in methane reforming by CO₂ and/or H₂O has been studied. Furthermore, the effect of the amount of Rh and feed composition on methane reforming has been elucidated.

2.2.1. Dry Reforming of Methane

Temperature has the same effect on the conversion of CH_4 and CO_2 and yield of hydrogen and carbon monoxide for all three Co-Rh compositions in DRM. The extents of the conversion of methane (X_{CH_4} , %) and carbon dioxide (X_{CO_2} , %), as well as the yield of hydrogen (Y_{H_2} , $\mu\text{mol}/\text{g}_{\text{cat}} \times \text{s}$) and carbon oxide (Y_{CO} , $\mu\text{mol}/\text{g}_{\text{cat}} \times \text{s}$), are raised with an increase in temperature as it shown for example the 5%Co-Rh(98:2)/ Al_2O_3 (Figure 6) catalysts. The eligible activity of the catalysts ($X_{\text{CH}_4} > 25\%$) in the DRM is occurred at temperatures above 500 °C. Both reactants converted up to extents of 90–99% at 700–800 °C depending on the content of Rh.

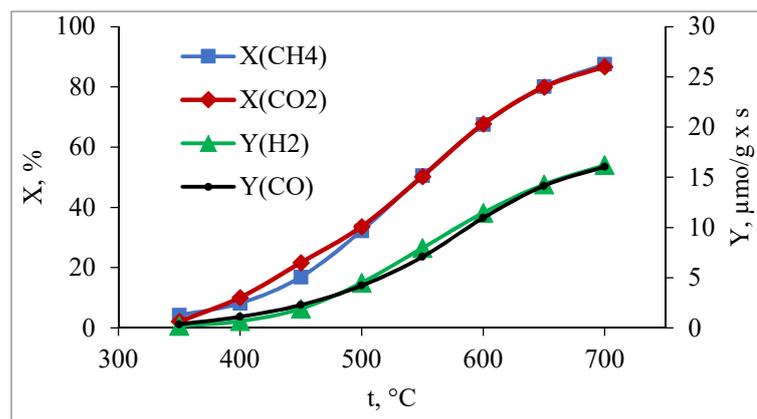


Figure 6. Effect of temperature on CO_2 - CH_4 conversion and yield of H_2 - CO in DRM over 5%Co-Rh(98:2)/ Al_2O_3 at $\text{CH}_4:\text{CO}_2:\text{Ar}$, $P = 1$ atm, $\text{GHSV} = 1000$ h^{-1} .

In Table 3, the data on all three reactions are listed for three compositions of Co:Rh studied. As it can be seen, the increase in Rh content from 0.1 to 0.5 mass% leads to no substantial growth of conversion of both reactants: X_{CH_4} is raised from 87.6 to 94.4%, while X_{CO_2} from 86.8 to 91.1% at 700 °C (Table 3). As it was earlier shown, the monometallic Co catalyst is much less active than Rh modified ones [31,39]. Thus, for the 2.5%Co/ Al_2O_3 catalyst $X_{\text{CH}_4} = 60.4$, $X_{\text{CO}_2} = 44.3\%$ and $\text{H}_2/\text{CO} = 0.7$ at higher temperature—900 °C. That corresponds to the results of Erdohelyi et al. reported the promoting effect of Rh on 10%Co/ Al_2O_3 in DRM [20].

Table 3. Comparison of the performance of 5%Co-Rh/ Al_2O_3 catalysts in methane reforming processes at $t = 700$ °C, $P = 1$ atm, $\text{GHSV} = 1000$ h^{-1} .

Process	Feed, $\text{CH}_4:\text{CO}_2:\text{H}_2\text{O}$	Co:Rh, mass.	Extent of Conversion, %		Yield, $\mu\text{mol}/\text{g}_{\text{cat}} \times \text{s}$		Ratio of H_2/CO
			CH_4	CO_2	H_2	CO	
DRM	1:1:0	98:2	87.6	86.8	16.2 *	16.4 *	0.99
		95:5	90.3	90.6	3.2	3.2	1.0
		9:1	94.4	91.1	3.2	3.2	1.0
BRM	1:1:1	98:2	95.2	80.3	19.6 *	15.0 *	1.3
		95:5	94.3	90.6	4.3	3.1	1.4
		9:1	99.0	92.6	4.5	2.5	1.8
SRM	1:0:1	95:5	92.6	-	4.7	1.5	3.1
		9:1	92.2	-	4.7	1.3	3.6

* Undiluted feed (CH_4 - CO_2 , no inert dilutant like Ar) was used.

The ratio of H_2/CO in the syngas formed on the catalysts with lower Rh content (0.1–0.5 mass %) is less in comparison with the Co-Rh(1:1) [31], H_2/CO is 0.99–1.0 and 1.1 respectively. Higher than stoichiometric H_2/CO ratio may be the result of the WGS reaction (Equation (3)), which is strengthened with an increase in Rh content. In contrast, monometallic 2.5%Co/ Al_2O_3 is prone to RWGS (Equation (4)), which is responsible for

decreasing H₂ yield and accordingly for lower ratio of H₂/CO, which is equal to 0.7 in DRM at 900 °C [39].

2.2.2. Bireforming of Methane

For bireforming of methane, temperature has the same effect on the catalyst performance as for DRM, as is shown in, for example, the 5%Co-Rh(98:2)/Al₂O₃ (Figure 7).

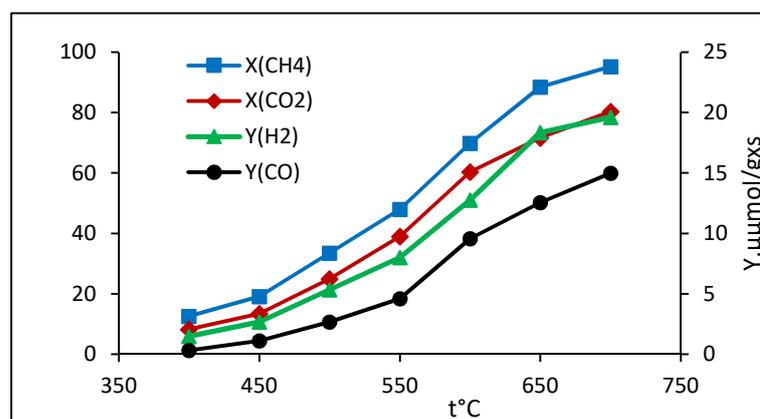


Figure 7. Effect of temperature on CO₂-CH₄ conversion in BRM over 5%Co-Rh(98:2)/Al₂O₃ at CH₄:CO₂:H₂O = 1:1:1, P = 1 atm, GHSV = 1000 h⁻¹.

The subsequent twofold increase in the amount of Rh from 0.25 to 0.5 wt% does not lead to a noticeable increase in activity. The close values of methane conversion—99.2 and 98.8% and carbon dioxide conversion—97.3 and 96.5% for Co-Rh(9:1) and Co-Rh(95:5) respectively were reached at 800 °C and CH₄/CO₂/H₂O = 1/1/1.

The data on the effect of steam amount on methane reforming studied for the two Co-Rh compositions, 95:5 and 9:1, are summarized in Table 4. As it can be seen, the increase in steam volume from 0 to 2 parts in a feed of CH₄:CO₂ = 1:1 leads to enhancing the H₂/CO ratio in syngas formed from 1.0 to 2.7–3.1. The higher conversions of methane and carbon dioxide were observed at adding of 1.5–2 vol. parts of steam depending on Rh amount. At a lower volume of steam, CH₄:CO₂:H₂O = 1:1:0.5, the extents of conversions of carbon dioxide and methane are almost the same for the Co:Rh(95:5), at following increase in steam volume from 0.5 to 2 the difference between X_{CH₄} and X_{CO₂} become more notable and methane conversion prevails. This effect is more pronounced for composition, with higher Rh amount, Co:Rh(9:1) (Table 4). The possible reason of that is the WGSR (Equation (3)) accelerating by Rh. It is obviously that the rate of WGSR is enhanced in excess of steam. Running the two competitive reactions—CO₂ and H₂O decomposition over the same active sites may also be a reason for decline of CO₂ conversion.

Table 4. Effect of steam and Rh amount on CO₂-CH₄ conversion over the 5%Co-Rh/Al₂O₃ catalysts at CO₂:CH₄ = 1:1, t = 700 °C, P = 1 atm, GHSV = 1000 h⁻¹.

Steam in a Feed, Vol. Part	Co-Rh(95:5)			Co-Rh(9:1)		
	X _{CH₄} , %	X _{CO₂} , %	H ₂ /CO	X _{CH₄} , %	X _{CO₂} , %	H ₂ /CO
0	90.3	90.6	1.0	94.4	89.8	1.0
0.5	91.1	91.5	1.2	94.8	90.0	1.2
1	94.3	90.6	1.4	99.0	92.6	1.8
1.5	97.9	90.6	1.6	99.2	90.4	2.1
2	98.3	88.7	2.7	98.3	81.3	3.1

The data on hydrogen and carbon oxide yields in BRM are given in Table 3. In comparison with DRM, hydrogen yield grows up over all catalysts studied when steam is added to the CH₄-CO₂ = 1:1 feed, while the CO content is decreased. These are

two reasons of enhancing H_2/CO ratio. For example, the Y_{H_2} is increased from 3.2 to 4.2–4.3 $\mu\text{mol}/\text{g}_{\text{cat}} \times \text{s}$ for the catalysts with 0.25–0.5 mass % of Rh, while CO yield are decreased from 3.2 to 2.5–3.1 $\mu\text{mol}/\text{g}_{\text{cat}} \times \text{s}$. The same behaviour was observed for the catalyst with the smaller amount of Rh—0.1 mass %: Y_{H_2} is increased, while Y_{CO} is decreased from 16.2 and 16.4 to 19.6 and 15.0 $\mu\text{mol}/\text{g}_{\text{cat}} \times \text{s}$ respectively (Table 3). It needs to note that the concentrated feed of CH_4-CO_2 without dilution with inert gas was used for this catalyst testing, that is why a higher yield of products occurred.

WGS (Equation (3)) is the most likely reason for a lowering conversion of CO_2 in BRM in comparison with DRM. In fact, the values of CO_2 have been calculated on a base of Formula (7), which considers only the content of CO_2 in inlet and outlet flows but does not consider the formation of CO_2 by WGS and its contribution to carbon dioxide amount in the outlet flow. That is why a real conversion of carbon dioxide may be higher than the calculated one for BRM.

Comparison of DRM and BRM over $Co-Rh/Al_2O_3$ (Table 3) demonstrates such benefits of the BRM reaction as a controllable syngas composition and deeper conversion of methane. Intensification of methane reforming is caused by reducing carbon formation because of increased gasification [2,8,10]. Nevertheless, the steam amount to be added is limited for Co-based catalysts. It is known that excess of water can poison the catalyst surface; therefore, the catalysts with a good performance in DRM may be inactive in BRM. By TEM, the formation of Co hydroxide due to the water effect in BRM was found for monometallic 2.5%Co/ Al_2O_3 . The cobalt hydroxide is not active in DRM and cause the drastic decreasing activity of the catalyst, $X_{CH_4} < 5\%$ at 900 °C. The addition of Rh not only increases the activity of Co-based catalyst in DRM, but also makes it active in BRM. So, this is evidence of synergistic effect of Co and Rh interaction.

2.2.3. Steam Reforming of Methane

Due to the revealed high activity of $Co-Rh/Al_2O_3$ in BRM, the catalysts have been tested in the steam reforming of methane (SRM)—a method of industrial hydrogen production. The feed with ratio of $CH_4/H_2O = 1/1$ has been used that corresponds to the stoichiometry (Equation (2)). It has been observed that the Co-Rh systems performed high activity in SRM process too. In Figure 8a,b, the typical pattern of temperature effect on methane conversion is presented for catalysts with content of Rh—0.25 and 0.5%. X_{CH_4} are 98.4 and 97.4% for Co-Rh (95:5) and Co-Rh(9:1) respectively at 800 °C. The yield of carbon monoxide in SRM is substantially less than in DRM and BRM, 1.3–1.5 and 2.5–3.2 $\mu\text{mol}/\text{g}_{\text{cat}} \times \text{s}$ respectively. This is due to a half lower intake of C from a feed consisting only of CH_4 , there is no CO_2 as the second supplier of C. The yield of hydrogen for SRM is slightly higher than for BRM: 4.7 and 4.3–4.5 $\mu\text{mol}/\text{g}_{\text{cat}} \times \text{s}$ respectively (Table 3).

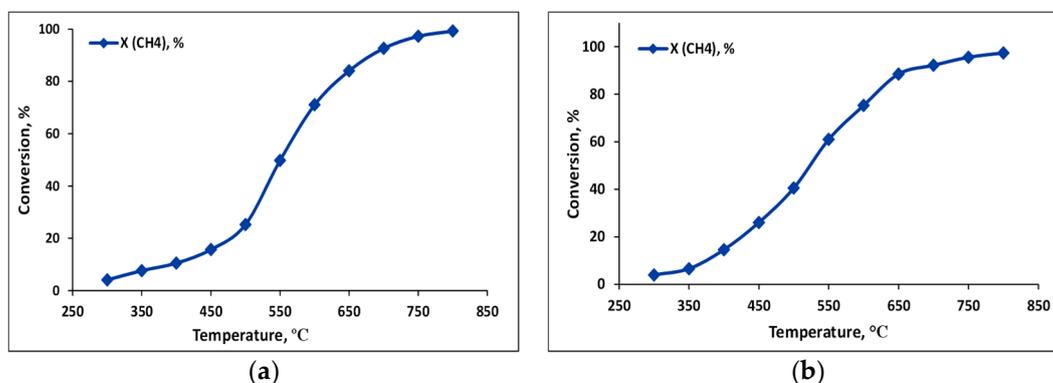


Figure 8. Effect of temperature on CH_4 conversion in SRM over 5%Co-Rh/ Al_2O_3 at $CH_4:H_2O = 1:1$, $P = 1$ atm, $GHSV = 1000$ h^{-1} : (a) Co:Rh = 95:5, (b) Co:Rh = 9:1.

The ratio of H_2/CO in SRM reaction is grown from 3.1 to 3.6 with an increase in Rh content from 0.25 to 0.5 mass%, while the yield of hydrogen is approximately the same—

4.7 $\mu\text{mol}/\text{g}_{\text{cat}} \times \text{s}$. As for CO yield, it is moderately decreased from 1.5 to 1.3 $\mu\text{mol}/\text{g}_{\text{cat}} \times \text{s}$ (Table 3). The activity of both compositions is almost the same: $X_{\text{CH}_4} = 92.2\text{--}92.6\%$.

The higher H_2/CO ratio in SRM in comparison with BRM and DRM occurs due to decrease in CO content in products formed. The SRM does not give a much higher yield of hydrogen than BRM.

In Figure 9, the comparison of methane reforming either by carbon dioxide or steam, or by their mixture is presented. As can be seen, all three processes may proceed with approximately the same activity over the same catalyst—5%Co-Rh(95:5)/ Al_2O_3 at 700 °C with production of syngas with H_2/CO ratio varied in a wide region—1–3.

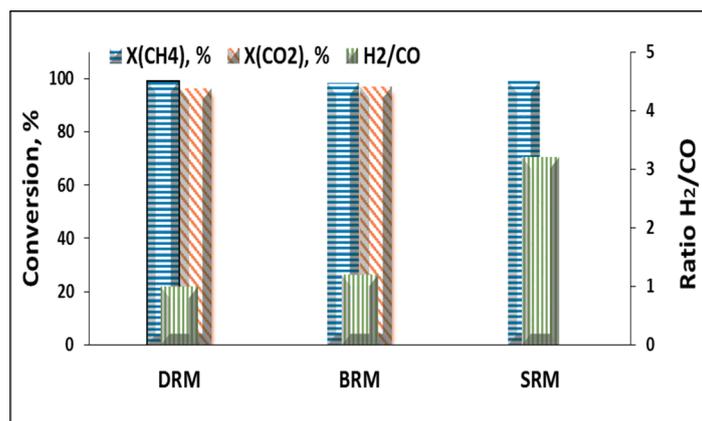


Figure 9. Comparative characteristics of methane conversion by dry ($\text{CH}_4/\text{CO}_2 = 1/1$), bireforming ($\text{CH}_4/\text{CO}_2/\text{H}_2\text{O} = 1/1/1$), and steam ($\text{CH}_4/\text{H}_2\text{O} = 1/1$) reforming over 5%Co-Rh(95:5)/ Al_2O_3 catalyst at $t = 700\text{ }^\circ\text{C}$, $P = 1\text{ atm}$, $\text{GHSV} = 1000\text{ h}^{-1}$.

2.2.4. Stability Test

To determine the stability, the catalysts with less amount of Rh—0.1–0.25 mass % performed the activity and yield of products comparable with the catalysts containing higher Rh content were selected for long-term testing in the dry reforming and in bireforming of methane under $P = 1\text{ atm}$, $t = 670\text{--}700\text{ }^\circ\text{C}$, $\text{GHSV} = 1000\text{--}1250\text{ h}^{-1}$, and $\text{CH}_4/\text{CO}_2 = 1/1$ for DRM and $\text{CH}_4/\text{CO}_2/\text{H}_2\text{O}_g = 1/1/1$ for BRM. The 5%Co-Rh(95:5)/ Al_2O_3 catalyst with $V_{\text{cat}} = 12\text{ mL}$ was tested in a quartz reactor in DRM and then without stopping and regeneration in BRM for 25 h each process. The 5%Co-Rh(98:2)/ Al_2O_3 with $V_{\text{cat}} = 100\text{ mL}$ was tested in the pilot reactor made from Inconel in BRM and DRM for 100 h each.

In Figure 10, the dependence of CH_4 and CO_2 conversion (Figure 10a) and products yields (Figure 10b) on time on stream is presented for the DRM on 5%Co-Rh(95:5)/ Al_2O_3 catalyst.

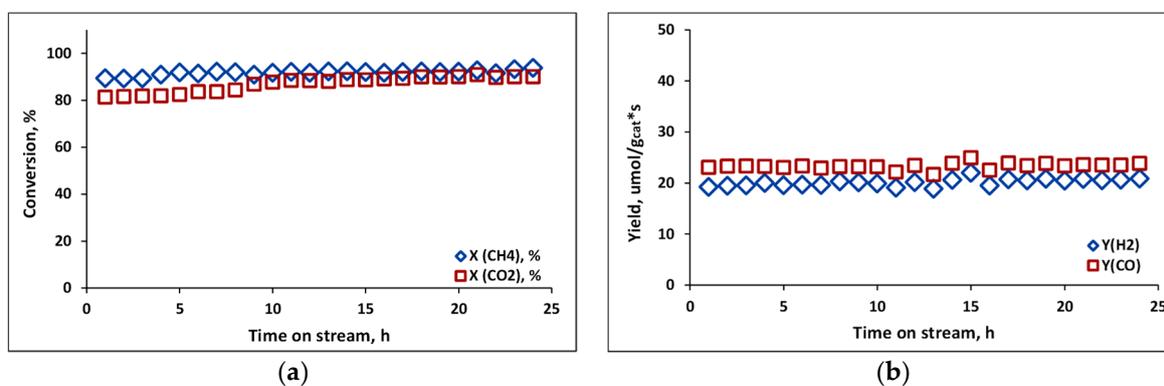


Figure 10. Dependence of (a) $\text{CO}_2\text{--CH}_4$ conversion and (b) H_2 and CO yield on TOS in DRM over the 5%Co-Rh(95:5)/ Al_2O_3 catalyst at $\text{CH}_4:\text{CO}_2 = 1:1$, $t = 700\text{ }^\circ\text{C}$, $P = 1\text{ atm}$, $\text{GHSV} = 1500\text{ h}^{-1}$.

Syngas formed has a ratio of $H_2/CO = 0.9$. There was no loss of the catalyst activity for 25 h in DRM. Moreover, the conversion of both reactants was slightly increased with TOS: X_{CO_2} from 81 to 90 and X_{CH_4} from 90 to 93%. It may occur because of the ‘catalyst elaboration’ accompanied by changing such catalyst surface characteristics as dispersion, composition, and state of the active centres due to effect of the reaction medium during the first hours of the catalyst operation. Such phenomena, which is typical for Co-based FTS catalysts, was found for the 5%Co-Pt/ Al_2O_3 - ZrO_2 catalysts tested in DRM and BRM [42]. This is evidence of the significant influence of the DRM reaction medium (mix of initial, intermediate, and final products— CO_2 , CH_4 , CO , H_2 , H_2O , etc.) on the catalyst surface, as a result of which the catalyst is completely structured. In particular, this can be accompanied by an increase in dispersion or the formation of new active sites.

After 25 h testing in DRM, steam was added to a $CH_4/CO_2 = 1/1$ feed flow to carry out bireforming. The data on reagents conversion and products yield are presented in Figures 11a and 11b respectively. As it can be seen, after previous 25 h operation in DRM the conversion of methane and carbon dioxide were stabilised in BRM. Their values were negligible fluctuated within 92.0–93.9 and 88.5–89.9% for X_{CH_4} and X_{CO_2} respectively. In comparison with DRM, the yield of CO was slightly decreased, in opposite, the yield of hydrogen was substantially increased, $H_2/CO = 1.6$. This is evidence of H_2O decomposition and contributing H_2 from water. The 5%Co-Rh(95:5)/ Al_2O_3 catalyst demonstrated stability in BRM with producing H_2 -rich syngas for all entire period of 25 h.

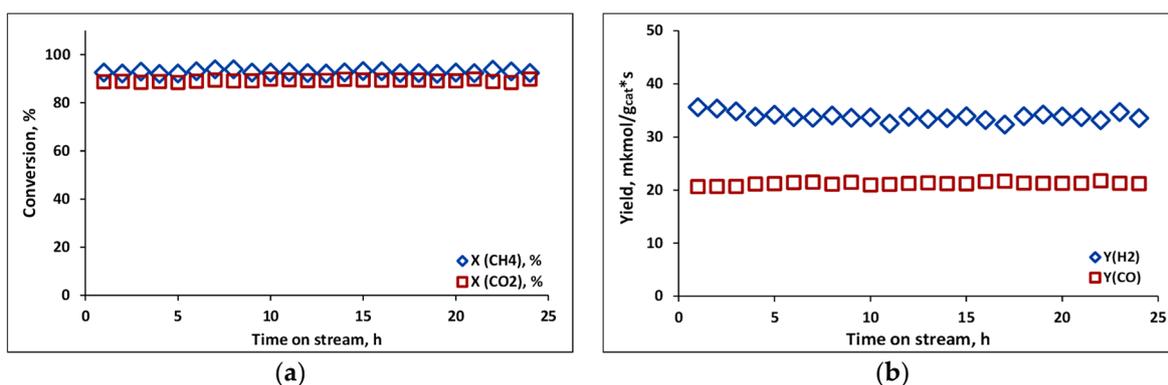


Figure 11. Dependence of (a) CO_2 - CH_4 conversion and (b) H_2 and CO yield on TOS in BRM over the 5%Co-Rh(95:5)/ Al_2O_3 catalyst at $CH_4:CO_2 = 1:1$, $t = 700$ °C, $P = 1$ atm, $GHSV = 1500$ h^{-1} .

On the whole, the 5%Co-Rh(95:5)/ Al_2O_3 catalyst worked continuously without regeneration for about 70 h in DRM and BRM. No visible carbon formation was observed, by TEM and SEM any carbonaceous species were not found.

These results demonstrate the possibility to use the same catalyst for the production of syngas with any desirable H_2/CO ratio by changing feed composition— $CH_4:CO_2:H_2O$ and the easy transition from one reforming process to another one depending on requirements. The additional technological benefit may be in mitigating coke formation in case of its accumulation in DRM by providing periodically BRM/SRM. Such alternation of processes $DRM \leftrightarrow BRM/SRM$ will promote the removal of coke by water as a mild oxidizing agent and allow it to work without stops.

To develop the effective stable catalyst with a low content of noble metal, the 5%Co-Rh(98:2)/ Al_2O_3 with Rh content of 0.1 mass % ($V_{cat} = 100$ mL) was selected to be tested in DRM and in BRM. Average values of degrees of CH_4 and CO_2 conversion in DRM are almost the same and equal to 89.0 and 89.7% respectively. Syngas formed has a ratio of $H_2/CO \sim 1$ (Figure 12).

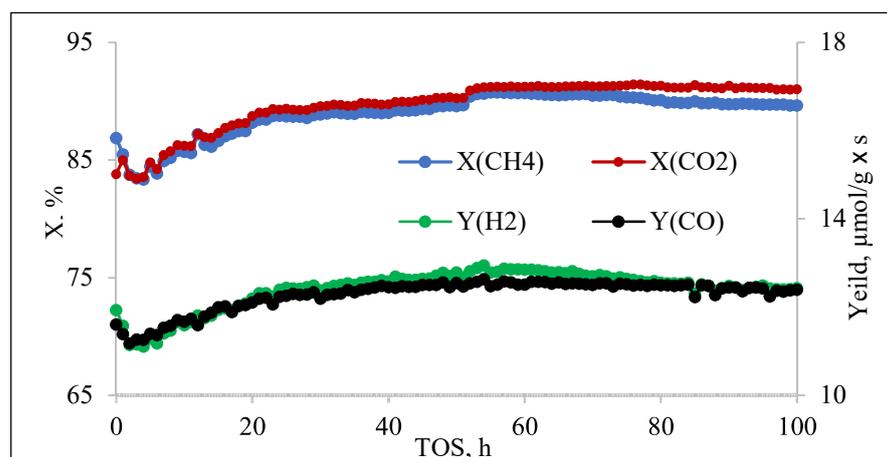


Figure 12. Dependence of CO₂-CH₄ conversion and H₂ and CO yield on TOS in DRM over the 5%Co-Rh(98:2)/Al₂O₃ at CH₄:CO₂:H₂O = 1:1, t = 700 °C, P = 1 atm, GHSV = 1000 h⁻¹.

The substantial changes in activity and productivity were observed, when steam in the amount of 0.5 volume parts was added to a feed of CH₄:CO₂ = 1:1 (Figure 13). If the extent of conversion of carbon dioxide slightly decreased from 89.7 to 87% on average then X(CH₄) was increased by almost 10% from 89 to 98.7%. The yield of reaction products, carbon oxide and hydrogen, were also grown. The last increased in higher degree, due to enhancing methane conversion and water contribution. It should be noted that such improved catalyst performance was reached at lower temperature—670 °C, which is less by 30 °C in comparison with DRM at the same catalyst. As far as it can be concluded on the basis of stable extent of conversion and product yields, the 5%Co-Rh(98:2)/Al₂O₃ catalyst worked with the stable activity and selectivity for 100 h of its testing.

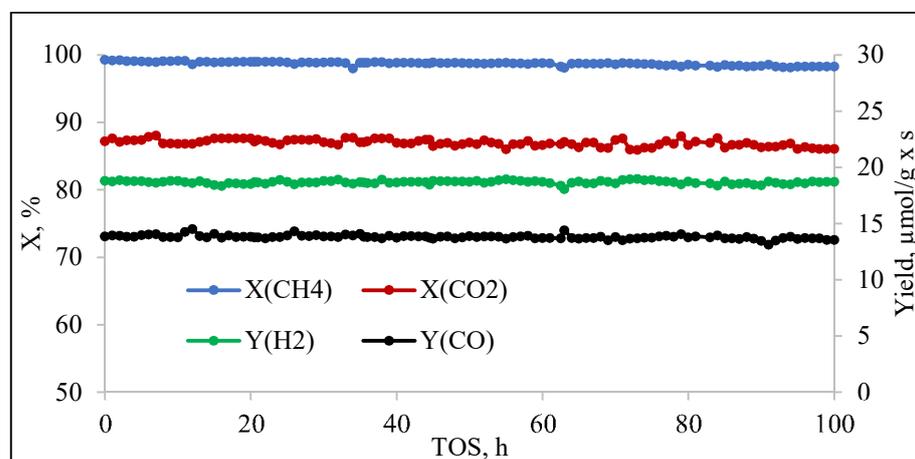


Figure 13. Dependence of CO₂-CH₄ conversion and H₂ and CO yield on process duration in BRM over the 5%Co-Rh(98:2)/Al₂O₃ catalyst at CH₄:CO₂:H₂O = 1:1:0.5, t = 670 °C, P = 1 atm, GHSV = 1250 h⁻¹.

The results obtained demonstrate the ability of bimetallic Co-Rh-based catalysts with low content of Rh—0.1–0.25 mass% to catalyse methane reforming by either CO₂, H₂O, or combined CO₂-H₂O. It allows to apply the 5%Co-Rh/Al₂O₃ catalyst with low content of Rh for producing syngas with a wide range of H₂/CO ratios from the various dry or wet feedstock—natural gas or biogas.

3. Materials and Methods

3.1. Catalyst Preparation and Characterisation

The catalysts were prepared by wet co-impregnation of γ -alumina with aqueous solutions of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{RhCl}_3 \cdot n\text{H}_2\text{O}$, purity is 99% for both compounds. Support is γ -alumina (XRD-pattern in Figure 1b) being granules in the form of balls with a diameter of 3–5 mm and BET surface area is $140 \text{ m}^2/\text{g}$ (IC-02-200, Novosibirsk, Russia, purity—99%). After drying the catalysts were calcined at 400°C for 3 h and then prior testing was reduced by hydrogen at $300\text{--}400^\circ\text{C}$ for 1–3 h. The total nominal content of Co and Rh metals was equal to 5% of the total catalyst mass. The mass ratio of Co:Rh was 98:2, 95:5, and 9:1, which corresponds to 0.1, 0.25, and 0.5 mass% of Rh and 4.9, 4.75, and 4.5 mass% of Co respectively. Element analysis provided by means of the scan electron microscope JSM 6610 LV JOEL, Japan showed a correlation between nominal and actual weight and deviation of no more than 2% on average for each element involved.

The physico-chemical studies of the catalysts were, as a rule, undertaken prior to the reaction (fresh sample) and after the reaction (spent sample) to understand the effects of the reaction feed and process conditions on the catalyst characteristics, such as the specific surface area, reducibility of Co, morphology, particle size, element distribution, etc.

Specific surface area measurements were performed with a Micromeritics Accusorb apparatus, USA. Samples were preliminarily degassed in an Ar flow at 220°C for 3.5 h. The BET specific surface area was deduced from the N_2 adsorption/desorption isotherms at 77 K.

X-ray diffraction (XRD) measurements were performed with the fresh and used catalysts using the CuK_α or CoK_α radiation of a “Dron-4” upgraded powder diffractometer, USSR.

Transmission electron microscopy at a resolution of approximately 0.5 nm was used to characterize the sizes of the metal particles, their distribution and state in the fresh and spent samples of catalysts. Electron microscopy studies were provided with a JEM-100CX unit, Japan. Phase identification was performed with the help of the ASTM (American Society for Testing and Materials).

Scanning electron microscopy (SEM) images were taken using the JSM 6610 LV JOEL, Equipment, Japan using a secondary electron detector operating under high and low vacuum. The external surface of the entire catalyst granule as well as the inner surface of a catalyst granule divided in half have been scanned.

Investigation of catalysts by the XPS method was carried out using the VG ESCALAB electron spectrometer from VG Scientific at the Boreskov Institute of Catalysis, Novosibirsk, Russia. The emission of electrons from the sample was carried out using the soft X-ray radiation of AlK, so that the average mean free path of electrons was 2.0–3.0 nm depending on the line analysed. Thus, the surface thickness of the samples studied was 6–9 nm. Before spectroscopic measurements, the samples were evacuated in a preliminary preparation chamber to $P = 10^{-7}$ mb and then moved to an analyser chamber, where the base vacuum was not higher than 10^{-9} mb. The spectra were recorded using a hemispherical electron energy analyser in the FAT (Fixed Analyzer Transmission) mode. The binding energy obtained were compared with the tabular empirical data given in [40].

To determine the effect of Rh on Co reducibility, the temperature programmed reduction (H_2 -TPR) was provided for the bimetallic Co-Rh/ Al_2O_3 and for mono-metallic catalysts for comparison. TPR measurements were performed on equipment CETARAM, France using a thermal conductivity detector (TCD) and a 5% H_2/N_2 mixture at a flow rate of 20 ccm/min. The catalyst samples were heated from ambient temperature to 800°C at $5^\circ\text{C}/\text{min}$.

3.2. Catalyst Test

The catalysts were tested in a flow quartz reactor supplied with programmed heating, a controlled feed velocity, a programmable syringe pump (Braun Melsungen AG, Melsungen, Germany), and GCs. To provide the stability test, the pilot flow installation included the

tubular reactor made from Inconel-600 (USA), folding tubular furnace, mass flowmeters, microprocessor temperature controllers, separator, water tank, and steam evaporator was used. The volume of the catalysts tested was 6–12 or 50–100 mL for the quartz and pilot reactors respectively. The processes were carried out under atmospheric pressure, gas hourly space velocity (GHSV) was varied within 1000–2000 h⁻¹ and temperature varied within 300–800 °C.

The feed was composed of gases with purity 99.9% taken from cylinders in the molar ratio of CH₄/CO₂ = 1/1 (DRM) or CH₄/H₂O = 1/1 (SRM). To provide the bireforming of methane (BRM), steam has been added in an amount of 0.5–2 volume to methane volume, which corresponds to the gas composition of CH₄/CO₂/H₂O = 1/1/(0.5 ÷ 2). The duration of the process was varied within 10–25 h. The stability was continuously tested for 50–100 h. The initial and final reaction products were online analysed using the GCs with a TCD (Chromatek-Krystall-5000, Russia and Chromatek-Gazochrom-2000, Russia using columns: Hayesep N, Valco Instruments Co. Inc., NaX, CaX and activated carbon, Russia; carrier gases are Ar and air). A special cooling trap was supplied to collect liquid products in case of their formation. Liquid products were analysed using the GC Agilent-7820A, EU with flame ionization detector (FID). However, no liquid products except water were found over the studied catalysts under the process conditions (t = 700–800 °C, P = 1 atm).

The extent of conversion of carbon dioxide (X_{CO₂}) and methane (X_{CH₄}) were calculated according to Formulas (7) and (8), respectively, and thus the activities of the catalysts were compared.

$$X_{\text{CO}_2} = (1 - f[\text{CO}_2]_{\text{out}}/[\text{CO}_2]_{\text{in}}) \times 100\% \quad (7)$$

$$X_{\text{CH}_4} = (1 - f[\text{CH}_4]_{\text{out}}/[\text{CH}_4]_{\text{in}}) \times 100\% \quad (8)$$

where *f* is the ratio of the measured outlet molar flow to the inlet molar flow, [CH₄]_{in} and [CO₂]_{in} are the concentrations of the reactants in the initial (introduced) feed and [CH₄]_{out} and [CO₂]_{out} are the concentrations of the same compounds in the effluent flow.

The conversion of water was not calculated because of the difficulties in differentiating unreacted water and water formed by the secondary reaction. Water is always present in the reaction products.

Due to side reactions, it is rather difficult to determine the selectivity for the main reaction product hydrogen and carbon monoxide. Therefore, the product yields were calculated and presented, this shows the real amount of final products obtained and dynamics of their changes over time after all reactions occurred. Since the yield of the product is a value that depends on the degree of conversion and selectivity, the latter can be indirectly estimated on a base of yield values.

The yields of the reaction products, hydrogen and carbon oxide expressed in micro-moles formed by 1 g of the catalyst per second, were calculated to assess the catalyst selectivity and productivity.

The ratio of H₂/CO in syngas formed was defined as follows: [H₂]/[CO], where [H₂] and [CO] are their concentrations in the outlet gas.

4. Conclusions

The overall goal of this research was the development of the highly active and stable catalysts for their effective application in production of syngas with desirable and controlled composition by either dry, steam or bireforming of methane.

The bimetallic 5%Co-Rh/Al₂O₃ catalysts studied in detail exhibit a number of beneficial effects at relatively low loading of Rh (0.1–0.5 mass %), such as improved methane and carbon dioxide conversion in conjunction with catalyst stability in DRM. Both methane and carbon dioxide are almost completely converted at 700–800 °C.

Besides DRM, the bimetallic 5%Co-Rh/Al₂O₃ catalysts provide BRM with higher hydrogen production, and consequently, with higher H₂/CO ratio in the syngas formed. BRM gives a possibility to control the quality of syngas produced by adjusting the feed composition. Thus, by varying the ratio of CO₂:H₂O within (0 ÷ 1)/(0 ÷ 2) the resulting

H₂:CO ratio is tuned from 0.9 to 3.9 covering a wide range of syngas ratios relevant to various applications.

The strong improvement in the activity and stability of Co-Rh catalysts in DRM, BRM, and SRM occurs due to the synergetic effect of Co-Rh interaction accompanied with an increase in the metal dispersion, the formation of more reactive intermediate carbonaceous species, and enhanced Co reducibility. No coke was observed on the studied bimetallic Co-Rh alumina supported catalyst.

Therefore, the bimetallic Co-Rh systems are considered as a potential and promising base for the catalyst to convert methane with producing syngas with desirable composition. Several additional topics should be studied in future work: lower Rh loading, optimisation of method of preparation, the following modification of the catalyst composition, etc.

Author Contributions: Conceptualization: S.S.I.; Methodology: S.S.I., Y.A.B. and K.A.V.; Software: K.A.V. and Y.A.B.; Validation: K.A.V., Y.A.B. and S.S.I.; Formal Analysis: S.S.I., K.A.V. and Y.A.B.; Investigation: K.A.V., Y.A.B. and S.S.I.; Resources: S.S.I., K.A.V. and Y.A.B.; Data Curation: K.A.V. and Y.A.B.; Writing—Original Draft Preparation: K.A.V., Y.A.B. and S.S.I.; Writing—Review and Editing: S.S.I.; Visualization: K.A.V. and Y.A.B.; Supervision, Project Administration and Funding Acquisition: S.S.I. All authors have read and agreed to the published version of the manuscript.

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