

CO₂ Reforming of Methane over Co-Pd/Al₂O₃ Catalysts

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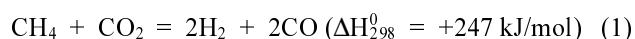
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The supported bimetallic Co-containing catalysts promoted by the different amount of noble metal (Pd) have been studied in the dry reforming of methane. The activity, selectivity, stability and resistance to the carbon deposition of Co-Pd/Al₂O₃ catalysts depend on both the catalyst composition and process conditions. It has been observed that the Co-Pd/Al₂O₃ catalysts produce the various oxygenates from CO₂ + CH₄ at moderate pressures.

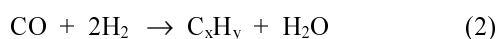
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Introduction

The catalytic process of dry reforming of methane, running according to an equation (1), is one of the promising ways for the utilisation of greenhouse gases such as carbon dioxide and methane:



This reaction allows producing two volumes of synthesis gas from 1 volume of CH₄ + CO₂ mix. Synthesis gas is an alternative source for the producing the various hydrocarbons and oxygenates (eqs. 2, 3).



Since natural gas can contain up to 30% of carbon dioxide, it can be used as an independent source for the production of synthesis gas on condition that some amount of any oxidising agent (carbon dioxide or oxygen/water) will be added (step 1). At the second step synthesis gas may be converted to the high-value products (high hydrocarbons or oxygenates) by the Fischer-Tropsch synthesis (eq. 2, 3). It is reasonable to suggest that under certain conditions (appropriate catalyst and process conditions) synthesis gas, formed during the first reaction (eq. 1), can participate in the following reactions (eq. 2, 3) over the same catalyst. In this case high value products will be formed by one step. This route appears to be more promising.

Ni, Co and noble metals were found to have the high catalytic activity in the process of dry reforming of methane.¹ But the strong surface carbonisation of non-noble metal catalysts, causing their rapid deactivation, on the one hand and the expensiveness of noble metals on the other hand prevent the practical use of the process. At present, the ways for improvement of the Ni-containing catalysts are widely developed. The Co-containing catalysts are incomparably less studied. At the same time, the Co-containing catalysts are very active catalysts in the Fischer-Tropsch synthesis. Besides, it has been shown that oxygenates (acetic

acid) may be produced in the process of dry reforming of methane over Co-containing catalysts.² Thus, the Co-containing catalysts, being active in both processes, are of interest.

Earlier in order to improve the catalytic properties and stability of Co-containing catalyst we have introduced noble metals into their composition.^{3,4} It was shown, that the bimetallic Co-containing catalysts promoted by noble metals and supported on alumina have the high activity, selectivity and resistance to coke formation in the process of dry reforming of methane. In addition to synthesis gas oxygenates (basically C₁-C₂ alcohols) were produced over catalysts under pressure. In this work with a purpose to reduce the catalyst cost and to determine the optimum content of noble metal one of those catalysts, namely Co-Pd/Al₂O₃, was studied in dry reforming of methane at varying the amount of second metal (Pd). For comparison the data on monometallic catalysts tested in the process are presented too.

Experimental Section

The process was carried out in the laboratory flow reactors (usual quartz reactor and stainless steel reactor allowing to work under pressure) combined with the gaseous chromatographs at varying experiment conditions: pressure from 0.1 to 2.0 MPa, temperature from 200 to 1200 °C, space velocity from 500 to 2000 hr⁻¹. Ratio of CO₂/CH₄ was constant 1/1, content of each gas in mix with argon was 10%.

Bimetallic Co-containing catalysts promoted by the various amount of the second metal (Pd) and supported on alumina (sum of metals is 5 weight %, content of Pd varies within 2-50 wt. % from the total metal content) were prepared by impregnation method. For comparison the monometallic 2.5%Co/Al₂O₃ and 2.5%Pd/Al₂O₃ prepared by the same manner have been studied too.

The initial reactants and reaction products were analysed on-line by using GC's. Liquid products were collected in a special cooling trap and were analysed after reaction by using the GS and IR-spectroscopy. To detect the carbon formation the thermoprogrammed reduction of catalyst was

carried out after reaction. The surface both of the fresh and used catalysts was investigated by using the transmission electron microscopy. Also, the thermoprogammed reduction (TPR), TGA, BET and IR-spectroscopy were carried out. The methods were described earlier.^{3,4}

Results and Discussion

Catalysts characterization. By the electron microscopic investigation it has been established that the addition of palladium into Co/Al₂O₃ leads to dispersion of both metals. Size of bimetallic particles in fresh catalysts is 1.0-1.5 nm, that less than the size of Co and Pd in the corresponding monometallic catalysts (3-7 nm and 2-10 nm, respectively).

The non-significant graphitisation occurs over monometallic 2.5%Pd/Al₂O₃ catalyst used in the process. Very strong graphite formation is observed over the monometallic Co-containing catalyst, which increases with growth of pressure. Figure 1 shows graphite formed over 2.5%Co/Al₂O₃ used in the reaction at atmospheric pressure (T=1100 °C).

The size of bimetallic particles in bimetallic catalysts was



Figure 1. Micrograph showing graphite formation on the surface of 2.5% Co/Al₂O₃ used in the reaction of CO₂ + CH₄. The scale bar is 30 nm.

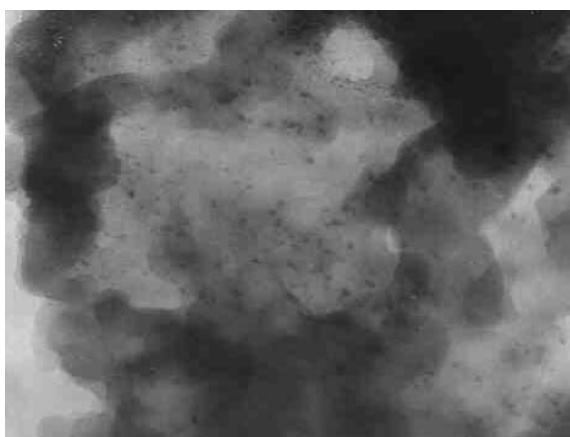


Figure 2. Micrograph of 5%Co-Pd(1 : 1)/Al₂O₃ used in the reaction of CO₂ + CH₄ under pressure (P = 1.0 MPa). The scale bar is 30 nm.

Table 1. TPR data for 5% Co-Pd/Al₂O₃ catalysts

Content of Pd, wt. %	Reduction temperature of Co, °C
0	386, 538 (shoulder), and 594
5	230 and 420
10	230, 380
30	220, 328
50	221, 321

not changed after their using in the reaction (Figure 2). The formation of the amorphous form of carbon during the carbon dioxide reforming of methane is observed over all the bimetallic catalysts. This carbon does not give the micro-diffraction pattern and is easily removed at a treatment by hydrogen. It has been supposed, that this form of carbon actively participates in the following reactions with the formation of carbon oxide and oxygenates.

In addition to the “active” carbon, the non-significant formation of graphite occurs over catalysts with a low content of Pd (< 10 wt.%).

By TGA it has been shown that a loss of weight of bimetallic catalysts by 1.4-3.2% occurs at 100 °C that can be attributed to the evaporation of water produced at the reaction and accumulated by the catalyst.

TPR indicates that Pd promotes the reduction of Co. Even the small Pd loading facilitates the reduction of Co (Table 1). At addition of 5 wt.% Pd, the reduction temperature of Co decreases by about 150 °C. Increasing the Pd content in catalysts is accompanied by a shift of the reduction temperature of Co into the lowest values (Table 1).

By IR-spectroscopy it has been established, that carbon dioxide and methane are dissociatively adsorbed on the surface of bimetallic catalysts. The presence of adsorption bands at 2090 cm⁻¹ and at 2800-2900 cm⁻¹, which are attributed to CO- and CH_x- adsorbed species respectively, are evidence of that.

The comparison of the BET surface area of the fresh and used catalysts shows that a significant loss of the BET surface area occurs over the monometallic Co/Al₂O₃ (from 101.48 to 24.30 g/cm²) and bimetallic catalyst with a low content of Pd (2 wt.%) (from 163.77 to 108.19 g/cm²). No change of the BET surface area is observed for the bimetallic catalysts with highest Pd content and for the monometallic Pd/Al₂O₃.

Catalyst testing in the CO₂ + CH₄ reaction. The process of dry reforming of methane occurs over all the catalysts studied. Their activity, selectivity and stable work in the dry reforming of methane depend on the catalyst composition and temperature and pressure.

The process of dry reforming of methane over all the bimetallic catalysts begins to run with the appreciable activity from temperature of about 400-450 °C at atmospheric pressure. Figure 3 illustrates the typical temperature dependence of the conversion of CO₂ and CH₄ on an example of two compositions of Co-Pd/Al₂O₃ catalyst (Co : Pd = 80 : 20 and 90 : 10). As it is shown from Figure 3, the process attains a significant activity at temperature is about 600 °C.

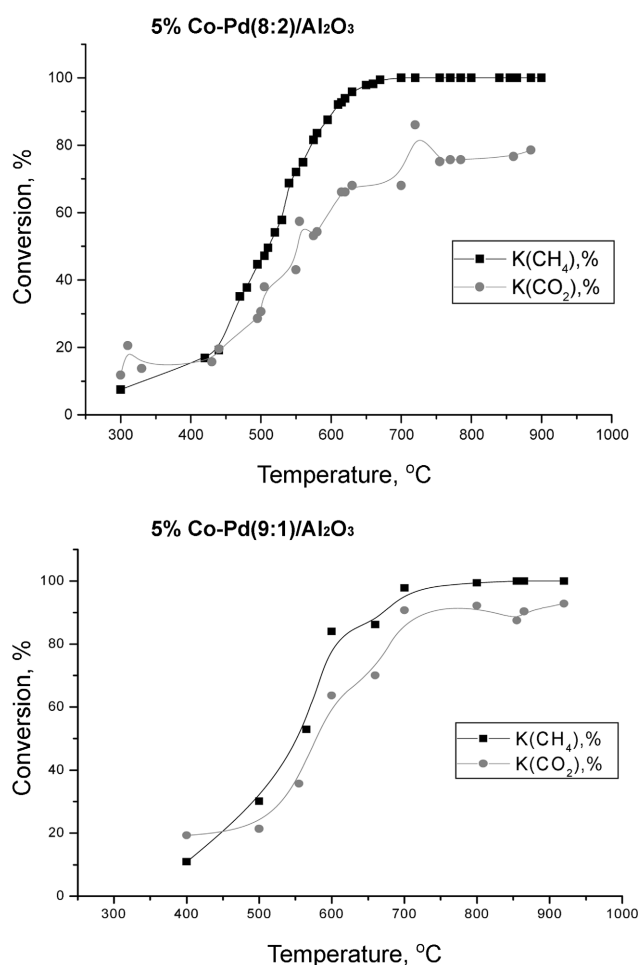


Figure 3. The effect of temperature on conversion of CH₄ and CO₂ over Co-Pd/Al₂O₃ catalysts at atmospheric pressure.

The similar results were observed at other loadings of Pd.

The results of dry reforming of methane over the mono- and bimetallic catalysts obtained at the highest temperatures and atmospheric pressure are summarised in Table 2. The comparison is given at two temperatures: 600 °C is the same for all catalysts and the second one is temperature, when 100% conversion of methane is observed over each catalyst. It is shown that monometallic Pd/Al₂O₃ and all the bimetallic Co-containing catalysts have a high activity in the process. Complete methane conversion (K_{CH_4}) over above catalysts is reached at temperature region of 700–800 °C. While 100% methane conversion over monometallic Co/Al₂O₃ is observed only at $T=1060$ °C. At the same time, the conversion of carbon dioxide never gets 100% over all the catalysts even at the highest temperatures (1200 °C), probably, due to the formation of carbon dioxide as a result of the secondary reactions.

Synthesis gas and water are the main reaction products at atmospheric pressure.

Testing the catalysts under higher pressure showed that catalyst activity is decreasing with pressure growth. Figure 4 shows the effect of pressure on conversion of carbon dioxide and methane over 5%Co-Pd(1 : 1)/Al₂O₃. The same behavi-

Table 2. The effect of the metal content on activity and selectivity of the 5%Co-Pd/Al₂O₃ catalysts (CO₂ : CH₄ = 1 : 1, $P = 0.1$ MPa, space velocity – 1000 hr⁻¹)

Ratio Co:M	T, °C	K_{CH_4} , %	K_{CO_2} , %	T, °C	K_{CH_4} , %	K_{CO_2} , %
100:0	600	7.8	7.1	1060	100	70.4
98:2	600	76.0	66.1	750	100	93.3
95:5	600	87.5	63.8	770	100	84.6
90:10	600	87.5	63.5	755	100	87.5
80:20	600	84.0	60.6	800	100	87.6
70:30	600	84.9	61.7	800	100	87.5
50:50	600	90.2	62.4	700	100	66.7
0:100	600	73.7	63.5	790	100	82.3

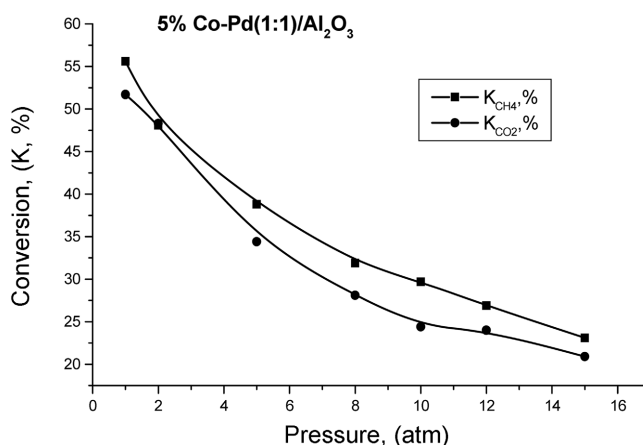


Figure 4. Effect of pressure on conversion of CO₂ and CH₄ over Co-Pd(1 : 1)/Al₂O₃ ($T = 580^\circ$, S.V. = 1000 hr⁻¹).

our is observed for other bimetallic catalysts. The reason of that is unfavourable effect of pressure growth for the reactions, running with volume expansion (eq. 1). No coke formation was observed on the catalysts used under pressure and temperature < 600 °C. Exception is the monometallic Co/Al₂O₃ catalyst, which drastically loses its activity under higher pressure due to a significant graphite formation.

Selectivity of catalysts is significantly changed under higher pressure. Various oxygenates are formed over the bimetallic catalysts under pressure > 0.1 MPa. Their yield and composition strongly depend on the catalyst composition and reaction conditions.

In Table 3 the data on the effect of pressure on the yield of oxygenates are presented for 5% Co-Pd(1 : 1)/Al₂O₃ catalyst. The main oxygenates for the catalyst with high content of Pd (50 wt.% from total metal content) are C₁–C₂ alcohols. Their yield is increased up to about 9% at pressure growth from 0.2 to 1.0 MPa. At the further pressure increase from 1.0 to 1.5 MPa their yield slightly decrease (Table 3).

Decreasing the Pd content from 50 to 5 wt.% leads to a change of the composition of oxygenates. Acetic acid was found to be the main oxygenate. Its yield increases with decreasing the Pd content. Maximum yield of acetic acid is

Table 3. The effect of pressure on yield of oxygenates in CO₂+CH₄ reaction over Co-Pd(1 : 1)/Al₂O₃ (CO₂ : CH₄ = 1 : 1, S.V. = 1000 hr⁻¹, T=580 °C)

P, MPa	Conversion, %				Selectivity, %		
	CO ₂	CH ₄	CO	H ₂	CH ₃ OH	C ₂ H ₅ OH	aldehydes + acids + high alcohols
0.1	51.7	55.6	97.8	97.7	—	—	—
0.2	48.3	48.1	96.1	98.7	—	—	—
0.5	34.4	38.8	96.2	91.6	0.4	traces	—
0.8	28.1	31.9	90.2	98.3	2.2	2.2	traces
1.0	24.4	29.7	82.5	81.7	8.0	0.6	0.2
1.2	24.0	26.1	92.4	89.3	6.0	0.1	0.1
1.5	20.9	23.1	92.2	87.3	6.0	0.2	0.2

observed over 5% Co-Pd/Al₂O₃ with a loading of Pd is 5 wt. % from total metal content at P=1.0 MPa, T=580 °C. In this case, the content of acetic acid among oxygenates reaches 63%.

The study of duration of catalyst work under higher pressure showed that only bimetallic catalysts with a high content of Pd (> 10 wt.% from total metal content) are stable during all the period of testing (100 hours). The catalysts with smaller Pd content are slightly lost their activity due to coke formation.

Conclusion

Thus, all the Co-containing bimetallic catalysts studied are active in the process of dry reforming of methane. They carry out the reaction with the complete methane conversion at 700-800 °C at atmospheric pressure.

Stability and resistance to the graphite formation increase with increasing the Pd content. No graphite formation and

loss of activity for catalysts with high Pd content (> 10 wt.%) were observed.

Oxygenates can be produced from CO₂+CH₄ over the bimetallic catalysts studied by one step under pressure (> 0.1 MPa). Their yield and composition depend on the catalyst composition and reaction conditions.

The further works will be devoted to the choice of conditions are optimal for both the processes (dry reforming of methane and Fischer-Tropsch synthesis).

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