

CO₂ Reforming of CH₄ on Co-Containing Supported Catalysts

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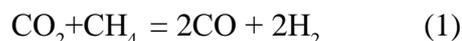
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Abstract

Mono- and bimetallic cobalt-containing catalysts supported on alumina have been investigated in the reaction of interaction between carbon dioxide and methane at variation of experiment temperature and pressure. It was shown, that the bimetallic catalysts have a high activity in this reaction in compare with monometallic ones. The main reaction products are carbon oxide, hydrogen, water and oxygenates. The yield of latter reaches 30% at certain conditions ($P > 0.5$ MPa, $T < 853$ K). The maximum conversion of both methane (100%) and carbon dioxide (94%) is reached at lower pressure (0.1MPa) and 1023K. In these conditions the synthesis-gas is a main reaction product. One of the advantages of the bimetallic catalysts is their resistance to coke formation.

Introduction

Recently reaction between carbon dioxide and methane attracts an attention as a perspective process for synthesis-gas production and a way for utilization of green-house gases (equation 1). Both carbon dioxide and methane are green-house gases.



The interaction between carbon dioxide and methane was investigated by Fischer and Tropsch yet in 1926 [1]. From all metals studied by them cobalt and nickel catalysts were the most preferable for this process [1]. But there is a very strong coke formation on these catalysts. The noble metals are characterized by a low level of coke formation and more promising for process. Nevertheless the coke formation occurs on all catalysts. It discourages the use of catalysts under high pressure.

In this paper the interaction between carbon dioxide and methane on mono- and bimetallic cobalt-containing catalysts modified by different noble metals and supported on alumina has been investigated. The choice of catalysts was based on the literature data about preference of Co in this reaction [1] and noble metals as stable to coke formation [2-6]. Moreover the same catalysts have been investigated

in our previous works and showed high activity in Fisher-Tropsch Synthesis [7-11]. It was supposed that synthesis-gas in case of its formation is able to following reactions with formation of different organic compounds under moderate temperature and pressure.

Experimental

Catalysts (content of each metal is 2.5 weight %) were prepared by impregnation method. Co:M ratio in the bimetallic catalysts was 1:1. Temperature of catalyst reduction was 473-673K. The process was carried out in a flow stainless steel reactor under pressure 0.1 - 2.0 MPa and varying experiment temperature from 473 to 853K, and in a quartz flow micro-reactor in the temperature range of 473-1373K at atmospheric pressure. Space velocity was varied from 500 to 2000 hr⁻¹. Ratio CO₂:CH₄ was constant 1:1, content of each gas in the initial reacting mixture with Ar was 10%.

The sets were combined with gas chromatographs (GC) equipped with thermal conductivity detector for analysis of H₂, Ar, CO, CH₄, O₂, CO₂ (columns: molecular sieves and activated coal) and flame-ionization detector (FID) for analysis of hydrocarbons (column: modified alumina) during the reaction. Analysis of oxygenates and water after reaction and their collection in special cooled trap (separator) was carried out by GC equipped with FID on columns: Carbowax/

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Carbopak and Poropak N, as well as by IR-spectroscopy. The degree of surface carbonization was determined by TGA. In addition, after reaction the thermo-programmed hydrogenation was carried out for definition of carbon-containing species on catalyst surface.

Catalysts were investigated by X-Ray analysis, TPR and IR-spectroscopy.

Results and discussion

a) CO₂ + CH₄ reaction

Some results of CO₂ + CH₄ reaction study on mono- and bimetallic Co-containing catalysts are summarized

in the Table 1. Co/Al₂O₃-catalyst has the lower activity in this process in compare with bimetallic ones (see Table 1). Introduction of the second metal to the composition of catalyst implies the significant increase of their activity. Conversion degree of initial compounds depends on the nature of catalyst and experiment conditions. Basically an unequal consumption of both carbon dioxide and methane is observed on all catalysts. The main reaction products are carbon oxide, hydrogen, water and oxygenates. In some cases oxygen is formed at the beginning of process. It has been shown that the yield of oxygenates depends on the nature of the second modified metal and experiment conditions (Table 1).

Table 1

The comparative characteristics of activity of 5% Co-M (1:1)/Al₂O₃ catalysts in the reaction of CO₂+CH₄ (CO₂: CH₄=1:1; space velocity = 1000hr⁻¹)

Catalyst	P, MPa	T, K	Conversion of CO ₂ , %	Conversion of CH ₄ , %
Co/Al ₂ O ₃	0.1	853	7.1	7.8
Co/Al ₂ O ₃	0.1	1323	79.8	100
M ₄ /Al ₂ O ₃	0.1	853	46.0	54.0
M ₄ /Al ₂ O ₃	0.1	1023	83.9	100
Co-M ₁ /Al ₂ O ₃	0.1	853	73.8	65.8
Co-M ₁ /Al ₂ O ₃	1.0	853	30.0	29.5
Co-M ₂ /Al ₂ O ₃	0.1	853	46.5	46.7
Co-M ₂ /Al ₂ O ₃	1.0	853	37.3	33.3
Co-M ₃ /Al ₂ O ₃	0.1	853	49.9	57.4
Co-M ₃ /Al ₂ O ₃	1.0	853	39.0	37.1
Co-M ₄ /Al ₂ O ₃	0.1	853	72.6	56.4
Co-M ₄ /Al ₂ O ₃	0.1	1023	94.0	100
Co-M ₄ /Al ₂ O ₃	1.0	853	32.4	31.2

On all catalysts the conversion of both reactants grows with increase of experiment temperature and decrease of pressure. It needs to note that ethane formation and increase of oxygenates' yield over these catalysts are observed with pressure increase. There are no oxygenates at atmospheric pressure. The maximum yield of oxygenates (20-30%) is observed on catalyst modified with M₄. Oxygenates consist of C₁-C₂ alcohols (≥ 95%) and traces

of acids (T_{exp}= 853 K, P= 0.1-1.5 MPa, space velocity =1000 hr⁻¹). On other catalysts the liquid fraction consists basically of water.

The advantage of the investigated catalysts is their resistance to coke formation. The coke formation is not verified by TGA. The weight loss during increase of temperature up to 1173K is less than 4%. It occurs because of water elimination at ~ 373K. The formation of carbon-containing species is not

observed during thermo-programmed hydrogenation of catalysts after reaction at temperature increase from 298 to 1373K. Water always produced during reaction on these catalysts may promote the suppression of coke formation. According to [12] oxygen suppresses coke formation to a greater degree than water. Oxygen is produced on the investigated catalysts at the reaction beginning.

b) The mechanism of $CO_2 + CH_4$ interaction

By IR-spectroscopic measurements of both combined adsorption of CO_2 and CH_4 and reaction between CO_2 and CH_4 over 5% Co- M_4/Al_2O_3 the weak absorption bands have been detected in the region of 2800-2900 cm^{-1} assigned to adsorbed CH_x -species ($x=1-3$). Also in the IR-spectrum the bands are present at 2330 cm^{-1} , which could be assigned to physically adsorbed CO_2 . The bands at 2000 and 2090 cm^{-1} could be assigned to bridgely and linearly adsorbed CO respectively and intensive bands at 1410 and 1580 cm^{-1} are concerned to carbonate- carboxylate species.

The reactions of separate decomposition of carbon dioxide and methane over 5% Co- M_4/Al_2O_3 have been studied. It was shown that 100% decomposition of methane occurs at $T=1273K$ and atmospheric pressure. While the maximum degree of CO_2 decomposition reaches 25% at $T=673K$. With further temperature increase until 1273K CO_2 conversion does not increase and varies from 16 to 20%.

At interaction of CO_2+CH_4 the maximum conversion of both CH_4 (100%) and CO_2 (94%) is observed at lower temperature (1023K). With further increase of temperature until 1273K the conversion degree of both components does not change.

It is possible to suppose, that the process of interaction between CO_2 and CH_4 on these catalysts represents two parallel reactions of decomposition of each initial compound (equations 2 and 3). The different conversion degree of both reagents may be an indirect evidence of it in some cases, when only synthesis-gas is formed. Each of these reactions is promoted by intermediates produced during the other reactions (equations 4 and 5):



The obtained results are in agreement with mechanism suggested by other authors for $CO_2 + CH_4$ interaction on supported Pd catalysts [4].

At medium pressures (0.5-1.5 MPa) and not too high temperatures (773-873K) produced $CO_{\text{ ads}}$ and $H_{\text{ ads}}$ involve into further interaction on the studied catalysts with alcohol and acid formation.

Nevertheless these results do not exclude the formation of «active» carbide, which immediately involves in further interactions.

Conclusions

Earlier we have reported that cobalt is able to form the nano-structures of cluster type at interaction with such noble metals as Ir and Pt on the surface of alumina [7-11]. The properties of bimetallic catalysts drastically differ from monometallic ones. It was observed that bimetallic clusters were very stable and showed the high activity in reactions with participation of C_1 -molecules, in particular in Fischer-Tropsch Synthesis and CO_2 hydrogenation.

The study of the similar catalysts in CO_2+CH_4 reaction demonstrates that the adding of second metal to the composition of Co-containing catalysts increases their activity in this process too. At moderate conditions ($T_{\text{exp}}=853K$, $P=1.0$ MPa) the conversion of both carbon dioxide and methane is 30-40% depending on the nature of the second metal. The maximum conversion of both methane and carbon dioxide reaches 100 and 94% respectively at 1023K and $P=0.1$ MPa.

It was shown that it is possible to produce some organic compounds by one step during the process CO_2+CH_4 on the same catalyst. The yield of oxygenates reaches 30% at certain conditions ($P=1.0$ MPa, $T \leq 853K$).

The advantage of the synthesized catalysts is their resistance to coke deposition.

The obtained data allow to consider these catalysts as high effective ones for reforming of CH_4 by CO_2 and their further industrial use.

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