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NOTE

CO_2 reforming of CH_4 over bimetallic supported catalysts†

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Cobalt-containing catalysts promoted by noble metals and supported on alumina have been investigated in the reaction of interaction between carbon dioxide and methane at various experimental temperatures and pressures. It was shown that catalysts have a high activity in this reaction. At moderate conditions (T_{exp} = 853 K, P = 1.0 MPa) the conversion of both carbon dioxide and methane is 30–40% depending on the nature of the second metal. The main reaction products are carbon oxide, hydrogen, water and oxygenates. The yield of the latter reaches 30%. The maximum conversion of both methane (100%) and carbon dioxide (94%) is reached at lower pressure (0.1 MPa) and at 1023 K. In these conditions the synthesis gas is the main reaction product. One of the advantages of the synthesized catalysts is their resistance to coke formation. Copyright © 2000 John Wiley & Sons, Ltd.

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INTRODUCTION

Recently, the reaction between carbon dioxide and methane has attracted attention as a prospective process for synthesis-gas production and a way for utilization of greenhouse gases (Eqn [1]). Both carbon dioxide and methane are greenhouse gases.

$$CO_2 + CH_4 = 2CO + 2H_2 \qquad [1]$$

The interaction between carbon dioxide and methane was investigated by Fischer and Tropsch in 1926.[1] Of all the metals studied by them, cobalt and nickel catalysts were found to be the most preferable for this process.[1] However, there is a very strong coke formation on these catalysts. The noble metals are characterized by a low level of coke formation and thus are more promising for this reaction. 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 has been investigated on bimetallic cobalt-containing catalysts modified by different noble metals (iridium, rhodium, platinum, palladium) and supported on alumina. The choice of catalysts was based on the literature data about preference of cobalt in this reaction[1] and noble metals as stable to coke formation.[2–4] Moreover, the same catalysts have been investigated in our previous studies and showed high activity in Fisher–Tropsch synthesis.[7] It was supposed that synthesis gas in the case of its formation is able to react with formation of different organic compounds under moderate temperature and pressure.

EXPERIMENTAL

Catalysts (total metal content is 5 wt%, ratio Co:M = 1:1) were prepared by the co-impregnation method. The temperature of the catalyst reduction was 473–673 K. The process was carried out in a continuous flow stainless steel reactor under pressures of 0.1–2.0 MPa and varying experimental temperatures from 473 to 853 K, and in a quartz flow micro-reactor in the temperature range 473–

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Table 1 The activity of 5% Co–M(1:1)/Al_2O_3 catalysts in the reaction of $CO_2 + CH_4$ (CO_2:CH_4 = 1:1; T_{exp} = 853 K, space velocity: 1000 h^{-1})

Second metal	*P* (MPa)	Conversion (%)	
		CO_2	CH_4
Ir	0.1	73.8	65.8
Ir	1.0	30.0	29.5
Rh	0.1	46.5	46.7
Rh	1.0	37.3	33.3
Pt	0.1	49.9	57.4
Pt	1.0	39.0	37.1
Pd	0.1	72.6	56.4
Pd	1.0	32.4	31.2

1273 K at atmospheric pressure. Space velocity was varied from 500 to 2000 h^{-1}. The ratio of CO_2:CH_4 was constant at 1:1; the content of each gas in the initial reacting mixture with argon was 10%.

The sets were combined with gas chromatographs (GCs) equipped with a thermal conductivity detector for analysis of H_2, Ar, CO, CH_4, O_2, CO_2 (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 a special cooled trap (separator) was carried out by a GC equipped with an FID on columns Carbowax/Carbopak and Poropak N, as well as by IR spectroscopy. The degree of surface carbonization was determined by thermogravimetric analysis (TGA). In addition, after reaction the thermo-programmed hydrogenation was carried out for definition of carbon-containing species on the catalyst surface.

Catalysts were investigated by X-ray analysis, temperature-programmed reduction (TPR) and IR-spectroscopy.

RESULTS AND DISCUSSION

The conversion degree of initial compounds depends on the nature of the catalyst and the experimental 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 the process. It has been shown that the yield of oxygenates depends on the nature of the second modified metal and experiment conditions (Table 1).

On all catalysts the conversion of both reactants grows with increasing experimental temperature and decreasing pressure. It should be noted that ethane formation and an increase of oxygenates yield over these catalysts are observed with pressure increase. There are no oxygenates at atmospheric pressure. The maximal yield of oxygenates (20–30%) is observed on a catalyst modified with palladium. Oxygenates consist of C_1–C_2 alcohols ($\geq$95%) and traces of acids (T_{exp} = 853 K, P = 0.1–1.5 MPa, space velocity = 1000 h^{-1}). On other catalysts the liquid fraction consists basically of water.

It should be noted that at low pressure (0.1–0.5 MPa) the hydrogen formation is significantly higher than the theoretical yield, which was calculated from methane consumption according to reaction [1]. This phenomenon may be attributed to a second reactions resulting in additional hydrogen production and has to be investigated further.

The advantage of the catalysts investigated is their resistance to coke formation. The coke formation is not verified by TGA. The weight loss with increasing temperature up to 1173 K is less than 4%. It occurs due to water elimination at ~373K. The formation of carbon-containing species is not observed during thermo-programmed hydrogenation of catalysts after reaction at temperatures increased from 298 to 1273 K. Water, which is always produced during reaction on these catalysts, may promote the suppression of coke formation. According to Ref. [8] oxygen suppresses coke formation to a greater degree than water. Oxygen is produced on the catalysts investigated at the beginning of the reaction.

From IR spectroscopic measurements of both combined adsorption of CO_2 and CH_4 and reaction between CO_2 and CH_4 over 5% Co–Pd/Al_2O_3, weak absorption bands have been detected in the region 2800–2900 cm^{-1}; these were assigned to adsorbed CH_x species (x = 1–3). Nevertheless, these results do not exclude the formation of 'active' carbide, which's immediately involved in further interactions. Also, in the IR spectrum a band is present at 2330 cm^{-1} that could be assigned to physically adsorbed CO_2. The bands at 2000 cm^{-1} and 2090 cm^{-1} could be assigned to bridgely-adsorbed and linearly adsorbed CO respectively and intensive bands at 1410 and 1580 cm^{-1} are concerned with carbonate–carboxylate species.

The reactions of separate decomposition of carbon dioxide and methane over 5% Co–Pd/

Al_2O_3 have been studied. It was shown that 100% decomposition of methane occurs at $T = 1273$ K and atmospheric pressure, whereas the maximum degree of CO_2 decomposition reaches 25% at $T = 673$ K. With further temperature increase until 1273 K the 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 (1023 K). With further increase of temperature until 1273 K 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 (Eqns [2] and [3]). The different conversion degree of both reagents may be indirect evidence of it in some cases, when only synthesis gas is formed. Each of these reactions is promoted by intermediates that are produced during the other reactions (Eqns [4] and [5]):

$$CH_4 \rightarrow CH_{x\text{ads}} + H_{\text{ads}} \rightarrow H_2(g) \qquad [2]$$

$$CO_2 \rightarrow CO_{\text{ads}} + O_{\text{ads}} \rightarrow CO(g) \qquad [3]$$

$$CH_4 + O_{\text{ads}} \rightarrow CH_{x\text{ads}} + OH_{\text{ads}} \qquad [4]$$

$$CO_2 + H_{\text{ads}} \rightarrow CO_{\text{ads}} + OH_{\text{ads}} \qquad [5]$$

$$OH_{\text{ads}} \rightarrow H_2O + O_{\text{ads}} \qquad [6]$$

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

At medium pressures (0.5–1.5 MPa) and not too high temperatures (773–873 K) the CO_{ads} and H_{ads} produced is involved into further interaction on the catalysts with alcohol and acid formation.

CONCLUSIONS

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

The study of these catalysts in the $CO_2 + CH_4$ reaction demonstrates their high activity in this process too. At moderate conditions ($T_{\text{exp}} = 853$ K, $P = 1.0$ MPa) the conversion of both carbon dioxide and methane is 30–40%, depending on the nature of the second metal. The main reaction products are carbon oxide, hydrogen, water and oxygenates. The yield of the latter reaches 30%. The maximal conversion of both methane and carbon dioxide reaches 100% and 94% respectively at 1023 K and $P = 0.1$ MPa. The advantage of the synthesized catalysts is their resistance to coke deposition.

The data obtained allow are to consider these catalysts as being highly effective ones for reforming of CH_4 by CO_2.

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