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Reforming of Light Alkanes by CO₂ Over Bimetallic Supported Catalyst

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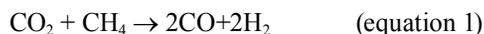
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The bimetallic cobalt-containing catalyst supported on alumina has been investigated in the reaction of interaction between carbon dioxide and light alkanes (mix of C₂-C₄ hydrocarbons) or individual methane at varying experiment temperature and pressure. It has been shown that the catalyst possesses the high activity in reforming of alkanes. The reactants' conversion and products' yield and composition depend on composition of initial feed and process conditions. The main product of CO₂+CH₄ reaction is synthesis-gas at atmospheric pressure, also water and oxygenates are produced at higher pressure. The yield of oxygenates (mainly methanol and ethanol) is about 2 % under the certain conditions (P= 2-5 atm). In addition to above products olefins are formed at the interaction between carbon dioxide and alkanes (C₂-C₄). One of the advantages of the synthesized catalyst is its resistance to coke formation.

Keywords: CO₂ reforming, bimetallic catalyst, light alkanes, synthesis-gas

Introduction

One of new widely developing methods of methane (CH₄) utilization is its catalytic interaction with carbon dioxide (CO₂) so called dry reforming of methane according to the reaction (equation 1) [1-4]:



Synthesis-gas (or syngas – CO+H₂) produced by this reaction is recognized as the most real alternative raw material for producing the various hydrocarbon fractions including motor fuel, hard hydrocarbons, olefins, and oxygenates to be used in different directions of energetic and chemistry [1-5]. The development of methods of combined utilization of carbon dioxide and alkanes can also

solve the ecological problem. Both carbon dioxide and methane are “green-house” gases. `

The interaction between light alkanes (C₂-C₄) and carbon dioxide is performed as a prospective process too, because they are components of the real natural, associated and petrochemical gases. CO₂ reforming of alkanes (C₂₊) is not widely investigated. The reason of that is high coke formation due to cracking of hydrocarbons strengthened with increase in number of carbon atoms of hydrocarbon. Carbon can be produced during decomposition of carbon dioxide too. As a result the catalysts covered by carbon deposition lose their activity in process of CO₂ reforming that discourages their use especially under high pressure. For commercial application the

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active catalysts with a low or absence of carbon deposition should be developed.

In this paper the catalytic interactions between carbon dioxide and light alkanes (C₂-C₄) or methane have been studied over the new cobalt-containing catalyst modified by a noble metal and supported on alumina. Choice of metals – cobalt and noble metal for the catalyst design was based on the following. Cobalt is an active metal for both processes – reforming of methane and Fischer-Tropsch synthesis [6]. It is known that the noble metals have high resistance to coke formation [7-9]. 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 over the same catalyst by one step.

Experimental

Catalyst with total metal content – 5 weight % and ratio Co:M = 1:1 was prepared. The process was carried out in a flow stainless steel reactor under varying pressure within 1- 20 atm and varying experiment temperature from 200 to 600 °C and in quartz reactor at atmospheric pressure and varying temperature from 300 to 800 °C. Space velocity was varied from 200 to 2000 hr⁻¹. Ratio CO₂:CH₄ and CO₂: alkanes (C₂-C₄) were constant 1:1. Content of each gas (except alkanes: their total content was 10 %) in initial reacting mixture with Ar was 10 %. The composition of a mix of light hydrocarbons, vol. %: ethane (C₂) – 12.9, propane (C₃) – 29.9, and butane (C₄) – 57.2.

The sets were combined with gas chromatographs (GC) equipped with thermal conductivity detector for on-line analysis of H₂, Ar, CO, CH₄, O₂, CO₂ (columns: molecular sieves and activated coal) and flame-ionization detector (FID) for on-line analysis of hydrocarbons (column: modified alumina). Liquid phase was collected in a special cooled trap (separator)

and then analyzed by GC equipped with FID on columns: Carbowax/Carbopak and Poropak N, as well as by IR-spectroscopy. The carbon formation was controlled by thermogravimetric analysis (TGA), thermo-programmed reduction (TPR) and electron microscopy.

The physico-chemical properties of the catalyst was studied with using BET, IR-spectroscopy and electron microscopy.

Results and discussion

Conversion degree of initial compounds depends on the composition of initial reactants and experiment conditions. Dependence of conversion degree of methane and carbon dioxide is demonstrated in Fig. 1. As it is shown in Fig. 1, with growing pressure from 1 to 20 atm the conversion of initial reacted gases – CH₄ and CO₂ over the 5 % Co-M(1:1)/Al₂O₃ catalyst is decreased from 57.4 to 20.7 % and from 55.7 to 24.7 respectively at T= 580 °C. It is no wonder, because the reaction carries out with twofold increase in volume (eq.1) consequently pressure would shift reaction to reverse direction.

The yield of products is shown in Table 1. The main product of the reaction between carbon dioxide and methane (dry reforming of methane) at atmospheric pressure is syngas. Also, water and oxygenates are formed at elevated pressure. The basic oxygenates are C₁-C₂ alcohols. The traces of other oxygenate such as acetic acid and C₃-C₄ alcohols and acids are produced. The maximum yield of methanol and ethanol reaches 2 % at P=2 atm (Table 1).

The ratio of H₂/CO is decreased from 1.2 to 0.7 with raising pressure from 1 to 20 atm (Table 1). Hydrogen yield is becoming less than carbon oxide at P=5 atm, when degree of methane conversion starts to be less than conversion of carbon dioxide. Thus, pressure increase suppresses the methane conversion in greater degree than carbon dioxide conversion that leads

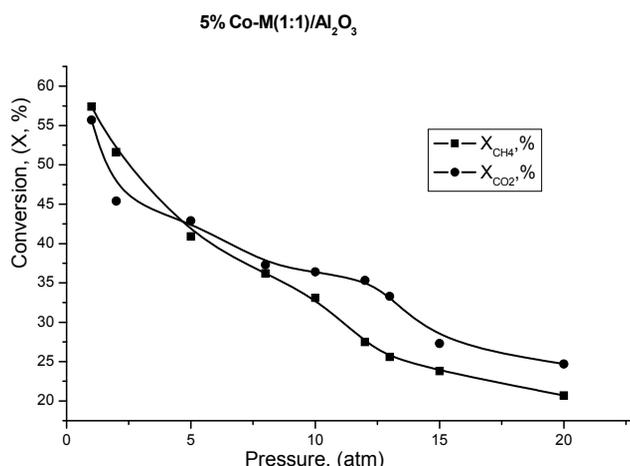


Fig. 1. The effect of pressure on conversion of methane and carbon dioxide over 5 % Co-M (1:1)/Al₂O₃ catalyst (CH₄:CO₂ = 1:1; T=580 °C; V=1000 hr⁻¹)

Table 1. Effect of pressure on formation and yield of products in CO₂+CH₄ reforming over 5 % Co-M(1:1)/γ-Al₂O₃ catalyst (CH₄:CO₂ = 1:1; T=580 °C; V=1000 hr⁻¹)

P, atm	Ratio H ₂ /CO	Yield of oxygenates, %*		
		CH ₃ OH	C ₂ H ₅ OH	CH ₃ COOH + Σ C ₃ -C ₄ alcohols
1	1.2	0	0	0
2	1.1	1.4	0.6	traces
5	0.9	1.1	0.5	traces
8	0.9	0.4	0.4	traces
10	0.8	0.2	0.4	traces
15	0.8	traces	traces	0
20	0.7	traces	traces	0

* % from theoretical yield at complete methane conversion

to decrease in hydrogen yield, which is formed due to decomposition of methane (equation 2):



The maximum conversion of both methane (100 %) and carbon dioxide (94 %) is reached at lower pressure – 1 atm and higher temperature – 750 °C. The data on effect of temperature on conversion of methane and carbon dioxide and composition of syngas at P=1 atm are presented in Table 2. Under these conditions the synthesis-gas is only one reaction product. The ratio of H₂/CO is decreased from 1.2 to 1.1 with temperature increase from 580 to 750 °C.

In case of CO₂ reforming of alkanes (C₂-C₄) in addition to above products olefins (ethylene, propylene, n- and iso-butylene, pentene and hexene) are formed at T=580 °C and P=1-10 atm. The conversion degree of CO₂ is 40-75 % and alkanes are 10-40 % for each depending on reaction conditions (Table 3). The formation of small amount of olefins indicates that dehydrogenation of hydrocarbons occurs prior than their decomposition to adsorbed carbon species to form carbon oxide.

The C₅-C₆ olefins and C₁-C₂ oxygenates (3.6-3.9 %) are produced under pressure. Their formation indicates that reactions of

Table 2. Effect of temperature on the activity of 5 % Co-M (1:1)/Al₂O₃ catalyst in the reaction of CO₂+CH₄ (CO₂:CH₄=1:1; P=1 atm; space velocity = 1000hr⁻¹)

Temperature, °C	Conversion of CO ₂ , %	Conversion of CH ₄ , %	H ₂ /CO
580	72.6	56.4	1.2
650	91.8	92.5	1.2
700	97.3	94.3	1.1
750	94.4	100	1.1

 Table 3. Effect of pressure on formation and yield of products in CO₂ reforming of light alkanes over 5 % Co-M(1:1)/γ-Al₂O₃ catalyst (T=580 °C; V=1000 hr⁻¹; (Σ C₂-C₄)/CO₂ = 1/1)

P, atm	Degree of conversion, %				H ₂ /CO	Yield of olefins and oxygenates, %				
	CO ₂	C ₂	C ₃	C ₄		=C ₂	=C ₃	=C ₄	Σ=C ₅ -C ₆	C ₁ -C ₂ alcohols
1	75.7	35.0	33.2	41.5	1.3	1.3	8.1	1.8	0	0
5	53.4	22.7	21.1	24.4	1.3	1.5	8.9	0.9	0.3	3.6
10	41.1	10.3	15.1	11.5	1.4	0.7	5.0	1.4	traces	3.9

polymerization of CH_{xads} groups and their interactions with CO_{ads} and CO_{2ads} adsorbed can take place over the catalyst under pressure.

The degree of CO₂ conversion is much higher (by 2-4 times) than conversion of individual hydrocarbons (Table 3). The reason of that may be the formation of C₂-C₆ alkanes due to secondary reactions and CO hydrogenation. That's why the real degree of C₂-C₄ conversion may be higher than calculated one.

The advantage of the synthesized catalyst is its resistance to coke formation. The coke formation is not verified by TGA. The weight loss of the catalyst used in reaction with increase in temperature up to 900 °C is less than 4 % and occurs at ~ 100 °C due to water elimination. The formation of carbon-containing species was not observed during thermo-programmed reduction of the catalyst after reaction at temperature increase from 300 to 900 °C. The catalyst keeps its high-dispersed state after reaction. By electron microscopy it has been observed that the metal particles uniformly distributed have a size of 2-3 nm.

Water always produced during reaction over these catalysts may promote the suppression of coke formation. Also, the reaction conditions are relatively mild: T << 800 °C.

Conclusions

The new Co-containing catalyst modified with noble metal and supported on alumina has been developed. The catalyst performs activity in reforming of light hydrocarbons by carbon dioxide with producing syngas, oxygenates, and olefins under moderate conditions: P=1-10 atm, T=580 °C.

The results obtained allow considering that the catalyst is the high effective one for reforming of natural and associated gases by CO₂ and can be recommended for further industrial test.

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References

1. Wilhelm, D.J., Simbeck, D.R., Karp, A.D., Dickenson, R.L. Syngas production for gas-to-liquids applications: technologies, issues and outlook // Journal Fuel Processing Technology. V. 71 (2001) 139-148.
2. Ashcroft, A. T., Cheetham, A. K., Green, M. L., and Vernon, P. D. F. Partial oxidation of methane to synthesis-gas using carbon dioxide // Nature. V. 352, No 6332 (1991) 225-226.
3. Chang, J.-S., Park, S.-E., Yoo, J.W., and Park, J.-N. Catalytic behavior of supported KNiCa catalyst and mechanistic consideration for carbon dioxide reforming of methane // J. Catalysis. V. 195 (2000) 1-11.
4. Ruckenstein, E., and Wang, H. Y. Carbon deposition and catalytic deactivation during CO₂ reforming of CH₄ over Co/Al₂O₃ catalyst // J. Catalysis V. 205, N 2 (2002) 289-293.
5. Арутюнов В.С., Крылов О.В. Окислительная конверсия метана // Успехи химии, №12 (2005) 1216-1243.
6. Fischer, F. and Tropsch, H. Conversion of methane into hydrogen and carbon monoxide // Brennstoff.Chem., V. 9 (1928) 39-46.
7. Mark, M.F. and Maier, W.F. CO₂-reforming of methane on supported Rh and Ir catalysts // J.Catal., 164 (1996) 122-130.
8. Kroll V. C. H., Swaan H. M., and Mirodatos C. Methane Reforming reaction with carbon dioxide over Ni/SiO₂ catalyst. I. Deactivation Studies // J. Catal., V.161 (1996) 409-422.
9. Erdoehelyi, A., Cserenyi, J., Papp, E., and Solymosi, F. Catalytic reaction of methane with carbon dioxide over supported palladium // Appl.Catal., 108A (1994) P. 205-219.

Риформинг легких алканов диоксидом углерода на биметаллическом нанесенном катализаторе

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Биметаллический кобальтсодержащий катализатор, нанесенный на оксид алюминия, был использован в реакции взаимодействия между диоксидом углерода и легкими алканами (смесь C₂-C₄ углеводородов) или только метаном при варьировании температуры и давления. Показано, что катализатор является высокоактивным в риформинге алканов. Степень конверсии реактантов, состав и выход продуктов зависят от состава исходной смеси и условий процесса. Основным продуктом при атмосферном давлении реакции CO₂+CH₄ является синтез-газ; при повышенном – также образуются вода и кислородсодержащие соединения. Выход кислородсодержащих соединений (в основном метанола и этанола) составляет около 2 % при определенных условиях (P= 2-5 атм). При взаимодействии легких алканов (C₂-C₄) кроме вышеперечисленных продуктов образуются олефины. Одним из достоинств синтезированного катализатора является его устойчивость к образованию кокса.

Ключевые слова: риформинг диоксидом углерода, биметаллический катализатор, легкие алканы, синтез-газ.
