Carbon Dioxide Reforming of Methane over Zeolite-containing Catalysts

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Abstract

Reforming of methane by carbon dioxide (dry reforming of methane) has been studied over the series of the 5% Co-M/Al_2O_3+ zeolite catalysts. The effect of zeolite (type, module, and amount) added to support composition on performance of the Co-M/Al_2O_3 catalyst in dry reforming has been examined. It has been shown that syngas is a main product of dry reforming over the zeolite-containing catalysts. Also, some amount (up to 3%) of acetic acid is produced. The yield of syngas and acetic acid depends on nature and amount of zeolite and process conditions.

Nomenclature

CH_4 – methane
CO_2 – carbon dioxide
GTL – gas-to-liquids process
IR-spectroscopy – infrared spectroscopy
P, atm – pressure, atmosphere
S.V. – space velocity
T,°C – temperature
TEM – transmission electron microscopy
TGA – thermogravimetric analysis
X_{CH4},% – degree of methane conversion:
X_{CO2},% – degree of carbon dioxide conversion:

Introduction

The main gas-to-liquids (GTL) interest now is in Fischer–Tropsch (F–T) synthesis of hydrocarbons from so called synthesis-gas or syngas (mix of CO+H_2). While synthesis gas for GTL can be produced from any carbon-based feedstock hydrocarbons, coal, petroleum coke, biomass, the lowest cost routes to syngas so far are based on natural gas [1]. Natural gas, the main component of which is methane, is an abundant fossil fuel resource found all over the world and is predicted to outlast oil reserves by a significant margin [2]. Syngas can be produced from natural gas by the main 3 ways widely described in literature [2-10]: i) steam reforming; ii) partial oxidation; and iii) dry reforming (eqn.1) or their combination.

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2$$
$$\Delta H = 247.3 \text{ kJ/mol} \qquad \text{(eqn.1)}$$

Methane reforming using carbon dioxide (dry reforming) has been of interest for a long time, and it has grown for both environmental and commercial reasons [11]. This process offers important advantages compared to steam reforming of methane. Namely, (a) it yields lower H_2/CO product ratios, which are preferable feeds for Fischer–Tropsch plants and for synthesis of oxoalcohols and acetic acid and dimethyl ether; (b) it reduces CO_2 and CH_4 emissions, which are both greenhouse gases; and (c) it is well suited for chemical energy transmission systems.

Most of the group VIII metals are more or less catalytically active toward this reaction. Due to the inherent inertness of methane, a high temperature (typically, 800–900°C) is needed to achieve a meaningful yield. Under such severe conditions, an excess carbon deposition occurs on the surface of the catalyst, and this constitutes a major drawback of CH_4–CO_2 reforming [12]. Much effort has been directed toward development of catalysts resistant to coke formation and capable of operating under severe deactivation conditions.

The noble metal-based catalysts (such as Rh, Ru, Pd, and Pt) can provide high activity and selectivity with little or no carbon deposition [3]. While Ni- and Co-based catalysts are easily available, they deactivated rapidly when the conventional supports, such as Al_2O_3 and SiO_2, were employed. Noble metals, which are active and comparatively resistant to coke formation, due to their expensiveness can

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be supposed only as a promoter. Earlier it has been shown by us that the combination of Co and noble metal allows avoiding the coke deposition in dry reforming of methane over the alumina supported catalysts [13-16].

It has been generally observed that the nature of the support greatly affects catalytic performance in dry reforming [4, 17-19]. The selection of a suitable support is regarded as one of the key aspects for designing a stable catalyst for the reaction. It was found that the composite support, which is composed of a highly siliceous NaZSM-5 zeolite and an alumina binder offers high catalyst stability for the KNiCa catalyst compared with a highly siliceous NaZSM-5 zeolite itself, Al_2O_3 and SiO_2 supports [12, 20].

This study deals with a design of a number of Co-containing catalysts supported on a matrix containing alumina promoted by various zeolites and their testing in dry reforming of methane. One of the Co-M/Al_2O_3 catalysts previously performed the high efficiency in dry reforming of methane [13-16] was used as a base for synthesis of new catalysts, where composition of support was varied depending on nature and amount of zeolite.

Experimental

The Co-containing bimetallic catalysts supported on alumina promoted by zeolites (NaZSM/HZSM or NaY) have been used in dry reforming of methane. The catalysts were prepared by impregnating the matrix – alumina + zeolite preliminary produced with a solution of metal salts. HZSM-zeolites were prepared by decationizing the appropriate NaZSM-5-zeolites. The content of metals (Co and Pt-Group metal) is 5 wt. % from total catalyst amount. The content of zeolites in the support is 10-20 wt. % from total mass of support (Al_2O_3 + zeolite). Si/Al ratio for the samples containing ZSM-5 zeolite was 35 except the sample 2, where Si/Al= 80. Also, the catalyst containing no zeolite (5% Co-M/Al_2O_3) has been used to define the effect of zeolite. The catalysts used are listed in Table 1.

Dry reforming of methane were carried out at a flow quartz reactor supplied with the programmed heating and controlled feeding velocity and operated at atmospheric pressure. The volume ratio of gases in feeding of $CO_2/CH_4/Ar = 10/10/80$. The process was carried out at atmospheric pressure, space velocity (S.V.) - 1000 hr^{-1}, and varying temperature from 200 to 900°C.

The catalysts were tested at the same process conditions. The conversion degrees of carbon dioxide (XCO_2,%) and methane (XCH_4,%) calculated according to the formulas 1 and 2 respectively were used in order to compare the catalyst activity. The effect of temperature on catalysts activity was studied. Temperature of complete methane conversion was determined for each catalyst.

$$XCO_2 = ([CO_2]_{init} - [CO_2]_{fin}) \times 100\%/[CO_2]_{init}, \quad (1)$$

where $[CO_2]$ – concentration of CO_2, init – initial, fin - final

$$XCH_4 = ([CH_4]_{init} - [CH_4]_{fin}) \times 100\%/[CH_4]_{init}, \quad (2)$$

where $[CH_4]$ – concentration of CH_4,

Table 1.

List of the catalysts used

Sample	Composition	Zeolite loading into matrix, wt. %	Si/Al
1	5%Co-M/Al_2O_3-NaZSM	10%	80
2	5%Co-M/Al_2O_3-NaZSM	10%	35
3	5%Co-M/Al_2O_3-NaZSM	20%	35
4	5%Co-M/Al_2O_3-HZSM	10%	35
5	5%Co-M/Al_2O_3-HZSM	20%	35
6	5%Co-M/Al_2O_3-NaY	10%	4
7	5%Co-M/Al_2O_3	-	-

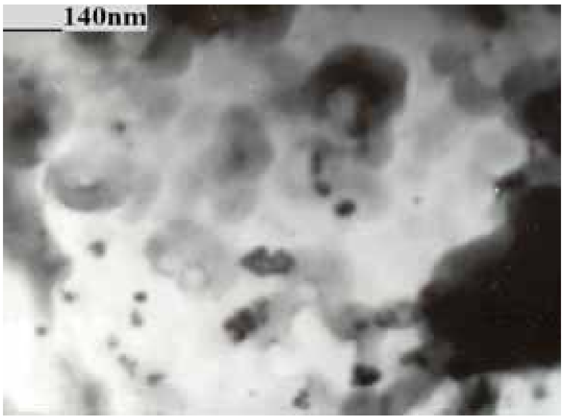

Fig. 1. TEM pattern of 5% Co-M/Al_2O_3-NaZSM (9:1) (Si/Al=35) - fresh sample.

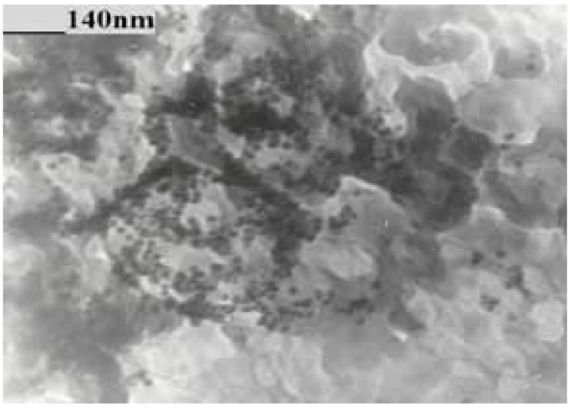

Fig. 2. TEM pattern of 5% Co-M/Al_2O_3-NaZSM (9:1) (Si/Al=35) - after dry reforming of methane.

The gaseous initial and final reaction products have been on-line analysed by the gaseous chromatographs equipped with a TCD and a FID using 5A molecular sieve, activated coal, and activated γ-Al_2O_3 columns. Liquid products were collected in a special cooling trap and analysed after reaction by using the GC (FID, carbopack/carbowax and Porapak columns) and IR-spectroscopy. To detect the carbon species, the used catalysts were analysed by TGA method.

The physico-chemical properties of catalysts were studied by an electron microscopy, IR-spectroscopy, and BET. Specimens for TEM-analysis were prepared with a conventional method.

Results and Discussion

TEM-study

The effect of a reaction medium on the catalyst surface has been observed by TEM. In a fresh sample, a size of metal particles is larger than in the catalyst used in dry reforming of methane.

Thus, the particles size in the fresh 5%Co-M/90%Al_2O_3-10%NaZSM (Si/Al=35) is about 3.0-5.0 nm. The particles are not uniformly distributed (Fig.1). After the reaction CO_2+CH_4, the particles size is decreased to ~ 2.0 nm and their uniform distribution is observed (Fig.2).

Amorphous carbon has been observed after dry reforming of methane over the catalysts with high content of zeolite – 20% ZSM. No graphite formation was observed over all the catalysts except the sample 1 with high ratio of Si/Al=80 used in dry reforming of methane.

IR-study

The weak bands at 2850-3000 cm^{-1} attributed to CH_{ads} groups have been detected in IR-spectra of the catalysts treated by CO_2-CH_4 at 350°C. This is an evidence of dissociative character of CH_4 adsorption.

The adsorption band at 2320-2350 cm^{-1} corresponding to physically adsorbed CO_2 and strong bands in region of 1380-1650 cm^{-1} attributed to the carbonate-carboxylate species have been found. The significant strengthening of bands at 1380-1650 cm^{-1} after CO_2–CH_4 adsorption in comparison with the fresh sample confirms the associative adsorption of CO_2.

Also, in IR-spectra the weak bands attributed to the COads at 1920-1960 and 2000-2070 cm^{-1} were presented. CO adsorbed may appear due to direct dissociation of adsorbed CO_2 or can be originated from carbonate species or both can take place.

In addition, OH_{ads} groups have been identified by presence of a broad band in region of 3200-3600 cm^{-1} over all the catalysts. OH_{ads}-groups can appear due to the secondary surface reactions.

Catalyst testing in dry reforming of methane

The reaction of dry reforming of methane runs with a slight activity at 300°C over all the catalysts studied (S.V.=1000 hr^{-1}, CH_4/CO_2=1/1, P=1 atm). Under these conditions, the degree of conversion of CH_4 and CO_2 is not higher than 5 and 10% respectively.

The process is significantly activated at temperature above 500°C over all the catalysts. The data obtained at T > 500°C are summarized in Table 2.

The complete conversion of methane is occurred at higher temperature - 725-810°C depending on the catalyst composition. While degree of CO_2 conversion does not reach 100% and varied within 88.4-96.6% under the same conditions (Table 2). The complete CO_2 conversion was not observed even at increasing temperature up to 850-900°C.

It needs to take into account that degree of carbon dioxide conversion - XCO_2 was calculated on a base of difference between the CO_2 content in an initial feeding mix and end gaseous flow (Formula 1). Carbon dioxide may be a product of the secondary reactions such as a water-gas shift reaction running with a sufficient probability at high temperatures (eqn.2) or the Boudouard reaction (eqn.3) at lower temperature ~ 400°C. For this reason, contribution of CO_2 produced complicates evaluating its actual conversion degree, which might be higher than calculated one.

Table 2.

Comparative characteristics of 5% Co-M/Al_2O_3+zeolite catalysts in dry reforming of methane (CO_2:CH_4=1:1; S.V. = 1000 hr^{-1}; P = 1 atm)

Catalysts	Sample	T,°C	X_{CH4},%	X_{CO2},%	H_2/CO
5%Co-M/Al_2O_3	7	500	23.8	17.4	2
		600	79.9	60.6	1.1
		700	93.1	94.0	1.1
		740	~100	96.6	1.0
5%Co-M/Al_2O_3+NaZSM (9:1)	1	500	13.5	4.6	-*
		600	21.9	23.3	1.7
		700	95.1	81.6	1.0
		810	~100	93.4	0.9
5%Co-M/Al_2O_3+NaZSM(9:1)	2	500	34.5	39.5	1.5
		600	77.3	70.9	0.9
		700	97.9	92.1	0.9
		725	**~100**	**94.0**	**0.8**
5%Co-M/Al_2O_3+NaZSM(8:2)	3	500	16.9	46.7	1.5
		600	87.8	86.5	1.1
		700	98.6	90.9	1.0
		745	~100	94.9	0.96
5%Co-M/Al_2O_3+HZSM(9:1)	4	500	40.0	27.0	1.3
		600	74.7	69.1	0.97
		700	97.7	88.1	0.95
		800	~100	91.2	0.92
5%Co-M/Al_2O_3+HZSM(8:2)	5	**500**	**70.8**	**35.5**	**1.2**
		600	94.0	69.7	1.0
		700	99.5	87.5	1.0
		750	~100	92.1	0.9
5%Co-M/Al_2O_3+NaY(9:1)	6	500	18.9	22.7	1.6
		600	81.8	56.8	0.9
		700	94.3	80.1	0.9
		755	~100	88.4	0.9

* - CO is not formed while H_2 is already produced

$$CO + H_2O \rightarrow CO_2 + H_2 \quad \Delta H = +41.2 \text{ kJ/mol} \qquad \text{(eqn.2)}$$

$$2CO \rightarrow CO_2 + C \quad \Delta H = -172.5 \text{ kJ/mol} \qquad \text{(eqn.3)}$$

Practically, the no-zeolite containing catalyst - 5%Co-M/Al_2O_3 at dry reforming of methane produces synthesis-gas only. Negligible traces of acids and ketone are produced at temperature range – 400-500°C. While over the zeolite containing catalysts, synthesis-gas is a main but not only one product. Selectivity toward H_2/CO is varied within 96-100% depending on the catalyst nature and conditions. Ratio of H_2/CO is varied within 0.7-2.0 depending on nature and amount of zeolite but first of all on temperature. Actually, at temperature $\leq$ 500°C the ratio of H_2/CO is significantly higher than 1.0 due to the prevalent hydrogen formation over all the catalysts. Producing CO is starting at higher temperature and at T $\geq$ 600°C its formation is comparable with hydrogen yield. With the following increase in temperature up to 700-800°C, the ratio of H_2/CO is about 1 ± 0.2 depending on zeolite nature and amount (Table 2).

Also water, acetic acid, and non-significant amount of various oxygenates such as ethers, aldehydes, alcohols, ketone, and higher molecular carboxylic acids are formed over the ZSM-zeolite containing catalysts at comparatively low temperatures 300-600°C. Traces of oxygenates were detected over the NaY-containing catalyst (sample 6). Content of acetic acid in liquid phase is 40-70%. Selectivity to acetic acid is about 0.4-3% depending on nature and content of zeolite. The highest yield – 3.0% of acetic acid is produced over the catalyst promoted with 10% NaZSM (sample 2, Si/Al=35). Acetic acid may be produced due to the interaction of the adsorbed intermediates, which formation was observed by IR-spectroscopy, for example according to the reaction (eqn. 4):

$$CH_{ads} + COOH_{ads} \rightarrow CH_3COOH \qquad \text{(eqn.4)}$$

This reaction requires strong acid as a solvent [21]. Zeolites possessing more acidic properties than alumina alone possibly promote the producing acetic acid in dry reforming of methane over zeolite-containing catalysts.

The various types of adsorbed species over the zeolite-containing catalysts are provided the formation of other oxygenates.

In addition to syngas and oxygenates also traces of C_2-C_4 hydrocarbons are formed over the catalysts promoted by NaZSM (sample 1,2,3) at 300-400°C.

Comparison of the catalyst performance with point of view of complete methane conversion shows that the catalyst prepared with using 10% of NaZSM with Si/Al=35 (sample 2) is the most active one. Complete conversion of CH_4 over this catalyst is reached at T= 725°C that less by 15 and 20-85° in comparison with no-zeolite and other zeolite-containing catalysts respectively (Table 2).

At the same time at lower temperature the catalysts synthesized on a base of HZSM prepared by decationizing of appropriate NaZSM perform higher activity than others. At 500°C over the catalysts with adding 10 and 20% of HZSM, the degree of methane conversion is 40 and 70.8% respectively. The last is much higher than for the rest catalysts, where XCH_4 lies within 13.5-34.5% at the same temperature (Table 2).

At 600°C, the catalysts with additives of 20% HZSM (sample 5) and 20% NaZSM (sample 3) perform the high efficiency in dry reforming of methane in comparison with other samples: degree of CH_4 conversion are 94.0 and 87.8%, and degree of CO_2 conversion are 69.7 and 86.5%, syngas with appropriate H_2/CO ratio – 1.0 and 1.1 respectively is produced (Table 2).

At 700°C, all the zeolite-containing catalysts show the high activity in syngas production from CH_4-CO_2. The degree of methane conversion is varied within 94.3-99.5% that higher than for the no-zeolite containing catalyst, where XCH_4=93.1% (Table 2).

At selecting zeolites for the present study it was assumed that doping of Co/Al_2O_3 with ZSM should improve the catalyst properties in reforming of methane, because the ZSM-5- type zeolite is considered as the most thermally stable among many zeolite molecular sieves in dry reforming of methane [22]. Therefore the good performance of the catalysts promoted with ZSM (samples 2-5; Si/Al=35) tested in this study is not surprising.

There is general agreement that increase in alkalinity of the catalyst leads to improving its performance in dry methane reforming due to suppression of coke formation. In [24] it has been reported that addition of basic metals to Ni/Al_2O_3 catalyst caused decrease in the ability of Ni catalyst for CH_4 decomposition. From this point of view the efficiency of HZSM promoted catalysts seems rather not expected. But it needs to note that HZSM-based catalysts operate with the sufficient activity (XCH_4= 40-99.5%) at low temperature - 500-700°C, when coke is not formed. Therefore, there is no necessity for decrease in ability of the catalysts to CH_4 decomposition.

The catalyst with additive of NaZSM with high Si/Al ratio = 80 (sample 1) was found to be the least effective among the tested samples (Table 2). At T=600°C, the degree of methane conversion is only 21.9% over the sample 1, while for other catalysts XCH_4 is varied within 74.7-94.0% at the same conditions. Besides, the complete methane conversion is occurred at high temperature – 810°C and syngas formed has a lower ratio – 0.9. One of the reasons of lower activity of the catalyst may be a decrease in content of alumina over the catalyst with high both of content of zeolite and Si/Al ratio. Alumina is a good adsorbent for carbon dioxide with formation of carbonate species, which produce carbon oxide.

It needs to note that adsorbed CO_2 can play an additional role. It been considered that the abundance in adsorbed CO_2 is an unfavourable condition for the direct decomposition of CH_4 [23,24] and as a result, carbon deposition is suppressed during CO_2-reforming by the carbonate species produced [22,23]. In addition, the oxidation step of surface carbon with gaseous CO_2 or surface carbonates over the catalyst is also considered to eliminate surface carbon species effectively [22].

In [25], zeolite NaY is considered the most promising catalyst for producing synthesis gas and liquid hydrocarbons (C_{5+}) with high methane and carbon dioxide conversions (67 and 40% respectively). In this study, the NaY based catalyst (sample 6) shows the good characteristics but its performance does not exceed the original catalyst 5%$Co-M/Al_2O_3$, where the high ratio of H_2/CO and conversion of CO_2 is observed (Table 2).

It is known that the catalytic deactivation during the CO_2 reforming of methane is caused by carbon deposition and/or sintering of the metal particles [3, 11, 26-31]. Sintering accelerates the carbon deposition since large metal ensembles stimulate coke formation [21]. Among factors affected coke deposition, temperature probably is most significant. According to the TEM-studies no sintering of metal particles and no coke were observed over the catalysts treated at T < 800°C.

In order to determine the amount of coke deposited, after reaction all the catalysts were analyzed by TGA within temperature region from Tamb to 900°C. It has been observed that the weight loss of all the catalysts treated at T ≤ 800°C is not more than 3-4% and occurs at T ~ 100°C when water formed during the reaction evaporates. No weight loss has been observed for the catalysts without zeolite (sample 7) and containing 10% NaZSM (Si/Al-35) (sample 2) undergone the thermal treatment at higher temperature > 800°C.

Non-significant coke formation was observed over some samples with high content of zeolites (20 wt.%) treated at T >800°C. The catalysts work with the stable activity during all period of their exploitation (> 48 hours) at T < 800°C.

Conclusions

The results obtained show that that adding the 10% NaZSM or 10-20% HZSM zeolite with Si/Al=35 into the $Co-M/Al_2O_3$ improves its performance in dry reforming of CH_4. At comparatively low temperature – 700°C, the ZSM-zeolite (Si/Al=35) containing catalysts with high conversion – XCH_4=97.7-99.5 and XCO_2=87.5-92.1% selectively (SH_2/CO=100%) produce synthesis-gas with ratio of H_2/CO=0.9-1.0. Methane completely converted at 725^{o}C over the catalyst with a matrix promoted with 10% NaZSM that is substantially less than 800-900°C usually needed for meaningful methane conversion [12]. At lower temperature – 400-600°C small amount of acetic acid (up to 3%) and non-significant amount of other oxygenates are formed over the zeolite-containing catalysts. Because of the catalysts perform high activity at temperature < 800°C no coke formation is occurred. Obviously, that the low operating temperature is an advantage of these catalysts.

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