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Methane Decomposition over Iron-based Catalysts
in the Presence of O₂ and CO₂

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Methane decomposition was carried out using Fe/Al₂O₃ catalyst in the absence and presence of O₂ and CO₂. Even in the presence of O₂ and CO₂ (CH₄/O₂/CO₂ = 80/10/5 vol ratio), the deactivation of Fe/Al₂O₃ catalyst at temperatures below 1100 K was caused mainly by accumulation of carbon products as well as oxidation of non-oxide iron species (α -Fe and Fe₃C), as confirmed by X-ray diffraction, TG/DTA, and *in-situ* DRIFT-IR analyses. The stability of Fe/Al₂O₃ catalyst in the presence of O₂ and CO₂ was improved by the addition of some metals into the catalyst (M/Fe = 1/1 wt ratio). Methane conversion decreased monotonously from 95 to 79% after 6 h for Fe/Al₂O₃ catalyst. In contrast, the activity of Fe/Mg/Al₂O₃ catalyst at 973 K remained unchanged after 6 h (CH₄ conversion 95%). This effect could be associated with the formation of MgFe₂O₄. The effectiveness of other metal additives on the catalyst stability was Ce, Y > Eu, La > Pr, none > V > Nb.

KeywordsIron based catalyst, Methane decomposition, Hydrogen production, Magnesium additive,
Oxidizing gas effect, Catalyst stability**1. Introduction**

Decomposition of methane to form hydrogen and carbon is currently of great interest, since no CO_x is formed^{1)~7)}. The conventional catalysts used for methane decomposition are nickel-based systems, since these provide the highest activity. However, a large amount of carbon is formed on the used catalyst. Use of an iron-based catalyst for methane decomposition would allow disposal of the used catalyst containing carbon in the steel-making process.

Methane decomposition catalyzed by iron is usually carried out at high temperatures above 1200 K or at moderate temperatures of 850 to 1000 K⁸⁾. Presumably the active phase catalyzing the decomposition at above 1200 K is γ -Fe (austenite) supersaturated with carbon, whereas the active phase at lower temperatures is α -Fe⁹⁾.

The final goal is to develop an iron-based methane decomposition process occurring at temperatures below 1100 K. However, catalyst deactivation occurs rapidly in iron-based as well as nickel-based catalysts because of the formation of carbon by-products including filamentous carbon. Addition of a small amount

of CO or CO₂ improves catalyst stability in the conversion of methane into benzene and hydrogen catalyzed by Mo-H-ZSM-5¹⁰⁾. Therefore, *in-situ* partial removal of carbon product by O₂ and CO₂ might be also effective for iron-catalyzed decomposition, even though small amounts of CO_x would be formed. The characteristics of the iron-catalyzed decomposition of methane in the presence of O₂, CO₂, and H₂O are not well known^{11),12)}. The present study investigated the performance of Fe-based catalysts for methane decomposition in the absence and presence of O₂ and CO₂.

2. Experimental

Fe catalysts supported on Al₂O₃ were prepared by impregnation of iron nitrate into Al₂O₃, followed by drying at 373 K and calcination at 973 K for 3 h. Fe/M/Al₂O₃ catalysts were prepared by impregnation of iron and metal nitrates into Al₂O₃, followed by the same calcination procedure. These catalysts were tested using a fixed-bed reactor with an alumina tube (inner diameter 10 mm). The catalyst (1 g) was diluted with quartz sand (5 g) for methane decomposition. The catalysts were reduced with H₂ at 873 K for 3 h, then premixed CH₄/N₂ (95/5 vol%, W/F = 29.9 g-cat.h. mol⁻¹ at 873 K) or premixed CH₄/O₂/CO₂/N₂ (80/10/5/5 vol%) were introduced under atmospheric pressure.

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The gaseous products were analyzed by on-line gas chromatography (GC) equipped with a Porapack Q and MS 5A columns for the thermal conductivity detector (TCD) and another Porapack Q column for the hydrogen-flame ionization detector (FID). The fresh and used catalysts were analyzed by powder X-ray diffraction (XRD) and scanning electron micrograph (SEM). The carbonaceous material on the used catalysts was analyzed by thermal-gravimetric (TG)/differential-thermal analysis (DTA) methods in air in the temperature programmed mode at a rate of temperature increase equal to 10°C/min. TG/DTA used 10 mg of the catalyst.

In-situ infrared spectroscopy (IR) measurements of the catalyst surface were performed with a JEOL 680-type spectrometer, equipped with a diffuse reflectance infrared fourier transform (DRIFT) accessory with an evacuation system and a liquid nitrogen cooled mercury-cadmium-telluride (MCT) focal-plane array detector. After pre-reduction at 873 K with hydrogen using a conventional fixed-bed reactor, the sample was cooled to room temperature and transferred into the DRIFT accessory. The sample was pretreated at 573 K under a nitrogen flow and cooled to 373 K and the gaseous mixture of $\text{CH}_4/\text{CO}_2/\text{N}_2 = 92.5/5/2.5$ (vol%) was introduced to the DRIFT cell. DRIFT spectra were taken at the prescribed temperature.

3. Results and Discussion

3.1. Methane Decomposition in the Absence of O_2 and CO_2

Methane decomposition over 10 wt%Fe/ Al_2O_3 occurred at 750–1050 K and hydrogen and carbon were formed without C2–C3 hydrocarbons as shown in **Fig. 1A**. The product composition is shown in **Fig. 6**. Methane conversion over 10 wt%Fe/ Al_2O_3 was as high as 75% at 1023 K, but the catalytic activity was dependent on the support. The effectiveness of catalyst supports was in the order 10 wt%Fe/ Al_2O_3 > 10 wt%Fe/ZSM-5 > 10 wt%Fe/ SiO_2 . The methane conversion was also affected by the iron salts at an iron content of 10 wt%. The activity was in the order: $\text{Fe}(\text{NO}_3)_3$ > FeCl_3 > FeSO_4 (**Fig. 1B**). $\text{Ni}/\text{Al}_2\text{O}_3$ catalyst was a little more active for the decomposition reaction than Fe/ Al_2O_3 (**Fig. 1**)², but the activity fell at the end of the test.

Methane decomposition over Fe/ Al_2O_3 at 773 K decreased from 8.5 to 7.5% with the accumulation of carbonaceous deposits over 5 h (**Fig. 2**). Catalyst deactivation occurred much more rapidly for Fe/Ca/ Al_2O_3 and Fe/H-ZSM-5 catalysts than for Fe/ Al_2O_3 (**Fig. 2**).

3.2. Methane Decomposition in the Presence of Oxidizing Agents

Fresh Fe/ Al_2O_3 catalyst exhibits the XRD character-

Reaction conditions: $W/F = 29.9$ g-cat.h.mol⁻¹, $\text{CH}_4/\text{N}_2 = 95/5$. Inset: Effect of iron precursor on the reaction.

Fig. 1 Temperature Dependence of CH₄ Decomposition

Reaction conditions: $W/F = 29.9$ g-cat.h.mol⁻¹, $\text{CH}_4/\text{N}_2 = 95/5$.

Fig. 2 Time Course of CH₄ Decomposition

istics of Fe_2O_3 , as shown in **Fig. 3A**. After methane decomposition at 873 K, both α -Fe and Fe_3C were detected, as shown in **Fig. 3B**. Methane conversion over Fe/ Al_2O_3 catalyst at 873 K decreased from 24 to 10% after 5 h, as shown in **Fig. 4**. In the presence of CO_2 ($\text{CH}_4/\text{CO}_2/\text{N}_2 = 92.5/5/2.5$ vol%), the methane conversion was slightly higher than that without CO_2 because of the removal of deposited carbon, but the activity was still decreased as shown in **Fig. 4**. In the

A: Fresh catalyst. B: After decomposition of CH₄ at 873 K. C: After reaction with CH₄/H₂O at 873 K. D: After reaction with CH₄/CO₂/O₂ at 1073 K.

Fig. 3 Powder X-Ray Diffraction Patterns of Fe/Al₂O₃

Reaction conditions: $W/F = 29.9 \text{ g-cat.h.mol}^{-1}$ at 873 K.
□: CH₄/N₂ = 95/5 vol; ○: CH₄/CO₂/N₂ = 92.5/5/2.5 vol; ◇: CH₄/H₂O/N₂ = 92.5/2.5/5.0 vol.

Fig. 4 Effect of CO₂ and H₂O on the Activity of CH₄ Decomposition at 873 K

presence of H₂O (CH₄/H₂O/N₂ = 92.5/2.5/5.0), the activity remarkably decreased due to the formation of Fe₃O₄, as shown by XRD (Fig. 3C), which is consistent with the findings for Ni-based catalyst³⁾. Therefore, in the presence of oxidizing agents such as CO₂, H₂O and O₂ at 873 K, the oxidation of non-oxide iron species such as α-Fe and Fe₃C to form Fe₃O₄ occur predominantly over the reverse change of Fe₃O₄ into α-Fe and Fe₃C.

Methane conversion was then investigated at higher temperature (1073 K) in the presence of O₂ and CO₂. Methane decomposition over Fe/Al₂O₃ at 1073 K in the presence of O₂ and CO₂ was found 95%, in sharp contrast to the low conversions at 873 K, although the methane conversion decreased monotonously from 95

Reaction conditions: $W/F = 41.9 \text{ g-cat.h.mol}^{-1}$ at 1073 K, and CH₄/O₂/CO₂/N₂ = 80/10/5/5 vol.

▽: Fe/Mg/Al₂O₃; ■: Fe/Al₂O₃; ○: FeLi/Al₂O₃; ◇: FeCa/Al₂O₃; △: FeNa/Al₂O₃.

Fig. 5 Effects of Metal Additives in Fe/Al₂O₃ Catalysts on Catalyst Stability during CH₄ Decomposition in the Presence of O₂/CO₂

to 79% after 6 h, as shown in Fig. 5. XRD of used catalyst after 6-h reaction exhibited the characteristics of α-Fe and Fe₃C, as shown in Fig. 3D. Thus, both α-Fe and Fe₃C were probably associated with the catalyst species active for methane decomposition over iron-based catalyst in the absence and presence of O₂ and CO₂, good accord with the previous results⁴⁾.

3.3. Effect of Additives on Fe/Al₂O₃ Catalyst

In order to improve catalyst stability under O₂ and CO₂ conditions, removal of O₂ and CO₂ from catalyst surface will be required through methane and carbon combustion, to inhibit re-oxidation of active species (Eqs. (2), (2)' and (3), (3'))^{*1)}.

Methane combustion catalyzed by sulfated zirconia¹³⁾ is accelerated by additives such as alkali and alkaline-earth metals, and rare-earth metals are also effective, since mixed oxides formed from zirconia and additives promote combustion¹⁴⁾. Therefore, these additives were also examined for iron-based catalysts as summarized in Table 1.

The performance of the manganese-modified catalyst was almost the same as that of Fe/Al₂O₃ catalyst. Addition of tungsten and chromium resulted in dramatic drops in stability and Fe/SiO₂ catalysts were not effective. Rare earth and group VIII metals were added to the Fe/Al system. These additives increased catalyst stability in the order Ce, Y > Eu, La > Pr,

*1) There are two possible reasons for the deactivation of iron catalysts: Reoxidation of active species into Fe₂O₃ by O₂ and CO₂ (Eq. (1)); and carbon accumulation.

Table 1 Methane Conversion over Metal-modified Fe/Al₂O₃ at 1073 K^{a)}

Run No.	Catalysts	CH ₄ conversion [%]		Analyses of used catalysts		
		After 30 min	After 6 h	XRD ^{b)}	TG/DTA ^{c)}	
					DTA peak [K] ^{d)}	C mol/Fe mol ^{e)}
1	Fe/Al ₂ O ₃	94.9	79.0	α -Fe/Fe ₃ C	840.2	26.0
2	Fe/Mn/Al ₂ O ₃	94.9	84.2	α -Fe/Fe ₃ C	840.6	24.6
3	Fe/Cr/Al ₂ O ₃	69.9	18.0	Fe ₃ O ₄	901.8	6.7
4	Fe/Mn/W/Al ₂ O ₃	93.2	24.6	Fe ₃ O ₄	—	—
5	Fe/Cr/W/Al ₂ O ₃	98.7	18.8	Fe ₃ O ₄	—	—
6	Fe/SiO ₂	3.85	0.93	X-ray amorphous	—	—
7	Fe/Mn/SiO ₂	15.3	8.48	Fe ₂ O ₃ /Fe ₃ O ₄	—	—
8	Fe/V/Al ₂ O ₃	81.6	23.7	Fe ₂ VO ₄	796.6	1.2
9	Fe/Y/Al ₂ O ₃	92.4	92.9	α -Fe/Fe ₃ C	838.5	31.8
10	Fe/La/Al ₂ O ₃	92.7	85.4	α -Fe/Fe ₃ C	848.2	38.2
11	Fe/Ce/Al ₂ O ₃	95.2	94.8	α -Fe/Fe ₃ C	856.8	26.2
12	Fe/Nb/Al ₂ O ₃	3.42	0.43	Fe ₃ O ₄	—	—
13	Fe/Pr/Al ₂ O ₃	95.5	83.5	α -Fe/Fe ₃ C	864.8	15.9
14	Fe/Eu/Al ₂ O ₃	94.8	89.5	α -Fe/Fe ₃ C	853.2	24.0
15	Fe/Ca/Al ₂ O ₃	92.8	14.7	Fe ₃ O ₄	—	1.2
16	Fe/Li/Al ₂ O ₃	92.3	14.7	α -Fe/Fe ₂ O ₃	—	—
17	Fe/Na/Al ₂ O ₃	77.3	4.88	Fe ₃ O ₄	—	—
18	Fe/Mg/Al ₂ O ₃	95.4	95.3	α -Fe/Fe ₃ C	846.6	32.4
19	Ni/Al ₂ O ₃	88.2	83.7	α -Ni	912.0	5.2

a) Reaction conditions: CH₄/CO₂/O₂/N₂ for 6 h at 1073 K. b) All fresh catalysts exhibited XRD absorptions characteristic of hematite (Fe₂O₃). c) TG/DTA analyses were carried out at 300–1073 K under air flow. d) If the used catalyst have two DTA peaks, as shown in Fig. 10, the temperature of the sharp peak associated with Fe₃C is shown in this table. e) The amount of estimated carbon is the sum of Fe₃C and deposited carbon.

none > V > Nb. The effects of alkali or alkali-earth metals on the stability of Fe/Al₂O₃ catalysts are shown in Table 1 and Fig. 5. Mg-modified Fe/Al₂O₃ catalyst improved the stability and the activity of Fe/Mg/Al₂O₃ catalyst for CH₄ decomposition remained unchanged after 6 h. None of the other additives were effective (Fig. 5). Thus, Mg, Y and Ce were effective as additives under the conditions of CH₄/CO₂/O₂.

Carbon-based product compositions^{*2)} are shown in Fig. 6, for carbon and CO_x at 1073 K. Carbon product composition on the Fe/Al₂O₃ catalyst was slightly decreased, whereas CO increased as the reaction proceeded (Fig. 6A). In contrast, carbon-based product compositions on Fe/Mg/Al₂O₃ catalyst remained constant after 380 min, as shown in Fig. 6B. The hydrogen yields over these two catalysts as shown in Fig. 6C were in good accordance with those of Fig. 5 and Fig. 6A, B. The hydrogen yield in the presence of O₂ and CO₂, at the initial reaction stage, was found to be 35% lower than that in the absence of O₂ and CO₂, as seen in Fig. 6A, B and C. However, the activity dropped rapidly without oxidants, whereas the activity remained constant with oxidants even after 380 min using Fe/Mg/Al₂O₃ catalyst. Therefore, addition of O₂ and CO₂ is effective to promote methane decomposi-

tion to form hydrogen.

3. 4. Characterization of Used Catalysts

Figure 7 shows typical XRD patterns for modified-Fe/Al₂O₃ and Fe/Al₂O₃ catalysts used for 6 h at 1073 K in the CH₄/O₂/CO₂ reaction. The XRD data of the Fe/Mg/Al₂O₃ catalyst shows the weak absorptions characteristic of magnesium species such as MgFe₂O₄ and MgO together with α -Fe and Fe₃C absorptions. These magnesium species are possibly important in methane and carbon combustion by oxidants, as mentioned in section 3. 3. The XRD data of the Fe/Al₂O₃ catalyst also showed absorptions of α -Fe and Fe₃C. The mean sizes of these particles, calculated based on the semi-widths of diffraction peaks (110) for α -Fe and (104) for Fe₃C, were estimated as 15.9 nm and 5.44 nm, respectively. In contrast, Fe₂O₃ and Fe₃O₄ were formed for Fe/Na/Al₂O₃, Fe/Ca/Al₂O₃ and Fe/Li/Al₂O₃ catalysts, and α -Fe and Fe₃C were not detected (Fig. 7). Thus, the formation of α -Fe and Fe₃C species may be important in the decomposition of methane under CH₄/O₂/CO₂ conditions. These results are consistent with previous findings¹⁵⁾.

Figure 8(A) shows the SEM image of carbon filaments formed on Fe/Al₂O₃ under CH₄/CO₂/O₂ conditions. The continuous thick filaments with a diameter of about 100 nm, are bent and often twisted along their axis. The filaments formed under only CH₄ conditions are also bent, but not twisted (Fig. 8(B)) and have a slightly smaller diameter of about 60 nm.

*2) [Carbon] = ([CH₄] + [CO₂])_{initial} - ([CH₄] + [CO₂] + [CO] + 2 × [C₂])_{detected}
[Carbon] composition = [Carbon]/([Carbon] + [CO] + [CO₂] + [C₂]) × 100

Reaction conditions as in Fig. 5.

A: Fe/Al₂O₃. B: Fe/Mg/Al₂O₃. C: Hydrogen yield (mol.h⁻¹).
Inset: Hydrogen yield in the absence of O₂ and CO₂.

Fig. 6 Product Composition in the CH₄ Decomposition in the Presence of O₂ and CO₂

The used catalysts were prepared by CH₄ decomposition in the presence of O₂ and CO₂ at 1073 K for 6 h.

Fig. 7 Powder X-Ray Diffraction Patterns of Used Fe/Al₂O₃ and Modified Fe/Al₂O₃ Catalysts

Fig. 8 Scanning Electron Micrographs of Used Catalysts Prepared by CH₄ Decomposition in the Presence (A) and Absence (B) of O₂ and CO₂

The used catalysts were prepared by CH₄ decomposition in the presence of O₂ and CO₂ at 1073 K for 6 h.

Fig. 9 Differential Thermal Analyses for Oxidation of Used Catalysts by Air

TG/DTA analyses were carried out with used catalysts in air to examine the nature of the carbon filaments. These filaments probably consisted of carbonaceous and iron materials. So, by oxidation, the following two reactions could occur.

The C/Fe molar ratios, which were obtained from the overall weight loss by TG analyses up to 1073 K, were 26.0 for Fe/Al₂O₃ and 32.4 for Fe/Mg/Al₂O₃ (Table 1). There were two peaks in the DTA data for these catalysts (Fig. 9); a sharp peak and a broad shoulder, which are consistent with the presence of Fe₃C and carbon deposit^{*3)}. In fact, the used Fe/Cr/Al₂O₃ catalyst, which rapidly deactivated after 6 h, showed a broad

*3) TG weight loss for the sharp DTA peak of Fe/Al₂O₃ was estimated as 14.2%, in good accordance with 15.3% for Fe/Mg/Al₂O₃ catalyst. In contrast, the weight loss for the broad DTA peak of Fe/Al₂O₃ was 22%, higher than 17% for Fe/Mg/Al₂O₃ due to the difference in the carbon deposits between the two catalysts. These TG data are consistent with the peak identification based on DTA.

Catalyst: (A) Fe/Al₂O₃, (B) Fe/Mg/Al₂O₃, (C) Fe/Cr/Al₂O₃.
 Conditions: CH₄/CO₂/N₂ (92.5/5/2.5 vol) at 673 K.
 Catalyst pretreatment: Reduction of fresh catalyst with H₂ at 873 K for 3 h.

Fig. 10 In-situ DRIFT-IR Spectra of Iron-based Catalysts

peak only, indicating the absence of Fe₃C species. Also, the broad shoulder peak for Fe/Mg/Al₂O₃ catalyst was much smaller than that for Fe/Al₂O₃ catalyst, which may be consistent with the difference in catalyst stability between these two catalysts (see Fig. 5). TG/DTA analyses for typical catalysts are summarized in Table 1. The sharp DTA peaks of these catalysts with moderate stability appeared at 840-860 K.

3.5. In-situ IR (DRIFT) Measurements

DRIFT spectra measured in CH₄/CO₂/N₂ gas flow at 673 K are shown in Fig. 10. When the mixed gas was introduced, the spectra displayed C-O stretching (3) at 1583 cm⁻¹ and carbonate (4) at 1358 cm⁻¹, in addition to gaseous species such as CH₄ (3015 cm⁻¹ (1) and 1299 cm⁻¹ (5)), CO₂ (2363 cm⁻¹ (2)) and CO (2149 cm⁻¹ (6)).¹⁶⁾ The intensities of these adsorbed species (3 and 4) for Fe/Cr/Al₂O₃ were much stronger than those for Fe/Mg/Al₂O₃ and Fe/Al₂O₃. When a large amount of adsorbed CO and carbonate species were present over the catalyst surface, oxidation of α -Fe and Fe₃C species into iron oxides was possibly accelerated, whereas the reduction of iron oxides into α -Fe and Fe₃C species was inhibited, as seen in the footnote to section 3.3. (Eq. (4)). Therefore, rapid deactivation in Fe/Cr/Al₂O₃ could occur. These findings are con-

sistent with the view that α -Fe and Fe₃C species are important in CH₄ decomposition in the presence of O₂ and CO₂.

4. Conclusion

Methane decomposition was carried out over Fe/Al₂O₃ catalyst in the absence and presence of O₂ and CO₂. Even in the presence of O₂ and CO₂ (CH₄/O₂/CO₂ = 80/10/5 vol), the deactivation of Fe/Al₂O₃ catalyst at temperatures below 1100 K was caused mainly by the accumulation of carbon products as well as the oxidation of non-oxide iron species (α -Fe and Fe₃C), as confirmed by XRD, TG/DTA, and *in-situ* DRIFT-IR analyses.

The stability of the Fe/Al₂O₃ catalyst in the presence of O₂ and CO₂ was improved by the addition of some metals to the catalyst, in particular Mg was the most effective. The activity of Fe/Mg/Al₂O₃ catalyst for CH₄ decomposition at 973 K remained unchanged after 6 h (CH₄ conversion 95%), whereas the CH₄ conversion over Fe/Al₂O₃ catalyst decreased monotonously from 95 to 79%. This Mg effect could be attributed to the formation of MgFe₂O₄ which may promote carbon and methane combustion with O₂ and CO₂. The effectiveness of other metal additives on catalyst stability was Ce, Y > Eu, La > Pr, none > V > Nb.

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要 旨

O₂ および CO₂ の存在下における鉄系触媒上でのメタン分解

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O₂/CO₂ の共存下または不在下で鉄／アルミナ系触媒を用いてメタン分解を検討した。O₂/CO₂ の共存下 (CH₄/O₂/CO₂ = 80/10/5 体積比) でも, 1100 K 以下の温和な温度で, 鉄／アルミナ系触媒の活性低下が観察された。これは, 炭素蓄積と鉄の非酸化物種 (α -Fe, Fe₃C) の酸化によるものと推定した。なお, これらの鉄種の存在は, 粉末 X 線, TG/DTA および *in-situ* DRIFT-IR などにより確認した。O₂/CO₂ の共存下のメタン分解における鉄／アルミナ系触媒の安定性は, 他の金属の添加 (金

属／鉄 = 1/1 重量比) により改善した。すなわち, 鉄／アルミナ系触媒では, 6 時間の反応でメタン転化率は 95% から 79% に低下したのに対して, Mg 添加により効果は最も大きく, 鉄／Mg／アルミナ系触媒の 973 K におけるメタン転化率 (約 95%) は 6 時間後でも一定であった。Mg の添加効果は MgFe₂O₄ の生成と関連があることを推定した。Mg 以外の添加物効果は, Ce, Y > Eu, La > Pr, none > V > Nb という序列であった。

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