Studies on Manufacture of Synthesis Gas from Natural Gas by Use of Metallic Oxides*

I. Fixed Bed

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Summary: Investigations on the manufacture of synthesis gas by direct partial oxidation of methane with metallic oxides in a fixed bed were made. From the equilibrium consideration and the experimental results, it was known that iron oxide-alumina was the most adequate oxygen carrier and the addition of alumina to iron oxide had effects on the promotion of reactivity. The oxygen carrier capable of producing carbon monoxide and hydrogen was of two stages of reduction, namely $\text{FeO}_{1.33} \sim \text{FeO}$ and $\text{FeO} \sim \text{FeO}_{0.8}$. The rate of reaction was larger in the latter stage than in the former; the selectivity of carbon monoxide formation in the former attained to the equilibrium value in $\text{CO} + \text{FeO} \rightleftharpoons \text{CO}_2 + \text{Fe}$, while in the latter it was over the equilibrium value. In general, the degree of reduction of iron oxide was not uniform throughout the bed; the degree of reduction of the oxide at the inlet was larger than that at the outlet. Moreover, carbon monoxide and hydrogen formed at the inlet side of the bed might be further oxidized at the succeeding parts. Discussions are given on the conditions under which gases rich in carbon monoxide and hydrogen is obtainable.

Introduction

The following process is introduced for manufacturing synthesis gas from natural gas by oxidation, which is quite different from the conventional methods: that is, natural gas is oxidized with a suitable metallic oxide to carbon monoxide and hydrogen; and then, the reduced metallic oxide is reoxidized with air for use again. This process is shown by the following equation, in which the metallic oxide is indicated by MO_x :

After all, synthesis gas are manufactured from natural gas and air in this process. It is a process of exothermic as well as partial oxidation of natural gas, and its heat economy is better than the reforming of natural gas. Further, costly oxygen can be replaced by air in this process, and nitrogen in air is not mixed

with gases for synthesis, which shall be used for synthesis of methanol.

There has been but a little information of partial oxidation of natural gas with metallic oxides in the literature published so far. In 1938, Ogawa *et al.*¹⁾ reported that methane was partially oxidized with iron oxide and nickel catalyst at temperatures above 1220°C. In 1949, Lewis *et al.*²⁾ reported that methane was partially oxidized to carbon monoxide and hydrogen with a fine powder of silica carrying small quantity of cupric oxide in fluidized bed at about 900°C. Regeneration of the powder was not reported. However, m.p. of reduced copper is considerably low, and it is doubtful whether good fluidization will be maintained without agglomeration or not, when copper is used in cycle operation for reaction and regeneration for a long time at high temperatures as high as 900°C. On patents, TiO_2 and $\text{Cr}_2\text{O}_3 + \text{MgO}$ ³⁾ in 1929 and zinc oxide ore⁴⁾ in 1933 were claimed. After 1952, methods of using iron oxide, manganese dioxide, chromic oxide, etc. in fluidized bed⁵⁾ have been proposed. However, it has never been reported that this

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process was successful in industrial plant.

As mentioned above, information on the partial oxidation of natural gas with metallic oxides has been very imperfect. The authors made fundamental studies by investigating metallic oxides suitable to partial oxidation of methane, partial oxidation reaction of methane with iron oxide, its regeneration by oxidation, etc. in a fixed bed, and have obtained some new knowledges. Moreover, at present a continuous test plant of laboratory scale on fluidized bed is also being operated, and various data are summed up in order to compare with the hitherto methods. In this paper, results will be reported only on metallic oxides suitable to oxygen carrier and partial oxidation reaction of methane with oxygen carrier in fixed bed.

Metallic Oxides suitable to Oxygen Carrier

In partial oxidation of methane with oxygen, the ratio of oxygen to methane is adjusted to the stoichiometric ratio shown by following equation.

This reaction proceeds in two steps; primarily, the complete combustion of methane proceeds as follows:

Secondarily, reforming reaction of residual methane with carbon dioxide and water proceeds as follows:

In this process, methane is partially oxidized with oxygen in the metallic oxide instead of gaseous oxygen.

However, the ratio of oxygen in the metallic oxide to methane in surroundings is far more than the stoichiometric ratio in Eq. (1). Therefore, undesirable complete combustion of carbon monoxide and hydrogen to carbon dioxide and water may proceed under this condition.

Partial oxidation of methane with metallic oxide (Eq. 3) is the combination of the following equation (dissociation reaction of metallic oxide) and Eq. (1).

Complete combustion of methane with metallic oxide Eq. (4) is the combination of Eq. (5) and Eq. (2). Then, the following relations may be introduced.

$$K_3 = K^{1/2}_5 \cdot K_1 \quad K_4 = K^2_5 \cdot K_2 \quad (6)$$

$$K_3/K_4 = (1/K_5)^{3/2} \cdot (K_1/K_2) \quad (7)$$

where $K_1 \sim K_5$: equilibrium constants

Equilibrium constant (K_5) of the dissociation reaction of metallic oxide Eq. (5) is indicated as follows by Nernst's formula.

$$\log_{10} K_5 = -(W/4.58T) + 1.75 \log_{10} T + 2.8 \quad (8)$$

where W : heat of dissociation when 1 mole oxygen is dissociated from metallic oxide.

As K_1 and K_2 are equilibrium constants of the reactions (1) and (2) to which metallic oxides are not related, the following decision shall be brought from Eqs. (6), (7), and (8). When stable metallic oxides with large heat of dissociation are used, partial oxidation of methane is relatively superior to its complete combustion, but equilibrium constant of partial oxidation itself is smaller. While, when unstable metallic oxides with small heat of dissociation are used, equilibrium constant of partial oxidation of methane is larger, but its reaction is relatively inferior to complete combustion. Therefore, it should not be adequate to use stable metallic oxides with too large heat of dissociation or unstable oxides with too small heat of dissociation as oxygen carrier.

Assuming that reaction temperature of partial oxidation of methane with metallic oxide be $600 \sim 1,000^\circ\text{C}$, the value of W calculated to maintain $K_3 > 1$ and $K_3/K_4 > 1$ is $128 \sim 183$ kcal. Therefore, metallic oxides with W more than 200 kcal (A in Table 1) or less than 100 kcal (B in Table 1) are not suitable and to be

Table 1. Heat of Dissociation of Metallic Oxides

	W (kcal)	Metallic Oxide							
		MgO	BaO	SrO	Al ₂ O ₃	TiO ₂	Na ₂ O	etc.	
A	>200								
B	<100	Bi ₂ O ₃	Sb ₂ O ₃	Cu ₂ O	CuO	PbO ₂	Ag ₂ O	etc.	
C		B ₂ O ₃	V ₂ O ₅	ZnO	MoO ₂	SnO	CdO		
		WO ₂	Sb ₂ O ₃	As ₂ O ₃	PbO	etc.			
	104	6Fe ₂ O ₃	—→		4Fe ₃ O ₄	+ O ₂			
	110	2Mn ₃ O ₄	—→		6MnO	+ O ₂			
	115	2CoO	—→		2Co	+ O ₂			
D	117	2NiO	—→		2Ni	+ O ₂			
	129	2FeO	—→		2Fe	+ O ₂			
	146	2Fe ₃ O ₄	—→		6FeO	+ O ₂			
	193	2/3Cr ₂ O ₃	—→		4/3Cr	+ O ₂			
	193	2MnO	—→		2Mn	+ O ₂			

rejected. Moreover, metallic oxides which decompose, melt, or evaporate in such a region of reaction temperature and too costly oxides (*C* in Table 1) are also unsuitable from industrial standpoint and to be rejected.

As mentioned above, considering equilibrium and physical properties, metallic oxides possibly be used for oxygen carrier in this process are only confined to those in *D* in Table 1.

Experiment

Apparatus and Procedure: Apparatus used in the experiment is shown in Fig. 1. As the

Fig. 1 Apparatus

- 1) Dryer (CaCl_2)
- 2) Pt-Pt-Rh thermocouple
- 3) Reaction tube
- 4) Metallic oxide
- 5) Electric oven for heating
- 6) Cooler
- 7) Water separator
- 8) Sampling cock for analysis
- 9) Gas holder

reaction temperature was so high that the reaction tube was made of opaque quartz with inner dia. of 22mm., and was heated electrically. The metallic oxide was placed in the part of uniform temperature. The temperature was measured by Pt—Pt-Rh thermocouple whose junction was placed at the centre of the packing. Air was passed through the reaction tube to attain to the reaction temperature and then after the air in the apparatus was completely replaced with nitrogen. Raw methane, being regulated with needle-valve at constant flow rate, was introduced into the top of the reaction tube through flowmeter and dryer. Water vapour in the generated gas was condensed and separated away by cooler and water separator, and the gas was led to a gas-holder. Sample gas for analysis was sampled at sampling cock for almost a definite volume at any times, and it was subjected to ordinary absorption analysis.

Materials: Methane used was natural gas packed in a cylinder. Impurities contained were small amounts of oxygen and nitrogen. ($\text{CH}_4=96.0\sim97.5\%$, $\text{O}_2=0.3\sim0.6\%$, $\text{N}_2=2.2\sim3.4\%$). Nitrogen used was of high purity packed in a cylinder, and hydrogen was also packed in a cylinder ($\text{H}_2=99.8\sim99.9\%$).

Iron Oxide-Alumina—Dil. aq. ammonia was added to the mixed aq. solution of calculated quantity of ferrous nitrate and aluminum nitrate, and the both hydroxides were coprecipitated. After thoroughly washed with water, the precipitate was molded and calcined at 900°C for 30 min. in air (Coprecipitation Method).

Cupric Oxide-Alumina—After cupric hydroxide and aluminum hydroxide were mixed in wet state, being molded as above and calcined at 900°C for 30 min. in air (Wet Mixing Method).

Iron Oxide-Alumina-Chromic Oxide—Iron oxide-alumina (wt. ratio 7 : 3) obtained by

Table 2. Samples of Metallic Oxides

Metallic Oxide	Wt. ratio	Preparation
Iron oxide-alumina	7:3	Co-precipitation
" "	98:2	"
Iron oxide		Precipitation
Cupric oxide-alumina	7:3	Wet Mixing
Manganese dioxide-alumina	7:3	"
Nickel oxide-alumina	7:3	"
Chromic oxide-alumina	7:3	"
Cobalt oxide-alumina	7:3	"
Iron oxide-alumina-alkali	Addition of 2%	Impregnation
" " " -manganese dioxide	" 10%	Wet Mixing
" " " -chromic oxide	" 40%	Impregnation

co-precipitation method was impregnated with chromium nitrate solution (Impregnation Method).

Other samples are shown in Table 2, and all these samples were calcined at 900°C for 30 min. in air.

Oxidation of Methane with various Kinds of Metallic Oxides

Among metallic oxides shown in *D* in Table 1, Ni and Fe are methane reforming catalysts. And Cu has also the same behavior. Therefore, the following six kinds of metallic oxides were used for experiment.

Fig. 2 Oxidation of Methane with Manganese Dioxide-Alumina, Chromic Oxide-Alumina, and Cupric Oxide-Alumina.

800°C, SV=200

-Δ- CH₄ conversion, -○- CO selectivity

- (1) Manganese dioxide-alumina (7:3)
- (2) Chromic oxide-alumina (7:3)
- (3) Cupric oxide-alumina (7:3)

Assuming conversion of methane: $(\text{CO}_2 + \text{CO})/(\text{CO}_2 + \text{CO} + \text{CH}_4)$ and selectivity of carbon monoxide: $\text{CO}/(\text{CO} + \text{CO}_2)$, in Fig. 2 are shown variations of methane conversion and carbon monoxide selectivity with time, in the runs with manganese dioxide-alumina, chromic oxide-alumina and cupric oxide-alumina were used. When manganese dioxide-alumina was used, conversion was large at the beginning, and most of the gas was carbon dioxide, which showed the complete combustion of methane. After nearly 10 min. selectivity was increased to about 80%, but conversion was decreased to about 10%, which gave practically no good

result. Almost the same result as that of the former was obtained with chromic oxide-alumina and also with cupric oxide-alumina, and no depositing of carbon was seen in any experiments.

The results using nickel oxide-alumina and cobalt oxide-alumina are shown in Fig. 3. In

Fig. 3 Oxidation of Methane with Nickel Oxide-Alumina and Cobalt Oxide-Alumina.

800°C, SV=200

-Δ- CH₄ conversion, -○- CO selectivity
-●- fraction of carbon deposition

- (1) Nickel oxide-alumina (7:3)
- (2) Cobalt oxide-alumina (7:3)

this Figure, the fraction of carbon depositing was determined by $(\text{H}_2 - 2(\text{CO}_2 + \text{CO}))/\text{H}_2$. When nickel oxide-alumina was used, methane was subjected to complete combustion in the initial period and then remarkable deposition of carbon with producing almost 10% of carbon monoxide. Almost the same result as the former was obtained by cobalt oxide-alumina, but the combustion of methane was slightly less complete than the former, and a smaller quantity of carbon monoxide was produced.

Changes in the composition of generated gases with time in the run with iron oxide-alumina are shown in Fig. 4 and changes of methane conversion and carbon monoxide selectivity with time are shown in Fig. 5.

This oxide is different from any others mentioned above; complete combustion of methane happened as before at first, and then carbon monoxide and hydrogen were generated for a considerable period. Calculating the oxygen transferred from iron oxide to the generated gas, it is seen that the oxide has the average

Fig. 4 Oxidation of Methane with $\text{Fe}_2\text{O}_3\text{--Al}_2\text{O}_3$ (7:3), 800°C, SV=200

compositions of $\text{FeO}_{1.33}(\text{Fe}_3\text{O}_4)$ at about 5~6 min. and FeO at nearly 25~27 min. Therefore, in the reduction beyond FeO both of methane conversion and carbon monoxide selectivity were increased, and carbon deposition started after nearly 40 min. It is desirable that metallic oxides suitable in this process have the following characteristics: both of methane conversion and carbon monoxide selectivity are large, and no depositing of carbon occurs. As the result of the above experiments, it is known that iron oxide-alumina is the most suitable for oxygen carrier than any other oxides.

A comparison between the results mentioned above and the values of dissociation heats in (D) of Table 1 shows the following relations. (1) Complete combustion happened at the steps in which dissociation heat was considerably small as $\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4$, $\text{Mn}_3\text{O}_4 \rightarrow \text{MnO}$, $\text{CoO} \rightarrow \text{Co}$, $\text{NiO} \rightarrow \text{Ni}$. (2) High selectivity and low conversion were obtained at the steps in which dissociation heat was considerably large as $\text{Cr}_2\text{O}_3 \rightarrow \text{Cr}$, $\text{MnO} \rightarrow \text{Mn}$. (3) At the steps in which dissociation heat was in the middle degree as $\text{FeO} \rightarrow \text{Fe}$, $\text{Fe}_3\text{O}_4 \rightarrow \text{FeO}$, both values of conversion and selectivity were in the middle of the former two.

By Ogawa *et al.*¹¹, methane was appreciably oxidized with pure iron oxide under the condition of 900°C and SV=10. However, better results were obtained in the case of iron oxide-alumina at lower temperature than the former and it will be discussed later in this report.

Fig. 5 Oxidation of Methane with $\text{Fe}_2\text{O}_3\text{--Al}_2\text{O}_3$ (7:3) 800°C, SV=200

— Δ — CH_4 conversion, — $\circ$ — CO selectivity
— $\bullet$ — fraction of carbon deposition

It was supposed that, it was caused by the difference in reduction grade of iron oxide that composition of generated gases showed remarkable change with time in the reaction between methane and iron oxide-alumina. In order to confirm the supposition, the partially reduced oxides of $\text{FeO}_{1.29}$, $\text{FeO}_{0.89}$, and $\text{FeO}_{0.68}$ in average composition, all of which had been previously produced by reduction with hydrogen, were examined; the results are shown in Fig. 6. When these results were compared with Fig. 4 in which $\text{Fe}_2\text{O}_3\text{--Al}_2\text{O}_3$ was used, it was known that the composition of generated gases was determined by the reduction grade of iron oxide, independent of the kinds of reducing gases. When $\text{Fe}_2\text{O}_3\text{--Al}_2\text{O}_3$ was used, the carbon deposition started at the time of maximum carbon monoxide content in generated gases. The average composition of iron oxide at this time was nearly $\text{FeO}_{0.8}$ calculated by the results in Fig. 6. Therefore, it is at the reduction grade of iron oxide of $\text{FeO}_{1.33} \sim \text{FeO}_{0.8}$ in average composition that desirable gases of low residual methane and rich in carbon monoxide without depositing of carbon are produced from methane.

As mentioned above, methane was easily oxidized to carbon monoxide and hydrogen with iron oxide-alumina (30% alumina was added) at much lower temperature than that of Ogawa *et al.* in which pure iron oxide was used. This would be caused by the addition of alumina to pure iron oxide. And then the

Fig. 6. Oxidation of Methane with $\text{FeO}-\text{Al}_2\text{O}_3$, $\text{FeO}_{0.99}-\text{Al}_2\text{O}_3$ and $\text{FeO}_{0.69}-\text{Al}_2\text{O}_3$. 800°C , $\text{SV}=200$

additional results of experiments to confirm this respect are as follows. The results using pure iron oxide and iron oxide-alumina with 2% of alumina are shown in Fig. 7.

Fig. 7 Oxidation of Methane with Iron Oxide and Iron Oxide-Alumina (98:2) 800°C , $\text{SV}=200$
 Δ — CH_4 conversion, $\circ$ — CO selectivity
 $\bullet$ — fraction of carbon deposition
 (1) Iron oxide
 (2) Iron oxide-alumina (98:2)

In the both cases, complete combustion of methane happened at the beginning of reaction, and soon after methane conversion was rapidly decreased. And then generation of traces of carbon monoxide and hydrogen continued for a long time. When pure iron oxide was used, the stage of low methane conversion continued for more than 3 hr., and then methane conversion was gradually increased. Comparing Fig. 7 with Fig. 5, the content of carbon monoxide was fairly increased just before the carbon deposition in the case of pure iron oxide as well as in that of iron oxide-alumina

(7:3). However, both methane conversion and CO content in the former were inferior to those in the latter, and carbon monoxide selectivity in both cases was nearly equal to each other. Moreover, when only 2% of alumina was added, the time until content of carbon monoxide in generated gas became maximum was slightly but clearly shortened, and when 30% was added, it was very much shortened. It was also observed that by the addition of 2% of alumina both methane conversion and CO content just before the carbon deposition increased more than those in pure iron oxide.

As mentioned above, it was confirmed that reactivity at the stage of $\text{FeO}_{1.33}\sim\text{FeO}$ was remarkably increased and reactivity after the stage of FeO was also somewhat increased by the addition of alumina.

From the same viewpoint, the effects of the addition of various kinds of metallic oxides to iron oxide-alumina (7:3) was examined. The results of the addition of alkali (K_2O), chromic oxide, and manganese dioxide are shown in Fig. 8. When these results were compared with Fig. 5, following effects were observed.

Fig. 8 Effects of Addition of Alkali, Chromic Oxide and Manganese Dioxide. 800°C
 Δ — CH_4 conversion, $\circ$ — CO selectivity
 $\bullet$ — fraction of carbon deposition
 (1) Alkali (2% addition) $\text{SV}=200$
 (2) Chromic oxide (10% addition) $\text{SV}=200$
 (3) Manganese dioxide (40% addition) $\text{SV}=100$

The addition of only 2% of alkali decreased considerably methane conversion throughout the whole stage. Either methane conversion or CO content at the beginning of the carbon deposition was somewhat less. Therefore, addition of alkali was not desirable. And also, the addition of chromic oxide or manganese dioxide was not desirable as that of alkali, which made methane conversion lower.

Partial Oxidation of Methane with Iron Oxide-Alumina

As mentioned above, iron oxide-alumina was the most adequate oxygen carrier. In the reaction of partial oxidation of methane with iron oxide-alumina, the effects of reaction temperature and SV on the composition of generated gases were examined.

Effects of Reaction Temperature: The effects of reaction temperature, with 10g of $\text{Fe}_2\text{O}_3\text{—Al}_2\text{O}_3(7:3)$ and $\text{SV}=100$, were examined and the results are shown in Fig. 9 and Fig. 10.

Fig. 9 Relation between Reaction Temperature and CH_4 conversion, $\text{SV}=200$

Methane conversion at the stage of $\text{FeO}_{1.33}\sim\text{FeO}$ was considerably increased with the rise of reaction temperature. For example, it was increased about twofold during each rise of 100°C . The point, at which the balance of carbon in the generated gas was just lost, was indicated in this Figure, which was extrapolated to the fraction of carbon deposition = 0%. The conversion of methane at the beginning of carbon deposition was only about 30% at 700°C , but considerably increased to 70 or 90% at 800 or 900°C .

As shown in Fig. 10, selectivity was very small at the beginning of reaction, and then increased rapidly and maintained a constant value for a while. These values for various temperatures increased with the rise of reaction

Fig. 10 Relation between Reaction Temperature and CO Selectivity, $\text{SV}=200$

- (1) 1000°C (2) 900°C
(3) 800°C (4) 700°C

Fig. 11 Relation between Flow Rate of CH_4 and CH_4 Conversion or CO Selectivity, 800°C

- (1) $\text{SV}=400$ (2) $\text{SV}=200$
— Δ — CH_4 conversion, — $\circ$ — CO selectivity

temperature, but the tendency was not so remarkable as that of conversion.

Effects of Methane Flow Rate: Effects of methane flow rate, with 10g of iron oxide-alumina and at a reaction temperature of 800°C , were examined and the results are shown in Fig. 11.

Fig. 12 Relation between Layer Thickness and CH_4 conversion 800°C

Methane conversion at the stage of $\text{FeO}_{1.33} \sim \text{FeO}$ was considerably decreased with increasing of flow rate. But it was rather rapidly increased at the stage beyond FeO , and also the period of carbon separation was clearly shortened. Selectivity maintained constant values for a while at the stage of $\text{FeO}_{1.33} \sim \text{FeO}$, and these values were not changed with increasing of flow rate. And selectivity at the stage beyond FeO was gradually increased and then carbon was separated.

Effects of Layer Thickness: At constant flow rate of methane the quantity of the oxide in reaction tube was increased twofold. The results are shown in Fig. 12 and Fig. 13.

From Fig. 12 it was known that when layer thickness was increased, the period of complete combustion of methane was elongated, and then conversion during the next stage was fairly increased; but the time of carbon deposition was hardly changed.

After all, it was concluded as follows; when the layer thickness was increased twofold, the amount of carbon dioxide and water produced by complete combustion was increased, while the period of constant selectivity was shortened, because the time of carbon deposition was not affected at all.

Discussion

i) Conversion of Methane

When methane is partially oxidized with iron oxide-alumina, the reactions in which methane is concerned in the presence of no reduced metallic iron at the stage beyond Fe_3O_4 are as

Fig. 13 Relation between Layer Thickness and CO Selectivity 800°C

follows:

The reactions of producing metallic iron are as follows:

The formation of metallic iron by reduction make possible the following reactions in which reduced iron acts as catalyst.

As these reactions are fully possible thermodynamically at $700 \sim 1,000^\circ\text{C}$, conversion is determined by the rate of these reactions. In fact, it was shown by the results of experiments that methane conversion was increased with rising of reaction temperature and decreasing of SV without exception.

At the stage of $\text{FeO}_{1.33} \sim \text{FeO}$, reactivity is considerably low at low temperatures as 700°C , but is considerably increased at $1,000^\circ\text{C}$ and residual methane falls to a small quantity. Therefore, it is required high temperature such as $1,000^\circ\text{C}$ to conduct good partial oxidation of methane at this stage. The higher is the reaction temperature, the more increase of reactivity is seen at the stage beyond FeO ; then, in general, it should be adequate to adopt higher reaction temperature at the stage beyond FeO .

ii) Selectivity.

The measured values of partial pressure ratio ($P_{CO_2} \cdot P_{H_2} / P_{CO} \cdot P_{H_2O}$) during the stage beyond $FeO_{1.33}$ are shown in Fig. 14. It is known that this reaction is at equilibrium. However, this fact does not determine the selectivity of carbon monoxide or hydrogen, but controls the two selectivities to satisfy the equilibrium relation of water gas shift reaction.

Fig. 14 Measured Value of ($P_{CO_2} P_{H_2} / P_{CO} P_{H_2O}$)
○ 800°C ● 900°C

The reduction of pure iron oxide with reducing gas was explained by Wagner's theory,⁶⁾ most popular in metallo-chemistry as follows: Fe_2O_3 is reduced to Fe_3O_4 almost quantitatively, and then Fe_3O_4 is reduced to form Wüstite layer on the surface, which is so compact that even gaseous hydrogen is not permeable. Therefore, it is recognized that reducing gas reduces Fe_3O_4 by the agent of Wüstite layer.

When hydrogen is present as a reducing gas, the surface contact to hydrogen is not Fe_3O_4 but Wüstite layer, and the following reaction proceeds (Wüstite will be indicated as FeO).

The produced Fe diffuses as Fe^{++} due to the concentration gradient from FeO layer to internal Fe_3O_4 to reduce the latter.

Accordingly, the following reduction reaction proceeds practically as the combination of reaction (8), diffusion of Fe^{++} in FeO layer, and reaction (9).

If the reaction in this experiment proceeds in practical as Wagner's theory, hydrogen and carbon monoxide present in the generated gases react with FeO respectively as Eq. (8) and the following equation at the stage of $FeO_{1.33} \sim FeO$.

The summarized reactions are indicated by

Eq. (10) and the following equation.

Methane also reacts as Eq. (3) or (4) on the surface at the stage of $FeO_{1.33} \sim FeO$. As shown in Fig. 10, selectivity of carbon monoxide maintains an almost constant value after attained to the equilibrium value of Eq. (11) at each reaction temperature. As shown in Fig. 11, it is known that constant value is not changed though methane flow rate is changed. Accordingly, it is concluded that at the stage of $FeO_{1.33} \sim FeO$, when selectivity of carbon monoxide is in equilibrium value at each reaction temperature, the both reactions of Eq. (8) and (11) are at equilibrium; while, it is shown by the experiment that methane conversion is considerably small at this stage. Therefore, it is supposed that reaction (3) or (4) is the rate-determining step and reaction (8) and (11) are at equilibria at the latter stage of $FeO_{1.33} \sim FeO$, and also that reduced metallic iron is gradually accumulated on the surface.

At the stage beyond FeO, in general, selectivity of carbon monoxide has a tendency to exceed the value obtained from the equilibrium of reaction (11). At this stage, FeO is reduced to be decreased and at the same time metallic iron is gradually increased, so it is supposed that it is difficult to attain to the equilibria of the reaction (8) and (11). However, it should be impossible to conclude that primary reaction of methane is not Eq. (3) but Eq. (4), merely on the experimental result that equilibrium is unbalanced in the direction of selectivity increase of carbon monoxide. Because, metallic iron formed by reduction is a catalyst which promotes any reactions of (5), (6), or (7), and increases the selectivity of carbon monoxide. In addition, it is difficult to consider clearly the mechanism of reaction at the stage beyond FeO, which will be described in detail in the later report made on fluidized bed.

iii) Increase of layer thickness

Though SV was small as seen in Fig. 11, the values of selectivities were equal to the equilibrium value of the reactions (8) and (11). By the above results, it is considered to make SV smaller for the purpose of increasing conversion at low reaction temperature without loss in selectivity. In addition, it is desirable practically to diminish the frequency of Blow and Make.

Iron oxide is a reaction material in this case, and the compositions of iron oxide at inlet

and outlet are not equal. When methane is introduced into the reaction tube, at first it is perfectly oxidized by $\text{Fe}_2\text{O}_3\text{--Al}_2\text{O}_3$ at the inlet to generate carbon dioxide and water, while Fe_2O_3 at the outlet or middle parts will not be reduced at all. However, after several minutes a considerable residue of unreacted methane is found in the generated gases, by the time $\text{Fe}_2\text{O}_3\text{--Al}_2\text{O}_3$ at the outlet will become reduced to $\text{Fe}_3\text{O}_4\text{--Al}_2\text{O}_3$. Therefore, when it is reduced to Fe_3O_4 in average composition, there will be some differences in the reduction grade of iron oxide-alumina at inlet, middle parts, and outlet; in general, the state of inlet is more reduced than that of outlet.

In the next, the stage more reduced than $\text{FeO}_{1.33}$ (corresponding to Fe_3O_4) will be considered. Unless the reaction is zero order for methane, quantity of methane which reacts at inlet is considered to be larger than that at outlet. Therefore, at the stage beyond $\text{FeO}_{1.33}$, also the state of inlet is more reduced than that of outlet, and this difference of reduction grade is more remarkable with the increase of the layer thickness.

When the layer thickness is increased, it is supposed that the difference of reduction grade is more remarkable and carbon is separated by reduced metallic iron at inlet, by which the carbon balance is lost in generated gases. The above argument is supported by the result of experiment: the time until the carbone deposition starts is not affected at all by the increase of the layer thickness. Accordingly, with the increase of layer thickness, conversion of methane is surely increased, but the selectivity of generating gases will be smaller because of the larger difference of reduction grade of iron oxide. Then, when layer thickness is too large, carbon dioxide and water are generated at first, and then the product gas containing mainly carbon dioxide and water, in which the carbon balance is lost, will be generated.

Conclusion

1) From the considerations of equilibrium and physical properties, the kinds of metallic oxides being possible to be used for oxygen carrier are not so many. On comparing these oxides by experiments, iron oxide-alumina is the most adequate.

2) The reactivity of iron oxide with methane is promoted by the addition of alumina to iron oxide. In particular, it is remarkable at the stage of $\text{FeO}_{1.33}\sim\text{FeO}$ and the reactivity at the stage beyond FeO is also promoted.

3) Reactivity is decreased by each addition of alkali, chromic oxide, and manganese dioxide to iron oxide-alumina. However, selectivity of carbon monoxide is somewhat promoted by the addition of manganese dioxide or chromic oxide.

4) When methane is partially oxidized with iron oxide-alumina to generate carbon monoxide and hydrogen, there are two stages of average composition; namely $\text{FeO}_{1.33}\sim\text{FeO}$ and $\text{FeO}\sim\text{FeO}_{0.8}$. Conversion of methane is higher at the latter stage than at the former; selectivity of carbon monoxide at the former stage gets to the equilibrium value of

but increased gradually at the latter stage. Water gas shift reaction is at the equilibrium at the both stages.

5) When reaction temperature is higher, conversion of methane at the both stages is increased. Fairly good gases are generated at above $1,000^\circ\text{C}$ at the stage of $\text{FeO}_{1.33}\sim\text{FeO}$, and at above 900°C at the stage of $\text{FeO}\sim\text{FeO}_{0.8}$.

6) Assuming that Fe_3O_4 is reduced by the agent of FeO (Wüstite), selectivity of carbon monoxide is increased to get to the following equilibrium value with the thicker layer of FeO ,

and then it is supposed that reduced metallic oxide begins to be accumulated on the surface. The rate-determining step is supposed to be following reaction,

and following reactions are at equilibrium.

7) At the stage beyond FeO , the following equilibria will be difficult to establish because of the decrease of FeO :

The proceeding of decomposition reaction or reforming reaction of methane by catalytic reaction of metallic iron formed by reduction will be also taken into consideration.

8) The difference of reduction grade of iron oxide throughout the bed is seen; that is iron oxide at inlet is more reduced than at outlet.

It is supposed that gases, of which the carbon balance is lost, are generated when iron oxide at inlet is reduced to a certain state. Therefore, when layer thickness is too large, the yields of carbon monoxide and hydrogen will be smaller.

Refereces

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