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Rapid catalytic reforming of methane with CO_2 and its application to other reactions†

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First, indispensable requisites of the catalytic technologies for moderating the CO_2 problems are enumerated. Among various conditions, high conversion rates to treat a huge amount of the feed and high tolerance against coke deposit are most important. In spite of many advantages, CO_2 reforming of methane has the following general problem. Different from steam reforming, the deposited coke due to the disproportionation reaction of CO and the cracking of methane in CO_2 reforming cannot be volatilized by the reaction with steam. Based on the mechanisms of the coke formation mentioned above, a number of methods to reduce or prevent the coke deposit have been tried by many researchers. Many of them compared the results by using different kinds of catalyst components and their supports. Taking into account the catalytic performance and cost of catalyst materials, nickel supported on alkaline earth oxides and rare earth oxides, especially magnesia, were studied extensively. Sufficient stability to magnesia supported catalysts was observed; however, the conversion rate is still not high enough. Steam–CO_2 co-reforming and other approaches involving membrane reactors were also investigated; however, these results were basically affected by the intrinsic performance of the catalysts used and limit of diffusion in the case of the membrane. Another essential approach has been done by the author and coworkers. A nickel-based four-component composite catalyst was designed for high promotion of hydrogen spillover during the reaction progressing with high rates. Plenty of hydrogen on the catalyst surface prevented coke deposition and achieved an extraordinarily high reaction rate and high tolerance due to no covering of coke on the active catalytic sites. The large endothermic reaction heat of CO_2 reforming of methane could be compensated by simultaneous combination of catalytic combustion of a low concentration of easily combustible hydrocarbons.

In this plenary lecture, almost all the studies on CO_2 reforming done in the recent decade were surveyed and summarized in the light of the above requisites to contribute to the further improvement in the catalysts and their reaction processes of CO_2 reforming of methane and/or natural gas. Copyright © 2001 John Wiley & Sons, Ltd.

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1. GENERAL INTRODUCTION FOR CATALYTIC CONVERSION OF CO_2

1.1 Indispensable requisites of the catalytic technologies for moderating CO_2 problems

Before reviewing the subject of CO_2 reforming of methane or natural gas, general considerations on CO_2 conversion are necessary, and then rational criteria to evaluate the works will be given.

High conversion rate is the most important condition for treating large quantities of CO_2. High selectivity to targeted compounds is also necessary from the viewpoint of production economy. Since coke deposition and accompanying deactivation of the catalyst is a general problem, a catalyst without coke formation is also indispensable to keep high reaction rates. A low cost charge for catalyst preparation and conducting the reaction must not be overlooked.

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1.2 Key factors to promote the highly rapid rate of catalytic reaction

In linear controlling factors, suitable pore-structures to allow faster mass transfer for the feeds and products are essential to progress the reactions. In order to compensate for the large endothermic reaction a combination with an exothermic reaction on the same catalyst surface would assist in maintaining the proper catalyst temperature and the reaction rates.

As for non-linear factors to enhance the reaction, a proper utilization of the hydrogen spillover effect, is required. This might change the catalyst surface to a very reductive state, resulting in the prevention of coke formation and the realization of a high reaction rate as a level of space-time yield of syngas, above 4 000 mol l^{-1} h^{-1} at a space velocity of at least 200×10^3 h^{-1}.

2. INTRODUCTION FOR CO_2 REFORMING OF METHANE

2.1 Recent trend of the research work

Catalytic reforming of methane with CO_2 for converting to syngas (Eq. [1]) is one of the significant subjects among various methods of chemical conversion of CO_2, although this reaction

$$CH_4 + CO_2 = 2CO + 2H_2, \Delta H_{773\ K} = 259\ kJ\ mol^{-1} \quad [1]$$

itself is not so effective for the purpose of direct mitigation of the CO_2 accumulation, because CO_2 needs an equivalent mole of methane to progress the reaction. However, still it has a variety of intriguing new aspects. Reflecting this situation, several elaborative reviews on this subject have been done by Fox[1] in 1993, Rostrup-Nielsen[2] in 1994, Ross *et al.*[3] in 1996, and by Halmann and Steinberg[4] in 1999. However, since the number of studies on CO_2 reforming of methane has rapidly increased in recent years, it is necessary to review at the present level of studies. During the past decade up to the end of July 1999, the number of original papers published in major catalysis journals amounted to 103, and 81 papers among them, i.e. *ca* 80%, appeared in the two and a half years after 1996. Although not all of them can be mentioned in this paper by the reason of the limit on space, the results obtained are introduced as much as possible.

2.2 Significance of the subject

Expensive hydrogen is not needed to reduce CO_2. Syngas can be synthesized by dry gas conditions, which allow simple reaction processes and saving energy for the use of steam. Syngas having a lower H_2/CO molar ratio can be directly synthesized from the natural gas involving CO_2. Syntheses of valuable compounds from two inexpensive resources could be achieved.

2.3 Advantage of the subject

As a thermodynamical reason, methane conversion in CO_2 reforming can reach higher than that in steam reforming. H_2O–CO_2-co-reforming and partial oxidation reforming can be designed by using a highly active catalyst for CO_2 reforming. An advanced reforming process, which involved *in situ* heat supply by catalytic combustion, could be established. Direct regulation of appropriate ratios of $H_2/CO/CO_2$ for fitting objective reactions could be achieved by a one-pass operation.

2.4 Disadvantage of the subject

More vigorous coke formation than in steam reforming is expected by the use of a conventional reforming catalyst. This is because deposited coke formed by the following equations has no chance to be removed by reaction [4], which occurs in steam-reforming.

$$2CO \rightarrow C + CO_2 \quad [2]$$

$$CH_4 \rightarrow C + 2H_2 \quad [3]$$

$$C + H_2O \rightarrow CO + H_2 \quad [4]$$

3. TRIALS TO AVOID EQUILIBRIUM-LIMITED CONVERSION

In trials to avoid a lower equilibrium conversion for reaction [1] at lower temperatures, the performance of a membrane reactor was tested by using suitable catalysts for less coke formation, i.e. rhodium or ruthenium and Ni/La_2O_3 or $Ni_{0.03}Mg_{0.97}O$.[6] It was observed that the conversion exceeded the equilibrium conversion; however, as hydrogen transport through the membrane limits the performance of the membrane reactor, an extremely low space velocity must be adopted and a corresponding low space-time yield of hydrogen was obtained.

4. KINETIC AND MECHANISTIC STUDIES

Not so many studies on mechanism have been conducted, mainly because the ultimate objective of the study on CO_2 reforming would be that to find and develop a high performance catalyst for realizing the rapid conversion without coke formation. Most of the studies are still in the state of catalyst development. The role of La_2O_3 was revealed by kinetic-isotope measurements as its strong chemisorption of CO_2.[7] It was concluded that Ni/TiO_2 catalyst exhibited the highest activity in both kinetic studies by pulse surface reaction rate analysis[8] and evaluation based on the specific activities on a turnover frequency: [9] however, both of them were conducted at fairly low conversion levels and the results are not directly related to the performance, exhibiting a high space-time yield of product at a high conversion level of the feed. Transient kinetic techniques,[10] and measurement of the isotope effect[11] gives the same insufficiency.

5. COMPARISON OF THE INTRINSIC ACTIVITY OF NICKEL AND NOBLE METALS BELONGING TO GROUP VIII

The comparison of the specific activities among platinum-group metals such as platinum, iridium, rhodium, palladium and ruthenium, and iron-group metals, nickel, cobalt, and iron, has been made for CO_2-reforming as single metal-component catalyst.[12–17] Rostrup-Nielsen and Hansen[12] compared the catalytic activity among nickel, ruthenium, rhodium, palladium, iridium, and platinum supported on MgO, and concluded that replacing steam by CO_2 has no significant impact on the reforming mechanism. The order of activity for these metals was similar to each other, as follows:

Ru, Rh$\gg$Ir$>$Ni, Pt, Pd for steam reforming, and Ru, Rh, Ni$\gg$Ir$>$Pt$>$Pd for CO_2 reforming. Rates of carbon formation in the $CH_4/H_2 = 95/5$ feed were compared by thermogravimetric analysis measurements, and a striking contrast among catalysts was observed. The order of deposited coke was Ni, Rh$>$Ir = Ru$>$Pt, Pd at 500 °C, and Ni$>$Pd = Rh$>$Ir$>$Pt$\gg$Ru at 650 °C.

As a result, they concluded that rhodium and ruthenium show high selectivity for carbon-free operation, but from the viewpoint of cost of these resources a major impact cannot be expected on the total reforming catalyst market. Even apparent results were somewhat different, caused by the combination of different supports, the essential result being that rhodium, ruthenium, and nickel are highly active catalyst metal components with the same properties.[13–17]

Detailed studies on rhodium[18–24] and iridium[21,25] catalysts have been made, using different kinds of support, such as, Al_2O_3, TiO_2, SiO_2 and MgO. Erdöhelyi *et al.*[18] showed that the order of catalytic activity was the same order as described above. Other than these supports, yttria-stabilized zirconia (YSZ),[19,20] Zr–SiO_2,[21] and zeolites (NaY and NaZSM-5)[22] were used.

Ruthenium[26–30] and platinum[31–39] catalysts were also studied extensively, reflecting their high activity and less coke formation in the CO_2 reforming. Ruthenium catalyst was supported on γ-Al_2O_3[26,28,29] η- Al_2O_3,[27] TiO_2,[27] SiO_2,[29] carbon black,[27] graphite,[28] La_2O_3,[30] Y_2O_3,[30] active carbon,[26] and ZrO_2.[30] Platinum catalyst was supported on Al_2O_3,[31,37] γ-Al_2O_3,[32,36] TiO_2,[32,35] ZrO_2,[32–38] Cr_2O_3[35] and SiO_2.[35]

Bradford and Vannice[27] showed the order of turnover frequencies of ruthenium catalyst supported on different supports for CO_2 reforming of CH_4 in the absence of heat and mass transfer effects. These values were in the order of $TiO_2 > Al_2O_3 \gg C$ as expressed with the kind of supports. On the other hand, the most popular support for platinum catalyst was ZrO_2. One reason would be less coke formation on Pt/ZrO_2 than others.[32,35,36,39] A very limited number of cobalt catalysts was studied using carbon and SiO_2[40] and alumina[41,42] as the supports. The coke deposition was markedly reduced by the presence of MgO[40].

Catalysts MoS_2 and WS_2 for CO_2 reforming of CH_4 were found to suppress carbon deposition but the performance was inferior to Ni/SiO_2; however, the activity of these catalysts was much less than nickel catalyst.[43,44]

6. PERFORMANCE OF NICKEL CATALYST SUPPORTED ON DIFFERENT KINDS OF SUPPORT

From the practical viewpoint, the most inexpensive catalyst is nickel, and attention has been focused on improving this among the highly active catalysts: rhodium, ruthenium, and nickel for CO_2 reforming of methane. One of the most popular supports used for nickel catalyst was alumina.[45–53] In order to avoid nickel particle growth, NiAl spinel was tested. Stability increased at the sacrifice of high activity. The effect of additives to nickel catalyst supported on α-Al_2O_3 upon activity was tested; however, no enhancement was obtained, as recognized by the following order of the activity:

$$\text{Ni, Ni–Co, Ni–Ce} > \text{Ni–Cu} >> \text{Ni–Fe}^{46}$$

The carbon deposition during CO_2 reforming was markedly suppressed by the addition of alkali metal oxides such as Na_2O and K_2O, and alkaline-earth-metal oxides such as MgO, and CaO, but the activity of Ni decreased in the order of

$$\text{None} \simeq Na_2O > MgO >> CaO > K_2O^{50}$$

The effect of nickel precursor for Ni/γ-Al_2O_3 catalyst was tested using $Ni(NO_3)_2$, $NiCl_2$, and nickel acetylacetonate $[Ni(C_5H_7O_2)_2]$. However, the latter two precursors gave considerably lower activities than $Ni(NO_3)_2$.[51]

Nickel catalysts have been supported on SiO_2,[54,55] perovskite,[56] high siliceous ZSM-5 zeolite,[57] and $AlPO_4$.[58] In the case of ZSM-5 support,[57] coke deposition was remarkably diminished with the addition of potassium and calcium, and stability was confirmed up to 140 h, although the space-velocity of the experiment was fairly low, such as $(4.4-6)\times 10^4\ h^{-1}$ from the viewpoint of the rapid conversion criteria mentioned above. Choudhary *et al.*[58] investigated partial oxidation of methane to syngas with or without simultaneous CO_2 and steam reforming reaction over Ni/$AlPO_4$. As discussed later, this kind of reaction control would be one of the promising directions for practical operation.

7. PREVENTION OF COKE FORMATION BY COMBINING ALKALINE-EARTH OR RARE-EARTH OXIDES

The effect of the addition of alkaline-earth oxides or rare-earth oxides to supported nickel catalysts on the prevention of coke formation and consequent enhancement in methane to syngas conversion was widely recognized recently, and a number of studies have been focused on this point.[59–80]

Gadalla and Bower[59,60] compared various commercial nickel catalysts supported on different kinds of support and found that in the presence of $MgAl_2O_4$, calcium aluminate, or CaO–TiO_2–Al_2O_3 gave high conversion. Takayasu *et al.*[61] observed that by merely mechanical mixing of Ni/MgO with other supports, such as SiO_2, deactivation was markedly prevented. Choudary *et al.*[63] found that precoating with MgO for the commercial low surface area porous catalyst carriers was also effective.

Ruckenstein and Hu[62] reported that MgO inhibits the disproportionation reaction $2CO \rightarrow C + CO_2$ over nickel, probably due to the formation of NiO–MgO solution, as a result of the similar crystalline structures of NiO and MgO. The same conclusion was drawn by Bradford and Vannice[64].

Unique characteristics of NiO–MgO solid solution were studies in detail especially by Ruckenstein and Hu,[62,65–67,73] and Fujimoto and coworkers.[68,70,75,76] Ruckenstein and Hu[62] showed the striking contrast between Ni/MgO and others in the stability of the catalyst, Ni/MgO kept the conversion level constant up to 12 h, whereas other catalysts lost their activity abruptly. The problem is its low intrinsic activity. At a space velocity of $6 \times 10^4\ ml\ g^{-1}\ h^{-1}$ the conversion almost coincided with the equilibrium one; however, when the space velocity was increased 4.2 times, the conversion decreased from 95 to 60% at 790 °C.

Tomishige *et al.*[70] also showed the stable catalytic performance of $Ni_{0.03}Mg_{0.97}$ catalyst. At a space velocity of $18\,670\ l\ kg^{-1}\ h^{-1}$, methane conversion was *ca* 82% for 100 days, although nickel (3 mol%)/Al_2O_3 lost its activity within 1 day. However, at a space velocity of $224\,000\ l\ kg^{-1}\ h^{-1}$, methane conversion decreased to a level below 11%,[76] or space-time yield of CO was as low as 66.7 $mol\ kg^{-1}\ h^{-1}$.

8. PERFORMANCE OF NICKEL-BASED COMPOSITE CATALYST TO REALIZE ULTRA-RAPID RATE OF CO_2 REFORMING OF METHANE

Two decades ago Inui *et al.*[81] had developed a highly active catalyst for CO_2 methanation. The catalyst was composed of Ni–La_2O_3–Ru with the atomic ratios of 100:20:3 supported on spherical silica particles having a meso–macro bi-modal pore structure. La_2O_3 and ruthenium could be replaced by Ce_2O_3 and rhodium, respectively. The catalyst allowed CO_2–CO co-methanation with total conversion at considerably lower temperature than the conventional CO methanation catalyst.[82] The role of each catalyst component was elucidated as that

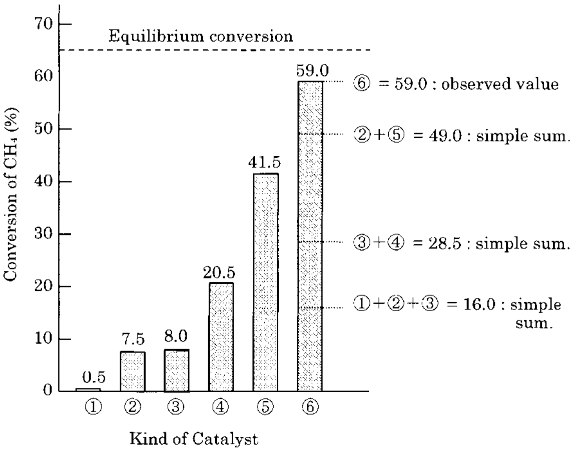

Figure 1 Synergistic effect of Rh-modified Ni-Ce_2O_3-Pt four-component catalyst on CO_2 reforming of methane. Catalyst composition: ① = 10wt% Ni – 6.0wt% Ce_2O_3, ② = 1.0wt% Pt, ③ = 0.2wt% Rh, ④ =① +② = 10wt% Ni – 6.0wt% Ce_2O_3 – 1.0wt% Pt, ⑤ =① +③ = 10wt% Ni – 6.0wt% Ce_2O_3 – 0.2wt% Rh, ⑥ =① +② +③ = 10wt% Ni – 6.0wt% Ce_2O_3 – 1.0wt% Pt – 0.2% Rh; catalyst support: alumina-wash coated ceramic fiber plate; feed gas: 10 vol% CH_4 – 10 vol% CO_2 – 80 vol% N_2; space velocity: 730,000 h^{-1}; contact time: 4.93 ms; furnace temperature: 600 °C; numerals on bar graph: conversion of methane (%); numerals indicated at right-hand side postulated simple summation of methane conversion for each catalyst component indicated as its number.

lanthanide oxides increase the adsorption of CO_2 by their weak basicities and dispersion of nickel, and ruthenium or rhodium play the role of the porthole for hydrogen spillover during the reaction with high rates. The spillover hydrogen keeps the nickel catalyst surface in a very reduced state and prevents coke deposition.[83] This catalyst concept was applied to the rapid purification of hydrogen containing a low concentration of oxygen to the ultrahigh purity one using Ni–Ce_2O_3–Pt catalyst supported on alumina-washcoated ceramic fiber plate.[84] This catalyst also exhibited high performance in methanol to syngas conversion.[85] These kinds of catalyst exerted high performance in both CO_2 reforming[86] and partial-oxidation reforming of methane.[87,90] This kind of catalyst was then applied to CO_2 reforming of methane.[86–99] Even at a considerably high space velocity of 73 000 h^{-1} or contact time of 49.3ms, conversions of methane and CO_2 on the Ni–Ce_2O_3-Pt catalyst were strictly along the equilibrium conversion at a range of catalyst temperature from 350 to 650 °C or corresponding conversion from 0 to 80% for a feed gas composed of 10% CH_4–10% CO_2–80% N_2.[86] However, as shown, bar graph 4 in Fig. 1, the conversion decreased to 1/3 at a high space velocity 730 000 h^{-1} or contact time of 4.93 ms on this catalyst. The Ni–Ce_2O_3–Pt catalyst was then

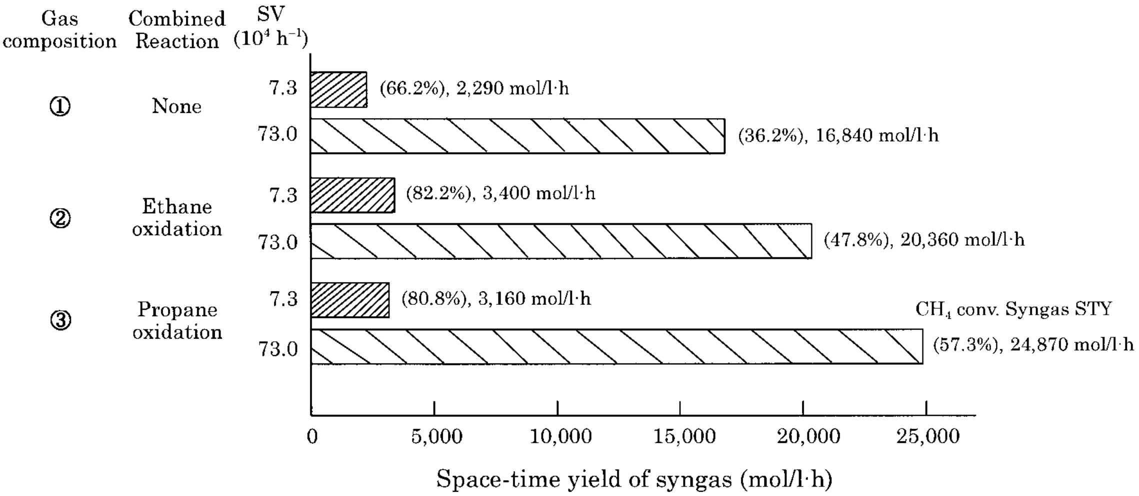

Figure 2 Effect of catalytic oxidation of ethane or propane on the CO_2 reforming of methane at two examples of space-velocities 73 000 and 730 000 h^{-1}. Catalyst: Rh-modified four-component catalyst; Gas composition: ① 35% CH_4 - 10% CO_2 - 55% N_2, ② 35% CH_4 - 10% CO_2 - 5% C_2H_6 - 17.5% O_2 - 32.5% N_2, ③ 35% CH_4 - 10% CO_2 - 3.3% C_3H_8 - 16.5% O_2 - 35.2% N_2; catalyst-bed temperature: 700 °C (furnace temperature: 500 °C); pressure: 1 atm.

modified with a very low concentration of rhodium. The rhodium-modified nickel-based four-component catalyst, which is designated as 6 in Fig. 1, exhibited a high reaction rate. The conversion increased to a level as high as the equilibrium conversion, even under such high space velocity or short contact time due to two-stage hydrogen spillover from rhodium to platinum and then from platinum to nickel. The conversion on catalyst 6 was several percent lower than the equilibrium one. This is attributed to the decrease of the catalyst-bed temperature from the furnace temperature due to the large endothermic reaction heat.[86]

In order to compensate the large endothermic reaction heat by partial oxidation reforming of methane (Eq. 5) or complete combustion (Eq. 6) they were combined with CO_2 reforming of

$$2CH_4 + O_2 \rightleftharpoons H_2 + 2CO,\ \Delta H_{773K} = -48.8\text{kJmol}^{-1} \tag{5}$$

$$CH_4 + 2O_2 \rightleftharpoons CO_2 + 2H_2O,\ \Delta H_{773K} = -800\text{kJmol}^{-1} \tag{6}$$

methane, and much higher conversion beyond equilibrium conversion was achieved.[90] The principle was then applied to CO_2–H_2O coreforming of methane as Eq. (7), and a very high space-time yield of hydrogen 12 190 mol l^{-} h^{-1} or syngas 17 070 mol l^{-1} h^{-1} was obtained.[90]

$$6CH_4 + CO_2 + H_2O + 2O_2 \rightleftharpoons 13H_2 + 7CO,\ \Delta H_{773K} = 383\text{kJmol}^{-1} \tag{7}$$

This concept was then progressed to adopt more combustible hydrocarbons. Ethane and propane are involved in natural gas, and these hydrocarbons are much more easily combustible on the catalyst, generating high combustion heat as Eqs. (8) and (9)

$$C_2H_6 + 3.5O_2 \rightarrow 2CO_2 + 3H_2O,\ \Delta H_{773K} = -1424\text{kJmol}^{-1} \tag{8}$$

$$C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O,\ \Delta H_{773K} = -2040\text{kJmol}^{-1} \tag{9}$$

The total reaction heats are neutralized as Eqs. (10) and (11).

$$(x + 5y)CH_4 + xCO_2 + yC_2H_6 + 3.5yO_2 \rightarrow (2x + 7y)CO + (2x + 13y)H_2,\ \Delta H_{773K} = 259x - 240y\text{kJmol}^{-1} \tag{10}$$

$$(x + 7z)CH_4 + xCO_2 + zC_3H_8 + 5zO_2 \rightarrow (2x + 10z)CO + (2x + 18z)H_2,\ \Delta H_{773K} = 259x - 375z\text{kJmol}^{-1} \tag{11}$$

In fact, as shown in Fig. 2, the reaction progressed smoothly and the effect of this *in situ* heat supply gave a marked increase of conversion and consequently, space–time yield of syngas.[95] By controlling the feed composition, a syngas having an appropriate composition to fit the successive reaction would be obtained without the process of CO–H_2O shift reaction or CO_2–H_2 partial reduction reaction.

Since no coke formation occurs even with a nickel-based catalyst owing to the vigorous hydrogen spillover effect and catalytic combustion by oxygen, an ultra high conversion rate of CO_2 reforming of methane was achieved with enough stability, even under medium pressure conditions. An industrial application is now being developed, and detailed reports will be presented in the future. The combination of oxidation reaction with CO_2 reforming of methane was followed by O'Connor and Ross[37] using Pt/ZrO_2, and confirmed the marked effect of oxygen addition into the feed on the prevention of catalyst deterioration due to diminishing of the coke deposit.

9. APPLICATION TO OTHER REACTIONS

By using CO_2 reforming of methane with a combination of steam reforming and oxidation reaction, syngas having appropriate ratios of hydrogen and carbon oxides can be obtained with a high efficiency. The syngas was then allowed to introduce directly to the second reactor connected in series. The second reactor, in which methanol synthesis catalyst[93,97,99] or ethanol synthesis catalyst[100] was packed, produced methanol or ethanol. The total effluent gas from the methanol synthesis reactor was directly introduced to the third reactor, in which zeolite catalysts were packed, and produced low aromatic but high octane number gasoline or light olefins with high selectivities.[97,99]

10. CONCLUSION

Recent papers on CO_2 reforming of methane were reviewed. In order to overcome the easiness of coke deposition in this reaction, ruthenium and rhodium catalysts were selected in the early stage of the study. Simultaneously, the effect of catalyst support was investigated, and it was found that alkaline-earth or rare-earth oxides have the role of suppression of coke deposition. Recently, nickel supported on MgO and Ni–MgO solid solution catalysts were studied extensively owing to their characteristics of low coke deposition. Another solution has been realized by the different principles that nickel-based catalyst combined with a small concentration of Ce_2O_3 was modified with very small concentrations of platinum and rhodium, which are expected to act in the role as porthole for hydrogen spillover. Furthermore, to compensate the large endothermic reaction heat of the reforming, catalytic combustion of easily combustible hydrocarbons was carried out on the same catalyst surface, resulting in ultra rapid reforming.

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