Novel Synthesis Routes for Clean Fuels through Ultra-Rapid Synthesis of Syngas as the Trigger Technology

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Abstract

Recently, much more efficient method for hydrogen and/or syngas production has been requested by the reasons of not only usage for petroleum refinery processes and synthetic fuel production but also usage for fuel cells. After 70 years improvements in steam reforming processes, recent investigations seem to be focused on the Auto-thermal reforming (ATR), because the huge burden of conventional steam reformers can be replaced by fairly smaller size reformers, which are combining partial oxidation of the fed hydrocarbons and successive steam reforming by using the exothermic heat of the partial oxidation. Although various improvements have been done, not so drastic change in reformer size can be achieved yet.

Most recently, an innovative steam- and/or CO\textsubscript{2}-reforming designated as Thermo-Neutral Reforming (TNR) has been introduced by the author after 30 years studies on ultra-rapid catalytic reactions. The reformer can be reduced two-order magnitude compared with traditional steam reformers, because the large endothermic heat of reforming is compensated by the large exothermic heat of complete combustion on the same catalyst surface without supply of heat from out side of the reactor.

By applying the extremely compact size of the TNR system to the successive syngas converters packed newly developed catalysts, highly effective ultra clean fuels such as MeOH, DME, and sulfur-free & non-aromatic high octane number gasoline can be produced effectively with non-expensive costs. These future challenges and opportunities will be emphasized comprehensively in this presentation.

1. Introduction

1.1. Status of Production of Oil and Building Blocks for Petrochemical Industry in Middle East Countries

As well known, the proved reserves of oil in the area of Middle East, 673 billion bbl, is an overwhelming majority, and it occupies 2/3 that of the world\textsuperscript{1}. The percentages of these are Saudi Arabia 25.0, Iraq 10.7, UAE 9.3, Kuwait 9.2, Iran 8.5, and Qatar 1.5. Reflecting these distinguishes status of reserves and production of oil, recently, advances towards the downstream of the petroleum industry has become remarkable\textsuperscript{2}. The comparison of the global ethylene-producing capacities gives us an impression that Japan is as No. 2 after United State. Saudi Arabia is No. 3 at that moment. It is also surprising and respective status. Because, only 5 years ago, that of Saudi Arabia was less than half
size that of Japan. The recent tendency of ethylene production can be compared from the change in ethylene capacities of Asian countries from 5 years ago and 2 years future\(^3\). Japan has already attained a plateau level (748 to 726 10M tons), and Saudi Arabia is now the midway of remarkable increase along the logistic curve (340 to 840 10M ton). Saudi Arabia has stood the strongest position from the viewpoint of the producing price of ethylene. The cheapest ethylene among the world is now producing from ethane source in Saudi Arabia\(^4\). It is only about 1/6 of Far East countries like as Japan and Korea. Such a great advantage of Saudi Arabia can be applied to new industries, which cannot be established in other Asian countries and Western countries.

1.2. Status of Hydrogen Production Technologies

Hydrogen production is the most fundamental subject in the petroleum industry, because hydrogen is used in many basic processes of petroleum refinery such as hydrocracking and hydrotreating. Moreover, in most recent years, hydrogen and/or syngas production by a variety of methods is enthusiastically pursuing in many countries, mainly because, hydrogen and/or syngas can be provided to fuel cell, as the ideal fuel of highly efficient electric power generator without any pollutant.

In the case of steam reforming for the industrial hydrogen production, for example, in the past 70 years, tremendous efforts have been done to improve the process\(^5\), such as Enhanced Heat Transfer Reformer (Air Products & Chemicals Co.), Gas Heated Reformer (ICI-Synetix), Convective Reforming (Halder Topsoe), Advanced Reforming Technology (Technip), Kellog Reforming Exchange System (Kellog), Fluid-Bed Reforming (Exxon), and Partial Oxidation (Shell, Texaco). Main reasons of these efforts due to the common understanding that the steam reforming reaction needs a large endothermic heat, and there is no much room in the improvement in catalyst performance. Therefore, the device for heat transfer has been targeted to improve. But unfortunately, a dramatic and innovative improvement could not be achieved yet through these efforts, because these pursuits have been done consistently based on the same principle mentioned above.

Experimental

2.1. Creation of the Novel Poly-functional Composite Catalyst for \(\text{CO}_2\)- and/or Steam-Reforming

A new incentive has come from an unexpected direction. That is to say; recent advances in the steam reforming catalyst have been done through the \(\text{CO}_2\) reforming associated with the \(\text{CO}_2\) mitigation against the global warming crisis\(^6\). The common sense of the steam reforming has been that the excess steam is necessary to prevent coke formation by the reaction between deposited carbon and steam to convert carbon mono oxide and hydrogen. On the other hand, if \(\text{CO}_2\) is used instead of \(\text{H}_2\text{O}\), it has been thought that there is no opportunity to avoid coke formation. Then new studies aimed to investigate the novel catalyst to avoid coke formation even under the reaction condition of \(\text{CO}_2\) reforming. As the criteria to develop this ideal catalyst, the following performances have been required. (1) No coke formation, (2) High sulfur tolerance, (3) Ultra-rapid reaction rate, (4) High-temperature resistance, (5) Low temperature start-up in a very short time, (6) Non toxic, and (7) Low production cost.

Only the Rh-modified Ni-based four-component composite catalyst supported on an appropriate high thermal resistant support satisfied all the criteria\(^6\).
2.2. Creation of the Novel Thermo-neutral Reforming (TNR) Method

Since the novel catalyst mentioned above has both catalytic functions of combustion and steam reforming for hydrocarbons, the thermo-neutral reactions on the same catalyst surface could be realized. As the result, the reactor size could be reduced to two-order magnitude that of traditional hydrocarbon steams reforming (HSR) method. The thermo-neutral reforming has been designated as TNR.

2.3. Creation of the Novel Effective Catalysts for New Synthesis Routes of Ultra Clean Fuels

By applying the extremely compact size of the TNR system to successive syngas converters packed newly developed catalysts, highly effective ultra clean fuels such as MeOH, DME, and sulfur-poor & non-aromatic high octane number gasoline can be produced effectively with non-expensive costs. These future challenges and opportunities are comprehensively explained in the next section.

3. Results and Discussion

3.1. Feature of the Four-component Composite Catalyst and the Thermo-Neutral Reforming (TNR)

The synergistic effect of the four-component catalyst on CO$_2$-reforming of methane is shown in Figure 1, which exhibits far beyond the catalytic activities of summation of each catalyst activity. Configuration of the catalyst components and the working state of the catalyst during the thermo-neutral reforming is illustrated in Figure 2. This catalyst possesses both catalytic activities of combustion and steam reforming with a good balance. Both activities are markedly enhanced by oxygen spillover and hydrogen spillover, respectively, and therefore, can exhibit on the same catalyst surface. It could realize the surprising reduction of the catalyst volume.

A demonstration pilot plant on the novel reforming of natural gas by the new catalyst and the thermo-neutral reforming method to produce five-nine grade hydrogen with a scale of 20 Nm$^3$/h has been conducted until 2003 by Air Water Inc. The size of reformer was as small as 1/80 that of the conventional steam reformer.

Heat balance between the exothermic heat of catalytic combustion and the endothermic heat of steam reforming in the TNR reformer for natural gas under a steady-state reaction operation is shown in Figure 4. The catalyst-bed temperature elevated within 20 seconds up to 850ºC after the reactants introduced into the catalyst bed at 407ºC. The catalyst-bed temperature and the heat for steam reforming were kept by the catalytic combustion of a part of hydrocarbons fed without any heat supply from the out side of the reactor wall during the steady state of the reactions.

Figure 5 shows the feature of the TNR reforming process by comparison with other conventional reforming processes through the heat transfer phenomena during the steady state of the reactions. The illustration is as follows;

**HSR:** Heat of steam reforming in the traditional reformer is supplied from the outside of the reactor, and therefore, very small amount of heat can be injected to the catalyst bed. It needs a huge reactor...
Figure 1  Comparison of the catalytic performance in CO₂ reforming of methane for various catalyst components --- Synergy appeared by proper combination of catalyst components

Catalyst composition of the four-components catalyst (wt%): 10Ni-6.0Ce₂O₃-1.0Pt-0.2Rh supported on alumina-washcoated ceramic fiber. Other catalysts contained the same concentrations described in the four-component catalyst. Feed gas (mol%): 10CH₄-10CO₂-80N₂, Furnace temperature: 600°C, SV: 730,000 h⁻¹, in case of Ni-Ce₂O₃-Pt catalyst SV was 73,000 h⁻¹ shown with the thin-bar graph was also shown.

Figure 2  Configuration of the catalyst components and the effects of spillover during the thermo-neutral ultra-rapid reforming
Figure 3 Schematic flow sheet of the AWI's pilot plant with the thermo-neutral reformer for 20 Nm$^3$/h 99.999% H$_2$ production

C$_4$-C$_2$ combustion heat (74.1%)

H$_2$ & CO combustion heat (23.6%)

Heat from furnace (2.3%)

C$_4$-C$_2$ Combustion $\text{CH}_2\text{CH}_2 + 1.68 \text{O}_2 = \text{CO}_2 + 1.36 \text{H}_2\text{O}$, ($\Delta H = -695 \text{ kJ/h}$)

Steam reforming of CH$_4$, $\text{CH}_4 + \text{H}_2\text{O} = 3\text{H}_2 + \text{CO}$, ($\Delta H = +220 \text{ kJ/h}$)

Combustion of CO formed. CO + 0.5 O$_2$ = CO$_2$, ($\Delta H = -285 \text{ kJ/h}$)

Combustion of H$_2$ formed. H$_2$ +0.5 O$_2$ = H$_2$O, ($\Delta H = -242 \text{ kJ/h}$)

Figure 4 Heat balance in the steam reforming of natural gas by TNR method under a steady state reaction operation

Reactor diameter 5.0 cm, Length of catalyst bed 10 cm, Vol. of catalyst 196 ml, Size of catalyst: 2.4–4.0 mm, Feed gas: Natural gas 23.48%, O$_2$ 15.0%, H$_2$O 61.5%, SV 203,800 h$^{-1}$, Pressure 0.77 MPa, Temperature at the catalyst-bed entrance 407°C, Conversion of C$_2$ – C$_4$ 100%, Conversion of CH$_4$ in the natural gas 92.8%, H$_2$ Space-time yield (STY) 4,730 mol/l/h, CO STY 1,440 mol/l/h, CO$_2$ STY 974 mol/l/h
and furnace to provide the heat.

**POR:** Partial oxidation of the hydrocarbons is conducted using catalytic combustion catalysts such as gauze-shaped Pt-Rh wires with extremely short (m-sec order) contact time, but combustion of some parts of hydrocarbon fed and once produced H₂ and CO cannot be eliminated and therefore, selectivities to obtain objective H₂ and CO are apt to decrease.

**ATR:** Even the most advanced auto thermal reforming, in principally, the rate of catalytic partial oxidation is limited up to around 1,100°C by heat elevation due to the limit of transformation temperature of the catalyst supports. As the result, space velocity cannot increase so much, in other wards, the catalyst volume cannot decrease so much.

**TNR:** On the other hand, in thermo-neutral reforming, by the catalytic combustion theoretically or imaginary, catalyst-bed temperature elevates as high as 3,000°C, however, in practically, the catalyst-bed temperature forced decrease by the large endothermic heat of the steam reforming and as the results, catalyst-bed temperature can be maintained proper and safe temperature range. As the result, the reactor size can be reduced two orders of magnitude compared with the traditional steam reformers.

In Figure 6) the reactor sizes of these typical four kinds of reformer are comprehensively compared with key conditions, and these figures evidently show the big difference of each technology.

By realization of the TNR reforming, there are many tasks towards the mid-stream of petroleum industry can be designed. In the Middle East countries, the special fortunate conditions should be taking account as follows; overwhelming amount of fissile fuel can convert natural gas or syngas to
valuable compounds very cheaply, world cheapest cost of ethylene production enables to convert ethylene to valuable compounds easily, world cheapest cost of methanol and/or dimethyl ether production enables to convert them to valuables very efficiently, and abundant production of LPG and naphtha enables those hydrocarbon conversions efficiently.

3.2. New Usage of Cheap Hydrogen and/or Syngas as the Most Fundamental Ultra Clean Fuels for Fuel Cells

First of all, the effect of hydrogen production itself can be anticipated as indicated in Figure 7\textsuperscript{17}. Cheap hydrogen produced by the TNR method would have high potential to supply to a variety of the petroleum refinery processes. As for fuel cell use, including fuel cell cars, the minimized size of the reformer can be applied very smartly. Actually, in Japan LPG-based TNR reformer is applying to the PEFC towards the application of co-generation systems of 1 kW scale for domestic use\textsuperscript{18}. Also CO\textsubscript{2}-TNR reforming of a variety of the fuel sources can be designed successfully to the application of high-temperature fuel cells, because these fuel cells, not only hydrogen but also CO can be used as the fuel for the fuel cells\textsuperscript{7}.

3.3 New Synthesis Routes of Ultra Clean Fuels Using Cheap Hydrogen and/or Syngas with Novel Catalysts

Next, as shown in Figure 8\textsuperscript{17}, the building blocks for petrochemicals and/or ultra clean liquid fuels can be produced much more efficiently by applying the TNR technology associated with each
Cheap and pure hydrogen and/or syngas produced by TNR method

Hydrocracking and hydrotreating processes in Petroleum refinery

Cogeneration systems for the use of domestic and/or residence assembly (1 – 25 kW) with high temperature fuel cells such as PEFC

Combined electric power generation systems (100 – MkW) with high temperature fuel cells such as SOFC, MCFC

Fuel cell cars equipped the liquid-fuel reformer

Figure 7  New usages of cheap and pure hydrogen and/or syngas produced by TNR method as the most fundamental ultra clean fuels
Figure 8  New synthesis routes of ultra clean fuels adopting novel catalysts
novel catalyst for each compound synthesis\textsuperscript{19}. New catalysts developed in Kyoto University can be applied to each process. As for example, it should be considered the possible change in GTL process. Now the term GTL is very popular. GTL is abbreviation of “Gas To Liquids synthesis \textit{via} syngas formation by reforming and successive Fisher-Tropsh synthesis or MeOH and/or DME syntheses”. As compared in Figure 9\textsuperscript{17}, so-called Mobil MTG process has been operated a quarter century ago in New Zealand based on the great innovation of ZSM-5 zeolite catalyst. This Zeolite of Socony Mobil Number 5 produced aromatic-rich high octane-number gasoline from methanol and dimethyl ether synthesized from natural gas \textit{via} steam reforming. However, the major part of the production cost depended on the process of steam reforming of natural gas to convert syngas.

Now main rout of GTL uses partial-oxidation reforming of natural gas instead of steam reforming, like as the project of Oryx GTL by Shell group at Qatar, Sasol/Chevron project at Nigeria, and Shell/NPC project at Iran. It can be seen in the comparison of Figure 9, the reactor size of the natural gas reforming reduced very much by applying partial oxidation reforming, but still the conventional Fischer-Tropsh synthesis needs considerable large volume of the reactors and optional equipments. On the other hand, an ultimate GTL process can be illustrated in the light-hand side of this figure. When TNR reactor will be adopted as the steam reformer, it will be able to reduce into extremely small size, and moreover successive reactors using newly developed catalysts will be applied, then the total system become very compact size and the total efficiency will be optimized, and the cost of the process could be minimized.

A Cu-based Cu-Zn-Cr-Al-Ga mixed oxide catalyst was prepared by uniform gelation method,
which was mixed with Pd supported alumina calcined at 1,060°C. The composite catalyst exhibited activity much higher than that of conventional catalyst prepared by precipitation method, and

![Diagram of gasoline synthesis from carbon oxides via methanol as intermediate product using reactors connected in series](image)

Figure 10  Gasoline synthesis from carbon oxides via methanol as intermediate product using reactors connected in series

space-time yields of methanol amounted to 6,620 and 1,410 g/l/h, from CO-rich and CO₂-rich syngases under conditions of 80 atm, at 290°C and 270°C, respectively. Finally, all of the products, obtained CO-rich or CO₂-rich and the syngases, were introduced into the reactor, which was connected in series, and the methanol was totally converted into hydrocarbons. As shown in Figure 10(19), in case of H-Ga-silicate catalyst, gasoline was obtained in space-time yields of 1,860 and 308 g/l/h, at selectivity of 63 and 54%, respectively from the CO-rich and the CO₂-rich syngas.

3.4 New Synthesis Routes of Ultra Clean Fuels Using Cheap Light Olefins with Novel Catalyst

The major starting materials for matured modern petrochemical industries consist of light olefins and simple aromatics. Light olefins are produced by thermal cracking of various resources formed in refinery processes, natural gas and petroleum-associated gas. For many industrialized countries, in which olefin production depends on petroleum, after the oil crisis investigation of new synthetic routes of light olefins from alternative resources becomes urgent and significant. Therefore, syngas conversion on various modified FT synthesis-type catalysts, oxidative coupling of methane, and methanol conversion by using zeolite catalysts had been conducted. Among these various kinds of reaction routes, methanol conversion on zeolite catalysts seems to be the most promising due to its high selectivity to olefins. In deed using H-Fe-silicate and Ni-SAPO-34, methanol could converted to ethylene, propylene and butens very selectively and efficiently(20).

The ultra rapid conversion of light olefins such as ethylene, propylene, and butens to gasoline
achieved using Fe-silicate having a pentasil pore-opening structure\textsuperscript{10).}

The Fe-silicates were prepared using a novel rapid crystallization method by replacing the Al ingredient in ZSM-5 with Fe salt at the gel formation stage. Different from other kinds of metallosilicates, the Fe-silicate were highly effective for selective formation of liquid products in the

Table 1 Comparison of product distribution between those of directly connected 1\textsuperscript{st} and 2\textsuperscript{nd} reactors in conversion of propylene

<table>
<thead>
<tr>
<th>Distribution (wt%)</th>
<th>1\textsuperscript{st} reactor H-Fe-silicate</th>
<th>2\textsuperscript{nd} reactor Pt(1.0)/MFI-type Non-metal silicate</th>
<th>2\textsuperscript{nd} reactor 0.5wt%/Pt H-Al-beta</th>
<th>2\textsuperscript{nd} reactor 0.5wt%/Pt(imp.)/Mesoporous silicate</th>
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<td>C\textsubscript{1}</td>
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<td>C\textsubscript{2}</td>
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<td>C\textsubscript{3}</td>
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<td>14.09</td>
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<tr>
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<td>C\textsubscript{5,8} Naphtene</td>
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<td>5.64</td>
<td>6.11</td>
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<td>6.86</td>
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<td>5.92</td>
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</table>

gasoline fraction. For example, 95.6% propylene fed was converted under the space velocity of 4,500 h\textsuperscript{-1} and at 300°C to the liquid products with a space-time yield as high as 8.09 kg/l/h. The octane-number of the gasoline produced was as high as 95 because of the high percentage of branched internal-olefins found in the liquid products. The Fe-silicate exhibited high activity and selectivity under various conditions, and maintained its steady performance at least 100 h on stream.

The olefin-rich gasoline produced by light olefin conversion on the MFI-type H-Fe-silicate packed in the first-stage reactor was successively converted to the isoparaffin-rich gasoline on various Pt-modified catalysts packed in the second-stage reactor\textsuperscript{12).} The results are shown in Table 1\textsuperscript{19).} The Pt supported by an incipient impregnation method on a nonmetal silicate showed a lower dispersion and lower hydrogenation activity. Although the dispersion of Pt in Pt-ion-exchanged H-ZSM-5 (Pt/H-Al-silicate) was higher than that of Pt-modified nonmetal silicate, the selectivity to iso-paraffins in the gasoline range was lower owing to the hydrogenolysis and isomerization of iso-paraffins to n-paraffins. Since nonmetal silicate possess a very small number of strong acid sites, the very strong catalytic activities of Pt and/or Pt/zeolite were moderated, and the undesirable reactions like hydrogenolysis proceeded minimally. Consequently, MFI-type nonmetal silicate modified with a small amount of Pt by means of adsorption treatment (almost same procedure as the ion-exchange
method) showed a higher dispersion of Pt, and was the most effective in the hydrogenation of olefins in the gasoline range even at very low temperatures in the range of 100 -150°C.

3. Conclusion

In the Middle East countries, such as Saudi Arabia have begun 2nd phase development in petroleum industry with focusing the downstream. Imbalance and inconsistency between the upstream and the downstream would exhibit explicitly, if appropriate improvements towards the midstream will be not adopted. The singular-point technology, such as TNR, enables it and extends a great influence in the midstream. All these new factors inevitably depend on the development of novel catalysts and their using technologies.

Acknowledgments

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