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Highly effective conversion of carbon dioxide to valuable compounds on composite catalysts

T. Inui

Division of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University, Sakyo-ku, Kyoto 606-01, Japan

Abstract

The highly effective catalytic conversion of CO_2 into valuable compounds was investigated by multi-functional catalysts composed of base-metal oxides as the main components promoted by a low concentration of precious metals and gallium oxide. The desired reduced state of catalyst metal oxides for exhibiting the optimum catalytic performance could be controlled by both the hydrogen spillover on the precious metal parts and the inverse-spillover from the Ga parts. By applying those principal concepts in the catalyst structure-design, the rapid CO_2 reforming of methane, the rapid CO_2 methanation, the effective synthesis of methanol and/or ethanol from CO_2 and H_2, and selective syntheses of high quality gasoline and/or light olefins by means of one-pass conversion of CO_2–H_2 mixture via methanol as the intermediate product, were respectively realized. Those novel catalytic reactions would have a high potential to moderate the accumulation of CO_2 come from fossil fuel combustion, while compensating the cost of hydrogen as the reducing reagent.

Keywords: precious metals catalysts; CO_2 catalytic conversion

1. Introduction

Carbon dioxide is the final oxidation product of organic compounds and, therefore, CO_2 itself has little value, and in order to obtain new products by means of the CO_2 reduction, the large amount of additional energy, in particular expensive hydrogen gas is necessary. In this context, a considerable number of scientists have considered that the catalytic hydrogenation of CO_2 is almost nonsense, if the objective is in mitigation of CO_2 accumulation in the atmosphere of globe. However, the catalytic hydrogenation of CO_2 is superior to other chemical conversion methods for CO_2 as the following advantageous features. Namely, CO_2 can be converted with an extremely higher rate on the well designed solid catalysts than other chemical conversion methods and desired highly valuable compounds can be synthesized very selectively on those catalysts. Moreover, the highly concentrated CO_2 in flue gas, which comes out from large facilities in the electric power generation plants, the steel industry, the petroleum industry and the cement industry, occupies about one third of total CO_2 emission by fossil fuel combustion.

The largest problem in the catalytic hydrogenation would be concentrated in the effective and economic production method of the huge amount of H_2 as the reducing reagent for CO_2. The thermal decomposition of water by the high temperature supplying from the furnace for the nuclear fuel and the electrolysis of water by the

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electricity generated by the water-power generation system and the solar cell, would be realized far and near futures, respectively, and they still have much problems to be solved. The most practical new production method of H_2, which could be developed within a short period is considered that the innovation in the catalyst technology of the conventional industrial method.

In this study, then the highly active Ni-based composite catalyst which works at much lower temperatures than that of the conventional catalyst was developed. Since the novel catalyst has high activity for not only steam-reforming but also CO_2-reforming of methane, H_2 for CO_2 hydrogenation could be replaced by CH_4 and H_2O. In this study, the focus has been concentrated to the CO_2 reduction by H_2 or CH_4 to synthesize highly valuable major building blocks for petrochemical industries such as ethylene, propylene, methanol, ethanol, aromatic hydrocarbons, and high quality gaseous and liquid fuels such as substituted natural gas and high octane-number gasoline. These high value products have a potential to compensate the cost of reducing reagents, hydrogen or methane, and these CO_2-conversion routes lead to a new system for chemical industries and energy usage cycles in many fields.

2. Rapid CO_2-reforming of methane

The major conventional production method of H_2 is the steam reforming of saturated hydrocarbons, on the stabilized Ni catalyst, in which Ni is sintered to stabilize and supported on the ceramic carrier having a very low surface area, and the reaction is operated at a high temperature around 900°C. Since the coke deposit owing to the decomposition of hydrocarbon is unavoidable, and in order to moderate the coke deposit, a larger concentration of steam than that needed from the reaction stoichiometry is added in the feed [1]. Consequently, an excess energy to evaporate water is needed and economic load in the process is heavy and the objective reaction is markedly retarded by the predominant covering of coke on the most active sites. Furthermore, the activity is so low that CO once formed by Eq. (1) is successively converted into CO_2 reacting with the excess H_2O by the water gas shift reaction (Eq. (2)).

$$CH_4 + H_2O \rightleftharpoons 3H_2 + CO \quad + 221.8\,\mathrm{kJ/mol}\ (500^\circ\mathrm{C}) \tag{1}$$

$$CO + H_2O \rightleftharpoons H_2 + CO_2 \quad - 37.1\,\mathrm{kJ/mol}\ (500^\circ\mathrm{C}) \tag{2}$$

$$CH_4 + 2H_2O \rightleftharpoons 4H_2 + CO_2 \quad + 184.7\,\mathrm{kJ/mol}\ (500^\circ\mathrm{C}) \tag{3}$$

As the conventional catalyst has no ability for CO_2 activation, CO_2 once formed by the reaction (2) cannot convert to other molecules by both the inverse reaction of Eq. (2) and CO_2-reforming of methane (Eq. (4)).

$$CH_4 + CO_2 \rightleftharpoons 2H_2 + 2CO \quad + 258.9\,\mathrm{kJ/mol}\ (500^\circ\mathrm{C}) \tag{4}$$

It seems to be in contradiction that in order to obtain H_2 for CO_2 hydrogenation, the fuel is necessary to maintain the high reaction temperature and CO_2 is additionally produced as the by-product. However, if by the innovative improvement in catalyst structure, on which no coke deposit occurs and exhibits a very high reaction rate even at the medium temperature range around several hundred °C. The heat to maintain that medium-range temperature could be supplied by the waste heat of large scale facilities of industries. Furthermore, the large endothermic heat of reaction could be supplied on-site by the catalytic combustion of a part of methane fed.

A number of researches on CO_2-reforming has been done recently, and reviewed by Nakamura and Uchijima [2] for example. However, many of them [3–8] were concerned with the comparison in catalytic properties of various single component supported metal or metal oxide catalysts and the effect of the sort of support materials upon the performance of catalytic reaction, and the focus was not in the rapid catalytic reaction. As for the rapid catalytic reaction, Huff et al. [9] addressed the importance of the experiment and analysis in ms order catalytic partial oxidation of methane and light paraffins.

In the present study, for the rapid synthesis of hydrogen through methane reforming, the synergistic effect of composite catalysts and the combined reactions to compensate the large amount of endothermic heat were investigated.

A Ni-based three-component catalyst such as Ni–La_2O_3–Ru or Ni–Ce_2O_3–Pt supported on alumina-wash-coated ceramic fiber in a plate shape [10] was very suitable for both reactions. The catalyst composition was set at 10 wt.-% Ni, 5.6 wt.-% La_2O_3 and 0.57 wt.-% Ru for example, or molar ratios of these components were 1:0.2:0.03. Even with such a low concentration, the precious metal enhanced the reaction rate markedly and this synergistic effect was ascribed to the hydrogen spillover effect through the part of precious metal and it resulted in a more reduced surface of the main catalyst component. In particular, a marked enhancement in the reaction rate of CO_2-reforming of methane was observed by the combination of a low concentration Rh to the Ni–Ce_2O_3–Pt catalyst. Very high space-time yields of H_2 (i.e., 8300 mol/l h in partial oxidation of methane at 600°C with a methane conversion of 37.5% and 3585 mol/l h in CO_2 reforming of methane at 600°C with a methane conversion of 58%) were realized in those reactions. By combining the catalytic combustion reaction, methane conversion to syngas was markedly enhanced, and even with a very short contact time (10 ms) the conversion of methane increased more than that at 50 ms. The space-time yield of hydrogen amounted to 2780 mol/l h with a methane conversion of 90% at 700°C. Furthermore, in a reaction of CH_4–CO_2–H_2O–O_2 on the four components catalyst, an extraordinarily high space-time yield of hydrogen, 12 190 mol/l h, could be realized under the conditions of very high space velocity (5 ms) [11].

3. Rapid CO_2-methanation

Since in CO_2 methanation, the inverse reaction of the reaction (3), H_2 is needed four times of CO_2, it seems to be disadvantageous from the view points of energy and economical consideration. However, as far as it is known the formation rate of methane by catalytic hydrogenation of CO_2 can be realized far beyond all other methods for chemical conversion of CO_2. The large consumption of hydrogen per unit CO_2 mole corresponds to that the accumulation of internal energy into methane molecules is large and the methane synthesized by hydrogenation of CO_2 is expected as the transportation media of the energy injected to the reaction. When the rapid CO_2 methanation progress at a low temperature range around 250–450°C, the large exothermic reaction heat itself can be used and, furthermore, when the methane formed is used as the fuel, a high temperature even 1000°C can be obtained. Therefore, it is thought that the rapid CO_2-methanation is significant as one kind of the chemical heat pump, by which a low temperature, i.e., a low-value energy, can be transformed into a high temperature, i.e., a high-value energy, through chemical reactions.

We have studied on the CO_2 methanation since 1970's, and developed the Ni-based three components composite catalyst supported on the spherical silica support having meso–macro bimodal pore structure [12]. The catalyst contained La_2O_3 by 1/5 mol of Ni, and Ru by 1/30 mol of Ni. The Ni–La_2O_3–Ru catalyst exhibited the high conversion rate to synthesize methane exclusively, and the catalyst made possible the CO–CO_2 co-methanation [13]. The cause of the high performance was elucidated as follows; the adsorption capacity of catalyst for CO_2 was increased by the weak basicity of La_2O_3, and hydrogen adsorption was markedly enhanced by combining Ru, which worked as the porthole of hydrogen spillover. The meso and macro bimodal pore structures have the roles of the supported bed for catalytic substances and the pass for quick diffusion of the reactants, respectively [14]. In order to apply this catalyst to much higher space velocity of the reaction gas, we have investigated the catalyst support and the reaction devises and succeeded to increase CO_2 methanation rate up to extraordinary high levels [15] as described below. In order to reduce the resistance to high flow rates of reaction gases, Fiberfrax (FF), produced by Toshiba Monoflax Co. Ltd., was adopted as the catalysts support. This support is formed in a plate shape of 1 mm thickness with ceramic fibers of ca. 5–10 μm in diameter and has a void space of 88%. Before impregnation of the catalyst components, Fiberfrax was coated with fine silica spherical particles of ca. 6–7 nm in diameter by 17.8 wt.-% to increase the surface area as the catalyst support. Nickel-based three-component catalyst 13.9 wt.-% Ni–3.4 wt.-% La_2O_3–0.4 wt.-% Ru was prepared by the stepwise supporting method [16]. The catalyst in sheet shape was cut in three kinds forms, doughnut type (10 mm outer diameter, 4.3 mm inner diameter; 5 sheets were used), rectangle type (10 mm width and 32.0 mm length), and cross plate type (1 mm width, 16.8 mm length, 2 sheets were crossed). The catalyst sheet volume was 0.32 ml irrespective of the catalyst type. The catalysts were packed to the pyrex glass tubular reactor of 10 mm inner diameter. The reaction gas composed of 12% CO_2, 88% H_2 was allowed to flow at 10 l/h and 50 l/h. The space velocities corresponded to 31 000 and 156 000 h^{-1}, respectively, on the basis of the total catalyst sheet volume. When the space of super macro channel of the catalyst sheet was eliminated in the calculation, i.e., on the basis of the net catalyst volume, these space velocities were 226 300 h^{-1} (or contact time 16 ms) and 1 138 800 h^{-1} (or contact time 3.2 ms), respectively. The three types of catalyst bed gave the largely different results as summarized in Table 1. The effect of mixing diffusion was remarkable in case of the cross type configuration of the catalyst packing compared with the others. When the SV was 226 300 h^{-1}, the CO_2 conversion reached as high as 96%, and at the very high SV 1 138 800 h^{-1} the CO_2 conversion at 450°C remained 67%, suggesting that the rate determined step was in the diffusion step. The corresponding space-time conversion of hydrogenation was 15 388 mol/l h.

4. Effective methanol synthesis from CO_2 and H_2

In methanol synthesis by CO_2 hydrogenation, one oxygen remains in the objective product (methanol), therefore, it is regarded as the equivalent of the hydrocarbon synthesis from syngas, from the view point of energy balance. The demand of methanol is now increasing and it would be possible to use as not only the fuel but also the alternative starting raw materials for the matured petrochemical industry, because methanol can be converted into a variety of important compounds. Methanol is now producing from syngas with large scale by using the Cu–Zn oxides-based precipitated catalysts. However, when the catalyst uses as it is to the

Table 1
Comparison of space-time yield for different types of catalyst shape in CO_2 methanation at extremely higher space velocities

	Space-time yield of methane (mol/l h)					
Net SV (h^{-1})	226 300			1 138 800		
Type of catalyst bed	Reaction temperature (°C)					
	300	400	450	300	400	450
Doughnut × 5	204	708	810	350	1591	1905
Rectangle	387	993	1015	358	2497	2825
Cross	672	1175	1205	971	3416	3847

CO_2 hydrogenation, the yield of methanol is much lower than that obtained from syngas conversion under the same temperature and pressure conditions. The equilibrium value for methanol synthesis from CO_2 is about one third, and moreover, below ca. 250°C the yield of methanol hardly reaches to the equilibrium [17].

Recently, a hundred papers concerned with methanol synthesis from CO_2–H_2 mixture have been presented, and the results were reviewed by Saito [18] and Ohyama [19]. In our study [17,20,21], Cu–Zn–Cr–Al mixed oxides catalyst was prepared by the uniform gelation method, in which the concentrated nitrate solution of the four components was changed into gel by the contact of NH_3 vapor and, followed by drying, thermal decomposition, calcination and hydrogen reduction. The catalyst exhibited 50% higher activity for methanol synthesis from CO_2 than the catalyst which was prepared by the conventional precipitation method [21].

The methanol synthesis activity was enhanced by the combination of La_2O_3 [17] and Pd or Ag [20]. The reasons of those improvements were considered as the weak basicity to increase of the adsorption capacity for acidic CO_2 and the effect of hydrogen spillover through the part of Pd or Ag, respectively. The hydrogen spillover gives an influence not only on the transportation rate of hydrogen as the reactant but also on the control of the reduction state of the catalyst surface during the reaction. On the other hand, Saito et al. found out the good effect of Ga_2O_3 combination to Cu–Zn oxides catalyst [18]. On the other hand, we have recognized through the investigation of paraffin aromatization that Ga ingredient has a catalytic property for an inverse spillover of hydrogen. In our most recent study [22], both effects, spillover effect with Pd and inverse-spillover effect with Ga, were then combined with an anticipating that the both effects could maintain with a good balance for the desired proper reduced state of the catalyst during the reaction giving the maximum methanol yield. The effect of Ga_2O_3 addition to the four component catalyst (Cat. 1); Cu–ZnO–Cr_2O_3–Al_2O_3 (38.1, 29.4, 1.6, 30.9 wt.-%), by substituting Ga_2O_3 for Al_2O_3 was investigated. The catalyst was calcined at 350°C for 10 min and reduced at 400°C for 30 min by H_2 diluted with N_2. The addition of Ga_2O_3 markedly enhanced the methanol synthesis activity and retarded the CO formation. When Ga_2O_3 added by 17.8 wt.-%, a very high space-time yield (STY) of methanol, 1483 g/l h, was obtained at 290°C with a CO_2 conversion to methanol 25.1% (Fig. 1). It is suggested that, from judging the decrease of CO selectivity, the Ga_2O_3 added plays the role of hydrogen inverse-spillover and excessive reduction of the catalyst surface is avoided. Effect of the calcination temperature was then tested. As shown in Table 2, in spite of the large decrease of BET surface area by 600°C calcination (Cat. 4), the

Table 2
Performance of Ga and Pd combined catalyst for methanol synthesis from CO_2

Cat.	Calcination T (°C)	BET surface area (m^2/g)	CU dispersion [a] (%)	Reaction T (°C)	CO_2 conversion to			MeOH STY (g/l h)
					MeOH	CO	H.C.	
3	350	114	5.4	250	13.7	2.7	0.0	810
				270	19.6	2.7	0.1	1158
4	600	46	4.3	250	12.8	3.3	0.0	756
				270	21.3	3.3	0.0	1261
5	Pd modifiedCat. 4	38	3.5	250	19.2	3.0	0.1	1135
				270	22.0	3.9	0.2	1300

Composition of catalysts 3 and 4; Cu:ZnO:Cr_2O_3:Al_2O_3:Ga_2O_3 = 38.1:29.4:1.6:13.1:17.8 (wt.-%), catalyst 5 was catalyst 4 modified with 1 wt.-% Pd by physical mixing of Pd/γ-alumina.

[a] Estimated by N_2O adsorption, Pressure 80 atm, SV 18800 h^{-1}.

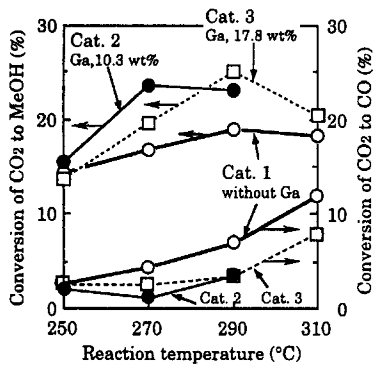

Fig. 1. Effect of Ga_2O_3 addition to the four component catalyst. Cat. 1: $Cu:ZnO:Cr_2O_3:Al_2O_3$ = 38.1:29.4:1.6:30.9 (wt.-%), BET surface area 172 m^2/g, Cu dispersion 7.3%, Cat. 2: $Cu:ZnO:Cr_2O_3:Al_2O_3:Ga_2O_3$ = 38.1:29.4:1.6:20.6:10.3, BET surface area 141 m^2/g, Cu dispersion 3.7%, Cat. 3: $Cu:ZnO:Cr_2O_3:Al_2O_3:Ga_2O_3$ = 38.1:29.4:1.6:13.1:17.8, BET surface area 114 m^2/g, Cu dispersion 5.4%, 80 atm, SV = 18 800 h^{-1}.

activity and STY of methanol rather increased at a higher reaction temperature indicating that the density of the effective active sites increases by the decrease of the surface area. The Pd modification to Cat. 4 enhanced the catalytic

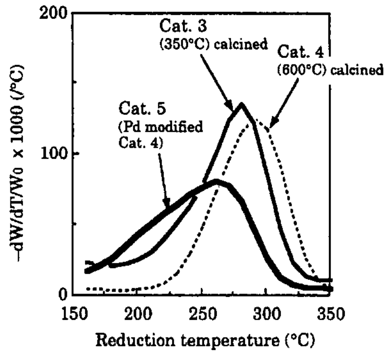

Fig. 2. TPR profiles for the catalysts appeared in Table 2.

activity, in particular at a lower temperature range indicating the effect of hydrogen spillover through Pd. The temperature-programmed reduction (TPR) profiles for catalysts 3, 4 and 5 are shown in Fig. 2. The effect of the higher temperature calcination and the Pd modification on the catalytic performance mentioned above are consistent with the features of the TPR profiles.

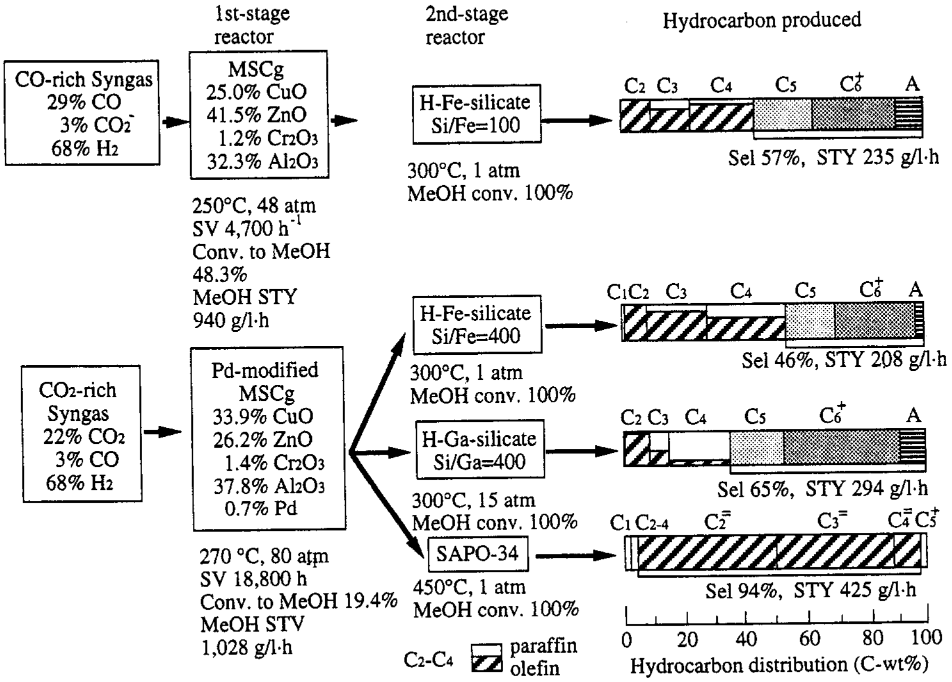

Fig. 3. Hydrocarbon synthesis from syngases having different content of carbon oxides using two-stage series reactor packed different type of catalysts.

5. Effective alcohol synthesis from CO_2–H_2 mixture

Ethanol is produced industrially by hydration of ethylene using a phosphoric acid type catalyst with a space-time yield of ethanol around 0.2 kg/l h. If ethanol could be directly produced by CO_2 hydrogenation with a comparable yield of the conventional method, it would have a potential as one of the alternative new route of ethanol synthesis. A number of studies on ethanol synthesis from syngas has been carried out. However, ethanol synthesis from CO_2 has not been studied extensively as reviewed by Arakawa and Okamoto [23]. They introduced themselves their results on K-modified Cu–Zn–Fe and Rh–Li catalysts.

Independently, we have studied on the subject by our intrinsic principle for the catalyst design without use of expensive precious metals, Rh, Ru and Ir as the main catalyst component. Two kinds of catalytic functions, i.e., carbon–carbon formation and hydroxyl group formation after partial reduction of CO_2 to CO were combined by using an iron-based catalyst composed of Fe:Cu:Al:K = 1:0.03:2:0.7 atomic ratio and Cu–Zn based catalyst composed of Cu:Zn:Al:K = 1:1:1:0.1, respectively. Both catalysts were prepared by the uniform gelation method [24] and the optimum composition of both catalysts were separately decided by varying the composition and evaluated their performance by the yield of ethanol from CO_2 and H_2. The effect of the method of combination of both catalysts on the catalytic performance was compared among (1) physical mixing, (2) mixing of the stage of mixed gels for both catalysts and (3) simultaneous gelation. The methods (1) and (2) gave similar results and they were better than that obtained on the catalyst prepared by method (3). In Table 3, the results [25] obtained by the composite catalyst prepared by method (1) are presented.

The selectivity to ethanol should be improved much more, however, the space-time yield of ethanol is rather higher than the expected value.

6. Selective synthesis of light olefins and gasoline from CO_2–H_2 mixture by one-pass conversion via methanol synthesis

The classical Fischer–Tropsch synthesis catalysts such as Co-based and Fe-based catalysts produce a variety of hydrocarbons and oxygen-containing compounds, which obey the Shultz–Flory polymerization law and when those kinds of catalyst use for CO_2 hydrogenation, only methane can be obtained, especially in higher CO_2 conversion levels. The zeolite ZSM-5 is used for Mobil MTG process to produce aromatic-rich gasoline with light paraffinic hydrocarbons from methanol. When ZSM-5 is used for the conversion of methanol formed from syngas or CO_2–H_2 mixture, only a very little gasoline fraction is obtained [17,20,26]. This is ascribed to the intrinsic property of H-ZSM-5, i.e., the strong hydrogen-shift function and consequently intermediate olefins easily hydrogenated into light saturated hydrocarbons before

Table 3
Results of ethanol synthesis from CO_2 and H_2 on the Fe–Cu-based composite catalystSVCO_2

SV (h^{-1})	CO_2 Conv. (%)	Selectivity (C-mol-%)					STY (g/l h)	
		EtOH	MeOH	Oxy. [a]	H.C. [b]	CO	EtOH	EtOH + MeOH
5000	27.5	16.7	15.6	8.43	45.0	14.2	58.7	129
20000	42.3	10.6	7.36	4.58	66.4	11.1	231	441

[a] Oxygen containing compounds, methyl acetate is the major component.

[b] Hydrocarbons obeying S–F-polymerization law.

Catalyst prepared by physical mixing of the two types catalyst with equivalent weight.

Reaction temperature 310°C, Reaction pressure 80 atm.

oligomerized to gasoline range fraction. Only the hydrogen inactive shape-selective microporous crystalline catalyst such as H/Fe-silicate having MFI (ZSM-5) structure [20] and the similar MFI-type metallosilicate which has the hydrogen inverse-spillover function such as H/Ga-silicate [27] have a potential to produce gasoline fraction with a higher selectivity. For the selective olefin synthesis, weak acidic narrow pore microporous crystalline catalyst such as SAPO-34 [28] would be suitable, on which olefin oligomerization could not occur due to its weak acidity and ethylene and propylene could be obtained exclusively. The results are summarized in Fig. 3.

In case of the CO-rich syngas, methanol could be synthesized under rather moderate reaction conditions on the methanol synthesis catalyst (MSCg). The methanol formed was totally converted in the 2nd-stage reactor packed with H/Fe-silicate at 300°C to a gasoline fraction with 57% selectivity, and 235 g/l h space-time yield [29]. The contents of this gasoline fraction were mainly iso-mono-internal olefins, and other products also still ca. C_2–C_4 olefins, which is markedly different from the results obtained by using H-ZSM-5.

Even in case of the CO_2-rich syngas, it is noteworthy that methanol could be synthesized rather higher space-time yield than from CO-rich syngas by using Pd-modified MSCg and at somewhat higher temperature and pressurized conditions. As shown in Fig. 3, by selecting the sort of catalysts and corresponding reaction conditions, gasoline and light olefins could be synthesized respectively with very high selectivities and space-time yields [30].

7. Conclusion

The significance and the practical improvements in catalyst behaviors for the CO_2 hydrogenation to obtain the valuable compounds, such as methane, methanol, ethanol, ethylene, propylene and gasoline were described. The rapid hydrogen production by the CO_2-reforming will support realization of the CO_2-hydrogenation mentioned above. Especially, the development of new usage routes for methanol synthesized by CO_2 hydrogenation with a large amount and the reorganization of the system of the energy use in large scale industry will be necessary to realize the new system for the CO_2 valorization.

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