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Structure and function of Cu-based composite catalysts for highly effective synthesis of methanol by hydrogenation of CO_2 and CO

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Abstract

A highly effective catalytic conversion of CO_2 and CO into methanol has been investigated by the multi-functional catalysts composed of Cu–Zn oxides as the main components with the modification of a low concentration of precious metals and gallium oxide. The desired reduced state of the catalyst metal oxides for exhibiting the optimum catalytic performance could be controlled by both the hydrogen spillover through the precious metal parts and the inverse-spillover from the Ga parts. As a result, an extraordinary high space-time yield of methanol, 1300 g/l · h, could be realized under conditions of 270°C, 80 atm, SV 18 800 h^{-1} with 22.0% CO_2 conversion to methanol. Furthermore, the catalyst also exhibited a very high performance in CO hydrogenation, and gave a space-time yield of methanol as high as 6340 g/l · h under conditions of 270°C, 80 atm, SV 37 600 h^{-1} with 39.4% CO conversion to methanol.

Keywords: Cu-based composite catalysts; CO_x hydrogenation; Methanol synthesis; Pd- and Ga-modification; Spillover; Inverse-spillover

1. Introduction

Carbon dioxide is the final combustion product of organic compounds, and, therefore, CO_2 itself has little value, and in order to obtain new products by chemical reduction, the large amount of additional energy, in particular expensive hydrogen 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 far 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 such as electrochemical, photochemical, and biochemical 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, is considered as the object of hydrogenation.

In methanol synthesis by CO_2 hydrogenation, one oxygen remains in the objective product (methanol), therefore, it is regarded as equivalent of the hydrocarbon synthesis from syngas, from the view point of energy balance. The

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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 a large scale by using the Cu–Zn oxides-based precipitated catalysts. However, when the catalyst is used as it is to the CO_2 hydrogenation, the yield of methanol is much lower than that obtained from syngas conversion under the similar reaction conditions. The equilibrium value for methanol synthesis from CO_2 is about one third that from CO, and moreover, below circa 250°C the yield of methanol hardly reaches to the equilibrium [1].

Recently, a hundred papers concerned with methanol synthesis from CO_2–H_2 mixture have been presented, and the results were reviewed by Saito [2] and Ohyama [3]. The Cu–Zn oxides-based catalysts have been widely investigated and modified with various metal oxides such as Zr [4–8], Cr [9], Ce [10], V [7,11], Ti [12,13], etc.; however, most of the catalysts used were prepared by the conventional precipitation method. On the other hand, in our study [1,14,15], Cu–Zn–Cr–Al mixed oxides catalysts had been prepared by our intrinsic uniform gelation method [16], and this catalyst exhibited 50% higher activity for methanol synthesis from CO_2 than the catalyst which was prepared by the conventional precipitation method [15]. The methanol synthesis activity was markedly enhanced by the combination of La_2O_3 [1] and Pd [14,17–19] or Ag [14]. The reasons of those improvements were considered as the weak basicity to increase in the adsorption capacity for 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 proper transportation rate of hydrogen as the reactant but also on the control of the intermediate oxidation state of the catalyst surface during the reaction giving the highest space-time yield of methanol. Recently, Saito et al. found out a good effect of Ga_2O_3 combination to Cu–Zn oxides catalyst for methanol synthesis from CO_2 [2,19]. Independently, we have accumulated the knowledge on the catalytic property of Ga ingredient, i.e., inverse spillover of hydrogen, through a sequential studies on aromatization of paraffinic hydrocarbons [20,21].

In this study, therefore, both effects, the spillover effect with Pd and the inverse-spillover effect with Ga, were then combined with an expecting that the both effects could maintain with a good balance for the desired proper state of the catalyst during the reaction giving the maximum methanol yield not only from CO_2 but also from CO.

2. Experimental

2.1. Catalyst preparation

Methanol synthesis catalysts (MSCg) were prepared by a newly developed our intrinsic uniform gelation method [16]. A mixed oxide catalyst composed of Cu-oxide, Zn-oxide, Cr-oxide and Al-oxide, which are widely known as the typical low-temperature active catalysts for methanol synthesis from syngas, was basically adopted. Mixed hydroxides prepared by the ordinary precipitation method from a multicomponent mixed metal-salts solution is apt to involve heterogeneities in their physical properties, and then catalytic properties, because of their different equivalent electric points. Moreover, during the course of washing of the precipitates with excess water to remove the alkaline ions used as the precipitating reagent, often mutual segregation among the mixed hydroxides would occur. To avoid the occurrence of this kind of heterogeneities, we adopted the uniform gelation method [16] for the formation of mixed hydroxides. The preparation procedure of a standard catalyst (Cat. 1) in detail was as follows; a 30 ml portion of the concentrated mixed aqueous solution contained of 7.24 g $Cu(NO_3)_2 \cdot 3H_2O$, 5.37 g $Zn(NO_3)_2 \cdot 6H_2O$, 0.42 g $Cr(NO_3)_3 \cdot$

$9H_2O$ and 11.37 g $Al(NO_3)_3 \cdot 9H_2O$ was put in an enamelled flat vat of 20 cm × 15 cm area and 3 cm height. This was placed at a larger enamelled flat vat of 40 cm × 35 cm area and 6 cm height for ca. 10 min until the pH of the mixture became 6.5–7. In this flat vat, 25% NH_3 aqueous solution had been spread by 3 mm depth and kept 60°C. The upper side of the flat bat was covered with a glass plate to prevent the vaporization of NH_3 and H_2O during the gel formation. With this treatment whole the mixed solution was transformed into a uniform gel. For the preparation of Cat. 2–4, $Ga(NO_3)_2 \cdot 8H_2O$ was introduced at the stage of gel formation instead of a determined amount of $Al(NO_3)_3 \cdot 9H_2O$. This was dried at 120°C overnight in an electric oven, and then crushed to the powder form. This was put in a porcelain boat and placed in a tubular Pylex glass of 20 mm inner diameter. It was heated in a stream of dried air with a flow rate of 100 ml/min, from room temperature up to 150°C, and then up to 350°C with a constant heating rate of 4°C/min and 1.7°C/min, respectively. It was maintained at 350°C for 3 h. Only Cat. 4 was calcined at 600°C for 30 min. By this treatment ammonium nitrate formed and partly unconverted metal nitrate were decomposed and afforded the mixed metal oxides of prescribed composition. The washing process was thus eliminated.

Moreover, in order to promote the catalytic activity, a small amount of precious metals were combined with MSCg with expecting the effect of hydrogen spillover, which could be seen in syngas to methanol conversion [22], on keeping an optimum oxidation state of the catalyst during the reaction. The precious metal is often effective and favourable as a porthole for hydrogen spillover when the metal particles are located at the vicinity of the main catalyst components of metal oxides but in isolation, and when the precious metals exist as a considerably larger particle size like 30 Å or more to keep their more reduced metallic state [22–24]. Therefore, the combination of precious metals with MSCg was conducted through simple physical mixing method. Pd was supported on a γ-alumina by an incipient impregnation method. The Pd-supported γ-alumina was heated in an air stream at 350°C for 10 min, and then treated in a stream of 10% H_2–90% N_2 at 400°C for 30 min before mixing with MSCg. 89.6 wt% Cat. 4 and 10.4 wt% Pd/γ-alumina were mixed manually for 15 min using a porcelain mortar of 8 cm in a diameter. The Pd content in the Cat. 5 (Pd/γ-alumina + Cat. 4) was set in 1 wt%.

2.2. Characterization

A TG-DTA Shimadzu Thermal analyzer DT-30 was used to measure the temperature programmed reduction (TPR). The catalyst sample was heated in 4% H_2–96% N_2 with a constant heating rate of 10°C/min.

2.3. Reaction method and analysis of product

The calcined mixed oxide was tabletted by using a tablet machine in a size of 6.0 mm in diameter and 5.0 mm height. The tablets were crashed and sieved to a range of 10 to 24 mesh to provide the reaction. Before use for the reaction, the catalyst was reduced in situ in a stream of 1% H_2 diluted with N_2 at a flow rate of 4700 h^{-1}, expressed as space velocity, from room temperature up to 250°C for 60 min and at that temperature for 4 h.

The reactor was stainless steel tube of 8 mm inner diameter and 60 cm length of heating zone. The reaction was operated under the following range of conditions; temperature: 230–310°C, pressure: 80 atm, space velocity 18 800 h^{-1} and 37 600 h^{-1}, and reaction gas: 3% CO–22% CO_2–75% H_2 for the CO_2-rich syngas conversion reaction and 30% CO–3% CO_2–67% H_2 for the CO-rich syngas conversion reaction. A portion of total reaction product was analyzed by three gas chromatographs equipped with integrators. H_2, CO and CO_2 were analyzed by the thermal-conductivity detector (TCD) with a column of activated charcoal. Methanol and dimethyl ether were analyzed by the flame ionization detector (FID) with a column of Porapack-T. Hydrocarbons were analyzed by FID with a column of OV-101 silicone.

3. Results and discussion

3.1. CO_2-rich syngas conversion

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 on the synthesis of methanol was investigated in the case of CO_2-rich reaction gas conversion, and the results are shown in Fig. 1. The addition of Ga_2O_3 markedly enhanced the methanol synthesis activity and retarded the CO formation. When Ga_2O_3 was added by 17.8 wt% (Cat. 3), a very high space-time yield (STY) of methanol, 1,483 g/l · h, was obtained at 290°C with a CO_2 conversion to methanol 25.1%.

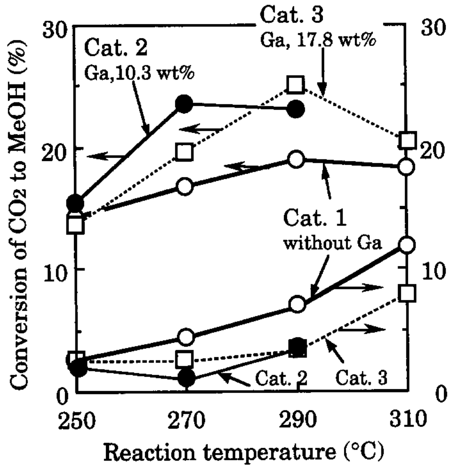

Fig. 1. Effect of Ga_2O_3 addition to the four component catalyst on the CO_2-rich syngas conversion. Cat. 1, Cu: ZnO: Cr_2O_3: Al_2O_3 = 38.1: 29.4: 1.6: 30.9 (wt%), BET surface area 172 m^2/g, Cu dispersion 7.3%; Cat. 2, Cu:ZnO:Cr_2O_3:Al_2O_3:Ga_2O_3 = 38.1:29.4:1.6:20.6:10.3, BET surface area 141 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%; Reaction gas 3% CO–22% CO_2–75% H_2, Pressure 80 atm, SV 18 800 h^{-1}.

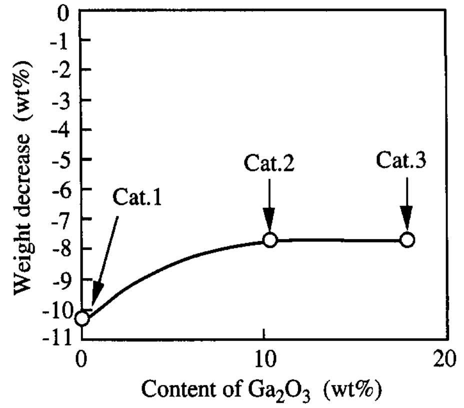

Fig. 2. Effect of Ga_2O_3 content on the decrease in catalyst weight measured by TPR.

The function of Ga_2O_3 part [2,19–21], could be considered as the controlling role of the oxidation state of copper component as the major catalyst part, because Ga has a property of inverse spillover of hydrogen. As shown in Fig. 2, the decrease in catalysts weight (Cats. 1–3) measured by temperature programmed reduction (TPR) of Cu-oxide parts in the catalysts decreased by the addition of Ga_2O_3 in the case of Cat. 2 and 3. It is suggested that from judging the decrease in CO selectivity in CO_2 hydrogenation (Fig. 1) and the weight decrease by reduction (Fig. 2), the Ga_2O_3 added plays the role of hydrogen inverse-spillover and excessive reduction of the catalyst surface would be avoided.

Effect of the calcination temperature was then tested. As shown in Table 1, in spite of the large decrease of BET surface area by 600°C calcination (Cat. 4), the activity and STY of methanol rather increased at a higher reaction temperature indicating that the density of the effective active sites increases by the contraction of the bulk of mixed metal oxides. The Pd modification to Cat. 4 enhanced the catalytic 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. 3. The Cu-oxide parts in Cat. 4 (Cat. 3 calcined at 600°C) was reduced at higher

Table 1
Performance of Ga and Pd combined catalyst for methanol synthesis from CO_2

Cat.	Calcination Temp. (°C)	BET surf. area (m^2/g)	Cu dispersion * (%)	Reaction Temp. (°C)	CO_2 conv. 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 modified Cat. 4	38	3.5	250	19.2	3.0	0.1	1135
				270	22.0	3.9	0.2	1300

Composition of Cats. 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%), Cat. 5; Cat. 4 was modified with 1 wt% Pd by physical mixing of Pd/γ-alumina, * estimated by N_2O adsorption, 3% CO–22% CO_2–75% H_2, Pressure 80 atm, SV 18,800 h^{-1}.

temperature than the Cat. 3, and the reduction peak was markedly shifted to lower temperature range for the Cat. 5 (Pd-modified Cat. 4). 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.

3.2. CO-rich syngas conversion

The syngas (including 3% CO_2) conversion reactions were investigated by using the Cats. 1, 3 and 5, and the result are shown in Fig. 4. Cat. 5 (modified with both Ga_2O_3 and Pd) showed a higher CO conversion involving of both CO conversions to methanol and dimethyl ether than Cats. 1 and 3 at above 290°C. As shown in Fig. 4, Cats. 1 and 3 showed a high selectivity to methanol, on the other hand, it decreased on the Pd-modified catalyst (Cat. 5), and dimethyl ether increased markedly. Since a γ-alumina was used as the support of Pd, and the fraction of γ-alumina in the Cat. 5 was higher than other catalysts. When the concentration of methanol produced was high, the formation of dimethyl ether by dehydration of methanol on the acid sites of γ-alumina considerably proceeded. There is a possibility that the amount of Brönsted acid sites increased by enhancement of hydrogen transfer by the spillover [25] to the γ-alumina surface through the Pd particles combined.

Since the CO conversion was ultimately limited by the equilibrium level for all the catalysts

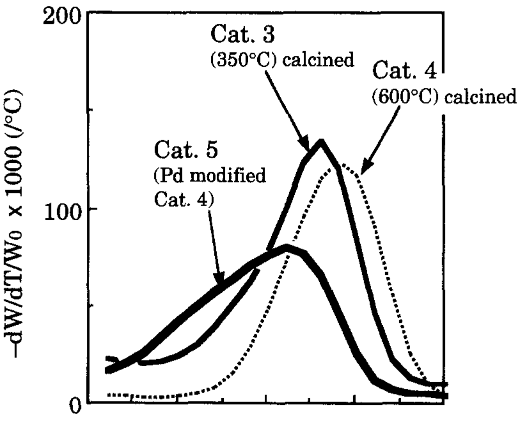

Fig. 3. TPR profiles for the catalysts given in Table 1.

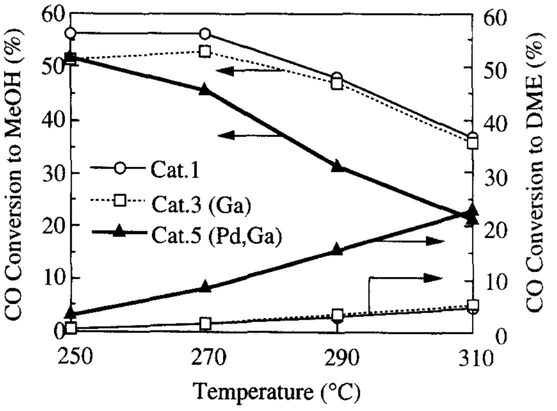

Fig. 4. Effect of modification with Pd and Ga_2O_3 on the CO-rich syngas conversion to methanol and dimethyl ether. Reaction gas 30% CO–3% CO_2–67% H_2, Pressure 80 atm, SV 18800 h^{-1}.

under a SV 18 800 h^{-1}, the effect of modification with Ga_2O_3 and Pd on the CO conversion hardly appeared. Therefore, in order to clarify the effect of modification with Ga_2O_3 and Pd, the CO-rich syngas conversion reaction was investigated under a higher SV condition (37 600 h^{-1}) and in Fig. 5 the results are compared with that of the lower SV condition (18 800 h^{-1}). Under the lower SV, the effect on CO conversion was not obvious, although Cat. 5 showed a slightly higher CO conversion only at higher temperature range above 290°C. The CO conversion on the non-modified four component catalyst (Cat. 1) decreased about 20% in the whole range of temperature tested. On the other hand, on Cat. 5, the high CO conversion was maintained at the high temperature range above 290°C even under the higher SV condition. The lower CO conversion at 230°C on the Cat. 5 could be due to the higher fraction of γ-alumina, i.e., lower fraction of methanol synthesis catalyst. As a result, the effect of Ga_2O_3 and Pd combination evidently appeared under the higher SV at around 290°C, and consequently, the yield of methanol and dimethyl ether markedly increased.

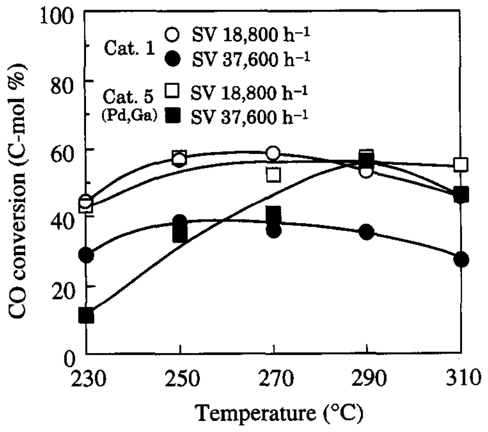

Fig. 5. Effect of space velocity in CO-rich syngas conversion on the Pd–Ga modified and non-modified catalysts. Reaction gas 30% CO–3% CO_2–67% H_2, Pressure 80 atm, SV 18 800 and 37 600 h^{-1}.

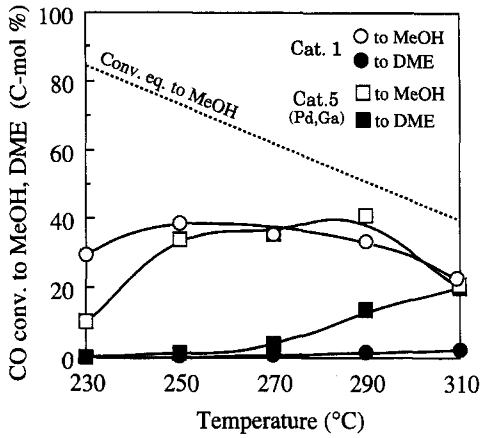

Fig. 6. Effect of modification with Pd and Ga_2O_3 on the CO-rich syngas conversion to methanol and dimethyl ether under a higher SV condition. Reaction gas 30% CO–3% CO_2–67% H_2, Pressure 80 atm, SV 37 600 h^{-1}.

Fig. 6 shows the CO conversion to methanol and dimethyl ether on the Cats. 1 and 5 under the higher SV (37 600 h^{-1}). The CO conversion to methanol on Cat. 5 was almost same as that on the Cat. 1, except only at lower temperature (230°C). Although the formation of dimethyl ether was partly due to the acid sites of γ-alumina, the effect of Ga_2O_3 and Pd combination was remarkable at the higher temperature range. In particular, the sum of CO conversion to methanol and dimethyl ether on Cat. 5 exceeded the equilibrium conversion to methanol at above 290°C.

Fig. 7 more clearly shows the influence of SV in CO-rich syngas conversion to methanol and dimethyl ether on the Ga_2O_3 and Pd modified catalyst (Cat. 5). Under SV 10 400 h^{-1}, the formation of dimethyl ether markedly increased with increase in reaction temperature, and accordingly, the selectivity to methanol was lower than that of higher SVs above 290°C. However, the formation of dimethyl ether decreased with increase in SV, and the high selectivity to methanol was maintained at higher temperature range. The CO conversion to methanol under lower SV (10 400 h^{-1}) was very close to equilibrium level at lower temperature range. The CO conversion to methanol was lowered by increase in SV to 37 600 h^{-1} at lower tempera-

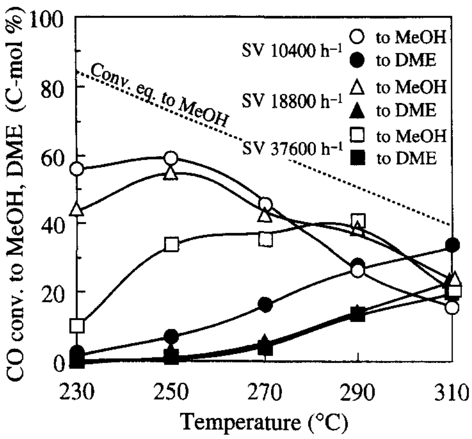

Fig. 7. Influence of SV in CO-rich syngas conversion on the Pd–Ga_2O_3 co-modified catalyst (Cat. 5). Reaction gas 30% CO–3% CO_2–67% H_2, Pressure 80 atm, SV 10400, 18800 and 37600 h^{-1}.

ture range. However, the high CO conversion to methanol and dimethyl ether was maintained at higher temperature range. The formation of dimethyl ether gave the increasing of CO conversion to methanol in case of CO-rich syngas conversion reaction, because the equilibrium limit of CO conversion to methanol could be relieved by the dimethyl ether formation.

Table 2 shows a space-time yield (STY) of methanol and dimethyl ether on the Cat. 5 in the CO-rich syngas reaction. It is noteworthy that a surprising high methanol STY, 6340 g/l · h, was obtained at 270°C with a CO conversion 41.1%. Moreover, the sum of space-time yield (STY) of both methanol and dimethyl ether reached the highest value (6490 g/l · h) at 290°C with a CO conversion 44.3% under the condition of SV 37600 h^{-1}. Consequently, not only for the CO_2-rich syngas conversion but also the CO-rich syngas conversion, it was clarified that the activity of methanol synthesis catalyst was largely promoted by simultaneous modification with Ga_2O_3 and Pd.

4. Conclusions

For the methanol synthesis from CO_2, the catalytic activity was enhanced by the combination of Ga_2O_3 and Pd, which are possessing an ability of depression of excessive reduction of the catalyst surface by hydrogen inverse-spillover and hydrogen spillover, respectively. Although the selectivity to methanol decreased with increase in the formation of dimethyl ether in the case of CO conversion, the prominent effect of modification with both Ga_2O_3 and Pd was also confirmed, especially under the higher SV condition.

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Table 2

Influence of SV on performance of Ga_2O_3 and Pd combined catalyst for methanol synthesis from CO-rich syngas

SV (h^{-1})	Temp. (°C)	CO conv. (%)	Selectivity to (C-mol%)				STY (g/l · h)	
			MeOH	DME	H.C.	CO_2	MeOH	MeOH + DME
18800	250	55.0	94.2	6.2	0.4	−0.8	4180	4380
	270	56.3	81.4	15.3	0.9	2.4	3690	4190
	290	52.9	59.6	29.8	1.9	8.7	2540	3460
37600	250	31.8	99.0	1.3	0.1	−0.4	5080	5110
	270	41.1	95.8	4.1	0.4	−0.3	6340	6440
	290	44.3	87.3	10.5	0.9	1.3	6220	6490

Reaction gas 30% CO–3% CO_2–67% H_2, pressure 80 atm.

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