

The optimization of methanol yield in direct selective oxidation of methane with O₂ and NO in the presence of Cu-ZnO/Al₂O₃

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Abstract

Cu-ZnO/Al₂O₃ catalyst was examined for the enhancement of methanol selectivity in the products of the direct selective oxidation of methane with O₂ and NO in the gas-phase. The precise study of effects of reaction pressures and CH₄/O₂ ratio on the yield of CH₃OH was performed with the Cu-ZnO/Al₂O₃ catalyst. The yield of CH₃OH had a maximum value at 0.4 MPa and CH₄/O₂ = 8.0. The yield of CH₃OH was enhanced with the Cu-ZnO/Al₂O₃ catalyst in all of the examined regions. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Direct oxidation of methane to C₁-oxygenates (methanol and formaldehyde) with oxygen is a potentially important process not only for the effective use of natural gas resources, but also for minimization of energy consumption. Various researches of non-catalytic or catalytic oxidation of methane to oxygenates have been carried out since early last century, but the main products were still carbon oxides [1–4]. The rate-determining step of the direct selective oxidation of methane is the first hydrogen abstraction from

methane. Therefore, many researches using initiators or sensitizers have been carried out in order to reduce the activation energy of the first hydrogen abstraction from methane. NO_x ($x = 1, 2$) has been reported as an effective initiator for the activation of methane [5–9]. Recently, Teng et al. [10] and Tabata et al. [11] systematically examined the effects of variation of reaction conditions on the yield of C₁-oxygenates in gas-phase selective oxidation of methane with O₂ and NO_x ($x = 1, 2$). The selectivity of both methanol and formaldehyde depended strongly on their reaction conditions, i.e. NO_x concentration, CH₄/O₂ ratio in the feed gas and space velocity (SV), these two C₁-oxygenates were always observed more or less in all the examined regions. It is quite worthwhile to control the selectivities of methanol and formaldehyde in the products for the application to a practical process for the gas-phase selective oxidation of methane.

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Very recently, we tried to enhance the selectivity of methanol in the products using a Cu-ZnO based catalyst in addition to the gas-phase selective oxidation of methane with O₂ and NO [12–14]. Both CH₃OH and CH₂O were observed as C₁-oxygenates at 550 °C in the gas-phase selective oxidation of methane with O₂ and NO, but only CH₃OH was observed in the products as C₁-oxygenate in the presence of Cu-ZnO/Al₂O₃ catalyst at 250 °C in addition to the gas-phase reaction at 550 °C. We suggested that the formation of CH₃OH through the hydrogenation of CH₂O and the water gas shift reaction (WGSR) of CO-H₂O progressed simultaneously on the Cu-ZnO/Al₂O₃ catalyst [12]. Furthermore, we suggested that the complete exhaustion of oxygen in the region of gas-phase reaction was a key for the effective use of the Cu-ZnO/Al₂O₃ catalyst. All the reactions were carried out at 0.5 MPa so as to use up oxygen during the gas-phase reaction. The highest yield of CH₃OH was around 1.6% at 0.5 MPa in the presence of Cu-ZnO/Al₂O₃ catalyst, and this value was smaller than that of total oxygenates (ca. 6%) at 0.1 MPa in the absence of the catalyst [10]. The higher ratio of CH₄/O₂ in the feed gas (CH₄/O₂ = 13.3) at 0.5 MPa in comparison to the ratio at 0.1 MPa (CH₄/O₂ = 2.0) was assumed to retard the yield of CH₃OH in the products. This higher value of CH₄/O₂ was selected so as to avoid explosions.

We consider that the precise study of variation effects of reaction pressures and CH₄/O₂ ratio on the yield of CH₃OH is worthwhile for enhancing the CH₃OH selectivity. We therefore examine the catalytic performance of Cu-ZnO/Al₂O₃ catalyst under various reaction pressures and CH₄/O₂ ratios so as to optimize methanol yield.

2. Experimental

2.1. CH₄-O₂-NO reaction

Highly purified methane (>99.9995%), oxygen (>99.9999%), and 3.0% NO (Ar balance) were mixed with argon (>99.9999%). The standard feed gas composition (CH₄, 77.5%; O₂, 5.8%; NO, 0.5%; Ar, 16.2%) was controlled with a mass flow controller. A quartz tube (7 mm i.d.) was mounted inside of a stainless tube (13.8 mm o.d.) in order to minimize the

effects of reactor wall. This quartz tube was heated for the gas-phase selective oxidation of methane with an electric furnace from the outside of the stainless tube, the length of the heated zone was 100 mm. The temperature of gas-phase reaction was measured at the center part of the electric furnace with a thermocouple, which was mounted at the center part of the reactor. The thermocouple was covered with a quartz tube (3 mm o.d.) so as to avoid any reactions on the surface of the thermocouple. The same Cu-ZnO/Al₂O₃ catalyst in the previous work [12] was used. The catalyst was mounted at 150 mm downstream from the end of the heater. The temperature of catalyst was measured from the outside of the reactor with a thermocouple. The temperature of the mounted catalyst was less than 150 °C during the gas-phase reaction at 550 °C. We prepared the second heater and controlled the temperature of the catalyst at 250 °C. The length of this heater was 100 mm.

We used mechanical seals for connecting the quartz tube and the stainless one, avoiding direct contact between reaction gas and the stainless tube. Flow rate of feed gas was stabilized at 120 ml min⁻¹ (SV = 15700 h⁻¹). The SV was calculated by dividing the gas flow volume per 1 h at 25 °C and atmospheric pressure by the volume of the catalyst (0.5 g). The mixed gas was fed from the bottom side of the reactor. Products were analyzed with two on-line gas chromatography. CO, CO₂, ethane, ethene, CH₂O, CH₃OH and nitromethane were detected with FID (Gaskuropack 54) using a methanator. Methane, hydrogen and oxygen were detected with TCD (activated carbon). Carbon balance between the reactants and the products exceeded 95%. Every feed gas was mixed just before the inlet of the reactor. All of the gas lines from the exit of the reactor up to the gas chromatograph were heated at 120 °C in order to avoid condensation. All the experiments were repeated at least three times to check the reproducibility. The deviation of experimentally obtained results was less than ±1%.

2.2. Characterization of Cu-ZnO/Al₂O₃ catalyst

The procedures of characterization of Cu-ZnO/Al₂O₃ were performed in the same manner as reported in the previous paper [12]. The atomic ratio of Cu:Zn:Al of the sample was measured by energy-dispersion X-ray spectroscopy (EDX,

KEVEX, Sigma). BET specific surface area was determined by N_2 adsorption at 77 K. XRD (powder X-ray diffraction) patterns were recorded by X-ray diffractometry (RINT 2000, Rigaku) using $Cu\ K\alpha$ radiation. The surface of sample was examined by X-ray photoelectron spectroscopy (XPS, ESCA-3200, Shimadzu) with an $Mg\ K\alpha$ X-ray source operating at 8 kV and 20 mA. The $Cu\ 2p$, $Zn\ 2P$, $Al\ 2p$, $O\ 1s$ and $C\ 1s$ levels' spectra were investigated and their binding energies were calibrated using the main peak of the $C\ 1s$ level spectrum of contaminated carbon at 284.8 eV as an internal reference.

3. Results and discussion

3.1. Characterization of $Cu-ZnO/Al_2O_3$

The atomic proportion of $Cu:Zn:Al$ in the bulk of the obtained sample was 39.7:40.8:19.5, respectively. The specific surface area was $68.7\ m^2\ g^{-1}$. Several peaks assignable to ZnO and CuO and some other peaks were observed in the XRD pattern of the untreated sample, showing that the sample was a mixture. The surface atomic ratio of Cu/Zn was calculated from the ratio of the peak area of the $Cu\ 2p$ level and that of the $Zn\ 2p$ level in XPS [12], using the set of elemental sensitivity factors of the equipment. The ratio of Cu/Zn was 0.88. We reported the change of the catalyst surface

observed by XPS [13]. The spectra of $Cu\ 2p$ showed the amount of $Cu(I)$ increased at the expense of $Cu(II)$ after the reaction. We assumed that the active site was the reduced copper species on ZnO .

3.2. The effects of reaction pressures on CH_4 activation and C_1 -oxygenates selectivity in the absence of $Cu-ZnO/Al_2O_3$ catalyst

The increase of reaction pressures lowered the initiation temperature of methane activation in the selective oxidation of methane with O_2 and NO (Fig. 1). This enhancement of methane activation under a higher reaction pressure was similar to that reported in the gas-phase selective oxidation of methane with O_2 [2]. The leveling-off of methane conversion around 6% shows that all of the oxygen in a feed gas ($CH_4/O_2 = 13.3$) was used up at around these reaction temperatures. The obtained selectivity of total C_1 -oxygenates and the ratio of CH_3OH/C_1 -oxygenates in the products was shown as functions of reaction pressures (Fig. 2). We measured the selectivity of C_1 -oxygenates under the conditions where O_2 conversion exceeded 99%. The ratio of CH_4/O_2 was kept constant at 13.3. All conversions were included in the region of 5.3–5.7%. C_1 -oxygenates selectivity was raised in a lower region than 1.0 MPa, and it had a maximum value

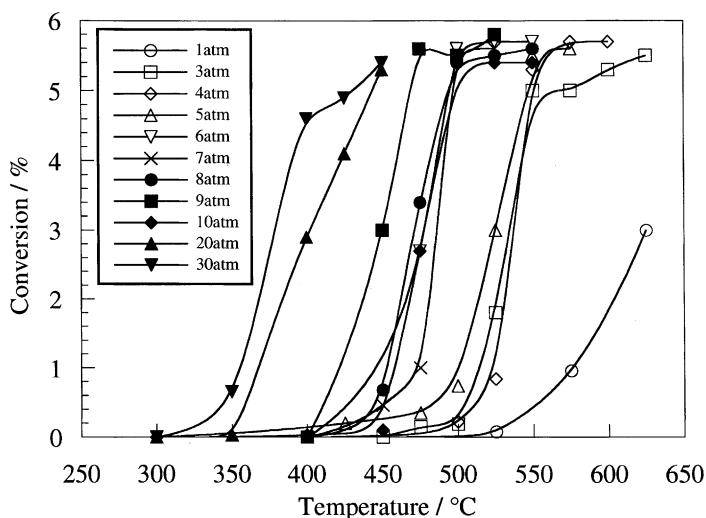


Fig. 1. Effects of reaction pressures on CH_4 conversions in the absence of the $Cu-ZnO/Al_2O_3$ catalyst. Feed gas composition: CH_4 , 77.5%; O_2 , 5.8%; NO , 0.5%; Ar , balance; and flow rate: $120\ ml\ min^{-1}$.

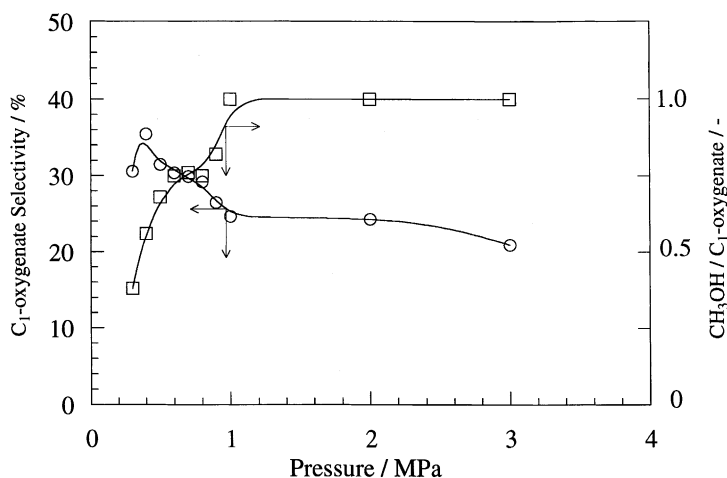


Fig. 2. Effects of reaction pressures on C₁-oxygenates selectivities and the ratio of CH₃OH to C₁-oxygenates in the absence of the Cu-ZnO/Al₂O₃ catalyst. Feed gas composition: CH₄, 77.5%; O₂, 5.8%; NO, 0.5%; Ar, balance; and flow rate: 120 ml min⁻¹; gas-phase reaction temperatures: 625 °C (0.3 MPa), 575 °C (0.4 MPa), 550 °C (0.5 MPa), 525 °C (0.6–1.0 MPa), 450 °C (2.0 and 3.0 MPa), respectively. All of the O₂ conversions were higher than 99%. All of the CH₄ conversions were in the range of 5.3–5.7%.

at 0.4 MPa. The decrease of C₁-oxygenate selectivity at 0.3 MPa could be derived from its higher reaction temperature (625 °C), the reaction at 0.4 MPa was conducted at 575 °C. In contrast, the ratio of CH₃OH/C₁-oxygenates decreased in the same region. This means the selectivity of CH₂O increased in this region. The increase of CH₂O selectivity in a lower pressure region was also reported by Arutyunov et al. in the selective oxidation of methane with O₂ [2].

3.3. The effects of reaction pressures on the selectivities of products in the presence of Cu-ZnO/Al₂O₃ catalyst

All of the product selectivities at our reaction pressures are examined in the presence and absence of the Cu-ZnO/Al₂O₃ catalyst were listed in Table 1. The catalyst temperature was kept constant at 250 °C because the selectivity of produced CH₃OH had a maximum

Table 1

The effects of reaction pressures on the selectivities of products in the presence and absence of Cu-ZnO/Al₂O₃^a

Number	Pressure (MPa)	Temperature (°C)	Catalysis (g)	Conversion (%)		Selectivity (%)						
				CH ₄	O ₂	CH ₃ OH	CH ₂ O	CO	CO ₂	C ₂ H ₄	C ₂ H ₆	CH ₃ NO ₂
1	0.4	575	0 ^b	5.5	99	20	15.5	58.9	4.8	0	0.5	0.3
2	0.4	575	0.5	5.5	99.7	32.1	0	51.8	15.2	0	0.5	0.4
3	0.5	550	0 ^b	5.5	99	21.4	10.1	63.3	4.4	0	0.8	0
4	0.5	550	0.5	5.4	99.5	28.8	0.1	60.2	9.5	0	1	0.4
5	0.6	525	0 ^b	5.6	99	22.9	7.5	59.9	5.6	0.5	0.5	3.2
6	0.6	525	0.5	5.5	99.7	26.1	0	58.7	14	0	0.8	0.4
7	1	525	0 ^b	5.4	99.5	24.7	0	65.5	5.2	0	4.2	0.4
8	1	525	0.5	5.6	99.7	24.7	1.8	59.7	8	0.3	4.3	1.2
9	2	450	0 ^b	5.3	99.7	24.3	0	59.9	8	0.1	3.7	4
10	2	450	0.5	5.4	99.6	25.4	0	56	13.7	0.9	2	2
11	3	450	0 ^b	5.4	99.4	20.9	0	60.4	12.6	0.6	3.4	2.1
12	3	450	0.5	5.5	99.7	24.5	0	55.9	15.1	0.4	1.2	2.9

^a Catalyst, Cu:Zn:Al = 39.7:40.8:19.5, flow rate: 120 sccm, reaction time: 180 min, catalysts bed temperature: 250 °C and feed gases composition: CH₄, 77.5%; O₂, 5.8%; NO, 0.5%; Ar, 16.2%.

^b In the absence of Cu-ZnO/Al₂O₃ catalyst.

value at around 250 °C in our previous work [12]. The conversions of CH₄ were around 5.5% irrespective of whether the catalyst was present or not. All the oxygen in the feed gas was used up in the presence of the Cu-ZnO/Al₂O₃ catalyst. The selectivities of CH₃OH and CO₂ in the products were raised in the presence of the Cu-ZnO/Al₂O₃ catalyst, while those of CH₂O and CO decreased in the presence of the catalyst.

Concerning the increase of CH₃OH selectivity, we confirmed the presence of hydrogenation reaction between the produced CH₂O and H₂



on the Cu-ZnO/Al₂O₃ catalyst from both experimental results and theoretical calculations of thermodynamic equilibrium values [12]. Concerning the production of H₂ in Eq. (1), we suggested the coexistence of the WGS between CO and H₂O on the Cu-ZnO/Al₂O₃ catalyst from the experiments between CO and H₂O.

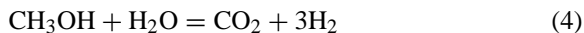


Furthermore, we also suggested the dissociation reaction of CH₂O on the catalyst as follows:



3.4. The effects of catalyst temperatures on the selectivities of products

Fig. 3 shows the effects of catalyst temperatures on the selectivities of products at 0.4 MPa in the presence of Cu-ZnO/Al₂O₃ catalyst because the selectivity of CH₃OH had a maximum value at 0.4 MPa in Table 1. The reaction conditions other than pressure and temperature were the same as those in Table 1. The conversions of O₂ exceeded 99% at any temperature. CH₂O was hardly observed in all of the examined regions. CH₃OH selectivity increased up to 250 °C, then decreased. CO selectivity slightly decreased with increase of catalyst temperatures, and decreased remarkably over 300 °C. CO₂ selectivity rapidly increased over 250 °C. Breen et al. [15] reported that the reactivity of the steam reforming of methanol over the Cu-ZnO/ZrO₂/Al₂O₃ catalyst was raised over around 350 °C. We assumed that the steam reforming reaction between the produced CH₃OH and H₂O on Cu-ZnO/Al₂O₃ progressed over 250 °C at 0.4 MPa.



Figs. 4–6 show the effects of catalyst temperatures on the selectivities of CH₃OH, CO and CO₂, respectively. The reaction conditions other than

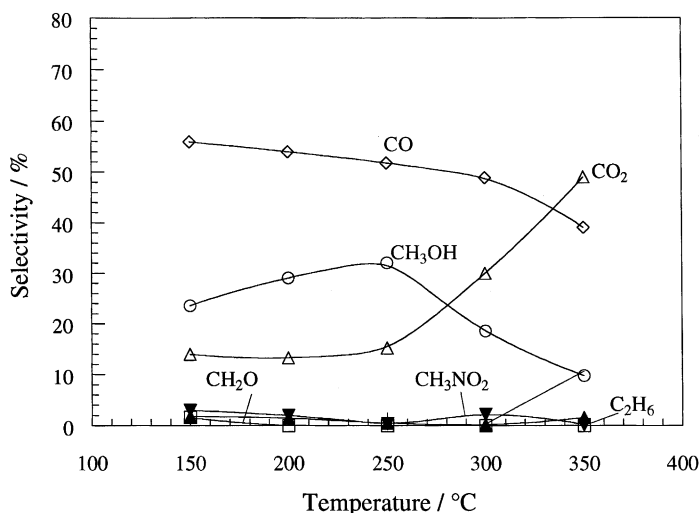


Fig. 3. Effects of catalyst temperatures on the selectivities of products at 0.4 MPa in the presence of the Cu-ZnO/Al₂O₃ catalyst. Feed gas composition: CH₄, 77.5%; O₂, 5.8%; NO, 0.5%; Ar, balance; flow rate: 120 ml min⁻¹; and gas-phase reaction temperatures: 575 °C, respectively. All of the O₂ conversions were higher than 99%. All of the CH₄ conversions were in the range of 5.5–5.7%.

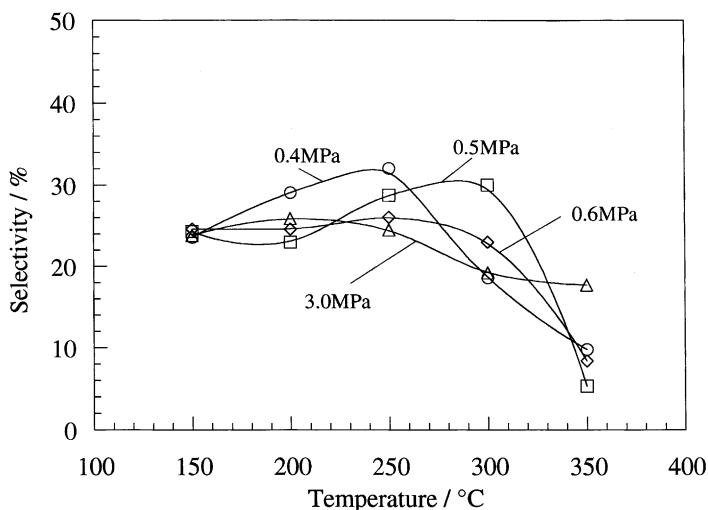


Fig. 4. Effects of catalyst temperatures on CH₃OH selectivity at 0.4 MPa in the presence of the Cu-ZnO/Al₂O₃ catalyst. Feed gas composition: CH₄, 77.5%; O₂, 5.8%; NO, 0.5%; Ar, balance; flow rate: 120 ml min⁻¹; and gas-phase reaction temperatures: 575 °C (0.4 MPa), 550 °C (0.5 MPa), 525 °C (0.6 MPa), 450 °C (3.0 MPa), respectively. All of the O₂ conversions were higher than 99%. All of the CH₄ conversions were in the range of 5.3–5.7%.

pressure were the same as those in Fig. 3. CH₃OH selectivity increased up to 250 °C at 0.4 MPa (Fig. 4). This increase of CH₃OH selectivity in a lower temperature region was suppressed under a higher pressure. The decrease of CH₃OH selectivity in the

region over 250 °C was clearly observed but this decrease was mitigated under a higher pressure. These results show that not only the hydrogenation reaction of CH₂O, but also the steam reforming reaction was retarded in a higher pressure region. The maximum

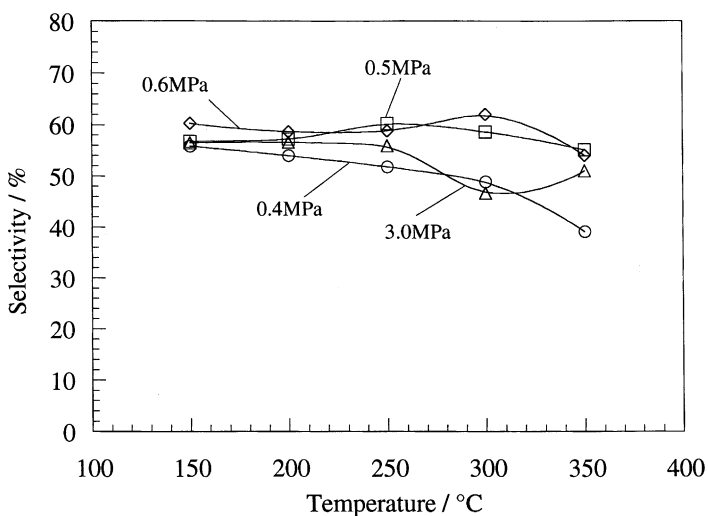


Fig. 5. Effects of catalyst temperatures on CO selectivity at 0.4 MPa in the presence of the Cu-ZnO/Al₂O₃ catalyst. Feed gas composition: CH₄, 77.5%; O₂, 5.8%; NO, 0.5%; Ar, balance; flow rate: 120 ml min⁻¹; and gas-phase reaction temperatures: 575 °C (0.4 MPa), 550 °C (0.5 MPa), 525 °C (0.6 MPa), 450 °C (3.0 MPa), respectively. All of the O₂ conversions were higher than 99%. All of the CH₄ conversions were in the range of 5.3–5.7%.

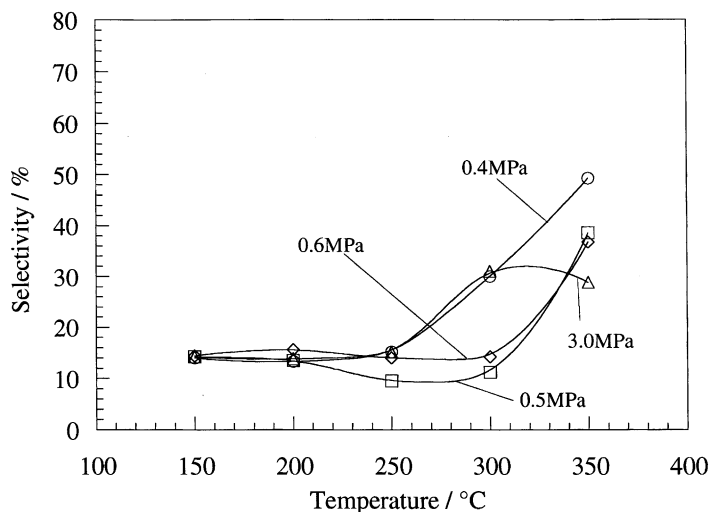


Fig. 6. Effects of catalyst temperatures on CO₂ selectivity at 0.4 MPa in the presence of the Cu-ZnO/Al₂O₃ catalyst. Feed gas composition: CH₄, 77.5%; O₂, 5.8%; NO, 0.5%; Ar, balance; flow rate: 120 ml min⁻¹; and gas-phase reaction temperatures: 575 °C (0.4 MPa), 550 °C (0.5 MPa), 525 °C (0.6 MPa), 450 °C (3.0 MPa), respectively. All of the O₂ conversions were higher than 99%. All of the CH₄ conversions were in the range of 5.3–5.7%.

value of CH₃OH selectivity (32.1%) was obtained at 0.4 MPa and at 250 °C.

The variations of CO selectivities were not clear in all the examined reaction temperatures and pressures (Fig. 5). This means that the effects of catalyst temper-

atures and pressures on the CO related reactions, i.e. Eqs. (2) and (3) were small in the examined region.

As mentioned above, the steam reforming reaction was favorable over 350 °C. The variation of CO₂ selectivities increased in that region (Fig. 6). However,

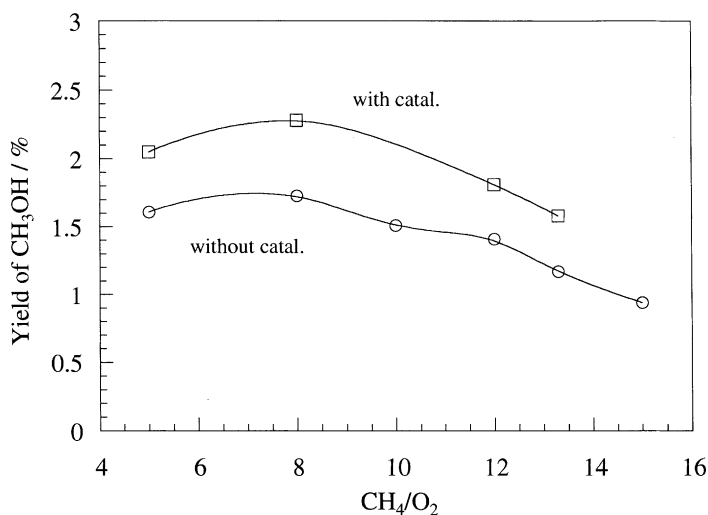


Fig. 7. Effects of CH₄/O₂ ratios on CH₃OH yield at 0.4 MPa in the presence of the Cu-ZnO/Al₂O₃ catalyst. Feed gas composition: CH₄, 77.5%; O₂, 5.8%; NO, 0.5%; Ar, balance; flow rate: 120 ml min⁻¹; and gas-phase reaction temperatures: 575 °C (0.4 MPa), respectively. All of the O₂ conversions were higher than 99%. All of the CH₄ conversions were in the range of 5.3–5.7%.

this increase was suppressed under a higher pressure as suggested in Fig. 4.

3.5. The effects of CH_4/O_2 ratios on the selectivities of products

Finally, we examined the effects of CH_4/O_2 ratio on CH_3OH yield at 0.4 MPa in the presence and absence of the $\text{Cu-ZnO}/\text{Al}_2\text{O}_3$ catalyst. The variations of CH_3OH yields as functions of CH_4/O_2 ratio in the presence and absence of the catalyst were almost the same. In the presence of the catalyst, CH_3OH yields were larger than in the absence of $\text{Cu-ZnO}/\text{Al}_2\text{O}_3$ (Fig. 7) in the examined region. CH_3OH yield had a maximum value at $\text{CH}_4/\text{O}_2 = 8.0$ in the presence of the catalyst.

4. Conclusions

The yield of CH_3OH from $\text{CH}_4\text{-O}_2\text{-NO}_x$ was enhanced by using the $\text{Cu-ZnO}/\text{Al}_2\text{O}_3$ catalyst in all the examined reaction pressures from 0.4 up to 3.0 MPa. The optimum reaction conditions of the catalyst for the highest yield of CH_3OH were 250°C at 0.4 MPa. The highest yield of CH_3OH was 2.3% at 0.4 MPa and $\text{CH}_4/\text{O}_2 = 8.0$.

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