

EVALUATION OF LOW-TEMPERATURE METHANOL SYNTHESIS IN THE LIQUID PHASE

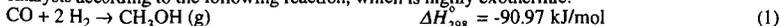
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INTRODUCTION

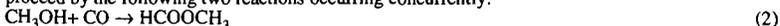
Methanol has recently attracted much public attention as one of the possible alternate fuels for oil. The electric power industry is considering the introduction of methanol as a fuel for gas turbines and fuel cells. Also, coproduction of methanol and electricity in an integrated gasification combined-cycle power plant (IGCC) has been proposed for operating IGCC at levels corresponding to peak demand¹. The electric power industry in Japan projects methanol power generation to be 1,000 MW in 2010. To employ methanol as a power plant fuel, a more efficient and more economical methanol production process, which can reduce methanol cost, is required.

Conventionally, methanol is produced in the gas-solid phase process over copper-zinc-based oxide catalysts according to the following reaction, which is highly exothermic:



This reaction is thermodynamically favorable at lower temperatures. Thus, if a catalyst that is highly active at low temperature is available and the reaction heat is removed efficiently, methanol production with high conversion per pass is achieved, which would result in a reduction of methanol cost.

Recently, low-temperature methanol synthesis in the liquid phase has been proposed and received considerable attention, since it has the potential to overcome problems in the conventional methanol processes. Two processes have been proposed: the Brookhaven National Laboratory (BNL) low-temperature methanol process^{2,3} and the process⁴⁻⁶ through methyl formate (MF) formation (hereafter referred to as "methanol synthesis via MF"). Methanol synthesis via MF is supposed to proceed by the following two reactions occurring concurrently:



The BNL process employs a homogeneous Ni catalyst and alkoxide in an organic solvent, while methanol synthesis via MF employs a mixture of copper-based oxide and alkoxide as a catalyst. Both processes are operated at around 373 K, where high equilibrium conversion of carbon monoxide to methanol is expected. The processes have been reported to show excellent activity even at such low temperatures.

Believing that these low-temperature methanol processes show future promise, the author has examined their catalytic activities and their possibilities as industrial processes were estimated in terms of the space time yield (STY).

EXPERIMENTAL

Experimental System

All experiments were carried out in batch operation in a 465 cm³ stainless steel autoclave. A mixture of carbon monoxide and hydrogen with a stoichiometric ratio for methanol synthesis (H₂/CO = 2) was employed as feed gas. The feed gas was admitted to the reactor and pressurized to a certain pressure at ambient temperature. The reaction conditions were temperatures from ambient temperature to 433 K and initial pressures from 1.1 MPa to 5.0 MPa. The time courses of the pressure and the temperature were monitored during the run. After the run, the components of the gas phase and the liquid phase were withdrawn and analyzed by gas chromatography.

The carbon monoxide conversion and the selectivity to methanol were determined on the basis of the amount of carbon-containing products. The approximate STY was determined from the amount of methanol produced, the reaction time at which the catalyst showed a pressure decrease, and the total volume of the catalyst system. (In this paper, "catalyst system" indicates a mixture of the catalyst and the solvent.)

Catalyst Preparation

The BNL Catalysts. The BNL low-temperature methanol synthesis catalysts were prepared according to their patent reports³. They were prepared from three compounds, *i.e.*, sodium hydride, alcohol and metal acetate. In this work, 60 mmol of sodium hydride, 52 mmol of *tert*-amyl alcohol as the alcohol component and 2.5-30 mmol of nickel acetate (typically 10 mmol) that was fully dried and dehydrated, were employed as standard starting materials. The catalysts were suspended in a 50 or 100 cm³ solvent (triethylene glycol dimethyl ether, *i.e.*, triglyme). A mixture of nickel acetate (10 mmol) and sodium hydride (60 mmol) was also used as a catalyst to study the active species of the catalyst.

Catalysts for Methanol Synthesis via MF. A mixture of oxide and alkoxide was employed as a catalyst for methanol synthesis via MF. The catalyst was suspended in triglyme (90 cm³). Oxides used in this study (normally 4 g) were CuO (Wako Pure Chemical Industries), Cr₂O₃ (Wako Pure Chemical Industries), a mixture of CuO and Cr₂O₃ (CuO/Cr₂O₃ = 1 and 2, molar ratio), copper chromite (CuO/Cr₂O₃, Aldrich Chemical Company, Inc.) and Ba-promoted copper chromite (CuO/Cr₂O₃/BaO, Aldrich Chemical Company, Inc.). Copper-based oxide commercial catalysts,

N203SD (Nikki Chemical Co.), KMB (Toyo CCI Corp.), G66B and G89 (Nissan Girdler Catalyst Co.) were also employed. Potassium methoxide solution (10 cm³, 30% in methanol solution) was employed as an alkoxide component.

RESULTS AND DISCUSSION

The BNL Methanol Process

The performance of the BNL Ni catalysts at 373 K and 433 K is summarized in Table 1. Methanol was formed quite selectively over the BNL catalysts at 353-433 K and 1.1-5.0 MPa of initial pressure. (Experiments could not be carried out at temperatures above 433 K because the pressure started to decrease in the course of the heating process. Also, it is reported³ that the catalyst works only below 423 K.) The maximum STY was obtained at 433 K and at 5.0 MPa because higher temperatures and higher initial pressures tended to enhance methanol productivity under the studied conditions. The STY with the BNL catalysts also varied with Ni concentration in the catalyst system and reached 0.89 kg l⁻¹ h⁻¹ at the optimum concentration. At 433 K, the BNL catalysts yielded almost 90% for CO conversion and over 99% for selectivity to methanol. Ni is a well-known catalyst for methanation of carbon oxides and Fischer-Tropsch synthesis. However, to the author's knowledge, it has never been reported that a Ni-based compound catalyzes methanol synthesis from CO + H₂. Thus, the BNL catalyst is quite novel at this point. Since the catalyst was highly active even at temperatures much lower than the operating temperature of the conventional methanol process (503-543 K), with this catalyst, it should be possible to eliminate recycling facilities for unconverted gas, which would reduce the production cost of methanol.

Small amounts of methyl formate and dimethyl ether were also produced. They were considered to be formed by the carbonylation of methanol (equation 2) and dehydration of methanol (equation 4), where produced methanol was a reactant:



Sodium *tert*-amyl alkoxide that could possibly be formed and exist in the catalyst system, might be responsible for equation 2 since alkoxide is known to catalyze carbonylation of methanol⁷.

Figure 1 indicates the effect of methanol concentration in the catalyst system on the STY. In these experiments a certain amount (1-8 cm³) of methanol was initially added to the catalyst system and the reaction was carried out at 373 K and 5 MPa. As shown in Figure 1, methanol addition did not affect catalytic activity significantly under the studied conditions although the STY showed a slight tendency to decrease with methanol concentration. A 99% selectivity to methanol was obtained, independent of methanol concentration. Therefore, constraints from chemical equilibrium or inhibition of the reaction by adding methanol was not recognized. On the other hand, a large amount of methyl formate was formed in the experiments with methanol addition at ambient temperature. Carbonylation of methanol (equation 2) seemed to prevail at such low temperatures, where sodium alkoxide functioned as a catalyst. Figure 2 shows the time courses of the temperature and the pressure during the multiple-charging experiment. Even when the pressure decrease became small, the pressure started to decrease again by recharging the feed gas, which suggested that the reaction continued to proceed. However, a marked pressure decrease was not observed after the second recharge of syngas (in the 3rd reaction). Methanol of 167 mmol was formed at the end of the entire reaction. Such an amount of methanol was not found to affect or inhibit the methanol productivity as shown in Figure 1. Therefore it was because of deactivation of the catalyst that only a slight pressure decrease was observed in the 3rd reaction.

To clarify the active species of the BNL catalyst, experiments with a mixture of sodium hydride and nickel acetate as a catalyst were carried out. Figure 3 shows the results. With sodium hydride and nickel acetate, methanol synthesis proceeded as well as with the BNL catalyst. The sodium hydride and nickel acetate catalyst exhibited a slightly lower STY than the BNL catalyst, but it showed almost the same value in CO conversion and selectivity as the BNL catalyst. On the other hand, in the experiments using a mixture of *tert*-amyl alcohol and sodium hydride as a catalyst (the nickel acetate component of the BNL catalyst was not employed), methanol synthesis did not occur at temperatures where the BNL catalyst works. Methyl formate and dimethyl ether were formed only when methanol was initially added into the catalyst system. Therefore, the nickel species that is activated or reduced by sodium hydride is responsible for methanol synthesis.

The BNL catalyst exhibited activity in several subsequent experiments, while a mixture of sodium hydride and nickel acetate that was employed in the previous experiment, did not show activity in the second experiment. Hence, *tert*-amyl alcohol, which is a component of the BNL catalyst and was not used in the experiments in Figure 3, may play a role in re-activating the nickel species and making the BNL catalyst function again in the subsequent reactions.

Methanol Synthesis via MF

Methanol was formed rapidly at around 373 K using a mixture of copper-based oxide and alkoxide. Figure 4 shows the STY of methanol and methyl formate at 373 K and 5 MPa with various oxides and potassium methoxide as a catalyst. It should be noted that the catalyst system initially contains methanol (ca. 220 mmol) because potassium methoxide in methanol solution was employed as an alkoxide component. N203SD and G89, the copper-chromite-based catalysts, showed activity for methanol among the commercial catalysts. In particular, N203SD exhibited high STY. Copper chromite (unpromoted and Ba-promoted) also had the STY values comparable to N203SD. On the other hand, methanol was consumed and only methyl formate was formed over the CuO/ZnO-based catalysts (KMB and G66B), which are the conventional catalysts for methanol synthesis. Since all the oxides exhibiting high activity for methanol were copper-chromite-based compounds, it was considered that copper chromite is quite effective for methanol synthesis *via* MF. It is generally known that copper chromite promotes hydrogenation of carbonyl compounds. Thus, in this study,

copper chromite might catalyze hydrogenolysis of methyl formate that resulted from carbonylation of methanol.

When CuO or Cr₂O₃ was employed as an oxide component, only methyl formate was formed with consumption of methanol, which suggested the progress of carbonylation of methanol. However, amounts of methanol and methyl formate were produced using a mixture of both. Thus it is suggested that an active site for hydrogenolysis of methyl formate might be yielded by mixing of CuO and Cr₂O₃.

Figure 5 shows the dependence of the STY on temperature and initial pressure using N203SD and potassium methoxide. Methanol was formed rapidly and selectively over 353 K (CO conversion: 87-94%, selectivity to methanol: 87-98%). However, a significant amount of methyl formate was formed at ambient temperature, which indicated carbonylation of methanol proceeded rapidly at such low temperature. As seen in the figure, higher temperatures and higher initial pressures enhanced methanol productivity, while lower temperatures and higher pressures increased methyl formate formation.

The STY Evaluation of Low-Temperature Methanol Synthesis

The STY of low-temperature methanol synthesis and that of the conventional methanol production process are compared in Figure 6. In the conventional process⁸, copper-zinc-based oxide catalysts (CuO/ZnO/Al₂O₃ or CuO/ZnO/Cr₂O₃) are employed under the conditions of temperature of 503-573 K, pressure of 5-20 MPa, and space velocity of 10,000-40,000 h⁻¹. In the ICI process, a typical methanol process, the STY of 0.5-0.77 kg l⁻¹ h⁻¹ (average 0.66 kg l⁻¹ h⁻¹) is obtained under the conditions of 500-523 K and 5-10 MPa. The BNL process showed the STY of 0.89 kg l⁻¹ h⁻¹ at the optimum Ni concentration (433 K, 5 MPa), which was almost the same value as that in the ICI process. Thus, the BNL process has the possibility of producing methanol more efficiently than the conventional process. On the other hand, methanol synthesis via MF showed the STY of 0.13 kg l⁻¹ h⁻¹ at 423 K and 5 MPa (feed: H₂/CO = 1), which is 1/5 of the STY in the ICI process. However, the STY is expected to be improved by optimizing reaction conditions and catalyst concentration in the liquid phase, and by searching for an active catalyst system.

CONCLUSIONS

Low-temperature methanol synthesis in the liquid phase has been studied and its possibility as an industrial process was evaluated in terms of the STY. Methanol productivity comparable to that of the conventional methanol process is anticipated under much milder conditions by using the BNL catalyst. It was suggested, however, that extension and stability of the catalyst life are the important subjects in the BNL process. Methanol synthesis via MF also showed activity for methanol at low temperatures but its productivity was still quite low. It is necessary to explore an active catalyst system and examine the catalytic behavior in more detail to improve the STY value.

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Table I. Catalytic activity for low-temperature methanol synthesis over BNL Ni catalysts.

Temp. (K)	P ^a (MPa)	Time (h)	Ni conc ^b (mol l ⁻¹)	Conv. ^c (%)	Select. ^d (%)	Products ^e (mmol)					STY (kg-MeOH l ⁻¹ h ⁻¹)	
						MeOH	Me ₂ O	HCOOCH ₃	CO ₂	CH ₄		H.C.
373	1.1	1	94.6	80.0	93.4	54.4	0.001	0.662	0.059	trace	---	0.016
373	3.0	1	94.6	60.3	98.4	50.7	trace	0.403	---	0.003	---	0.024
373	5.0	1	94.6	87.8	99.5	140	0.010	0.353	0.017	---	---	0.043
433	1.6	1	94.6	86.7	99.3	33.0	trace	0.049	---	0.005	---	0.025
433	3.0	1	94.6	95.5	99.8	98.8	0.013	0.046	---	0.004	---	0.12
433	5.0	1	94.6	90.7	99.8	203	0.017	0.237	---	0.004	---	0.25
433	5.0	1	23.7	98.9	99.7	213	0.196	0.031	---	0.004	0.026	0.24
433	5.0	1	94.6	90.7	99.8	203	0.017	0.237	---	0.004	0.001	0.25
433	5.0	1	94.6	93.0	99.9	237	0.044	0.025	---	0.007	0.004	0.47
433	5.0	1	180	96.3	99.1	257	0.378	0.777	---	0.005	0.005	0.89
433	5.0	1	284	88.6	99.0	136	trace	0.588	0.132	0.005	---	0.41

Catalyst: NaH/tert-amyl alcohol/Ni(CH₃COO)₂. Catalyst amount = 2.5-30 mmol as Ni(CH₃COO)₂. Volume of solvent = 50-100 cm³.

^aInitial pressure at ambient temperature. ^bNi concentration in the catalyst system.

^cConversion of carbon monoxide. ^dSelectivity to MeOH.

^eProducts: Me₂O = dimethyl ether; H.C. = hydrocarbons except CH₄.

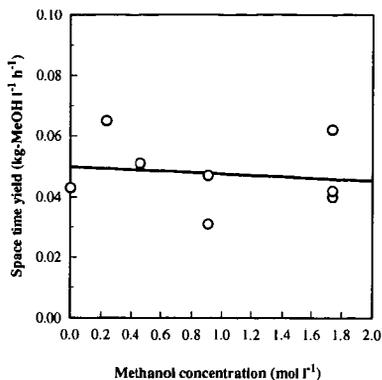


Figure 1. Effect of methanol addition on space time yield over BNL Ni catalysts
Catalyst: $\text{NaH/ert-amyI alcohol/Ni(CH}_3\text{COO)}_2$. Catalyst amount: 10 mmol as
 $\text{Ni(CH}_3\text{COO)}_2$. Solvent: triglyme (100 cm^3). Reaction conditions: temperature =
373 K, initial pressure = 5 MPa, $\text{H}_2/\text{CO} = 2$.

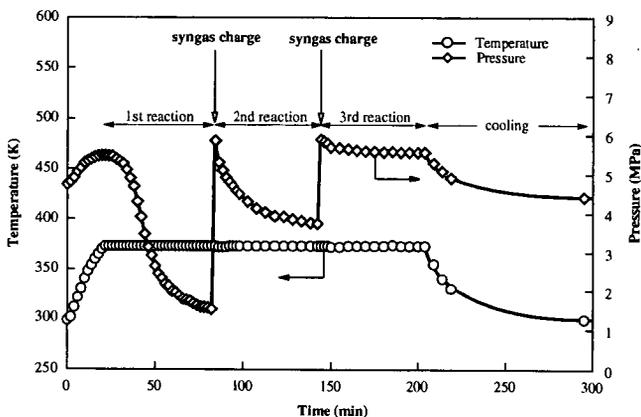


Figure 2. Temperature and pressure profiles using a BNL Ni catalyst (multiple-charging experiment).
Catalyst: $\text{NaH/ert-amyI alcohol/Ni(CH}_3\text{COO)}_2$. Catalyst amount: 10 mmol as $\text{Ni(CH}_3\text{COO)}_2$. Solvent:
triglyme (100 cm^3). Reaction conditions: initial pressure = 5.0 MPa, reaction temperature = 373 K.

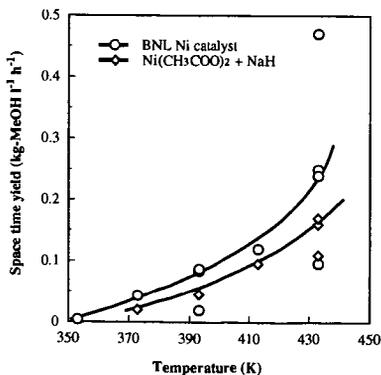


Figure 3. Space time yield over BNL Ni catalysts and nickel acetate + sodium
hydride catalysts. Catalyst amount: 10 mmol as $\text{Ni(CH}_3\text{COO)}_2$. Solvent: triglyme
(100 cm^3). Reaction conditions: initial pressure = 5 MPa, $\text{H}_2/\text{CO} = 2$.

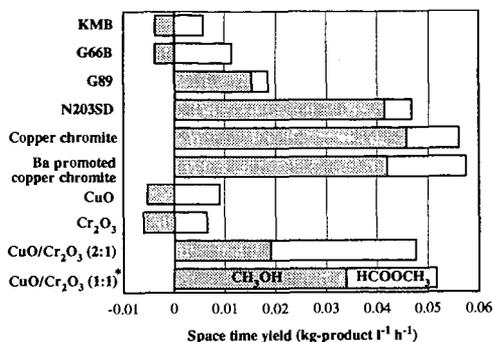


Figure 4. Space time yield over a mixture of metal oxide and potassium methoxide, Catalyst: metal oxide 4 g (* 6 g) + CH₃OK 10 cm³ (30% in methanol solution). Solvent: triglyme (90 cm³). Reaction conditions: reaction temperature = 373 K, initial pressure = 5.0 MPa (at ambient temperature), H₂/CO = 2.

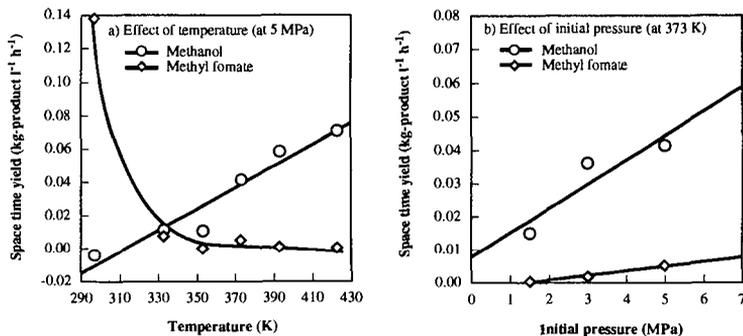


Figure 5. Effect of reaction parameters on space time yield for low-temperature methanol synthesis via methyl formate a) Effect of temperature (initial pressure: 5 MPa), b) Effect of initial pressure (reaction temperature: 373 K). Catalyst: N203SD 4 g + CH₃OK 10 cm³ (30% in methanol solution). Solvent: triglyme (90 cm³). Feed gas: H₂/CO = 2.

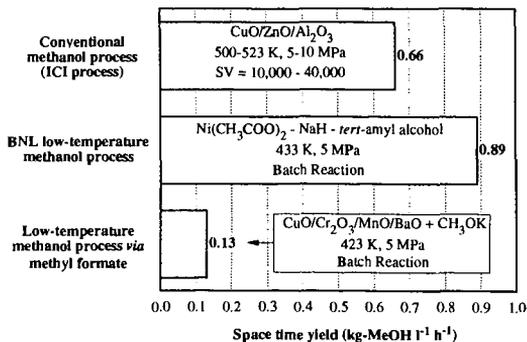


Figure 6. Space time yield of various methanol synthesis technologies