Articles

Concurrent Production of Methanol and Dimethyl Ether from Carbon Dioxide Hydrogenation : Investigation of Reaction Conditions

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The concurrent production of methanol and dimethyl ether from carbon dioxide hydrogenation has been studied under various reaction conditions. First, the methanol synthesis was compared with the concurrent production method. For the methanol synthesis, the ternary mixed oxide catalyst ($CuO/ZnO/Al_2O_3$) was used and for the coproduction of methanol and dimethyl ether, silica-alumina was mixed with the methanol synthesis catalyst to be a hybrid catalyst. The results show that the co-production provides much higher per-pass yield than methanol synthesis even at very short contact time. The effects of temperature, contact time, pressure and catalyst hybrid ratio on the product yields and selectivities were also determined in the co-production.

Introduction

Since carbon dioxide accumulation in the atmosphere is feared as the major cause of global warming, the subject on the utilization of carbon dioxide has attained great importance in recent years. When hydrogen is able to be obtained readily, the catalytic hydrogenation of CO_2 will probably be the most efficient route among the methods of CO_2 fixation. Moreover, the CO_2 conversion to a clean liquid fuel such as methanol (MeOH) and dimethyl ether (DME) could provide a way to produce a secondary energy carrier for using renewable energy or off-peak electricity more efficiently. Although the methanol synthesis from H_2/CO_2 has not been studied as extensively as the commercialized methanol synthesis from synthesis gas ($H_2/CO/CO_2$), there has been considerable progress, especially in the development of effective catalysts for the CO_2 conversion to methanol.[1-4] However, methanol formation from the hydrogenation of CO_2 is much more thermodynamically unfavorable than that of CO under operating conditions of interest.[3]

In order to overcome the equilibrium limitation, the third reaction can be added to shift the equilibrium to more conversion of methanol synthesis reaction. Some reports have been cited on the simultaneous production of methanol and dimethyl ether (DME) from CO_2 or CO hydrogenation over hybrid catalysts, that is, combination of methanol synthesis and solid acid catalysts.[5-7] The improvement in per-pass conversion can be achieved by turning methanol into DME on solid acids.

DME can be used as a clean fuel because of its LPG-like physical property as well as a raw material for the conversion to hydrocarbons like methanol. Moreover, recently it has been known that DME can be used as an attractive alternative fuel for diesel engines.[8]

In the present work, it has been tried to develop one-step process of the MeOH+DME co-production from H_2/CO_2 feed stock using a hybrid-catalytic system. First the MeOH+DME co-production was compared with methanol synthesis, and then the effects of temperature, contact time, pressure and catalyst-mixing on the product yields and selectivities were investigated in the co-production. This work is an extension of the preliminary report which was given as a proceeding paper.[9]

Experimental Section

Catalysts. A $CuO/ZnO/Al_2O_3$ (Cu : Zn : Al molar ratio = 1 : 0.81 : 0.16) methanol synthesis catalyst was prepared by the conventional coprecipitation method. An aqueous solution of copper nitrate, zinc nitrate and aluminum nitrate and an aqueous solution of sodium carbonate were added to water simultaneously with constant stirring. During the precipitation, the temperature and pH were maintained at room temperature and 7.0, respectively. After the completion of precipitation the suspension was kept for two hours in the mother liquid, followed by filtering and washing with water. The precipitate was then dried at 393 K overnight and calcined in air at 623 K for 12 hours. Total surface area and Cu surface area of the prepared catalyst were found to be 58.5 m^2/g and 16.1 m^2/g, respectively, from BET measurement and N_2O surface titration.[10]

A commercially available silica-alumina (Aldrich: SiO_2 86 wt%, surface area = 540.4 m^2/g) was used as a solid acid catalyst for the *in-situ* conversion of methanol formed from hydrogenation of CO_2. This catalyst was calcined at 773 K overnight before using. In the preparation of hybrid catalysts, silica-alumina (60-80 mesh) was physically mixed with $CuO/ZnO/Al_2O_3$ methanol synthesis catalyst (60-80 mesh) in desired weight ratios.

Testing Apparatus. Prior to the reaction, the catalyst was

reduced in a H_2/N_2 (10% H_2) gas stream of 100 mL/min · g_{cat} at 523 K for 4 h under atmospheric pressure. The catalytic hydrogenation of CO_2 was carried out in a high-pressure stainless-steel tubular reactor by feeding a gas mixture of H_2/CO_2 (3/1 mole ratio). The gases used for reduction and reaction in this work were high purity and premixed to desired compositions. The reactor is constructed of a 10.2 mm i.d. stainless steel tube and equipped with a 3.2 mm o.d. thermocouple well in the catalyst bed, permitting a volume of catalyst samples ranging in size from 1.0 to 10 cm^3. For each reaction experiment 0.5-1.0 g of $CuO/ZnO/Al_2O_3$ catalyst was loaded. In the case of DME synthesis the methanol dehydration catalyst was also loaded as being mixed with the methanol synthesis catalyst at a desired ratio. The catalysts were diluted by inert quartz sand of the same particle size. The pressure in the reactor was adjusted with a back pressure regulator. The flow rate of feed gas mixture was controlled by a mass flow controller. Effluent gas from the reactor was analyzed by on-line gas chromatograph (Donam model DS 6200) using carbosphere column (connected to TCD) for CO_2 and CO and Porapak T column (connected to FID) for methanol, DME and hydrocarbons. The product lines were heated electrically where necessary in order to avoid unwanted condensation of methanol and water.

The yield (%) of a product is expressed as following: 100 × number of moles of CO_2 converted into a product (MeOH, DME or CO)/initial number of moles of CO_2. Each reaction data here represents an average value taken from several gas chromatographic measurements of the reactor effluent composition at several different times up to 10 hours during steady-state operations.

Results and Discussion

Comparison of Methanol Synthesis and MeOH+DME Co-production. In the CO_2 hydrogenation using $CuO/ZnO/Al_2O_3$, the products were found to be CO and methanol almost exclusively. Only a trace of methane formation was observed. When the hybrid catalyst was employed, DME was found as an additional product. Generally, in the methanol synthesis (reaction 1) from CO_2 hydrogenation, the reverse water gas shift (RWGS: reaction 2) also occurs simultaneously. Therefore, the reactions (1) and (2) make the total reaction system of methanol synthesis.

$$CO_2 + 3H_2 \rightleftharpoons CH_3OH + H_2O \quad (1)$$

$$CO_2 + H_2 \rightleftharpoons CO + H_2O \quad (2)$$

Carbon monoxide could be formed from the methanol decomposition also.

$$CH_3OH \rightleftharpoons CO + 2H_2 \quad (3)$$

The addition of solid acid to methanol synthesis catalyst makes methanol dehydration to DME.

$$2CH_3OH \rightleftharpoons CH_3OCH_3 - H_2O \quad (4)$$

The combination of reactions (1) and (4) gives overall reaction (5).

$$2CO_2 - 6H_2 \rightleftharpoons CH_3OCH_3 - 3H_2O \quad (5)$$

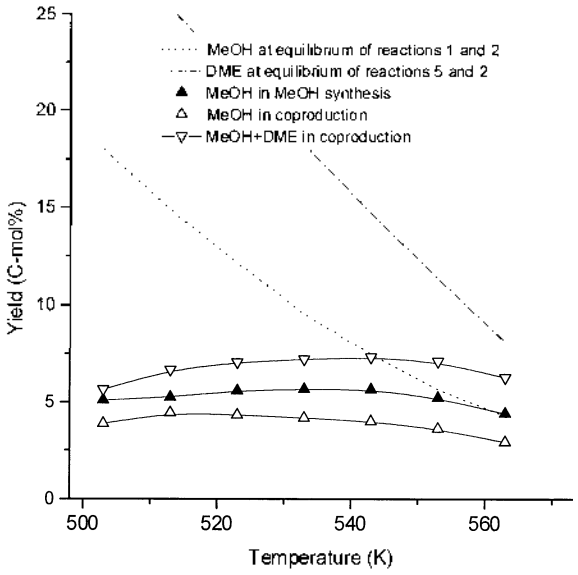


Figure 1. Comparison of oxygenate yields between methanol synthesis and MeOH+DME co-production: pressure 3 MPa; catalyst ($CuO/ZnO/Al_2O_3$; silica-alumina) hybrid = 1 : 1 wt. ratio; contact time = 0.125 s · g/mL (contact time is based on only $CuO/ZnO/Al_2O_3$).

In the primary stage of this work, the CO_2 hydrogenation was carried out on the hybrid of $CuO/ZnO/Al_2O_3$ and silica-alumina (1 : 1 wt. ratio) at different temperatures and the results were compared with the results from the reaction on the methanol synthesis catalyst alone. Figures 1-3 illustrate the results of two modes of reactions for comparison. From Figure 1, it is readily seen that the MeOH+DME co-production always gives higher yield of total oxygenates (MeOH and DME) than methanol synthesis. When the reactions are conducted at the high temperatures, the benefit of increasing oxygenate yield appears more clearly. This shows that the co-production method removes the equilibrium constraint of methanol synthesis by converting methanol to DME and that it is more effective under the reaction condition which is close to equilibrium as predicted by the comparison between the equilibrium yields of methanol and DME achievable in the reaction systems consisted of reactions 1 and 2 and reactions 5 and 2, respectively. It is also to be noted that the co-production gives higher yield even at the low temperatures which scarcely seems to be close to equilibrium condition. The conversion of methanol to DME would lower the methanol concentration on the catalyst surface and this would increase the forward reaction rate of methanol synthesis (reaction 1). As a consequence, the higher oxygenate yield can be obtained when the solid acid is added to methanol synthesis catalyst. The results clearly show that the co-production of methanol and DME plays a very important role in alleviating the chemical equilibrium limitation by which the forward reaction of methanol synthesis is limited.

From Figure 2, it can be seen that the co-production gives

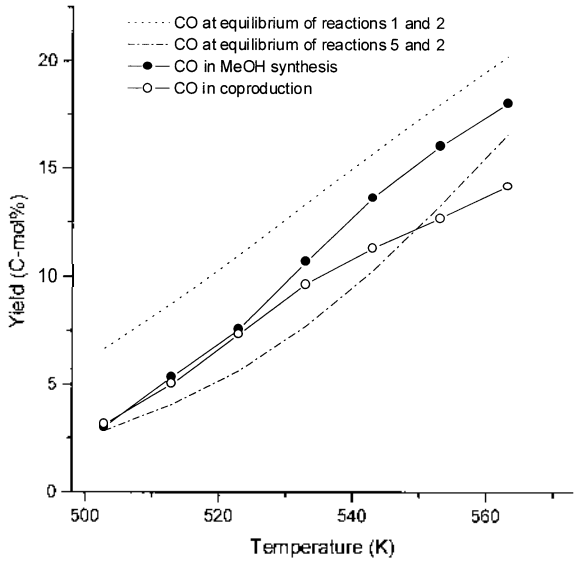


Figure 2. Comparison of CO yield between methanol synthesis and MeOH+DME co-production: pressure = 3 MPa; catalyst ($CuO/ZnO/Al_2O_3$: silica-alumina) hybrid = 1 : 1 wt. ratio; contact time = 0.125 s · g/mL (contact time is based on only $CuO/ZnO/Al_2O_3$).

lower yield of CO than the simple methanol synthesis. This is in agreement with the fact that the equilibrium CO yield achievable in the reaction systems consisted of reactions 5 and 2 is lower than that in the reactions 1 and 2. Since both methanol formation and CO formation (reactions 1 and 2) produce the same product (water), two reactions compete in the restricted CO_2 conversion. In other words, a favorable condition for methanol formation becomes an unfavorable condition for CO formation and vice versa. In case of the co-production, the water concentration on the catalyst surface

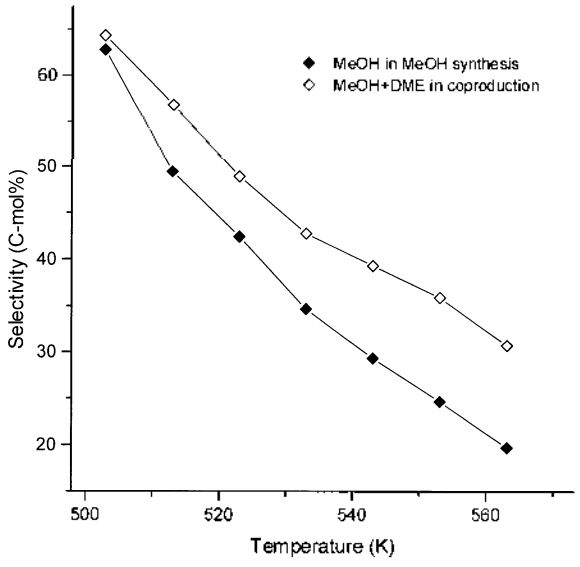


Figure 3. Comparison of oxygenate selectivity between methanol synthesis and MeOH+DME co-production: pressure = 3 MPa; catalyst ($CuO/ZnO/Al_2O_3$: silica-alumina) hybrid = 1 : 1 wt. ratio; contact time = 0.125 s · g/mL (contact time is based on only $CuO/ZnO/Al_2O_3$).

would be increased with the formation of DME, because methanol formation is enhanced and methanol dehydration to DME (reaction 4) produces another molecule of water. Because of this, the CO formation in the co-production would be diminished as compared to the simple methanol synthesis. As a consequence, the co-production provides the enhancement in oxygenate selectivity (see Figure 3).

The apparent benefit of MeOH+DME co-production is the enhancement of per-pass conversion: that is, higher CO_2 conversion per single pass of reactant gas through the reactor is obtained. Under the condition of the same temperature (543 K) and contact time (0.5 s · g_{cat}/mL based on methanol synthesis catalyst), the total CO_2 conversion was 20.76% for the methanol synthesis way, whereas it was 22.31% for the co-production way. The percent increase in the total CO_2 conversion was 7.47%. However, a significant portion of the total CO_2 conversion corresponds to CO formation. Therefore, it is necessary to compare the performance by CO_2 conversion to total useful products. By excluding the CO formation through the RWGS, it was observed that 6.78% of CO_2 was converted to oxygenate in case of the methanol synthesis. With MeOH+DME co-production, 10.80% of CO_2 was converted to oxygenates. The percent increase in per-pass CO_2 conversion to oxygenates was actually 59.29 %, while the percent decrease in per-pass CO_2 conversion to CO was 17.67%. Along with this, the reactor productivity for case of the co-production was increased by 59.29% over that of the methanol synthesis. Although the co-production way does not give any advantage in view of the productivity based on total catalyst mass, the efficiency of single reactor is clearly improved by using the hybrid catalyst. This would diminish the recycling of unconverted reactant and carbon monoxide as employing the recycling reaction mode, which should be essential in the industrial process.

Temperature Effect. Figure 4 shows the yields and the selectivities as functions of reaction temperature in the MeOH+DME co-production from H_2/CO_2. It can be seen that the oxygenate yield, which is defined as (DME + MeOH, based on carbon atom), increases up to about 543 K and then decreases with increasing temperature. The decrease in oxygenate yield at high temperature can be explained as follows: for the methanol synthesis from CO_2 hydrogenation, a maximum yield of methanol is expected to be observed with the increase of temperature due to the transformation from kinetic control to thermodynamic control. On the other hand, the methanol dehydration to DME is an almost kinetically controlled process because equilibrium constants are quite high in the temperature range investigated.[7-11] The combination of these two successive reactions, $H_2/CO_2 \rightarrow CH_3OH \rightarrow DME$, may result in the increase in the total oxygenates yield at first as increasing temperature and then the decrease after passing the maximum point. From Figure 4(A), it can be further found that the methanol yield decreases a little as temperature increases, but the DME yield increases at first with temperature. This result demonstrates that the DME formation from CH_3OH is not a thermodynamically controlled process, and that the DME

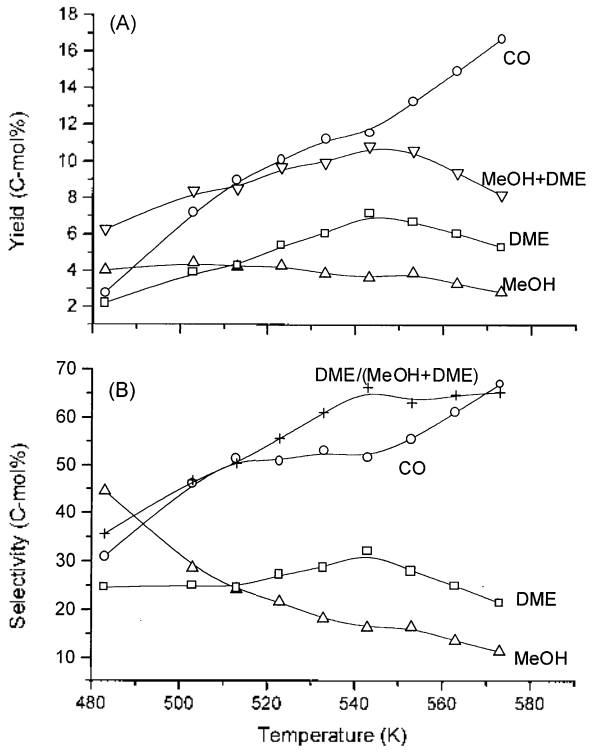


Figure 4. Dependence of yields and selectivities on reaction temperature in MeOH+DME co-production: pressure 3 MPa; catalyst ($CuO/ZnO/Al_2O_3$; silica-alumina) hybrid = 1 : 1 wt. ratio; contact time = 0.5 s · g/mL (contact time is based on only $CuO/ZnO/Al_2O_3$).

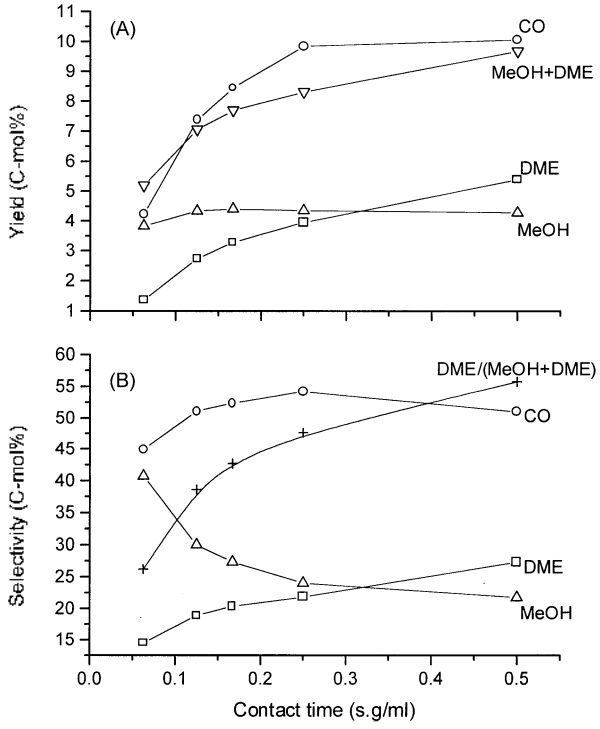


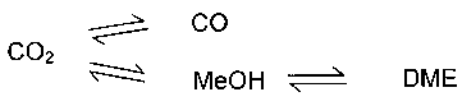
Figure 5. Dependence of yields and selectivities on contact time in MeOH+DME co-production (contact time is based on only $CuO/ZnO/Al_2O_3$): pressure 3 MPa; catalyst ($CuO/ZnO/Al_2O_3$; silica-alumina) hybrid = 1 : 1 wt. ratio; reaction temperature =523 K.

formation can effectively accelerate the methanol synthesis (reaction 1) to the right side.

By observing the corresponding CO yield, one can find that the CO yield increases monotonously with temperature, especially at high temperature. This is natural considering that high reaction temperature favors the CO formation through reaction 2 thermodynamically as well as kinetically.

From Figure 4(B), it is seen that the selectivity for methanol decreases as temperature increases, but the selectivity for DME increases initially and subsequently decreases. Initial decrease in methanol selectivity is partly due to the increase in DME selectivity. However, the decrease in methanol selectivity and the decrease in DME selectivity at the temperature higher than 543 K are mainly due to the increase in CO selectivity. It seems that the temperature higher than 543 K should be avoided to get high selectivities for the oxygenates.

Contact Time Effect. Figure 5 shows the yields and the selectivities as functions of contact time in the MeOH–DME co-production, which was conducted at 523 K over the hybrid of $Cu/ZnO/Al_2O_3$ and silica-alumina catalysts (1 : 1 wt. ratio). It is apparent that the yields of DME and CO on the hybrid catalytic system increase with the increase in contact time, while that of methanol is kept almost at a constant level, almost irrespective of contact time. These product selectivity phenomena suggest the following reaction scheme: (1) The methanol synthesis reaches its equilibrium level on $Cu/ZnO/Al_2O_3$ single catalyst under the reaction conditions adopted; (2) Successive reactions, $H_2/CO_2 \rightarrow CH_3OH \rightarrow$ DME proceed quickly on the hybrid catalyst, which lowers the methanol concentration by converting it into DME and thus keeps the methanol synthesis far from its equilibrium state. Thus, the reverse direction of reaction 1 is suppressed; (3) The formation of CO, of which yield is almost parallel to that of DME, can be attributed to the RWGS reaction occurring simultaneously with methanol formation over the $Cu/ZnO/Al_2O_3$ catalyst. This reaction produces one molecule of water along with one molecule of CO. Produced water depresses both the methanol synthesis from H_2/CO_2 and the successive DME formation from CH_3OH. The variation of methanol and DME yields agree with typical reaction pathway of reversible serial reactions. The reaction scheme can be established as follows:



Pressure Effect. The co-production of methanol and DME was carried out at 523 K under different pressures and contact times. The results is shown in Table 1. As the reaction pressure increases at the contact time of 0.25 s · g/mL, the yields of DME and methanol increase, but the related CO yield decreases, being agreement with thermodynamic calculation. Since the formation of methanol (reaction 1) is a molecular-decreasing reaction, high pressure gives high methanol yield, and in turn DME. As for CO yield, the

Table 1. The effect of pressure on MeOH+DME co-production[a]

Contact time[b], s·g/mL	0.0625			0.25		
Pressure, MPa	1.0	3.0	5.0	1.0	3.0	5.0
CO_2 conversion (%)	10.27	14.73	14.99	15.82	18.13	18.55
Yield (C-mol %)						
CO	6.42	8.42	8.26	11.68	9.83	8.52
MeOH	3.13	4.38	4.67	2.63	4.35	5.20
DME	0.72	1.92	2.07	1.51	3.95	4.83
MeOH+DME	3.84	6.31	6.73	4.15	8.30	10.03
Selectivity (C-mol %)						
MeOH+DME	37.43	42.81	44.92	26.20	45.77	54.06
DME/(MeOH+DME)	18.67	30.49	30.71	36.52	47.63	48.16

[a]Reaction temperature = 523 K, hybrid catalyst mixing ratio = 1 : 1 wt. ratio. [b]The contact time is based on only CuO ZnO/Al_2O_3.

RWGS readily reaches its equilibrium at longer contact time under 1.0 MPa, the decrease of CO yield with increasing pressure is attributed to the depression of methanol decomposition (reaction 3). Because the secondary reaction of methanol decomposition to carbon monoxide is a molecular-increasing reaction, it is unfavorable at higher pressure, and thus the increase of pressure will certainly inhibit this reaction and decrease the CO yield. Both the increase in methanol synthesis and the decrease of methanol decomposition are responsible for the decrease of CO yield with increase of pressure. Meanwhile, the increase in water concentration due to methanol and DME formation also drives the RWGS (reaction 2) to the left side and thus decreases CO yield. Consequently, the selectivity for oxygenate formation increases with the reaction pressure. It is also noteworthy that high pressure favors the selectivity for DME among oxygenates even though the reaction 4 does not gives the change of molecular number.

On the other hand, at the short contact time, the reactions are controlled mainly by kinetics, the thermodynamic limitation is lowered. Thus the pressure effect on CO formation becomes less significant.

Hybrid Catalyst Ratio Effect. The method of MeOH+DME co-synthesis is expected to be very flexible in the sense that any fixed mole ratio of methanol and DME can be obtained. This mole ratio can be effectively controlled by varying the methanol synthesis: methanol dehydration catalyst ratio. If the same amount of methanol catalyst is used, reaction systems with higher loading of methanol dehydration catalyst would lead to higher DME yield at the expense of lower methanol yield. This fact is borne out in Table 2. As increasing the loading amount of silica-alumina with the same amount of methanol synthesis catalyst loaded, DME yield increases concurrently, but methanol yield decreases. Depending on the process requirements, the co-synthesis of methanol and DME can be adjusted to a mixture of DME and methanol in any fixed mole proportion, at significant synthesis rate of methanol and DME.

As seen in Figure 1, the initial addition of silica-alumina improves the oxygenate yield significantly, but further increase in the amount of silica-alumina does not provide additional benefit for oxygenate yield. This indicates that the oxygenate synthesis is not severely limited by equilibrium because of short contact time under the reaction condition employed in this work. From the viewpoint of productivity, this solid addition effect is not so remarkable at high space velocity, but it may shift the product distribution to some degree.

Table 2. The effect of hybrid catalyst ratio on MeOH+DME co-production[a]

Contact time[b], s·g/mL	0.125			0.50		
CuO/ZnO/Al_2O_3:silica-alumina wt.-ratio	1:1	1:2	1:4	1:1	1:2	1:4
CO_2 conversion (%)	14.41	15.82	15.63	19.72	19.84	20.02
Yield (C-mol %)						
CO	7.36	8.35	8.30	10.05	10.26	9.83
MeOH	4.33	3.68	2.62	4.28	3.49	2.98
DME	2.72	3.78	4.71	5.39	6.09	7.21
MeOH+DME	7.05	7.46	7.33	9.67	9.58	10.21
Selectivity (C-mol %)						
MeOH+DME	48.93	47.19	46.90	49.04	48.29	50.92
DME/(MeOH+DME)	38.59	50.68	64.23	55.75	63.53	70.75

[a]Reaction temperature = 523 K, reaction pressure = 3.0 MPa. [b]The contact time is based on only CuO/ZnO/Al_2O_3.

Conclusions

When the forward reaction of methanol synthesis is limited by chemical equilibrium, the co-production of methanol and DME plays a very important role in alleviating the limitation - thereby, the co-production gives higher per-pass oxygenate yield than the methanol synthesis even at the very short contact time. It seems that the temperature higher than 543 K should be avoided to get high selectivities for the oxygenates and long contact time is preferable to get high oxygenate yield. The yield and the selectivity of oxygenates increase with reaction pressure. By changing the hybrid catalyst ratio, the DME:MeOH ratio in the product mixture can be controlled. Although the way of co-production does not give a favorable productivity based on total mass of hybrid catalyst, it may be concluded that the simultaneous production of methanol and DME clearly provides more effective way to convert CO_2 to useful products than the conventional methanol synthesis.

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