# Continuous Supercritical Low-temperature Methanol Synthesis with *n*-Butane as a Supercritical Fluid

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A process of supercritical low-temperature methanol synthesis from syngas containing $CO_2$ was carried out at 443 K and 60 bar. The 2-butanol and *n*-butane was used as catalytic solvent and supercritical medium, respectively. The results showed that the total carbon conversion, especially the $CO_2$ conversion of the methanol synthesis was increased significantly under the supercritical condition.

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Supercritical fluid (SCF) as a new technology has unique properties such as superior solubility and transfer characteristics. The use of SCF in heterogeneous reactions can increase the reaction rates because the products and reaction heat can be removed out rapidly while the multiphase interface is eliminated and the molecules diffusivity is increased. Moreover, better selectivity can be achieved in supercritical reactions owing to the possibility of uncoupling process variables and the deactivation of catalyst can be mitigated through better heat and mass transfer.[1,2]

Methanol, as one of the primary chemicals, is commercially produced via the ICI process under extreme conditions, such as 573 K and 100 bar. Under these conditions, one-pass conversion is only 15–25% because of severe thermodynamic limitation of this exothermic reaction.[3,4] Zhu et al. conducted the ICI methanol synthesis under supercritical conditions with *n*-hexane as the supercritical medium.[5] The conversions and methanol mole fraction are obviously higher than those of gas–solid reaction. Similar results were also reported by Zhong et al.[6] Han et al. simulated the methanol synthesis in supercritical *n*-hexane using the Monte Carlo (MC) method.[7] The results indicated that the catalyst activities depended not only on the number of active sites, but also on the ratio of different adsorbed species on the catalyst surface.

Previous studies of our group have developed a new route of low-temperature methanol synthesis.[8,9] This process consists of three steps: (1) water–gas shift reaction; (2) esterification reaction; and (3) hydrogenation of ester to form methanol and alcohol. Herein, ROH acts as a catalytic solvent, which participates in the reaction but is not consumed by the overall reaction.

$$CO + H_2O = (HCOOH) = CO_2 + H_2 \qquad (1)$$

$$HCOOH + ROH = HCOOR + H_2O \qquad (2)$$

$$HCOOR + 2H_2 = CH_3OH + ROH \qquad (3)$$

$$CO + 2H_2 = CH_3OH \qquad (4)$$

Through the new path, methanol can be produced with high one-pass conversion and specific selectivity at 423–443 K and 30 bar. To investigate the promotional effects of SCF on this low-temperature–catalysis process, supercritical *n*-butane with lower $T_c$ was employed to accompany ROH where the latter acted like an entrainer. The results showed that the reaction rate of low-temperature methanol synthesis can be improved significantly under the supercritical conditions.

The Cu/ZnO catalyst with Cu/Zn molar ratio of 1 was prepared by the coprecipitation from copper nitrate and zinc nitrate, using sodium carbonate as precipitant.[8] The obtained precursor was reduced at 473 K for 13 h by flowing 5% $H_2$ in $N_2$ and passivated by 2% $O_2$ in Ar. The reaction was carried out in a continuous flow fixed-bed reactor. The feed gas was $CO/H_2/CO_2/Ar = 31.6/60.7/4.8/2.9$. The balance gas was helium in the gas-phase reaction. 2-Butanol and *n*-butane were used as the solvent and SCF, respectively. Detailed information on the experimental setup and the product analysis has been reported elsewhere.[10]

The applicability of ester, alcohol, ketone, and saturated hydrocarbon as supercritical medium was studied by Zhong et al. The results showed that only saturated hydrocarbon has preferable appetency to methanol under the supercritical condition.[11] In this work, the *n*-butane was selected as the supercritical medium due to its low critical point ($T_c = 425.2$ K, $P_c = 37.7$ bar). Additionally, *n*-butane in the supercritical phase at the range of reaction temperature has favorable stability and preferable diathermancy. The reaction results are shown in Table 1. In general, the catalytic conversions are relatively low owing to the low partial pressure of feed gas and alcohol solvent. Only CO and $CO_2$ were the carbon-containing gas components after reaction. The reaction without 2-butanol and *n*-butane had a low conversion. The intermediate formic acid was the only product and no methanol was detected, which might be due to the low temperature and short contact time. The total carbon conversion increased when the supercritical *n*-butane was introduced. With only the presence of 2-butanol, the intermediate ester which was formed by the esterification as described in step (2),[9] was the only liquid product and no methanol was detected because of the short contact time. When conducting the reaction in the supercritical *n*-butane as in Reaction No. 4, the total carbon conversion increased from 2.6 to 4.2%. At a higher $W/F$ value of 30 $g \cdot h \cdot mol^{-1}$, the methanol selectivity of the super critical reaction was high up to 98.4% and the total carbon conversion was 8.6%, much higher than that of the reaction without *n*-butane. The 2-butanol, acted as the catalytic solvent, was almost not consumed during the reaction, except only a little was converted to the intermediate ester. These findings indicated that the utilization of SCF in the low-temperature-methanol synthesis increased the reaction rate significantly.

The catalytic solvent effect of 1-butanol and 2-butanol on the activity was compared in Table 2. 2-Butanol exhibited higher conversion and selectivity than that of the 1-butanol. It is sug-

**Table 1.** Reaction results for supercritical low-temperature methanol synthesis[a]

| No. | Partial pressure/bar | | | | $W/F$ | Conversion/% | | | Selectivity/% | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Syngas | He | 2-Butanol | $n$-Butane | /g·h·mol$^{-1}$ | CO | $CO_2$ | Total C[b] | MeOH | HCOOR | HCOOH |
| 1 | 10 | 50 | 0 | 0 | 10 | 2.3 | 1.2 | 2.2 | 0 | 0 | 100 |
| 2 | 10 | 10 | 0 | 40 | 10 | −0.1 | 46.2 | 6.0 | 0 | 0 | 100 |
| 3 | 10 | 40 | 10 | 0 | 10 | 5.5 | −16.2 | 2.6 | 0 | 100 | 0 |
| 4 | 10 | 0 | 10 | 40 | 10 | −2.1 | 45.7 | 4.2 | 0 | 100 | 0 |
| 5 | 10 | 40 | 10 | 0 | 30 | 6.4 | −1.2 | 5.4 | 95.5 | 4.5 | 0 |
| 6 | 10 | 0 | 10 | 40 | 30 | 3.8 | 40.2 | 8.6 | 98.4 | 1.6 | 0 |

[a]Reaction conditions: $T = 443\,K$, $P(\text{total}) = 60$ bar, $P(CO/H_2/CO_2) = 10$ bar, Catalyst weight: 0.5 g. [b]Total carbon conversion = CO conv. × 31.6/(31.6 + 4.8) + $CO_2$ conv. × 4.8/(31.6 + 4.8).

**Table 2.** Effects of 1-butanol and 2-butanol on the methanol synthesis activity[a]

| Alcohol | Conversion/% | | | Selectivity/% | |
|---|---|---|---|---|---|
| | CO | $CO_2$ | Total C | MeOH | Ester |
| 2-Butanol | 11.0 | 53.5 | 16.6 | 97.7 | 2.3 |
| 1-Butanol | 3.8 | 64.2 | 11.7 | 94.3 | 5.7 |

[a]Reaction conditions: $T = 443\,K$, $P(\text{total}) = 60$ bar, $P(CO/H_2/CO_2) = 10$ bar, $P(n\text{-butane}) = 40$ bar; $P(\text{alcohol}) = 10$ bar; Catalyst weight: 1.5 g, $W/F = 90\,g{\cdot}h{\cdot}mol^{-1}$.

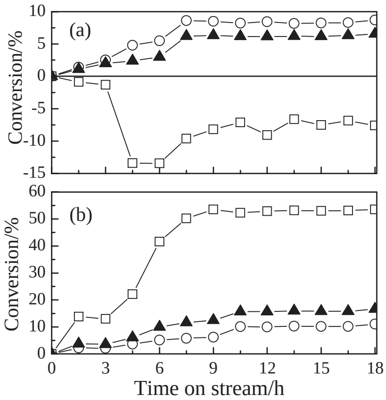

**Figure 1.** Variations of CO, $CO_2$, and total carbon conversions with reaction time. Reaction conditions: $T = 443\,K$, $P(\text{total}) = 60$ bar, $P(CO/H_2/CO_2) = 10$ bar, $P(\text{2-butanol}) = 10$ bar, $P(\text{He or } n\text{-butane}) = 40$ bar, $W/F(CO/H_2/CO_2) = 90\,g{\cdot}h{\cdot}mol^{-1}$, Catalyst weight: 1.5 g. (a) With only the presence of 2-butanol; (b) with the coexistence of 2-butanol and supercritical $n$-butane. (○) CO conv.; (□) $CO_2$ conv.; (▲) Total carbon conv.

gested that different alcohol affected the esterification reaction, step 2, by both electronic and spatial effects.[9] High electron density of oxygen atom in branched ROH makes it more efficient for the ROH to attack the carbon atom of HCOOCu, the intermediate of step (2). Low steric hindrance in linear ROH is favorable to the nucleophilic attack in the esterification reaction. As a balanced effect between electronic factor and spatial factor, 2-butanol exhibited higher promoting effect.

Figure 1 shows the variations of CO, $CO_2$, and total carbon conversions with reaction time. For comparison purpose, the reaction without $n$-butane was also tested. At the initial stage of the reaction, since the dead volume of the reactor and the ice-trap were filled by the pressurized feed gas, the apparent conversions were low but increased gradually. After reaction for 10 h, the dilution effect disappeared and the conversions were stable. It is noted that with only the presence of 2-butanol, $CO_2$ conversion was negative, while in the supercritical $n$-butane, $CO_2$ conversion was high up to 53.5%. From the reaction steps (1–4), CO was converted to $CO_2$ firstly through the water–gas shift reaction, step (1), and then $CO_2$ was converted to methanol via other steps. This suggested that without supercritical $n$-butane, the formation rate of $CO_2$ was higher than its consumption rate, resulting in the accumulation of $CO_2$ and the negative conversion. Under supercritical conditions, the high $CO_2$ conversion indicated that the conversion rate of $CO_2$ was increased more significantly than that of CO, which might be attributed to the fact that the nonpolar $CO_2$ has higher solubility in the nonpolar supercritical $n$-butane due to the rule of "like dissolves like."

In summary, the introduction of supercritical $n$-butane in the low-temperature methanol synthesis can increase the catalytic conversion, especially the $CO_2$ conversion significantly. The present study provides an experimental foundation for the industrial application of supercritical low-temperature methanol synthesis.

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