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Liquid phase methanol synthesis from CO_2 utilizing liquid–liquid separation

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Abstract

The liquid phase methanol synthesis from CO_2 over $Cu/ZnO/Al_2O_3$ catalyst was studied in a hydrophobic solvent. The products were collected continuously by liquid–liquid separation. The main operating conditions, the solvent recycling rate, and the separation temperature had appreciable effect on the catalytic performances. The separation factor was estimated from calculating the liquid–liquid equilibrium by the UNIFAC activity coefficient model. Water produced appreciably influence the catalytic activity, and the separation temperature changed water concentration in the recycling solvent.

Keywords: Copper; Methanol synthesis; Liquid–liquid separation; UNIFAC

1. Introduction

The methanol synthesis from CO_2 and H_2 has recently attracted much attention as one of promising processes for converting CO_2 into chemicals. Methanol is industrially produced from synthesis gas ($CO + H_2$) using gas phase fixed bed reactors. This conventional process should recycle a large quantity of unconverted gas, because of the limitation of chemical equilibrium [1]. Furthermore, the single pass conversion is limited by the large heat release in the reaction.

Recently, a liquid phase methanol synthesis in solvent has received considerable attention, since temperature control is much easier in the liquid phase than in the gas phase one. Several types of reactors have been proposed such as the liquid entrained reactor [2] and the Trickle bed reactor [3]. However, in many of these liquid phase methanol syntheses, the methanol produced is discharged from the reactor in the vapour phase. In this case, the vapour phase remains within the chemical equilibrium composition. As for the CO_2 hydrogenation, the solubility of formed water and methanol into hydrophobic solvent is very low. Therefore, we could collect only products by a liquid–liquid separation.

In a previous paper [4] we have reported that the overall methanol yield was very high for the liquid phase methanol synthesis with a liquid–liquid separation. The purpose of the present work is to describe the main conditions for the production of methanol in the liquid phase system as environmental process.

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2. Experimental

2.1. Catalyst

The $Cu/ZnO/Al_2O_3$ catalyst (the atomic ratio of Cu/Zn/Al = 4:3:3) used in this study was prepared by the coprecipitation method [5]. A mixed aqueous solution of metal nitrates (total metal concentration 1 mol/l) and an aqueous solution of Na_2CO_3 (1.1 mol/l) were added dropwise to distilled water. Subsequently, the precipitate was filtered out, washed with distilled water, dried in air at 393 K overnight, calcined in air at 623 K for 2 h, pressurized at 20 MPa and crushed to the size of 1–2 mm. Before reaction, the catalyst was reduced in a gas mixture of H_2 (50%) and He (50%) at 523 K under atmospheric pressure.

2.2. Apparatus and procedures

The hydrogenation reaction of CO_2 was conducted using a 200 cm^3 autoclave under a pressurized condition. The continuous reactor consisted of a draft tube, a catalytic basket type impeller, a gas feed section, and a liquid–liquid separator (13 cm^3). The catalyst was charged to the catalyst basket type impeller. As a model solvent, n-dodecane (n-$C_{12}H_{26}$) 150 cm^3 was charged to the reactor. The mixture of gases (H_2/CO_2 = 3:1) was admitted into the reactor by operating a forward pressure regulator (Tescom Corporation), and its flow rate was measured by a mass flow meter (Oval F201S). The total pressure of H_2 and CO_2 was 15 MPa. A mixture of products was introduced to the liquid–liquid separator by a high pressure pump. Then, the liquid phase was separated into upper phase (solvent phase) and lower phase (aqueous methanol phase), according to the difference of specific gravity. After separation, the solvent phase was continuously recycled to the reactor. The operation pressure of the separation and the solvent recycling was not different from the reaction pressure. The separation temperature was controlled by heating the separator from the outside. The aqueous phase was sampled every hour for analysis. The methanol and water produced were analyzed by a gas chromatography (SHMADZU GC-8A, Detector: TCD) using a Porapak-T column with helium as a carrier.

2.3. Calculation of the liquid–liquid equilibrium

The liquid–liquid equilibrium for a ternary n-$C_{12}H_{26}/H_2O/CH_3OH$ system by the UNIFAC group contribution method was computed by PRODECE (Toyo Joho System Co., Ltd.). This program consists of the equilibrium condition equation, material balance equation and UNIFAC equations [6].

3. Results and discussion

In the CO_2 hydrogenation, the main reaction proceeds under Eqs. (1)–(3). The main condensed products are CH_3OH and an equal molar of H_2O. This hydrogenation occurs under the hydrophobic phase and the products are recovered by the liquid–liquid separation. Especially, the polar products of H_2O would be related to catalytic performance because this reaction system is based on the solubility of products in n-dodecane. We have reported in a previous paper [4] that the composition of the aqueous phase at liquid–liquid separator $H_2/CO/CO_2/H_2O/CH_3OH$ = 1.0/0.03/2.3/48.3/48.3 (conditions: reaction temperature, 523 K; pressure, 15 MPa; H_2/CO_2; solvent flow rate, 3 l-solv./l-cat · h; catalyst, $Cu/ZnO/Al_2O_3$) molar ratio was contained. In order to clarify the catalytic performance of this system, the main factors related to the main products of H_2O and CH_3OH were studied.

$$CO_2 + 3H_2 = CH_3OH + H_2O, \tag{1}$$

$$CO + 2H_2 = CH_3OH, \tag{2}$$

$$CO_2 + H_2 = CO + H_2O. \tag{3}$$

3.1. The effect of the solvent recycling rate

The result in Fig. 1 shows the effect of the solvent recycling rate. The production rate of methanol depended on the solvent recycling rate with a reaction temperature between 473 K to 543 K. The production rate was approaching to a steady value while increasing the solvent flow rate. This means that this steady activity nearly simulates the actual catalytic activity. But in the low flow rate region, the rate was sharply decreased.

Fig. 2 shows the water concentration in the reactor when the recycling rate was changed. The reaction fluid was directly sampled from the reactor. The production rate of methanol was sharply decreased with an increase in H_2O concentration. In the lower H_2O concentration region, the production rate was high and in the higher concentration region, the rate was low. Water concentration was changed to a relative low concentration in a series.

The effect of H_2O in the liquid phase methanol synthesis from syn-gas [7] has already been studied. The addition of large quantities of H_2O slowed down the hydrogenation, depressing the forward reaction. As for the CO_2 hydrogenation in hydrophobic solvent, the solubility of formed H_2O was low. Hence, condensed water would be accumulated in the pores or on the surface of the catalyst, and reduce the potential for the forward reaction.

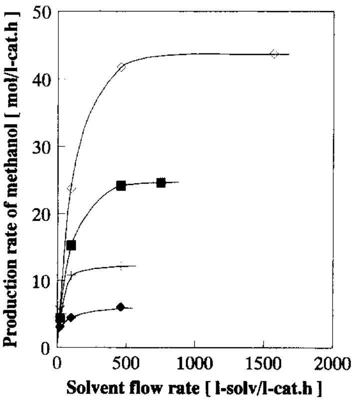

Fig. 1. The relationship between the solvent flow rate and the production rate of methanol. Reaction conditions: temperature, 473 K (◆), 503 K (+), 523 K (■), 543 K (◇); pressure 15 MPa; $H_2/CO_2 = 3$; catalyst $Cu/ZnO/Al_2O_3$ (Cu/Zn/Al, 4:3:3 molar ratio).

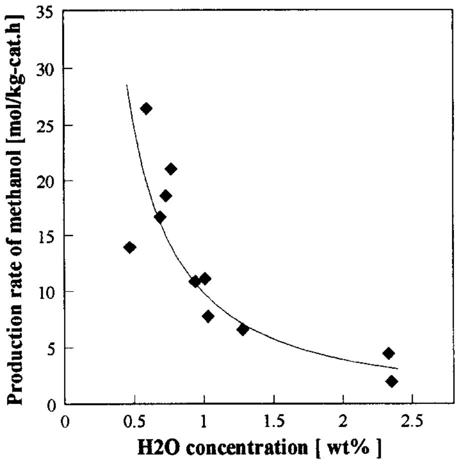

Fig. 2. The relationship between the water concentration and the production rate of methanol. Reaction conditions: temperature, 523 K; pressure 15 MPa; $H_2/CO_2 = 3$, catalyst $Cu/ZnO/Al_2O_3$ (Cu/Zn/Al, 4:3:3 molar ratio).

3.2. The effect of the separation temperature

Under the separation conditions, phase splitting occurs because the aqueous products are mixed with a hydrophobic solvent. It is well known that the equilibrium temperature affects the liquid–liquid equilibrium, and separation efficiency decreases with an increase in the temperature, because the solubility of each component in the separation phases has increased. In this liquid phase system, products are recovered from the liquid–liquid separation. Hence, it is necessary to optimize the separation condition to conform to be the actual operations. Fig. 3 shows the effect of the separation temperature on the production rate of methanol, examined under the steady state condition. In this condition, the ratio of main products reached a molar ratio of nearly $H_2O/CH_3OH = 1$. The rate was decreased with an increase in separation temperature. Especially, the rate was sharply decreased around 423 K and aqueous products were not collected from the separator at 523 K. There-

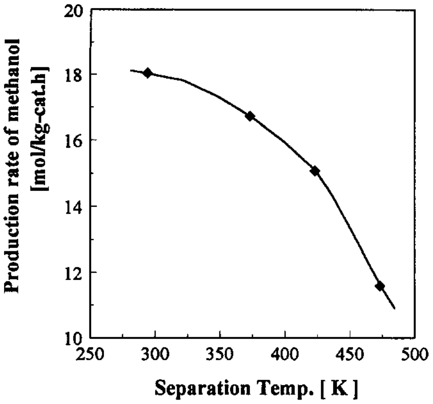

Fig. 3. The effect of the separation temperature on the production rate of methanol. Reaction conditions: temperature, 523 K; pressure 15 MPa; $H_2/CO_2 = 3$; solvent flow rate, 100 l-solv./l-cat · h; catalyst $Cu/ZnO/Al_2O_3$ (Cu/Zn/Al, 4:3:3 molar ratio).

fore, the separation temperature was very important for the recovery of the products.

In order to clarify the separation behaviour, we tried to calculate the ternary n-$C_{12}H_{26}/CH_3OH/H_2O$ liquid–liquid equilibrium by the UNIFAC group contribution method. It is well-known that equilibrium calculations by the UNIFAC method are often considered to be most effectual with the ASOG method [8]. Especially, these group contribution methods are indispensable for unknown systems. To calculate the ternary n-$C_{12}H_{26}/CH_3OH/H_2O$ systems, a liquid composition of reactor: n-$C_{12}H_{26}/CH_3OH/H_2O$ = 0.894:0.042:0.064 (conditions: reaction temperature, 523 K; pressure, 15 MPa; $H_2/CO_2 = 3$; solvent flow rate, 100 l-solv./l-cat · h; separation temperature, 294 K; catalyst $Cu/ZnO/Al_2O_3$) molar ratio was assumed as a feed point. And the distribution and the separation factor were estimated from calculating the liquid–liquid equilibrium results. The distribution and the separation factor were estimated from the following equations:

$$K_{H_2O} = (H_2O\text{ mol fractions in n-}C_{12}H_{26}\text{ phase}) / (H_2O\text{ mol fractions in }H_2O\text{ phase}),$$

$$K_{\text{solv.}} = (\text{n-}C_{12}H_{26}\text{ mol fractions in n-}C_{12}H_{26}\text{ phase}) / (\text{n-}C_{12}H_{26}\text{ mol fractions in }H_2O\text{ phase}).$$

The separation factor $\alpha = K_{H_2O}/K_{\text{solv.}}$.

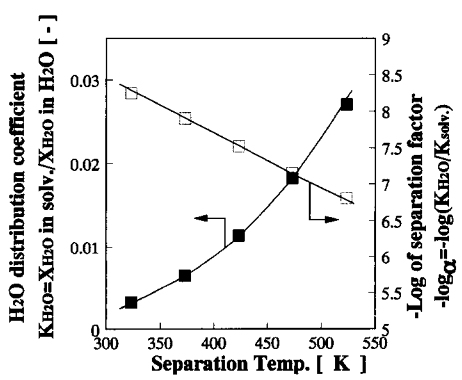

Fig. 4. Effect of the separation temperature on the water distribution coefficient and the − log of the separation factor. Calculation method: UNIFAC group contribution method. Program PRODECE was used.

As shown in Fig. 4, the ratio of H_2O distribution in n-dodecane phase to that in H_2O phase was increased with increasing separation temperature. Also the estimated separation factor was decreased with an increasing separation temperature. The − log of separation factor under 323 K was about 1.21 times higher than under 523 K. This fact implies that the separation efficiency decreased by increasing the temperature. Moreover, water concentration in the n-dodecane phase was increased at higher temperatures. Therefore, the catalytic performance as shown in Fig. 3 may be explained as follows: (1) The products recovered can be strongly affected by the temperature; (2) Water distribution can also be affected by the temperature. Therefore, a higher H_2O concentration results in a decrease of catalytic performance.

Thus, the formed H_2O would play an important role in this system. As for the usual liquid-phase methanol synthesis from synthesis gas, products are collected by vapour–liquid separation with a large amount of gas recycling. But in the method of the liquid–liquid separation, only the reaction fluid is introduced to the separator except for a trace amount of reactant gases.

Therefore, it is possible to consider that (1) recycling power would be lower than the usual liquid-phase methanol synthesis, and (2) recycling of solvent would serve to exchange the reaction heat outside of the reactor. And the heat recovery would be made by the distillation and heating up of recycling solvent.

4. Conclusion

The liquid phase methanol synthesis from CO_2 over $Cu/ZnO/Al_2O_3$ catalyst was studied in a hydrophobic solvent. Products were collected continuously by liquid–liquid separation. The main operating conditions, the solvent recycling rate and the separation temperature had appreciable effect on the catalytic performances. The separation factor was estimated from calculating the liquid–liquid equilibrium by the UNIFAC activity coefficient model. Water produced appreciably influence the catalytic activity, and the separation temperature changed water concentration in the recycling solvent. In this method, only the reaction fluid is introduced to the separator except for a trace amount of reactant gases. Recycling of solvent would serve to exchange the reaction heat outside the reactor, and recycling power would be lower than usual liquid-phase methanol synthesis.

Acknowledgements

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