

Control of surface area and activity with changing precipitation rate in preparation of Cu-Zn based catalysts for dimethyl ether direct synthesis

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Abstract—Cu-Zn based catalysts for the direct synthesis of dimethyl ether were prepared by the co-precipitation method, and the feeding rate of ammonium carbonate used as the precipitant was controlled in order to change the particle size of the active materials. SEM and XRD confirmed that the catalyst particles that were prepared have a small size when the precipitant is rapidly fed into the precursor solution. The crystal growth of the Cu-Zn based catalyst could be controlled by changing the feeding rate of the precipitant in the precipitation method, and the physical properties of the Cu-Zn based catalyst were improved by controlling the crystal growth rate in order to enhance the catalytic activity. The feeding rate of the precipitant solution was controlled in range of 1.5-10.0 ml/min in this study. When the feeding rate of precipitant was adjusted from 1.5 ml/min to 10.0 ml/min, the particle size of Cu-Zn catalysts decreased from 28 nm to 10 nm with increasing feeding rates of precipitant solution and their surface area increased from 28 m²/g to 80 m²/g. The conversion of CO obtained in the catalytic activity tests also increased from 13% to 60%. A high conversion of CO was obtained over the Cu-Zn based catalysts prepared by changing the feeding rate of the precipitate.

Key words: Dimethyl Ether, Co-precipitation, Cu-Zn Based Catalyst

INTRODUCTION

The best way to solve not only environmental pollution issues but also the limited energy supply is to suppress the consumption of fossil fuels. However, the global energy consumption is likely to gradually increase due to the industrial growth expected in the future. For this reason, it is necessary to develop various alternative energy technologies that can produce energy in a highly efficient and environmentally sustainable way. It is known that dimethyl ether (DME) is preferred over fossil fuels since it does not contain many toxic materials. Therefore, it is used either as a spray propellant instead of Freon gas or as an intermediate to produce chemicals such as dimethyl sulfate and methyl acetate [1]. Since the engine noise and air pollution that it causes are considerably less than those caused by the conventional fuels used for transportation, DME has been suggested as a clean alternative fuel for diesel engines. At present, DME is commercially produced by a two-step process in which methanol is synthesized from syngas in the first stage and then converted to DME by dehydration over solid-acid catalysts in the second stage. Studies on the STD (syngas to DME) process for the direct synthesis of DME from syngas in a single step have recently been performed by many researchers, because of its simplicity and advantageous economic aspects [2,3]. Since methanol is rapidly converted to DME and water by reaction (2) in the STD process, a higher conversion and yield would be expected in the single-step process than in the commercialized two-step process [4,5]. The syn-

thesis reactions of DME are as follows [6].



The hybrid catalysts used for the direct synthesis of DME are typically formulated by the physical mixing of a Cu-Zn-based catalyst used for the synthesis of methanol and $\gamma\text{-Al}_2\text{O}_3$ used for its dehydration [1,7-9].

In this study, the direct synthesis of DME from a coal derived synthetic gas, which is composed of CO and H₂, was carried out over the catalysts. The Cu-Zn based catalysts for the direct synthesis of DME were prepared by the co-precipitation method. The feeding rate of the precipitant injected into the precursor solution, which contained Cu and Zn, was controlled in order to decrease the size of the particles. The physical properties and catalytic activity of the catalysts produced in this study were also investigated.

EXPERIMENT

1. Preparation of Catalysts for Direct Synthesis of Dimethyl Ether

The Cu-Zn based catalysts used for the synthesis of methanol were prepared by the co-precipitation method and the procedure used for the preparation of the catalysts is shown in Fig. 1. The equipment used for the preparation of catalysts is also shown in Fig. 2. Copper acetate [$\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2$] and zinc acetate [$\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2$] at a

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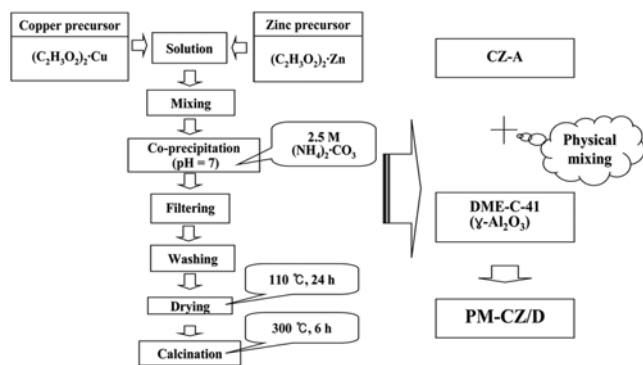


Fig. 1. Procedure used for the preparation of the catalyst.

concentration of 0.2 M as the precursors of the active components were used for the preparation of the Cu-Zn based catalysts. In this way, the mole ratio of Cu/Zn was fixed at 1. Ammonium carbonate $[(\text{NH}_4)_2\text{CO}_3]$ at a concentration of 2.5 M as the precipitant was added slowly at a pH of 7 into the solution containing the Cu and Zn precursors. The precipitate was formed as the pH in the precursor solution increased when the precipitant was added. The feeding rate of ammonium carbonate used as the precipitant was controlled in the range of 1.5–10.0 ml/min. The precursor solution used for the precipitation was heated to 50 °C by means of a mantle and temperature controller. The precursors and precipitant were well mixed by a mechanical agitator equipped with an electrical motor. The solid product obtained by precipitation was dried for 24 h at 110 °C in a dry oven after filtration and washing, and was calcined for 6 h at 300 °C in a muffle furnace. A commercial acid catalyst ($\gamma\text{-Al}_2\text{O}_3$) from Süd-Chemie Inc. was used for the dehydration of methanol

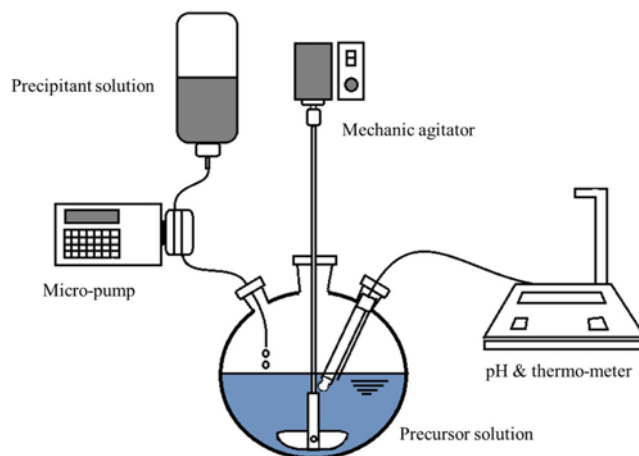


Fig. 2. Schematic diagram of equipment for the catalyst preparation by co-precipitation method.

in this study. A hybrid catalyst, which consisted of $\gamma\text{-Al}_2\text{O}_3$ and the Cu-Zn based catalyst prepared by the co-precipitation method, was prepared by physical mixing for the direct synthesis of DME. The prepared Cu-Zn based catalyst and $\gamma\text{-Al}_2\text{O}_3$ were mixed at a ratio of 1 : 1. The above-mentioned Cu-Zn based catalysts were prepared by varying the feeding rate of the precipitant in the precipitation process. The hybrid catalysts prepared in this study were used to investigate their activity.

2. Catalytic Activity Tests for Direct Synthesis of Dimethyl Ether

The catalytic activity tests for the direct synthesis of DME were carried out in a high pressure catalytic reaction system of the fixed-bed type, as shown in Fig. 3. A tubular reactor consisting of a 1/2

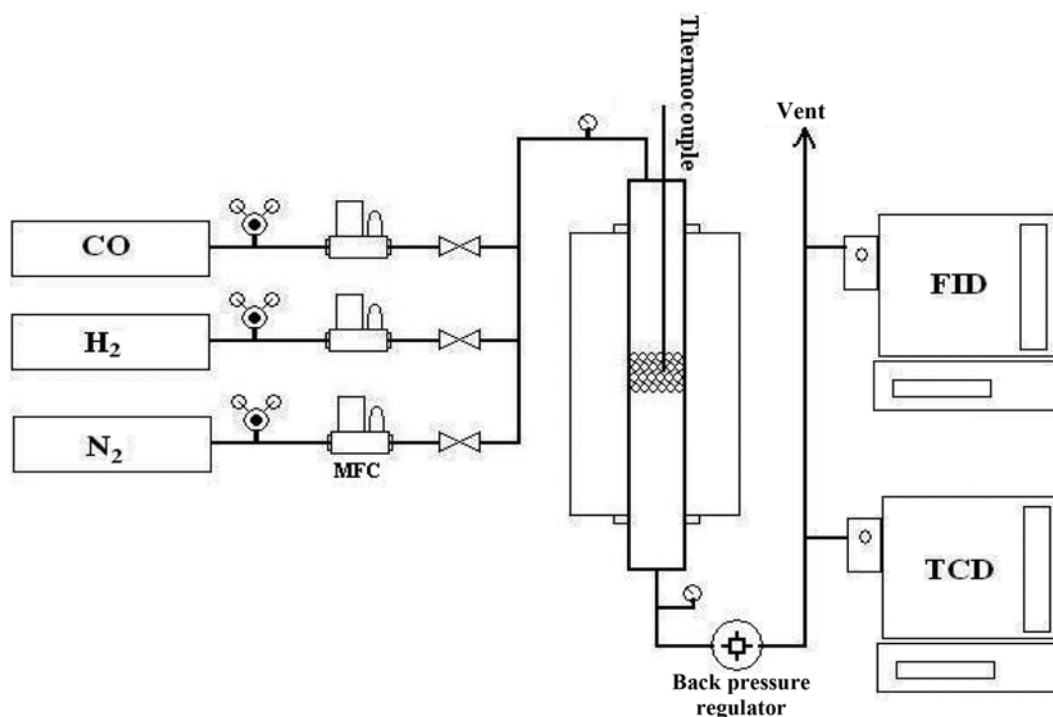


Fig. 3. Schematic diagram of experimental setup.

inch stainless steel (SUS-316) tube was used as the catalytic reactor and about 1.0 g of the hybrid catalyst was packed in the center of the reactor. A thermocouple was also located in the catalyst bed. This high pressure catalytic reactor was placed in a tubular furnace of the vertical type.

The catalytic activity tests for the direct synthesis of DME over the hybrid catalysts were performed under the following experimental conditions. The temperature and pressure in the catalytic reactor were maintained at 260 °C and 50 atm, respectively. The purities of the CO and H₂ used as the reactants were 99.5% and 99.9%, respectively. The H₂/CO mole ratio of the reactant gases flowing into the catalytic reactor was fixed at 1, corresponding to the stoichiometric coefficient. The space velocity (GHSV: Gas Hourly Space Velocity)

was 3,000 ml/g_{cat.}·h. The catalyst was pretreated before the catalytic activity tests. In the pretreatment process, the hybrid catalyst was reduced with 5 vol% of hydrogen under atmospheric pressure conditions for 3 h at 260 °C.

RESULTS AND DISCUSSION

1. Particle Size Measurement of Catalyst by TEM

In the preparation of the catalyst used for the synthesis of methanol, the precursors of zinc and copper are co-precipitated at a pH of about 7 with ammonium carbonate by the co-precipitation method. The role of ammonium carbonate is to produce the precipitants of the active components. In this study, the feeding rate of ammonium

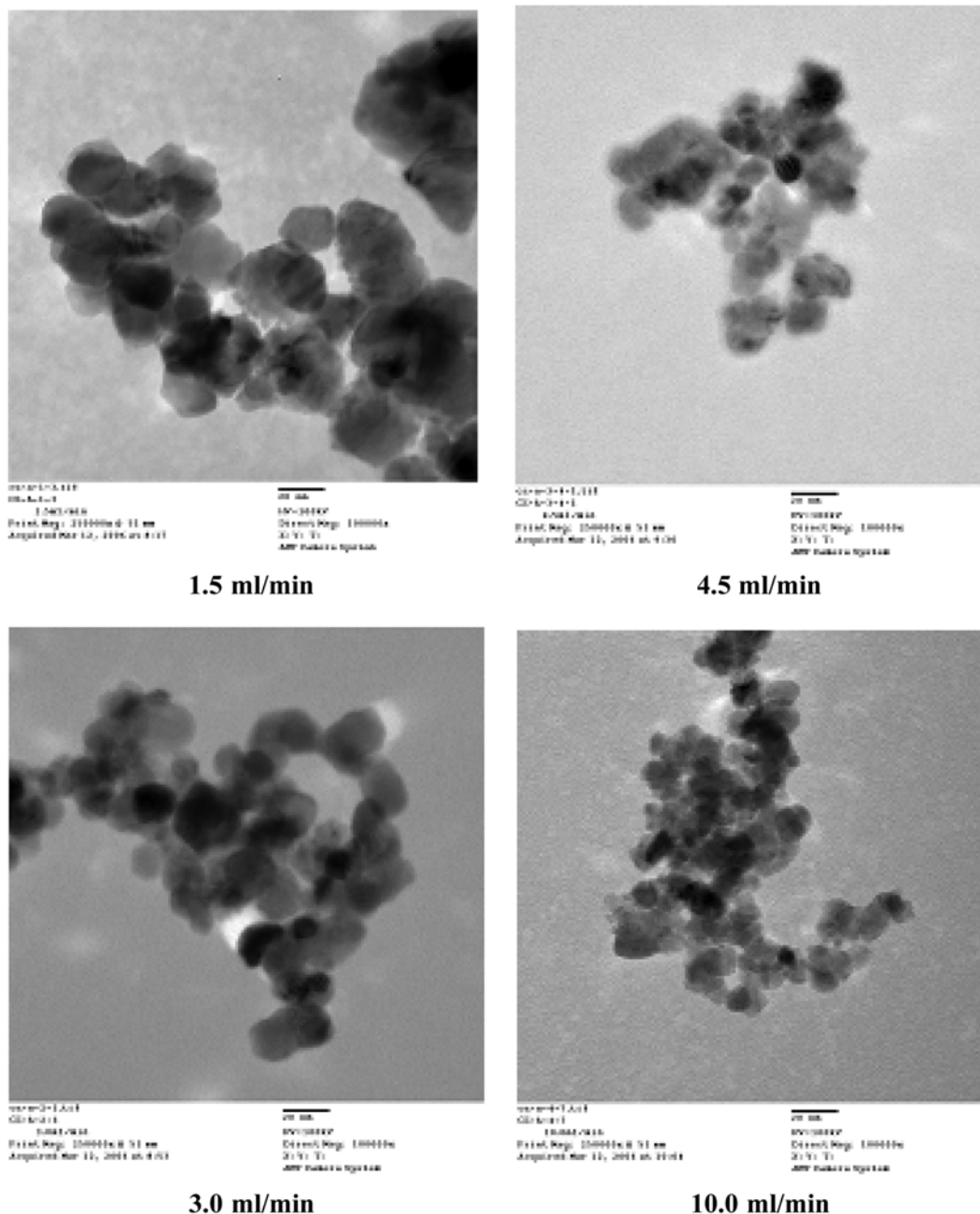


Fig. 4. TEM images of Cu-Zn based catalysts prepared by varying the feeding rate of the precipitant.

carbonate used as the precipitant was controlled. The catalytic active material produced by the precipitation method was treated by washing, drying, and calcination. The surface morphologies of the catalysts were investigated by TEM, as shown in Fig. 4. The Cu-Zn based catalysts synthesized by the precipitation method were prepared with different particle sizes by adjusting the feeding rate of ammonium carbonate. Ammonium carbonate was injected into the precursor solution at rates of 1.5–10.0 ml/min. The particle size of the catalyst was about 18–25 nm when the feeding rate of ammonium carbonate was 1.5 ml/min. Meanwhile, the particle size of the catalyst decreased to 7–10 nm when the feeding rate of ammonium carbonate was increased to 10 ml/min. It was confirmed that the particle size of the catalyst decreased with increasing feeding rate of ammonium carbonate. If the particle size of the catalyst is decreased, a catalyst with a higher surface area would be expected to be obtained.

2. BET Surface Area of Catalyst

It was forecasted that the surface area of the catalyst, which was prepared by adjusting the feeding rate of the precipitant into the precursor solution, would vary with its particle size. The surface area of the Cu-Zn based catalysts prepared for the synthesis of methanol was measured by the BET method using nitrogen adsorption, as shown in Table 1. It was found that the surface area of the Cu-Zn based catalysts increased with increasing feeding rate of the precipitant. The surface area of the catalyst was 28.1 m²/g, when ammonium carbonate was injected at a feeding rate of 1.5 ml/min into the precursor solution. The surface area of the catalyst was increased to 80.8 m²/g, when the feeding rate of ammonium carbonate was increased to 10.0 ml/min. It was concluded that the surface area of the catalysts was enhanced due to the reduction of the particle size.

3. EDX Analysis

The components on the surface of the Cu-Zn based catalysts prepared with various feeding rates of the precipitant were analyzed by EDX. It was confirmed that all of the catalysts prepared in this study had a similar composition of Cu and Zn, as shown in Table 2. The active materials, copper and zinc, in the precursor solution were mixed at a mole ratio of 1 with the addition of copper acetate and

Table 1. BET surface areas of catalysts prepared with various feeding rates of the precipitant by the co-precipitation method

Catalysts	Feeding rate of precipitant, ml/min	BET surface area, m ² /g
CZ-A-I	1.5	28.1
CZ-A-II	3.0	46.5
CZ-A-III	4.5	67.4
CZ-A-IV	10.0	80.8

Table 2. The compositions of the active materials on the surface of the catalysts determined by EDX analysis

Catalysts	Feeding rate of precipitant, ml/min	Atomic %	
		Cu	Zn
CZ-A-I	1.5	37.3	62.7
CZ-A-II	3.0	41.3	58.7
CZ-A-III	4.5	40.7	59.3
CZ-A-IV	10.0	39.9	60.1

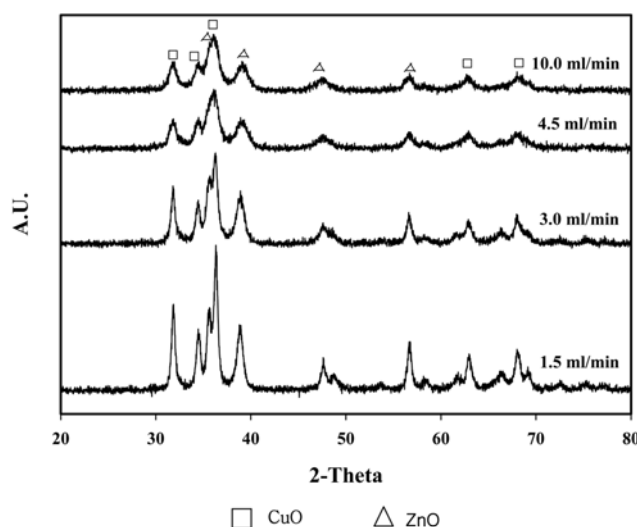


Fig. 5. XRD patterns of Cu-Zn based catalysts prepared by varying the feeding rate of the precipitant.

zinc acetate used as the precursors, respectively. However, the atomic ratio of Cu:Zn over the surface of the catalysts was 4 : 6. This result shows that the amount of the Cu compound precipitated as a solid substance at pH 7 is lower than that of the Zn compound. However, the rate of precipitation of Cu and Zn was found not to be related to the feeding rate of ammonium carbonate, due to the high reaction rate leading to the precipitation of the active materials. Therefore, we concluded that the physical properties of the catalysts prepared by the co-precipitation method are determined by the crystal growth time, which is the time consumed until a pH of 7 is reached after the start of precipitation.

4. XRD Analysis

XRD analysis was performed to investigate the crystal structure of the catalysts prepared with various feeding rates of the precipitant in the co-precipitation process, and the XRD patterns of the catalysts are shown in Fig. 5. The XRD patterns show the typical structure of CuO (2 theta=35.5°, 38.6°) and ZnO (2 theta=31.7°, 34.4°, 36.2°) and no change of the XRD pattern was observed in the XRD analysis of the catalysts prepared with various feeding rates of the precipitant. However, the peak width in the XRD pattern became narrower with decreasing feeding rate of the precipitant and the peak intensity increased. The width and intensity of the XRD peaks were also reversed when the feeding rate of the precipitant was increased. This increase of the peak intensity and decrease of the peak width in these XRD patterns means that the crystal is grown from the active components. In our previous study [9,10], amorphous Cu-Zn based catalysts had a high catalytic activity for directly synthesized of DME. Thus, the crystal growth time of the catalytic active components should be shortened, in order to enhance the catalytic activity of the Cu-Zn based catalyst. We concluded that amorphous Cu-Zn based catalysts, which have low peak intensity in their XRD peak pattern, can be obtained by controlling the crystal growth time.

5. Catalytic Activity for DME Synthesis

The activity of the prepared catalysts, whose particle size, surface area and crystallinity vary with the feeding rate of the precipitant, was investigated in a high-pressure fixed bed catalytic reactor,

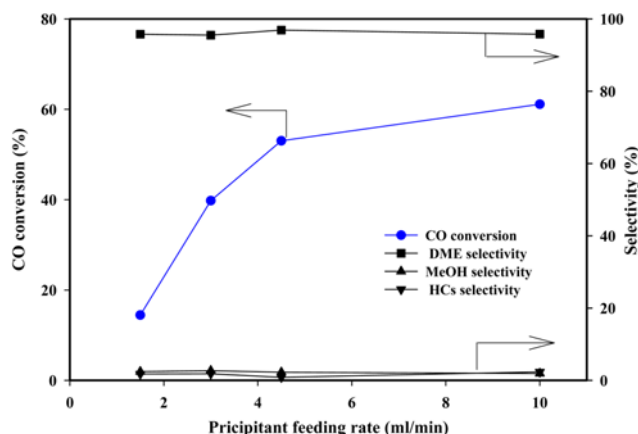


Fig. 6. Effect of the feeding rate of the precipitant on the reactivity of the catalysts used the synthesis of methanol.

as shown in Fig. 3. The activity test of the Cu-Zn based catalysts for the direct synthesis of DME was conducted at a space velocity of 3,000 ml/h g-cat at 260 °C and 50 atm. The molar ratio of the reactants, H₂ and CO, was maintained at 1, which corresponds to the stoichiometric ratio for the direct of synthesis of DME. The catalysts used for methanol synthesis were mixed with γ -Al₂O₃ and used as the catalyst for methanol dehydration: the physical mixing ratio of the two catalysts was 1 : 1. The conversion of CO and the selectivity of DME obtained from the activity tests of the Cu-Zn based catalysts varied with the feeding rate of the precipitant used for the preparation of the Cu-Zn-based catalysts, as shown in Fig. 6. The conversions of CO over the hybrid catalysts, which contained the Cu-Zn based catalysts prepared with feeding rates of 1.5, 4.5, and 10.0 ml/min, were 15%, 55%, and 60%, respectively. The selectivity of DME also remained above 95% over most of the catalysts prepared in this study. Since the same amount of γ -Al₂O₃ as the catalyst for the dehydration of methanol was added to all of the hybrid catalysts, the same selectivity of DME was obtained in all of the activity tests. From these results, it can be concluded that the conversion of CO and the selectivity of DME are dependent on the catalysts used for methanol synthesis and methanol dehydration, respectively. The selectivity of DME was independent of the Cu-Zn based catalyst. We concluded that the rate determination step (RDS) is the methanol synthesis process over the hybrid catalyst used for direct DME synthesis, which consisted of methanol synthesis, methanol dehydration and the water gas shift reaction. Therefore, the physical properties of the Cu-Zn based catalyst contained in the hybrid catalyst are important for the production of DME. In this study, the physical properties of the Cu-Zn based catalysts were varied by adjusting the feeding rate of the precipitant, ammonium carbonate, in the precipitation process and their catalytic activity was improved by changing their physical properties, such as their particle size and surface area.

CONCLUSIONS

To improve the catalytic activity of the hybrid catalyst used for

direct synthesis of DME, Cu-Zn based catalysts were prepared with various feeding rates of the precipitant in the co-precipitation method in this study. The feeding rate of the precipitant solution was controlled in the range of 1.5-10.0 ml/min. When the feeding rate of precipitant was adjusted from 1.5 ml/min to 10.0 ml/min, the particle size of Cu-Zn catalysts decreased from 28 nm to 10 nm with increasing feeding rates of precipitant solution and their surface area increased from 28 m²/g to 80 m²/g. The conversion of CO obtained in the catalytic activity tests also increased from 13% to 60%. The particle size of the Cu-Zn based catalysts decreased due to the low crystal growth of the active materials, and their surface area increased, when the ammonium carbonate used as the precipitant was quickly fed into the precursor solution. Because the fast feeding rate of the precipitant caused the pH of the precursor solution to rapidly reach 7, the crystal growth time for the solid active materials produced by the precipitation method was shortened. Therefore, the crystal growth of the Cu-Zn based catalyst could be controlled by varying the feeding rate of the precipitant in the precipitation method and the physical properties of the Cu-Zn based catalysts were improved by controlling the crystal growth to enhance the catalytic activity. A high conversion of CO was also obtained over the Cu-Zn based catalysts in this study.

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