A New Method for Synthesizing Co-precipitated Cu–ZnO Catalyst and Its Activity for Methanol Decomposition at High Temperature

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Cu–ZnO–Al2O3 catalyst was prepared by introducing fine bubbles of ammonia into a mixed aqueous solution of metal nitrates under carbon dioxide flow and its activity was tested for the methanol decomposition reaction. Specific surface area of the newly developed fine bubble catalyst (FBC) was 94 m²/g and 1.5 times larger than that of conventional catalyst (CVC) prepared by co-precipitation of mixed metallic aqueous solution and sodium carbonate. SEM revealed that the FBC particles were spherical of around 3 μm diameter and homogeneous. The particles of CVC were irregular in size and shape. SEM-EDX showed aggregation of copper in the CVC but good dispersion of all elements in the FBC. FBC had higher activity and less deactivation in the methanol decomposition reaction compared with CVC even at 623-673 K although the reaction time was only 10 hours.

Keywords
Co-precipitation, Copper zinc catalyst, Methanol decomposition, Fine bubble

1. Introduction

Global warming caused by increased emissions of greenhouse gases, especially CO2, is a pressing global problem. Atmospheric CO2 concentration rose above 400 ppm in 2015, and continues to increase. Therefore, CO2 emissions must be drastically reduced or eliminated entirely to prevent an increase in global temperature of more than 2 K by 2100. One solution is to recycle CO2 into fuel using hydrogen produced from renewable energy sources. Previous studies have examined the synthesis of hydrocarbons such as methane, methanol, gasoline, and diesel fuel from CO2. Methane and methanol can be effectively synthesized from CO2; but the methanol yield is strongly limited by the thermodynamic equilibrium of the reaction. For example, the yield of methanol from synthesis gas at 4 MPa is only 30 % at 473 K, and 13 % at 523 K. Conversion of methanol to dimethyl ether (DME) may increase the yield of methanol and DME. The highest yield of methanol and DME was 24 % at 543 K, achieved by combining a methanol synthesis catalyst with γ-Al2O3. Similar possibilities can be applied to the conversion of CO2 to hydrocarbons, which are currently a more important fuel.

Other studies have reported hydrocarbon synthesis from syngas4)–6). Use of a combination of Cu–ZnO and ultra-stable Y-type zeolite catalyst at 623 K and 2.1 MPa obtained a yield of hydrocarbons of 30 %, about 75 % of which were C3 and C4 paraffins, or liquefied petroleum gas (LPG). These techniques can be applied to hydrocarbon synthesis from CO2; but methanol synthesis catalysts such as Cu–ZnO–Al2O3 have low thermal stabilities at the conditions under which the zeolite catalyst actively forms hydrocarbons from methanol/dimethyl ether. Therefore, development of a new methanol synthesis catalyst with high thermal stability is required.

Fine bubbles smaller than 100 μm show unique behavior. Fine bubbles have a large specific surface area, so gas molecules inside the bubble will easily and rapidly contact with the surrounding liquid. Here we describe a new method for the preparation of precipitated catalyst by passing fine bubbles through a solution. Mixed metal salts solution will quickly react with ammonia in fine bubbles but the resulting metal hydroxide is unlikely to aggregate into large particles because the precipitate is generated only at the interface of the liquid and fine bubbles. Consequently, the particle diameter of the precipitate prepared by this fine bubble method is thought to be very fine with a large specific surface area. A Cu–ZnO–Al2O3 catalyst, prepared with...
this method, was found to have high thermal stability, even at temperatures of 623-673 K.

The methanol decomposition reaction has generally been used to evaluate the catalytic activity of newly developed methanol synthesis catalysts because the methanol synthesis reaction is strongly limited by the thermodynamic equilibrium, and pressures above 3 MPa are required for testing methanol synthesis activity. Here we report the characteristics and activity of the newly developed catalyst for methanol decomposition at high temperatures.

2. Experimental

2.1. Catalyst Preparation

2.1.1. Preparation of Fine Bubble Catalyst

The new type of fine bubble catalyst (FBC) was prepared using ammonia fine bubbles as follows. Ion-exchanged water 2000 cm$^3$ was poured into a beaker and circulated through an aspirator (Fig. 1). Copper nitrate trihydrate 45.0 g, zinc nitrate hexahydrate 55.5 g and aluminum nitrate nonahydrate 12.2 g were dissolved into ion-exchanged water 3000 cm$^3$. This mixed metal nitrate solution was fed into the beaker at around 30 cm$^3$/min with a tube pump. Just after starting the tube pump, ammonia gas was also introduced into the nitrate solution through the aspirator as fine bubbles approximately 100 $\mu$m in diameter at a flow rate of 150 cm$^3$/min controlled by a thermal mass flow controller. Carbon dioxide was introduced through a ceramic filter at a flow rate of 200 cm$^3$/min. The feeding rate of the nitrate solution was controlled to maintain pH 7 in the beaker. Ammonia gas and carbon dioxide flows were stopped when the nitrate solution was consumed. After titration, the solution was kept at room temperature for 24 h for aging. The resulting cake was filtered, rinsed, dried and calcined as described above for the FBC.

2.1.2. Preparation of Conventional Catalyst

For comparison, a conventional catalyst (CVC) was also prepared as follows. Copper nitrate trihydrate 15.0 g, zinc nitrate hexahydrate 18.5 g and aluminum nitrate nonahydrate 4.1 g were dissolved into ion-exchanged water 1000 cm$^3$. Sodium carbonate 28 g was dissolved into ion-exchanged water 600 cm$^3$ in another beaker. The mixed metal nitrate solution was introduced into the nitrate solution through the aspirator as fine bubbles containing ammonium carbonate solution 0.15 mmol/cm$^3$ with a tube pump, and stirred with a magnetic stirrer. The sodium carbonate solution was also added to the system with a separate tube pump, until the pH was 7. After titration, the precipitated solid was kept at room temperature for 24 h. The cake was filtered, rinsed, dried and calcined as described above for the FBC.

2.2. Catalyst Characterization

The exterior surface of the catalyst was observed by scanning electron microscopy (SEM, SU-6600 Hitachi High-Tech Corp.) with an energy-dispersive X-ray (EDX) device. The SEM-EDX image was observed by the same apparatus. The specific surface area was measured by BEL-CAT (MicrotracBEL Corp.) using the one point BET method with 30 % N$_2$ (helium balance) gas in liquid nitrogen. The sample was heated at 473 K for 2 h in helium gas flow before measurement.

2.3. Decomposition Reaction of Methanol

The apparatus shown in Fig. 2 was used for the decomposition reaction of methanol. Cu-ZnO-Al$_2$O$_3$ catalyst 2.8 g was crushed and sieved to particle sizes of 2-4 mm and placed in a stainless tube reactor. The catalyst was reduced in a 100 cm$^3$/min flow of N$_2$/H$_2$ (95 : 5) at 493 K for 10 h. The reactor temperature was subsequently increased to 623 K in a pure nitrogen flow, and methanol was introduced to the reactor with a pump. The molar ratio of nitrogen to methanol was...
1:1. W/F was adjusted to 5 g-cat·h/mol, and the decomposition reaction was executed under ambient pressure. A second experiment was performed at 673 K. Product gas was analyzed by gas chromatography with thermal conductivity detector (TCD). Flow rate of the product gas was calculated using N₂ as an internal standard.

3. Results and Discussions

3.1. Catalyst Characterization

SEM images of the FBC and CVC are shown in Figs. 3 and 4. The particles of FBC are spherical, with diameters of approximately 3 μm, and relatively homogeneous. In contrast, the particles of CVC are irregularly shaped and have formed aggregates. SEM-EDX images of Cu and Zn in the FBC and CVC are shown in Figs. 5 and 6. Cu is homogeneously distributed in the FBC particles, but locally aggregated in the CVC particles. The specific surface area of the FBC, 94 m²/g, is 1.5 times larger than that of the CVC, 63 m²/g.

3.2. Activity for Methanol Decomposition

Activity and selectivity for methanol conversion to carbon monoxide were used as parameters to evaluate the catalytic activity of the methanol decomposition reaction. Methanol decomposes to carbon monoxide and hydrogen according to the following reaction:

\[
\text{CH}_3\text{OH} \rightarrow \text{CO} + 2\text{H}_2 \tag{1}
\]

However, methane and carbon dioxide are also observed as products. The methane and some CO₂ may be the products of a reaction between CO produced by the reaction of (1) and methanol:

\[
\text{CO} + \text{CH}_3\text{OH} \rightarrow \text{CH}_4 + \text{CO}_2 \tag{2}
\]

CO₂ may also be produced via the disproportionation reaction of carbon monoxide:

\[
2\text{CO} \rightarrow \text{C} + \text{CO}_2 \tag{3}
\]

The results of methanol decomposition at 623 K with FBC, FBC-b and CVC are shown in Fig. 7. Average methanol conversion after 3 h was around 62 % with the FBC and FBC-b. On the other hand, average methanol conversion with CVC was around 43 %. Although the reaction time was only 10 h, methanol conversion seemed to cause deactivation of all catalysts. However, the rates of deactivation were clearly lower with FBCs than with CVC. Therefore, FBC shows
higher activity and less deactivation.

Figure 8 shows the selectivity for CO in the methanol decomposition reaction at 623 K with FBC, FBC-b and CVC. The product gas from all three experiments was stable at approximately 90 % CO after 10 h of reaction. Methane and carbon dioxide were also observed in the product gas at contents of less than 10 %. In more detail, the content of carbon dioxide was approximately 5-7 %, and the content of methane was approximately 3-5 %. Therefore, we assumed that both reactions (2) and (3) had also proceeded simultaneously with reaction (1).

Figure 9 shows methanol conversion at 673 K with the FBC and CVC. Average methanol conversion with FBC was about 73 %; higher than that achieved at 623 K as expected. However, methanol conversions with CVC were again unstable with average of only 38 %; lower than the average at 623 K. Figure 10 shows the selectivity for CO produced at 673 K. As for the experiments at 623 K, selectivities for CO were stable at approximately 90 %.

Previous studies have indicated that Cu-ZnO catalysts have low thermal stabilities, and should not be employed above 573 K. Consequently, methanol conversions with CVC were unstable even at 623 K. In contrast, FBC showed high and stable catalytic activity even at 673 K. To understand the high thermal stability of FBC, the specific surface areas of FBC, FBC-b and CVC after 10 h of reaction at 623 K were measured as listed in Table 1. Before the reaction, the specific surface area of FBC was 1.5 times larger than that of the CVC. However, after 10 h of reaction, both had similar specific surface areas of approximately
55-60 m²/g. Unfortunately, the reason for the high thermal stability of FBC remains unclear.

Aggregations of Cu was found in the CVC by SEM-EDX analysis. In a Cu-ZnO-Al₂O₃ catalyst, Cu(I) is the active agent for methanol synthesis and decomposition, and ZnO prevents over-reduction of Cu. Therefore, Cu and ZnO should ideally be distributed homogeneously within the catalyst particle. The FBC particles were more chemically homogeneous, which is likely the reason FBC retained stable activity in the methanol decomposition reaction even at high temperature.

4. Conclusions

A new method for catalyst preparation is described, in which a precipitated catalyst is formed at the interface of fine bubbles and a liquid, and catalyst evaluation provided the following conclusions.

(1) Catalyst particles formed by this new method are roughly spherical, around 3 μm in diameter, and homogeneous.
(2) Catalyst specific surface area is 1.5 times larger than that of a catalyst prepared with a conventional method.
(3) Catalyst activity is high even at 623-673 K, with high thermal stability.

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Table 1 Specific Surface Area before and after the Reaction

| Catalyst [m²/g] | FBC | FBC-b | CVC |
|----------------|-----|-------|-----|
| Before reaction | 94  | 89    | 63  |
| After reaction  | 60  | 78    | 55  |

Measured by BET one point method (N₂ conc. = 30 %).