Activity and stability of $Cu/ZnO/Al_2O_3$ catalyst promoted with B_2O_3 for methanol synthesis

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The addition of B_2O_3 to a $Cu/ZnO/Al_2O_3$ catalyst increased the activity of the catalyst for methanol synthesis after an induction period during the reaction. The stability of the B_2O_3-containing $Cu/ZnO/Al_2O_3$ catalyst was greatly improved by the addition of a small amount of colloidal silica to the catalyst.

Keywords: promoting effect, B_2O_3, $Cu/ZnO/Al_2O_3$ catalyst, methanol synthesis, stability

1. Introduction

Methanol synthesis is one of the most important reactions in chemical industries. Furthermore, as methanol is expected to be used for fuel cell automobiles and for power plants in the future, methanol synthesis could be more important even in the energy field. So far methanol has been commercially produced from syngas [1–3]. Recently, methanol synthesis from CO_2 and H_2 has received much attention because it has been considered to be one of the promising ways for CO_2 mitigation. Many researchers have been devoted to the study of methanol synthesis from CO_2 hydrogenation [4–20]. So far, the authors have been trying to develop Cu/ZnO-based high performance catalysts for methanol synthesis [14–20]. Recently, the authors have newly found out that the addition of B_2O_3 to a $Cu/ZnO/Al_2O_3$ catalyst improved the activity of the catalyst for methanol synthesis after an induction period observed during the reaction. The present paper reports the following three points: (1) promoting effect of B_2O_3 contained in a $Cu/ZnO/Al_2O_3$ catalyst on the catalyst activity, (2) induction period observed during methanol synthesis due to the addition of B_2O_3, and (3) improvement of the catalyst stability by the addition of a small amount of colloidal silica.

2. Experimental

A $Cu/ZnO/Al_2O_3$ (40/55/5) catalyst containing B_2O_3 was prepared according to the following steps. In the first step, the precipitate containing the components of the catalyst was prepared by a coprecipitation method using Na_2CO_3 as a precipitant, as described in detail elsewhere [14]. In the second step, the precipitate prepared was thoroughly washed with distilled water and mixed with an aqueous solution of B_2O_3. Finally, without further filtering, the precipitate containing B_2O_3 was dried overnight at 393 K, calcined at 873 K for 2 h, and then the dry powder was crushed and pelletized before use for methanol synthesis.

A $Cu/ZnO/Al_2O_3$ (40/55/5) catalyst without B_2O_3 was prepared in the same way as the preparation of the B_2O_3-containing catalyst, except that no B_2O_3 was added. Silica was introduced into the catalyst by adding colloidal silica into the aqueous solution of metal nitrates used for coprecipitation in the first step described above. The colloidal silica was supplied by Nissan Chemical Co.

The catalysts prepared were tested for methanol synthesis using a fixed-bed downflow reactor. 1 ml of catalyst was loaded in the reactor and then reduced in a stream of a gas mixture of H_2 (10%) and He (90%) at 573 K for 2 h under the pressure of 5 MPa. After cooling the catalyst bed to the reaction temperature (523 K), the reaction gas, which consisted of CO (3%), CO_2 (22%) and H_2 (75%), was fed at 167 ml/min from a mass controller. The reaction gas containing 3% of CO was used in the present study because CO concentration in the inlet gas to the reactor in a recycle plant for methanol synthesis from CO_2 and H_2 was around 3% [18,20]. Methanol synthesis was carried out at the pressure of 5 MPa. The reactor effluent was analyzed by on-line gas chromatographs equipped with a Porapak Q column and a TCD detector for analysis of CO and CO_2, and with a CBP20 capillary column and a FID detector for analysis of methanol. The methanol synthesis activity of the catalyst was expressed by space time yield of methanol (STY).

The total surface area of the catalyst after reaction was measured by flow N_2 adsorption at 77 K. The Cu sur-

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face area of each catalyst after reaction was determined by the technique of N_2O reactive frontal chromatography (RFC) [21] after re-reducing the post-reaction catalyst with H_2 at 523 K. X-ray diffraction (XRD) experiments were carried out on a Rigaku diffractometer, Cu Kα radiation was used at 30 kV and 20 mA. The sample scans were collected between 10° and 80° 2θ. The content of B_2O_3 in the catalyst was determined by the ICP method.

3. Results and discussion

3.1. Activity and an induction period

Figure 1 presents the change in the methanol synthesis activity of silica-free $Cu/ZnO/Al_2O_3$ catalysts without B_2O_3 and with an initial B_2O_3 content of 5.8 wt% with increasing time on stream. The activity of the $Cu/ZnO/Al_2O_3$ catalyst without B_2O_3 was 551 g-methanol/kg-cat h as STY after 1 h reaction, and then decreased with increasing time on stream. On the other hand, the initial activity of the $Cu/ZnO/Al_2O_3$ catalyst with B_2O_3 was quite low (STY $=$ 214 g-methanol/kg-cat h) after 1 h reaction. Then, the activity gradually increased with an increase in time on stream and reached its maximum (STY $=$ 636 g-methanol/kg-cat h) after 120 h reaction, which was much higher than that of the $Cu/ZnO/Al_2O_3$ catalyst without B_2O_3.

Table 1 shows the activity, the surface areas and the B_2O_3 content of the $Cu/ZnO/Al_2O_3$ catalyst containing B_2O_3 as a function of time on stream of methanol synthesis along with the activity and the surface areas of the catalyst without B_2O_3 after 1 h reaction. Each sample shown in table 1 was taken after the fresh catalyst was used for a given time on stream. The Cu surface area (21.5 m^2/g) of the catalyst with an initial B_2O_3 content of 5.8 wt% after 120 h reaction was much higher than that (15.0 m^2/g) of the catalyst without B_2O_3 after 1 h reaction, whereas their BET surface areas were almost the same. As displayed in figure 2, X-ray diffraction measurements showed that the diffraction peaks assigned to metallic copper were sharper for the catalyst without B_2O_3 after 1 h reaction than those for the catalyst with B_2O_3 after 120 h reaction, indicating that the copper dispersion in the catalyst was improved by the addition of B_2O_3 to the catalyst. The Cu surface area of the catalyst without B_2O_3 should be lower in 120 h reaction than in 1 h reaction, as suggested from our previous finding that both the activity and the Cu surface area of a Cu/ZnO-based catalyst decreased with time on stream [16]. The findings described above strongly suggest that B_2O_3 added to the $Cu/ZnO/Al_2O_3$ catalyst should enhance the catalyst activity for methanol synthesis from CO_2 hydrogenation in a way of improving the copper dispersion in the catalyst as a dispersing agent.

It is also clearly shown in table 1 that the content of B_2O_3 in the catalyst decreased from 5.8 wt% after 1 h reaction to 1.3 wt% after 120 h reaction with an increase in time on stream, while the Cu surface area and the activity increased. The total surface area of the catalyst slightly

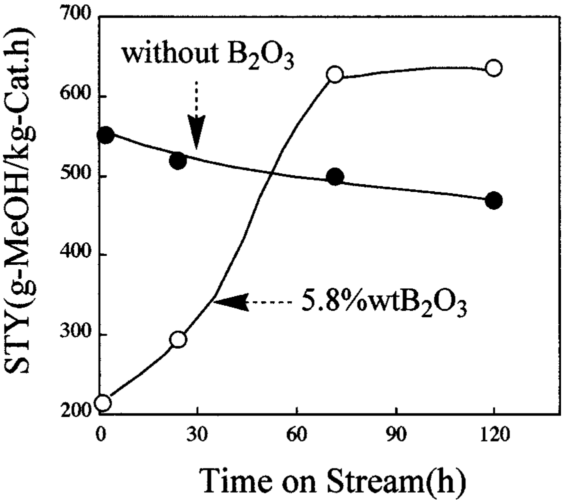

Figure 1. Change in the methanol synthesis activity of $Cu/ZnO/Al_2O_3$ catalysts without B_2O_3 and with an initial B_2O_3 content of 5.8 wt% calcined at 873 K with time on stream. Reaction conditions: 523 K, 5 MPa, SV $= 10\,000\ h^{-1}$, $CO_2/CO/H_2 = 22/3/75$.

Table 1

Activity, surface areas and B_2O_3 content of a $Cu/ZnO/Al_2O_3$ catalyst with an initial B_2O_3 content of 5.8 wt% as a function of time on stream of methanol synthesis and comparison with the catalyst without B_2O_3.[a]

Catalyst	Time on stream (h)	B_2O_3 content (wt%)	Activity (g-MeOH/ kg-cat h)	Surface area (m^2/g-cat)	Cu surface area (m^2/ml-cat)
$Cu/ZnO/Al_2O_3$ containing B_2O_3	1	5.8	214	55.4	16.5
	24	4.8	295	50.4	14.3
	72	2.9	627	49.9	19.8
	120	1.3	636	48.3	21.5
Without B_2O_3	1	0	551	48.3	15.0

[a] Reaction conditions: 523 K, 5 MPa, GHSV $= 10\,000\ h^{-1}$, $CO_2/CO/H_2 = 22/3/75$.

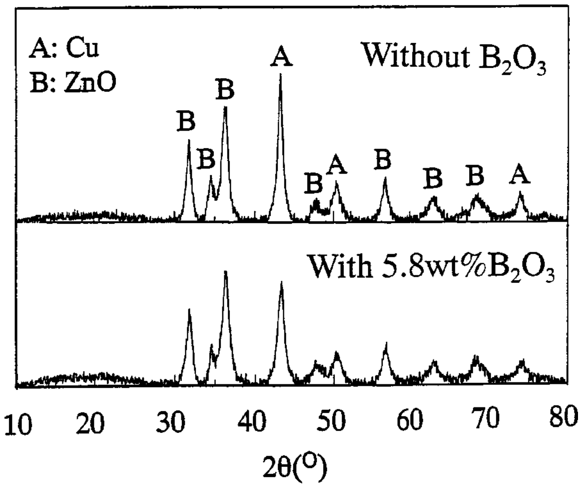

Figure 2. X-ray diffraction patterns of $Cu/ZnO/Al_2O_3$ catalyst without B_2O_3 after 1 h reaction and $Cu/ZnO/Al_2O_3$ catalyst with 5.8 wt% B_2O_3 after 120 h reaction in methanol synthesis from CO_2 hydrogenation.

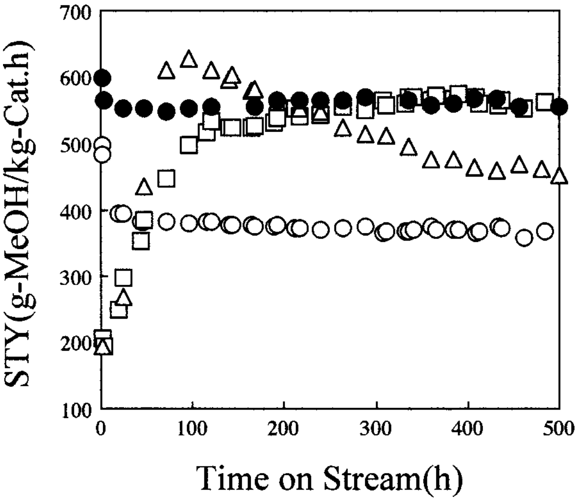

Figure 3. The effect a small amount of colloidal silica added to B_2O_3-containing $Cu/ZnO/Al_2O_3$ catalyst calcined at 873 K on its long-term stability in methanol synthesis from CO_2 hydrogenation. Reaction conditions: 523 K, 5 MPa, SV = 10 000 h^{-1}, $CO_2/CO/H_2 = 22/3/75$. (○) $Cu/ZnO/Al_2O_3$ catalyst with 1.0 wt% SiO_2, (△) $Cu/ZnO/Al_2O_3$ catalyst with 5.8 wt% B_2O_3, (□) $Cu/ZnO/Al_2O_3$ catalyst with 5.8 wt% B_2O_3 and 1.0 wt% SiO_2, and (●) $Cu/ZnO/Al_2O_3$ catalyst with 5.8 wt% B_2O_3 and 1.0 wt% SiO_2 pretreated *in situ* with H_2 and methanol for 2 h before the reaction gas was fed.

decreased during the reaction. Since it is well known that B_2O_3 reacts with methanol to produce trimethyl borate [22], it is suggested that the decrease in the content of B_2O_3 in the catalyst during methanol synthesis should be due to the removal of B_2O_3 from the catalyst through the formation of volatile trimethyl borate by the reaction between B_2O_3 and methanol produced during the reaction. In addition, the XRD pattern for the catalyst with an initial B_2O_3 content of 5.8 wt% remained almost unchanged during 120 h reaction, suggesting that the increase in Cu surface area of the catalyst with decreasing content of B_2O_3 in the catalyst could be due to the removal of B_2O_3 from Cu surface covered with B_2O_3.

To verify the above speculation, the catalyst with 5.8 wt% B_2O_3 was pretreated *in situ* at 523 K with a gas mixture of methanol and $H_2(10\%)/He(90\%)$ for about 2 h before reaction gas was fed into the reactor. The results are shown in figure 3 (●). The results will also be discussed later in the section of stability improvement since the catalyst investigated here contained colloidal silica. In this case, no induction period was observed, and almost the same initial activity as the highest one obtained on 5.8 wt% B_2O_3–$Cu/ZnO/Al_2O_3$ (as (△) in figure 3). This result strongly suggests that the induction period for a B_2O_3-containing catalyst could be avoided by the pretreatment of the catalyst with methanol to remove B_2O_3 from the catalyst by its reaction with methanol.

In summary, the addition of B_2O_3 to a $Cu/ZnO/Al_2O_3$ catalyst increased its Cu dispersion, resulting in the improvement of the catalyst activity. An induction period observed during methanol synthesis over a B_2O_3-containing catalyst can be explained by the removal of B_2O_3 from the catalyst due to the formation of trimethyl borate between B_2O_3 and methanol.

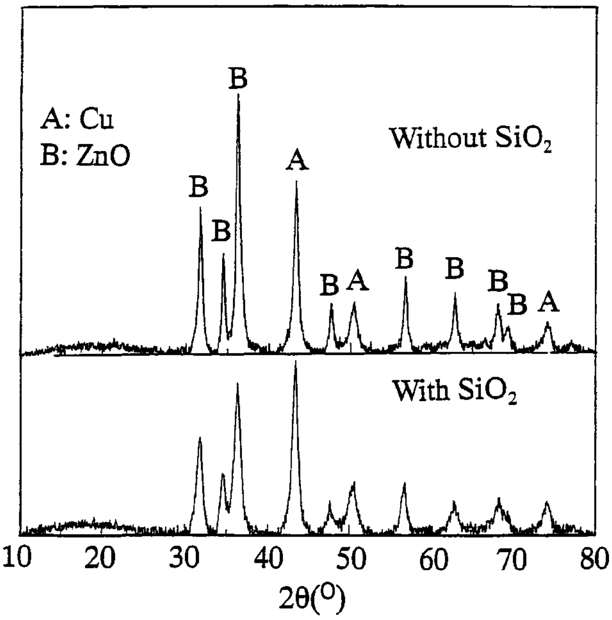

Figure 4. X-ray diffraction patterns of 5.8 wt% B_2O_3–$Cu/ZnO/Al_2O_3$ catalysts without silica and with 1.0 wt% silica after 500 h in methanol synthesis from CO_2 hydrogenation.

3.2. Stability improvement

A methanol synthesis catalyst used in a practical process should be not only highly active, but also stable for a long period in a continuous operation. The addition of a small amount of colloidal silica to a $Cu/ZnO/Al_2O_3$ catalyst with 5.8 wt% B_2O_3 was found to greatly improve its long-term stability in methanol synthesis from CO_2 hydrogenation. The activity of the 5.8 wt% B_2O_3–$Cu/ZnO/Al_2O_3$ catalyst without colloidal silica reached its maximum due to the induction period of catalyst activation, and then decreased monotonously with time on stream and was not stabilized until 500 h (as (△) in figure 3). The activity after 500 h was 28% lower than its highest activity. On the other hand, the activity of the 5.8 wt% B_2O_3–$Cu/ZnO/Al_2O_3$ catalyst containing 1.0 wt% SiO_2 remained almost unchanged after the induction period (as (□) in figure 3).

Figure 4 shows XRD patterns for the 5.8 wt% B_2O_3–$Cu/ZnO/Al_2O_3$ catalysts without and with 1.0 wt% SiO_2 after 500 h in methanol synthesis from CO_2 hydrogenation. The peaks assigned to ZnO were much sharper for the catalyst without SiO_2 than those for the catalyst with SiO_2, clearly indicating that ZnO in the catalyst without SiO_2 was more crystallized than that in the catalyst with SiO_2. As previously reported by the authors [16], it is suggested that the catalyst deactivation should result from the crystallization of the metal oxides contained in the catalyst, especially ZnO, that could be caused by the steam produced during methanol synthesis from CO_2 hydrogenation, and that the silica added to the catalyst could suppress the crystallization of ZnO, leading to the improvement of the catalyst stability. In the previous study [19], the authors found out that the surface area of ZnO containing silica after its treatment with a feeding gas containing steam was almost the same as that after its treatment with the feeding gas without steam, whereas the surface area of ZnO without silica after its treatment with a feeding gas containing steam was 20% lower than that after the treatment with feeding gas without steam. XRD measurements also indicated that the crystallization of ZnO without silica was much larger than that of ZnO containing silica after the treatment with the feeding gas containing steam.

From practical viewpoints, the induction period due to the addition of B_2O_3 discussed above should be avoided. To achieve this purpose, the 5.8 wt% B_2O_3–$Cu/ZnO/Al_2O_3$ catalyst containing 1.0 wt% of SiO_2 was pretreated *in situ* with a mixture of methanol and H_2(10%)/He(90%) for 2 h before the reaction gas was fed into the reactor, as described before. The catalyst activity slightly decreased at the very beginning and then remained unchanged until 500 h on stream of methanol synthesis from CO_2 hydrogenation (as (●) in figure 3). Both the activity and the stability of the 5.8 wt% B_2O_3–$Cu/ZnO/Al_2O_3$ catalyst containing 1.0 wt% of SiO_2 remained almost unchanged in spite of its pretreatment with methanol, while the induction period was avoided. For comparison, the addition of colloidal silica to a $Cu/ZnO/Al_2O_3$ catalyst without B_2O_3 was also investigated. The results are also shown in figure 3 (○). Although the activity of the 1.0 wt% SiO_2–$Cu/ZnO/Al_2O_3$ catalyst without B_2O_3 was also stable in methanol synthesis, it was much lower than that of the catalyst with 5.8 wt% B_2O_3. This finding clearly indicates that the addition of B_2O_3 into the catalyst can improve the activity of the catalyst, as described above.

4. Conclusions

(1) The addition of B_2O_3 to a $Cu/ZnO/Al_2O_3$ catalyst increased its activity by increasing Cu dispersion in the catalyst. An induction period was observed due to the removal of B_2O_3 from the catalyst by the formation of trimethyl borate by the reaction between B_2O_3 and methanol.

(2) The stability of a $Cu/ZnO/Al_2O_3$ catalyst with 5.8 wt% of B_2O_3 was greatly improved by the addition of a small amount of colloidal silica to the catalyst by suppressing the crystallization of the metal oxides contained in the catalyst, especially ZnO.

(3) The induction period observed over a $Cu/ZnO/Al_2O_3$ catalyst with 5.8 wt% of B_2O_3 could be avoided without the change in its activity and stability by the *in situ* pretreatment of the catalyst with methanol and H_2.

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