Adaptation of Cu/ZnO/Al\(_2\)O\(_3\) to Temperature Change in Methanol Synthesis from CO\(_2\) Hydrogenation

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Abstract: The induction behavior in CO\(_2\) hydrogenation was studied by varying the reaction temperature to investigate the adaptation of the Cu/ZnO/Al\(_2\)O\(_3\) catalyst to the temperature change. The results indicated that a used catalyst had a tendency to keep the last running state in new reaction conditions for MeOH formation, and that this tendency was related to the difference in Cu/Cu\(^{2+}\) ratio caused by CO\(_2\) and CO produced at different reaction temperatures. However, the reverse water-gas shift reaction (RWGS) induced at four temperatures was completely different from that of methanol synthesis. It implied that the two so-called competitive reactions in CO\(_2\)+H\(_2\), RWGS and methanol synthesis, have different active centers.

Key words: induction, Cu/ZnO/Al\(_2\)O\(_3\) catalyst, methanol, adaptation

1. Introduction

The induction phenomenon is very common in catalytic processes, because it is related to almost all catalytic aspects including the formation of active sites, the adsorption and desorption equilibria of reactants and products, the migration of components in catalysts, the catalyst preparation, and even impurities in catalysts, etc. In methanol synthesis from CO+H\(_2\), the induction phenomenon over Ru/Al\(_2\)O\(_3\) [1], CeCu\(_2\) [2], Pd/SiO\(_2\) [3] and Cu/ZnO [3] has been studied, however, few studies on the induction behavior of methanol formation using CO\(_2\)+H\(_2\) as the feed gas over the Cu/ZnO/Al\(_2\)O\(_3\) catalyst have been carried out. Furthermore, the previous studies usually paid attention to the steady-state transient kinetic analysis of the induction phenomenon, but not to the response to reaction temperature changes. In CO\(_2\) hydrogenation, CO\(_2\) and H\(_2\)O shown in reactions (1) and (2) can oxidize metallic Cu in practical operations [4], while the H\(_2\)O adsorbed on the catalyst surface is difficult to desorb [5]. The oxidation ability of CO\(_2\) or H\(_2\)O and the possibility of H\(_2\)O desorption are all related to the reaction temperature. Useful information can be obtained from the study of the induction phenomenon in CO\(_2\) hydrogenation by changing the reaction temperature to investigate the adaptation of the Cu/ZnO/Al\(_2\)O\(_3\) catalyst to the temperature change.

\[
\begin{align*}
\text{CO}_2 + 3\text{H}_2 &= \text{CH}_3\text{OH} + \text{H}_2\text{O} \\
\text{CO}_2 + \text{H}_2 &= \text{CO} + \text{H}_2\text{O}
\end{align*}
\]

2. Experimental

2.1. Catalyst preparation and characterization

The Cu/ZnO/Al\(_2\)O\(_3\) catalyst was prepared by the conventional co-precipitation method. An aqueous solution of Cu, Zn and Al nitrates and an aqueous solution of sodium carbonate (all first grade GR Reagent, D.S.P., Korea) were simultaneously added
into warm water (65–70 °C) with constant stirring and a pH value between 6.8–7.0. After completion of co-precipitation, the suspension, the pH of which had been adjusted to 7.0 was maintained for one hour under the same condition, then filtered and washed with cool water. The precipitate was dried at 120 °C overnight and calcined at 350 °C for 12 h. $S_{BET}$ of Cu/ZnO/Al$_2$O$_3$ (mass ratio: 50/45/5) was 64 m$^2$/g.

2.2. Evaluation of catalytic activity

The reactor was a 3/8 inch stainless steel tube equipped with a 1/8 inch O.D. thermowell in the catalyst bed. The Cu-based catalyst was pelleted and crashed into 60–80 mesh, and 0.5 g of the Cu-based catalyst was mixed with 1.5 g of quartz sand (50–70 mesh) and loaded each time. Prior to the reaction, the Cu-based catalyst was reduced with a 10%H$_2$/N$_2$ gas stream at 100 ml/(min·g) and 250 °C for 6 h under atmospheric pressure, then cooled to room temperature. The reaction pressure was controlled by a back pressure regulator, and the flow rate of the feed gas was controlled by a mass flow controller. The effluent gas from the reactor was electrically maintained at 150 °C to avoid condensation and adsorption of methanol and water on the wall of the tube connecting the reactor and the 6-port valve (tube: 1.8 m, 1/4 inch, and with a back-pressure regulator). CO$_2$ and CO were analyzed by an online GC equipped with a Carbosphere column connected to a TCD. Analysis of methanol, DME and hydrocarbons was carried out by using a Porapark T column connected to an FID. The concentrations of the components in the effluent gas were measured according to the external standard method and the carbon balance. All gases (99.995%) were supplied by Korea Industrial Gases, LTP.

2.3. Temperature programming of the reaction

Route A: After the reduction of the catalyst, the reaction temperature was raised to 190 °C within 1.5 h and held for a certain time to reach a steady methanol yield. Then, it was raised to 210 °C within 1 h, and held for a period of time to reach a steady methanol yield, followed by 230 °C, 250 °C, and finally 190 °C.

Route B: Contrary to route A, the reaction temperature followed the sequence: 250 °C to 230 °C, to 210 °C, to 190 °C, and finally to 250 °C. The reaction pressure and space velocity (SV) in Route B were the same as in Route A.

The schemes of Route A and Route B are shown in Figure 1.

For each constant temperature segment, the outgas was taken for analysis after 0.5 h on-stream at the reaction temperature and then once during each successive hour.

3. Results

3.1. Catalyst stability

The catalyst must be very stable during a continuous evaluation at several temperature points. In order to investigate the catalyst stability, a durable test of the catalyst was carried out at 3.0 MPa with a space velocity of 10,000 ml/(g·h). Deactivation of the Cu-based catalyst is sensitive to reaction temperature [6], and a higher reaction temperature can lead to a faster deactivation. A durability test of the catalyst was carried out at a temperature of 270 °C, which was higher than those used in the following experiments, in order to determine the

![Figure 1. The programming of the reaction temperature.](image1)

![Figure 2. Stability of the Cu/ZnO/Al$_2$O$_3$ catalyst.](image2)
effect of temperature on the stability of the catalyst. As depicted in Figure 2, after the 10 h induction period, the catalyst activity was maintained at a steady state for 100 h. Therefore, the results proved that the catalyst was stable enough to carry out the continuous evaluation.

3.2. Adaptation of the catalyst to reaction temperature change

Evaluation of the fresh catalyst was conducted according to the two routes of temperature change shown in Figure 1 using a feed gas of $\text{H}_2/\text{CO}_2$ (mole ratio 3/1). After the four temperature points were reached in the two temperature routes, the change of catalyst activity from the initial to the steady state was plotted against reaction time in Figures 3, 4, 5 and 6, respectively.

The induction behavior at 250 °C is shown in Figure 3. For the RWGS reaction, no induction period appeared at 250 °C. Similarly for MeOH formation, no induction period appeared as the temperature was raised from 230 °C to 250 °C. However, two long induction periods existed as the temperature was increased directly from ambient temperature or from the 190 °C thermostatic state to 250 °C within 1 h and 1.5 h, respectively. Furthermore, the bigger the rise in temperature, the longer the induction period. All phenomena in Figure 3 (also Figures 4 and 6) were not caused by catalyst deactivation, due to the very close MeOH yields at the steady states.

From Figure 4, the induction period for MeOH formation did not exist, while a short induction period for CO formation occurred in the RWGS, as the reaction temperature changed from 250 °C to 230 °C. As the temperature was changed from 210 °C to 230 °C, the induction period for MeOH formation appeared, while that for CO formation did not.

Figure 3. Reaction activity at the 250 °C thermostatic segment.
Reaction conditions: $SV = 6,150 \text{ ml/(g.h)}$, $p = 3.0 \text{ MPa}$.

Figure 4. Reaction activity at the 230 °C thermostatic segment.
Reaction conditions are the same as those in Figure 3.
Figure 5 exhibits that when the temperature change routes were different, the yields of CO and MeOH at the steady state of 210 °C differed as well. The MeOH yield in the route of 230 °C to 210 °C was higher than that in the route of 190 °C to 210 °C, but CO yield was reversed. These results show that the interior states of the catalyst reached according to the two temperature routes were different or irreversible.

In Figure 6, as the temperature increased from room temperature to 190 °C, a steady state was reached after 9 h, and the induction period for CO formation was not found. As the reaction temperature changed from 210 °C and 250 °C to 190 °C, respectively, similar methanol yields under the above two routes could be achieved when running for 0.5 h. However, methanol yields went through different declining ways or induction behaviors, which showed that the catalysts experienced different interior paths when approaching the steady states, in which the methanol yields were slightly different. This is supported by the fact that the former had an induction period for CO formation for 1 h, while the latter did not.

3.3. Calculation of the real RWGS equilibrium constant

In this work, the actual equilibrium constant $K_p$ of the RWGS reaction and MeOH formation was calculated, in which CO, CO$_2$ and H$_2$ were regarded as ideal gases [7], while the fugacity coefficients of methanol and water were not included. Analytical errors, even within an acceptable range, can drastically effect the accuracy of $K_p$. Nevertheless, the value can still be used to roughly show the changes in the real equilibrium. The theoretical equilibrium constant $K_p$ was calculated according to the equation in ref. [8]. The $K_p$/ $K_p$ of MeOH formation and RWGS reaction as a function of temperature is shown in Figure 7. Figure 7(1) shows that the RWGS reaction
in the feed gas of CO\(_2\) and H\(_2\) is far away from the equilibrium state at temperatures below 250 °C, and only when the reaction was carried out at temperatures higher than 250 °C, could \(K_{p}^{\text{a}}/K_{p}\) be close to 1/1 and near the equilibrium state. Figure 7(2) and Figure 7(3) exhibit the \(K_{p}^{\text{a}}/K_{p}\) of MeOH formation and the RWGS reaction in the feed gas containing CO as a function of temperature, and some results have been further discussed in the following section.

**Figure 7. Reaction equilibrium constant as a function of temperature.**
Reaction conditions are the same as those in Figure 3.
(1) RWGS reaction with feed gas of CO\(_2\)+H\(_2\);
(2) RWGS reaction with feed gas containing CO;
(3) MeOH formation with feed gas containing CO.
\(K_{p}^{\text{a}}\): actual equilibrium constant;
\(K_{p}\): theoretical equilibrium constant.

4. Discussion

Generally, for MeOH formation, a long induction period exists before reaching the steady state, when the reaction temperature is raised from a temperature below 230 °C to a higher temperature. There is almost no induction period when the reaction temperature is reached starting from a higher temperature above 230 °C. However, an induction period exists below 230 °C when the reaction temperature is reached either from a lower or higher temperature. A used catalyst seems to have a tendency to "remember" the last running state, possibly caused by a change in the Cu/Cu\(^{n+}\) ratio of the catalyst. The ratio of Cu/Cu\(^{n+}\) is dependent on CO formation in the RWGS reaction, because the reaction temperature is favorable to enhance CO yield (as shown in Figures 3, 4, 5, 6). It is shown that the states of the Cu surfaces were different at varied temperatures because of the distinct declining routes of MeOH yields at 190 °C from 250 °C and 210 °C (Figure 6). Strong evidence, reported by Chinchen et al. [9], indicated that both metallic and oxidized Cu existed on the surface of the Cu/ZnO/Al\(_2\)O\(_3\) in real methanol synthesis from CO\(_2\)-containing syngas, and that the ratio of Cu/Cu\(^{n+}\) on the surface depended on the precise CO\(_2)/\text{CO}\) ratio in the feed gas. This tendency can be attributed to a reduction capability of CO at a particular temperature, and the change in the Cu/Cu\(^{n+}\) ratio. The later changed slowly with a long induction period at a temperature lower than 230 °C, while it varied quickly at a temperature higher than 230 °C, because there is almost no induction period for CO formation.

However, the Cu/Cu\(^{n+}\) ratio at different temperatures and the tendency to keep the last running state was insufficient to explain the difference of MeOH and CO yields in the steady states at 210 °C reaching from different temperatures (Figure 5), because they should generally affect the induction period and not the yields of products in the steady states. It was suggested that the state of the Cu surfaces could not reappear at a particular temperature, regardless if it was reached from a lower or higher temperature. A recent study [10] demonstrated that Cu(111), Cu(110) and Cu(211) on the surface of the catalyst existed on a catalyst reduced by H\(_2\) at 513 K. When the catalyst was oxidized by CO\(_2\) at 213 K followed by CO reduction at 473 K, the initial state could not be restored because of the loss of Cu(110), while a six-fold increase occurred for the surface population of Cu(211), which was less active in CO\(_2\) decomposition at 213 K. However, when treated by H\(_2\) at 513 K the initial state could be restored. A more recent study [13] by a combination of XPS and a high pressure reaction of Zn vapor deposited Cu(111), Cu(100) and Cu(110) showed that Zn had a promotional effect on the Cu(111) activity for MeOH formation, but no effects for the Cu(110) and (100) activities. The above suggestions were supported by other studies and our experiment.

For the CO formation from CO\(_2\)+H\(_2\) on the Cu/Zn/Al\(_2\)O\(_3\) catalyst, induction behaviors in the RWGS reaction at four temperature points were completely different from those of methanol formation. This observation implies that the two competitive CO\(_2\)+H\(_2\) reactions, RWGS and MeOH synthesis, proceed on Cu (atom or ion) sites [11], but must take place on different centers with different environments such as Zn-doping [13]. If they proceeded on the same
sites, the induction periods should be the same since the RWGS reaction is still far from thermodynamic equilibrium (Figure 7). Therefore, a competitive process may be responsible for the water produced in the two reactions through backward processes.

In order to confirm this assumption, a test in which CO was added to the feed gas to inhibit the RWGS reaction was conducted. In this test, the following conditions were a prerequisite. a) The catalyst must have high activity for methanol formation. The reaction was far from equilibrium, so as to make the difference of MeOH formation rates from different feed gases much larger especially when the RWGS reaction was inhibited. The Cu/Zn/Al$_2$O$_3$ catalyst can meet this demand. b) The RWGS reaction must proceed with little CO yield to reduce the possibility of other explanations. Obviously, only when the RWGS reaction is close to the equilibrium state, can this condition be satisfied. c) The rates of methanol formation at a definite reaction temperature must be at a steady state at which the equilibrium of the Cu crystal surface redox circle can be reversibly reached to reduce the CO concentration effect on the proportions of the Cu surfaces. d) The chemical adsorption of water is reduced as soon as possible. Therefore, a feed gas containing 3.98% CO and 21.81% CO$_2$ was used at reaction temperatures above 230 °C. The results are shown in Figure 7 and Table 1.

### Table 1. The effect of CO in feed gas on reaction activity

<table>
<thead>
<tr>
<th>Feed gas</th>
<th>Temperature</th>
<th>CO$_2$ Conversion (%)</th>
<th>MeOH yield$^a$ (%)</th>
<th>MeOH yield$^b$ (%)</th>
<th>CO yield (%)</th>
<th>MeOH formation rate (mmol/(g·h))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>230</td>
<td>15.70</td>
<td>8.20</td>
<td>8.20</td>
<td>7.40</td>
<td>5.50</td>
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<tr>
<td>25.1% CO$_2$</td>
<td>240</td>
<td>17.50</td>
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<td>8.90</td>
<td>8.70</td>
<td>6.10</td>
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<tr>
<td></td>
<td>250</td>
<td>18.80</td>
<td>8.50</td>
<td>8.50</td>
<td>10.70</td>
<td>5.90</td>
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<td>3.98%CO + 21.81%CO$_2$</td>
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<td>10.80</td>
<td>10.50</td>
<td>9.20</td>
<td>0.30</td>
<td>6.50</td>
</tr>
<tr>
<td></td>
<td>250</td>
<td>11.70</td>
<td>11.30</td>
<td>9.80</td>
<td>0.40</td>
<td>6.90</td>
</tr>
</tbody>
</table>

Reaction conditions are the same as those in Figure 3. MeOH yield $^a$: based on carbon dioxide; MeOH yield $^b$: based on carbon oxides.

Table 1 and Figure 7(2) demonstrate that the RWGS reaction, when the feed gas consisted of 3.98% CO and 21.81% CO$_2$, is close to the equilibrium at 230 °C, and CO yield was below 1%. Although the CO yields remarkably decreased with the increase of temperature, the MeOH formation rates increased slightly, especially at 230 °C and at 240 °C, at which methanol yields were far away from those at the equilibrium states (Figure 7(3)). The slight increase may be attributed to a decrease of water that can inhibit reaction (1), because RWGS is retarded by CO. The above assumption is supported by the experimental results. In a very recent study [12] with TPD-MS and TPSR-MS, it was also indicated that CO could suppress CO$_2$ adsorption, leading to the RWGS reaction. This means that reactions (1) and (2) must proceed on different active sites, because if they occurred on the same site, CO suppression should be the same for both.

Additionally, it can be clearly concluded that catalyst preparation may have strong effects on the catalytic behavior by influencing the distribution and local population of Cu atoms and Cu crystal planes on the surface.

**References**
