Synthesis-Gas Formation from Methanol over Ni Based Composite Catalysts

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The catalytic decomposition of methanol on the Group VIII metal catalysts was studied using a conventional flow reactor. From the comparison of activity and selectivity for \(2\text{H}_2+\text{CO}\) formation, Ni was found to be a suitable main catalyst component. The partial pressure dependence of the decomposition rate showed that methanol was strongly adsorbed on the catalyst surface at higher pressures, resulting in substantial retardation. However, it decreased with increasing temperature. For this reason, Ni catalysts showed a considerable range of change in the rate at 350°C, while a three-component catalyst, Ni-La\(_2\text{O}_3\)-Ru, exhibited stable activity during the reaction, and it is suitable catalyst for synthesis-gas formation.

1. Introduction

In the near future, it is expected that methanol would be supplied in large quantities because it is readily obtainable from abundantly natural gas, available coal, or via synthesis gas, and it has many applications such as organic synthesis, fuel cell, and in particular, on-board reforming.

Some studies on catalytic decomposition of methanol to \(2\text{H}_2+\text{CO}\) by Group VIII metal catalysts\(^1\)) and by Ni-Cu catalysts\(^2\)) have been made but not yet extensively.

The purpose of this study is to develop a highly active catalyst for decomposition of methanol. The authors had found that some three-component catalysts such as Ni-La\(_2\text{O}_3\)-Ru showed high activity for hydrogenation of carbon oxides to form meth-\(\text{H}_4\)ane\(^3\),\(^4\)) and direct hydrogenation of carbon\(^5\)). The activity of Ni-La\(_2\text{O}_3\)-Ru was far beyond the sum of the activities of the single component catalysts\(^6\)). The reason for this phenomenon is elucidated by the adsorption study that indicated that a marked increase in CO- and \(\text{H}_2\)-adsorption occurred in the three-component catalyst\(^6\)). This fact suggested that the three-component catalyst could be highly active for methanol decomposition and this suggestion was ascertained\(^7\)). So, to clarify the phenomenon more in detail, the reaction characteristics of various kinds of Ni-based composite catalysts and some platinum-group-metals catalysts were investigated. In addition, an industrial catalyst used for methanol synthesis from \(\text{H}_2+\text{CO}\), was also used in this study for comparison, because the catalyst could be one of the possible catalysts\(^8\),\(^9\)) to achieve the purpose of this study.

2. Experimental

2.1 Catalysts

A silica support having meso (5 nm) and macro (600 nm) bimodal pore structures\(^3\)) was prepared and used in this study. Research grade Ni(\(\text{NO}_3\))\(_2\)-\(6\text{H}_2\text{O}\), La(\(\text{NO}_3\))\(_3\)-\(6\text{H}_2\text{O}\), and RuCl\(_3\)-\(3\text{H}_2\text{O}\) were used as impregnating materials. The catalyst was prepared by incipient impregnation of aqueous solutions, followed by drying, ammonia-water vapor treatment, thermal decomposition, and hydrogen reduction\(^3\)). The industrial catalyst used for methanol synthesis (ZnO-Cr\(_2\text{O}_3\)) was obtained from Kurare Co., Ltd.

2.2 Apparatus and Procedure

Kinetic studies were carried out in a continuous flow system\(^10\)) of ordinary type under atmospheric pressure. Methanol was injected with a micro-tube pump into the evaporator and after mixing with \(\text{N}_2\), carrier gas, the mixture was introduced into the catalyst bed. The catalyst was pretreated in a stream of 10\% \(\text{H}_2\) at 450°C, and the reaction was conducted under the methanol vapor pressure of 0.15～0.80 atm at 200～450°C. The effluent gases were analyzed by gas chromatographs with columns of MS-5A and Porapak T.

3. Results and Discussion

3.1 Comparison of Catalytic Activity of Various Catalysts

Table 1 shows the activity of each catalyst at

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the same reaction conditions under which methanol conversion was below 20%, and the main products were H2 and CO with a ratio of 2:1. The data were obtained by continuously raising the catalyst temperature from 200°C to 450°C, and the conversion of methanol was compared at 330°C.

It can be seen from this table that activities of Ni-based catalysts (Cat. Numbers: 1, 4, 5, 6, 7) were higher than those of Ru, Rh, and the industrial catalyst. These results indicate that Ni is a suitable catalyst component for methanol decomposition.

### 3.2 Effect of Partial Pressure of Methanol

It might be expected that Ni-based composite catalysts show high activities in the formation of methane from CO and H2 produced by methanol decomposition. However, the formation of considerable quantities of methane was not observed until at temperatures above 400°C and under methanol partial pressure of 0.80 atm, suggesting that the catalyst had adsorbed methanol more strongly than CO and H2, and the adsorbed methanol retarded the formation of methane. This suggestion was confirmed by the rate dependence of H2 formation on the partial pressure of methanol in the temperature range of 250~400°C.

The results are shown by log-log plots in Fig. 1. In the partial pressure range of methanol less than 0.4~0.5 atm, the slope of the straight line at each temperature was almost the same, and the order with respect to methanol was shown to be 0.7. CO and H2 formed seem to have no effect on methanol decomposition rate. These observations suggest that in this partial pressure range, the catalyst surface was always in a reductive state, thus the dependence of the rate on partial pressure showed a constant order irrespective of the change in the reaction temperature. However, each line turns toward the negative slope at partial pressure higher than 0.4~0.5 atm. The kinetic order obtained from the slopes at methanol partial pressure of 0.80 atm increased from −1.5 to −0.7 with increasing temperature. In this partial pressure range, the adsorbed methanol covered a larger portion of the catalyst surface on which retardation of the reaction became predominant, and under such a condition, oxidation on the catalyst surface may proceed and this would enhance methanol adsorption. This synergic effect may bring about a large negative pressure dependence of the decomposition rate. The cause for the decrease in retardation with increasing temperature is probably the decrease in methanol adsorption.

### 3.3 Time Dependence of Catalyst Activity

Fig. 2 shows the change in the H2 formation rate with reaction time under the same flow conditions used for four typical kinds of catalysts listed in Table 1.

The initial activity of Ni catalyst (1) at 350°C was the highest of all the catalysts used in this study. This initial activity markedly decreased with reaction time, but after raising the reaction temperature up to 450°C, the activity was recovered and maintained nearly constant for several hours. On the other hand, although the activity of the Ni–La2O3–Ru catalyst (7) was smaller than that of the Ni catalyst (1), the decrease in activity
with time was very small at 350°C, and exhibited
a higher steady-state activity than that of Ni
catalyst at 450°C. These results indicate that the
adsorption capability of each catalyst is different.
That is to say, methanol or some other products
are adsorbed more strongly on the surface of the
Ni-La₂O₃-Ru catalyst than on the surface of Ni,
resulting in strong retardation of Ni-La₂O₃-Ru
catalyst activity from an early stage of reaction
at low temperatures, while at higher temperatures
such as 450°C this retardation becomes minor due
to the decrease in the adsorbates. Under such
conditions the intrinsic high activity of Ni-La₂O₃-
Ru must exert itself freely. The behavior of Rh
catalyst (3) and that of ZnO-Cr₂O₃ industrial
catalyst (8) were approximately the same at 350°C,
but at higher temperatures the steady-state activity of the former increased and that of the latter rather
decreased.
The steady-state rate of H₂-formation at various
temperatures are shown in Table 2. As the results
indicate, the Ni-La₂O₃-Ru catalyst exhibited the highest activity. The behavior of the industrial
catalyst for methanol synthesis differs from
that of other catalysts. This difference seems to
tem from the catalyst composition and pore struc-
ture.

### 3.4 Product Distribution

Products analyses including small quantities of
by-products were conducted on four kinds of cat-
alysts used in the previous section. The results
are summarized in Table 2. Catalysts 1, 7, and
3 gave considerable amounts of HCHO and small
amounts of dimethyl ether and C₁-C₄ hydro-

| Table 2 Rate of Formation of Decomposition Products (mol/l·hr) |
|-----------------|-----------------|-----------------|-----------------|-----------------|
| Temp. (°C)      | 350             | 400             | 450             | 350             | 400             | 450             |
| Methanol        | 8.7%Ni-4.9%La₂O₃-0.53%Ru/SiO₂ | 2.8%Ni/SiO₂ | 5.0%Rh/SiO₂ | ZnO-Cr₂O₃ Industrial Catalyst |
| Conversion (%)  | 4.2             | 8.3             | 15.2            | 4.2             | 8.3             | 15.2            |
| H₂              | 170             | 330             | 621             | 170             | 330             | 621             |
| CO              | 81.9            | 147             | 269             | 81.9            | 147             | 269             |
| HCHO            | 0.16            | 0.17            | 25.9            | 0.16            | 0.17            | 25.9            |
| CH₃CHO          | 0.28            | 0.86            | 1.73            | 0.28            | 0.86            | 1.73            |
| CH₃COCH₃        | 0.01            | 0.05            | 0.02            | 0.01            | 0.05            | 0.02            |
| CH₃COOCH₃       | 0.02            | 0.14            | 0.59            | 0.02            | 0.14            | 0.59            |
| CO₂             | 0.00            | 0.01            | 0.00            | 0.00            | 0.01            | 0.00            |
| CO              | 0.00            | 0.01            | 0.00            | 0.00            | 0.01            | 0.00            |
| CH₃CHO          | 0.00            | 0.00            | 0.00            | 0.00            | 0.00            | 0.00            |
| CH₃COCH₃        | 0.00            | 0.00            | 0.00            | 0.00            | 0.00            | 0.00            |
| CH₃COOCH₃       | 0.00            | 0.00            | 0.00            | 0.00            | 0.00            | 0.00            |
| CO₂             | 0.00            | 0.00            | 0.00            | 0.00            | 0.00            | 0.00            |

For reaction conditions see Fig. 2.
carbons, however, oxygen-containing compounds such as HCOOCH$_3$, CH$_3$COOCH$_3$, and CO$_2$ were not detected. On the other hand, the industrial catalyst 8 for methanol synthesis formed detectable amounts of oxygen-containing compounds besides the products formed in catalysts 1, 7, and 3. This result suggests the reason for the slight temperature dependence of the activity of catalyst 8, that is the adsorption of oxygen-containing products strongly retards the reaction.

Hydrogen, CO, HCHO, and CH$_4$ were probably formed according to Eqs. (1)–(3). Reaction (2) was experimentally confirmed to occur rapidly on those catalysts.

$$
\text{CH}_3\text{OH} \rightarrow \text{H}_2 + \text{HCHO} \quad (1)
$$

$$
\text{HCHO} \rightarrow \text{H}_2 + \text{CO} \quad (2)
$$

$$
3\text{H}_2 + \text{CO} \rightarrow \text{CH}_4 + \text{H}_2\text{O} \quad (3)
$$

From the material balance between H$_2$, CO, HCHO, and CH$_4$, the amount of H$_2$ should be equal to the amount of (2CO+HCHO−CH$_4$). The results in Table 2 satisfy this relationship.

From the above observations, it was concluded that Ni-based composite catalysts, especially a three-component catalyst such as Ni-La$_2$O$_3$-Ru, is favorable for synthesis-gas formation from methanol because of its high selectivity and stability even at high operating temperatures.

### References


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**Keywords**

Decomposition, Methanol, Nickel based catalyst, Retardation, Synthesis gas formation