

## Dynamic Behavior in Methanation Activity During the Reaction on Supported Nickel-based Catalysts

By

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### Abstract

Increase in the methanation activity of supported Ni-based composite catalysts during the  $\text{H}_2\text{-CO}_2$  reaction was studied. A gradual increase in the activity with repeated use was observed in the Ni- $\text{La}_2\text{O}_3$  catalysts supported on alumina, whereas the Ni- $\text{La}_2\text{O}_3$  catalysts supported on silica gave an almost constant activity through repeated use. This difference was attributed to the reducibility of the catalysts. The nickel oxide part in the composite catalyst supported on silica was reduced sufficiently to nickel metal by hydrogen reduction at  $400^\circ\text{C}$ . On the other hand, some portion of the nickel oxide in the composite catalyst supported on alumina was considered to have formed some  $\text{NiAl}_2\text{O}_4$  spinel which was difficult to be reduced with hydrogen at  $400^\circ\text{C}$ . However, this  $\text{NiAl}_2\text{O}_4$  spinel was reduced gradually during the methanation reaction even at a much lower temperature,  $300^\circ\text{C}$ , with the aid of coexisting water vapor formed by the reaction, resulting in the increase in activity.

### 1. Introduction

Nickel or nickel-based catalysts have been studied extensively as reforming catalysts<sup>1-3)</sup> and methanation catalysts<sup>4-10)</sup>. However, little attention has been paid to the dynamic behaviors of the catalytic activity during the reaction.

Atkinson and Nicks<sup>11)</sup> observed a remarkable increase in the activity with a marvellous increase in the surface area of a misch-metal Ni alloy catalyst during CO methanation. In this case, the misch-metal Ni changed through the reaction into a mixture of rare-earth oxide and  $\text{Ni}_3\text{C}$ , resulting in a high dispersion of active sites. Similar observations have recently been reported on Th-Cu intermetallics for methanol synthesis<sup>12)</sup>, and on Pd-Zr alloy for methanation reaction<sup>13)</sup>. One of the authors has reported that the Ni- $\text{La}_2\text{O}_3$ -Ru composite catalyst had an excellent methanation activity<sup>6-9)</sup>, and verified the role of  $\text{La}_2\text{O}_3$  and Ru<sup>10)</sup>. In a recent paper<sup>14)</sup>, we showed the influence of the pore structure of the alumina support on the  $\text{CO}_2$ -

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methanation performance. In subsequent experiments, we found a prominent increase in the methanation activity when a Ni-La<sub>2</sub>O<sub>3</sub> catalyst supported on alumina was tested repeatedly.

In this paper, the cause of increase in activity will be discussed from the viewpoint of the reduction degree of the supported nickel oxide-lanthanum oxide catalyst, especially comparing two kinds of supports, alumina and silica.

## 2. Experimental

### 2.1. Materials

Two kinds of  $\gamma$ -alumina supports designated ALO-3 and ALO-4, presented by the Catalysis Society of Japan, were used as the catalyst supports. ALO-3 had spheres of 3.4 mm in diameter and ALO-4 had pellets of 1.5 mm diameter and 10 mm length. The BET-surface area (m<sup>2</sup>/g), porosity (%) and average pore diameter (nm) were 133, 70.2 and 18 for ALO-3, and 177, 68.0 and 17 for ALO-4, respectively<sup>15)</sup>. A spherical silica support of 3.0 mm diameter was prepared by ourselves. It had a BET-surface area of 313 m<sup>2</sup>/g, a porosity of 64.6%, and a meso (5 nm) and macro (600 nm) bimodal pore structure<sup>8)</sup>. Guaranteed grade Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and La(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O were used as the starting materials for the catalyst preparation.

### 2.2. Catalyst preparation

Catalysts, 5.0 wt% Ni-2.8 wt% La<sub>2</sub>O<sub>3</sub>, supported on  $\gamma$ -alumina or silica, were prepared according to the conventional pore-fill impregnation method. The support, pre-dried at 300°C, was impregnated dropwise with a mixed solution of nickel nitrate and lanthanum nitrate of the prescribed concentration till the outer surface of the support was completely saturated. The superfluous solution was removed by wiping with a filter paper. This material was weighed to determine the amount of the catalyst components, and then dried in air by continual rolling. After the drying and thermal decomposition of nitrates, it was reduced at 400°C for 30 min in a pure hydrogen stream.

### 2.3. Characterization of catalysts

X-Ray diffraction (XRD) patterns were measured by a Rigaku Geigerflex-2013 diffractometer employing Cu K $\alpha$  radiation with a Ni filter. The surface area of the reduced Ni was calculated, based on the CO uptake obtained by the pulse method<sup>15)</sup>. The value of 13.0 Å<sup>2</sup> was assumed for the metallic surface area occupied by the linearly adsorbed CO molecule<sup>17)</sup>.

### 2.4. Methanation reaction and product analysis

Methanation of CO<sub>2</sub> was carried out in an ordinary micro flow-reactor. A 0.07 ml portion of the catalyst was packed into a Pyrex glass tubular reactor of 6 mm inner diameter. The catalyst was standardized by an *in situ* hydrogen treatment before

use. The temperature was raised by  $10^{\circ}\text{C}/\text{min}$  to  $400^{\circ}\text{C}$  in a pure hydrogen stream. After the temperature reached  $400^{\circ}\text{C}$ , the reactor was cooled down to room temperature, and the hydrogen stream was replaced by a flow of mixed gas composed of 12%  $\text{CO}_2$  and 88%  $\text{H}_2$  with a space velocity of  $43000\text{ h}^{-1}$ . The temperature was raised by  $1.5^{\circ}\text{C}/\text{min}$  to the upper limit of the reaction temperature (usually  $310^{\circ}\text{C}$ ). The effluent gas was analyzed every 10 min by a gas chromatograph with an X-28 column. The selectivity of methane was above 98%, irrespective of the reaction conditions. As by-products, small amounts of ethane, ethylene and propane were detected in the lower temperature range, and a trace of CO was detected in the higher temperature range. When the reproducibility of the catalyst performance was tested repeatedly, the reactor at around  $300^{\circ}\text{C}$  was cooled down to room temperature immediately. Then, hydrogen was introduced instead of the reaction gas mixture, and the procedure mentioned above was followed.

Methanation activity was represented by a Space-Time Yield of Methane,  $\text{STY}_M$ . It was defined by the moles of methane formed on the unit volume of the catalyst per hour.

### 3. Results and Discussion

#### 3.1. Increase in methanation activity by repeated use of the catalyst

In order to confirm the reproducibility of the catalytic activity of the  $\text{Ni-La}_2\text{O}_3$

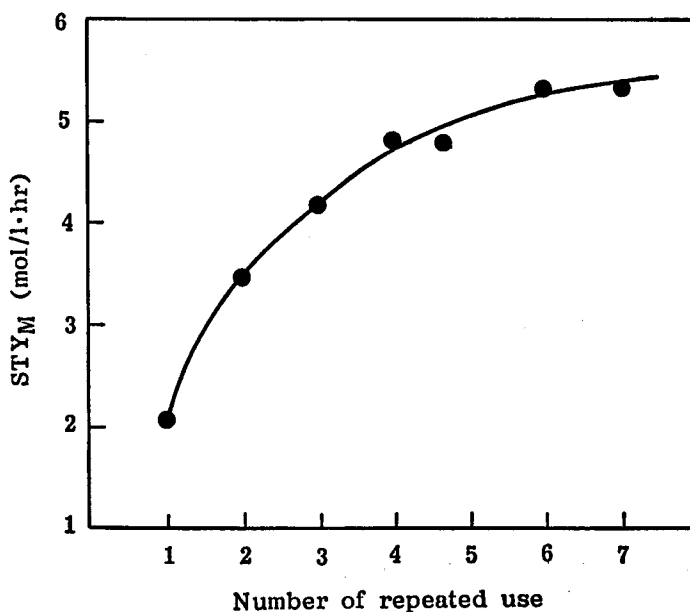


Fig. 1. Increase in the  $\text{CO}_2$ -methanation activity of 5%  $\text{Ni}$ -2.8%  $\text{La}_2\text{O}_3$  catalyst supported on ALO-4 alumina by the repeated use.

supported on ALO-4 alumina, the  $\text{CO}_2$ -methanation activity of the catalyst was measured repeatedly by varying the temperature from room temperature to ca.  $310^\circ\text{C}$ . The activity in each sequential run was compared at  $200^\circ\text{C}$ . The results are shown in Fig. 1. The  $\text{STY}_M$  increased gradually and levelled off at around the 6th and 7th runs. The  $\text{STY}_M$  of the 7th run was about 2.5 times higher than the first run. Explanations are possible for this increase in the activity. The first one is the effect of the repeated hydrogen reduction before the subsequent reaction. However, the contribution of this effect seems to be small, because the reduction temperature was the same as that adopted for the preparation of the catalyst, and the treated period in the hydrogen stream was short. The second one is the effect of water produced at temperatures of high  $\text{CO}_2$  conversion and the high percentage of remaining hydrogen. As was reported<sup>18,19</sup>, water can remarkably accelerate the hydrogen reduction of supported metal oxides. Therefore, we can have the hypothesis that during the reaction at high temperatures giving high  $\text{CO}_2$  conversion, produced water accelerated the hydrogen reduction of nickel oxide or  $\text{NiAl}_2\text{O}_4$ .

To confirm this hypothesis, the following experiments were conducted. First, the

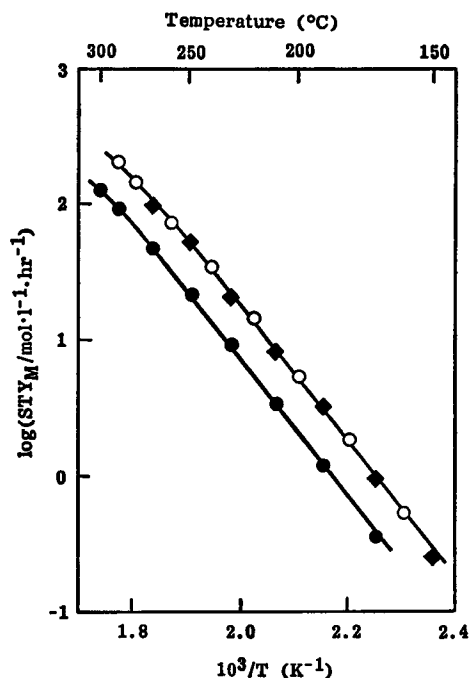


Fig. 2. Arrhenius type plots for  $\text{CO}_2$  methanation on non-treated and reaction-treated 5% Ni-2.8%  $\text{La}_2\text{O}_3/\text{ALO-4}$  alumina catalyst. ●: 1st run, ○: 7th run, ◆: after reaction-treatment at  $300^\circ\text{C}$  for 2.5 hr

activity change during the course of the reaction was examined at a constant temperature ( $278 \pm 1^\circ\text{C}$ ), using the fresh catalyst of the same batch as was used repeatedly. No change in activity (about 25% conversion of  $\text{CO}_2$ ) was observed for one hour. Then, the temperature was raised to  $300^\circ\text{C}$ . At this temperature, the reaction rate is controlled by diffusion of reactant gases. Therefore, no change in activity (more than 80% conversion of  $\text{CO}_2$ ) was observed explicitly during the reaction period (2.5 hr). The temperature was lowered to  $150^\circ\text{C}$ , and again the activity was tested by raising the temperature to a constant heating rate. As can be seen in Fig. 2, this "reaction treated" catalyst exhibited almost the same activity as the catalyst used 7 times repeatedly. These experiments clearly show that the increase in activity occurs when the catalyst is used at around  $300^\circ\text{C}$ , namely in temperatures giving a higher conversion of  $\text{CO}_2$ .

### 3.2. Different behavior between $\text{Al}_2\text{O}_3$ and $\text{SiO}_2$ supports

The effects of the different kinds of supports on the dynamic behavior are shown in Table 1. A marked difference between the alumina and silica supports was found in the degree of the increase in activity by the reaction treatment or repeated use. The activity increase of the catalyst supported on  $\text{SiO}_2$  was only about 20% even after the reaction treatment, whereas the activity increase of the catalyst supported on  $\text{Al}_2\text{O}_3$  in the 2nd run was more than 50% compared with the 1st run. The difference shown in Table 1 can be attributed to the easiness of reduction of the metal oxides on the support. Morikawa *et al.*<sup>20)</sup> indicated that the use of an alumina carrier gave support to nickel catalysts which were difficult to reduce, while silica gave easily reducible ones. Reinen and Selwood<sup>21)</sup> have examined the reducibility of impregnated or coprecipitated nickel oxide, and reported that the reduction of impregnated  $\text{Ni-Al}_2\text{O}_3$  was much more difficult to reduce than that of impregnated  $\text{Ni-SiO}_2$ . Holm and Clark<sup>22)</sup> also showed that among the impregnated catalysts, the resistance to reduction of  $\text{NiO}$  increased in the following order on the respective supports:  $\text{SiO}_2$ ,  $\text{SiO}_2\text{-Al}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$ . One of the authors<sup>23)</sup> has reported in the study of methanol conversion that the

Table 1. Comparison of alumina support with silica support for the increase in  $\text{CO}_2$ -methanation activity

| Catalyst                                                  | STY <sub>M</sub> (mol/1·hr) at $200^\circ\text{C}$ |                    | Ratio<br>$\left(\frac{1\text{st}}{2\text{nd}}\right)$<br>(—) |
|-----------------------------------------------------------|----------------------------------------------------|--------------------|--------------------------------------------------------------|
|                                                           | 1st run                                            | 2nd run            |                                                              |
| 5%Ni-2.8%La <sub>2</sub> O <sub>3</sub> /ALO-3            | 2.04                                               | 3.07               | 1.5                                                          |
| 5%Ni-2.8%La <sub>2</sub> O <sub>3</sub> /ALO-4            | 2.09                                               | 3.47               | 1.7                                                          |
| 5%Ni-2.8%La <sub>2</sub> O <sub>3</sub> /SiO <sub>2</sub> | 4.68                                               | 4.93               | 1.1                                                          |
| 5%Ni-2.8%La <sub>2</sub> O <sub>3</sub> /SiO <sub>2</sub> | 4.68                                               | 5.60 <sup>a)</sup> | 1.2                                                          |

a) After the reaction treatment at  $310^\circ\text{C}$  for 2.5 hr.

Ni/SiO<sub>2</sub> catalyst has no strong metal support interaction (SMSI), while the Ni/Al<sub>2</sub>O<sub>3</sub> catalyst showed a strong SMSI. Besides these studies, it is often reported that nickel oxide supported on alumina can easily form a surface spinel NiAl<sub>2</sub>O<sub>4</sub> by calcination, and that this NiAl<sub>2</sub>O<sub>4</sub> is difficult to reduce<sup>20,24,25</sup>. On the other hand, a silica supported nickel catalyst is easy to be reduced because nickel oxide does not interact with silica support and exists as the bulk nickel oxide<sup>20,22,26,27</sup>.

When our reduction conditions in the catalyst preparation are compared with the conditions applied in the papers mentioned above, we can conclude that the reduction condition in our catalyst preparation was almost suitable for reduction of the silica supported nickel catalyst. However, in the alumina supported nickel catalysts, there remained some NiAl<sub>2</sub>O<sub>4</sub> that could not be reduced. Then in the course of methanation reaction, this remaining NiAl<sub>2</sub>O<sub>4</sub> has been reduced gradually resulting in an increase in activity.

### 3.3. Change in XRD patterns of catalysts by calcination and reduction

XRD patterns of calcined and reduced catalysts supported on ALO-4 alumina are shown in Fig. 3, and those of calcined and reduced catalysts supported on SiO<sub>2</sub> are shown in Fig. 4. Although the intensity of the peaks is weak, we can see the peak of NiAl<sub>2</sub>O<sub>4</sub> in the curve of the calcined catalyst (Fig. 3-a). Even in the XRD pattern of the reduced catalyst (Fig. 3-b), we can find no clear nickel peaks. This means that nickel is finely dispersed and can not be detected by XRD, or that only a small portion of NiAl<sub>2</sub>O<sub>4</sub> was reduced. In our catalysts, both NiAl<sub>2</sub>O<sub>4</sub> and bulk nickel oxide are expected to exist on the alumina surface of the as-calcined catalyst<sup>25</sup>. Most of the bulk nickel oxide and some part of NiAl<sub>2</sub>O<sub>4</sub> would have been reduced. It is, therefore, most probable that the absolute quantity of reduced nickel was too

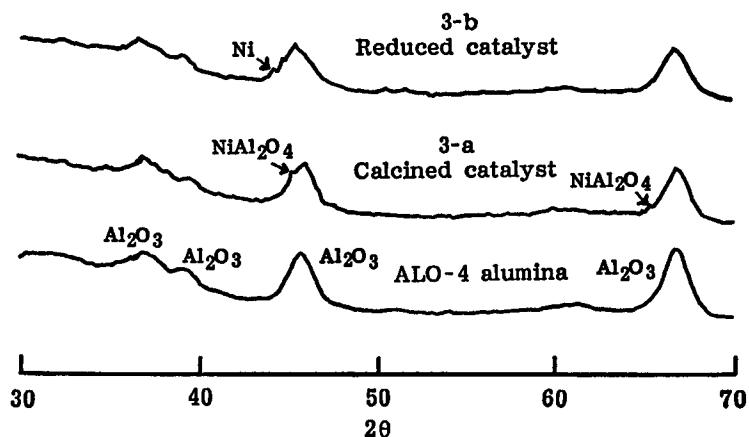


Fig. 3. XRD patterns of 5% Ni-2.8% La<sub>2</sub>O<sub>3</sub> catalyst supported on ALO-4 alumina.

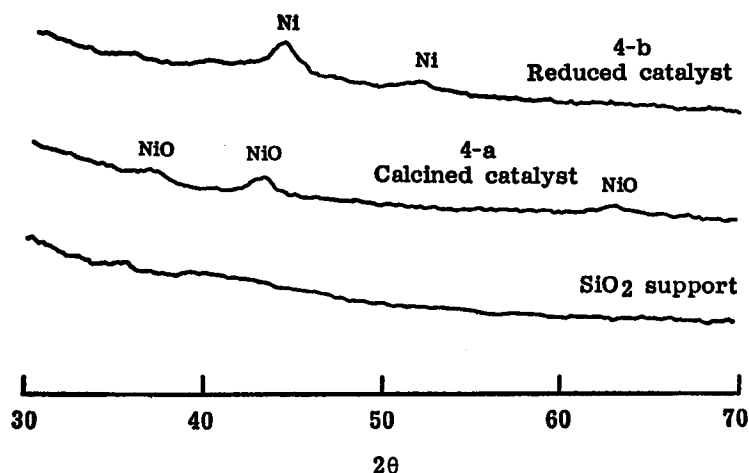


Fig. 4. XRD patterns of 5% Ni-2.8%  $\text{La}_2\text{O}_3$  catalyst supported on  $\text{SiO}_2$ .

small to be detected by XRD. Comparing curve-a with curve-b in Fig. 4, it is clear that the nickel oxide on the silica support was easily almost substantially reduced to metallic nickel.

From the discussion in the foregoing section, one can expect that the intensity of  $\text{NiAl}_2\text{O}_4$  peaks in XRD will decrease by repeated use. However, no conclusive evidence could be obtained because the intensity of the  $\text{NiAl}_2\text{O}_4$  peaks themselves in the XRD pattern of the reduced catalyst was too weak.

### 3.4. Effect of reduction temperature on the methanation rate

In the previous section, it was indicated that  $\text{NiAl}_2\text{O}_4$  was formed when  $\text{Ni(II)}$  salt was impregnated with alumina and calcined, and this  $\text{NiAl}_2\text{O}_4$  was reduced during the methanation reaction. Then, the effect of the hydrogen-reduction temperature at the preparation stage was investigated. The results are shown in Table 2, together with the metallic surface areas estimated by CO adsorption. When the catalyst was reduced at  $450^\circ\text{C}$  which was  $50^\circ\text{C}$  higher than usual, the activity was about 3.7 times higher. When reduced at  $475^\circ\text{C}$ , the activity increased still more. As was mentioned

Table 2.  $\text{CO}_2$ -methanation activity of 5%Ni-2.8% $\text{La}_2\text{O}_3$ /ALO-4 catalyst for various treatments and Ni-surface area of the reduced metallic part

| Condition                                 | $\text{STY}_M(200^\circ\text{C})$<br>(mol/l·hr) | Ratio<br>(—) | Metal-surface area<br>$\text{m}^2/\text{g-Ni}$ |
|-------------------------------------------|-------------------------------------------------|--------------|------------------------------------------------|
| 1st run                                   | 2.09                                            | 1.0          | 54.2                                           |
| 7th run                                   | 5.31                                            | 2.5          | 82.3                                           |
| Reaction treatment (300°C for 2.5 hr)     | 5.10                                            | 2.5          | 96.2                                           |
| Reduced at $450^\circ\text{C}$ for 10 min | 7.75                                            | 3.7          | 72.2                                           |
| Reduced at $475^\circ\text{C}$ for 10 min | 8.61                                            | 4.1          | 141                                            |

above, the XRD did not give conclusive evidence for the catalysts supported on alumina. Then, the CO adsorption was measured as a means to compare the degree of reduction. When the catalyst was reduced at the higher temperature, the nickel-surface area increased. The increase in activity is, therefore, best explained by the increase in the amounts of reduced metallic nickel. Although the change in the nickel-surface area is not proportional to the change in activity, the catalyst having a larger metallic surface area gave higher activity in general.

The  $STY_M$  of 7 times "reaction-treated" catalyst was lower than that of the 475°C reduced catalyst, and this is the predominant effect of the reduction temperature. It must nevertheless be noted that the increase in activity occurred at a much lower temperature, at least 100°C lower than the reduction temperature. The "reaction-treatment" is expected to be valid for the reduction of the catalyst without sintering of catalyst metals at high temperatures. Moreover, as can be seen in Table 2, the effect of the reduction may be different between "reaction-treatment" and high-temperature reduction. This is because the catalyst reduced at 450°C had a higher activity than the "reaction-treated" catalyst as well as the catalyst used 7 times repeatedly in spite of the smaller nickel-surface area.

In conclusion, the increase in the methanation activity of a nickel catalyst supported on alumina during the methanation reaction was caused by the gradual reduction of  $NiAl_2O_4$ , with the aid of co-existing water and hydrogen. Nickel oxide supported on silica was reduced easier than that supported on alumina. Probably, nickel oxide does not interact with silica. When nickel oxide is supported on alumina, it can easily form a  $NiAl_2O_4$  spinel which is difficult to be reduced. The methanation activity of a nickel catalyst supported on alumina can be improved by the hydrogen reduction at higher temperatures. "Reaction-treatment" is another way to reduce the catalyst mass in a mild condition, and can also improve the methanation activity.

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