Development of High Throughput Screening Method of Ni-supported Catalysts for the Decomposition of Methane to Hydrogen and Carbon

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A high throughput screening (HTS) method for identifying supported nickel catalysts for the decomposition of methane was developed. Porous materials such as H-beta(SiO₂/Al₂O₃ = 150), H-beta(25), and H-ZSM-5(90) were highly effective supports for methane decomposition. The total time to find 3 active catalysts among 18 catalysts could be reduced to about one-third of that required with the conventional method. A Ni content of 5-10 mmol g-support⁻¹ was adequate. The HTS results were consistent with the results obtained using a conventional reactor.

Keywords
High throughput screening, Nickel catalyst, Zeolite support, Methane decomposition, Hydrogen

1. Introduction

Hydrogen formation by catalytic decomposition of methane has received much recent attention as an alternative to hydrogen formation by steam reforming and partial oxidation of light hydrocarbons. Catalytic decomposition of methane has two important advantages: lower requirement of energy than steam reforming for producing hydrogen; no formation of CO, so product hydrogen can be directly supplied to a fuel cell without pretreatment. Typical catalysts for hydrogen formation by decomposition of methane are Ni or Fe supported on metal oxides such as SiO₂, Al₂O₃, TiO₂, and ZrO₂, but little is known about other supports. We have already reported that zeolites, which have characteristic acidities and crystal structures, especially USY, are more effective than conventional SiO₂ supports for the catalytic decomposition of methane.

Recently, high throughput screening (HTS) of heterogeneous catalysts by a combinatorial approach has been used to identify high-performance solid catalysts. Rapid detection of catalytic activity is the key to successfully exploiting this method. Various techniques for detecting the catalytic activities of a large number of catalysts in a short time have been reported.

Catalytic decomposition of methane involves the reaction CH₄ = C + 2H₂. In this reaction, hydrogen flows out with the reactant gas whereas the carbon formed remains on the surface of the catalyst. Moreover, no CO or CO₂ is formed. Thus, the amount of H₂ formed can be calculated accurately from the amount of carbon formed on the catalyst without analysis of the outlet gas. Therefore, many catalysts can be placed in a single reactor and simultaneously treated under the same conditions. We believe that this method constitutes a novel HTS technique for discovering high-performance solid catalysts.

This study used the HTS method to identify supported Ni-based catalysts for the decomposition of methane. The zeolite supports (and other metal oxides), were expected to be better supports for Ni catalysts, based on our previous study. The HTS results were consistent with the results obtained using a conventional reactor.

2. Experimental Procedure

Catalysts were prepared by the impregnation method. A ceramic plate (120 mm × 90 mm × 10 mm) with 12 depressions (diameter 20 mm, depth 5 mm, matrix 4 × 3) was used for the experiments. Supports (0.1 g) as described in Table 1 were placed in each of the depressions, nickel nitrate solution was dropped onto the supports, and the slurry on the plate was stirred with a glass rod. The Ni content was con-
trolled by the amount and concentration of the Ni(NO₃)₂ solution. The precursors of the catalysts were dried at 373 K, then calcined at 1023 K for 5 h in air.

The catalysts (2-5 mg) were put in quartz cups (outside diameter 7.0 mm, inside diameter 5.5 mm, height 11.0 mm) as shown in Fig. 1 (a). The weights of the catalysts were not precisely measured prior to reaction, as the accurate weights of the catalysts were measured with a thermogravimetric analyzer (TGA) after the reaction. The cups containing the catalysts were placed in a ceramic boat (Fig. 1 (b)), which could hold up to 12 cups. The boat was set in a quartz tube reactor (outside diameter 28 mm, inside diameter 24 mm) in a tube-type heater (Fig. 1 (c)). The temperature in the reactor was measured with a thermocouple. After the catalysts were activated with H₂(10 vol%)/Ar(90 vol%) mixed gas at 823 K for 1 h, the reactant gas (CH₄(10 vol%)/He(90 vol%), 150 ml min⁻¹) was introduced into the reactor. When the reaction was finished, the methane flow was stopped and the reactor was cooled to ca. 373 K under a He flow. A conventional tubular down-flow reactor (quartz, inside diameter 11.0 mm, outside diameter 14.0 mm) and a side-flow reactor (quartz, inside diameter 24 mm, outside diameter 28 mm) were also used.

The amount of H₂ formed was obtained by measuring the weight of carbon deposited on the surface of the catalyst during the dehydrogenation with a TGA 2950 thermogravimetric analyzer (TA Instruments, New Castle, DE) using the dynamic rate mode. The conditions were as follows: base rate, 50 K min⁻¹; temperature range, room temperature to 1123 K; feed gas, dried air, 30 ml min⁻¹. The weights of absorbed water and deposited carbon were interpreted from the TGA profiles, and the amount of H₂ formation was calculated.

### 3. Results and Discussion

The error associated with the catalyst position in the reactor was determined before performing HTS experiments on supported Ni-based catalysts. Three quartz cups containing the same catalyst (Ni/AlPO₄-5, No. 15 (Table 1), 1.25 mmol-Ni g-support⁻¹) were placed at the inlet side, the center, and the outlet side of the ceramic boat. Reaction was carried out under the conditions in Table 2. After the reaction, the amounts of carbon on the catalysts were determined to be within 5% of each other, indicating that the error was acceptable for screening catalysts for decomposition of methane (DM).

Figure 2 shows the initial activities (0-30 min) of various supported Ni catalysts after 30 min reaction at 723, 773, and 823 K. Since the activities of catalysts 12-15 were very low at 773 K, no activity was observed at 723 K and 823 K. The activities of catalysts 16-18 were zero, because no carbon was deposited

### Table 1 List of Supports for the Ni-based Catalysts for Hydrogen Formation by Decomposition of Methane

<table>
<thead>
<tr>
<th>No.</th>
<th>Support</th>
<th>SiO₂/Al₂O₃ ratio</th>
<th>Origin</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H-mordenite</td>
<td>20</td>
<td>JRC-Z-HM-20abl</td>
</tr>
<tr>
<td>2</td>
<td>Na-mordenite</td>
<td>20</td>
<td>JRC-Z-M-20abl</td>
</tr>
<tr>
<td>3</td>
<td>H-mordenite</td>
<td>240</td>
<td>Tosoh</td>
</tr>
<tr>
<td>4</td>
<td>H-ZSM-5</td>
<td>29</td>
<td>Tosoh</td>
</tr>
<tr>
<td>5</td>
<td>H-ZSM-5</td>
<td>90</td>
<td>JRC-ZS-90Habl</td>
</tr>
<tr>
<td>6</td>
<td>H-ZSM-5</td>
<td>190</td>
<td>Tosoh</td>
</tr>
<tr>
<td>7</td>
<td>H-Y</td>
<td>5.6</td>
<td>JRC-Z-HY-5.6abl</td>
</tr>
<tr>
<td>8</td>
<td>USY</td>
<td>360</td>
<td>Tosoh</td>
</tr>
<tr>
<td>9</td>
<td>H-beta</td>
<td>150</td>
<td>JRC-Z-HB-150abl</td>
</tr>
<tr>
<td>10</td>
<td>H-beta</td>
<td>25</td>
<td>JRC-Z-HB-25abl</td>
</tr>
<tr>
<td>11</td>
<td>Na-beta</td>
<td>25</td>
<td>JRC-Z-B-25abl</td>
</tr>
<tr>
<td>12</td>
<td>Silica/magnesia</td>
<td>—</td>
<td>JRC-SM-1abl</td>
</tr>
<tr>
<td>13</td>
<td>Silica/alumina</td>
<td>2.5</td>
<td>JRC-SAL-2abl</td>
</tr>
<tr>
<td>14</td>
<td>Silica/alumina</td>
<td>6.3</td>
<td>JRC-SAH-1abl</td>
</tr>
<tr>
<td>15</td>
<td>AlPO₄⁻₅</td>
<td>—</td>
<td>Our laboratory</td>
</tr>
<tr>
<td>16</td>
<td>Ga₂O₃/MgO</td>
<td>—</td>
<td>Our laboratory</td>
</tr>
<tr>
<td>17</td>
<td>Ga₂O₃/ZnO</td>
<td>—</td>
<td>Our laboratory</td>
</tr>
<tr>
<td>18</td>
<td>Al₂O₃/ZnO</td>
<td>—</td>
<td>Our laboratory</td>
</tr>
</tbody>
</table>

a) Reference catalyst of the Catalysis Society of Japan.
b) Calcined hydrotalcite-like compound.

### Table 2 Influence of Location of Sample on the Ceramic Boat on the Amount of Carbon Deposited on the Catalyst

<table>
<thead>
<tr>
<th>Location of quartz cup</th>
<th>Amount of carbon deposited on the catalyst [g-carbon g-catalyst⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inlet side</td>
<td>0.122</td>
</tr>
<tr>
<td>Center</td>
<td>0.120</td>
</tr>
<tr>
<td>Outlet side</td>
<td>0.128</td>
</tr>
</tbody>
</table>

a) Catalyst, Ni(1.25 mmol g-support⁻¹)/AlPO₄-5. H₂ treatment, 873 K, 1 h, H₂(10 vol%)/Ar(90 vol%), 50 ml min⁻¹. Reaction conditions, 773 K, 30 min, CH₄(10 vol%)/He(90 vol%), 150 ml min⁻¹.
on the surface of the catalysts. The catalysts are set in only one tube in this HTS method, so the catalytic activities are indicated by the rate of formation of hydrogen instead of conversion of methane. The decomposition rates with catalysts 1-11 increased with increasing reaction temperature. Comparison of catalysts 1 and 2, and catalysts 10 and 11, shows that the activities of H-type zeolites are higher than those of Na-type zeolites. These findings indicate that the surface acidity of the catalyst support is associated with the decomposition of methane. Comparison of catalysts 4-6, which have the same MFI crystal structure, reveals that the SiO2/Al2O3 ratio affects activity. The most active of these catalysts (catalyst 5) had a SiO2/Al2O3 ratio of 90. Comparison of catalysts 1, 4, and 10, with almost the same SiO2/Al2O3 ratios, reveals that activity is affected by the crystal structure. The six most active catalysts in Table 1 (catalysts 1, 4, 5, 8, 9, and 10) were identified after the first screening.

The total time spent in obtaining the data presented in Fig. 2 was about 40 h, which we estimate is about one-third of the time that would be required with the conventional method. One experiment required 3.5 h, and four experiments were required to measure the activities of all 18 catalysts presented in Fig. 2. Also, measurement of the carbon deposits by TGA took 40-50 min. We believe that more rapid measurements of catalytic activities can be achieved by using a larger boat (containing more samples) and an automated high-performance TGA or precision balance. Such measurements could result in a total time of 1/5 to 1/10 of that required by conventional methods.

There are two procedures for the HTS of catalysts. One procedure involves selecting about 100 to 10,000 catalysts and simply determining whether they are active or inactive. The other procedure, which provides more information about the catalysts, involves initial screening of dozens of samples. We believe that the method in this report is suitable for the latter procedure.

We studied the influence of Ni content on the initial activities of the catalysts and found that a Ni content of 5-10 mmol g-support−1 was sufficient for catalytic activity (Fig. 3). The most active of the 18 supports were the Ni/zeolite catalysts H-beta(150), H-beta(25), and H-ZSM-5(90).

The time courses of the activities of six catalysts (catalysts 1, 4, 5, 8, 9, and 10) are presented in Fig. 4, in which the Ni content was 5.0 mmol g-support−1. Pretreatment, H2(10 vol%)/Ar(90 vol%), 50 ml min−1, 873 K, 1 h. Reaction, CH4(10 vol%)/He(90 vol%), 150 ml min−1, 773 K.

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lysts that formed the largest amount of hydrogen over the 240-min reaction period were H-beta(150), H-beta(25), and H-ZSM-5(90), which correspond to the catalysts with the highest initial activities. The total amount of hydrogen until the activities are lost during long-term reaction (over 8-10 h) can be determined using this HTS method; in this case, we could not find when the lives of the catalysts end.

To check the validity of the HTS method, we tested the catalytic activities of six active catalysts (H-beta(150), H-beta(25), H-ZSM-5(90), USY(360), H-ZSM-5(29), and H-mordenite(20)) by using conventional tubular down-flow and side-flow reactors (Table 3). The side-flow reactor included space over the catalyst powder. The order of the activities for the conventional down-flow reactor was as follows: H-beta(150) > H-beta(25) > H-ZSM-5(90) > USY(360) > H-ZSM-5(29) > H-mordenite(20). This order is in good agreement with the order of activities determined by the HTS method, although the activities determined by the HTS method are higher than those determined with the conventional down-flow reactor. The difference in activities might be amplified by the HTS method. The three most active catalysts selected by the HTS method (H-beta(150), H-beta(25), and H-ZSM-5(90)) were about 15-20% more active than the other catalysts (USY(360), H-ZSM-5(29), and H-mordenite(20)). On the other hand, the activity of Ni/H-beta(150) was almost the same as that determined with the side-flow reactor. Catalyst performance seemed to be greatly influenced by reactor type. Possible causes include diffusion of formed hydrogen, and the contact efficiency between the methane and the surface of the catalyst.

4. Conclusions

(1) A novel, convenient, low-cost HTS method for screening catalysts for decomposition of methane was designed which is suitable for screening dozens of samples.

(2) The three most effective supports among a diverse group of 18 supports for catalytic decomposition of methane were rapidly determined by the HTS method as H-beta(150), H-beta(25), and H-ZSM-5(90). A Ni content of 5-10 mmol g-support⁻¹ was sufficient for catalytic activity.

(3) The HTS results were consistent with results from conventional reactors.

References

7) Inaba, M., Murata, K., 88th Debate Meeting of the Catalysis Society of Japan, 2001, 1P08.
要  旨
メタンの水素と炭素への分解反応に有効なニッケル系触媒の迅速探索法の開発

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ハイスクリーニング（HTS）手法をメタン分解に用いられるニッケル系触媒の探索に適用した。その結果、
H-beta（SiO2/Al2O3 = 150）、H-beta（25）、およびH-ZSM-5（90）が高活性な触媒担体として見い出され、18の担体から三つの
高活性な担体を選び出すのに要した時間は従来と比較して約1/3に減少した。また、最適なニッケル担持量は5〜10 mmol g−1
support1であった。HTSによって得られた結果は、従来型反応器による結果と整合性があった。