

# Catalyst Screening for Oxidative Reforming of Methane in Direct Route using High Pressure HTS Reactor with Syngas Detection System by Colorimetric Reaction and Gas Chromatograph

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A high-throughput screening (HTS) reactor for high-pressure oxidative reforming of methane in a direct reaction route was developed. With a combination of catalyst preparation by a split-and-pool method and HTS, Ni-K/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> catalyst was found to show high activity under 1 MPa at 650 °C with high selectivity even when O<sub>2</sub> conversion is less than 100%. The HTS reactor required a new simple syngas detector operable under high pressure because the number of parallel reactor is limited when equipped with the conventional detection system. The complexity of the pressure reducing unit is the main reason of the limitation. Reduction of metal oxide accompanied with the color change was applied to the detection system. Copper oxide was supported on the filter disk made of alumina, and the filter was placed underneath the catalyst bed. After the methane was oxidatively reformed under 1 MPa at 650 °C, color change of spots from dark brown to light brown was observed just under the catalyst which produced hydrogen. Color change of the disk can be used to detect hydrogen formation from the reforming catalyst under pressure.

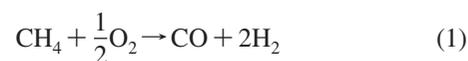
## Introduction

Combinatorial chemistry attracts much attention in research field of solid catalyst development. The technology consists of high-speed library synthesis, high-throughput screening (HTS), and informatics.<sup>1</sup> Among them, the most demanding is HTS because the environment of the catalyst in a laboratory should be similar to those in an industrial process. When the discrepancy between the laboratory application and the industry application is not negligible, ultra-HTS, such as thermographic observation of a thin film catalyst,<sup>2,3</sup> Q-mass detection of products at surface,<sup>4,5</sup> and a reactor system using 384 well microplate,<sup>6</sup> are valid. However, the industrial catalysts are often tailor-made to give the best performance under constrained conditions. To estimate the in situ catalytic performance under near-industrial conditions, that is, pressurized conditions, other types of HTS with smaller library scales were also reported.<sup>7–9</sup>

In the present study, new catalysts have been screened for high-pressure oxidative reforming of methane to produce synthesis gas (syngas). For reforming catalysts, it was reported that both oxidation state of the catalyst and deactivation by coke formation strongly depend on reaction pressure.<sup>10</sup> In such a case, an HTS system operable under pressure and at high temperature is required. We also reported a methanol detection system, where methanol synthesized from syngas in a high-pressure reactor was transferred through capillary tube into a water trap and was analyzed by reagent oxidation with color change.<sup>11</sup> Such a

colorimetric reaction was proven to be useful for simultaneous detection, and other detection systems were reported for pH,<sup>12</sup> NO<sub>x</sub>,<sup>13</sup> acetic acid,<sup>14</sup> aniline,<sup>15</sup> and olefin.<sup>16</sup> Hydrogen was also detected by a colorimetric reaction of tungsten oxide reduction by spillover hydrogen<sup>17</sup> or of molybdenum oxide reduction in hydrogen detector-tube.<sup>18</sup> Because such a color change of metal oxide seemed applicable under high pressure and high temperature, an in situ colorimetric reaction for hydrogen detection was investigated in the present study.

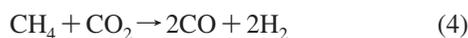
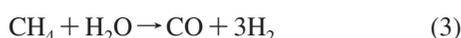
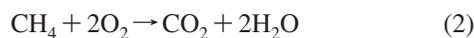
Methane is the main component of natural gas, and steam reforming of methane is currently used industrially on a large scale to produce hydrogen and syngas. Whereas the steam reforming process is currently the most prevalent method, the heat requirement is huge, and the heat is supplied by many external burners heating the tubular reactors by combustion of natural gas. An attractive alternative process for syngas production is the oxidative reforming of methane.<sup>19</sup> If the reaction proceeds as is presented by eq. 1, the reaction is mildly exothermic, and therefore the reforming process would be more economical from viewpoint of heat supply. In addition, the H<sub>2</sub>/CO ratio produced in stoichiometry is around 2, and this ratio is ideal for downstream processes, such as methanol synthesis and Fischer–Tropsch reaction with cobalt catalysts. Thus the oxidative reforming reaction is suitable for gas to liquid (GTL) processes.



To take full advantage of oxidative reforming, the reaction should proceed in a direct route. Usually the oxidative

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reforming proceeds in an indirect route on Ni catalyst,<sup>20</sup> where methane is first combusted by eq 2 and then reformed by eqs 3 and 4. While total reaction is same, the indirect route reaction spoils the advantages of oxidative reforming reaction. Only few Ni catalysts were reported as a direct route catalyst, such as Ni/Ca-Al-O<sup>21</sup> and Ni-Ca hydroxyapatite<sup>22</sup> in steady state reaction and Ni/Al<sub>2</sub>O<sub>3</sub><sup>23</sup> in pulse reaction.



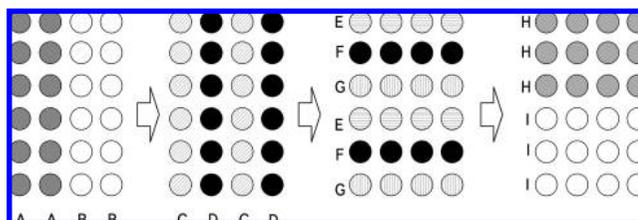
Activity tests were conducted using a diluted gas and a diluted catalyst bed under the criteria developed by Verykios<sup>24</sup> to suppress the hot-spot formation and to decrease the influence of diffusion. High hydrogen selectivity at O<sub>2</sub> conversion <100% is the index of direct route reaction. Catalysts for screening were prepared by a conventional split-and-pool method and a quasi-split-and-pool method.

### Experimental Section

**Catalyst Library Preparation.** Commercially available Pt/Al<sub>2</sub>O<sub>3</sub> and Rh/Al<sub>2</sub>O<sub>3</sub> (Wako Pure Chemical Industries, Ltd.) were used as standard catalysts to check the detection system.  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> was prepared by calcination of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> in air at 1200 °C for 5 h and identified by XRD analysis.

A catalyst library for the first screening was prepared by an impregnation method designed by the conventional split-and-pool method. The support was  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, and the active metal was selected from Ni, Co, Fe, or Mn. As an additive for surface carbon removal and promotion of the activity, one rare earth metal was selected from La, Ce, Pr, Nd, or Yb. As third metal for suppression of carbon formation and for the activity stabilization, one alkali metal was selected from Li, Na, K, Mg, or Ca. A fourth metal was also selected from B, Si, Sc, Ti, or Re. An amount of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> was equally split into 5 groups, and 4 groups were impregnated with metal salt solutions. The last group was impregnated with water without metal salt. After the mixtures were dried on hot plate, they were dried in air at 120 °C for 3 h, followed by calcination at 600 °C for 5 h. The 5 groups were pooled into one and then split equally into 6 groups. The second, third, and fourth metals were impregnated in the similar way. This procedure is hereafter denoted as {Ni, Co, Fe, Mn, bl} × {La, Ce, Pr, Nd, Yb, bl} × {Li, Na, K, Mg, Ca, bl} × {B, Si, Sc, Ti, Re, bl}. After impregnation of the fourth metal, the library was not pooled, and so, a library with 6 groups with 1080 kinds of catalysts was obtained. They were reduced in hydrogen prior to the reaction.

While a large library is effectively synthesized by a split-and-pool method, an excess amount of catalyst should be prepared to guarantee that all combinations were prepared because the library is split in a stochastic process. Another drawback of the method is that the catalyst composition should be identified by other procedures after library synthesis or after screening. To remove the drawback of the split-and-pool method, the method was modified by using of a parallel method on multiwell microplate. The procedure for the quasi-split-and-pool method is demonstrated in Figure



**Figure 1.** Schematic procedure of a quasi-split-and-pool method.

1. Metal salts solutions are mixed step by step in multiwell microplate according to the patterns determined for split-and-pool. All the 24 combinations are synthesized in 4 steps on the plate. Then the support is impregnated with the mixed solution.

In the second screening in this study, 144 kinds of catalysts of {Ni, Co, Fe, Mn} × {La, Ce, Pr, Nd, Yb, bl} × {Li, Na, K, Mg, Ca, bl} were prepared by this quasi-split-and-pool method. Aqueous solutions of these metal salts were mixed on 384-well plate according to the pattern in Figure 2 from a to c, and then  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> was added. After the mixtures were dried in a vacuum rotary evaporator at 60–90 °C for 24 h and in air at 120 °C for 3 h, the library was calcined in air at 600 °C for 5 h. Thus, for example, Ni-La-Li/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> and Co-Pr-Mg/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> were prepared at the 2B and 13D wells in Figure 2, respectively. Catalysts were reduced in hydrogen prior to the reaction.

In the third screening of Ni catalysts, a spotting method was applied to the catalyst preparation. Solution of nickel salt (2 mol/L) and additives (0.2 mol/L) were prepared by a quasi-split-and-pool method, and the 96 combinations were prepared as {Ni} × {Li, Na, K, Mg, Ca, Sr, Sc, bl} × {La, Ce, Pr, Nd, Dy, Ho, Er, Yb, Lu, Sc, Y, bl}. An Anodisc (Whatman) was covered by an aluminum plate with punched holes, and then the metal solutions were plotted using a Teflontube ( $\phi$  0.3/0.5 mm) in the holes as shown in Figure 3. After they were dried in air at 120 °C for 3 h and at 400 °C for 5 h, the catalysts were reduced in hydrogen before the reaction.

For the preparation of catalysts in a laboratory scale, a sequential impregnation method using aqueous solution of nitrates was applied. The library was {Ni} × {La, Ce, Pr, Nd, Yb, Sc, bl} × {K}. After each step, catalysts were dried at 120 °C for 3 h and calcined at 600 °C for 5 h. Ni loading was 10 wt %, and the amount of each additive was one tenth of Ni. The catalysts were reduced in hydrogen before the reaction.

**Activity Test.** Conventional oxidative reforming of methane was carried out in a fixed bed reactor at 650 °C, 1 MPa. An alumina tube ( $\phi$  3 mm/5 mm) was inserted in a stainless steel tube. Reaction gas (CH<sub>4</sub>/O<sub>2</sub>/N<sub>2</sub> = 5/3/92) was introduced inside the alumina tube. Conversions of CH<sub>4</sub> and O<sub>2</sub> were calculated with an N<sub>2</sub> internal method. H<sub>2</sub> and CO were analyzed by a gas chromatograph equipped with a TCD detector (Shimadzu GC-8A, MS13X column, Ar carrier).

In the HTS reaction, the CuO-supported disk was applied as hydrogen detector. Copper nitrate was impregnated on a porous alumina disk filter (Whatman, Anodisc, O.D. 13 mm) and was used after calcination at 400 °C for 1 h as a detector disk. An aluminum plate with punched holes was overlapped

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	(a)	(b)	
A																		La	La
B		Ni	Ni	Ni	Ni	Ni	Ni			Co		Ce	Ce						
C		Ni	Ni	Ni	Ni	Ni	Ni			Co		Pr	Pr						
D		Ni	Ni	Ni	Ni	Ni	Ni			Co		Nd	Nd						
E		Ni	Ni	Ni	Ni	Ni	Ni			Co		Yb	Yb						
F		Ni	Ni	Ni	Ni	Ni	Ni			Co		bl	bl						
G		Ni	Ni	Ni	Ni	Ni	Ni			Co									
H																			
I																			
J		Mn	Mn	Mn	Mn	Mn	Mn			Fe									
K		Mn	Mn	Mn	Mn	Mn	Mn			Fe		Li	Na						
L		Mn	Mn	Mn	Mn	Mn	Mn			Fe		K	Mg						
M		Mn	Mn	Mn	Mn	Mn	Mn			Fe		Ca	bl						
N		Mn	Mn	Mn	Mn	Mn	Mn			Fe		Li	Na						
O		Mn	Mn	Mn	Mn	Mn	Mn			Fe		K	Mg						
P																		Ca	bl

Figure 2. Catalyst preparation for second screening by a quasi-split-and-pool method.

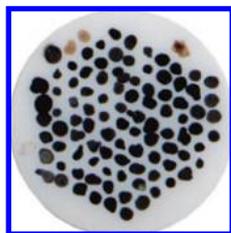


Figure 3. Ni spotted catalyst disk using a quasi-split-and-pool method.

on the detector disk, and each catalytic oxide was placed in the hole. The plate and disk were fixed horizontally in a Swagelok connector (SS-8-VCR-3-4MTW). After reformate gas of oxidative reforming of methane passed through the filter at reaction pressure (1 MPa) and temperature (650 °C), light brown spots formed by the oxide reduction were observed detecting the activity of the catalyst oxides.

**Temperature Programmed Reduction (TPR).** Temperature-programmed reduction of  $\text{Cu}_2\text{O}$  and  $\text{Ni}/\alpha\text{-Al}_2\text{O}_3$  catalysts were conducted in a conventional fixed bed reactor apparatus at normal pressure in 7%  $\text{H}_2$  (Ar balance). The temperature ramp was carried out at 5 °C/min, and hydrogen consumption was monitored by a gas chromatograph (Shimadzu, GC-8A, TCD detector).

## Results and Discussion

**Assembly of Detector Disc, Catalyst Bed, and Catalyst Disc.** Gibbs energy change of oxide formation is plotted in Figure 4.<sup>25,26</sup> Oxides above the  $\text{H}_2\text{O}$  and  $\text{CO}_2$  formation lines can be reduced by  $\text{H}_2$  and  $\text{CO}$ , respectively. Among metal oxides, those of Cu, Pb, Co, Mo, and Mn are probably available to detect hydrogen and carbon monoxide using their own reduction as shown in the Ellingham diagram, and  $\text{CuO}$  has an advantage in the viewpoints of color change, toxicity, and so on. Despite the thermodynamic equilibrium,  $\text{Cu}_2\text{O}$  was reduced at 600 °C as shown in TPR profile in Figure 5. The detector disk coated with  $\text{CuO}$ , therefore, should be used near reaction temperature.

Assembly of the detector disk was considered,<sup>27</sup> and the outlines are illustrated in Figure 6. Figure 6a is the principal

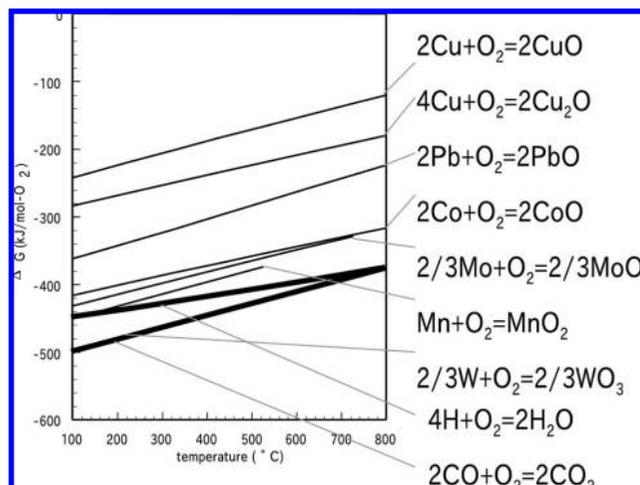


Figure 4. Ellingham diagram of metal oxides.

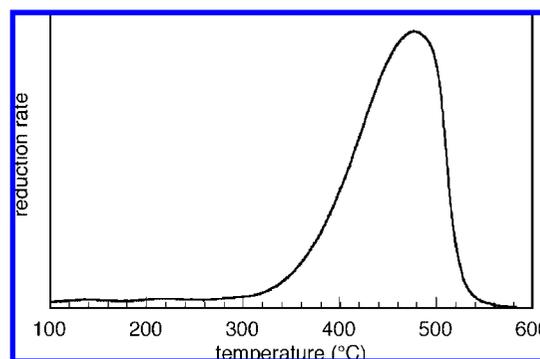
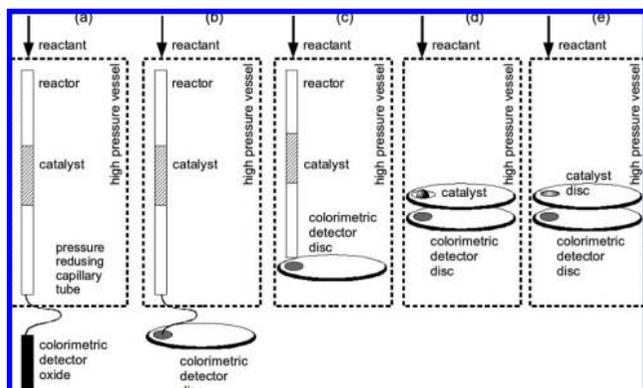
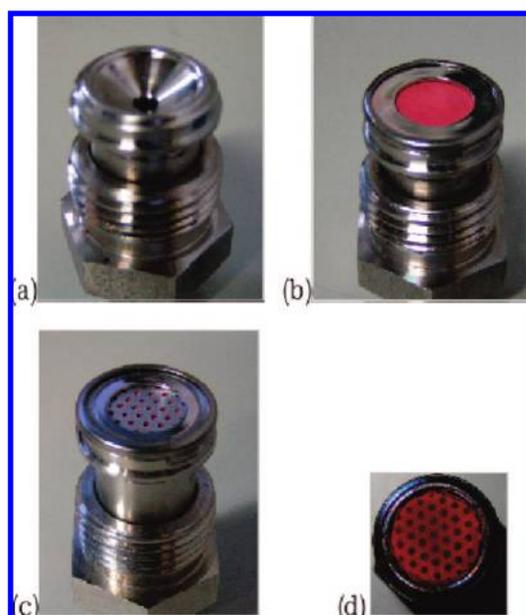


Figure 5. TPR of copper oxide.

design. The product gas at 650 °C and 1 MPa is regulated to normal pressure to determine the amount of color-changed oxide. To eliminate the connection capillary tubes and simplify the system,  $\text{Cu}_2\text{O}$  was coated on glass fiber filter (Whatman, GF/F), and the filter was overlapped with an aluminum plate with punched holes. After reformate gas from a  $\text{Pt}/\text{Al}_2\text{O}_3$  catalyst was supplied to the disk and plate at 550 °C for 30 min, reduction of the  $\text{CuO}$  only at the hole of the alumina plate was observed (Figure 6b and Figure 7). The results show no difference from gas distribution on the disk.



**Figure 6.** Variations of reactor configuration for HTS with colorimetric detector.



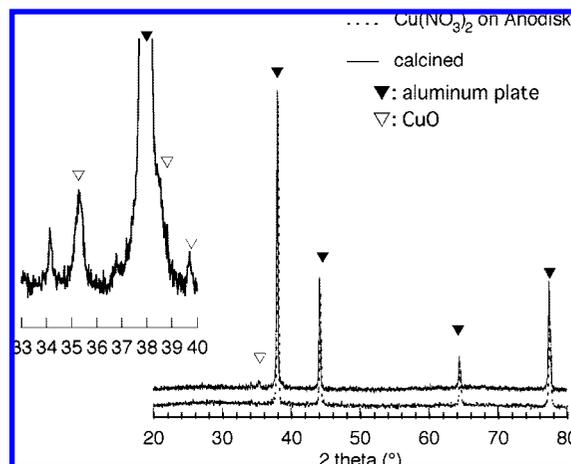
**Figure 7.** Reactor configuration for HTS with VCR connector and detector disk.

To check the presence of the activity, this is enough, while quantitative estimation of catalytic activity would be difficult in this HTS reactor.

Because gas flow was limited and went through the holes of the aluminum plate, the holes could be the acceptor of the end of many quartz tubes used as catalyst vessels in the reactor (in Figure 6c). However, the connection between the quartz tube ends and the punched holes was troublesome.

Then catalysts were charged directly in the punched holes of the aluminum plate as in Figure 6d. CuO was coated on a thermally stable alumina filter disk (Anodisc) instead of glass filter as shown in Figure 8. The disk was overlapped with an aluminum plate and placed in a VCR connector with Pt/Al<sub>2</sub>O<sub>3</sub> catalysts in the 4 holes. During the oxidative reforming reaction under 1 MPa at 650 °C, light brown spots were formed where Pt/Al<sub>2</sub>O<sub>3</sub> was loaded. The result in Figure 9 shows that the detector disk can be applied to the HTS detector.

Catalyst metal can be coated on another Anodisc, namely, an Anodisc can be used as a catalyst support instead of alumina sphere. This simple coating method can be applied to screen the alumina supported catalysts. For example, chloroplatinic acid was coated and calcined as shown in



**Figure 8.** X-ray diffractogram of CuO-coated Anodisc.



**Figure 9.** Pt/Al<sub>2</sub>O<sub>3</sub> in punched holes of aluminum plate and detector disk after reaction.



**Figure 10.** Pt/Al<sub>2</sub>O<sub>3</sub> disk and detector disk after reaction.

Figure 10 (left). During the reforming reaction, CuO-coated disk detected the hydrogen formation just underneath the catalyst plate where Pt was coated as shown in Figure 10 (right). Thus, both type of catalysts can be available in the screening of reforming catalysts with CuO-detector disk.

**First Screening.** Six groups of catalysts were prepared as {Ni, Co, Fe, Mn} × {La, Ce, Pr, Nd, Yb, bl} × {Li, Na, K, Mg, Ca, bl} × {B, Si, Sc, Ti, Re, bl}. After the fourth metal salts were impregnated and calcined, the library was not pooled, and 6.6 mg samples from each group were charged in the HTS reactor. The aluminum plate was not overlapped on detector disk because as many as 500–600 catalyst particles were charged. Flow rate of reactant gas was controlled for 1 h to keep SV = 2.1 × 10<sup>6</sup> mL/g/h for O<sub>2</sub> conversion <100%.

A detector CuO/Anodisc for each group after the HTS reaction is shown in Figure 11. Three colored spots were observed in the “Ti” library, where the fourth metal was Ti, and 5 spots were observed in “bl” library. The contrast of the latter spots are better than others, and it suggests that the fourth metals in these library are not adequate to enhance the catalytic activity. Because 3–5 particles of the identical catalyst are included among the 6.6 mg samples, only 1–2 kinds of catalysts in bl library produce syngas even

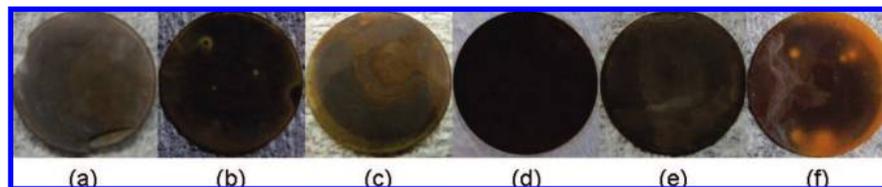


Figure 11. CuO disk after the reaction by 6 catalyst groups. The last impregnated metal is (a) B, (b) Re, (c) Sc, (d) Ti, (e) Si, (f) bl.

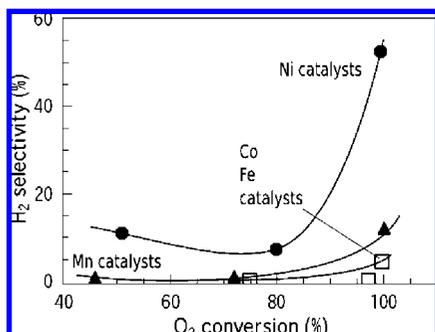


Figure 12. H<sub>2</sub> selectivity of 4 catalyst groups.

when O<sub>2</sub> conversion is less than 100%. Thus, at least one “hit” catalyst should be included in the 1080 kinds of catalyst library.

The bl library was separated into 4 groups to identify the active catalyst. New libraries of {La, Ce, Pr, Nd, Yb, bl} × {Li, Na, K, Mg, Ca, bl} were synthesized for each of the Ni, Co, Mn, and Fe catalysts in the second screening. Total 144 (= 4 × 36) kinds of catalysts were prepared and screened.

**Second Screening.** Four catalyst groups containing Ni, Co, Fe, or Mn were submitted to HTS reaction, separately. Hydrogen selectivity as a function of O<sub>2</sub> conversion is illustrated in Figure 12. Cobalt and Fe catalysts were tested together.

In the region where O<sub>2</sub> conversion was less than 50%, H<sub>2</sub> formation was hardly observed with Co, Fe, and Mn catalysts, whereas Ni catalysts showed H<sub>2</sub> selectivity of ~10%. The selectivity is relatively high considering that the stainless steel wall shows high activity for hydrogen combustion, and it was concluded that Ni was the main catalyst component that caused color change spots in the first screening. Unfortunately the most active nickel catalyst was not identified in the second screening because the color of entire area of CuO disk was changed. If an active catalyst particle is surrounded by inactive catalysts, as is the case in the first screening, the contrast of color change should appear clearly. In the next screening, the gas flow was constrained by aluminum plate, and the disk catalysts prepared by a spotting method were screened.

**Third Screening.** Screening of 96 (= 8 × 12) kinds of Ni catalysts of {Ni} × {Li, Na, K, Mg, Ca, Sr, Sc, bl} × {La, Ce, Pr, Nd, Dy, Ho, Er, Yb, Lu, Sc, Y, bl} was conducted. A catalyst disk was prepared by a spotting method as shown in Figure 3. During oxidative reforming of methane, the entire CuO disk was reduced to Cu<sub>2</sub>O because of hydrogen formation. Twelve color changed spots corresponding to K containing catalysts and 3 black points corresponding to Rh catalysts used as position marker were observed after the reaction as shown in Figure 13. The result



Figure 13. CuO disk after the reaction by catalyst disk with 96 Ni spots.

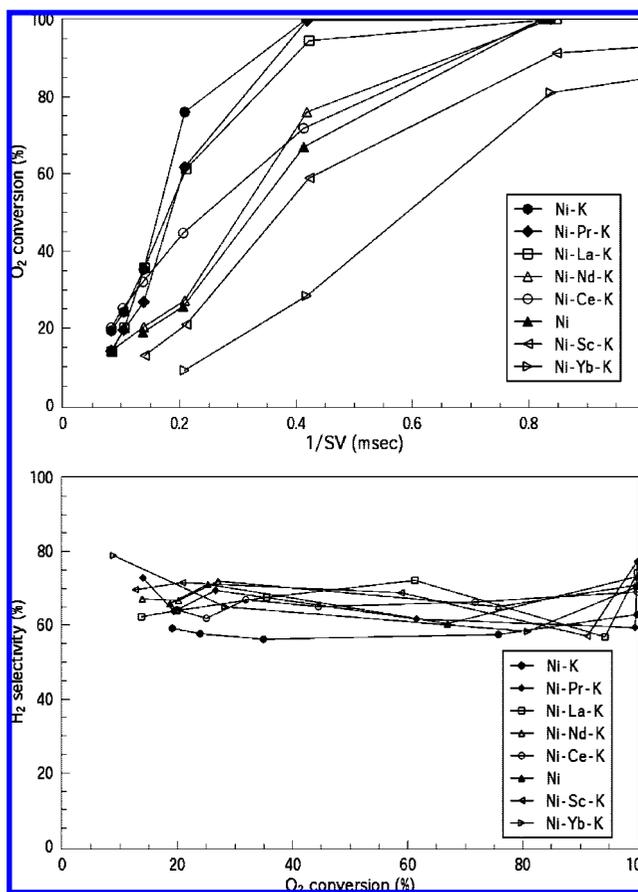
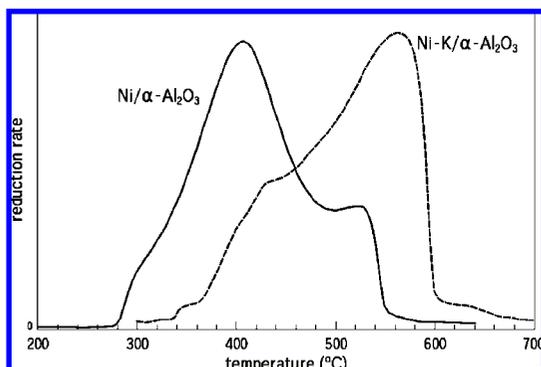


Figure 14. Catalytic activity and selectivity of supported Ni catalyst.

suggests that all Ni-X-K catalysts on the disk show activity for H<sub>2</sub> formation at high SV, where O<sub>2</sub> conversion is less than 100%. The hit catalysts were then submitted to the conventional activity test in a laboratory scale.

**Scale-up of Catalyst to Laboratory Scale.** α-Al<sub>2</sub>O<sub>3</sub>-supported {Ni} × {La, Ce, Pr, Nd, Yb, Sc, bl} × {K} catalysts were prepared by the sequential impregnation. The result of individual activity test is shown in Figure 14. Oxygen conversion and H<sub>2</sub> selectivity as a function of SV<sup>-1</sup> are illustrated. While the deviation of H<sub>2</sub> selectivities are not significant, O<sub>2</sub> conversion was affected by the additives. When only Ni was supported on α-Al<sub>2</sub>O<sub>3</sub>, the conversion rapidly decreased at shorter contact time. K clearly promoted



**Figure 15.** TPR profile of Ni and Ni-K catalyst.

the activity and oxidation resistance keeping high contribution of a direct route reaction while the promotion effect was slightly inhibited by rare earth metals.

It was reported, on the basis of both experimental results and DFT calculations, that K inhibits the dissociative adsorption of methane on nickel metal.<sup>28</sup> The result<sup>28</sup> suggests that K addition usually suppresses the carbon formation for prolonged catalytic life and simultaneously reduces the activity of a nickel catalyst by slowing the rate determining step. It was also reported that reduction of nickel oxide supported on Al<sub>2</sub>O<sub>3</sub> is accelerated by K addition.

Contrary to these conventional reports, reduction temperature of Ni/Al<sub>2</sub>O<sub>3</sub> was increased as shown in Figure 15 in the present study. These extraordinary effects of K would be closely related each other, and further studies are under consideration.

### Conclusion

The high-throughput screening reactor for high-pressure oxidative reforming of methane in a direct route was developed. Copper oxide was supported on a porous Anodisc alumina filter, and the filter was placed underneath the catalyst bed to detect the hydrogen formation. Using this HTS reactor with a combination of catalyst preparation by a split-and-pool method, over 1000 catalysts were screened, and the Ni-K/α-Al<sub>2</sub>O<sub>3</sub> catalyst was found to show high activity under 1 MPa at 650 °C with high selectivity, even when O<sub>2</sub> conversion was less than 100%. An extraordinary effect of K was found to promote the activity of a nickel catalyst hindering the reduction of nickel oxide.

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