Carbon Dioxide Reforming of Methane over a Novel Ni/Al_2O_3 Catalysts

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Introduction

A lot of attentions have been recently paid to the CO_2 reforming of methane to syngas. A major reason for it is that this reaction can provide us a syngas with a 1/1 ratio of H_2 and CO, which is typically suitable for the synthesis of valuable oxygenated chemicals.[1] Among the catalysts developed, Al_2O_3 supported Ni catalysts were extensively investigated due to their relatively high activity and low cost. The major problem for the further practical application of these nickel catalysts is the deactivation of the catalyst, suffered from carbon deposition on the catalyst during reactions. Many investigators are working on the improvement in this nickel catalyst by using the addition of promoters,[2-5] using novel reactor configurations,[6,7] and using different supports.[3] In this work, we attempt to use a glow discharge plasma treatment following by thermal calcinations to achieve a better catalyst with higher activity at lower temperatures and better stability.

Experimental

The preparation or the plasma treatment of catalyst has been described elsewhere.[8,9] The principal procedure of the catalyst preparation includes: 1) impregnation conventionally; 2) drying; 3) glow discharge plasma treatment; and 4) calcination thermally. During the plasma treatment, we use argon glow discharge plasma to treat the catalyst. The loading amount of nickel on the alumina support is 9 wt.%. The reaction of CO_2 reforming of methane was carried out at atmospheric pressure in a 6 mm i.d quartz-tube fixed-bed reactor. A thermocouple placed in the center of the catalyst bed was used to measure the reaction temperature. The reaction temperature was maintained at 873 K, 923 K and 973 K, respectively. The reaction time is 48 h for all the temperatures. Argon was used as the dilution gas during the reaction. The ratio of the feeding gases is 1:1:2 of methane/carbon dioxide/argon. The total flow rate is 40 ml/min with a space velocity of 48000 ml/h·gcat. The reactants and products were analyzed with an online gas chromatography (Agilent 4890D) with a Porapak Q column. An ice-cold trap was set between the reactor exit and the GC sampling valve to remove the water formed during the reaction. CO_2, CH_4 conversions and H_2, CO selectivities were calculated according to the following formulas:

$$X(CH_4)\% = (FCH_{4,IN} - FCH_{4,OUT})/FCH_{4,IN} \times 100\%$$

$$X(CO_2)\% = (FCO_{2,IN} - FCO_{2,OUT})/FCO_{2,IN} \times 100\%$$

$$S(H_2)\% = FH_{2,OUT}/[2\times(FCH_{4,IN} - FCH_{4,OUT})]\times 100\%$$

$$S(CO)\% = FCO,_{OUT}/[(FCH_{4,IN} - FCH_{4,OUT}) + (FCO_{2,IN} - FCO_{2,OUT})]\times 100\%$$

$$F_i = Ci*F_{total}$$

where X, S and F are conversion, selectivity and gas flow rate, respectively. F_{total} is the total feed rate or the gas effluent flow rate. C_i is the molar fraction of component i in the feed gas or in the gaseous effluent that is detected by GC.

The morphology of the used catalysts was observed by TEM with a JEOL JEM –100CXII transmission electron microscope.

Results and Discussion

The stability test was investigated at 873K, 923K and 973K, respectively. Figure 1 and Figure 2 present the conversions of methane and carbon dioxide at different reaction temperatures. Evidently, the catalyst prepared with glow discharge plasma treatment following by calcination thermally is very stable, especially, at the reaction temperature of 923 K. At lower temperatures, the stability of the catalyst is also very well but the catalytic activity is lower. At higher temperature, however, the catalytic activity reduces slightly with the reaction time. Compared to the reported results with Ni/Al_2O_3 catalysts, [2,5] the catalyst reported in this work shows a better low temperature activity.

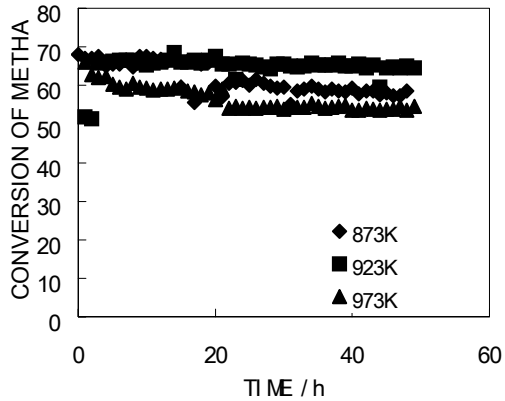

Figure 1. Catalytic activity and stability of Ni/Al_2O_3 catalyst represented by methane conversion (reaction conditions: CH_4:CO_2:Ar=1:1:2, space velocity=48000 ml/h·gcat.)

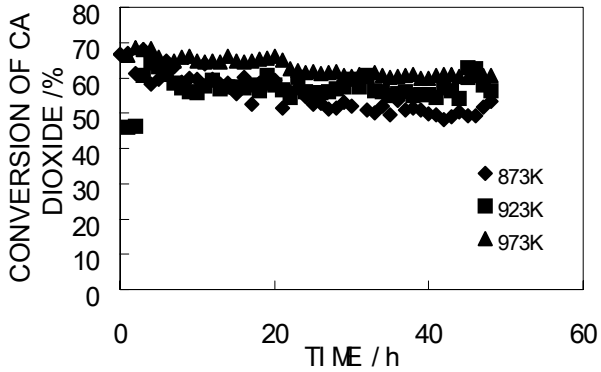

Figure 2. Catalytic activity and stability of Ni/Al_2O_3 catalyst represented by carbon dioxide conversion (reaction conditions: CH_4:CO_2:Ar=1:1:2,space velocity=48000 ml/h·gcat.)

Figure 3 and Figure 4 show the selectivities of hydrogen and carbon monoxide at reaction temperature of 873 K, 923 K and 973 K. With temperature varying from 873 K to 973 K, the selectivities of products increased significantly. Parvery *et al.*[5] have reported a promoted mixed $LaNi_xAl_{1-x}O_3$ perovskite catalysts prepared by a sol-gel related method for dry reforming of methane. Compared to their results, both of the two works achieved good activities of catalysts. However, the catalyst prepared with glow discharge plasma in this work showed a better stability. This means that the glow discharge treatment followed by calcinations thermally leads to a plasma-

enhanced catalytic stability. The TEM provides us evidence with this enhanced stability. It is well known that the carbon deposition is the main reason for the deactivation of the conventional catalysts with the dry reforming of methane. However, the glow discharge treated catalysts exhibit an excellent anti-carbon deposit performance, as shown in Figure 5. Figure 5 shows a TEM image of the used plasma-treated catalyst, taken from the stability test at 923 K. Evidently, some well defined facets of Ni can be observed. This suggests that the carbon deposition is not serious under this reaction condition over the plasma-treated catalyst. Further investigation is being conducted for a better understanding of the plasma-enhanced catalytic stability.

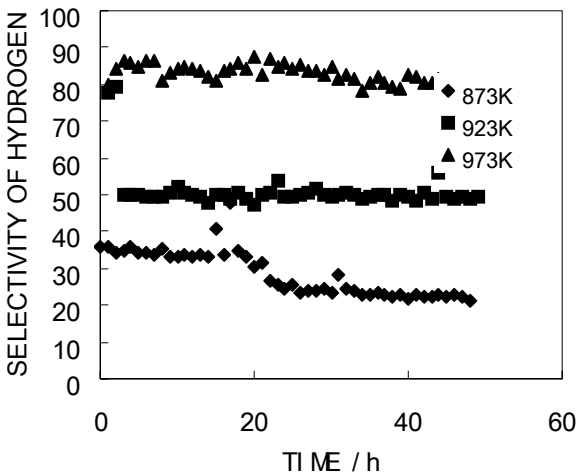

Figure 3. Catalytic activity and stability of Ni/Al_2O_3 catalyst represented by hydrogen selectivity (reaction conditions: CH_4:CO_2:Ar=1:1:2, space velocity=48000 ml/h·gcat.)

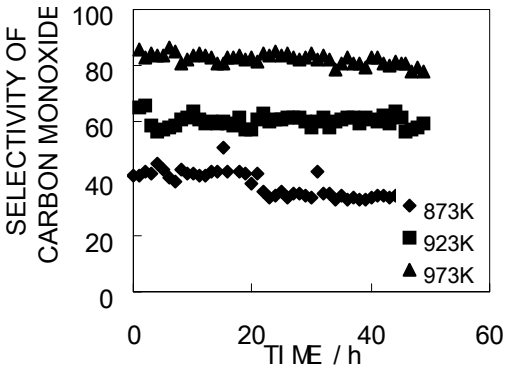

Figure 4. Catalytic activity and stability of Ni/Al_2O_3 catalyst represented by carbon monoxide selectivity (reaction conditions: CH_4:CO_2:Ar=1:1:2, space velocity=48000 ml/h·gcat.).

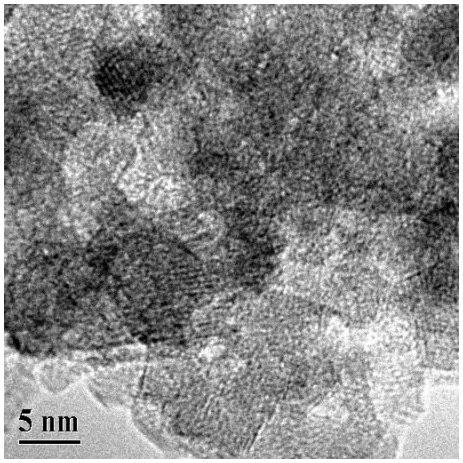

Figure 5. TEM image of used catalyst taken after the stability test (reaction conditions: reaction temperature=923 K, CH_4:CO_2:Ar=1:1:2, space velocity=48000 ml/h·gcat.)

Conclusion

The present investigation confirms that the plasma catalyst preparation described in this work can lead to a production of catalyst with a better low temperature activity and an enhanced catalytic stability for CO_2 reforming of methane. Such prepared catalyst exhibits some well-defined Ni facets after the stability test. This means that the glow discharge plasma treatment would improve the metal-support interaction significantly and induce a better anti-carbon deposit performance.

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