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Direct Methane Reforming: Characterization and Improvement of Fe-SiO_2 catalysts

Keisuke Fugane, Taichi Matsunaga, Noriyasu Okazaki and Akio Tada
Kitami institute of technology, 165 Koen-cho, Kitami, Hokkaido, 090-8507
Fax: 0157-24-7719, e-mail: tada@catal.chem.kitami-it.ac.jp

Fe-SiO_2 catalysts for direct methane reforming were investigated. Low Fe-loading catalysts showed low activity; most of Fe formed inactive Fe silicate. The addition of NiO into Fe-SiO_2 significantly improved the activity.
Key words: methane, direct reforming, Fe catalyst, silica support.

1. INTRODUCTION

As hydrogen is a clean gas fuel, the demand for it is steadily increasing.[1] An ideal source of hydrogen is methane CH_4, because of its large abundance and the highest H/C ratio among saturated hydrocarbons.

Hydrogen is currently produced by steam reforming, partial oxidation and auto-thermal reforming of hydrocarbons, but CO_2 is also produced as by-product.[2]

On the other hand, a direct methane reforming reaction enables us to convert methane to hydrogen without CO_2 emission.[3-4]

Fortunately, the by-product of the direct reforming of methane is mainly carbon nanofibers, a material that has an array of potential applications as electronic components, as polymer additives, and as catalysts/ catalyst supports.[5]

The direct reforming of methane are catalyzed by Fe, Co, and Ni supported on hard-reduced metal oxides such as SiO_2, Al_2O_3, and MgO.[6-14]

Of those Ni has been extensively investigated. Takenaka et al.[15] examined the effect of different catalyst supports, such as MgO, Al_2O_3, SiO_2, TiO_2 and ZrO_2, on the Ni activity for methane reforming, reporting that silica was one of the most effective supports studied. However, yields of hydrogen and carbon nanofibers by supported Ni catalysts decreased significantly with the rise of reaction temperatures of methane decomposition.[15]

On the other hands, Fe-based catalysts have been used at temperatures[16-18] higher than those for Ni-based catalysts. Generally, SiO_2, Al_2O_3, TiO_2, and ZrO_2 are used as supports of Fe.[19-20] Takenaka et al.[21] investigated a direct methane reforming over Fe_2O_3/Al_2O_3 and Fe_2O_3/SiO_2 (77 wt% as Fe_2O_3) at 1073 K and revealed that the carbon yield for Fe_2O_3/Al_2O_3(22.5 g-C/g-Fe) was greater than that for Fe_2O_3/SiO_2 (7.5 g-C/g-Fe). The difference of the catalytic performance between the two catalysts was ascribed to the particle size of the catalytically active iron species. This findings remind us that an interaction between iron metal and its support is crucial for the activity of catalysts, especially supported iron catalysts for the direct reforming of methane.

Supported metal catalysts have been mostly prepared by the conventional impregnation method and those for the direct reforming of methane also without exception. Alternative method for the preparation of catalysts for this reaction could improve the above interaction. Thus there seems to be still a room for improvement of silica supported Fe catalyst for the direct methane reforming.

In this work, the effects of supports, catalyst preparation methods on the activity of Fe-based catalysts were investigated. In addition, the influence of a small quantity of NiO into Fe_2O_3-SiO_2 physically mixed catalysts was studied.

2. EXPERIMENTAL

2.1 Preparation of catalyst

2.1.1 *SiO_2 supported Fe catalyst*:

SiO_2-supported Fe catalysts (Fe/SiO_2) were prepared by impregnating SiO_2 (SIO-6) with an aqueous solution containing Fe cation. $Fe(NO_3)_3 \cdot 9H_2O$ was used as Fe precursor. The impregnated sample was dried over night at 100 °C and then calcined for 5 h at 500 °C in air.

2.1.2 *Fe_2O_3-SiO_2 mixed catalysts*:

Fe_2O_3-SiO_2 mixed catalysts (Fe_2O_3-SiO_2) were prepared by mixing Fe_2O_3 with SiO_2 (SIO-6) using a planetary ball mill for 15 minutes.

2.2 Activity tests

The direct methane reforming reaction was carried out at 750 °C using a flow-type fixed-bed tubular reactor made from quartz (an inner diameter and length 2.5 and 70 cm, respectively) by passing pure methane over the catalysts at 30ml/min. In order to reduce Fe precursors to Fe metal, prior to the activity tests, all catalysts were subjected to a reduction pre-treatment using methane (30 ml/min) at temperatures increasing continuously from 20 °C to 750 °C with the rate of 10 °C/min.

The composition of the outlet gas from the reactor was determined by gas chromatography using activated carbon column and a TCD detector. Conversion of methane was evaluated from the amounts of hydrogen formed, assuming that the reaction, $CH_4 = C + 2H_2$, occurs selectively. In fact, hydrogen only was detected as a gaseous product.

2.3 Characterization of the catalysts

X-ray diffraction (XRD) patterns of the catalyst samples were measured by a Rigaku RINT-1200 diffractmeter using Cu-$K\alpha$ radiation at room temperature. The scanning rate was 4.0 degree/min.

3. RESULTS AND DISCUSSION

3.1 Fe/SiO_2 catalysts

Figure 1 shows the effect of percentage fraction by weight of Fe in Fe/SiO_2 catalysts on the activity for DMR. The 20.0%-loading catalyst was inactive and the 40.0%-loading catalyst was slightly active. The percentage conversion of methane did not reach 30% until the percentage fraction of Fe was raised to 67.7%. On the other hand, in the case of Fe/Al_2O_3, not only a 40.0%-loading catalyst but also a 20.0%-loading catalyst was quite active (not shown). A 30.0%-loading catalyst was active; the percentage conversion of methane reached 67% (not shown). The results that the activity of Fe/Al_2O_3 was higher than that of Fe_2O_3/SiO_2, in accord with the findings by Takenaka et al.,[8] suggest that an interaction between Fe and its support greatly affect the respective catalysts.

Figure 2 shows the powder XRD patterns of the Fe/SiO_2 catalysts used for the reaction. The 20.0%-loading catalyst contained not Fe metal but Fe silicate, while the 40.0%-loading catalyst contained a small amount of Fe metal together with Fe silicate and Fe_3C. In the case of the 67.7%-loading catalyst, the contents of Fe metal and Fe_3C increased, while that of Fe silicate almost remained.

In the case of Fe/Al_2O_3, even a 20.0%-loading catalyst formed no Fe aluminate; there was Fe metal and Fe_3C found (not shown). In other words, an interaction between Fe metal and SiO_2 in Fe/SiO_2 was confirmed to be very strong compared to that in Fe/Al_2O_3.

Since 20.0%-loading Fe/SiO_2 which has not Fe metal but Fe silicate was inactive, Fe silicate is found to be catalytically inactive. It is clear that active iron species is Fe metal, because all active Fe-based catalysts involved Fe metal as shown above.

3.2 Fe_2O_3-SiO_2 catalysts

Figure 3 shows the effect of percentage fraction by weight of Fe in Fe_2O_3-SiO_2 catalysts on the activity. Although the 25.9%-loading catalyst was also inactive, the 40.0%-loading catalyst was highly active; the methane conversion was apparently higher than that of 40.0%-loading Fe/SiO_2. In the case of 67.7%-loading, Fe_2O_3-SiO_2 catalyst was much higher than Fe/SiO_2.

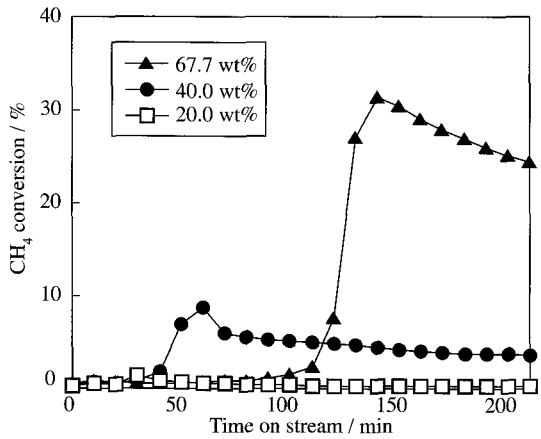

Fig. 1 The activity of Fe/SiO_2 catalysts for direct methane reforming at 750 °C.

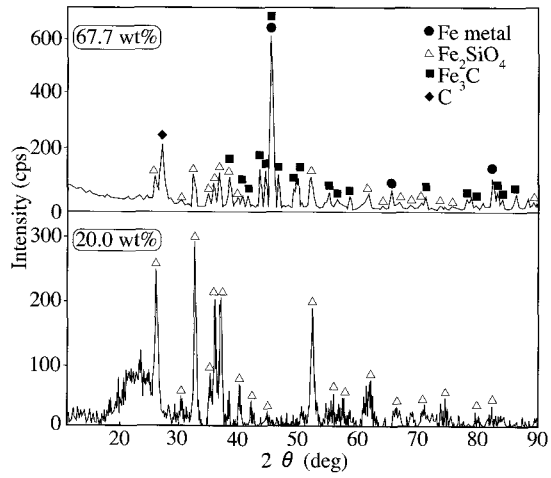

Fig. 2 The powder XRD patterns of the Fe/SiO_2 catalysts used for the reaction.

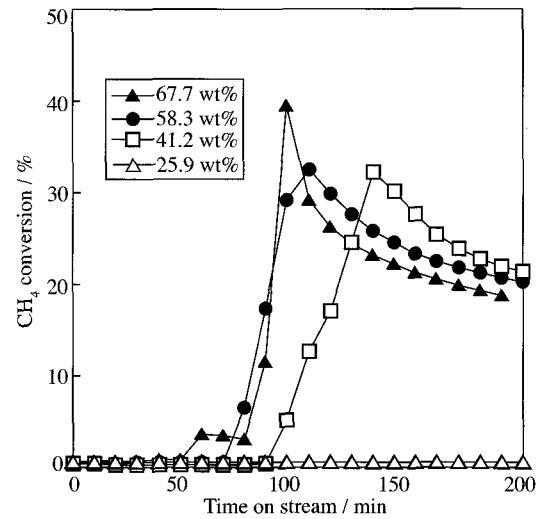

Fig. 3 The activity of Fe_2O_3-SiO_2 catalysts for direct methane reforming at 750 °C.

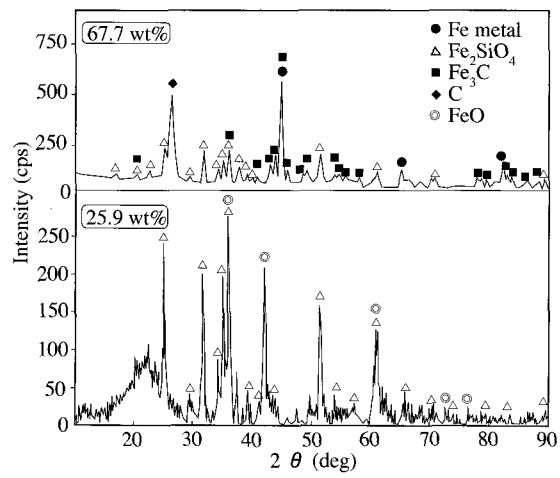

Fig. 4 The powder XRD patterns of the Fe_2O_3-SiO_2 catalysts used for the reaction.

Figure 4 shows the powder XRD patterns of the Fe_2O_3-SiO_2 catalysts used for the reaction. The 25.9%-loading catalyst contained FeO and Fe silicate, while the 40.0% and more-loading catalyst contained considerable amount of Fe and Fe_3C. The amounts of those components increased with Fe loading but that of Fe silicate remained. The reason the 25.9%-loading Fe_2O_3-SiO_2 was inactive is because it had no Fe metal.

3.3 Preparation method of Fe-SiO_2 catalysts

A comparison of Fig. 1 and Fig. 3 shows that the activity of a Fe/SiO_2 catalyst is lower than that of a Fe_2O_3-SiO_2 catalyst having comparable Fe loading.

A detailed comparison of the XRD pattern of 40.0%-loading Fe/SiO_2 and that of 41.2%-loading Fe_2O_3-SiO_2 in Fig. 5 shows that the ratio of the height of the main peak assignable to Fe to that assigned to Fe silicate for the Fe/SiO_2 is lower than that for the Fe_2O_3-SiO_2. This suggests that an interaction between Fe and SiO_2 in Fe/SiO_2 is stronger than that in Fe_2O_3-SiO_2. Similar tendency was also confirmed for respective 67.7%-loading catalysts. Therefore, the lower activity of a Fe/SiO_2 compared to a Fe_2O_3-SiO_2 having comparable Fe loading will be ascribed to the stronger interaction of Fe with SiO_2; the stronger the interaction, the lower the content of catalytically active Fe.

Either 20.0%-loading Fe/SiO_2 or 25.9%-loading Fe_2O_3-SiO_2 contained no Fe. This is the reason why both catalysts showed no activity. However, there is considerable difference in XRD pattern between those: The 20.0%-loading Fe/SiO_2 contained Fe silicate, while 25.9%-loading Fe_2O_3-SiO_2 contained not only Fe silicate but also FeO. The presence of FeO gives evidence that the interaction of Fe with SiO_2 in Fe/SiO_2 is rather weak.

The fact that 20.0%-loading Fe/SiO_2 was inactive but 40.0% or more-loading Fe/SiO_2 was active suggests that the amount of Fe which can react with SiO_2 to form Fe silicate is limited, and so excess amount of Fe can behave as catalytically active species.

Takenaka et al.[21] assumed that Fe_3C as well as α-Fe metal are the catalytically active species and the decomposition of Fe_3C into α-Fe and carbons produced filamentous carbons, as proposed by several research groups.[19, 22]

This explanation holds true for our results that Fe_3C is found together with α-Fe in most active Fe-based catalysts.

3.4 Addition of NiO to Fe_2O_3-SiO_2 catalysts

Figure 6 shows that the activity of Fe_2O_3-SiO_2 was remarkably enhanced by the addition of a small amount of NiO (0.1 g or 0.05 g): The induction period was greatly shortened, the maximum conversion of methane was increased and besides, the significant decrease in activity with respect to time on stream was improved. Regarding binary oxide catalysts, Fe_2O_3-SiO_2 and NiO-SiO_2 were active but Fe_2O_3-NiO inactive contrary to expectation.

The remarkable change of the induciton period due

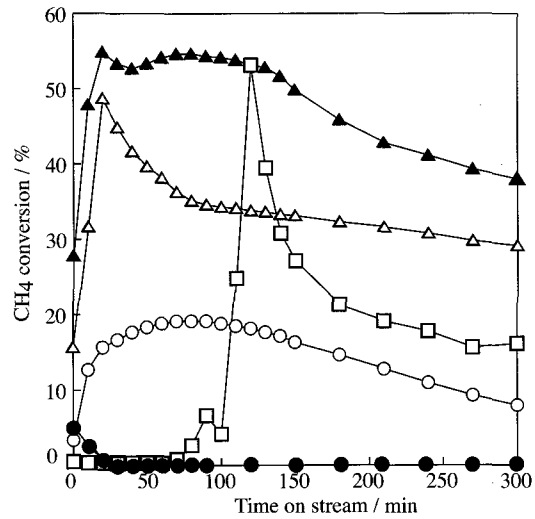

Fig. 6 The activity of Fe_2O_3-NiO-SiO_2 for direct methane reforming at 750 °C. ▲: Fe_2O_3(0.4 g)-NiO(0.1 g)-SiO_2(0.1 g); △: Fe_2O_3(0.4 g)-NiO(0.05 g)-SiO_2(0.1 g); □: Fe_2O_3(0.4 g)-SiO_2(0.1 g); ○: NiO(0.1 g)-SiO_2(0.1 g); ●: Fe_2O_3(0.4 g)-NiO(0.1 g).

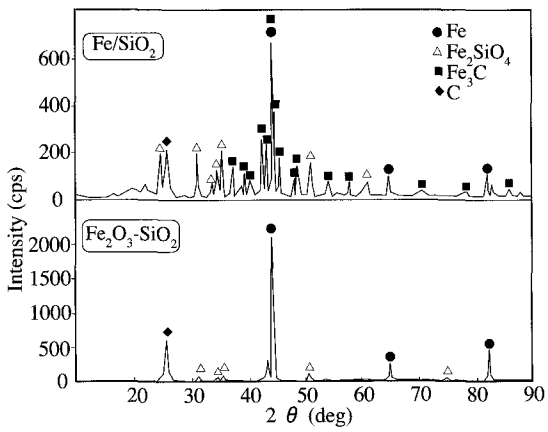

Fig. 5 The powder XRD patterns of the Fe(40.0 wt%)/SiO_2 catalyst and Fe_2O_3(41.2 wt%)-SiO_2 catalyst used for the reaction.

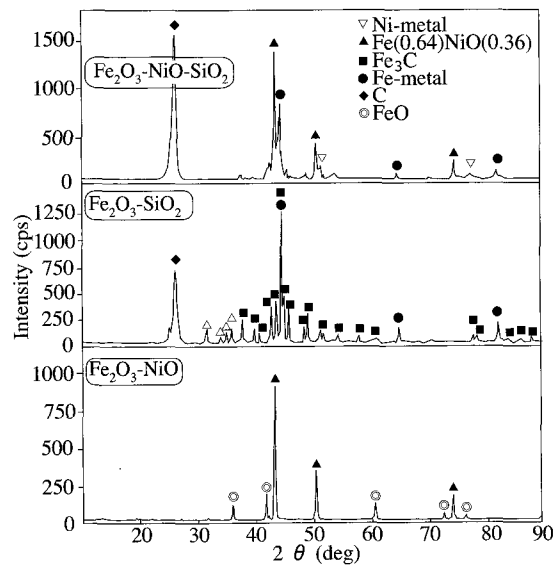

Fig. 7 The powder XRD patterns of Fe_2O_3(0.4 g)-NiO(0.1 g)-SiO_2(0.1 g), Fe_2O_3(0.4 g)-SiO_2(0.1 g) and Fe_2O_3(0.4 g)-NiO(0.1 g) catalysts used for the reaction.

to the addition of NiO could be caused by the easier reduction of Fe_2O_3 to Fe because of abandunt hydrogen gas formed by the DMR over Ni metal which is produced earlier than Fe metal, as will be demonstrated elsewhere.[23]

3.5 XRD profile of Fe_2O_3-NiO-SiO_2 catalyst

Figure 7 shows the powder XRD patterns of both Fe_2O_3-NiO-SiO_2 and Fe_2O_3-NiO that were used for the reaction.

The XRD patterns revealed that Fe_2O_3-NiO-SiO_2 catalysts had both Fe metal and Ni metal together with Fe-Ni alloy; there was no Fe silicate. NiO-SiO_2 that was active contained Ni metal; no Ni silicate was formed. Fe_2O_3-NiO having no activity involved Fe-Ni alloy and FeO, indicating that Fe-Ni alloy is inactive, because FeO has been already known to be inactive.

3.6 Role of NiO in Fe_2O_3-NiO-SiO_2 catalysts

The NiO addition to Fe_2O_3-SiO_2 prevented the formation of Fe silicate. This can be explained as follows: catalytically inactive Fe-Ni alloy could lie between Fe metal and SiO_2 and disturb their direct contact.

The activity of Fe_2O_3-NiO-SiO_2 will be essentially ascribed to the Fe metal and Ni metal.

4. Conclusion

On the basis of the results described above, we concluded as follows;

1. The activity of Fe_2O_3-SiO_2 for the direct methane reforming was higher than that of Fe/SiO_2. The content of Fe silicate formed in Fe_2O_3-SiO_2 during the reaction was lower than that in Fe/SiO_2.
2. The activity of Fe/Al_2O_3 and Fe_2O_3-Al_2O_3 for the direct methane reforming was higher than those of Fe/SiO_2 and Fe_2O_3-SiO_2, respectively. No Fe aluminate was formed in Fe/Al_2O_3 and Fe_2O_3-Al_2O_3 during the reaction.
3. The activity of Fe-based catalysts depended strongly on the interaction between the Fe metal and the support.
4. The catalytically activity of Fe_2O_3-SiO_2 was greatly improved by the addition of NiO.

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