

# Syn Gas and Hydrogen Production from 2-step Thermochemical Methane Reforming over Cu/Fe/Ce/Zr Mixed Oxides Medium

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**ABSTRACT:** Thermochemical 2-step methane reforming, involving the reduction of metal oxide with methane to produce syn-gas and the oxidation of the reduced metal oxide with water to produce pure hydrogen, was investigated on iron oxide based metal oxide mediums. The mediums, Cu/Fe/Zr mixed oxide were composed as an active component and ZrO<sub>2</sub> as a binder, respectively. The reaction characteristics on the added amounts of Cu in Cu/Fe/Zr mixed oxide mediums and the cyclic tests were investigated. With the increase of the added amount of Cu in Cu/Fe/Zr mixed oxide mediums, the conversion of CH<sub>4</sub> and the selectivity of CO<sub>2</sub> were increased with the increase of the added amount of Cu in Cu/Fe/Zr mixed oxide mediums. The Cu<sub>0.7</sub>Fe<sub>2.3</sub>O<sub>4</sub>/ZrO<sub>2</sub> medium showed the good performance in the ten cycles, indicating that the medium had high durability. Moreover, the gasification of the deposited carbon in the water-splitting step was promoted with the addition of Cu to the mediums. In addition, we investigated the addition of Ce to Cu/Fe/Zr medium for improvement of reactivity.

**Keywords:** syn-gas, hydrogen, thermochemical, methane reforming, iron oxide

## 1. INTRODUCTION

Thermochemical conversion of high temperature heat from concentrated solar radiation into chemical fuels has an advantage of producing energy carriers for storing and transporting solar energy from sun-belt to the remote population centers [1].

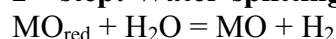
Correspond to this, various processes were proposed. Notably, two-step methane reforming process using metal oxide medium is favorable process for an effective conversion from solar energy to chemical energy. This process consists of two steps as

follows, and an overall reaction equals the conventional steam reforming of methane.

### 1<sup>st</sup> step: Syn-gas production step



### 2<sup>nd</sup> step: Water-splitting step



In syn-gas production step, methane reacts with metal oxide (MO) and then produces a reduced metal oxide (MO<sub>red</sub>) and the syn-gas with H<sub>2</sub>/CO ratio of two, which is suitable for synthesis of methanol,

dimethyl ether (DME) and liquid fuel by Fischer-Tropsch process. The concentrated solar radiation heat can be utilized to supply reaction heat in this endothermic step. The produced syn-gas is calorifically upgraded by ideally 28% and the emitted carbon dioxide caused green house effect can be reduced about 21% by utilizing of solar radiation heat [2]. For the conventional steam reforming of methane, a large amount of carbon dioxide was released because methane itself is burned with oxygen in a reformer to supply reaction heat.

In subsequent water-splitting step, the reduced metal oxide ( $\text{MO}_{\text{red}}$ ) reacts with water vapor and then produces metal oxide (MO) and hydrogen. Because methane and vapor as reactant were introduced to a reactor separately, the production of pure hydrogen, suitable for application to polymer electrolyte membrane fuel cell, is possible.

The technical key aspects for this process to practical use are the technique for the concentrated solar heat and the development of metal oxide medium. At present, the technique for utilizing the concentrated solar heat has been achieved in practical use below 1273 K. Therefore, it is important to develop the metal oxide medium suitable for 2-step methane reforming. As a favored medium for 2-step methane reforming, it should have high oxygen storage capacity, good redox property, high reactivity and resistance against carbon deposition.

Notably, preventing carbon deposition on surface of medium in syn-gas production step is important because it causes the deactivation of medium and leads to produce the hydrogen contaminated with  $\text{CO}_x$  in water-splitting step.

Related to develop metal oxide medium for 2-step methane reforming, Kodama et al. [2~4] evaluated the possibility of various metal oxides such as  $\text{In}_2\text{O}_3$ ,  $\text{SnO}_2$ ,  $\text{V}_2\text{O}_5$ ,  $\text{MoO}_3$  and  $\text{WO}_3$  and found  $\text{WO}_3$  medium had a good redox property, high CO selectivity and an appropriate ratio of  $\text{H}_2/\text{CO}$

in syn gas production step, while it had low reactivity and stability in repeated cycles. Hence, to suppress the sintering of metal oxide in high temperature, they attempted the addition of  $\text{ZrO}_2$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{SiO}_2$  as binder to  $\text{WO}_3$  medium and found the addition of  $\text{ZrO}_2$  to  $\text{WO}_3$  medium suppressed the sintering of metal oxide medium with repeated cycling in high temperature.

The Ferrite system, transition metal substituted to magnetite ( $\text{Fe}_3\text{O}_4$ ), having good redox property was also considered as medium for 2-step methane reforming [5,6]. Notably,  $\text{ZrO}_2$  added to Ni-ferrite showed the quite high activity, while it showed the fast carbon deposition on surface of medium.

In our previous study [7], we investigated the screening of the favorable medium in 2-step methane reforming. As the medium, various transition metals such as Co, Cu and Mn substituted to magnetite, ferrite system was considered and  $\text{ZrO}_2$  was added to ferrite for stability of medium. In the results, Cu-ferrite/ $\text{ZrO}_2$  showed the lowest carbon deposition although it showed the low reactivity.

In this study, we evaluated the effect of Cu added to iron oxide/ $\text{ZrO}_2$  with increasing Cu content and examined cyclic test for the medium adding appropriate content of Cu. In the result, we found the considerable result in terms of durability of medium. In addition, we investigated the addition of Ce to Cu/Fe/Zr medium for improvement of reactivity. The addition of Ce to medium in steam reforming of methane has been identified to improve the reactivity and the resistance of carbon deposition.

## 2. EXPERIMENTAL

### 2.1 Preparation of mediums

Cu/Fe/Zr mixed oxides with various content of Cu were prepared by modified co-precipitation method. Water solutions (0.5 M) dissolving  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (Kanto, 99%),  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  (Junsei, 99.5%), and  $\text{Zr}(\text{OCH}_2\text{CH}_2\text{CH}_3)_4$  (Fluka, 70 wt%) were

used as precursors of metal species Fe, Cu, Mn and Zr, respectively. For  $\text{Cu}_x\text{Fe}_{3-x}\text{O}_4/\text{ZrO}_2$  as expected product, the composition of Cu,  $x$ , varied to 0~1.5 mol. The  $\text{ZrO}_2$  content in the medium was determined to 45 wt%.

The mixed solution containing precursors of metal species was stirred drastically with dropping 1 M of sodium hydroxide water solution as the precipitant at 60 °C and then it was reacted for 60 min. The obtained precipitate was washed and filtered with deionized water more than three times, dried for 24 h at 100 °C, and calcined in air for 3 h at 900 °C. Prepared mediums with a particle size range of 180 to 425  $\mu\text{m}$  were used in reaction.

## 2.2 2-step methane reforming

Figure 1 shows an experimental apparatus for 2-step methane reforming. Reaction was carried out in a fixed bed reactor under atmospheric pressure. 1 g of the medium was packed in the reactor of quartz tube with a diameter of 11 mm. The reactor was heated in an infrared furnace to desired temperature within 5 min while passing an Ar gas at a flow rate of 30  $\text{ml min}^{-1}$ . 15%  $\text{CH}_4$  (Ar balance) was introduced to the reactor at a flow rate of 30  $\text{ml min}^{-1}$  to carry out the syn-gas production step. For subsequent water-splitting step, Ar introduced to a steam generator at a flow rate of 30  $\text{ml min}^{-1}$ . The partial pressure of water vapor in steam generator was maintained to 31.1 kPa. The reaction temperatures were determined to 900 and 700 °C as syn-gas production step and water-splitting step, respectively. The reactive gases ( $\text{CH}_4$  or  $\text{H}_2\text{O}$ ) were introduced to the reactor when the reaction temperatures were constant. The effluent gases during reaction were analyzed at an interval of 8 min by gas chromatography (Donam, DS6200) equipped with thermal conductivity detector (TCD) and carboxphere column in on-line. The structural investigation of the mediums

before and after reaction was confirmed by means of an X-ray diffractometry (XRD, Philips, X'Pert, MPD).

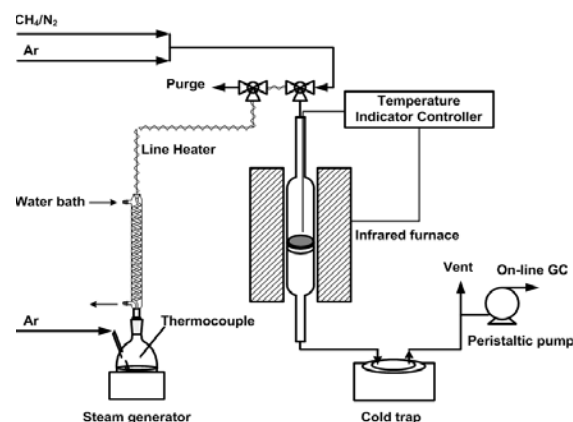


**Figure 1:** Schematic diagram of the experimental apparatus for 2-step methane reforming.

## 3. RESULTS AND DISCUSSION

### 3.1 Carbon deposition on surface of medium

The expected carbon deposition in syn-gas production step strongly affects to 2-step methane reforming. As aforementioned, the significant deactivation of medium be caused and the production of pure hydrogen is impossible in water-splitting step due to carbon deposition on surface of medium. Therefore, it is very important to reduce carbon deposition or to determine the reaction time considering starting point of carbon deposition in syn-gas production step.

The carbon deposition could be caused by an oxygen deficiency in metal oxide medium during reduction with  $\text{CH}_4$ . To evaluate the starting point of carbon deposition, syn-gas production step was performed with Fe oxide/ $\text{ZrO}_2$  as a reference medium for 72 min. The variation of moles of the effluent gases during syn-gas production step was shown in Figure 2(a). Methane as reactive gas was fast converted for 8 min, and then it was converted until the end of reaction, gradually. The generation rates of  $\text{H}_2$  and CO as desired product increased until 64 min, gradually. Hereafter, CO generation was decreased in

spite of consecutive conversion of  $\text{CH}_4$ , while  $\text{H}_2$  generation was increased remarkably. It indicates that microscopic deposition of carbon was started with time on stream and carbon deposition was increased remarkably at a specific point. To decide a clear point of carbon deposition, total carbon balance was calculated by summation of molar flows of  $\text{CH}_4$ ,  $\text{CO}$ , and  $\text{CO}_2$  as effluent gases containing carbon. As shown in Figure 2(b), whereas total carbon molar flow maintained  $0.2 \text{ mmol min}^{-1}$  from the beginning of reaction to ca. 56 min, it decreased remarkably after 56 min. In other words, carbon deposition started from point of decreasing  $\text{CO}$  in Figure 2(a), ca. 56 min, in this reaction. With this method, the starting point of carbon deposition was determined by the point of decrease of total carbon molar flow. Furthermore, the reaction times of all the mediums were determined by considering the start point of carbon deposition.

### 3.2 The effect of the additive in Cu/Fe/Zr mixed oxide medium with content of Cu

Cu/Fe/Zr mixed oxide mediums with various Cu content were designated to  $\text{Cu}_x\text{Fe}_{3-x}\text{O}_4/\text{ZrO}_2$  ( $x=0, 0.3, 0.7, 1.0, 1.5$ ). XRD analysis for the mediums as  $x=0.3, 0.7$ , and  $1.5$  in  $\text{Cu}_x\text{Fe}_{3-x}\text{O}_4/\text{ZrO}_2$  is shown in Figure 3. As-prepared  $\text{Cu}_{0.3}\text{Fe}_{2.7}\text{O}_4/\text{ZrO}_2$  (a) showed the structures,  $\text{ZrO}_2$ ,  $\text{Fe}_2\text{O}_3$ , and  $\text{Cu}_{0.67}\text{Fe}_{2.33}\text{O}_4$ . The added Cu to medium does not formed the phase of oxide. On the other hand, it showed  $\text{Fe}_2\text{O}_3$  due to the excess Fe species. For  $\text{Cu}_{0.7}\text{Fe}_{2.3}\text{O}_4/\text{ZrO}_2$  (b), whereas  $\text{Fe}_2\text{O}_3$  was not observed, the only  $\text{Cu}_{0.67}\text{Fe}_{2.33}\text{O}_4$  phase was observed with  $\text{ZrO}_2$ . It indicates that the structure of medium showed  $\text{Cu}_{0.67}\text{Fe}_{2.33}\text{O}_4$  as stoichiometric ferrite phase when  $0.7 \text{ mol}$  of Cu added to medium. For  $\text{Cu}_{1.5}\text{Fe}_{1.5}\text{O}_4/\text{ZrO}_2$  (c),  $\text{CuO}$  was observed with  $\text{Cu}_{0.67}\text{Fe}_{2.33}\text{O}_4$  due to the excess Cu. It deduced that the peak intensity of  $\text{CuO}$  become strong with increase of Cu content.

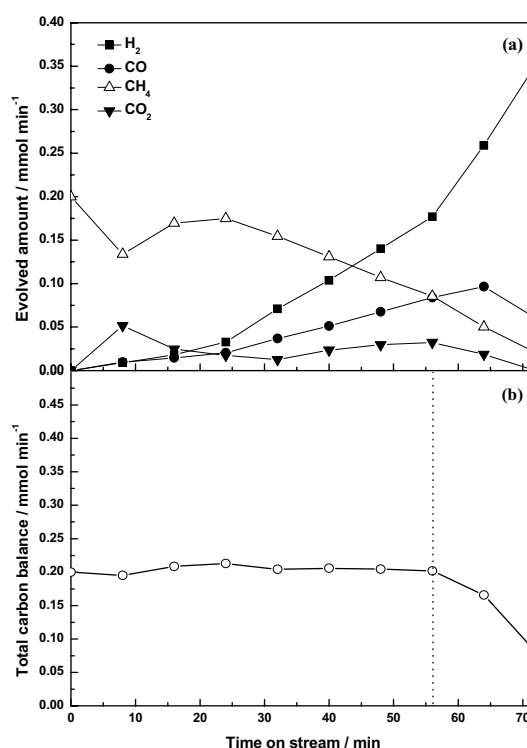


**Figure 2:** The experimental results after syn-gas production step using Fe oxide/ $\text{ZrO}_2$ ; (a) variation of the evolved gaseous amounts (b) variation of total carbon balance (sample: 1 g, reaction temp:  $900^\circ\text{C}$ , reaction time: 72 min, concentration of reactive gas: 15%  $\text{CH}_4$ ).

The experimental results of 2-step methane reforming over  $\text{Cu}_x\text{Fe}_{3-x}\text{O}_4/\text{ZrO}_2$  ( $x=0\sim 1.5$ ) mediums are listed in Table I.

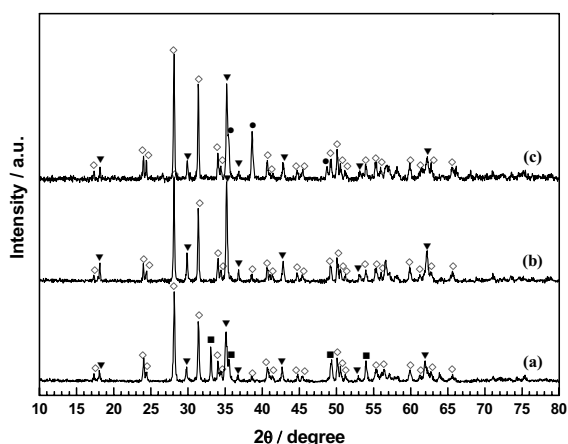
In terms of reaction time indicating the starting point of carbon deposition ( $T_{\text{deposit}}$ ) in syn-gas production step, Fe-oxide/ $\text{ZrO}_2$  showed  $T_{\text{deposit}}$ , 56 min, while  $\text{Cu}_{0.3}\text{Fe}_{2.7}\text{O}_4/\text{ZrO}_2$  showed 136 min. From this result, it evaluated that the addition of Cu to medium plays a role of make delay the carbon deposition. With increase of Cu content,  $T_{\text{deposit}}$  decreased remarkably from 136 min to 48 min. The conversion of methane increased from 13.1% to 29.5% and the selectivity of  $\text{CO}_2$  increased relatively by the decrease of  $\text{CO}$  selectivity from 60.2% to 42.7%.

**Table I:** The experimental results for two-step methane reforming over  $\text{Cu}_x\text{Fe}_{3-x}\text{O}_4/\text{ZrO}_2$  and Fe oxide/ $\text{ZrO}_2$  mediums.

| Mediums<br>/ $\text{ZrO}_2$                | Step | Total evolved gaseous<br>amounts (mmol/g) |             |               | $\text{H}_2/\text{CO}$ | $\text{CH}_4$ Conversion<br>(%) | Selectivity<br>(%) |               | Reaction time<br>(min) |
|--------------------------------------------|------|-------------------------------------------|-------------|---------------|------------------------|---------------------------------|--------------------|---------------|------------------------|
|                                            |      | $\text{H}_2$                              | $\text{CO}$ | $\text{CO}_2$ |                        |                                 | $\text{CO}$        | $\text{CO}_2$ |                        |
| Fe oxide                                   | S.P  | 3.27                                      | 1.78        | 1.25          | 1.84                   | 25.36                           | 58.75              | 41.25         | 56                     |
|                                            | W.S  | 7.06                                      |             |               |                        |                                 |                    |               | 120                    |
| $\text{Cu}_{0.3}\text{Fe}_{2.7}\text{O}_4$ | S.P  | 3.90                                      | 2.47        | 1.63          | 1.58                   | 13.13                           | 60.21              | 39.79         | 136                    |
|                                            | W.S  | 6.19                                      |             |               |                        |                                 |                    |               | 120                    |
| $\text{Cu}_{0.5}\text{Fe}_{2.5}\text{O}_4$ | S.P  | 3.42                                      | 2.26        | 1.63          | 1.51                   | 12.76                           | 58.13              | 41.87         | 136                    |
|                                            | W.S  | 6.05                                      |             |               |                        |                                 |                    |               | 120                    |
| $\text{Cu}_{0.7}\text{Fe}_{2.3}\text{O}_4$ | S.P  | 3.26                                      | 1.98        | 1.66          | 1.65                   | 15.59                           | 54.31              | 45.69         | 104                    |
|                                            | W.S  | 5.66                                      |             |               |                        |                                 |                    |               | 120                    |
| $\text{Cu}_{1.0}\text{Fe}_{2.0}\text{O}_4$ | S.P  | 2.45                                      | 1.49        | 1.61          | 1.65                   | 18.57                           | 48.02              | 51.98         | 80                     |
|                                            | W.S  | 4.81                                      |             |               |                        |                                 |                    |               | 120                    |
| $\text{Cu}_{1.5}\text{Fe}_{1.5}\text{O}_4$ | S.P  | 2.45                                      | 1.28        | 1.72          | 1.91                   | 29.47                           | 42.68              | 57.32         | 48                     |
|                                            | W.S  | 4.37                                      |             |               |                        |                                 |                    |               | 120                    |

\* The weights of samples were 1g.

\* Syn-gas production step (S.P) and water splitting step (W.S) were accomplished at 900 °C, 700 °C, respectively.

**Figure 3:** XRD patterns of as-prepared  $\text{Cu}_x\text{Fe}_{3-x}\text{O}_4/\text{ZrO}_2$  [(a)  $x=0.3$ , (b)  $x=0.7$  and (c)  $x=1.5$ ] mediums; (■):  $\text{Fe}_2\text{O}_3$ , (▼):  $\text{Cu}_{0.67}\text{Fe}_{2.33}\text{O}_4$ , (●):  $\text{CuO}$ , (◇):  $\text{ZrO}_2$ .

In other words, increase of Cu content in  $\text{Cu}_x\text{Fe}_{3-x}\text{O}_4/\text{ZrO}_2$  mediums caused the improvement of reactivity, fast carbon deposition, and the increase of complete oxidation to  $\text{CO}_2$ .  $\text{H}_2/\text{CO}$  molar ratio increased from 1.5 to 1.9 as stoichiometric value by increase of Cu content. On the other hand, the amounts of evolved hydrogen decreased gradually by increase of Cu content in water splitting step. Because it is difficult that Cu metal converted to CuO in water splitting reaction, thermodynamic ally.

Consequently, it suggests that the amounts of evolved hydrogen were decreased in water splitting step with increase of Cu content in medium. In general, Cu has been used widely as the active component of hydrogenation catalysts and it enhances the hydrogen mobility [8,9]. It has been also proposed that Cu has high affinity with the graphite structure, thereby inhibiting the formation of a graphite layer on active species surface [10] and, thus, showing Cu to be good third component when in an appropriate amount. Moreover, for methane direct decomposition using Ni/Al based catalyst, these effects of Cu may reduce the growth rate of carbon layers and therefore, the encapsulation of catalyst particles by carbon layer is retarded, which is regarded as the main reason of catalyst deactivation, but the continual increase of Cu content led to a great decrease of the stability [11,12].

Furthermore, the Cu/Ce/O and Cu/Zr/O composites were used active catalysts [13] and deposition of CuO onto  $\text{MgAl}_2\text{O}_4$  leads to an efficient catalyst for the total oxidation of methane with a selectivity of 100% to carbon dioxide in appropriate condition [14]. Based the above results, it deduced that the addition of Cu to the medium has the effect

of depressed carbon deposition and improved total oxidation to carbon dioxide.

### 3.3 Properties in the repeated cycles over $\text{Cu}_{0.7}\text{Fe}_{2.3}\text{O}_4/\text{ZrO}_2$

We performed the cyclic tests for 2-step methane reforming using Cu/Fe/Zr mixed oxide to evaluate the stability of the medium. As the suitable medium, we selected  $\text{Cu}_{0.7}\text{Fe}_{2.3}\text{O}_4/\text{ZrO}_2$  because it shows mainly  $\text{Cu}_{0.67}\text{Fe}_{2.33}\text{O}_4$  structure, ferrite structure, as shown in Figure 3. It indicated that the added Cu was dispersed well to medium. The result of ten cycles for 2-step methane reforming over Fe-oxide/ $\text{ZrO}_2$  and  $\text{Cu}_{0.7}\text{Fe}_{2.3}\text{O}_4/\text{ZrO}_2$  is shown in Figure 4. For Fe-oxide/ $\text{ZrO}_2$ , the evolved amounts of the gaseous products ( $\text{H}_2$ , CO,  $\text{CO}_2$ ) were remarkably decreased during three cycles. It indicated that the deactivation of the medium was occurred significantly. On the other hand, for  $\text{Cu}_{0.7}\text{Fe}_{2.3}\text{O}_4/\text{ZrO}_2$ , the amounts of evolved gaseous products were gradually increased up to five cycles, and then they were gradually decreased from 6<sup>th</sup> cycle.

Figure 5 shows the XRD patterns for (a) as-prepared  $\text{Cu}_{0.7}\text{Fe}_{2.3}\text{O}_4/\text{ZrO}_2$ , (b) after syn-gas production step, (c) after water-splitting step.

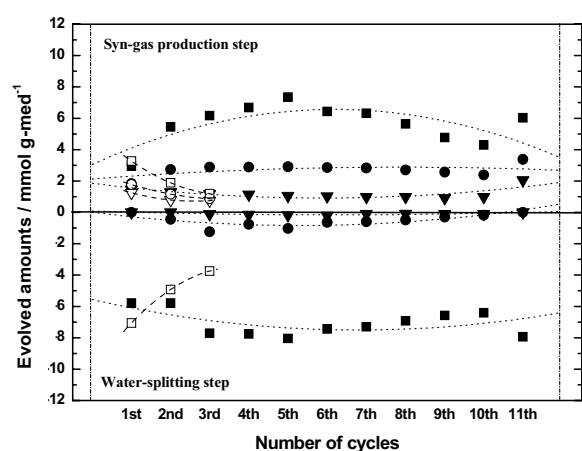


**Figure 4:** Variations of the amounts of evolved gaseous products in cyclic test for 2-step methane reforming over Fe oxide/ $\text{ZrO}_2$  and  $\text{Cu}_{0.7}\text{Fe}_{2.3}\text{O}_4/\text{ZrO}_2$ ; (■:  $\text{H}_2$ , ●: CO, ▼:  $\text{CO}_2$ , ; solid shape:  $\text{Cu}_{0.7}\text{Fe}_{2.3}\text{O}_4/\text{ZrO}_2$ , empty shape: Fe oxide/ $\text{ZrO}_2$ ).

After first syn-gas production step (b), it showed Cu and Fe phases. The structure of ferrite was observed with Cu structure after one of water-splitting step (c). Considering the structure of Cu, ferrite structure likely to present  $\text{Cu}_{0.67}\text{Fe}_{2.33}\text{O}_4$  and  $\text{Fe}_{2.93}\text{O}_4$  mixed. Figure 5(d) shows the XRD pattern after 2-step methane reforming using the medium, which was calcined in air atmosphere at 1173 K for the regeneration of medium after ten cycles. It evaluated this pattern was similar with the medium after first cycles.

Consequently, it deduced that Cu existing after water-splitting step provided the reaction path of reactive methane by five times of cycles. Moreover, it seems that Cu played a role of catalytic agent to improve gasification of water vapor and deposit carbon in water-splitting step. It likely to the deactivation of the medium occurred gradually with the change of structure in the above five cycles, whereas the possibility of regeneration in the medium was confirmed through the above result. As a whole, the addition of Cu to the medium leads to maintain the durability of the medium with repeated cycles.

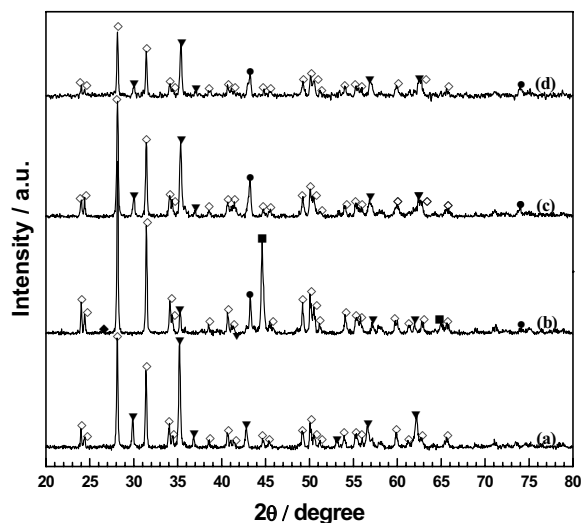


**Figure 5:** XRD patterns of  $\text{Cu}_{0.7}\text{Fe}_{2.3}\text{O}_4/\text{ZrO}_2$  (a) fresh sample, (b) after syn-gas production step, (c) after water-splitting step, (d) after 11th cyclic test; (▼:  $\text{Cu}_{0.67}\text{Fe}_{2.33}\text{O}_4$ , ■: Fe, ●: Cu, ◇:  $\text{ZrO}_2$ ).

#### 4. CONCLUSION

2-step methane reforming using Cu/Fe/Zr mixed oxides was carried out, and the additive effect of Cu and cyclic test were carried out. Some specific conclusions were drawn from this work as follows:

- 1) The syn-gas production step of 2-step methane reforming over  $\text{Cu}_x\text{Fe}_{3-x}\text{O}_4/\text{ZrO}_2$  ( $x=0\sim1.5$ ) were carried out, the deactivation of the mediums were shown by carbon deposition, and the starting points of carbon deposition were different by the mediums. The starting points of carbon deposition were shorter by the increase of reactivity generally.
- 2)  $\text{CH}_4$  conversion and  $\text{CO}_2$  selectivity were improved by the increase of Cu content in  $\text{Cu}_x\text{Fe}_{3-x}\text{O}_4/\text{ZrO}_2$  ( $x=0\sim1.5$ ) mediums, while the evolved  $\text{H}_2$  in water-splitting step were decreased by increase of Cu content.
- 3)  $\text{Cu}_{0.7}\text{Fe}_{2.3}\text{O}_4/\text{ZrO}_2$  medium showed the property of comparatively good regeneration in ten cycles. The added Cu maintained to metal Cu as not oxidative after first cycle, and it promoted the gasification with deposit carbon in water-splitting step.

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