

# Effects of $\text{La}_2\text{O}_3$ , Cu and Fe addition on the catalytic performance of Ni-SiO<sub>2</sub> catalysts for methane decomposition

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Methane decomposition over four kinds of catalysts such as Ni-SiO<sub>2</sub>, Ni-La<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>, Ni-Cu-SiO<sub>2</sub> and Ni-Fe-SiO<sub>2</sub> prepared by co-impregnation method and sol-gel method, respectively, has been studied. The results indicated that Ni-La<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> catalyst with La/Ni = 0.3 prepared by co-impregnation method showed better catalytic performance compared with all the other Ni-La<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> catalysts during methane decomposition at 823 K. However, the temperature resistance of this catalyst was not very good. The introduction of Cu and Fe into Ni-SiO<sub>2</sub> enhanced the temperature resistance of the catalysts during methane decomposition at 923 K and the overall catalytic performance of the catalysts was Ni-Cu-SiO<sub>2</sub> (sol-gel method) > Ni-Fe-SiO<sub>2</sub> (sol-gel method) > 75%Ni-25%SiO<sub>2</sub> (sol-gel method) > Ni-La<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> (co-impregnation method). XRD studies of Ni-La<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>, Ni-Cu-SiO<sub>2</sub> and Ni-Fe-SiO<sub>2</sub> catalysts indicated that Ni species existed in the form of Ni metal in Ni-La<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>, while Ni-Cu alloy and Ni-Fe alloy appeared in Ni-Cu-SiO<sub>2</sub> and Ni-Fe-SiO<sub>2</sub> catalysts. The structure of the carbon filaments formed during methane decomposition changed a lot with the introduction of Cu and Fe. At 923 K, “bifurcate carbon filaments” formed over Ni-Cu-SiO<sub>2</sub> during methane decomposition, while “bamboo-shaped carbon filaments” formed over Ni-Fe-SiO<sub>2</sub> catalysts.

Keywords: Methane decomposition, Ni-SiO<sub>2</sub>, Ni-La<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>, Ni-Cu-SiO<sub>2</sub>, Ni-Fe-SiO<sub>2</sub>

## 1. Introduction

If graphite and carbon fiber composite are employed as plasma facing components for ITER, the deuterated and tritiated methane may be a considerable constituent of the impurity gas stream [1-6]. Methane decomposition is a safe and simple method for recovering deuterium and tritium from the deuterated and tritiated methane and an optional catalyst bed for methane decomposition is currently included into the design of the tokamak exhaust processing system (TEP) [7,8].

Lots of research on methane decomposition has been done by many researchers [9-11]. The ZrCo powder has already been found to decompose methane slowly at 573 K. A product of 0.05 molC/mol ZrCo was obtained after 80 h when the getter was exposed to 430 torr CH<sub>4</sub> [9]. Watanabe [10] *et al* investigated the decomposition of methane on Zr<sub>7</sub>Ni<sub>10</sub>, ZrNi, Zr<sub>2</sub>Ni, Zr<sub>4</sub>Ni and Zr in the temperature range 573 K–823 K and the alloy of Zr<sub>4</sub>Ni removed methane over 99% efficiently in 105 s at 673 K. Baker [11] *et al* discovered that a St 909 getter (Zr–Mn–Fe) could effectively remove 99% of NH<sub>3</sub>, CO<sub>2</sub> and O<sub>2</sub> at 673 K, CO at 873 K, and CH<sub>4</sub> at 973 K from an inert gas stream.

However, methane decomposition for recovering deuterium and tritium which was studied by the above researchers all focused on the static systems and the unsupported alloy catalysts, while the dynamic systems

were hardly investigated. Above all, the unsupported alloy catalysts in the dynamic systems will deactivate quickly. Methane decomposition over the supported catalysts to prepare H<sub>2</sub> and carbon filament in the dynamic system has been studied by many researchers and many achievements have been obtained in recent years [12-16]. However, the effects of the rare metal oxide, Fe and Cu addition on the temperature resistance of the Ni-based catalysts were little investigated. In view of this, methane decomposition over supported catalysts such as Ni-SiO<sub>2</sub>, Ni-La<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>, Ni-Cu-SiO<sub>2</sub> and Ni-Fe-SiO<sub>2</sub> catalysts in dynamic systems has been studied in this work. The influences of the preparation method, the reaction temperature and the contents of La, Cu and Fe in Ni-SiO<sub>2</sub> on methane decomposition were investigated.

## 2. Experimental

### 2.1. Catalyst preparation

Ni-La<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> catalysts were prepared by co-impregnation method [17] which was done through impregnating SiO<sub>2</sub> with the mixed aqueous solution of Ni(NO<sub>3</sub>)<sub>2</sub> and La(NO<sub>3</sub>)<sub>3</sub> for 1.5 h, and then drying up the impregnated samples at 413 K for 12 h, and finally calcined them at 873 K for 6 h. The Ni content in all the catalysts was Ni/Si = 0.67 (molar ratio) and the La contents in the catalysts were La/Ni = 0, La/Ni = 0.1,

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$\text{La}/\text{Ni} = 0.3$ ,  $\text{La}/\text{Ni} = 0.45$  and  $\text{La}/\text{Ni} = 0.6$  (molar ratio), respectively.

75%Ni-25% $\text{SiO}_2$ , 65%Ni-10%Fe-25% $\text{SiO}_2$ , 35%Ni-40%Fe-25% $\text{SiO}_2$ , 65%Ni-10%Cu-25% $\text{SiO}_2$ , and 35%Ni-40%Cu-25% $\text{SiO}_2$  catalysts (mass fraction) were prepared by sol-gel method [18,19]. The method was based on mixing the active components such as NiO or the mixtures of NiO and CuO (or  $\text{Fe}_2\text{O}_3$ ) in this case, with alcosol containing silica in a certain amount. The suspensions of the active components with alcosol were dried in flowing air at room temperature and were finally calcined at 923 K for 3 h. Alcosol was prepared by mixing 50 mL of TEOS, 40 mL of ethanol, 2 mL of water and 0.5 mL of 40% HCl. Silica content in the alcosol was 0.142 g/mL and could be diluted by ethanol. The mixture of NiO and CuO (or  $\text{Fe}_2\text{O}_3$ ) was originated from calcining the mixture of  $\text{Ni}(\text{NO}_3)_2$  and  $\text{Cu}(\text{NO}_3)_2$  (or  $\text{Fe}(\text{NO}_3)_3$ ) at 723 K and the  $\text{Ni}(\text{NO}_3)_2$  and  $\text{Cu}(\text{NO}_3)_2$  (or  $\text{Fe}(\text{NO}_3)_3$ ) mixture was obtained by evaporating the mixed solution of  $\text{Ni}(\text{NO}_3)_2$  and  $\text{Cu}(\text{NO}_3)_2$  (or  $\text{Fe}(\text{NO}_3)_3$ ).

## 2.2 Activity tests and catalyst characterization

Methane catalytic decomposition reactions were carried out in a fixed-bed quartz reactor (10 mm i.d.) under atmospheric pressure. Before the activity tests, Ni- $\text{La}_2\text{O}_3$ - $\text{SiO}_2$  catalysts were subjected to a reduction pre-treatment using pure hydrogen of 20 mL/min at 873K for 1h and Ni-Cu- $\text{SiO}_2$  and Ni-Fe- $\text{SiO}_2$  catalysts were reduced with pure hydrogen of 20 mL/min at 923 K for 1 h. The feed stream was high-purified methane (99.99%) of 15 mL/min. The gaseous reaction products were monitored by an off-line gas chromatography (GC) combined with a 5A molecular column, using a thermal conductivity detector (TCD) for hydrogen and methane analysis.

XRD patterns were recorded on a Bruker D8Advance diffractometer with Cu  $K\alpha$  radiation at 40 kV and 40 mA.

The detailed structure of the deposited carbons was observed using the FEI Inspect F scanning electron microscope (SEM) operated at 20 kV and the JEOL JEM-100CX Transmission electron microscopy (TEM), operated at 80 kV.

## 3. Results and discussion

### 3.1 The catalytic performance of the catalysts

Fig.1 depicts the kinetic curves of methane decomposition over Ni- $\text{La}_2\text{O}_3$ - $\text{SiO}_2$  catalysts with different contents of  $\text{La}_2\text{O}_3$  at 823 K. Only hydrogen was obtained as a gaseous product for all the catalysts. It could be observed that the catalytic activity of Ni- $\text{SiO}_2$  catalyst without  $\text{La}_2\text{O}_3$  decreased gradually with the time on stream and it was completely deactivated after 450 minutes. The addition of  $\text{La}_2\text{O}_3$  extended the lifetime

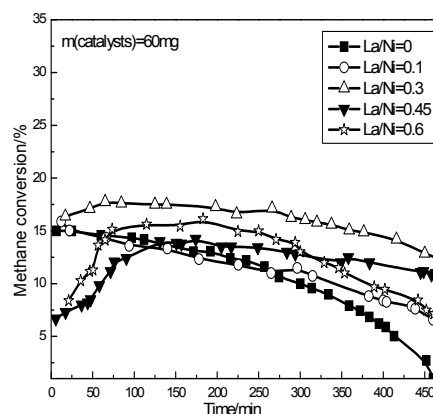


Fig.1 Kinetic curves of methane decomposition over Ni- $\text{La}_2\text{O}_3$ - $\text{SiO}_2$  catalysts at 823 K.

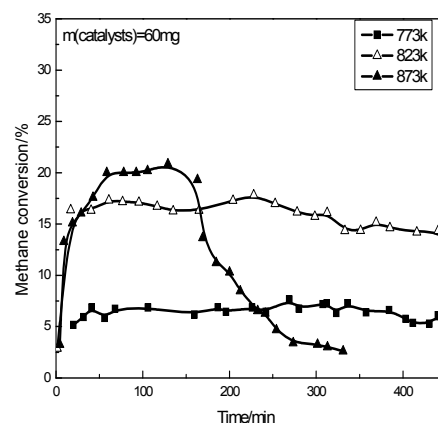


Fig.2 Effect of reaction temperature on methane decomposition over Ni- $\text{La}_2\text{O}_3$ - $\text{SiO}_2$  catalysts with  $\text{La}/\text{Ni} = 0.3$ .

of Ni- $\text{SiO}_2$  catalyst obviously. For the Ni- $\text{La}_2\text{O}_3$ - $\text{SiO}_2$  catalyst with  $\text{La}/\text{Ni} = 0.1$ , the methane conversion decreased from 16% to 7% after 450 minutes. With the increase of  $\text{La}_2\text{O}_3$  content from  $\text{La}/\text{Ni} = 0.1$  to  $\text{La}/\text{Ni} = 0.3$ , the catalytic performance of the catalyst was greatly improved and the methane conversion decreased from 17% to 13% with only 4% dropped after 450 minutes. However, when  $\text{La}_2\text{O}_3$  content in the catalyst exceeded  $\text{La}/\text{Ni} = 0.3$ , the catalytic performance of the catalysts dropped slightly. The methane conversion decreased from 15% to 7.5% for Ni- $\text{SiO}_2$  with  $\text{La}/\text{Ni} = 0.6$  after 450 minutes. Thus, a conclusion can be drawn that an optimum  $\text{La}_2\text{O}_3$  content exists in Ni- $\text{La}_2\text{O}_3$ - $\text{SiO}_2$  catalysts which can improve the catalytic performance of Ni- $\text{SiO}_2$  the most efficiently, while the introduction of more  $\text{La}_2\text{O}_3$  into Ni- $\text{SiO}_2$  catalyst will impair the catalytic activity and the lifetime of the catalysts and this optimum  $\text{La}_2\text{O}_3$  content is  $\text{La}/\text{Ni} = 0.3$ .

Fig.2 shows the effect of reaction temperature on methane decomposition over Ni- $\text{La}_2\text{O}_3$ - $\text{SiO}_2$  catalyst with  $\text{La}/\text{Ni} = 0.3$ . The catalytic activity of Ni- $\text{La}_2\text{O}_3$ - $\text{SiO}_2$  with  $\text{La}/\text{Ni} = 0.3$  increased remarkably from 773 K to 823 K. When the reaction temperature increased from 823 K to 873 K, the initial methane conversion increased to 20%,

however, the lifetime of the catalyst was reduced and the methane conversion decreased to 2% after 300 minutes. Therefore, a higher reaction temperature reduced the lifetime of the catalyst and another conclusion can also be drawn that the temperature resistance of Ni-La<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> was not so good even if the introduction of La<sub>2</sub>O<sub>3</sub> into Ni-SiO<sub>2</sub> greatly extended the lifetime of Ni-SiO<sub>2</sub> at a lower reaction temperature such as 823 K.

Fig.3 compared the catalytic performance of Ni-La<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> prepared by co-impregnation method with that of 75%Ni-25%SiO<sub>2</sub> prepared by sol-gel method and it demonstrated that the effect of the preparation method of the catalysts on methane decomposition was important. The catalytic activity of Ni-La<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> with La/Ni = 0.3 which showed the best catalytic performance among the Ni-La<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> catalysts was a little lower than that of 75%Ni-25%SiO<sub>2</sub>. The methane conversion of 75%Ni-25%SiO<sub>2</sub> catalyst at 823 K remained 21% and didn't change during the reaction. However, the methane conversion of Ni-La<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> with La/Ni = 0.3 decreased from 17% to 14% after 400 minutes. Therefore, both the catalytic activity and the stability of 75%Ni-25%SiO<sub>2</sub> were better than that of Ni-La<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> with La/Ni = 0.3 which indicated that the Ni-based catalysts prepared by sol-gel method showed better catalytic performance than that prepared by co-impregnation method during methane decomposition.

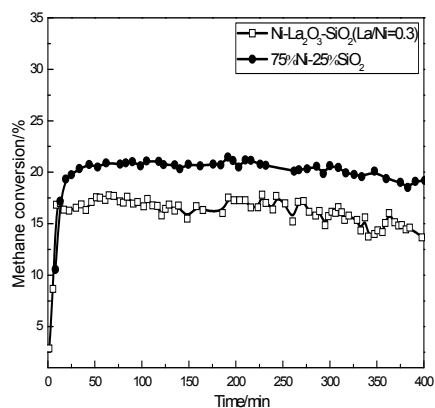


Fig.3 Effect of preparation method on methane decomposition at 823 K ( $m(\text{Ni-La}_2\text{O}_3\text{-SiO}_2) = 60$  mg, co-impregnation method;  $m(75\%\text{Ni}-25\%\text{SiO}_2) = 30$  mg, sol-gel method).

Fig.4(a) depicts the kinetic curves of methane decomposition over Ni-Cu-SiO<sub>2</sub> catalysts with different contents of Cu at 923 K. The lifetime of 75%Ni-25%SiO<sub>2</sub> catalyst was very short at 923 K unlike the catalytic behaviors at 823 K of which the methane conversion was kept at 21% for 400 minutes (Fig.3). After 70 minutes, the methane conversion of 75%Ni-25%SiO<sub>2</sub> decreased to around 5% and remained at this value. The addition of lower content of Cu improved the lifetime of Ni-SiO<sub>2</sub> catalyst apparently and the catalytic activity of

Ni-Cu-SiO<sub>2</sub> didn't change obviously during methane decomposition. The methane conversion of 65%Ni-10%Cu-25%SiO<sub>2</sub> catalyst was kept at around 40%, while when the Cu content increased to 40%, the methane conversion dropped to about 19%. Therefore, it was different from Ni-La<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> catalyst that Ni-Cu-SiO<sub>2</sub> catalysts could catalyze methane decomposition at a higher reaction temperature such as 923 K and the introduction of Cu into Ni-SiO<sub>2</sub> enhanced the temperature resistance of the catalysts.

Fig.4(b) shows the kinetic curves of methane decomposition over Ni-SiO<sub>2</sub> and Ni-Fe-SiO<sub>2</sub> catalysts at 923 K. The catalytic behaviors of Ni-Fe-SiO<sub>2</sub> catalysts were similar with that of Ni-Cu-SiO<sub>2</sub> catalysts. The introduction of Fe also improved the lifetime of Ni-SiO<sub>2</sub> catalysts obviously at 923 K. However, a deactivation period occurred for 65%Ni-10%Fe-25%SiO<sub>2</sub> catalyst and when methane decomposition over 65%Ni-10%Fe-25%SiO<sub>2</sub> catalyst proceeded to 200 min, the methane conversion decreased from 44% to 25%. While, the methane conversion of 35%Ni-40%Fe-25%SiO<sub>2</sub> was maintained at 19% all the time which indicated that with the increase of the Fe content in the Ni-Fe-SiO<sub>2</sub> catalysts the catalytic activity of the catalyst dropped and the stability of Ni-Fe-SiO<sub>2</sub> catalyst was enhanced. Therefore, Ni-Fe-SiO<sub>2</sub> could also catalyze methane decomposition at a higher reaction temperature such as 923 K which was similar with Ni-Cu-SiO<sub>2</sub>. However, the catalytic performance of 65%Ni-10%Fe-25%SiO<sub>2</sub> was a little poorer than that of 65%Ni-10%Cu-25%SiO<sub>2</sub> for the poorer stability.

The research on the temperature resistance of the catalysts is very important for methane decomposition is an endothermic reaction and the conversion rises with the increase of the reaction temperature [20]. Thus, a catalyst with high temperature resistance can catalyze methane decomposition more efficiently at a higher reaction temperature [21]. According to the above results, a conclusion can be drawn that the order of the catalytic performance of the four kinds of catalysts above is Ni-Cu-SiO<sub>2</sub> (sol-gel method) > Ni-Fe-SiO<sub>2</sub> (sol-gel method) > 75%Ni-25%SiO<sub>2</sub> (sol-gel method) > Ni-La<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> (co-impregnation method). Also, when methane decomposition over Ni-Cu-SiO<sub>2</sub> or Ni-Fe-SiO<sub>2</sub> catalysts is applied to TEP to recover deuterium and tritium from the deuterated and tritiated methane, a much higher reaction temperature can be adjusted to utilize the temperature resistance of the catalysts to improve the catalytic efficiency.

### 3.2 The characterization of the catalysts before and after methane decomposition

Fig.5(a) shows the XRD spectra of Ni-La<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>

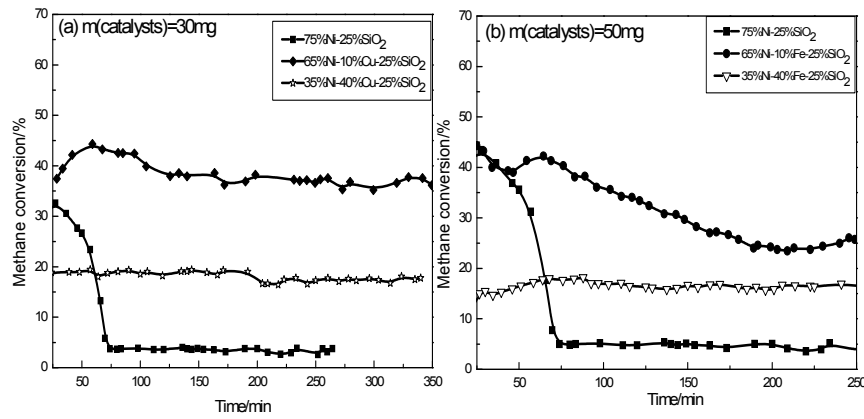


Fig.4 Kinetic curves of methane decomposition over Ni-Cu-SiO<sub>2</sub> and Ni-Fe-SiO<sub>2</sub> catalysts at 923 K.

catalysts reduced by hydrogen. The diffraction peaks at  $2\theta = 44.46^\circ$ ,  $51.81^\circ$  and  $76.36^\circ$  in the XRD spectra of Ni-SiO<sub>2</sub> revealed that the Ni species in the Ni-SiO<sub>2</sub> catalyst reduced by hydrogen existed mainly in the form of Ni metal. When lower content of  $\text{La}_2\text{O}_3$  was introduced into the catalysts such as Ni-La<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> with La/Ni = 0.1 and La/Ni = 0.3, no  $\text{La}_2\text{O}_3$  peaks were detected which meant that the lower contents of  $\text{La}_2\text{O}_3$  existed in an amorphous phase. However, as the contents of  $\text{La}_2\text{O}_3$  exceeded La/Ni = 0.3, the  $\text{La}_2\text{O}_3$  diffraction peaks appeared. In addition, with the increase of the  $\text{La}_2\text{O}_3$  content, the intensity of the diffraction peaks due to Ni metal turned weaker and weaker and the FWHM of the diffraction peaks turned wider and wider which indicated that the Ni crystallite size turned smaller and smaller. Therefore, the Ni dispersion degree was enhanced with the increase of  $\text{La}_2\text{O}_3$  content.

Fig. 5(b) shows the XRD spectra of Ni-SiO<sub>2</sub> and Ni-Cu-SiO<sub>2</sub> catalysts reduced by hydrogen. The diffraction peaks at  $2\theta = 44.46^\circ$ ,  $51.81^\circ$  and  $76.36^\circ$  in the

XRD spectra of 75%Ni-25%SiO<sub>2</sub> also demonstrated that the Ni species in the Ni-SiO<sub>2</sub> catalysts reduced by H<sub>2</sub> existed mainly in the form of Ni metal. The diffraction peaks due to Cu were not detected in Ni-Cu-SiO<sub>2</sub> catalysts even if the Cu content was very high. In fact, when Ni-Cu-SiO<sub>2</sub> was reduced by hydrogen, the Ni species was associated with the Cu species through the formation of Ni-Cu alloy in the catalysts and only Ni-Cu alloy metal phase existed in the Ni-Cu-SiO<sub>2</sub> catalyst.

Fig.5(c) shows the XRD spectra of Ni-SiO<sub>2</sub> and Ni-Fe-SiO<sub>2</sub> catalysts reduced by hydrogen. The Fe in the catalysts also appeared as Ni-Fe alloy which was similar with Ni-Cu-SiO<sub>2</sub> catalysts. However, the Ni-Fe-SiO<sub>2</sub> catalysts reduced by hydrogen had two metal phases: the Ni metal phase and the Ni-Fe alloy phase which was different from Ni-Cu-SiO<sub>2</sub>. The diffraction peaks due to Ni-Fe alloy and Ni metal overlapped with each other which indicated that the Ni-Fe alloy had identical structure with the Ni metal.

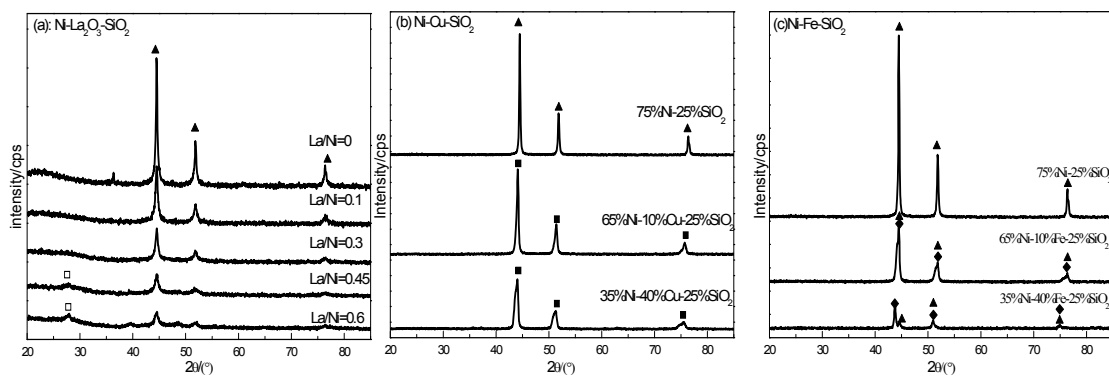


Fig.5 XRD spectra of the Ni-La<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>, Ni-Cu-SiO<sub>2</sub> and Ni-Fe-SiO<sub>2</sub> catalysts reduced by hydrogen (▲-Ni, □-La<sub>2</sub>O<sub>3</sub>, ■-Ni-Cu alloy, ◆-Ni-Fe alloy).

Fig.6 shows the SEM images of the Ni-SiO<sub>2</sub>, Ni-La<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>, Ni-Cu-SiO<sub>2</sub> and Ni-Fe-SiO<sub>2</sub> catalysts after methane decomposition at different reaction temperatures. It could be clearly observed that the

surfaces of all the catalysts were completely covered with the interlaced carbon filaments and the structure of the carbon filaments was seriously influenced by the reaction temperature and the introduced Cu and Fe. The

fundamental structure of the carbon filaments formed over Ni-La<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> with La/Ni = 0 and La/Ni = 0.3 at 823 K (Fig.6(a) and Fig.6(b)) was similar with that of 75%Ni-25%SiO<sub>2</sub> at 823 K (Fig.6(c)) except the thickness and the thickness of the carbon filaments formed over the three catalysts was 75%Ni-25%SiO<sub>2</sub> > Ni-La<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> with La/Ni = 0.3 > Ni-SiO<sub>2</sub> with La/Ni = 0.

From the performance of methane catalytic decomposition in Fig.1 and Fig.3, the order of the catalytic performance of the three catalysts was 75%Ni-25%SiO<sub>2</sub> > Ni-La<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> with La/Ni = 0.3 > Ni-SiO<sub>2</sub> with La/Ni = 0. It could be concluded that when thicker carbon filaments formed over the catalysts, the

catalysts showed better catalytic performance during methane decomposition.

The carbon filaments formed over 75%Ni-25%SiO<sub>2</sub> at 923 K turned shorter and thinner compared with those formed at 823 K. Thus, the increase of the reaction temperature lowered the carbon capacity of 75%Ni-25%SiO<sub>2</sub>. When Cu was introduced into Ni-SiO<sub>2</sub>, the carbon filaments turned much thicker and less homogeneous. The introduction of Fe into Ni-SiO<sub>2</sub> also changed the fundamental structure of the carbon filaments formed during methane decomposition at 923 K. They were much longer and thinner.

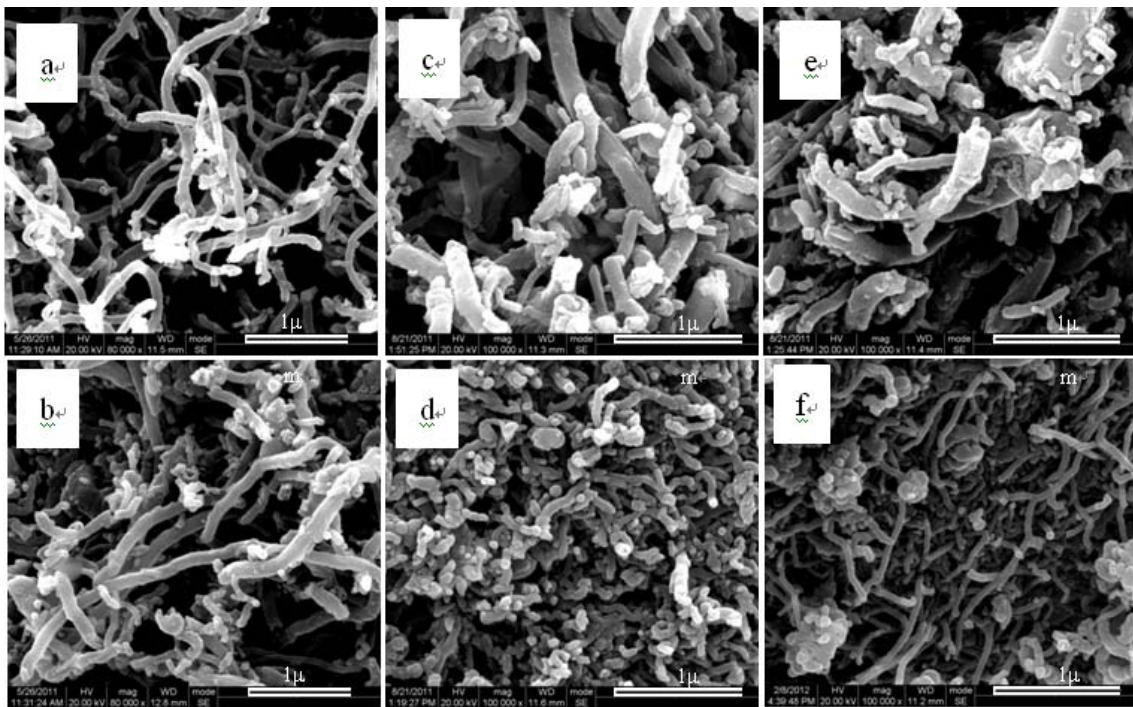


Fig. 6 SEM images of carbon filaments formed during methane decomposition (a: Ni-SiO<sub>2</sub> with La/Ni=0, 823 K; b: Ni-La<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> with La/Ni=0.3, 823 K; c: 75%Ni-25%SiO<sub>2</sub>, 823 K; d: 75%Ni-25%SiO<sub>2</sub>, 923 K; e: 65%Ni-10%Cu-25%SiO<sub>2</sub>, 923 K; f: 35%Ni-40%Fe-25%SiO<sub>2</sub>, 923 K).

Considering the great changes of the carbon filaments with the increase of the reaction temperature and the introduced Cu and Fe, TEM images of these carbon filaments were also investigated to analyze the differences of the detailed structure of these carbon filaments.

In the TEM images of 75%Ni-25%SiO<sub>2</sub> after methane decomposition at 823 K (Fig.7(a)), the carbon filaments with diameters from 70 nm to 110 nm were observed. The “pear-shaped” Ni metal particles were present at the tip of the carbon filaments. While in the TEM images of 75%Ni-25%SiO<sub>2</sub> catalyst formed during methane decomposition at 923 K (Fig.7(b)), the diameter range of the carbon filaments was 50 nm-90 nm and spherical Ni metal particles appeared at the tip of the carbon filaments. The diameters of both types of carbon

filaments were in agreement with their diameters of the catalyst particles at the tips.

The different shapes of the Ni metal particles at different reaction temperatures reflected the different carbon diffusion mechanisms during methane decomposition. Takenaka [22] *et al* pointed out that the formation of the “pear-shaped” Ni metal particles was due to the diffusion of carbon atoms through the bulk of Ni metal particles, while the formation of the spherical Ni metal particles resulted from the diffusion of carbon atoms on the surface of Ni metal particles. Thus, it could be speculated that the carbon atoms formed during methane decomposition was preferential to diffuse through the surface of the Ni metal particles at a higher temperature.

Another phenomenon which should be paid attention

to was that when the formed carbons during methane decomposition diffused through the bulk of the active metal at 823 K, the catalyst could keep active for methane decomposition for a long time, while, when the formed carbons during methane decomposition diffused through the surface of the active metal, the catalyst lost its activity in a short time (Fig.3 and Fig.4). As a result, the diffusion of the formed carbons through the surface of the catalysts wasn't beneficial for the long time methane decomposition.

Fig.7(c) and Fig.7(d) show the TEM images of the carbon filaments formed during methane decomposition over 65%Ni-10%Cu-25%SiO<sub>2</sub> at 923 K. It can be observed that “bifurcate carbon filaments” formed over 65%Ni-10%Cu-25%SiO<sub>2</sub> catalysts and the Ni-Cu alloy particle which was active for methane decomposition was not at the tip of the carbon filaments as it was in the carbon filaments formed over Ni-SiO<sub>2</sub> catalyst. A few carbon filaments grew from one Ni-Cu alloy particle and the Ni-Cu alloy particle was positioned among the carbon filaments.

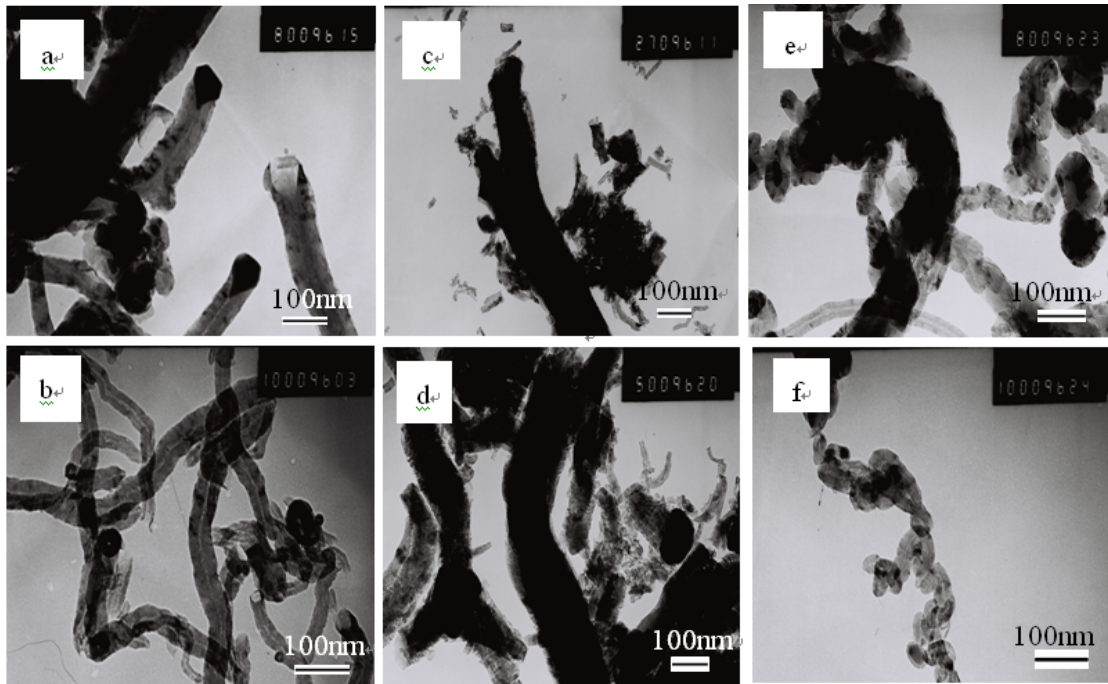


Fig.7 TEM images of carbon filaments formed over Ni-SiO<sub>2</sub>, Ni-Cu-SiO<sub>2</sub> and Ni-Fe-SiO<sub>2</sub> during methane decomposition (a: 75%Ni-25%SiO<sub>2</sub>,823 K; b:75%Ni-25%SiO<sub>2</sub>, 923 K; c,d: 65%Ni-10%Cu-25%SiO<sub>2</sub>, 923 K; e,f:35%Ni-40%Fe-25%SiO<sub>2</sub>, 923 K).

Compared with the Ni particles in Fig.7(b) which was formed over 75%Ni-25%SiO<sub>2</sub> after methane decomposition at 823 K, the Ni-Cu particles were also “pear-shaped” after methane decomposition over Ni-Cu-SiO<sub>2</sub> catalysts at 923 K. Thus, it could be speculated that the addition of Cu into Ni-SiO<sub>2</sub> catalyst changed the diffusion mechanism of the formed carbons. At a higher reaction temperature such as 923 K, the diffusion of the carbons formed over Ni-Cu-SiO<sub>2</sub> catalyst remained through the bulk of Ni-Cu particles. This might be the reason why the lifetime of Ni-Cu-SiO<sub>2</sub> catalysts was also very long at a higher reaction temperature such as 923 K.

Fig.7(e) and Fig.7(f) shows the TEM images of the carbon filaments formed over Ni-Fe-SiO<sub>2</sub> catalysts at 923 K. Carbon filaments of “bamboo-shaped” structure formed over Ni-Fe-SiO<sub>2</sub> catalyst. The walls of the “bamboo-shaped carbon filaments” were uneven and the

hollows of these carbon filaments were divided into many cells which was different from those formed over Ni-SiO<sub>2</sub> catalyst. The Ni-Fe alloy particles which were active for methane decomposition were not only present at the tip of the carbon filaments after methane decomposition, but also existed in the hollow cells of the “bamboo-shaped” structure.

Apparently, the addition of Fe also changed the carbon diffusion mechanism of Ni-SiO<sub>2</sub> catalyst during methane decomposition. The results of Ermakova and Takenaka [18, 23] *et al* indicated that the products of methane decomposition over Fe-SiO<sub>2</sub> catalysts were also “bamboo-shaped carbon filaments”. Thus, the carbon diffusion mechanism of Ni-Fe-SiO<sub>2</sub> catalyst during methane decomposition was similar with that of Fe-SiO<sub>2</sub> catalyst.

Since the carbon diffusion mechanism of Ni-Fe-SiO<sub>2</sub> is similar with that of Fe-SiO<sub>2</sub> catalyst, it can also be

believed that the characterization of methane decomposition over Ni-Fe-SiO<sub>2</sub> catalysts should be in agreement with that of Fe-based catalysts. As the activation temperature of the Fe-based catalysts is much higher than that of the Ni-based catalysts [23], the introduction of Fe also enhanced the temperature resistance of Ni-based catalysts and the lifetime of Ni-Fe alloy catalysts was much longer than that of the single Ni-based catalysts at a higher reaction temperature such as 923 K.

In addition, the temperature resistance of Ni-Cu alloy and Ni-Fe alloy catalysts was both stronger than that of the single Ni-based catalysts, while the stability of 65%Ni-10%Fe-25%SiO<sub>2</sub> catalyst during methane decomposition wasn't as good as that of 65%Ni-10%Cu-25%SiO<sub>2</sub> (Fig.4). The reason for this might be that not all of the Ni species in 65%Ni-10%Fe-25%SiO<sub>2</sub> catalyst existed in the form of Ni-Fe alloy (Fig.5), while Ni and Cu could form alloys over a wide composition range and this was proved by the results of Fig.5 and other researchers [24]. When the Fe content in Ni-Fe-SiO<sub>2</sub> increased to 40%, the stability of the catalyst was enhanced for the Ni species in 35%Ni-40%Fe-25%SiO<sub>2</sub> mainly existed in the form of Ni-Fe alloy although the catalytic activity of the catalyst decreased.

#### 4. Summary

1) The introduction of La<sub>2</sub>O<sub>3</sub> into Ni-SiO<sub>2</sub> catalysts obviously extended the lifetime of the catalysts during methane decomposition at 823 K. However, the temperature resistance of Ni-La<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> didn't change obviously and the catalytic activity of Ni-La<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> with La/Ni = 0.3 disappeared at a very short time at 873 K. While the introduction of Cu and Fe into Ni-SiO<sub>2</sub> enhanced the temperature resistance of the catalyst. The catalytic performance of the catalysts during methane decomposition was Ni-Cu-SiO<sub>2</sub> (sol-gel method) > Ni-Fe-SiO<sub>2</sub> (sol-gel method) > 75%Ni-25%SiO<sub>2</sub> (sol-gel method) > Ni-La<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> (co-impregnation method).

2) XRD studies of Ni-La<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>, Ni-Cu-SiO<sub>2</sub> and Ni-Fe-SiO<sub>2</sub> catalysts indicated that the Ni species existed in the form of Ni metal in Ni-La<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> catalyst and Ni-Cu alloy and Ni-Fe alloy appeared in Ni-Cu-SiO<sub>2</sub> and Ni-Fe-SiO<sub>2</sub> catalysts, respectively.

3) The fundamental structure of the carbon filaments formed over Ni-La<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> with La/Ni = 0 and La/Ni = 0.3 was similar with that of 75%Ni-25%SiO<sub>2</sub> at 823 K. While the carbon filaments formed over 75%Ni-25%SiO<sub>2</sub> at 923 K turned shorter and thinner than those formed at 823 K. "Bifurcate carbon filaments" formed over Ni-Cu-SiO<sub>2</sub>, while "bamboo-shaped carbon filaments" formed over Ni-Fe-SiO<sub>2</sub> catalysts during methane decomposition at 923 K.

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