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Hydrogen production by methane decomposition over Ni-Cu-SiO₂ catalysts: Effect of temperature on catalyst deactivation

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Catalytic decomposition of methane (CDM) is a simple process for the production of high-purity, CO_x -free (CO or CO₂) hydrogen. The CDM is a moderately endothermic reaction, and high temperature are thermodynamically favorable for achieving high methane conversion. However, Ni-Cu catalysts easily lose their activities at high temperature. To study the effect of temperature on the deactivation of Ni-Cu catalysts, 65%Ni-15%Cu-SiO₂ catalyst was prepared by the heterophase sol-gel method. A series of kinetic experiments (routes I, II, III) were designed to test the catalytic performance and generate by-products carbon structures. The effects of reaction temperature and methane dissociation rate on catalyst deactivation were studied. The phase transition temperature was estimated. Based on the kinetic experiments, TEM images, XRD data, TGA-DSC curves, and TEM-EDX data, a thoroughly deactivation study of the 65%Ni-15%Cu-SiO₂ catalyst was carried out. The results of this study proved that high degree of graphitization was the key factor contributing to the deactivation of Ni-Cu catalysts. Fragmentation and phase separation at high temperature were both responsible for carbon atom enrichment and high degree of graphitization, which in turn cause the 65%Ni-10%Cu-25%SiO₂ catalyst to lose activity at high temperature.

Keywords: Ni-Cu alloy particle, Catalyst deactivation, Methane decomposition, Kinetic study, Hydrogen production

1.Introduction

Recently, hydrogen is increasingly being considered as a promising and environmentally friendly energy source ¹, due to the rapid depletion of fossil-fuel resources and increased environmental pollution resulting from greenhouse gas emission. The large-scale industrial hydrogen production process is currently based on the well-known steam reforming of methane ^{2, 3}. However, this process and the partial oxidation of methane involve the formation of a certain amount of CO₂ and CO as by-products, which contribute to global warming ^{4, 5}. Moreover, for the effective use of hydrogen-derived energy, people are focusing on the use of fuel cells to generate electricity, as these cells can directly convert chemical energy into electricity ⁶⁻¹⁰. However, even low concentrations (a few ppm) of CO may act as poison for proton exchange membrane fuel cells (PEMFCs) ⁹. Moreover, CO₂ (at ppm levels) is detrimental to alkaline fuel cells (AFCs) ¹⁰. Hence, critical issues must be overcame for the successful application of hydrogen in fuel cells. Consequently, the

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aforementioned hydrogen production processes must include an additional purification step to remove CO_X , which in turn increases process cost. As opposed to the steam reforming of methane and partial oxidation of methane, catalytic decomposition of methane (CDM) is a direct means of hydrogen production, without the concomitant formation of CO_X ¹¹. In addition to generating CO_x -free hydrogen, CDM also affords highly valuable carbon structures, such as nanotubes (CNTs) and nanofibers (CNFs). These by-products, CNTs or CNFs, have significant potential due to their superior surface properties, high tenacity, high electron conductivity, as well as metallic and semiconductor characteristics ¹².

The CDM reaction is as follows ¹³:

 $CH_4 \rightarrow C + 2H_2$, $\Delta = 75.52 \text{ kJ/mol}$

(1)

Traditionally, Ni-based catalysts have been widely used in the CDM, because of their partially filled 3d-orbitals, which can facilitate the dissociation of hydrocarbon molecules through partial acceptance of electrons ¹⁴. Moreover, the CDM is a moderately endothermic reaction. Therefore, high temperature are thermodynamically favorable for achieving high methane conversion¹⁵. Although supported Ni catalysts show superior performance during the CDM at temperatures below 600 °C ¹⁶. Ni-based catalysts are deactivated immediately at temperatures above 600 °C ^{17, 18}. In order to enhance the catalytic stability at high temperature, copper is introduced into Ni-based catalysts ^{19, 20}. Previous reports state that the Ni-Cu catalyst exhibits better performance than the Ni catalyst at high temperature for the CDM, i.e., the carbon yields (gC/gNi) of the 75%Ni-15%Cu-Al₂O₃ catalyst was 700 at 625 °C and the 65%Ni-25%Cu/Nb₂O₅ catalyst resulted in the maximum carbon yield of 743 gC/gNi at 600 °C^{21, 22}. In general, the doping of Cu can have several effects on Ni-based catalysts. First, introduction of Cu can decrease the reduction temperature of Ni, since Cu has a lower reduction temperature than Ni¹⁵. The reduced Cu at low temperatures dissociates hydrogen molecules into hydrogen atoms. The hydrogen molecules can spread to the surface of the neighboring NiO species and facilitate the reduction of Ni species in the mixed oxide ²³. Second, in several reactions it has been reported the electronic interactions between Ni and a second metal can remarkably enhanced catalytic activity²⁵⁻²⁷. Therefore, due to Cu is richer in d electrons, it can exert an electronic effect on the Ni species ²⁴. Third, Cu affects the affinity of the Ni-metal surface toward graphite ^{28, 29}, i.e., Cu addition to Ni improves the desired resistance of the catalyst to carbon deposition by decreasing the amount of coke formed 30 .

Although doping of a Cu component can effectively improve the catalytic performance of Ni-based catalysts, the methane conversion decreases remarkably at temperatures beyond 750 °C ^{31, 32}. Some authors ^{15, 32-34} have reported that Ni catalysts easily aggregated into large clusters at high temperature during thermal treatment, and the enlargement of the metal particles results in poor catalytic performance ²³. Moreover, when the reaction temperature reaches a certain level, Ni-Cu alloy particles enter the so-called quasi-liquid state and lose their activities during the CDM reaction ^{32, 35}. In addition, when the Ni-Cu particles stay in the quasi-liquid state, bamboo-like

carbon nanotubes (BLCNTs) will be formed ³⁶. The growth of BLCNTs causes the Ni-Cu alloy particles break down into several pieces, and the balance between the methane dissociation rates and diffusion rates of carbon is disturbed with the change in the Ni-Cu particle size ^{15, 37}. As a result, the particles are encapsulated by carbon atoms in a very short time, leading to deactivation of the Ni-Cu catalyst.

Lots of reporters ^{15, 38} investigated the deactivation mechanism of Ni-Cu alloy particles. According to them, the Ni-Cu particles enter a quasi-liquid state, and fragmentation of these particles during BLCNT growth at high temperature may be a key factor for catalyst deactivation ³⁹. While others ³³ stated the excessive methane dissociation rate could lead to the formation of a large amount of carbon atoms on the surface of Ni-Cu particles, which was responsible for the notable loss of catalytic activity at high temperature. Although the structural damage of Ni-Cu particles and the high carbon production rate had been reported to make a significant contribution to catalyst deactivation at high temperature, some processes of them had not been studied in detail yet. Moreover, it was not clearly understand the effect of graphitization about catalyst deactivation. As a continuation of the authors' research on the properties and those well-known deactivation mechanisms of Ni-Cu alloy catalysts, we focused on the effects of temperature on Ni-Cu-SiO₂ catalysts during the CDM in the temperature range 600 °C-780 °C. A series of more precise reaction routes had been designed to test the performance of the catalysts, and we also analyzed the reaction kinetics and solved the above-mentioned issues. In addition, the morphology of the carbon structures and catalyst had been investigated, which could help us understand the detailed process of catalyst deactivation. Finally, the findings would try to be detailed in elaborating the deactivation mechanism of the Ni-Cu particles at high temperature.

2. Experimental

2.1. Catalyst preparation

65%Ni-10%Cu-25%SiO₂ catalyst (mass fraction) was prepared using the heterophase sol-gel method ^{40, 41}, by mixing the active components (mixture of NiO and CuO), with alcosol-containing silica in certain proportions. Suspensions of active components and alcosol were dried under a flow of air at room temperature and calcined at 650 °C for 3 h. The alcosol was prepared by mixing 50 mL of tetraethylorthosilicate (TEOS), 40 mL of ethanol, 2 mL of water, and 0.5 mL of 40% HCl. The silica content in the alcosol was 0.142 g/mL, and the alcosol could be diluted with ethanol. Mixtures of NiO and CuO were obtained from the mixtures of Ni(NO₃)₂ and Cu(NO₃)₂ calcined at 450°C, and the Ni(NO₃)₂ and Cu(NO₃)₂.

2.2. Catalyst performance tests

The catalyst performance was evaluated during the CDM in a fixed-bed quartz reactor (10 mm i.d.) under atmospheric pressure. A K-type thermocouple was placed in the catalyst bed to detect the temperature of the bed. Metallic Ni-Cu particles (15 mg) were placed in the quartz reactor, and hydrogen reduction reaction commenced when increasing the furnace temperature to 600 °C under a flow of N₂ at 20 cm³/min. Reduction treatment of the catalysts was continued for 1 h under 50% H₂ in N₂ at a flow rate of 20 cm³/min. After the reduction process, three routes were considered for the 65%Ni-10%Cu-25%SiO₂ catalyst performance tests.

Route I was a step-wise heating model for the CDM. The test was commenced at 600 °C, following the reduction process, and purified methane (99.99%) was passed through the reactor. After 20 min, the temperature was increased at a rate of 4 °C/min for 5 min (total of 20 °C), maintained at this level for 15 min, and then further increased to the next high preset temperature. The step-wise heating was continued until the temperature reached a certain level (600 °C, 620 °C, 640 °C, 660 °C, 680 °C, 700 °C, 720 °C, 740 °C, 760 °C, 780 °C), and this the temperature was maintained until a CDM reaction time of 200 min. In this route, the flow rate of methane (13 cm³/min) was constant during the CDM.

Route II was somewhat similar to route I. This test was commenced at 600 °C with purified methane at a flow rate of 13 cm³/min, and the temperature change was similar to the pattern in the step-wise heating model. When the furnace temperature reached the desired level, 640 °C, 660 °C and 680 °C, these temperatures were maintained until the CDM was complete, i.e., for 200 min. In addition, when the reaction time reached 100 min, the flow rate of methane would be changed from 13 cm³/min to 33 cm³/min, 25 cm³/min, and 20 cm³/min, corresponding to 640 °C, 660 °C, and 680 °C, respectively. After an additional 80 min, the methane flow rates would be reduced to 13 cm³/min and maintained at this level for 20 min.

Route III commenced from 600 °C, and temperature increase was similar to the pattern used in the step-wise heating model, under the same flow conditions. When the temperature was increased up to 640 °C, the methane flow was converted to a flow of Ar or H₂ at the rate of 13 cm³/min. Under Ar or H₂ flow, the temperature was increased to 720 °C at the rate of 10 °C/min and then maintained at this level until the reaction time reached 180 min. Then, the temperature was decreased from 720°C to 640 °C and the Ar (H₂) flow was changed to methane flow at the rate of 13 cm³/min. This temperature and methane flow were maintained for 300 min and 400 min, respectively.

In addition, when the catalyst was subjected to different thermal treatment processes, especially at high temperatures, the particle size changed as the result of aggregation. Moreover, the structure of the catalysts changed due to self-organizing which may regulate the size of particles to adapt to the reaction conditions ⁴²⁻⁴⁴. Therefore, for a more precise and detailed study of the catalyst deactivation and catalyst performance, the particle size and shape of the catalyst should be preserved during each experiment. In addition, it was clear that during the CDM over

Ni-Cu-SiO₂ catalysts, the carbon filament obeys the "tip-growth" model, and the metal particle is at the tip of the carbon filament ^{15, 32}. Because of this growth model, the carbon filament by-product can play as a the role of a living support and aid in the dispersion of the metal particles. Therefore, the catalyst particles can maintain their size and shape to a certain extent during the carbon filament growth even at high temperatures. Thus, if the initial methane conversion in the presence of a 65%Ni-10%Cu-25%SiO₂ catalyst at 600 °C can be controlled in the range of 22.5% –23.5%, the catalysts could be considered to have very similar size and shape in each experiment of using route X (X=I, II, III). Therefore, compared with traditional method of CDM reaction, the series of reaction routes can obtain more precise data from the test of catalytic performance.

The formation of gaseous reaction products was monitored using an on-line gas VARIAN CP-3800 chromatograph (GC) combined with a TDX-01 column, which was equipped with a thermal conductivity detector (TCD) for H_2 and CH_4 analysis. The concentrations of methane and hydrogen at the fixed bed outlet were determined, which were based on these calibrated data.



Fig. 1. Methane conversions using step-wise heating model

2.3. Catalyst characterization

Powder X-ray diffraction (XRD) patterns were recorded on an X-ray instrument (X' pert PRO) using CuK α (λ = 1.5406°A) radiation at 40 kV and 40 mA, in a continuous scan mode. The XRD patterns were recorded in the scan range of 2 θ = 10 ~ 90°, at a scan rate of 10 °/min. The mean crystallite sizes of the Ni-Cu particles were calculated from the Debye-Scherrer formula, where the particle shape factor was taken as 0.9⁴⁵.

The detailed structure of the deposited carbon was observed using a Tecnai G2 F20 S-Twin transmission electron microscope (TEM) operated at 200 kV. Samples for TEM analysis were prepared by drying the catalyst particles in ethanol on molybdenum grids. TEM-EDX (energy dispersive X-ray) observations was carried out for elemental analysis of the specimen surface.

Raman spectra were recorded on a Renishaw inVia confocal Raman microscope equipped with a 532 nm laser as the excitation source laser.

Thermal gravimetric analysis (TGA), differential thermal analysis (DTA), and differential scanning calorimetry (DSC) were used to characterize the thermal properties of carbonaceous materials such as graphite and CNTs. TGA and DTA experiments were performed between 25 °C and 900 °C with an SDT Q600 system, in air (80 cm³/min) at a heating rate of 20 °C/min. The mass of each sample was 5 mg.

3.Results and discussion

3.1. Catalytic performance



Fig. 2. Arrhenius plots for the investigated catalysts

Fig. 1 shows the methane conversion rates as a function of reaction time obtained in route I for a series of nearly equal masses of 65%Ni-10%Cu-25%SiO₂ catalysts at different reaction temperatures. Because the initial methane conversion rate was specified, the theoretical equilibrium methane conversion rates obtained during each CDM experiment in route I was consistent at the same temperature. It indirectly indicated that Ni–Cu particles in each experiment of route I had the same states and similar structures at the same reaction temperature.

For the 65%Ni-10%Cu-25%SiO₂ catalyst, due to the CDM is an endothermic reaction, an increase in reaction temperature greatly improved the methane conversion rate. However, within the temperature range of 600–780 °C, especially at 720 °C, the catalysts showed the highest activity during the step-wise heating process, and the methane conversion rate was increased by 65%. With the further increase in reaction

temperature, the methane conversion rates started to decrease. When the temperature was increased to 780 °C, the methane conversion rate was lower than 15%. The 65%Ni-10%Cu-25%SiO₂ catalyst exhibited similar properties as the unsupported Ni–Cu–Co ternary catalysts ³⁷. In addition, compared to the earlier reports on similar catalyst systems, the 65%Ni-10%Cu-25%SiO₂ catalyst exhibited higher H₂ formation rate at in the temperature range 600 °C-700 °C. The highest H₂ formation rate of the 65%Ni-10%Cu-25%SiO₂ catalyst reached to 34 mmol/(min g_{NiCu}), which far exceeded the H₂ formation rate of the Ni₇₈Cu₂₂-CNT catalysts (13.5 mmol/(min g_{NiCu}))¹⁵ and the Ni-Cu-catalysts (8 mmol/(min g_{NiCu}))²⁴.



Fig.3.TEM images of carbon deposits on Ni-Cu particles in route I at different temperatures: (a: 640 °C, b: 660 °C, c: 680 °C, d: 700 °C, e: 720 °C, f: 740 °C.)

3.2. Quasi-liquid state

In previous literature ^{35, 36}, researchers proposed that catalysts become unstable in a quasi-liquid state, and this state caused the catalysts to generate BLCNTs. Because of the growth of BLCNTs, the catalysts might undergo fragmentation. The fragmentation process could change the size of the particles, which was responsible for deactivation ¹⁵. Therefore, it is meaningful to determine a way to effectively obtain the phase transition temperature of the quasi-liquid state for Ni–Cu catalysts. To effectively obtain the phase transition temperature, the Arrhenius formula was taken into consideration and several temperatures (600–720 °C in route I) were selected. The Arrhenius plots (rCH₄) of the Ni–Cu alloy particles are represented in Fig. 2, where rCH₄ is the average methane conversion rate (mol/min) in the initial stage divided by the catalyst weight. In addition, the calculation method of Arrhenius plots references to the work of Wang et al and Reshetenko et al ^{46, 47}. It should be noted that when the temperature increased to higher than 680 °C, the slope of the Arrhenius curve started to decline. The decreased slope of the Arrhenius curve might imply that a few Ni–Cu particles started to enter the quasi-liquid state at a temperature of approximately 680 °C.



Fig. 4. XRD patterns of spent catalysts at different reaction temperatures in route I

(The crystal sizes of the Ni-Cu alloys were calculated from the peak due to the (2 0 0) plane at around 51°)

In order to validate this conjecture, the carbon structures deposited on the Ni–Cu particles were investigated by TEM. The micrographs of the carbon structures and Ni-Cu particles are shown in Fig. 3. In addition, the different states of Ni-Cu particles cause themselves generation of different carbon structures. For example, the Ni-Cu particle forms full CNTs and OLCNTs in crystalline state, but the Ni-Cu particle generates the BLCNTs in quasi-liquid state. Therefore, the state of Ni-Cu particle can be indirectly determined by detecting the carbon structure. Moreover, due to superior properties of those kinds of CNTs, the structure of them can be maintained after CDM reaction. A careful investigation of the carbon structures deposited on the 65%Ni-10%Cu-25%SiO₂ catalyst in route I at different temperatures, it revealed that BLCNTs were only observed at 700 °C, 720 °C, and 740 °C. However, at temperature below 700 °C, the Ni-Cu particles only formed full CNTs, hollow CNTs, and octopus-like carbon filaments (OLCNTs)⁴⁸. As noted above, the formation of BLCNTs could prove that the catalyst particles were in a quasi-liquid state, thus, a certain amount of Ni-Cu particles started to transform into the quasi-liquid state at approximately 680 °C.

As shown in Fig. 4, the size of the Ni–Cu particles decreased with the increase in temperature. When the reaction temperature was below 700 °C, the particle size was approximately 33 nm. However, the particle size of the Ni–Cu catalysts started to

decrease as the temperature increased and reached a minimum of 22.4 nm at 760 °C in route I. The phenomenon (Ni-Cu particle size decreased during the CDM reaction) was the so called fragmentation process, which often occurred when Ni-Cu alloy was in quasi-liquid state. Due to the Ni-Cu particle suffer fragmentation process, this result might also prove that Ni-Cu particles started to transform into the quasi-liquid state at approximately 680 °C. Therefore, those data combining the step-wise heating model with the Arrhenius equation could effectively be used to obtain the phase transition temperature with a reasonable degree of accuracy.



3.3. Effects of structural damage

Fig.5.TEM images of carbon deposits on Ni-Cu particles in route I at different temperatures after fragmentation: (a: 640 °C, b and C: 700 °C, d: 720 °C, e and f: 740 °C, g and h: 760 °C)

From the previously reported data, it is clear that the mechanism of deactivation of Ni-based catalysts is very complicated at high temperature, because of the change in the states of catalysts and the growth of the carbon structures ²³. However, in previous studies, the key factors that caused the deactivation of catalysts in the quasi-liquid state were found to be fragmentation and phase separation during the growth process ^{15, 31}. In addition, particle size, composition, and metal-supported interactions were responsible for Ni-Cu particles attaining a quasi-liquid state. According to some reports, when Ni-Cu particles attained a quasi-liquid state, BLCNTs started to generate and the Ni–Cu particles suffered periodical jumping ^{35, 49}. In this growth model, a particle in the quasi-liquid state was sucked into the hollow of the CNTs through a capillary force at the first stage ⁵⁰. Then, nucleation of bamboo-knot graphite sheets occurred at the graphene wall-catalyst junction ⁴⁹. Thus, the inner wall around the bottom of the Ni-Cu catalyst particles started to grow, and this process added to the growth of the inner wall edge through diffusion along the graphene sheet ⁵¹. When the surface tension of this particle became larger than the capillary force, the Ni-Cu particle jumped out of the hollow and BLCNTs was formed in these circles ²³. However, as Cu affects the affinity of the Ni-metal surface with graphite, the inner walls of the BLCNTs might become rough and form an irregular carbon layer, as shown in Fig. 5c and 5g. Moreover, the rough inner wall and high growth rate of the inner carbon layer could contribute to the generation of a tail, located at the bottom of a Ni–Cu particle during the BLCNT growth, as shown in Fig. 5d and 5f (red circle). During the periodical jumping of Ni–Cu alloy particles, the tails might be blocked in the interior of the BLCNT structure, and some fragmented Ni–Cu particles could be observed, as shown in Fig. 5b-5h. As the Ni–Cu particles suffered fragmentation during the growth of BLCNTs, the balance between the methane dissociation rate and the carbon diffusion rate was disturbed with the change in the size of the Ni–Cu particles. Smaller particles led to a higher methane dissociation rate and a lower carbon diffusion rate ⁵²; this would cause carbon enrichment on the surface of the Ni–Cu particle surface, resulting in deactivation. This phenomenon was one of the well-known factors for the deactivation of Ni–Cu–SiO₂ catalysts at high temperature.

Table 1.

Concentration of Ni and Cu over Ni-Cu-SiO2 catalyst at different temperatures, as de	etected by EDX.
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Number	Ni Content (%)	Cu Content (%)
1	84.4	15.6
2	83.6	16.4
3	32.2	67.8
4	74.8	25.2
5	86.5	13.5
6	51.8	48.2
7	56.8	43.2
8	66.6	33.4
9	81.8	18.2
10	1.6	98.4
11	83.1	16.9
12	70.3	29.7
13	73.4	26.6
14	76.8	23.2
15	70.7	29.2
16	8.5	91.5
17	87.7	12.3
18	62.6	37.4
19	48.2	51.8
20	54.3	45.7
21	26.7	73.3
22	32.7	67.3
23	74.6	25.4

To investigated in detailed the mechanism of fragmentation process and phase separation, TEM-EDX was used to evaluate the concentrations of Ni and Cu in the fragmented Ni-Cu alloy particles, as shown in Fig. 5. In addition, the concentrations are marked by red arrows numbered 1 to 23. The concentrations of Ni and Cu were also calculated by TEM imaging and an analysis software, and the results are shown in Table 1. As shown in Fig. 5a, when the Ni-Cu particles were in crystalline state, the Ni-Cu particles did not suffer fragmentation process and also did not have this phenomenon of phase separation. Though fragments of the catalyst were sucked into the same BLCNT, they had different Ni and Cu contents. This is called the phase separation phenomenon ^{15, 37}. Moreover, upon careful study the Ni content increased from the bottom of the BLCNT to the tip, while the Cu content decreased. By combining the details of the fragmentation process and the data shown in Table 1, the phase separation phenomenon can be described in detailed as follows: when the Ni-Cu particle suffered structural damage and generated a tail, a part of the head was enriched with Ni and the tail was enriched with Cu; Moreover, if the tail that was enriched with Cu was sucked into the interior of the BLCNT, the Ni content in the rest of the particle increased, as shown in Fig. 5d and 5f. In addition, a study ⁴⁶ proposed that Cu had negligible ability to crack methane and diffuse carbon atoms, which caused the selective diffusion of carbon atoms through the Ni particles. As a result, the rapid selective diffusion of carbon atoms might lead to fragmentation of the Ni-Cu particles. Based on this theory and the fact that the tail of the Ni-Cu particle has a higher Cu content and a lower Ni content, a Ni-Cu particle could undergo more serious structural damage through the selective diffusion of carbon atoms into the Ni-Cu structure.

Through above analysis, the rough inner wall of CNTs and a tail formed in Ni-Cu particles might be the key factors for fragmentation process of Ni–Cu–SiO₂ catalysts at high temperature. Moreover, the process of Cu content was enrichment in the tail not only made contribution to fragmentation process, but also caused the phase separation. Therefore, those factors acted on and influenced each other to cause the 65%Ni-10%Cu-25%SiO₂ catalyst to lose activity at high temperature.

3.4. Effect of excessive carbon formation



Fig. 6. Methane conversion in route II and route I at different temperatures

In addition to Ni-Cu structural damage, the excessive carbon generation is known to contribute significantly to the deactivation of the Ni-Cu catalysts ³⁸. The deactivation mechanism can be described like this: the high carbon production rate with the relatively low carbon diffusion rate causes the carbon enriched on the surface of particles, after that, the carbon atoms form carbon layers, which make the catalysts lose activity. In this work, the 65%Ni-10%Cu-25%SiO₂ catalyst showed superior methane conversion of about 65% at 720 °C; therefore, excessive methane dissociation could lead to the generation of a large amount of carbon atoms on the surface of the Ni-Cu particles, which might responsible for the notable loss of catalytic activity at high temperature.

To clearly investigate and validate whether the effect of excessive carbon generation play an important role in catalyst deactivation at high temperature, the maximum methane conversion at 720 °C in route I was taken as the reference to design the route II experiment. In this route, several temperatures (640 °C, 660 °C and 680 °C) were selected, and it was found that the 65%Ni-10%Cu-25%SiO₂ catalyst did not undergo fragmentation or phase separation. As shown in Fig. 6a, the carbon generation rate decreased with increasing reaction temperature for the reaction time of 100-200 min (zone 3). Although lower reaction temperatures caused the generation of more carbon atoms in route II, the methane conversion showed no notable decline after the methane flow rate was reverted to 13 cm³/min, as shown in Fig. 6b. For in-depth analysis of these data, the decreased methane conversion was used to evaluate the extent of activity reduction on the Ni-Cu particles (Table 2). As the temperature was increased from 640 °C to 680 °C in route II, the ratios of activity reduction increased from 0.5% to 13.0%.

Table 2.

samples	average methane	average methane	Ratios of activity
	conversion (Zone 1)	conversion (Zone 2)	reduction
	(X)	(Y)	((X-Y)/X)
Route II (640 °C)	34.5%	34.3%	0.5%
Route II (660 °C)	43.6%	42.3%	3.0%
Route II (680 °C)	54.5%	47.4%	13.0%
Route I (720 °C)	65.5%	53.2%	18.8%

Clearly, the maximum methane flow rate and carbon generation rate at the lower reaction temperature of 640 °C had almost no effect on the catalytic activity. This implies that the methane dissociation rate might not exceed the carbon diffusion and carbon deposition rates, or the enrichment of carbon atoms might not lead to complete coverage of the surface of the Ni-Cu particles. Because the structures of the Ni-Cu particles are stable at in the temperature range 640 °C-680 °C, only temperature would contribute to catalyst deactivation. Therefore, the deactivation mechanism of

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Ni-Cu particles at high temperature can't be explained by simple excessive carbon generation. However, the ratios of activity reduction increased with increasing of temperature, so it may need to take into account the other effect which bases on temperature. In addition, fragmentation process and phase separation might cause less than 5.8% of activity reduction of the 65%Ni-10%Cu-25%SiO₂ catalyst to lose their ability to cause cracking of methane in route I at 720 °C.

3.5. Effect of graphitization



Fig. 7. Raman spectra of carbon filaments obtained over 65%Ni-10%Cu-25%SiO₂ catalyst via route I.

From the above mentioned observations, it is clear that temperature plays an important role in the deactivation of the 65%Ni-10%Cu-25%SiO₂ catalyst by excessive carbon formation, and some other factors may make contribution to catalyst deactivation at high temperature. Some reports state ³⁰ that Cu addition to a Ni-based catalyst improved its desired resistance to carbon structure deposition by lowering the amount of coke formed. Moreover, since Cu affects the affinity of the Ni-metal surface toward graphite, it can inhibit the formation of a graphite layer on the nickel surface ²⁹. In addition, the graphite layer was very stable and could not be removed by reacting with hydrogen ⁵³. Since Cu inhibited the formation of the graphite layer, a large amount of disordered carbon was generated by the 65%Ni-10%Cu-25%SiO₂

catalyst in route I, as shown in Fig. 7. In addition, Two distinct peaks appear in the spectrum of each sample ⁵⁴, the G-band at 1582 cm⁻¹, assigned to the formed graphitized CNTs and the D-band at 1338 cm⁻¹, related to the existence of the disordered carbon such as amorphous carbon or defects in graphite layers ⁵⁵. The peak intensity ratio I_D/I_G ⁵⁵ is used as a direct measure for sample quality due to its relative response of graphite carbon to defective carbon. Therefore, from the date of Fig. 7, the Raman spectra showed that the disordered carbon content reduced with an increase in the temperature from 620 °C to 760 °C, as was evident from the change in the I_D/I_G ratio from 1.89 to 1.19, implying that the degree of graphitization is enhanced with increasing reaction temperature.

To clearly investigate the changes of the degree of graphitization, the TGA-DTA analysis had been taken consideration. Generally, the TGA-DTA analysis employed to study the graphitization degree, yield, thermal stability, and purity of accumulated CNTs over the current catalysts. In addition, the weight loss is attributed to the combustion of carbon in oxygen, and the oxidation temperature (inflection temperature) of the carbon structures can be used to analysis the graphitization degree ^{56, 57}. The TGA-DTA results in Fig. 8 revealed that the oxidation temperature of the carbon structures generated by the Ni-Cu particles in route I shifted to higher values with an increase in the CDM temperature. This indicates that high temperature enhanced the degree of graphitization.



Fig.8. TGA and DTA analysis of used 65%Ni-10%Cu-25%SiO₂ catalysts.

Previous studies showed that methane dissociation occurred at the active sites of the Ni-Cu (100 and 110) plane, while carbon deposition and carbon filament formation occurred on the precipitation planes (111)¹⁴. Because of the generation of excessive carbon atoms and the weak resistance of Cu to carbon structure deposition

at 720 °C in route I, some of carbon atoms might not diffuse to the precipitation planes and were enriched on the Ni-Cu (100 and 110) planes. High temperature enhanced the degree of graphitization; structural damage can cause a further increase in the degree of graphitization as phase separation can decrease the Cu content. Therefore, the carbon atoms could form graphite structures on the Ni-Cu (100 and 110) planes and cover the active sites. However, although the Ni-Cu particles generated a greater number of carbon atoms in route II at 640 °C than in route I at 720 °C and the carbon atoms might be enriched on the (100 and 110) planes, the low degree of graphitization might destabilize the carbon structure, so that the carbons were 58 removed by diffusion or reacting with hydrogen Therefore, the 65%Ni-10%Cu-25%SiO₂ catalyst could retain its activity even after excessive carbon formation for 100 min, as shown in Fig. 6.

Taking into account the fragmentation of the Ni-Cu particles and phase separation, the detailed deactivation mechanism of the 65%Ni-10%Cu-25%SiO₂ catalyst at high temperature could be explained as following. First, since the CDM is an endothermic reaction, high temperature contributes to excessive carbon formation, resulting in the formation of numerous carbon atoms on the surface of the Ni-Cu particles. Carbon atoms diffusion and methane atoms dissociation in copper are negligible, therefore they selectively diffuse into the Ni particles, causing fragmentation of the catalyst particles. Second, high temperature causes the Ni-Cu particles entering a quasi-liquid state, and Ni-Cu catalysts beginning to form BLCNTs. The growth of BLCNTs causes fragmentation and phase separation on Ni-Cu particles, both of which disturb the balance between methane dissociation and carbon diffusion. Hence, the carbon atoms are further enriched on the surface of the Ni-Cu particles. Third, high temperature and lower Cu content enhance the degree of graphitization, which promotes the formation of graphite layers from the enriched carbon atoms; these layers covered the active sites of the Ni-Cu particles. Therefore, the performance of the 65%Ni-10%Cu-25%SiO2 catalyst decreased markedly at high temperature during the CDM. By comparing these factors, although the structure damage and excessive carbon formation could make contribution to the activity reduction of Ni-Cu particles, this phenomenon of graphitization might be a key factor for the deactivation of Ni–Cu–SiO₂ catalysts at high temperature. Moreover, these factors interacted with one another and made a significant contribution to catalyst deactivation together.

3.6. Effect of carbon migration



Fig. 9. Methane conversions in route III under different conditions (temperature=720 °C in zone 4)

The 65%Ni-10%Cu-25%SiO₂ catalyst forms a large amount of disordered carbon structures, some of which might have migration ability ⁵⁹. Therefore, these carbon structures may act as sources of carbon and contribute to the catalyst deactivation at high temperature. In order to verify this conjecture, route III was taken into consideration. Fig. 9 shows the kinetic curves for the CDM over 65%Ni-10%Cu-25%SiO₂ catalyst at 640 °C. In this route, the carbon source was removed (not pass thought methane) to confirm that the CDM does not occur at a high temperature of 720 °C. Since the catalysts were located at the tip and the reaction condition was unchanged after re-passed though methane, the effect of self-organizing of the catalyst particles on the particle structure could be ignored. Hydrogen could react with carbon to form methane, the amount of methane formed was very small and hence may not contribute to the reduced activity of the 65%Ni-10%Cu-25%SiO₂ catalyst at high temperature under H_2 flow. From Fig. 9, when the catalysts were subjected to a high temperature of 720 °C under H₂ flow at 13 cm³/min for 120 min, the methane conversion increased from the lowest value of 34.5% to the highest value of 36.3%, which was closer to the initial methane conversion of 36.8%. This result confirms the above mentioned assumptions.

Under no matter what conditions, there existed a trend of covering catalytic activity process, which means that the methane conversion increased with reaction time after re-passed though methane. This might be attributed to the reaction between the generated hydrogen and the carbon atoms (not graphite carbon) covering the active sites. Due to hydrogen may inhibit the carbon atoms migration and prevent the formation of encapsulating coke ^{60, 61}, a few of carbon atoms migrated to the surfaces of catalysts. Therefore, 65%Ni-10%Cu-25%SiO₂ catalyst spent a short time on recovering activity. In contrast, argon does not react with the carbon atoms, and hence,

high temperatures allowed more carbon atoms to migrate to the surfaces of the Ni-Cu catalysts; therefore, the catalyst takes a long time to recover its activity. However, under Ar flow at 13 cm³/min for 120 min, in route III, the methane conversion increased from the lowest value of 15.6% to the highest value of 32.9%, which was much lower than the initial methane conversion of 35.8%. This result might be attributed to the formation of graphite layers from the carbon atoms migrated to the surface of the Ni-Cu particles.

4.Conclusions

A series of kinetic experiments (routes I, II, III) were designed to test the catalytic performance of Ni-Cu catalysts and to analyze the by-products, carbon structures. The effects of reaction temperature and methane dissociation rate on catalyst deactivation were studied. Based on such data as kinetic experiments, Arrhenius curve, XRD data, TEM images and so on, some results were obtained about the deactivation mechanism of 65%Ni-10%Cu-25%SiO₂ catalyst deactivation. First, it was found that the Ni-Cu particles were in the quasi-liquid state around 680 °C in route I, and when the Ni-Cu particles were in the quasi-liquid state, catalytic activity decreased remarkably with increasing temperature. Second, the detailed mechanism of fragmentation process and phase separation had been elaborated, moreover, a tail formed in Ni-Cu particles and enriched copper content might be the key factor for fragmentation process and phase separation. Third, although fragmentation process, phase separation, and graphitization together make a significant contribution to catalyst deactivation at high temperature, the high degree of graphitization might play the most important role in the deactivation of Ni-Cu catalysts at high temperature. In addition, because there existed a trend of covering catalytic activity process during route III, it was conjectured that some of these carbon structures might migrate to the surface of the Ni-Cu particles.

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The activities of 65%Ni-10%Cu-SiO₂ catalysts under different reaction temperatures using route I and route II