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Effect of Calcined Temperature on Coke Deposition for Autothermal Reforming of Methane with Ni-Cu Catalyst

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Ni-Cu/ZrO$_2$-CeO$_2$-Al$_2$O$_3$ catalysts were prepared by co-precipitation method at pH=9 and using Na$_2$CO$_3$ as the precipitant. The Ni loading (mass fraction) of the catalysts was 10%. The catalysts were characterized by X-ray diffraction, temperature-programmed oxidation (TPO), scanning electron microscope (SEM), and X-ray photoelectron spectroscopy (XPS). The effects of calcined temperature of support on coke deposition were studied. TPO, SEM and XPS results indicated there was no peak of higher temperature oxygen consumption on Ni-Cu/ZrO$_2$-CeO$_2$-Al$_2$O$_3$ catalyst (support was calcined at 800 °C), which could lead to the deactivation of the catalyst. The carbon species were carbonate and inactive carbon (filamentous carbon species) on the surface of catalyst reacting for 40 h which perhaps led to the deactivation of the catalyst.

Key words: Methane, Autothermal reforming, Hydrogen, Coke deposition

I. INTRODUCTION

In recent years, autothermal reforming of methane is regarded as an important way to converse methane to hydrogen [1–11]. In autothermal reforming of methane, exothermic partial oxidation of methane reaction and endothermic steam reforming of methane reaction are coupled to provide heat itself. Therefore, the reaction temperature can be reduced and different products can be obtained by controlling the reaction pathway and relative reaction speed of partial oxidation and steam reforming of methane.

Most of catalysts for autothermal reforming of methane are supported catalysts and the active components comprised of noble metal (Pt, Pd, Rh *etc.*) [4–9] and non-noble metal (Ni, Co *etc.*) [1–3]. In autothermal reforming of methane for hydrogen, the stability of catalyst is very important because of the existence of large amounts of water. The noble metal catalysts have drawn a lot of attention due to the advantages of high activity, high selectivity, high stability and resistance to carbon deposition *etc.* [4–9]. Compared to noble catalysts, non-noble metal catalysts, such as Ni/Al$_2$O$_3$-based catalysts have a good application perspective because they are more economical than precious metals and have higher activity in higher reaction temperature. But Ni/Al$_2$O$_3$-based catalysts are more sensitive

to coke formation in the course of reaction, which lead to the deactivation of the catalyst [11, 12].

Although the reaction conditions of coke deposition can be obtained through the thermodynamic equilibrium calculation, but in the actual reaction, the behavior of coke deposition is very complex, so in-depth study of coke deposition behavior is very important.

The problem of coke deposition in steam reforming of methane has been studied. Usually adding promoters to the catalyst or modifying the supports of the catalyst are used to improve the resistance of coke deposition. Rare earth oxides as promoters can change the crystal structure, modify the surface of the supports, inhibit the generation of inactive species of NiAl$_2$O$_4$, increase the dispersion of NiO and inhibit coke deposition of catalyst [11, 12]. Therefore, the addition of rare earth oxides can greatly improve the activity, thermal stability and resistance to coke deposition of the catalyst. It is indicated that the addition of alkali metal or alkaline earth metal could decrease the particle size and the binding energy of Ni, which is conducive to enhance the resistance of coke deposition [13, 14].

CeO$_2$ has the ability to store and release oxygen respectively in oxidizing and reducing conditions and it can stabilize the support Al$_2$O$_3$. The addition of CeO$_2$ can prevent the sintering of Ni based catalyst, enhance the activity of catalyst, reduce the coke deposition of catalyst and improve the stability of the catalyst [11]. The effects of CeO$_2$ on the catalyst are considered to be caused by the existence of metal-semiconductor interaction between CeO$_2$ and active site Ni. In the metal-semiconductor interaction, CeO$_2$ is partially reduced to

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oxygen vacancy with rich electron at high temperature, therefore, the oxygen vacancy is easy to release free electrons, and free electrons can transfer from CeO_2 to active site Ni^0 through the interface of Ni/CeO_2, resulting in the high electron of Ni atom. This interaction can inhibit the adsorption of CH_4 and C_2H_6 and reduce the coke deposition. ZrO_2 and alkaline earth metal (or rare earth oxides) solid solution supported Ni catalyst prepared by Atsuya was used for autothermal reforming of methane to hydrogen [12]. It was found that the Ni/CaO-ZrO_2 catalyst has higher activity because the combination of CaO and ZrO_2 is helpful for the reduction of NiO and can reduce the formation of carbon. On the Ni/CaO-CeO_2-ZrO_2 catalyst, there is a strong interaction between Ni particles and CaO-CeO_2-ZrO_2 solid solution, which can lead to the higher activity and stability in the reaction of autothermal reforming for hydrogen [12].

We had studied the effect of rare earth and transition metals (such as La, Ce, Zr, Fe, Co and Cu) on the catalytic performance of Ni/Al_2O_3 for autothermal reforming of methane (ATRM) to hydrogen and catalyst Ni-Cu/ZrO_2-CeO_2-Al_2O_3 ($m_{Al}:m_{Ce}:m_{Cu}:m_{Zr}$=65:20:10:5) showed good activity at low temperature [15, 16]. It was found that, in the reaction temperature of 650−850 °C of ATRM, calcination temperature of supports had great influence on the structure and properties of the catalyst [15, 16]. Therefore, in this work, the effects of calcination temperature of supports (600, 700, 800, and 900 °C, respectively) on the coke deposition behavior of Ni-Cu/ZrO_2-CeO_2-Al_2O_3 catalyst in autothermal reforming of methane to hydrogen were investigated and the properties of the catalysts were characterized by temperature-programmed oxidation (TPO), SEM, X-ray photoelectron spectroscopy (XPS). It was of great theoretical and practical significance on the aspects of understanding coke deposition behavior, eliminating the coke deposition and restoring the activity of the catalyst.

II. EXPERIMENTS

A. Preparation of support and catalyst

The support CuO-ZrO_2-CeO_2-Al_2O_3 were prepared by means of co-precipitation during the reaction of 1 mol/L Na_2CO_3 solution under vigorous stirring upon the aqueous solution of $Al(NO_3)_3 \cdot 9H_2O$, $ZrO(NO_3)_2$, $Ce(NO_3)_3$, and $Cu(NO_3)_2$, respectively. Both solution were simultaneously added at a constant rate of 50 mL/h. The addition of the precipitating agent (Na_2CO_3) was monitored using a stationary pH-meter, in order to maintain the pH value of the solution at 9.0 during precipitation. The temperature was kept at 80 °C. The precipitate obtained thereby was subjected to aging for 2 h with the mother liquor under vigorous stirring at the reaction temperature. Then the precipitate was filtered out, washed with deionized water, dried

at 120 °C for 12 h, and further calcined in air at 800 °C for 4 h. After this treatment, the support was ready for further experiments.

The Ni-Cu/ZrO_2-CeO_2-Al_2O_3 catalysts (with 10wt% of Ni loading apiece) were prepared via wet impregnation of the support CuO-ZrO_2-CeO_2-Al_2O_3 by $Ni(NO_3)_2$ solution at room temperature for 12 h. The resulting materials were dried at 120 °C for 10 h and subsequently calcined in air at 650 °C for 6 h.

B. Test of catalytic performance

ATRM reaction was carried out in a continuous flow fixed bed reactor at different temperatures (from 650 °C to 850 °C) under atmospheric pressure. The reactor temperature was measured by a K-type thermocouple with a thermowell placed in the center of the catalyst bed. Two sets of mass flow meters (D07, China) were used to control the flow rates of reactants (*i.e.*, CH_4, O_2). Deionized water was fed by a liquid micro-pump (SY-02A, China) and then, through a water evaporator. 1 mL of catalyst charge was used in a typical experiment and the particle size of catalyst was in the range of 20−40 mesh. Before catalytic reaction, the catalyst was reduced by a gas mixture consisting of 20%H_2 and 80%N_2 at 800 °C for 2 h. A gas mixture of CH_4, O_2 and H_2O with a molar ratio of 1:0.5:2.5 was introduced with a gas hourly space velocity of 4800 h^{-1}. The water in the tail gas was separated by a cold trap, and the product including H_2, CH_4, CO, and CO_2 was analyzed by one set of gas chromatograph equipped with a TDX-01 column and a thermal conductivity detector (TCD). The conversion of CH_4 where $n_{(CH_4)in}$ and $n_{(CH_4)out}$ are C_{CH_4} is as follows:

$$C_{CH_4} = \frac{n_{(CH_4)in} - n_{(CH_4)out}}{n_{(CH_4)in}} \times 100\% \qquad (1)$$

C. Characterization

XPS analysis was carried out on a VG MuiltiLab 2000 photoelectron spectrometer at room temperature under a vacuum of 10^{-8}−10^{-9} Torr, using Mg Kα radiation powered at 10 keV and 20 mA. The binding energies (BE) of $Ni2p_{3/2}$ were calibrated to the carbon with a C1s band at 284.6 eV.

In TPO experiment, 50 mg catalyst sample was loaded into a U-type quartz microreactor and the oxidation of the sample was carried out from 30 °C to 900 °C in a flow of 10%O_2-90%He (30 mL/min) at a heating rate of 15 °C/min. The consumption of O_2 was monitored continuously by a gas chromatograph equipped with TCD.

SEM was carried on LEO-1530VP, and samples were prepared on an aluminum slice, dried in a vacuum oven, and sputter-coated with gold.

Surface area of Ni-Cu/ZrO_2-CeO_2-Al_2O_3 catalysts was measured by N_2 adsorption-desorption at liquid nitrogen temperature using Quantachrome NOVA apparatus equipped with a thermal conductivity detector. Before nitrogen adsorption, samples were pre-treated at 423 K for 12 h. N_2 adsorption was carried out at liquid nitrogen temperature of 77 K.

III. RESULTS AND DISCUSSION

A. Effect of calcined temperature on performance of Ni-Cu/ZrO_2-CeO_2-Al_2O_3 catalyst

In order to investigate the effect of calcined temperature on the performance of catalyst Ni-Cu/ZrO_2-CeO_2-Al_2O_3 (in the catalyst m_{Al}:m_{Ce}:m_{Cu}:m_{Zr}=65:20:10:5), catalysts cat-6, cat-7, cat-8, and cat-9 were prepared (calcined temperature of the supports were 600, 700, 800, and 900 °C respectively).

The effects of calcined temperature on the performance of Ni-Cu/ZrO_2-CeO_2-Al_2O_3 catalysts for CH_4 conversion and H_2/CO are shown in Fig.1. As a shown in Fig.1(a), with the increasing of the reaction temperature from 650 °C to 850 °C, CH_4 conversion of all the catalysts increased. At the same reaction temperature, CH_4 conversion increased at first and then decreased with the increasing of calcined temperature of the supports. Therefore, calcined temperature of the supports had great influence on the catalytic activity and there existed an optimum calcined temperature for support. In this group of catalysts, 800 °C was the best calcined temperature for CH_4 conversion with Ni-Cu/ZrO_2-CeO_2-Al_2O_3 catalyst.

As shown in Fig.1(b), with the increasing of the reaction temperature from 650 °C to 850 °C, molar ratio of H_2/CO showed a decreasing trend. At the same reaction temperature and with the increasing of calcined temperature of support, molar ratio of H_2/CO showed the same trend as the conversion of methane, also increased at first and then decreased.

B. Effect of calcined temperature on the structure of Ni-Cu/ZrO_2-CeO_2-Al_2O_3

XRD profiles of cat-6, cat-7, cat-8 and cat-9 catalysts are shown in Fig.2. The results indicated that XRD profile of all the catalysts presented the same diffraction peaks. The peaks at 37.4° and 45.5° can be identified with $NiAl_2O_4$ species and that at 66.7° as Al_2O_3 species. The visible diffraction peaks of CeO_2 shifted to higher 2θ values compare to the indices of (111), (200), (220) and (311) phases of CeO_2, respectively. This could be attributed to the shrinkage of the corresponding lattice due to the replacement of Ce^{4+} by Zr^{4+} with smaller cation radius. ZrO_2 can incorporate into the CeO_2 lattice to form a solid solution CeO_2-ZrO_2. Only the cubic phases of CeO_2-ZrO_2 solid solution are detected in Fig.2, indicating that Ce and
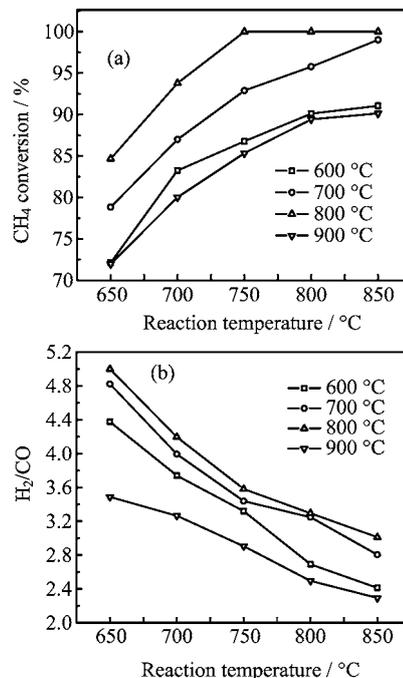
FIG. 1 Effect of calcined temperature on performance of Ni-Cu/ZrO_2-CeO_2-Al_2O_3 catalyst. (a) CH_4 conversion, (b) molar ratio of H_2/CO.
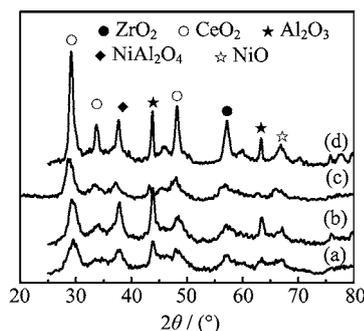
FIG. 2 XRD profiles of Ni-Cu/ZrO_2-CeO_2-Al_2O_3 catalysts. (a) Cat-6, (b) cat-7, (c) cat-8, (d) cat-9.

Zr are highly homogeneously distributed. In the XRD profile of cat-6, there is a weak peak of ZrO_2, which indicated that ZrO_2 can not get into CeO_2 lattice to form CeO_2-ZrO_2 solid solution calcined at lower temperature. With the increasing of calcined temperature, all the diffraction peaks of catalyst become sharper and more intensive which indicated that the size of the corresponding crystalline particles was increased. This may be due to the sinter of the supports. The diffraction peaks of NiO calcined at 800 °C become weaker and broader, indicating that the size of the particles of NiO is decreased and well dispersed. This may be due to the formation of solid solution CeO_2-ZrO_2. The solid solution CeO_2-ZrO_2 is a basic support with very good oxygen storage capacity and it can inhibit the formation of $NiAl_2O_4$, therefore makes the nickel species exist in
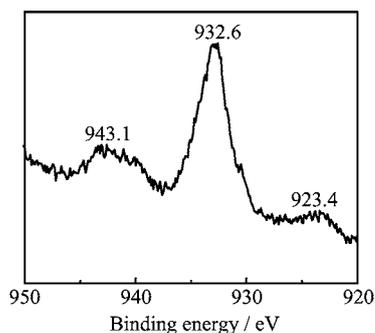
FIG. 3 XPS profiles of Ni-Cu/ZrO$_2$-CeO$_2$-Al$_2$O$_3$ (Cu2p).

FIG. 4 TPO spectra of Ni-Cu/ZrO$_2$-CeO$_2$-Al$_2$O$_3$ catalyst at different calcined temperature after reaction for 40 h.

the form of NiO [2]. There was no diffraction peak of CuO in the above catalysts, probably because CuO was highly dispersed on the surface of catalyst or got into the lattice of solid solution.

The Ni-Cu/ZrO$_2$-CeO$_2$-Al$_2$O$_3$ catalyst was characterized by XPS and the sample was used before reduction. Figure 3 shows XPS profiles of Ni-Cu/ZrO$_2$-CeO$_2$-Al$_2$O$_3$ (Cu2p). The result indicated that the binding energy peak of Cu2p was 932.6 eV in Ni-Cu/ZrO$_2$-CeO$_2$-Al$_2$O$_3$ catalyst, which was equal to the standard binding energy of Cu$_2$O. On the higher binding energy side of the main peak, there was a vibration excitation peak at 943.1 eV, which was the characteristic peak of Cu^{2+}. According to the literature [17–20], Cu2p BEs at 933−934.2 eV, in combination with the appearance of shake-up peaks, are typical characteristics of CuO. On the other hand, Cu2p BE at 932−933 eV are characteristics of more reduced copper species, primarily Cu$_2$O. The intensity ratio of the main peak at 932.6 eV to the vibration excitation peak at 943.1 eV reflected the change of chemical state of Cu species. Therefore, it could be argued, that the Cu species were in a more reduced state Cu$_2$O in bimetallic catalysts, which may be due to the existence of Ce^{4+}/Ce^{3+}.

The surface area of Ni-Cu/ZrO$_2$-CeO$_2$-Al$_2$O$_3$ catalysts calcined at different temperature of 600, 700, 800, 900 °C are 96.300, 88.926, 82.386, 79.649 m^2/g, which indicated that with the increasing of calcined temperature, the surface area of Ni-Cu/ZrO$_2$-CeO$_2$-Al$_2$O$_3$ catalysts decreased.

C. Effect of calcined temperature on coke deposition of Ni-Cu/ZrO$_2$-CeO$_2$-Al$_2$O$_3$

The calcined temperature of support can obviously affect the coke deposition on the Ni-Cu/ZrO$_2$-CeO$_2$-Al$_2$O$_3$ catalyst. Figure 4 shows the TPO spectra of Ni-Cu/ZrO$_2$-CeO$_2$-Al$_2$O$_3$ catalyst calcined at different temperature after reaction for 40 h.

For all samples, three oxygen consumption peaks of 200, 300, and 780 °C could be detected and they could be expressed as peak α, β, and γ. With the increasing of calcined temperature, the peaks of oxygen consump-

tion shifted to higher temperature and the consumption of oxygen increased gradually at lower temperature (peak α and β). When the calcined temperature reached 800 °C, the peak γ disappeared. It indicated that calcined temperature of support had great influence on coke deposition. The autothermal reforming of methane was carried out at 650−850 °C, therefore, the peaks of oxygen consumption may not exist stably for a long time, thus, the accumulation of coke on the catalyst could be avoided in the reaction conditions. The TPO spectra of cat-6, cat-7 and cat-9 presented the peaks of oxygen consumption at higher temperature (peak γ) could not be eliminated easily in the course of reaction, thus, leading to the deactivation of the catalyst. When the calcined temperature of the support was 800 °C, peak γ did not exist. Therefore, the deactivation of catalyst caused by coke deposition at higher temperature could be avoided.
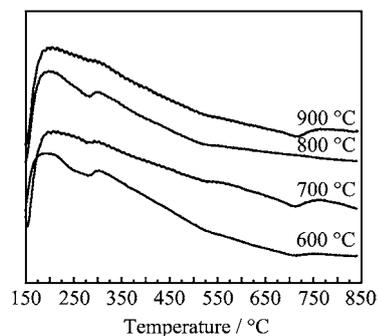
Zhang *et al.* have reported there were three coke species in Ni/Al$_2$O$_3$ catalyst and they were peak C$_\alpha$ (150−220 °C), C$_\beta$ (530−600 °C) and C$_\gamma$ (>650 °C) [21]. Peak C$_\alpha$ is active carbon species, which can not lead to the deactivation of catalyst. At lower temperature (<530 °C), peak C$_\beta$ can poison the surface of the catalyst. With increasing of the reaction temperature to higher than 660 °C, the carbon species of peak C$_\beta$ may participate in the generation reaction of CO. C$_\gamma$ is one of the key factors leading to the deactivation of catalyst. The reported results are consistent with the above results we have analyzed.

Figure 5 shows scaning electron microscope (SEM) results of Ni-Cu/ZrO$_2$-CeO$_2$-Al$_2$O$_3$ catalysts (calcined at different temperature) reacted for 40 h. Figure 5 indicated there was no obviously coke deposition on the surface of cat-6 after reaction for 40 h, while Ni species was easy to grow up and agglomerate, which led to the coke deposition to a certain extent. With the increasing of calcined temperature from 700 °C to 800 °C, Ni grain on the surface of the catalyst was fine and well dispersed, and agglomeration phenomenon almost did not happen after reacting for 40 h. When the calcined temperature increased to 900 °C, there was filamentous
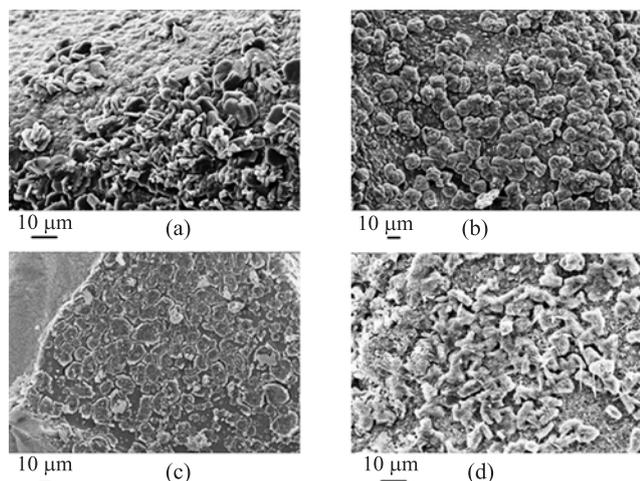
FIG. 5 SEM spectra of Ni-Cu/ZrO$_2$-CeO$_2$-Al$_2$O$_3$ catalyst reacted for 40 h at different temperature of (a) 600 °C, (b) 700 °C, (c) 800 °C, and (d) 900 °C.

FIG. 6 SEM spectra of NiO-CuO/ZrO$_2$-CeO$_2$-Al$_2$O$_3$ catalyst calcined at 800 °C. (a) Fresh, (b) 40 h, and (c) deactivation.

carbon on the surface of cat-9 after reacting for 40 h. Tesner *et al.* found that the coke deposition comprised of filamentous carbon and graphite carbon. Filamentous carbon was associated with metal Ni on the surface of the catalyst and in the growing course of filamentous carbon, metal Ni was always pulled out at the top of the filamentous carbon [22]. Baker *et al.* found that when the reaction temperature was more than 873 K, a part of the metal Ni could get into the tube formed by filamentous carbon and led to the deactivation of catalyst [23].

D. Effect of reaction time on coke deposition of Ni-Cu/ZrO$_2$-CeO$_2$-Al$_2$O$_3$ catalyst calcined at 800 °C

The above results indicated that Ni-Cu/ZrO$_2$-CeO$_2$-Al$_2$O$_3$ catalyst calcined at 800 °C had good resistance for coke deposition. Therefore, SEM and XPS were used to study the effect of reaction time on coke deposition and dispersion of Ni on Ni-Cu/ZrO$_2$-CeO$_2$-Al$_2$O$_3$ catalyst calcined at 800 °C.

SEM was carried out on Ni-Cu/ZrO$_2$-CeO$_2$-Al$_2$O$_3$ catalyst reacted for different time and deactivation respectively. The results are shown in Fig.6.

Figure 6 indicates that the fresh catalyst showed good dispersion of NiO and metal Ni species still kept a good dispersion after reacting for 40 h. When the catalyst lose activity, there was a great deal of filamentous carbon on the surface of the catalyst. Most of researches indicated that filamentous carbon which was connected with Ni could lead to the deactivation of the catalyst. [24].

In order to study the essence of coke deposition on NiO-CuO/ZrO$_2$-CeO$_2$-Al$_2$O$_3$ catalyst, XPS was used to study the difference between all kinds of carbon species. NiO-CuO/ZrO$_2$-CeO$_2$-Al$_2$O$_3$ catalyst calcined at 800 °C presented better stability, therefore, Fig.7
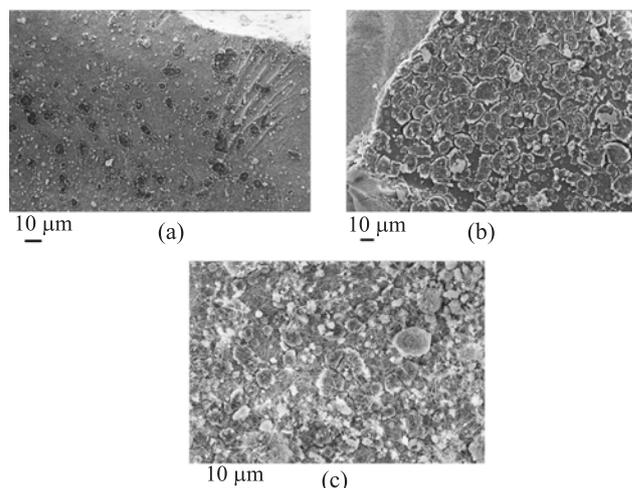
shows C1s bonding energy for Ni-Cu/ZrO$_2$-CeO$_2$-Al$_2$O$_3$ catalyst (calcined at 800 °C) after reacting for 4 and 40 h.

Figure 7 indicated the binding energy of C1s were 289.12 and 284.72 eV on Ni-Cu/ZrO$_2$-CeO$_2$-Al$_2$O$_3$ catalyst after reacting for 4 h, there were two kinds of carbon species on the surface of the catalyst. C1s bonding energy of carbonate on the surface of catalyst was 289.12 eV and C1s bonding energy of carbon polluted and metal carbides was 284.72 eV [25]. Metal carbides is one of the carbon species from the dissociation of Ni$_x$C (Ni$_x$C, x=1−3), which is a kind of active intermediate species. There are three types of active centers on the Ni-Cu/ZrO$_2$-CeO$_2$-Al$_2$O$_3$ catalyst, which are Ni metal site, Lewis acid site and basic site respectively. Carbonate species is the intermediate species when CO is adsorbed on the basic sites of catalyst. Metal carbides are formed in the course of dissociation of methane, which is necessary for autothermal reforming of methane and can not cause the deactivation of catalyst. Compared with Ni-Cu/ZrO$_2$-CeO$_2$-Al$_2$O$_3$ catalyst after reacting for 4 h, the peak area of carbonate species increased on the catalyst after reacting for 40 h. In addition, the peak at 284.72 eV became asymmetric and there was a shoulder peak at 282.4 eV, which was signed as the inactive carbon and this inactive carbon could lead to the deactivation of the catalyst.

The above results shown in Figs.3−7 indicated there was oxygen consumption peak at lower temperature on the surface of fresh Ni-Cu/ZrO$_2$-CeO$_2$-Al$_2$O$_3$ catalyst, which belonged to the intermediate species in the reaction, named as metal carbides. With the increasing of reaction time, the activity of Ni-Cu/ZrO$_2$-CeO$_2$-Al$_2$O$_3$ catalyst decreased and there was filamentous carbon on the surface of the catalyst, which belonged to the inactive carbon. The addition of Cu can form the alloy
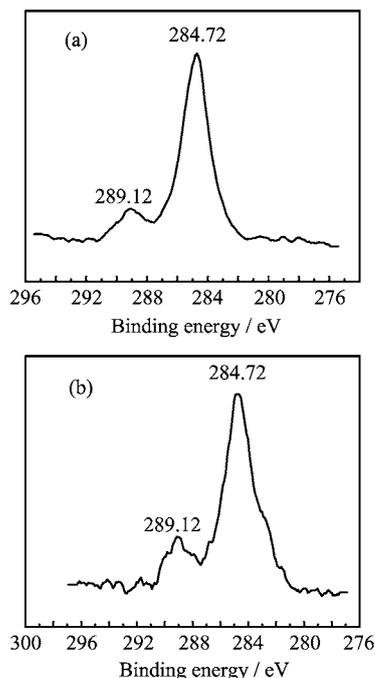
FIG. 7 C1s bonding energy for Ni-Cu/ZrO$_2$-CeO$_2$-Al$_2$O$_3$ catalyst calcined at 800 °C after reacting for (a) 4 h and (b) 40 h.

Ni-Cu, thus, hindering the loss of Ni species, but weakening the oxygen transfer on the surface of catalyst, leading to generation of filamentous carbon species from the decomposition of methane and resulting in carbon deposition.

IV. CONCLUSION

The effects of calcined temperature of support on catalytic performance of Ni-Cu/ZrO$_2$-CeO$_2$-Al$_2$O$_3$ catalyst were studied. It was found that the catalyst calcined at 800 °C showed the best activity. XRD results indicated that NiO was highly dispersed on the surface of the catalyst. The effects of calcined temperature on coke deposition of Ni-Cu/ZrO$_2$-CeO$_2$-Al$_2$O$_3$ catalyst were investigated. The results of TPO and SEM indicated there was no oxygen consumption peak at high temperature which could lead to the deactivation of the catalyst. When the catalyst reacted for 40 h, there was no agglomeration of Ni species. But when the catalyst was deactivated, there was a lot of filamentous carbon on the surface of the catalyst. XPS indicated the carbon species on Ni-Cu/ZrO$_2$-CeO$_2$-Al$_2$O$_3$ catalyst belonged to metal carbides. With the increasing of reaction time, the peak area of carbonate species increased and there was no active carbon which could lead to the deactivation of the catalyst.

V. ACKNOWLEDGMENTS

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