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Carbon dioxide reforming of methane reaction catalyzed by stable nickel copper catalysts

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Abstract

A long-term stable Cu/Ni/SiO_2 catalyst for carbon dioxide reforming of methane to produce synthesis gas at 800 °C was developed. The stability of the Cu/Ni catalysts depends on the reaction temperature and Cu/Ni ratio. Temperature programmed oxidation and temperature programmed reaction with CO_2 were applied to Ni and Cu/Ni catalysts to study the effect of Cu on Ni catalyst. The stability can not be fully explained by the ensemble effect of the Cu on Ni metal that may inhibit the carbon formation rate on Ni catalyst. Copper may stabilize the structure of the active site on Ni surface for methane cracking reaction, preventing the deactivation of the Ni catalyst caused by sintering or by loss of nickel crystallites. The addition of Cu into Ni catalyst system can fine-tune the catalytic activity so that the CH_4 cracking and removal of coke by CO_2 is balanced and prevent inactive coke accumulation on Ni particle. Thus encapsulated carbon layer does not formed on supported Cu/Ni giving the catalyst a stable activity.

Keywords: Copper; Nickel; Catalyst; CO_2; CH_4; Reforming

1. Introduction

The reaction of carbon dioxide reforming of methane to produce synthesis gas has attracted interest from both environmental and industrial perspectives. The environmental viewpoint stem from the fact that both CO_2 and CH_4 are viewed as harmful greenhouse gases. CO_2 reforming of CH_4 convert the two greenhouse gases into a valuable feedstock: CO and H_2. CH_4 and CO_2 are relatively inexpensive due to their rich natural abundance. CO_2 reforming of CH_4, therefore, provides potential incentives with economical and industrial benefits.

Most of the group VIII metals have promising catalytic performance for CO_2 reforming of methane reaction. A near thermal equilibrium conversion of CO_2 and over 90% selectivity to produce synthesis gas has been achieved when CO_2/CH_4 reforming reaction was catalyzed by Ni-based catalysts or supported noble metal catalysts [1]. It is practical to develop Ni-based catalysts for CO_2 reforming reaction from the view point of cost and availability. However, according to thermodynamic studies, carbon deposition via CO disproportionation reaction and methane cracking under reaction conditions of CO_2 reforming process (600–850 °C) was unavoidable on metallic catalysts, in particular for Ni [2,3]. The carbon formation rate on Ni catalysts was the highest among all group VIII metal catalysts. This carbonaceous deactivation problem inhibited the industrial application of Ni catalysts for CO_2 reforming of methane process. A lot of efforts therefore went into the development of an improved nickel based catalyst with stable long term high activity. Sulphur passivation of Ni catalyst decreases carbon formation rate more rapidly than reforming rate on Ni catalysts and thereby reducing the coking rate on Ni surface during the steam reforming methane reaction [4]. Zhang et al. showed that an appropriately activated Ni/La_2O_3 catalyst exhibited stable high CO_2/CH_4 reformation activity [5]. Tomishige et al. established carbon free operation of CO_2 reforming of methane at 850 °C with nickel-magnesia solid

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solution catalyst [6]. Here, we report results obtained on Cu/Ni/SiO_2 bimetallic catalysts which can be prepared by a simple impregnation method with low cost materials. Cu/Ni/SiO_2 have excellent catalytic performance and long-term stability for CO_2 reforming of methane reaction.

The special chemical, physical, and catalytic properties of Ni/Cu catalysts have been described extensively in the literature [7]. The activity of Cu/Ni catalysts for many reactions, such as ethylene hydrogenation reaction, had been reported to be much higher than that of the pure Ni catalyst [8]. However, little attention had been focused on the behavior of Cu/Ni catalysts for CO_2 reforming of methane reaction. Fischer and Tropsch had first studied the activity of Cu/Ni catalyst for CO_2 reforming of methane reaction [9]. They did not discuss the anti-deactivation effect of Cu on Ni catalyst. Pontic et al. studied the Cu/Ni catalysts for methanation reaction [10]. Although they did not discuss the CO_2 reforming reaction catalyzed by Cu/Ni catalysts, their results may be helpful for the understanding of the behavior of Cu/Ni catalysts for CO_2 reformation reaction.

We found that the inhibition of carbon formation can not be solely responsible for the stability of Cu/Ni catalysts. The stabilization of the Ni structure by the addition of Cu, the fine tuning of the relative rate of methane decomposition reaction and the dissociation rate of CO_2, the pathway of carbon formation, and the reactivity of the surface carbon on Cu/Ni surfaces, all play important roles on the anti-deactivation behavior of supported Cu/Ni catalysts for CO_2 reforming of methane reaction.

2. Experimental

The catalysts were prepared by impregnating the SiO_2 support (Cab-O-Sil M-5, 200 m^2/g) with aqueous solution of $Ni(NO_3)_2 2.5H_2O$ and $Cu(NO_3)_2 2.5H_2O$. The CO_2 reforming reaction was carried out in a conventional quartz fixed bed reactor under atmospheric pressure. A thermocouple was placed on the top of the catalyst to measure the catalyst temperature. The furnace temperature was controlled by a Eurotherm 818p temperature controller. 0.01–0.05 g of catalysts were loaded into a 1.0 cm inner diameter quartz tube reactor and pretreated in situ in flowing oxygen (30 cm^3/min) at 800 °C for 2 h, purged with Heat 800 °C for 30 min and reduced in flowing hydrogen (30 cm^3/min) at 500 °C for 12 h. The temperature was ramped from room temperature to the desired temperature at a rate of 10 °C/min. The XRD data shows that the freshly reduced catalysts consist of metallic Ni, Cu and Ni–Cu alloy crystalline. The reactants feed stream (CH_4/CO_2/He = 1:1:8, 100 cm^3/min) passed over catalysts for 10 min before the first products were taken for analysis. A Shimadzu GC-8A gas chromatograph equipped with a thermal conductivity detector (TCD) was used to analyze the products with an 18 ft 60/80 mesh Silica gel column. Product gas concentrations were determined by comparing the peak areas to those for a standard mixture. Product gas concentrations were determined by comparing the peak areas to those for a standard mixture. Minor amount of water was detected. Hydrogen production was not analyzed due to the poor hydrogen sensitivity of TCD under the He carrier gas environment.

The temperature programmed oxidation (TPO) and temperature programmed reaction (TPR) experiments were carried out in the same fixed bed reactor as the system used for catalytic activity measurement except that the analysis apparatus was replaced with a VG micromass 300D mass spectrometer. Samples of 0.05–0.2 g were pretreated with the same procedure as that for the catalytic activity measurement. The catalyst was then purged with helium at a rate of 100 cm^3/min after the pretreatment to remove any adsorbed hydrogen. The heating rate of the TPR was 10 °C/min. The flow rate of the reactant gas stream is 30 cm^3/min. The oxygen gas stream used for TPO experiment is 1% oxygen in He. The CO_2 gas stream used for TPR experiment is 1%CO_2 in He. The desorbed species were admitted into the mass vacuum chamber with the flowing helium through a VG MD6 leak valve at a pressure of 5.10^{-7} torr. The base pressure in the chamber was 1.10^{-9} torr. The pressure in the mass chamber was measured with a HPS 421 cold cathode ionization gauge uncorrected for relative ionization cross sections.

3. Results and discussion

Fig. 1 shows the variation of the reaction rate over Ni/SiO_2, Ni/Cu/SiO_2 and Cu/SiO_2 catalysts as a function of exposure time in reactant-stream obtained at 800 °C. As the results of previous studies, [1] Ni/SiO_2 catalyst exhibited high deactivation rates, presumably due to the blocking of the active sites by the deposition of inactive carbon. The activity of 8 wt.% Ni/SiO_2 catalyst dropped about 20% after

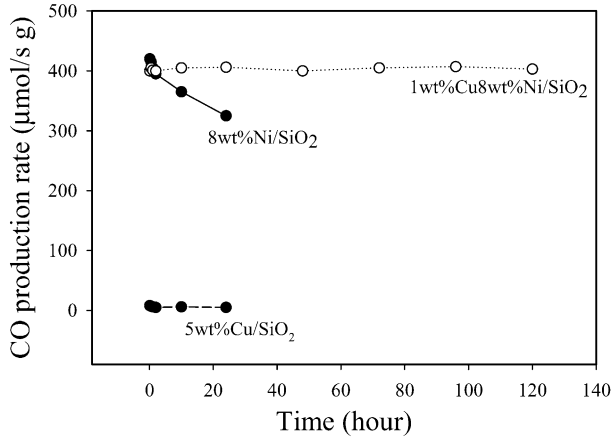

Fig. 1. Variations of the reaction rate as a function of time on stream over Cu, Ni and Cu/Ni/SiO_2 catalysts. Reaction conditions: CH_4/CO_2/He = 10/10/80 cm^3/min at one atmosphere, Temperature = 800 °C, M/F = 0.018 g s cm^{-3} for Ni and Cu/Ni catalysts. M/F = 0.18 g s cm^{-3} for Cu catalyst.

the catalyst was exposed to the reactant-stream for 24 h. The rate over Cu/SiO_2 catalyst was around 6 μmole/sec g catalyst, which was less than 2% of the initial activity of Ni/SiO_2 catalyst. In contrast, 1 wt.% Cu 8 wt.% Ni/SiO_2 catalysts show excellent stability and activity. The CO_2 and CH_4 conversion rate are over 90% with contact time of 0.018 g s cm^{-3}. The conversion rate over $Cu/Ni/SiO_2$ catalyst is similar to the initial rate of 8 wt.% Ni/SiO_2 catalyst and tends to be constant during the 120 h of reaction period. The stability of Cu/Ni catalysts for CO_2 reforming of methane reaction is temperature dependent. When the reaction temperature was between 760–850 °C, the stability of the catalysts can be maintained with on stream time for more than 100 h. However, the stability of the catalysts drops gradually when the reaction temperature was lower than 760 °C. The stability of the Cu/Ni catalysts was also Cu/Ni ratio dependent. When the copper loadings are higher than 2.0 wt.% on a 8 wt.% Ni/SiO_2 catalyst, the stability of the catalysts drops gradually with the increase of copper loading.

Because the ensemble size on the metal surface necessary for carbon formation is larger than the ensemble size for CH_4 reforming, [4,11] the effectiveness of the carbon suppression during the SPARG (sulphur-passivated reforming) process for CO_2 reforming of methane is attributed to control of the ensemble size on the metal surface. The suppression of carbon deposition on TiO_2 supported Pt catalysts for CO_2 reforming of methane has also been attributed to the deactivation of large ensembles of Pt atoms that are active for carbon deposition [12,13]. The copper atoms that added into the Ni catalyst system may also decorate the Ni metal surface and preferentially eliminate large ensembles of Ni metal atoms necessary for carbon deposition. The carbon formation rate on Ni catalyst may therefore be inhibited by the addition of Cu. This mechanism may contribute to the catalytic behavior of Cu/Ni catalysts for CO_2 reforming of methane reaction. However, the results of methane decomposition and carbon formation experiments suggest that the stability behavior of Ni/Cu catalysts for CO_2 reforming of methane reaction can not simply relate to the inhibition of carbon deposition phenomena.

Fig. 2 shows the results of temperature programmed decomposition of methane on Ni, Cu/Ni and Cu catalysts. The methane decomposition reaction takes place at temperature around 200 °C on Ni catalysts and the decomposition rate increases rapidly when temperature is higher than 400 °C. The decomposition rate reaches a maximum at temperature around 680 °C, then drops rapidly to near zero when temperature is higher than780 °C. The rapid dropping in methane decomposition rate is due, at least partially, to the carbon deposition on the metal surface. The methane decomposition rate on Ni/Cu catalysts take off at about the same temperature as that for Ni catalyst but with slower ascending pace. The maximum methane decomposition rate on 1 wt.% Cu 8 wt.% Ni/SiO_2 catalyst was about the same as that on pure Ni catalyst and was observed at temperature

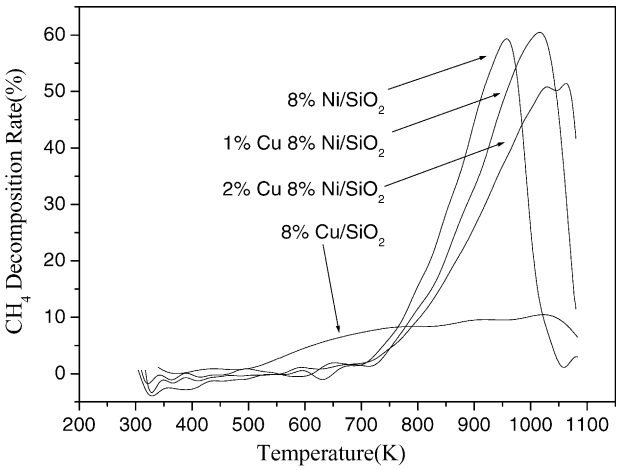

Fig. 2. Temperature programmed decomposition profiles of methane on 0.03 g Cu, Ni and Cu/Ni catalysts. Decomposition conditions: CH_4:He = 1:1, 30 cm^3/min, temperature programmed rate = 10 °C/min.

around 740 °C, which was 60 °C higher than that on pure Ni catalyst. The Cu/Ni catalysts still have some catalytic activity for methane decomposition reaction at temperature higher than 800 °C. Because the methane decomposition reaction is a key intermediate step for CO_2 reforming of methane reaction, the maintenance of the catalytic activity of Ni by the addition of Cu for methane cracking reaction at higher temperature may be an important factor in influencing the stability of Cu/Ni catalysts. The X-ray results (data not shown) suggested that no crystallized carbon species were formed, or the particle size of the crystallized carbon species was too small to be observed by X-ray diffraction under the experiment condition for methane decomposition reaction.

Fig. 3 shows the TPO profiles of the carbon on Ni/SiO_2 and $Cu/Ni/SiO_2$ after exposure to CH_4/He (1:9, 100 cm^3/min) for 30 s at 760 °C. The CO desorption profiles are not distinguishable from the background of $m/e = 28$ mass signal which are not shown here. Gas chromatograph analysis indicated that no CO was produced during the TPO experiment. Two desorption states of CO_2 peaked at 530 and 690 °C have been observed on a 8 wt.% Ni/SiO_2 catalyst with the 690 °C peak appearing as a shoulder of the 530 °C peak. Similar desorption peak temperatures have been observed during the course of TPO experiments on Cu/Ni catalysts but with different intensity distribution. The intensity of the 530 °C peak decreases gradually with the increasing of Cu loading while the intensity of the 690 °C peak increases rapidly with the increasing of Cu loading on a 8 wt.% Ni/SiO_2 catalyst. The different intensity distribution of CO_2 profiles during the course of TPO on Ni and Cu/Ni catalysts suggested that the pathway of the oxidation of the deposited carbon on Ni catalysts was changed by the addition of copper.

The differences in total CO_2 profile areas of the TPO on Cu/Ni catalysts and on pure Ni are less than 5% where the CO_2 profile areas on Ni catalysts with higher Cu loading are

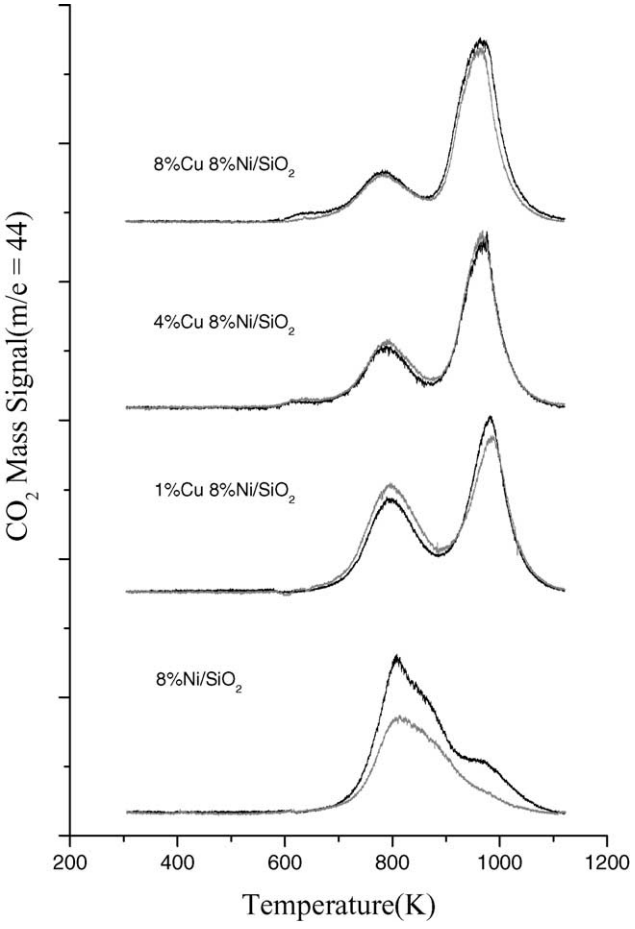

Fig. 3. Black trace: TPO profiles for 0.1 g freshly reduced Ni and Cu/Ni catalysts after exposure to CH_4/He (CH_4:He = 1:9, 100 cm^3/min) at 760 °C for 30 s. The temperature programmed rate was 10 °C/min. Gray trace: TPO following the first TPO and the catalysts had been regenerated again before the second methane exposure.

a little bit higher. Assuming that the oxygen oxidizes most of the deposited carbons during the TPO course, then the TPO results indicate that similar amounts of coke are formed on Ni and Cu/Ni catalysts during the methane cracking reaction at 760 °C. Bernardo et al. also reported that the carbon deposition rate depend only weakly on the copper concentration on a Cu/Ni catalyst during the methane reforming reaction in the absence of steam [14]. The similar amounts of coke formed on Ni and Cu/Ni catalysts would suggest that the addition of Cu into the Ni catalyst systems has little effect on the inhibition of the carbon formation, at least the carbon formation from the methane cracking at 760 °C. The inhibition of the carbon formation from methane decomposition may thus not that important for the stable CO_2 reforming reaction behavior of Cu/Ni catalysts. Isotope labeling experiments also suggested that methane decomposition was not the dominant carbon formation mechanism [15,16]. The influence of the reaction pathway of surface carbon by the addition of copper presumably play a more important role in the controlling of the stability of Cu/Ni for CO_2 reforming reaction.

The intensities of the CO_2 desorption profiles drops about 36% in the second TPO experiment (The gray trace in Fig. 3) as compared with the result of the first TPO experiment (the black trace in Fig. 3) where the Ni catalyst had been calcined and reduced again after the first TPO experiment. The intensities of the CO_2 desorption profiles remains nearly unchanged for the first and second TPO experiments on Cu/Ni catalysts. The lowering of the CO_2 desorption intensity suggested that part of the active sites on Ni surface have been destroyed during the methane cracking reaction or during the regeneration process and thereby diminish the amount of available Ni sites for carbon deposition during the second TPO experiment. Adsorbed carbon cause rearrangement of the Ni surface had been reported [17–19]. The loss of the nickel crystallites from the catalyst as the carbon burned off had also been confirmed previously [20]. The addition of copper into the Ni catalyst system can apparently stabilize the active site on Ni surface for methane cracking reaction and oxidation/reduction process, or the added copper can create a new active species that are more stable than Ni for catalyzing the methane decomposition reaction. The stabilization of the active center on Ni surface by the addition of copper must be an important factor in influencing the anti-deactivation behavior of Cu/Ni catalysts.

The TPR results comparing the activities of Ni and Cu/Ni/SiO_2 catalysts on the reaction of CO_2 with surface carbon are shown in Fig. 4. Two CO desorption peaks at 640 and 690 °C have been observed on a 8 wt.% Ni/SiO_2 catalyst where the peak at 690 °Cappears as a shoulder of the peak at 640 °C. The CO desorption peak on 1 wt.% Cu 8 wt.% Ni/SiO_2 catalyst appears as a broad band with a CO formation maximum around 760 °C. The broad band gradually becomes sharper and smaller with the increase of Cu loading on 8 wt.% Ni/SiO_2 catalysts. However, the temperature at the CO formation maximum does not change with the Cu loading. This observation suggests that a similar active site structure, most likely a Ni–Cu species, exist on the Cu/Ni/SiO_2 catalyst with various degree of Cu loading. The decrease of the CO profile intensity during the TPR indicated that coke on Ni and Cu/Ni catalysts had not been completely removed during the TPR course. This is confirmed by the results of TPO experiments taken right after the TPR experiment. Fig. 5 shows the TPO profiles of the residual carbon on Ni/SiO_2 and Cu/Ni/SiO_2 after the TPR experiments. The amount of the residual carbon increases with the increasing Cu loading on the Ni catalyst. The lowering of the CO formation rate on Ni catalyst with higher Cu loading is not relevant to the change of the active site structure as we point out above, but rather attributed to the covering of the active sites by the excess Cu. It appears that the surface of Ni–Cu particle is generally rich in copper [21]. The composition of the Cu–Ni alloy surface differs greatly from the average composition of the bulk [22,23]. The addition of small amounts of Cu may saturate the Ni surface with special Ni–Cu species that are active for CO_2 reforming reaction. Further addition of Cu will partially cover the

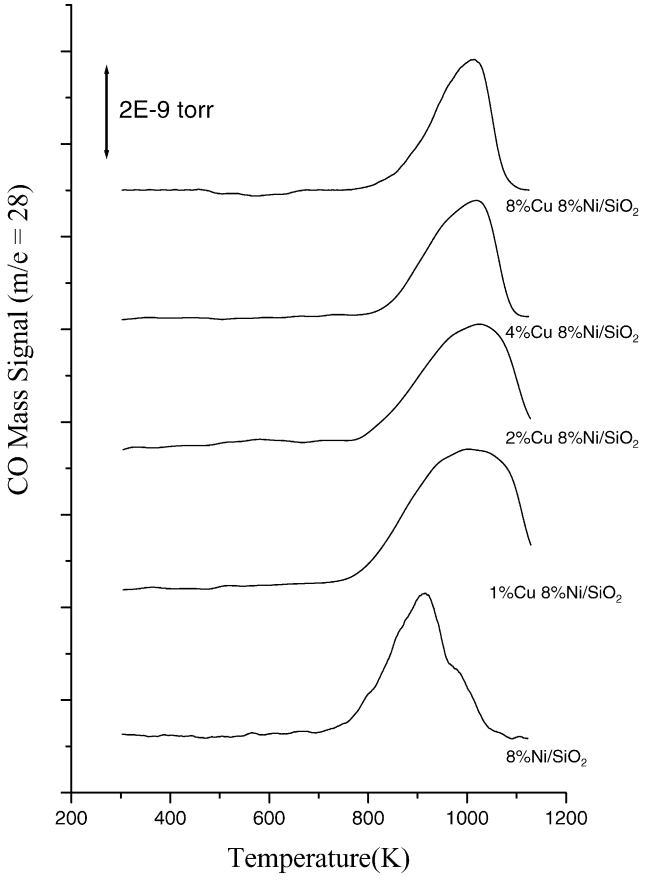

Fig. 4. TPR profiles with CO_2 for 0.1 g Ni and Cu/Ni catalysts after exposure to CH_4/He (CH_4:He = 1:9, 100 cm^3/min) at 760 °C for 30 s. The temperature programmed rate was 10 °C/min.

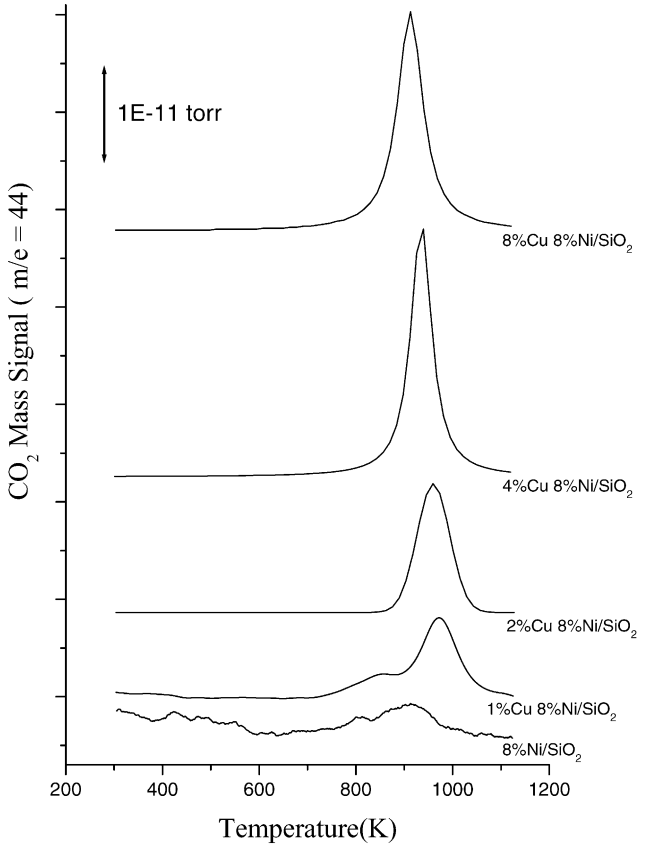

Fig. 5. TPO profiles for 0.1 g Cu and Cu/Ni catalysts after exposure to CH_4/He (CH_4:He = 1:9, 100 cm^3/min) at 760 °C for 30 s and TPR with CO_2 to 850 °C.

active site and inhibit the carbon scavenge ability of CO_2 on the Cu/Ni catalysts. This phenomenon can explain why the addition of a small amount of Cu into Ni catalyst induces a large change on the TPR profiles.

Recall that the stability of Cu/Ni catalysts for CO_2 reforming of methane reaction depends on Cu/Ni ratio and reaction temperature. The stability of the Cu/Ni catalysts drops gradually when the reaction temperatures were lower than 760 °C. The temperature effect on the deactivation behavior of the Cu/Ni catalysts is closely related to the temperature at CO formation maximum in TPR profiles and methane cracking rate on Cu/Ni catalyst. The CO_2 reforming of methane involves two key steps: the methane decomposition and CO_2 dissociation. The stability and activity of the catalysts corresponds to the ability of metals to crack methane and dissociate CO_2. The CO_2 dissociation produces adsorbed oxygen atoms that scavenge the carbon species formed from methane cracking and CO disproportionation. When the production rates of the carbon species on the surface are higher than the surface carbon oxidation rate, some carbon species would accumulate on the surface. The accumulated surface carbon species will eventually convert to an inactive type of carbon and poison the catalysts. The increasing of the reaction temperature can increase the rate of all types of reaction, such as the rate of methane cracking, the rate of CO_2 dissociation and the rate of surface carbon oxidation. The addition of Cu into Ni systems can reduce the temperature effect on the ascending rate of the methane cracking reaction that produces surface carbon species (see Fig. 2). When the reaction temperatures are higher than 760 °C, the CO_2 dissociation rate and the surface carbon oxidation rate can be increased to a level that the carbon removing rate is higher than the carbon formation rate. Then the formation of inactive type of carbon is inhibited and a stable CO_2 reforming of methane reaction is observed on Cu/Ni catalyst. Because the excess Cu on high Cu/Ni ratio catalysts may cover the active sites that catalyze the carbon oxidation reaction, the reaction rate of the surface carbon species would decrease gradually with the increasing Cu loading. The balance between carbon production and carbon removing rate would lose gradually with the increasing Cu loading, and thus a Cu/Ni ratio dependent stability was observed for the reaction of CO_2 reforming of methane.

The reactivity of the deposited coke formed during CO_2 reforming of methane and its influence on the stability of Cu/Ni catalysts are shown in Figs. 6 and 7. Fig. 6 shows TPO profiles of the carbon on Cu, Ni and Cu/Ni catalysts after exposure to CH_4/CO_2 for 12 h at 800 °C. A higher CH_4/CO_2

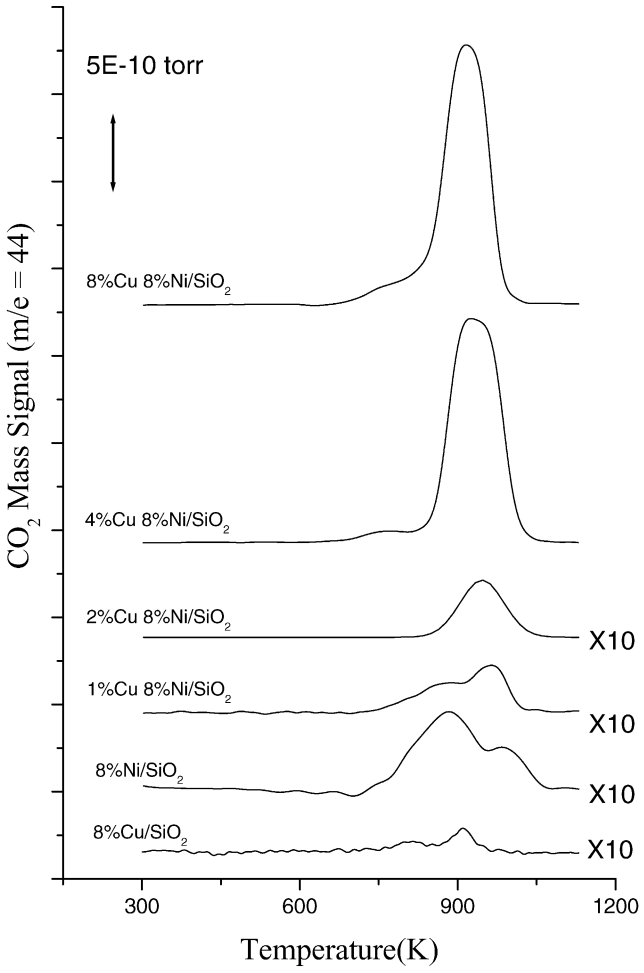

Fig. 6. TPO profiles for 0.1 g Cu and Cu/Ni catalysts after CO_2 reforming of methane (CH_4:CO_2 = 1:1, 30 cm^3/min) at 800 °C for 12 h.

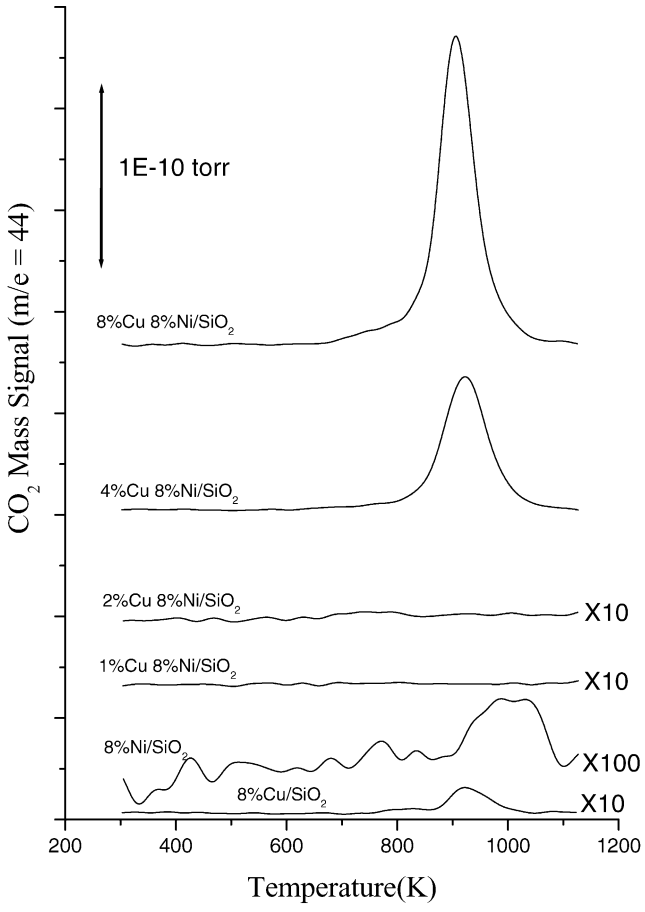

Fig. 7. TPO profiles for 0.1 g Cu and Cu/Ni catalysts after CO_2 reforming of methane (CH_4:CO_2 = 1:1, 30 cm^3/min) at 800 °C for 12 h and then in CO_2/He (CO_2:He = 1:1, 30 cm^3/min) at 800 °C for 30 min.

partial pressure was applied here to facilitate the coke formation on the catalytic surfaces. Coke formation was observed on all the Cu, Ni and Cu/Ni surface. Only residual amount of coke was observed on Cu catalyst presumably due to the low catalytic activity of Cu toward CO_2 reforming reaction. Less amounts of coke are formed on Cu/Ni catalysts as compared with the coke on pure Ni catalyst when the copper loading was lower than 2 wt.% on an 8 wt.% Ni catalyst. The amounts of deposited coke increase dramatically on Cu/Ni catalysts when the copper loading was higher than 2 wt.%. Because the results of methane decomposition experiments indicate that the carbon deposition rate on Ni and Cu/Ni catalysts at temperature higher than 760 °C is similar, the high coke formation rate on Ni catalysts with higher Cu loading during the CO_2 reformation is largely due to the lower carbon scavenge ability of CO_2 induced by the covering of the Cu–Ni active site by excess copper. X-ray data provided in Fig. 8 were taken for the catalysts after the reaction of CO_2 reforming of methane at 800 °C for 12 h. The X-ray diffraction results suggest that crystallized carbons ($2\theta = 26.3^\circ$) are formed on all of the catalysts where a smallest carbon signal is observed on the Ni catalyst with 1 wt.% Cu loading. The intensities of the carbon diffraction signal are not proportional to the CO_2 intensity observed on the TPO experiments, suggesting that different form of cokes are formed on Ni and Cu/Ni catalysts. Part of the carbon may be formed during the cooling process of the catalysts after the CO_2 reforming reaction. We therefore checked the reactivity between CO_2 and the coke after the reforming reaction vide infra.

Fig. 7 shows the TPO profiles of the carbon on Cu, Ni and Cu/Ni catalysts after exposure to CH_4/CO_2 for 12 h at 800 °C followed by exposure to CO_2/He for 30 min at 800 °C. The results of the TPO experiment indicate that all the carbon formed during the CO_2 reformed reaction can be removed by CO_2 on Ni catalyst with Cu loading lower than 2 wt.% while the coke on pure Ni, and Ni with Cu loading higher than 4 wt.% can not be removed completely by CO_2 at 800 °C. The inactive coke gradually accumulated on Ni surface and blocked the CO_2 access. The Ni surfaces would eventually be encapsulated by the inactive carbon and lost their activity. The addition of Cu into the Ni catalyst produced a Cu–Ni species that can inhibit the formation of the inactive carbon. Note also that the CH_4 decomposition

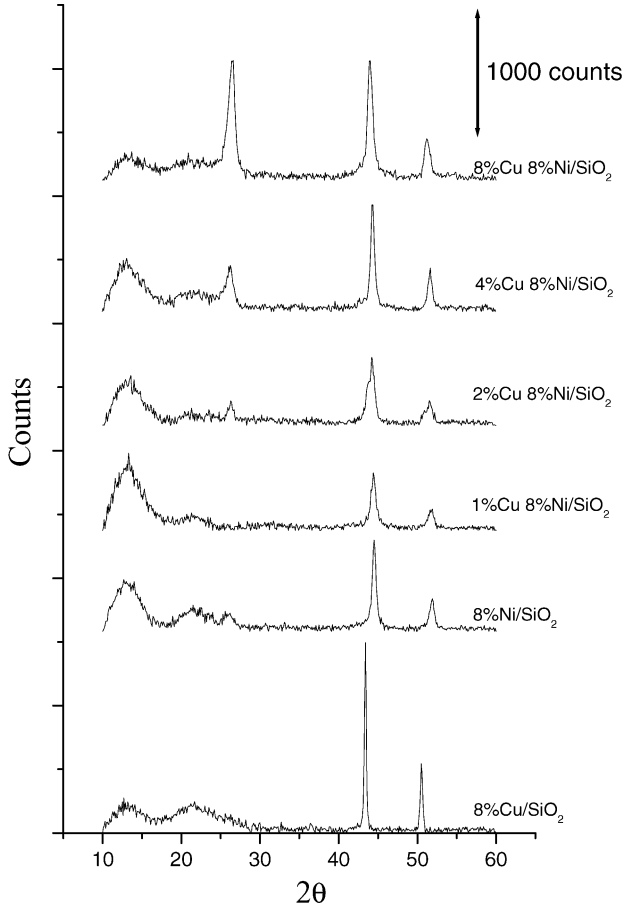

Fig. 8. X-ray diffraction patterns of catalysts after CO_2 reforming of methane (CH_4:CO_2 = 1:1, 30 cm^3/min) at 800 °C for 12 h.

rate on Cu/Ni catalyst was slower than that on Ni catalyst (Fig. 2). So CH_4 cracking and removal of coke by CO_2 is balanced and inactive coke does not accumulate on Ni particle when Cu loading is less than 2 wt.%. In addition, when the surface already covered with deposited carbon at 800 °C, the Cu/Ni metals are still capable of catalyzing the C–H bond scission reaction to produce the CH_x species (Fig. 2)—a key step to activate the CO_2 reforming reaction. As a result, encapsulated carbon layer does not formed on supported Cu/Ni given the catalyst a stable activity.

4. Conclusions

Many factors may vary with the addition of copper into supported Ni catalyst system. These factors, such as the surface geometry, the electronic structure of Ni–Cu, the extent of the CH_x species and hydrogen spillover on the Ni–Cu interfacial region and etc., may all contributed to the activity behavior of supported Cu/Ni catalysts on CO_2 reforming of methane reaction. All the factors together give a stable supported Cu/Ni catalyst for CO_2 reforming of methane reaction. The main conclusions of the present work can be summarized as follows:

1. 1 wt.% Cu 8 wt.% Ni/SiO_2 catalyst has excellent long-term stability for CO_2 reforming of methane reaction at temperatures higher than 760 °C. The stability drops gradually with the increases of Cu loading.
2. The addition of copper into the Ni catalyst system can stabilize the structure of the active site on Ni surface for methane cracking reaction and for regeneration process, preventing the deactivation of the Ni catalyst caused by sintering or by loss of nickel crystallites.
3. The carbon formation rate in methane decomposition reaction at 760 °C is similar for Ni and Cu/Ni catalysts except at high Cu content.
4. The inhibition of the carbon formation from methane decomposition may not be the major contributor for the stable activity of Cu/Ni catalysts. The influence of the reaction pathway of surface carbon by the addition of copper would be more important in the control of the stability of Cu/Ni.
5. The addition of Cu into the Ni catalyst produced a Cu-Ni species that can inhibit the formation of the inactive carbon during the CO_2 reforming reaction process.
6. When the surface already covered with deposited carbon at 800 °C, the Cu/Ni metals are still capable of catalyzing the C–H bond scission reaction to produce the CH_x species, which is a key step to activate the CO_2 reforming reaction.
7. The addition of Cu into Ni catalyst can fine tune catalytic activity so that the CH_4 cracking and removal of coke by CO_2 is balanced and inactive coke does not accumulate on Ni particle giving Cu/Ni catalyst a stable activity.

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References

[1] M.C.J. Bradford, M.A. Vannice, Catal. Rev. Sci. Eng. 41 (1999) 1.
[2] A.T. Ashcroft, A.K. Cheetham, M.L.H. Green, P.D.F. Vernon, Nature 352 (1991) 225.
[3] S. Wang, G.Q. Lu, Energy Fuels 10 (1996) 896.
[4] J.R. Rostrup-Nielsen, J. Catal. 85 (1984) 31.
[5] Z. Zhang, X.E. Verykios, J. Chem. Soc. Chem. Commun. 1 (1995) 71.
[6] K. tomishige, O. Yamazaki, Y. Chen, K. Yokoyama, X. Li, K. Fujimoto, Catal. Today 45 (1998) 35.
[7] K.C. Khulbe, R.S. Mann, A. Manoogian, Chem. Rev. 80 (1980) 417.
[8] J.S. Campbell, P.H. Emmett, J. Catal. 7 (1967) 252.
[9] F. Fischer, H. Tropsch, Brennstoff Chem. 3 (1928) 39.
[10] W.A.A. Van Barneveld, V. Ponec, J. Catal. 51 (1978) 426.
[11] J.R. Rostrup-Nielsen, Stud. Surf. Sci. Catal. 68 (1991) 85.

[12] M.C.J. Bradford, M.A. Vannice, Catal. Lett. 48 (1997) 31.
[13] M.C.J. Bradford, M.A. Vannice, J. Catal. 173 (1998) 157.
[14] C.A. Bernardo, I. Alstrup, J.R. Rostrup-Nielsen, J. Catal. 96 (1985) 517.
[15] H.M. Swaan, V.C.H. Kroll, G.A. Martin, C. Mirodatos, Catal. Today 21 (1994) 571.
[16] V.A. Tsipopuriari, A.M. Efstathiou, Z.L. Zhang, X.E. Verykios, Catal. Today 21 (1994) 579.
[17] C.H. Bartholomew, Catal. Rev. Sci. Eng. 24 (1982) 67.
[18] H.V. Thapliyal, J.M. Blakely, J. Vac. Sci. Technol. 15 (1978) 300.
[19] M. Eizenberg, J.M. Blakely, Surf. Sci. 82 (1979) 228.
[20] A.D. Moeller, C.H. Bartholomew, Prepr. ACS Fuels Chem. Div. 25 (2) (1980) 54.
[21] P.B. Shallcross, W.W. Russell, J. Am. Chem. Soc. 81 (1959) 4132.
[22] J.J. Burton, E. Hyman, J. Catal. 37 (1975) 114.
[23] D.H. Seib, W.E. Spicer, Phys. Rev. B 2 (1970) 167.