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The Influence of a Second Metal on the Ni/SiC Catalyst for the Methanation of Syngas

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Abstract – The catalytic performance of silicon carbide supported nickel catalysts modified with or without second metal (Co, Cu and Zn) for the methanation of CO has been investigated in a fixed-bed reactor using a feed consisting of 25% CO and 75% H_2 without any diluent gas. It has been found that the introduction of Co species can clearly improve the catalytic activity of Ni/SiC catalyst, whereas the addition of Cu or Zn can result in a significant decrease in the catalytic activity. The characterizations by means of XRD, TEM, XPS, CO-TPD and H_2-TPR indicate that the addition of Co could decrease the particle size of active metal, increase active sites on the surface of methanation catalyst, improve the chemisorption of CO and enhance the reducibility of methanation catalysts. Additionally, the special interaction between Co species and Ni species is likely favorable for the dissociation of adsorbed CO on the surface of catalyst, and this may also contribute to the high activity of 5Co-Ni/SiC catalyst for CO methanation reaction. For 5Cu-Ni/SiC catalyst and 5Zn-Ni/SiC catalyst, Cu and Zn species could cover partial nickel particles and decrease the chemisorption amount of CO. These could be responsible for the low methanation activity. In addition, a 150h stability test under 2 MPa and 300 °C showed that 5Co-Ni/SiC catalyst was very stable for CO methanation reaction.

Key words: CO Methanation, Ni/SiC Catalysts, Second Metal

1. Introduction

Natural gas is a clean fossil fuel that has a higher calorific value compared with petroleum and coal. Due to the exhaustion of natural gas and the wish for a renewable alternative to natural gas, the production of synthetic or substitute natural gas (SNG) from coal or dry-biomass has attracted more and more attention [1-3]. As a versatile energy carrier, SNG is inter-changeable with natural gas and therefore can be used as a green alternative fuel in transportation, power stations and heating [2,4]. On the other hand, the high conversion efficiency and the already existing gas distribution infrastructure such as pipelines also favor for the development of SNG projects [2,5-8]. It has been reported that a commercial SNG plant called Great Plains Synfuel Plant was commissioned in United States in 1984 and has been producing 4.8 Mio m^3 SNG per day by the coal-to-SNG technology [2]. Some institutes, such as the Energy Research Center of the Netherlands, Center for Solar Energy and Hydrogen Research in Stuttgart and Paul-Scherrer Institute in Switzerland, have developed different biomass-to-SNG technologies [2,4]. In China, a number of coal-to-SNG projects have also been proposed: Datang Hexigten SNG Project, Datang Huayin SNG Project, Shanxi SNG Project [2]. All of the plants and institutes produce SNG from coal or dry-biomass by thermo-chemical process, which includes gasification step, gas cleaning/conditioning step and subsequent methanation step. Most researchers focus their attention on the synthesis of methane from carbon monoxide and hydrogen because it is one of the most essential steps in the production of SNG.

It is well known that the noble and transition metal-based catalysts can efficiently catalyze the hydrogenation of carbon monoxide. Although, the supported noble metals such as Rh, Ru, Pd and Pt show high activity and selectivity toward methane in CO methanation reaction [9-14]. However, the high costs and restricted availabilities greatly limit their applications in industry [15]. Compared with noble metals, nickel-based catalysts have drawn much attention due to their low price and good activity for the methanation reaction [2].

Since the hydrogenation of carbon monoxide toward methane was first reported by Sabatier and Senderens in 1902 [16], the reaction mechanism of CO methanation reaction has also been investigated intensively. It is widely accepted that the CO is dissociated into CH_x as intermediate species by assistance of H after CO adsorbed on the surface of catalysts and then the CH_x is hydrogenated to produce methane [17,18]. Therefore, the introduction of promoters is possible to improve activity of catalysts by enhancing the adsorption amount of CO, by facilitating CO dissociation or by stabilizing intermediate species. It has been reported that the addition of La and Ce could form a new kind of active sites and promote the dissociation of carbon monoxide [19-22]. Some researchers found that the addition of Zr, V, Mo, W and Re had positive effect for the dissociation of CO and could enhance the formation of intermediate species on the catalyst surface [23-26]. Co, Cu and Zn were also widely investigated as promoters in the hydrogenation of carbon oxides. It has been reported

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that the activities of Fischer-Tropsch synthesis catalysts could be improved by introducing Co or Cu to form bimetallic nanoparticles [27,28]. Zhao *et al*. [29] reported that the addition of cobalt could increase the activity of Mn/SiO_2 catalyst for CO hydrogenation and enhance the selectivity toward light hydrocarbons. Hu *et al*. [21] demonstrated that the addition of Co into Ni/Al_2O_3 catalyst could promote the methanation reaction. Boellard *et al*. [30] found that the activity of CO hydrogenation could be enhanced by adding copper to active iron phase. Tsai *et al*. [15] investigated the CO hydrogenation reaction on CoCuZnO catalyst, and found that Cu could decrease the catalytic activity for CO hydrogenation while the addition of Zn could highly disperse active metal components and improve the catalytic activity for hydrocarbon synthesis. Fujitani *et al*. [31] investigated the effect of Zn in the promotion of methanol synthesis over Cu surfaces and found that a kind of special site was formed on the surface of Zn-doped catalyst, which could stabilize intermediate species during CO_2 hydrogenation reaction. Lin *et al*. [32] reported that Zn could be an electronic promoter to improve the performance of Cu-Fe catalyst for CO hydrogenation.

To resolve the highly exothermic problem of total methanation (methanation reaction with pure syngas as the feedstock [5]), we used SiC as support and found that the catalysts exhibited high activity and stability due to the excellent thermal stability and high thermal conductivity of the SiC support [33]. We modified Ni/SiC catalyst by a second metal Co, Cu or Zn to study the effect of the second metal on the performance of Ni/SiC catalysts for CO methanation reaction. The results were compared with those of pure Ni/SiC catalyst and Co/SiC catalyst, and the influences of Co, Cu or Zn on the performance of Ni/SiC catalyst were discussed.

2. Experimental Section

2-1. Catalyst preparation

$Ni(NO_3)_2{\cdot}6H_2O$, $Co(NO_3)_2{\cdot}6H_2O$, $Cu(NO_3)_2{\cdot}6H_2O$ and $Zn(NO_3)_2{\cdot}6H_2O$ were used as metal precursor salts. The SiC support was prepared by a sol-gel and carbothermal reduction route [34], and the catalyst referred to as Ni/SiC was prepared by the conventional impregnation method. SiC support was added into $Ni(NO_3)_2$ aqueous solution under stirring, and then the slurry was heated at 80 °C until nearly all the water was evaporated. After drying at 100 °C overnight, the sample was calcined in air at 550 °C for 4 h. The loading of Ni in the catalysts was 13 wt% (Elemental wt% relative to the weight of the catalyst).

The modified-Ni/SiC catalysts with Co, Cu or Zn were prepared by co-impregnation method. The SiC support was impregnated in $Ni(NO_3)_2$ aqueous solution mixed with a suitable amount of $Co(NO_3)_2{\cdot}6H_2O$, $Cu(NO_3)_2{\cdot}6H_2O$ or $Zn(NO_3)_2{\cdot}6H_2O$, and then stirred for 12 h. After heating at 80 °C to evaporate water, the mixtures were dried at 100 °C overnight. Finally, the samples were calcined at 550 °C in air for 4 h. The catalysts are denoted as *x*M-Ni/SiC (M=Co, Cu and Zn, respectively), where *x* is the loading of promoters. The loading of Ni over all these catalysts is 13 wt%.

2-2. Characterization Techniques

The crystalline phases of the catalysts were analyzed by a Rigaku D-Max/RB X-ray diffractometer (XRD) with Cu Kα radiation and a scanning rate of 6°/min. The morphology and structure of the catalysts were analyzed by JEOL-2010 transmission electron microscopy (TEM). X-ray photoelectron spectra (XPS) measurements were performed on a Kratos XSAM800 spectrometer using Al Kα X-ray source. The residual pressure inside the analysis chamber was below 2×10^{-7} Pa. All binding energies were referred to the C_{1s} line at 284.8 eV.

Temperature-programmed reduction of H_2 (H_2-TPR) was carried out in a continuous flow quartz reactor. About 50 mg (40-60 mesh) of the catalysts were packed between two layers of quartz wool in the reactor. Prior to the TPR measurements, the catalysts were pretreated in a following Ar gas at 500 °C for 1 h, and then cooled to room temperature in the Ar flow. After that, the temperature of the reactor was increased from room temperature to 900 °C at a constant rate of 5 °C/min and kept at 900 °C for 20 min in a 5% H_2/Ar mixture gas at a flow rate of 40 mL/min. The outlet gases were passed through 5A molecular sieve to eliminate water and then were analyzed by a gas chromatograph equipped with thermal conductivity detector.

The temperature programmed desorption of CO (CO-TPD) measurements were performed in the similar reactor as the above TPR. After being pre-reduced in a 5% H_2/Ar mixture gas at 400 °C for 1.5 h, the samples (100 mg with 40-60 mesh) were purged with Ar at the reduction temperature for 0.5 h, and then cooled to 40 °C in Ar flow. Pluses of CO were injected into the Ar flow through the samples until the adsorption of CO on the catalyst surface reached to saturation. After purging the samples with He for 1 h at 40 °C, the reactor was heated from 40 °C to 400 °C at a constant rate of 5 °C/min in He flow with a follow rate of 40 mL/min. The outlet gases were analyzed by a gas chromatograph.

2-3. Methanation measurement

The performance of the catalysts was tested in a fixed bed reactor with an inner diameter of 6mm using the mixed gases of H_2 and CO (molar ratio of H_2/CO=3, without diluent gas). In a typical experiment, about 0.8 ml of catalyst (40-60 mesh) was placed in the middle of the reactor, and then the mixed gases were fed into the reactor with a space velocity of 4,500 h^{-1}. All catalysts were reduced *in situ* at 500 °C in H_2 for 2 h prior to each reaction and all experiments were performed at 2 MPa. To achieve steady results, the reaction was kept at each temperature for 1 h. The outlet productions from the reactor were analyzed by GC-14B gas chromatograph with TDX-01 column and a GDX-104 column using thermal conductivity detector and flame ionization detector, respectively. The CO conversion (X_{CO}) and CH_4 selectivity (S_{CH4}) were estimated by the following equations:

$$X_{CO}(\%) = (F_{CO,in} - F_{CO,out}) / F_{CO,in} \times 100\% \quad (1)$$

$$S_{CH4}(\%) = F_{CH4,out} / (F_{CO,in} - F_{CO,out}) \times 100\% \quad (2)$$

3. Results and Discussion

3-1. Catalytic performance

3-1-1. Effect of Co, Cu and Zn on Ni/SiC catalytic performance

CO methanation reaction was investigated over pure Ni/SiC and modified Ni/SiC catalysts with Co, Cu and Zn under the same reaction conditions. Fig. 1 shows the CO conversion (X_{CO}) results of the methanation catalysts, which are plotted as functions of reaction temperature. It can be seen that the CO methanation reaction over Ni/SiC and 5Co-Ni/SiC started at 200 °C and the X_{CO} over the two catalysts increased with increasing temperature. From the figure, the X_{CO} is about 98% over 5Co-Ni/SiC at 290 °C, while it is only 68% over Ni/SiC at the same condition. For 5Cu-Ni/SiC and 5Zn-Ni/SiC, however, no methanation activity was detected until the reaction temperature was over 300 °C. The X_{CO} over 5Cu-Ni/SiC and 5Zn-Ni/SiC increased with increasing reaction temperature and then achieved a maximum of about 85% at 480 °C (Fig. 1A). The turnover frequency (TOF) values of CO defined as moles of carbon monoxide converted per surface metallic atom per second are shown in Table 1. The TOF value for 5Co-Ni/SiC (0.00306 s^{-1}) is more than three times as high as that for Ni/SiC (0.00091 s^{-1}) at 220 °C. While for 5Cu-Ni/SiC and 5Zn-Ni/SiC, the TOF values are 0.00133 s^{-1} and 0.00112 s^{-1}, respectively, even at 320 °C. Therefore, the addition of Co improves the methanation activity, whereas Cu and Zn play opposite roles for CO methanation reaction. Besides that, an obvious decrease of X_{CO} over the catalysts can be found when the reaction temperature is higher than 480 °C (Fig. 1A). This behavior can be explained by the thermodynamic limitation of CO methanation reaction [33]. Because the CO methanation reaction is a strongly exothermic reaction, too high reaction temperature is not favorable for this reaction.

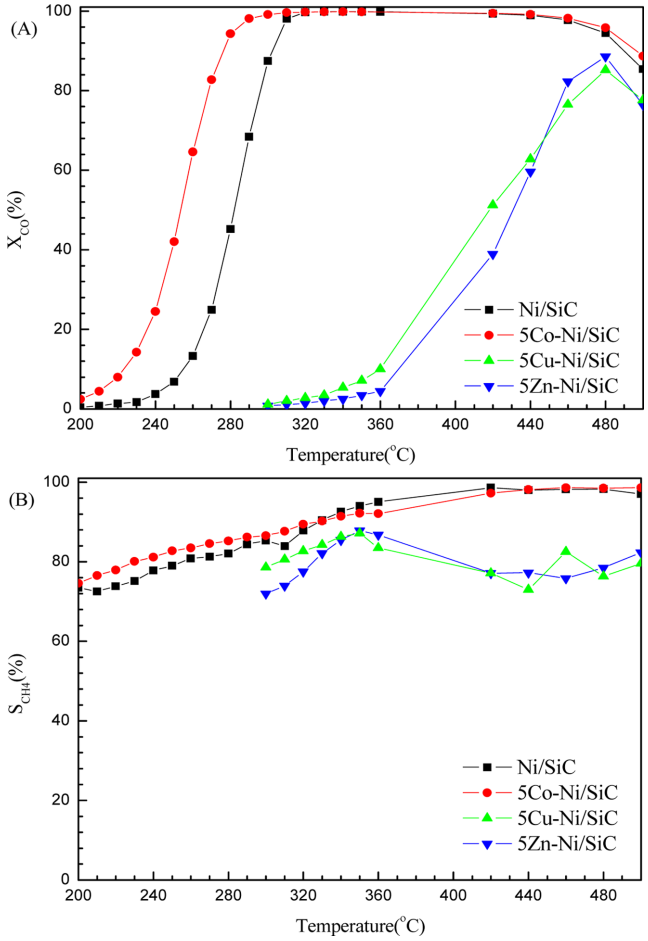

Fig. 1. Influences of Co, Cu and Zn modification on the catalytic performance of Ni/SiC catalysts for CO methanation reaction. (A) Conversions of CO (X_{CO}), (B) Selectivity of CH_4 (S_{CH4}). Reaction conditions: P=2.0 MPa, H_2/CO=3, GSV=4500 h^{-1}.

Fig. 1B shows the results of methane selectivity (S_{CH4}) over pure Ni/SiC and modified Ni/SiC catalysts. S_{CH4} over Ni/SiC and 5Co-Ni/SiC increases with increasing the reaction temperature and almost achieves a maximum above 440 °C. For 5Cu-Ni/SiC and 5Zn-Ni/SiC, however, the S_{CH4} is always lower than 80% even at high reaction temperature.

Except methane and water, the by-products of CO hydrogenation under present reaction condition are carbon dioxide (water-gas-shift reaction, $CO + H_2O = CO_2 + H_2$) and higher hydrocarbons, e.g., C_2H_6, C_2H_4, C_3H_8, C_3H_6, MeOH, EtOH. The selectivity of products over pure Ni/SiC and modified Ni/SiC catalysts at 420 °C is shown in Table 2. The addition of Cu and Zn clearly increases the by-product selectivity of CO hydrogenation reaction. Therefore, it is suggested that Cu and Zn have a negative effect on Ni/SiC catalyst for the methanation reaction in the present conditions.

Table 1. Metallic crystallite size and TOF results of CO over different methanation catalysts

Catalysts	Content of promoters (wt%)	NiO crystallite size (nm)[a]	Ni crystallite size (nm)[b]	NiO crystallite size (nm)[c]	TOF of CO at 220 °C ($\times 10^4$ s^{-1})
Ni/SiC	-	20.4	21.2	23.4	9.1
1Co-Ni/SiC	1	19.1	20.1	20.4	11.4
3Co-Ni/SiC	3	17.5	18.3	15.6	13.2
5Co-Ni/SiC	5	15.3	16.2	12.3	30.6
7Co-Ni/SiC	7	16.3	17.4	20.3	30.9
5Cu-Ni/SiC	5	19.7	20.6	22.1	13.3d
5Zn-Ni/SiC	5	20.0	22.7	21.9	11.2d

[a]Calculated from NiO (012) plane by Scherrer's equation from XRD results.
[b]Calculated from Ni (111) plane by Scherrer's equation from XRD results.
[c]Average size = $\Sigma n_i d_i^3 / \Sigma n_i d_i^2$ from TEM images.
[d]TOF results of CO at 320 °C.

Table 2. The selectivity of products over catalysts at 420 °C

	CH_4	C_2H_x	C_3H_x	CO_2	CHO
Ni/SiC	0.981087	0.000326	0.0000329	0.018541	0.000013
5Co-Ni/SiC	0.97546	0.005838	0.000323	0.018308	0.000071
5Cu-Ni/SiC	0.771266	0.027543	0.000953	0.200238	0.001939
5Zn-Ni/SiC	0.771372	0.037007	0.008405	0.183216	0.001743

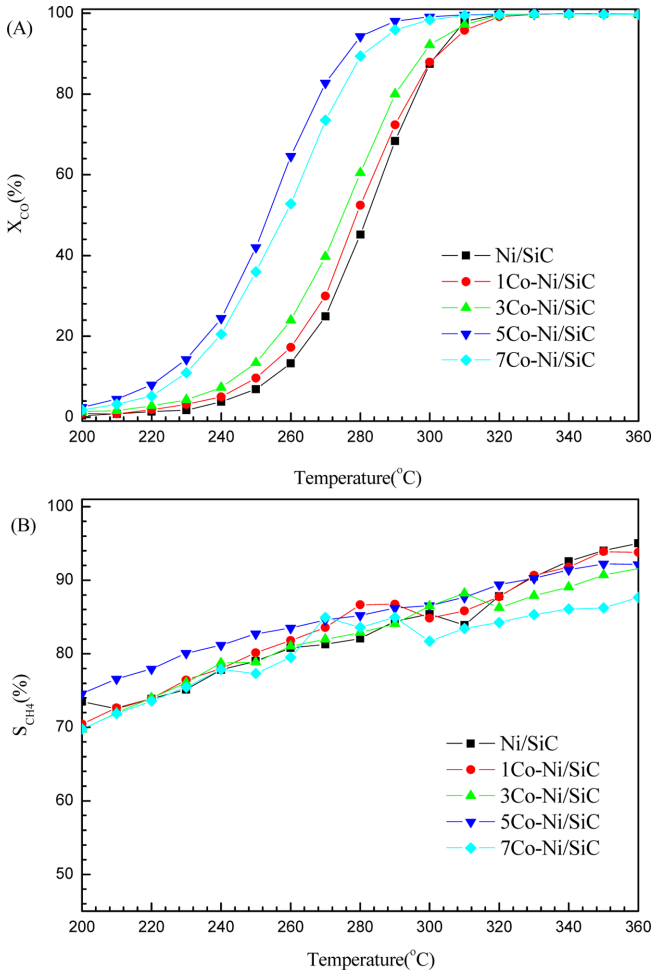

Fig. 2. Catalytic performance of Ni/SiC and Co-modified Ni/SiC catalysts with different Co loadings. (A) Conversions of CO (X_{CO}), (B) Selectivity of CH_4 (S_{CH4}). Reaction conditions: P=2.0 MPa, H_2/CO=3, GSV=4500 h^{-1}.

3-1-2. Effect of Co loading on methanation activity

To further study the influence of Co loading on the catalytic activity, we investigated Co-modified Ni/SiC catalysts with different Co contents (1-7 wt%) for CO methanation, and the results are shown in Fig. 2. The methanation activity is improved significantly when the Ni/SiC catalyst is modified with Co. In addition, Fig. 2 shows that the CO conversion curve is progressively shifted toward lower reaction temperature with increasing the loading of Co from 1 wt% to 5 wt%, and 5Co-Ni/SiC shows a similar S_{CH4} with that of pure Ni/SiC catalyst. However, when the loading of Co is further increased to 7 wt%, the methanation activity shows a little decrease. The results obtained from Table 1 show that the addition of Co can promote the TOF value of CO at 220 °C, and the TOF can significantly increase with increasing

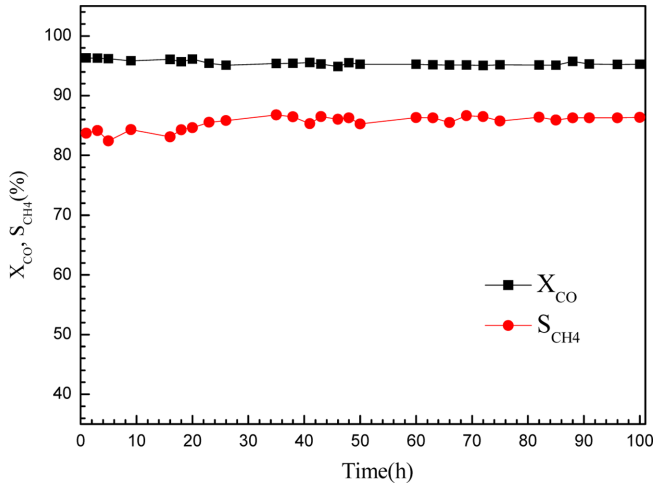

Fig. 3. Long-term stability test of 5Co-Ni/SiC catalyst. Reaction conditions: T=280 °C; P=2.0 MPa; H_2/CO=3; GSV=4500 h^{-1}.

Co loading to 5 wt%. For 7Co-Ni/SiC, however, there is no remarkable increase of the TOF value compared with 5Co-Ni/SiC. Therefore, 5 wt% is a suitable loading of Co for modifying the Ni/SiC catalyst.

3-1-3. Long-term stability test

Since 5Co-Ni/SiC shows the best performance for methanation reaction, a long-term stability test of 5Co-Ni/SiC was performed under 2MPa with H_2/CO=3. The reaction temperature was 280 °C and the space velocity was 4500 h^{-1}. The results are shown in Fig. 3, where X_{CO} and S_{CH4} are plotted as the function of time-on-stream. X_{CO} and the S_{CH4} are kept at about 95% and 85% for 100 h, respectively, indicating that 5Co-Ni/SiC is very stable in the CO methanation reaction.

3-2. Catalyst characterization

3-2.1. XRD

Fig. 4A shows the XRD results of fresh Ni/SiC and modified Ni/SiC catalysts with Co, Cu and Zn. It is demonstrated that the addition species have been highly dispersed on the SiC surface since no diffraction peaks of Co, Cu and Zn species can be found from the XRD patterns of catalysts. The average crystallite sizes of NiO particles calculated from NiO (012) plane by Scherrer's equation [35] are listed in Table 1. The particle sizes of NiO over 5Cu-Ni/SiC and 5Zn-Ni/SiC are 19.7 nm and 20.0 nm, respectively, almost the same as that over Ni/SiC (20.4 nm). For 5Co-Ni/SiC, however, the NiO particle size is about 15.3 nm. Fig. 4B shows the XRD results of used Ni/SiC catalysts modified with or without second metals. The diffraction peaks at $2\theta = 44.3°$ and 51.7° over the used catalysts are

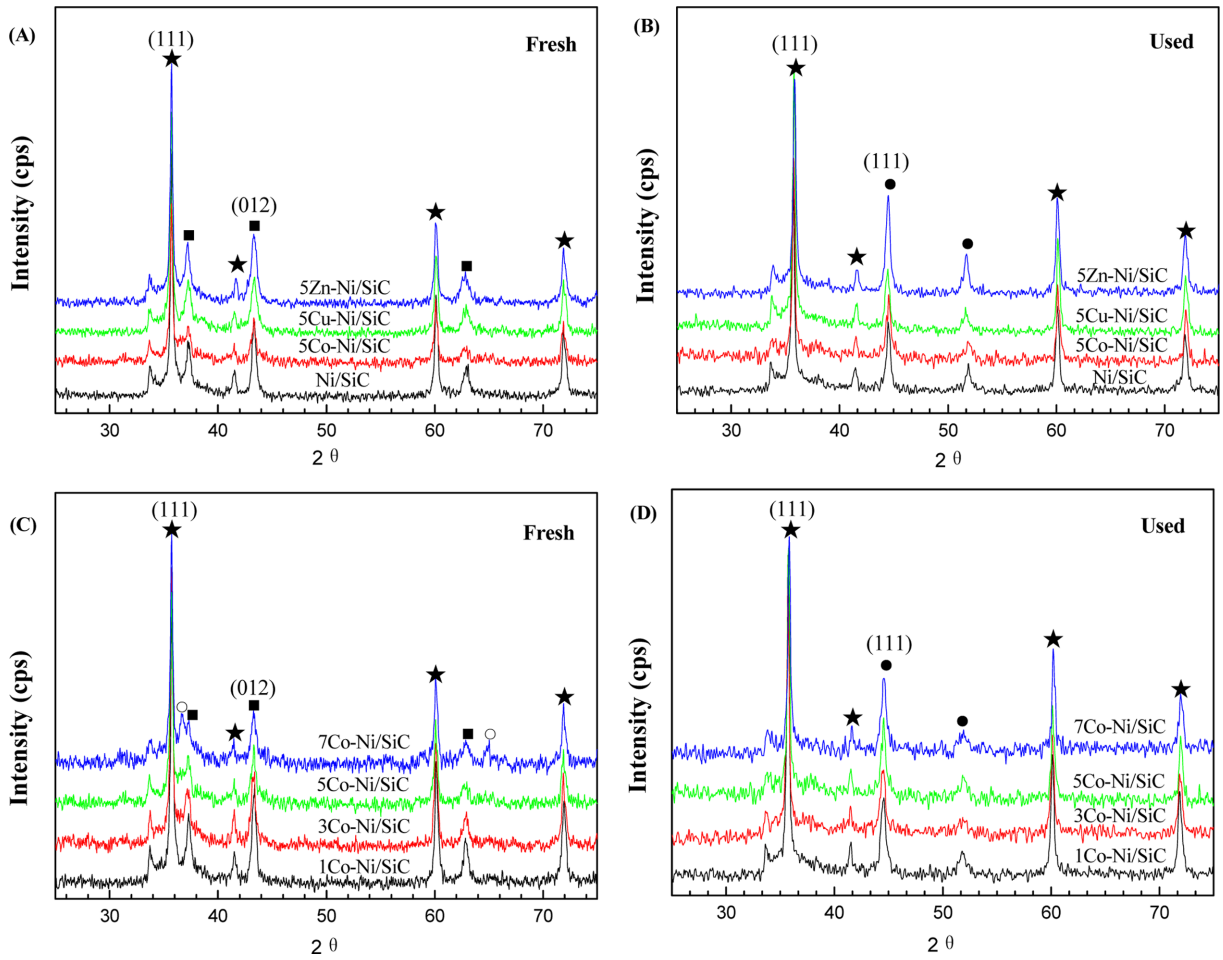

Fig. 4. XRD patterns of fresh and used pure Ni/SiC and modified Ni/SiC catalysts. (★) SiC; (■) NiO; (●) Ni; (○) Co_3O_4.

attributed to Ni, indicating the metallic nickel is the active phase for CO methanation reaction. From Table 1, interestingly, there is only a slight increment in the size of metallic nickel particles over the used catalysts. This suggests that no serious sintering occurred during the methanation reaction due to the excellent thermostability and heat conductivity of SiC support. Compared with Ni/SiC, 5Cu-Ni/SiC and 5Zn-Ni/SiC, metallic nickel particle on 5Co-Ni/SiC has a smaller size. Therefore, the addition of Co can enhance the dispersion of active metal. This is in accordance with the results reported by Zhang *et al.* [36], who found that the addition of Co increased the metallic surface and improved the metal dispersion, and thus resulted in a higher activity.

Fig. 4C and Fig. 4D show the XRD results of Co-modified Ni/SiC catalysts with the Co loading from 1 wt% to 7 wt% before and after methanation reaction, respectively. The loading of Co influences the intensities of NiO and metallic Ni diffraction peaks. The average particle sizes of NiO and metallic Ni are shown in Table 1. Table 1 shows that the metal particles over fresh and used Co-modified Ni/SiC catalysts are smaller than that over Ni/SiC. With increasing the loading of Co from 1 wt% to 5 wt%, the average particle sizes of NiO and Ni over fresh and used catalysts decrease from 19.1 nm and 20.1 nm to 15.3 nm and 16.2 nm, respectively. When further increasing Co loading, the particle size does not decrease. Therefore, 5 wt% is the suitable loading of Co for the dispersion of Ni species over catalysts. In addition, a new diffraction peak attributed to Co_3O_4 is interestingly detected over the 7Co-Ni/SiC (Fig. 4C), indicating that the Co species are not well dispersed and aggregate on the surface of catalyst in this case. This may result in the decrease of the amount of active sites and be responsible for the decreased activity of 7Co-Ni/SiC.

3-2.2. TEM

The average particle sizes of the methanation catalysts obtained from the TEM images are listed in Table 1, where the particle sizes are in good agreement with the crystallite sizes calculated from the XRD analysis.

Fig. 5 shows TEM results of the morphology and size distribution of metallic particles over pure and modified Ni/SiC catalysts before the methanation reaction. It is obvious that Ni/SiC has a wide size distribution ranging from 11 to 35 nm, and the percentage of large particles (larger than 25 nm) is about 19%. 5Cu-Ni/SiC and 5Zn-Ni/SiC have similar particle distribution with that of Ni/SiC. The percentage of large particles reaches about 18% and 15% for 5Cu-Ni/SiC and 5Zn-Ni/SiC, respectively. For 5Co-Ni/SiC, large metal particles are seldom detected and the portion of metal particles between 5 and 15 nm increases to about 86%. The relatively concentrated dis-

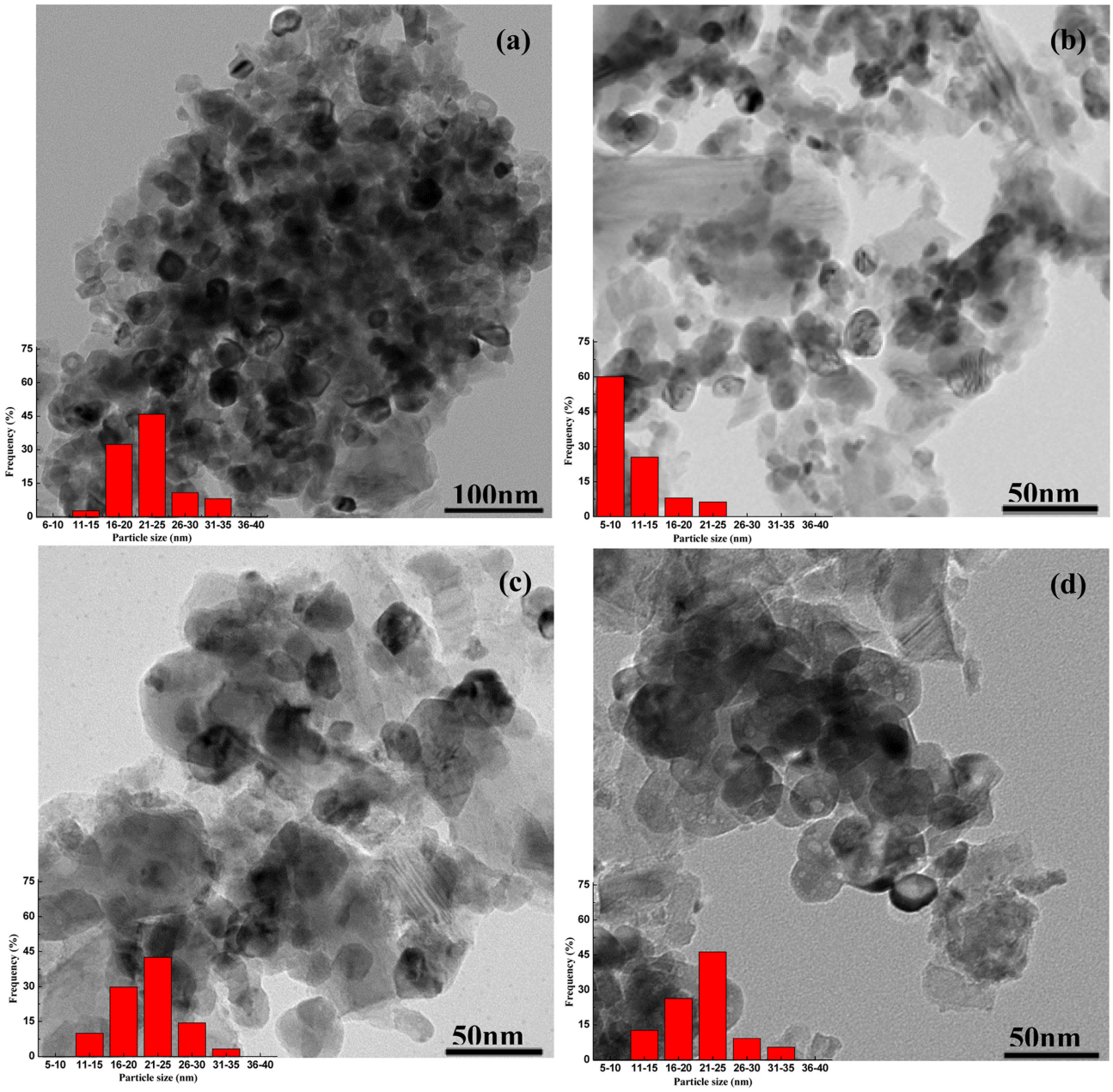

Fig. 5. TEM images and metal particle size distributions of the fresh catalysts. (a) Ni/SiC; (b) 5Co-Ni/SiC; (c) 5Cu-Ni/SiC and (d) 5Zn-Ni/SiC.

tribution of small metal particles further indicates that the active metal is highly dispersed over 5Co-Ni/SiC.

3-2.3. XPS

The relative atom ratios of Ni to Si on the used catalysts obtained from XPS analysis are given in Table 3. The Ni/Si atom ratio is 0.11 for Ni/SiC and 0.15 for 5Co-Ni/SiC, respectively. Obviously, the latter has a higher Ni/Si ratio. This illustrates that the introduction of Co enriches Ni species on the surface of catalyst, which results in the increase of active sites over 5Co-Ni/SiC. For 5Cu-Ni/SiC and 5Zn-Ni/SiC, the Ni/Si atom ratio is 0.09 and 0.07, respectively, which are lower than that of Ni/SiC. Since there is no significant increase of the metal particle sizes over 5Cu-Ni/SiC and 5Zn-Ni/SiC (according to the XRD and TEM results), the lower Ni/Si atom ratio is most likely because the nickel particles on 5Cu-Ni/SiC and 5Zn-Ni/SiC are partially covered by Cu or Zn species, resulting in the decrease of active sites over catalysts.

Fig. 6 shows the XPS results of Ni $2p_{3/2}$ for the used catalysts. The peak at about 853.0 eV should belong to the metallic Ni state [37]. Compared with Ni/SiC, 5Co-Ni/SiC shows a visible negative shift of Ni $2p_{3/2}$ binding energy, suggesting that the electron density on Ni increases. This may be due to the transfer of electrons from cobalt species to nickel species [36-39]. For used 5Cu-Ni/SiC and 5Zn-Ni/SiC, however, the shift of Ni $2p_{3/2}$ binding energy is not detected. Therefore, the addition of Cu and Zn does not influence the electron environment of Ni species. As reported in earlier literature, the dissociation

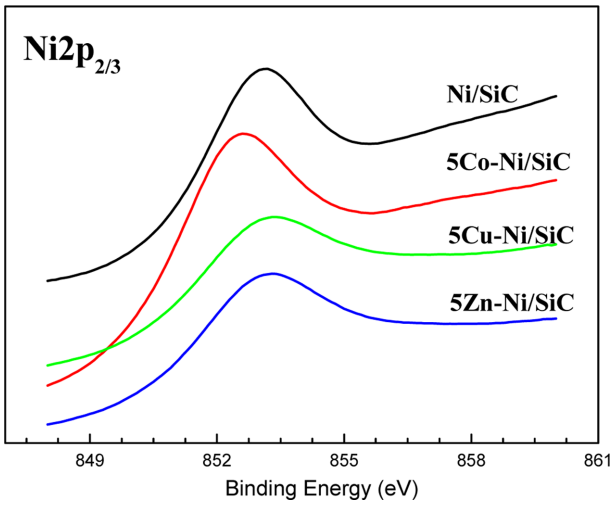

Fig. 6. XPS spectra of $Ni2p_{3/2}$ over the used methanation catalysts.

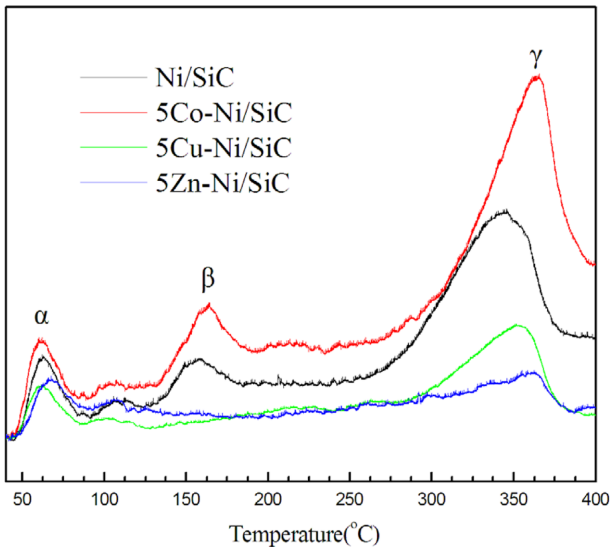

Fig. 7. CO-TPD profiles of pure Ni/SiC and Co-, Cu-, or Zn-modified Ni/SiC catalysts.

of C-O bond in adsorbed CO species is the rate-determining step in the CO methanation reaction [17,40]. When CO is adsorbed on the metal particles [41], a d-π feedback is formed by means of donation of the d-electron of nickel atoms to the vacant anti-bonding π* orbit of carbon monoxide molecule [20]. For 5Co-Ni/SiC, the d-electron density of the surface Ni atoms is increased by the effect of Co species, which can improve the proportion of d-π feedback bond and enhance the electron-feedback capacity of the metal to adsorbed CO. As a result, the Ni-C bond becomes stronger and then the C-O bond is more easily cleaved, making CO be activated more easily. Therefore, the introduction of Co improves the methanation activity of Ni/SiC catalyst.

3-2.4. CO-TPD

CO-TPD was carried out to study the effect of Co, Cu and Zn on the behavior of CO adsorption over the methanation catalysts, and the results are shown in Fig. 7. From the TPD profile of Ni/SiC, there are three desorption peaks (α, β, γ) at 62 °C, 157 °C and 344 °C, respectively. Peak α is generally assigned to the physical adsorption of CO. Peak β can be attributed to desorption of weakly chemisorbed CO. Since the CO methanation reaction occurred at a temperature lower than 200 °C over Ni/SiC (Fig. 2A), this kind of adsorption may play a role for CO activation of CO. Peak γ is probably attributed to desorption of CO which has a strong chemical interaction with metal nickel. This kind of adsorbed CO may be more active because CO can be completely converted at a temperature around 340 °C. For the 5Co-Ni/SiC, the CO-TPD profile is similar to that of Ni/SiC, in which three CO desorption peaks appear. Peaks β and γ in 5Co-Ni/SiC are shifted to higher temperature, compared with those of Ni/SiC, indicating that the introduction of Co species can enhance the interaction between adsorbed CO and active metal. The results obtained from volumetric CO desorption are shown in Table 3. The total amount of desorbed CO from 5Co-Ni/SiC is more than that from Ni/SiC, indicating that the addition of Co species increases the chemisorption amount of CO. On one hand, the introduction of Co enhances metal dispersion and thus results in the increase of active sites. On the other hand, the special interaction between Ni and Co produces a new kind of active site for CO adsorption. For 5Cu-Ni/SiC and 5Zn-Ni/SiC, except the physical adsorption of CO, only one desorption peak ranging from about 290 °C to 380 °C is detected. This indicates that only one type of chemisorbed CO exists on the surface of 5Cu-Ni/SiC and 5Zn-Ni/SiC. This type of CO can produce methane by reacting with H_2, since both 5Cu-Ni/SiC and 5Zn-Ni/SiC show methanation activity until the temperature is higher than 300 °C (Fig. 2A). In addition, from Table 3, the amounts of the chemisorption of CO (peak γ) over both 5Cu-Ni/SiC and 5Zn-Ni/SiC are lower than that over Ni/SiC. This is likely due to the partial coverage of Ni by Cu and Zn species, which results in a decrease of active sites over 5Cu-Ni/SiC and 5Zn-Ni/SiC. Similar results were reported by Mo *et al.* [19], who studied the role of promoters on Rh/SiO_2 catalyst in CO

Table 3. Surface atom ratio of Ni/Si and CO-TPD results over Ni/SiC and Co-, Cu- or Zn-modified Ni/SiC catalysts

Catalysts	Surface atom ratio (Ni/Si)[a]	Desorption temperature (°C)			CO uptake (μmol/g)		
		α	β	γ	α	β	γ
Ni/SiC	0.11	62	157	344	13.95	9.26	79.92
5Co-Ni/SiC	0.15	61	164	363	17.58	12.93	88.63
5Cu-Ni/SiC	0.09	61	-	354	9.96	-	39.83
5Zn-Ni/SiC	0.07	67	-	361	9.18	-	20.17

[a]Obtained from XPS results.

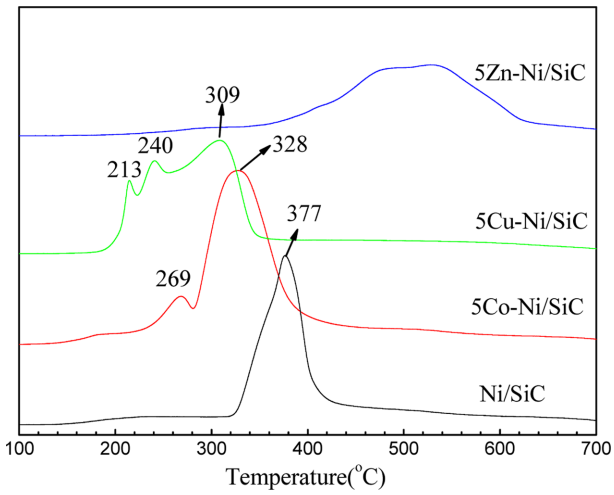

Fig. 8. TPR profiles of pure Ni/SiC and Co-, Cu-, or Zn-modified Ni/SiC catalysts.

hydrogenation reaction using DRIFTS and found that the addition of Cu and Zn suppressed the adsorption of CO on the catalyst significantly. They also investigated the activity of Co/CuZnO catalyst for CO hydrogenation and found that ZnO and Cu could cover/block a substantial number of active sites on Co [42].

3-2.5. H_2-TPR

H_2-TPR was employed to understand the reduction behavior of the methanation catalysts. Fig. 8 shows the TPR results of Ni/SiC and modified Ni/SiC catalysts. For Ni/SiC, only one reduction peak at about 377 °C is detected, indicating that NiO is reduced to metallic Ni. Compared with Ni/SiC, 5Co-Ni/SiC shows a lower reduction temperature at about 328 °C, indicating the addition of Co enhances the reducibility of Ni/SiC catalyst. This may be due to the interaction between Co and Ni species, which decreases the interaction between metal and SiC support [43-45]. In addition, a shoulder peak at about 269 °C is detected in the TPR profile of 5Co-Ni/SiC. In our earlier work, we found the reduction temperature of Co/SiC was about 353 °C [43]. Thus, it is difficult to discriminate the reduction of cobalt oxide from nickel oxide obviously. In the above XRD and XPS discussion, it was found that the introduction of Co species could enrich the Ni species on the surface of catalyst. Hence, the shoulder peak should be attributed to the reduction of surface NiO [43,46].

For 5Cu-Ni/SiC, three reduction peaks are detected. The two peaks at about 213 °C and 240 °C can be assigned to the reduction of different CuO species [47,48], and the reduction peak at 309 °C can be assigned to the reduction of NiO. The lower reduction temperature of NiO can be understood as follows. The reduced copper is able to activate and dissociate hydrogen, which can spill-over to, and subsequently reduce, the adjacent nickel oxide crystallite [49]. A similar result was also reported in the TPR experiment on Cu-Ni/ZrO_2 catalyst by Hernández *et al*. [47], who found that the presence of Cu facilitated the reduction of NiO. One point should be drawn here that although the addition of Cu species can decrease the reduction temperature of NiO, the methanation activity of 5Cu-Ni/SiC is not improved. This indicates the partial coverage of Ni by Cu, which decreases the amount of active sites, may be responsible for the decrease of the methanation activity for 5Cu-Ni/SiC. For 5Zn-Ni/SiC, on the contrary, it shows a wide reduction profile (starts at 380 °C and ends at 640 °C), which is much higher than that of Ni/SiC. This is agreement with the results reported by Zhu *et al*. [46], who found that the reduction temperature of Zn-Ni/SiO_2 catalyst was about 100 °C higher than that of Ni/SiO_2 catalyst. Chen *et al*. [50] also reported that the introduction of Zn could make reduction peak of Ni/Al_2O_3 catalyst shift to higher temperature. The higher reduction temperature of 5Zn-Ni/SiC suggests that the addition of Zn can increase the interaction between metal and support, and then decrease the reducibility of Ni/SiC catalyst.

4. Conclusion

Pure Ni/SiC and Co-, Cu- or Zn-modified Ni/SiC catalysts for CO methanation were prepared by conventional co-impregnation method. The Co-modified Ni/SiC exhibited higher catalytic activity and good selectivity towards CH_4. On the contrary, the addition of Cu and Zn could dramatically reduce the activity of Ni/SiC. In addition, a long-term stability test under 2 MPa and 280 °C showed that 5Co-Ni/SiC was very stable for CO methanation reaction.

To study the influence of Co, Cu and Zn on the catalytic performance of Ni/SiC for CO methanation reaction, XRD, TEM, XPS, CO-TPD and H_2-TPR characterizations were performed. The conclusions are as follows.

(1) The introduction of Co species could decrease the nickel crystallite size and enhance the dispersion of active nickel components, whereas the addition of Cu and Zn could cover partial nickel particles, resulting in a decrease of the active sites on the catalyst surface.

(2) The addition of Co could promote the chemisorption of CO, while the introduction of Cu and Zn could decrease the chemisorption amount of CO on the catalysts.

(3) There might be a special interaction between Co and Ni in 5Co-Ni/SiC and the electron density on nickel is increased. This could enhance the interaction between Ni and CO and promote the dissociation of adsorbed CO.

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References

1. Kustov, A. L., Frey, A. M., Larsen, K. E., Johannessen, T., Nørskov, J. K. and Christensen, C. H., "CO Methanation over Supported

Bimetallic Ni-Fe Catalysts: From Computational Studies Towards Catalyst Optimization," *Appl. Catal. A*, **320**, 98-104(2007).
2. Kopyscinski, J., Schildhauer, T. J. and Biollaz, S. M. A., "Production of Synthetic Natural Gas (SNG) from Coal and Dry Biomass - A Technology Review from 1950 to 2009," *Fuel*, **89**, 1763-1783 (2010).
3. Rostrup-Nielsen, J. R., Pedersen, K. and Sehested, J., "High Temperature Methanation: Sintering and Structure Sensitivity," *Appl. Catal. A*: *Gen*., **330**, 134-138(2007).
4. Vitasari, C. R., Jurascik, M. and Ptasinski, K. J., "Exergy Analysis of Biomass-to-synthetic Natural Gas (SNG) Process via Indirect Gasification of Various Biomass Feedstock," *Energy*, **36**, 3825-3837(2011).
5. Liu, Z. H., Chu, B. Z., Zhai, X. L., Jin, Y. and Cheng, Y., "Total Methanation of Syngas to Synthetic Natural Gas over Ni Catalyst in a Micro-channel Reactor," *Fuel*, **95**, 599-605(2012).
6. Meijden, C. M. V. D., Veringa, H. J. and Rabou, L. P. L. M., "The Production of Synthetic Natural Gas (SNG): A Comparison of Three Wood Gasification Systems for Energy Balance and Overall Efficiency," *Biomass Bioenergy*, **34**, 302-311(2010).
7. Gröbl, T., Walter, H. and Haider, M., "Biomass Steam Gasification for Production of SNG - Process Design and Sensitivity Analysis," *Applied Energy*, **97**, 451-461(2012).
8. Wirth, S. and Markard, J., "Context Matters: How Existing Sectors and Competing Technologies Affect the Prospects of the Swiss Bio-SNG Innovation System," *Technological Forecasting and Social Change*, **78**, 635-649(2011).
9. Shen, W. J., Okumura, M., Matsumura1, Y. and Haruta, M., "The Influence of the Support on the Activity and Selectivity of Pd in CO Hydrogenation," *Appl. Catal. A: Gen.*, **213**, 225-232(2001).
10. Takenaka, S., Shimizu, T. and Otsuka, K., "Complete Removal of Carbon Monoxide in Hydrogen-rich Gas Stream Through Methanation over Supported Metal Catalysts," *Int. J. Hydrogen Energy* **29**, 1065-1073(2004).
11. Panagiotopoulou, P., Kondarides, D. I. and Verykios, X. E., "Selective Methanation of CO over Supported Noble Metal Catalysts: Effects of the Nature of the Metallic Phase on Catalytic Performance," *Appl. Catal. A: Gen*., **344**, 45-54(2008).
12. Panagiotopoulou, P., Kondarides, D. I. and Verykios, X. E., "Selective Methanation of CO over Supported Ru Catalysts," *Appl. Catal. B: Environ*., **88**, 470-478(2009).
13. Kowalczyk, Z., Stołecki, K., Raróg-Pilecka, W., Miśkiewicz, E., Wilczkowska, E. and Karpiński, Z., "Supported Ruthenium Catalysts for Selective Methanation of Carbon Oxides at Very Low CO_x/H_2 Ratios," *Appl. Catal. A: Gen*., **342**, 35-39(2008).
14. Utaka, T., Takeguchi, T., Kikuchi, R. and Eguchi, K., "CO Removal from Reformed Fuels over Cu and Precious Metal Catalysts," *Appl. Catal. A: Gen*., **246**, 117-124(2003).
15. Tsai, Y. T., Mo, X. H. and Goodwin Jr, J. G., "The Synthesis of Hydrocarbons and Oxygenates During CO Hydrogenation on CoCuZnO Catalysts: Analysis at the Site Level Using Multiproduct SSITKA," *J. Catal*., **285**, 242-250(2012).
16. Sabatier, P. and Senderens, J. B., "New Synthesis of Methane," *Acad. Sci*., **134**, 514-516(1902).
17. Morl, T., Masuda, H. and Imal, H., "Kinetics, Isotope Effects, and Mechanism for the Hydrogenation of Carbon Monoxide on Supported Nickel Catalysts," *J. Phys. Chem*., **86**, 2753-2760(1982).
18. Fujitani, S.-I., Takezawa, N., Uchijima, T. and Nakamura, J., "Methanol Synthesis by Hydrogenation of CO_2 over a Zn-deposited Cu(111): Formate Intermediate," *Chem. Eng. J*., **68**, 63-38(1997).
19. Mo, X. H., Gao, J. and Goodwin Jr, J. G., " Effect of Component Interaction on the Activity of Co/CuZnO for CO Hydrogenation," *Catalysis*, **285**, 208-215(2012).
20. Znak, L., Stolecki, K. and Zieliński, J., "The Effect of Cerium, Lanthanum and Zirconium on Nickel/alumina Catalysts for the Hydrogenation of Carbon Oxides," *Catal. Today*, **101**, 65-71(2005).
21. Hu, X. and Lu, G. X., "Inhibition of Methane Formation in Steam Reforming Reactions Through Modification of Ni Catalyst and the Reactants," *Green Chem*., **11**, 724-732(2009).
22. Gao, J., Mo, X. H., Chien, A. C.-Y., Torres, W. and Goodwin Jr, J. G., "CO Hydrogenation on Lanthana and Vanadia Doubly Promoted Rh/SiO_2 Catalysts," *Catalysis*, **262**, 119-126(2009).
23. Wu, R. F., Zhang, Y., Wang, Y. Z., Gao, C. G. and Zhao, Y. X., *J. Fuel Chem. Tech*., **37**, 578-582(2009).
24. Wang, Y. Z., Wu, R. F. and Zhao, Y. X., "Effect of ZrO_2 Promoter on Structure and Catalytic Activity of the Ni/SiO_2 Catalyst for CO Methanation in Hydrogen-rich Gases," *Catal. Today*, **158**, 470-474(2010).
25. Karaselçuk, R., İnci İşli, A., Erhan Aksoylu, A., İlsen Önsan Z., "CO Hydrogenation over Bimetallic Nickel-vanadium Catalysts," *Appl. Catal. A: Gen*., **192**, 263-271(2000).
26. Kip, B. J., Smessts, P. A. T., Grondelle, J. and Van, Prins R., "Hydrogenation of Carbon Monoxide over Vanadium Oxide-promoted Rhodium Catalysts," *Appl. Catal*., **33**, 181-208(1987).
27. Ishihara, T., Eguchi, K. and Arai, H., "Hydrogenation of Carbon Monoxide over SiO_2-supported Fe-Co, Co-Ni and Ni-Fe Bimetallic Catalysts," *Appl. Catal*., **30**, 225-238(1987).
28. Wang, J. J., Chernavskii, P. A., Khodakov, A. Y. and Wang, Y., "Structure and Catalytic Performance of Alumina-supported Copper-cobalt Catalysts for Carbon Monoxide Hydrogenation," *Catalysis*, **286**, 51-61(2012).
29. Zhao, J. J., Zong, Z. M., Xie, H. S., Liu, T., Li, J. J., Wang, T. T. and Wei, X. Y., *Mining Science and Technology* (China), **20**, 296-311(2010).
30. Boellard, E., Scheur, F. Th., Kraan, and A. M., Geus, J. W., "Preparation, Reduction, and CO Chemisorption Properties of Cyanide-derived $CuxFe/Al_2O_3$ Catalysts," *Appl. Catal. A*, **171**, 333-350(1998).
31. Fujitani, T., Nakamura, I., Ueno, S., Uchijima, T., Nakamura, J., *J. Appl. Surf. Sci*., **122**, 583-586(1997).
32. Lin, M. G., Fang, K. G., Li, D. B. and Sun, Y. H., "CO Hydrogenation to Mixed Alcohols over co-precipitated Cu-Fe Catalysts," *Catal. Commun*., **9**, 1869-1873(2008).
33. Yu, Y., Jin, G. Q., Wang, Y. Y. and Guo, X. Y., "Synthetic Natural Gas from CO Hydrogenation over Silicon Carbide Supported Nickel Catalysts," *Fuel Process. Technol.*, **92**, 2293-2298(2011).
34. Jin, G. Q. and Guo, X. Y., "Synthesis and Characterization of Mesoporous Silicon Carbide," *Micropor. Mesopor. Mater*., **60**, 207-212(2003).
35. Ni, Y. H., Wang, F., Liu, H. J., Liang, Y. Y., Yin, G., Hong, J. M., Ma, X. and Xu, Z., "Fabrication and Characterization of Hollow Cuprous Sulfide (Cu_2-xS) Microspheres by a Simple Template-free Route," *Inorg. Chem. Commun*., **6**, 1406-1408(2003).
36. Zhang, J. G., Wang, H. and Dalai, A. K., "Development of Stable Bimetallic Catalysts for Carbon Dioxide Reforming of Meth-

ane," *Catalysis*, **249**, 300-310(2007).
37. Czekaj, I., Loviat, F., Raimondi, F., Wambach, J., Biollaz, S. and Wokaun, A., "Characterization of Surface Processes at the Ni-based Catalyst During the Methanation of Biomass-derived Synthesis Gas: X-ray Photoelectron Spectroscopy (XPS)," *Appl. Catal. A: Gen*., **329**, 68-78(2007).
38. Yu, Z. B., Qiao, M. H., Li, H. X. and Deng, J. F., "Preparation of Amorphous Ni-Co-B Alloys and the Effect of Cobalt on Their Hydrogenation Activity," *Appl. Catal. A: Gen*., **163**, 1-13(1997).
39. Petrov, K. and Will, G., "A New Cobalt-nickel Oxide Spinel Prepared Under High Pressure in An Oxygen Atmosphere," *J. Mater. Sci. Lett*., **6**, 1153-1155(1987).
40. Engbæk, J., Lytken, O., Nielsen, J. H. and Chorkendorff, I., "CO Dissociation on Ni: The Effect of Steps and of Nickel Carbonyl," *Surf. Sci*., **602**, 733-743(2008).
41. Hayes, R. E., Thomas, W. J. and Hayes, K. E., "A Study of the Nickel-catalyzed Methanation Reaction," *Catalysis*, **92**, 312-326 (1985).
42. Mo, X. H., Tsai, Y.-T., Gao, J., Mao, D. S. and Goodwin, Jr J. G., "Effect of Component Interaction on the Activity of Co/CuZnO for CO Hydrogenation," *Catalysis*, **285**, 208-215(2012).
43. Yu, Y., Jin, G. Q., Wang, Y. Y. and Guo, X. Y., "Synthesis of Natural Gas from CO Methanation over SiC Supported Ni-Co Bimetallic Catalysts," *Catal. Commun*., **31**, 5-10(2013).
44. Xu, J. K., Zhou, W., Li, Z. J., Wang, J. H. and Ma, J. X., "Biogas Reforming for Hydrogen Production over Nickel and Cobalt Bimetallic Catalysts," *Int. J. Hydrogen Energy*, **34**, 6646-6654(2009).
45. Li, L., Lu, P., Yao, Y. and Ji, W. J., "Silica-encapsulated Bimetallic Co-Ni Nanoparticles as Novel Catalysts for Partial Oxidation of Methane to Synga," *Catal. Commun*., **26**, 72-77(2012).
46. Zhu, J. Q., Peng, X. X., Yao, L., Shen, J., Tong, D. M. and Hu, C. W., "The Promoting Effect of La, Mg, Co and Zn on the Activity and Stability of Ni/SiO_2 Catalyst for CO_2 Reforming of Methane," *Int. J. Hydrogen Energy*, **36**, 7094-7104(2011).
47. Hernández, R. P., Galicia, G. M., Anaya, D. M., Palacios, J., Chavez, C. A. and Alatorre, J. A., "Synthesis and Characterization of Bimetallic $Cu-Ni/ZrO_2$ Nanocatalysts: H_2 Production by Oxidative Steam Reforming of Methanol," *Int. J. Hydrogen Energy*, **38**, 4569-4576 (2008).
48. Lee, J. H., Lee, E. G., Joo, O. S. and Jung, K. D., "Stabilization of Ni/Al_2O_3 Catalyst by Cu Addition for CO_2 Reforming of Methane," *Appl. Catal. A: Gen*., **289**, 1-6(2004).
49. Boellard, E., Scheur, F. Th., Kraan, A. M. and Geus, J. W., *Appl. Catal. A: Gen*., **171**, 333-350(1998).
50. Chen, J. L., Qiao, Y. H., Li, Y. D., "Methanation Sites on a Low Loading Ni/Al_2O_3 Catalyst," *Appl. Catal. A: Gen*., **337**, 148-154 (2008).