Stepwise conversion of methane over supported metal-boron amorphous alloy catalysts

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Received 5 July 2001; accepted 16 October 2001

The stepwise conversion of CH_4 to higher hydrocarbons over HMCM-22 zeolite supported metal-boron amorphous alloy catalysts has been investigated, including: (1) the influence of metals (Co, Ni, Pt, Rh and Ru) of the catalysts on the reaction; (2) the promotional effect of V on the catalytic behavior of the catalysts; (3) the influence of hydrogenation pressure and CH_4 decomposition temperature; and (4) the nature of carbon species. It is found that the yield of C_2^+ hydrocarbons is strongly dependent on the metals. Good yields of C_2^+ hydrocarbon are reached only on the supported NiB and CoB catalysts. The probability of C–C chain growth is increased by V promotion without seriously affecting the activities of CH_4 decomposition and hydrogenation. The ease of carbon removal *via* hydrogenation is strongly affected by the CH_4 decomposition temperature. Increasing hydrogenation temperature has a negative effect on the yield of C_2^+ hydrocarbons. XPS measurements show that a carbide(-like) carbon species is active and selective for hydrogenation to produce higher hydrocarbons. Its activity/selectivity is greatly reduced at high CH_4 decomposition temperatures, mainly due to transition of the reactive carbidic to un-reactive graphitic form. Graphite/filamental carbons were found to be formed at high CH_4 decomposition temperature.

KEY WORDS: stepwise conversion of methane; amorphous alloy catalyst; hydrogenation; hydrogen production; higher hydrocarbon formation; carbon

1. Introduction

Oxygen-free stepwise conversion of methane to higher hydrocarbons has been the objective of many studies since this process was proposed by three independent contributions in 1991 [1–3]. This process consists of two steps separated by time and temperature, with the first being the catalytic decomposition of methane on metal, followed by the subsequent hydrogenation of the carbon species at the same temperature (isothermal procedure) or a temperature lower than that of the exposure to CH_4 (dual temperature procedure):

$$CH_4 \rightarrow C_{ads}/[CH_x]_{ads} + H_2 \qquad \text{(Step I)}$$

$$C_{ads}/[CH_x]_{ads} + H_2 \rightarrow C_nH_{2n+2}, C_nH_{2n}, \text{Aromatics.} \qquad \text{(Step II)}$$

Clearly, this process shows advantages in production of *CO-free* hydrogen and higher hydrocarbons from CH_4 decomposition with 100% atom utilization. Recent studies [4–6] have shown that *CO-free* hydrogen can be produced successfully by a stepwise steam-reforming process.

In the preliminary work by Belgued *et al.* [1], an isothermal procedure at 250 °C over a standard Pt catalyst was carried out and 19.3% of carbon hydrogenated with 7.9% yield of C_2^+ was achieved. In addition, during exposure of CH_4 to this Pt catalyst, the continuous evolution of *CO-free* hydrogen could be obtained. In the experiments by Koerts and van Santen [2], CH_4 interacted with Ru or Co catalyst at a higher temperature (450 °C) while the subsequent hydrogenation was carried out at ~100 °C, and the maximum overall C_2^+ hydrocarbon yield of 13% was achieved. The above reports were extended to various group VIII metals and were confirmed by several authors [7–16]. The improvement of Ru/SiO_2 catalyst with Cu promotion was conducted by Goodman *et al.* [17] and Solymosi *et al.* [18]. On a Ru-Cu/SiO_2 ($Cu/Ru = 0.1$) catalyst ~80% of carbon hydrogenated with ~15% ethane selectivity was reported [17]. Comparative study on Ru/SiO_2 and Ru/SiO_2 promoted with V for labeled *n*-hexane production from 1-pentene and ^{11}CO was carried out by van Santen *et al.* [19] via a dual temperature procedure. They observed that total *n*-hexane selectivity based on the total quantity of adsorbed ^{11}C increased for the V-promoted Ru/SiO_2. Recently, supported NiB amorphous alloy catalysts were employed for this novel route for methane conversion by our group [20], because of their specific properties in catalysis, derived from the combination of their short-range order and long-range disorder in structure and nanoscale size [21]. It is found that on a supported NiB amorphous alloy catalyst, at 300 °C 60.1% of the carbon formed from CH_4 decomposition was converted *via* hydrogenation with a 16.1% yield of C2–C3 hydrocarbons during 10-min hydrogenation.

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Increasing hydrogenation time to 30 min, 94.3% of total carbon formed in Step I was gasified with a total yield of C2–C3 hydrocarbon of 24.9%.

In this work, a series of HMCM-22 zeolite supported metal-boron amorphous alloy catalysts prepared by a chemical reduction method were examined for catalytic performance in this stepwise CH_4 conversion. In order to improve the selectivity, V-promoted catalysts were also prepared and their activity/selectivity performance for this reaction was examined. In order to optimize the reaction conditions, the stepwise conversion of CH_4 as a function of CH_4 decomposition temperature and H_2 pressure was conducted. Moreover, the nature of carbon species formed from CH_4 decomposition was also studied using XPS and TEM.

2. Experimental

2.1. Catalyst preparation and treatment

A series of HMCM-22 (molar SiO_2/Al_2O_3 ratio: 50; SA: 380 m^2/g, supplied by RIPP, China Petrochemical Corporation) supported metal-boron amorphous alloy catalysts with a metal loading of 10 wt% (for Ni and Co) or 5 wt% (for Pt, Ru, Rh) were prepared by a chemical reduction method and denoted as MB/Z, where $NiCl_2{\cdot}6H_2O$, $CoCl_2{\cdot}6H_2O$, $H_2PtCl_6{\cdot}6H_2O$, $RuCl_3{\cdot}xH_2O$ (Ru = 39.15%, Alfa Aesar), and $RhCl_3{\cdot}2H_2O$ (Rh = 40.37%, Alfa Aesar) were used as starting precursors. Details of catalyst preparative procedures, storage and treatment prior to the reaction have been reported previously [20]. As for the preparation of V-promoted catalysts, three V-containing HMCM-22 supports with V-loading of 0.1 wt%, 0.5 wt% and 1.0 wt% were prepared by the incipient wetness impregnation method in advance. For instance, for the support with V-loading of 0.5 wt%, 5.0 g of HMCM-22 was impregnated using an equivalent volume of the solution (0.058 g of NH_4VO_3 was dissolved in 10% ammonia) and dried. This procedure was repeated until the solution was used up and then was followed by overnight drying at 100 °C. ICP-AES measurements indicated that the V contents for these three supports were 0.09 wt%, 0.53 wt% and 9.91 wt% respectively. Then, such zeolites were used as support to prepare V-promoted metal-boron amorphous alloy catalysts with a metal loading of 10 wt% via preparative procedures similar to those for the pure MB/Z catalysts.

2.2. Micro-reactor evaluation

The reaction was carried out on a stainless steel tube micro-reactor in the temperature range between 150 and 600 °C, using 100 mg of catalyst. Three types of experiments were carried out: (1) isothermal procedure at 300 °C under atmospheric pressure; (2) isothermal procedure at 300 °C where hydrogenation was performed at elevated pressure up to 60 bars; (3) dual temperature procedure, *i.e.*, CH_4 was decomposed at high temperatures (300–600 °C) and the reacted catalyst was then cooled rapidly to 300 °C or 150 °C where hydrogenation was carried out. In Step I, 2462 μmol of highly pure methane was allowed to flow over a catalyst bed at a flow rate of 6 ml/min for 10 min. In Step II, the above CH_4-reacted catalyst bed was flushed thoroughly with Ar and then was hydrogenated in a hydrogen flow (6 ml/min) for 10 min at appointed H_2 pressure. The gas flow rates were all controlled by Brooks 5850E thermal mass flow controllers. The outlet gases in Step I and Step II were collected respectively using a wet meter which can display the volume of the gases accurately and then analyzed by a GC equipped with a TCD and a FID in series. The TCD connected with a Porapak Q column (2.0 m; 60 °C) was used for the hydrogen analysis. The FID fixed with the same column was used for the hydrocarbon analysis. The amount of methane unreacted in Step I as well as the total amount of hydrocarbons including methane formed during hydrogenation were determined from the concentration results (from GC) and gas volume. Thus, methane conversion in Step I as well as carbon hydrogenated and yield of C2–C3 hydrocarbon in Step II could be determined on a C-atom basis. Only traces of C_4^+ hydrocarbons could be detected during hydrogenation and hence are not mentioned further in this study.

2.3. Catalyst characterization

TEM measurements of catalysts and filamental carbon were carried out using a JEM-1200EX/9100EDAX instrument. From the TEM images the particle size was found to lie in the range of 20–30 nm for Ni and Co based catalysts and 10–20 nm for precious metal based catalysts.

Powder XRD patterns were recorded on a Brucker AXS D8 using a scanning speed of 0.05°/s and an accelerating voltage of 40 kV. According to the XRD patterns of the as-synthesized catalysts, by subtracting the peaks resulting from the HMCM-22 zeolite support, only quite weak broad peaks corresponding to the metals were observed, indicating their typical amorphous character.

XPS analyses were carried out on VG ESCALAB MKII, using a Mg Kα X-ray source (1253.6 eV, 150W) at a constant analyzer pass energy of 20 eV. The charging effect was corrected by referring to contaminative C1s at 284.6 eV of binding energy. XPS measurements for a V-promoted NiB/Z catalyst with a V loading of 0.5 wt% show that the Ni2p binding energy of 853.1 eV is similar to that for non-promoted base catalyst reported by our previous work [20], suggesting that the electron deficiency of Ni is not affected obviously by V-modification.

3. Results and discussion

3.1. Comparison of metals for isothermal stepwise conversion of CH_4

The reaction results over a series of HMCM-22 zeolite supported catalysts are summarized in table 1. In each case the values quoted are results where the optimum conditions were used to maximize C_2^+ hydrocarbon yield. In our previous work [20], an optimum temperature for this reaction has been found at 300 °C where a maximum yield for C_2^+ hydrocarbon was obtained. In Step I, all catalysts behave in a very similar manner in terms of CH_4 conversion and yields of H_2 and surface hydrocarbonaceous species. The main carbon-containing product formed from CH_4 decomposition is carbon. C2–C3 hydrocarbons could also be formed with a low selectivity in this step. In Step II, all catalysts offer similar conversion of carbon; however, the yield of C2–C3 hydrocarbons attenuates in the following order for supported metal-boron amorphous alloy catalysts: Co, Ni > Pt, Ru, Rh. Note that both CoB/Z and NiB/Z catalysts show a similar product yield of ~16% which is ~3% higher than the maximum value (C_2^+ yield: 13%) achieved by Koerts and van Santen on a Ru catalyst [2]. Our previous work [20] showed that metalloid element boron exhibits a great promotional effect on the catalytic behavior for Ni-based catalysts, and pointed out that the higher yield of C_2^+ hydrocarbon on supported NiB amorphous alloy catalyst is attributed to its nanoscale size, short-range disorder in structure, and electron-deficiency. Here, precious metal amorphous alloy catalysts, however, give a lower product yield of ~7%, which is comparable to those reported by Belgued *et al.* [1] on a Pt catalyst and by Goodman *et al.* [17] on a Ru catalyst. Hence, Ni and/or Co based catalysts were employed in the following studies.

3.2. Promotional effect of V on the reaction

The catalytic behaviors of V-promoted NiB/Z and CoB/Z catalysts were examined for the isothermal stepwise conversion of methane. The methane conversion, yields of C2 and C3 hydrocarbons, and carbon hydrogenated at 300 °C as a function of V loadings are displayed in figure 1. Clearly, the V-promotional effect is the same on both supported NiB and CoB catalysts. For V-promoted NiB/Z catalysts, compared with the pure NiB/Z catalyst, V modification causes a slight loss in activity for CH_4 decomposition and hydrogenation but noticeably affects the selectivity of the C_2^+ hydrocarbon product. For the catalyst with V loadings of 0.1 wt%, methane conversion, C_2^+ hydrocarbon yield and carbon hydrogenated are similar to the corresponding pure catalyst. With increase of V loadings to 0.5 wt%, the activity for CH_4 decomposition and the percentage of carbon hydrogenated decrease slightly, the yield of C_2 and C_3 hydrocarbons however increases from 11.0% and 5.2% for the pure catalyst to 11.8% and 5.8% respectively. With further increase of V loadings up to 1.0 wt%, the activity for CH_4 decomposition and the percentage of carbon hydrogenated decrease to 1.7% and 45% respectively while the yield of C_2 hydrocarbon decreases by 1.2% compared with that for the V-promoted catalyst with V-loading of 0.5 wt%. However, note that the yield of C_3 hydrocarbon increases slightly and reaches 6.0%.

The above results suggest that the presence of V noticeably affects the nature of carbon intermediates formed during the hydrogenation. van Santen's group has shown that the activation energy for the hydrogenation of all carbon-containing surface species is increased by V modification on Ru [19] and Rh [22] catalysts. They reached a conclusion that the carbon species are more strongly bonded to the catalyst surface, and therefore more likely to take place in C–C coupling reactions, which is further confirmed by our observations.

3.3. Isothermal stepwise conversion of CH_4 at elevated hydrogenation pressure

The effect of hydrogen pressure on carbon hydrogenation and yield of C_2^+ hydrocarbon was studied via an isothermal procedure at 300 °C, using a V-promoted NiB/Z with V-loadings of 0.5 wt%. In each case, fresh catalyst

Table 1
Results of the isothermal stepwise conversion of CH_4 to H_2 and higher hydrocarbons over a series of HMCM-22 zeolite supported metal-boron amorphous alloy catalysts at 300 °C

Catalyst	Step I, mol%				Step II, mol%		
	X_{CH_4}	Y_{H_2}	$Y_{C2\text{-}C3}$	Y_C	X_C	Y_{C2}	Y_{C3}
CoB/Z [a]	2.0	1.4	0.3	1.7	61.9	10.8	5.1
NiB/Z [a]	2.1	1.2	0.4	1.7	60.1	11.0	5.2
PtB/Z [b]	1.9	1.3	0.3	1.6	62.3	4.5	3.1
RuB/Z [b]	1.8	1.2	0.3	1.5	62.0	4.2	2.3
RhB/Z [b]	1.9	1.2	0.4	1.5	61.1	5.4	2.0

X: conversion; *Y*: yield.

[a] With metal loading of 10 wt%.

[b] With metal loading of 5 wt%.

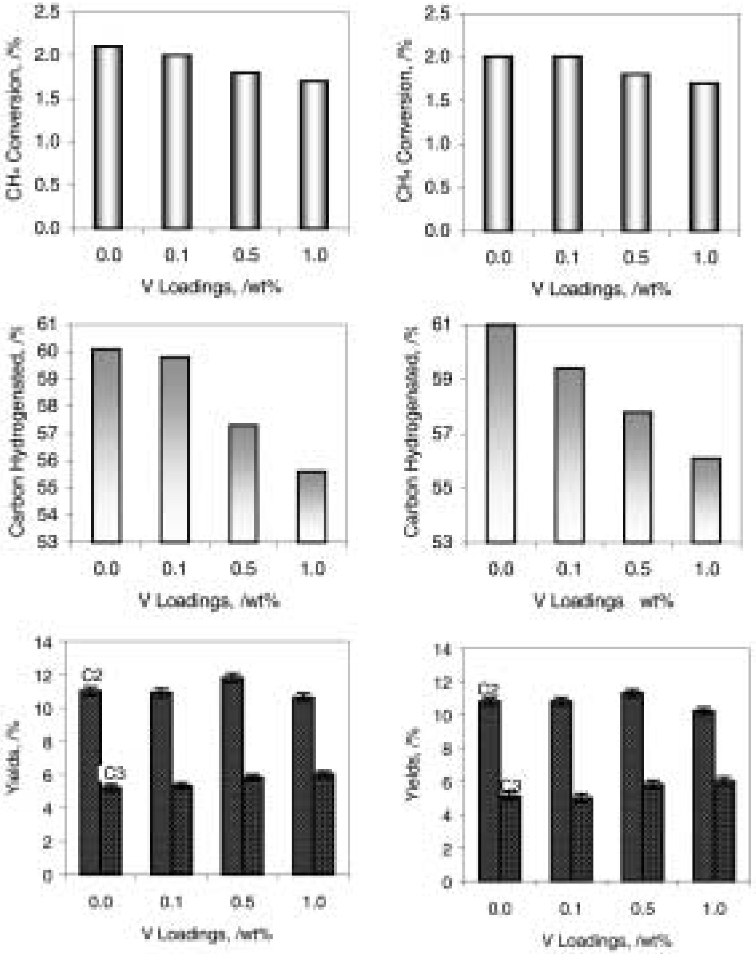

Figure 1. Methane conversion, yields of C2 and C3, and carbon hydrogenated at 300 °C as a function of V loadings for a series of NiB/Z and CoB/Z with V modification.

was used and reacted with methane at the same conditions prior to hydrogenation at the appointed pressure. The carbon hydrogenated and yield of C_2^+ hydrocarbon as a function of hydrogen pressure is displayed in figure 2. The carbon hydrogenated increases with the increase in hydrogenation pressure. However, the yield of C_2^+ hydrocarbon decreases significantly in such an operation. For example, increasing the hydrogen pressure from 1 bar to 30 bars decreases the yield of C_2^+ from 17.6% to 14.9%, and up to 60 bars only 12.4% is left. On the one hand, high pressure of hydrogen causes more hydrogen atoms to be adsorbed on the surface of the catalyst, which in turn suggests that the probability is higher for C–H formation to produce CH_4 but lower for the chain growth to produce C_2^+ hydrocarbon. High pressure of hydrogen, on the other hand, favors the hydrogenation cracking of the formed C_2^+ hydrocarbon product, which also results in the decrease of such desired products.

3.4. Dual temperature stepwise conversion of CH_4 over a V-promoted NiB/Z

A dual temperature reaction, where catalyst reacted with methane at temperatures between 300 and 600 °C followed by rehydrogenation at 300 °C or 150 °C, was also carried out in this work, using a V-promoted NiB/Z with V-loadings of 0.5 wt%. Methane conversion, yield of C_2^+ hydrocarbon and carbon hydrogenated as a function of methane decomposition temperature are displayed in figure 3. With increase of the temperature, CH_4 conversion increases slowly up to 500 °C and sharply from 500 °C to 600 °C. This is consistent with the trend observed by several authors [7,11–13,17,23]. However, carbon hydrogenated and yield of C_2^+ hydrocarbon decrease obviously with increase in methane decomposition temperature. The yield of C_2^+ product decreases from 17.6% at 300 °C to 1.3% at 600 °C while carbon hydrogenated decreases by over four fifths of the maximum conversion. Similar trends were observed also by Belgued and coworkers [7] on Pt/SiO_2 catalyst under methane decomposition temperature higher than 250 °C. This result suggests that carbon species from CH_4 decomposition rapidly transform to "inactive" carbon and this transformation is accelerated greatly with increasing methane decomposition temperature. A comparison of the yield of the C_2^+ hydrocarbon product under different hydrogenation temperatures at 150 °C and 300 °C is also presented in figure 3. It is

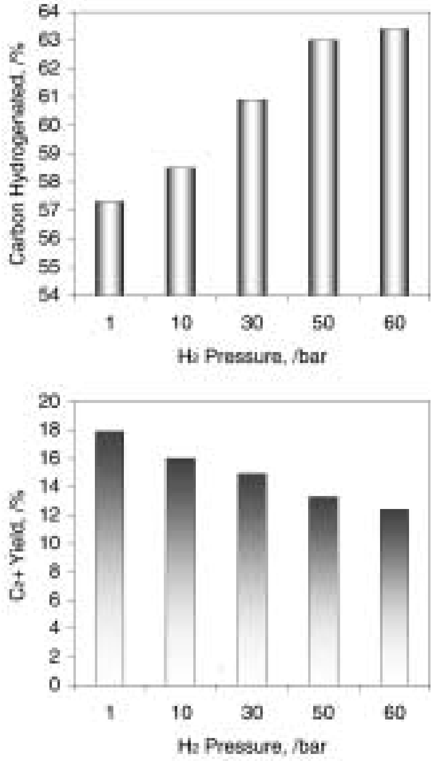

Figure 2. Methane conversion, yields of C2 and C3, and carbon hydrogenated at 300 °C as a function of the hydrogenation pressure for a V-promoted NiB/Z with a V loading of 0.5 wt%.

noticed that the yield obtained at 150 °C is lower than that at 300 °C for the reacted catalyst with CH_4 at 300 °C, confirming the optimum temperature for both CH_4 decomposition and subsequent hydrogenation is around 300 °C [20]. Belgued and coworkers [7] indicated that on a standard Pt catalyst the total C_2^+ production was maximum around 250–300 °C.

3.5. XPS and TEM studies on the nature of carbon species

To understand the nature of the carbon species, XPS measurements were carried out on a series of CH_4-reacted V-promoted NiB/Z before and after rehydrogenation at 300 °C. XPS spectra in the C1s region are displayed in figure 4. In comparison with the fresh catalyst, strong C1s peaks at ~283.4 eV appear for all the catalysts exposed to CH_4 for 10 min at various temperatures followed by fast cooling using ice (see figure 4(a), (b), (d) and (f)), which are assigned to carbide carbon. With the increase in the CH_4 decomposition temperature from 300 °C to 600 °C, the C1s peak intensity of the carbide carbon increases greatly, which is in agreement with the trend of the carbon yield in CH_4 decomposition with increasing temperature shown in figure 3. Several contributions [23–26] have shown that carbide carbon had been definitely detected by XPS on CH_4-reacted Ni and Co catalyst surfaces at 700 °C or higher temperature, while Auger analyses [23,24] showed that the shape of carbide C KVV peaks at 250–280 eV was very close to the carbide carbon on Ir [27]. Recently, Choudhary *et al.* [6] claimed that the carbidic form does not exist at 600 °C for Ni/SiO_2. Nevertheless it should be noted that their experiment was carried out on a completely deactivated Ni/SiO_2 for a stepwise steam-reforming process at 600 °C. In this case, CH_4 would not be activated further to form the carbidic form, while the carbidic carbon built up on the surface might have enough time to turn into the graphitic form during the slow cooling of the sample from 600 °C to room temperature.

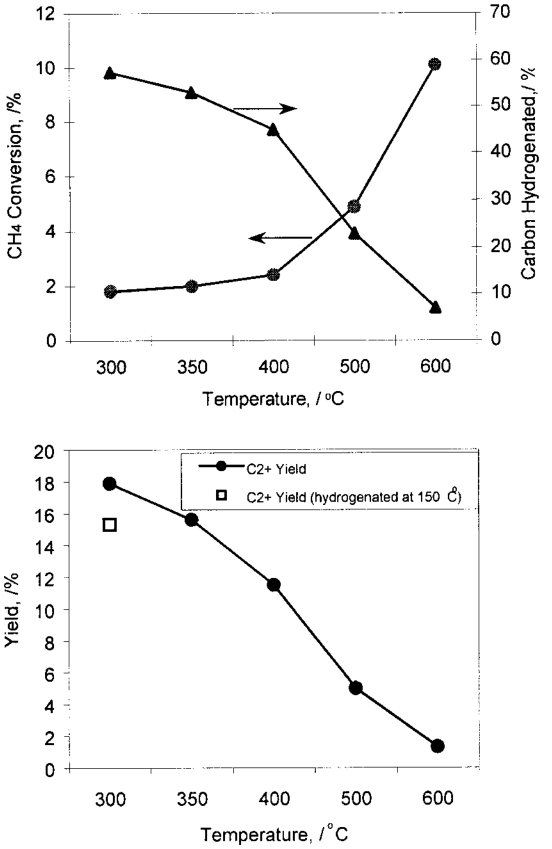

Figure 3. Methane conversion, C_2^+ yield, and carbon hydrogenated at 300 °C (and 150 °C) as a function of the methane decomposition temperature for the V-promoted NiB/Z with a V loading of 0.5 wt%.

However, after exposure of the CH_4-reacted catalysts in figure 4(b), (d) and (f) to hydrogen at 300 °C for 10 min, the C1s peak areas of the carbide carbon decrease by 51%, 40% and 12% respectively (see figure 4(c), (e) and (g)), indicating again that the carbon removal in the hydrogenation step becomes more and more difficult with increase in CH_4 decomposition temperature. Meanwhile, increasing the CH_4 decomposition temperature dramatically reduces the Ni2p peak intensity of the metallic Ni for the catalysts; even no detectable Ni2p XPS signals can be observed for the catalysts used in figure 4(f) and (g), suggesting that the catalyst surface is covered more and more seriously with the carbon formed at high temperatures. Goodman and coworkers [12] suggested that the nature of intermediates may be affected by the presence of "inactive" carbon. Hence, the difficulty in carbon removal at high temperatures is mainly due to the transition of the reactive carbide to un-reactive graphitic carbon. On the other hand, higher carbon coverage at high temperatures would result in a reduction in the number of metal sites, even total deactivation of the catalyst.

In contrast to the results shown in figure 4(b) and (c), the same C1s peak at 283.3 eV was observed for the basic non-promoted NiB/Z reacted with CH_4 at 300 °C for 10 min and its peak area decreased by ~53% after a 10-min hydrogenation. This means that the nature of the carbon species formed from CH_4 decomposition is not affected seriously by the V-modification. However, the yield behavior of the NiB/Z catalyst was improved indeed with the modification of V (see figure 2) while neither shift of the B.E. of the V element nor change of the V^{5+}/V^{4+} ratio on all catalyst surfaces used in figure 4 was detected by XPS. Thus, we believe that the presence of V noticeably affects the nature of carbon intermediates (*i.e.*, CH_x) formed during the rehydrogenation but not the carbon species formed from CH_4 decomposition: such CH_x species are more strongly bonded to such a catalyst surface than those to the surface of the non-promoted NiB/Z catalyst and therefore are more likely to take place in C–C coupling reactions.

Additionally, it is found that the peak intensity of the C1s peak at about 284.5 eV for the catalysts in figure 4(b) and (c) is close to that for the fresh catalyst in figure 4(a). With increase in the CH_4 decomposition temperature, the peak intensity of such a C1s peak for the catalysts in figure 4(d) and (f) increases pronouncedly, compared with that for the catalyst in figure 4(a), (b) or (c). Meanwhile, the charging effect decreases significantly from 7.2 eV for the catalyst in figure 4(b) to 2.1 eV for the one in figure 4(f). At the same time, filamental carbon with a diameter of 7 nm was observed by TEM on the catalyst used in figure 4(f) and (g) but not on the one used in figure 4(d) and (e). The above results reveal that the carbide carbon transfers to graphite carbon, even filamental carbon with the graphite structure, which contributes to the increase in the peak intensity of the C1s peak at ~284.5 eV, and high CH_4 decomposition temperature favors this transfer process. From figure 4, it can also be found that the peak intensity of the C1s peak at ~284.5 eV and the charging effect are quite close for the CH_4-reacted catalysts before and after rehydrogenation (see figure 4(d) and (e), or figure 4(f) and (g)), indicating that the formed graphite/filamental carbons in the CH_4 decomposition step cannot be gasified via hydrogenation at low temperature (*e.g.* 300 °C). Our previous work [20] has shown that such carbon is chemically inert and is not easily removed *via* hydrogenation at temperature lower than 600 °C. Undoubtedly, part of the metal sites are blocked permanently by the formed graphite/filamental carbons and this permanent blocking becomes more and more serious with increase in the CH_4 decomposition temperature.

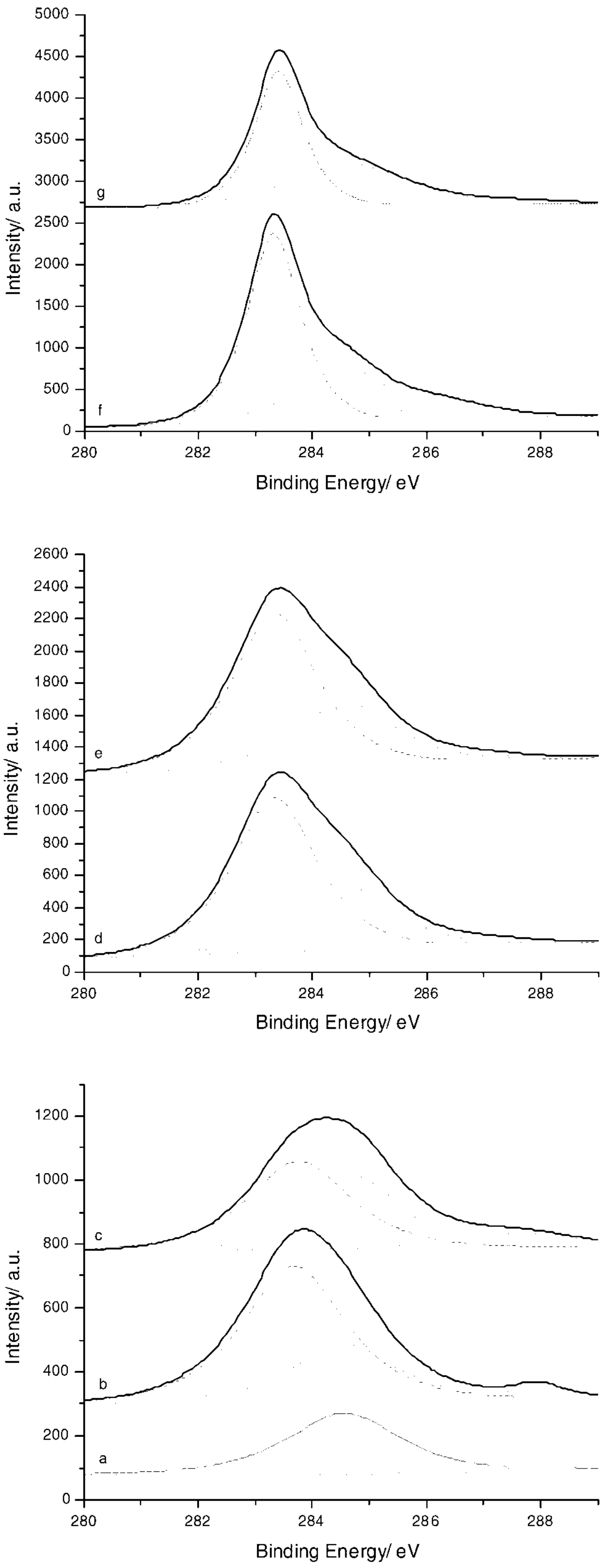

Figure 4. XPS spectra of the V-promoted NiB/Z with a V loading of 0.5 wt% in the C1s region: (a) fresh, (b) after 10-min exposure of CH_4 at 300 °C; (c) the sample (b) followed by a 10-min hydrogenation at 300 °C; (d) after 10-min exposure of CH_4 at 450 °C; (e) the sample (d) followed by a 10-min hydrogenation at 300 °C; (f) after 10-min exposure of CH_4 at 600 °C; (g) the sample (f) followed by a 10-min hydrogenation at 300 °C.

4. Conclusions

The following conclusions can be drawn regarding the oxygen-free stepwise conversion of CH_4 to higher hydrocarbons over supported metal-boron amorphous alloy catalysts:

(1) Both CoB/Z and NiB/Z catalysts give a similar product yield of ~16%, which is 3% higher than the maximum value (C_2^+ yield: 13%) achieved by Koerts and van Santen on a Ru catalyst [2]. Precious metal (Pt, Ru, Rh) amorphous alloy catalysts, however, give a lower product yield of ~7%, which is comparable to those reported by Belgued *et al.* [1] on a Pt catalyst and by Goodman *et al.* [13] on a Ru catalyst.

(2) For Ni(or Co)B/Z catalyst, V modification causes a slight loss in activity for CH_4 decomposition and hydrogenation but affects to a notable extent the yield/selectivity of C_2^+ hydrocarbon product, which is dependent on the V loadings. Total yield of C_2^+ product increases from ~16% for non-modified catalysts to 17.6% for V-promoted NiB/Z with V-loadings of 0.5 wt%.

(3) With increase in hydrogenation pressure, the carbon hydrogenated increases, but the yield and selectivity of C_2^+ hydrocarbon product decrease significantly. For a V-promoted NiB/Z catalyst with V-loadings of 0.5 wt%, increasing the hydrogen pressure from 1 bar to 30 bars decreases the yield of C_2^+ from 17.6% to 14.9%, and up to 60 bars only 12.4% is left.

(4) With increase of the CH_4 decomposition temperature, CH_4 conversion increases slowly up to 500 °C and sharply from 500 °C to 600 °C. However, the yield of C_2^+ hydrocarbon product and carbon hydrogenated at 300 °C decrease obviously. The selectivity of C_2^+ product decreases from 17.6% at 300 °C to 3.2% at 600 °C.

(5) Carbide(-like) carbon (with a B.E. of 283.3 eV) is active and selective for hydrogenation to produce high hydrocarbons. Its activity/selectivity is greatly reduced at high CH_4 decomposition temperatures, mainly due to the transition of the reactive carbide to un-reactive graphitic carbon. Graphite/filamental carbons (with a B.E. of ~284.5 eV) were found to be formed at high CH_4 decomposition temperatures, which would result in a reduction in the number of metal sites, even total deactivation of the catalyst.

Acknowledgments

Financial support from ABB Lummus Global Inc. is gratefully acknowledged. The authors also wish to thank Ms. Yan-Jiao Liu for assistance with XPS measurements.

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