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Reactive Intermediates or Inert Graphene? The Temperature and Pressure Determined Evolution of Carbon in the CH₄–Ni(111) System

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Abstract

Atomic-level identification of carbon intermediates under reaction conditions is essential for carbon-related heterogeneous catalysis. Using the *in operando* technique of near ambient pressure x-ray photoelectron spectroscopy, we have identified various carbon intermediates during the thermal decomposition of CH₄ on Ni(111), including *CH, *C₁ (Ni₃C), *C_n ($n \geq 2$) and clock-reconstructed Ni₂C at different temperature regions (300–900 K). These “reactive” carbon precursors can either react with probing molecules like O₂ at room temperature, or be etched away by CH₄. They can also develop into graphene flakes under controlled conditions: a temperature between 800–900 K, and a suitable CH₄ pressure (10^{-3} – 10^{-1} mbar, depending on temperature). The growth rate of graphene is significantly restrained at higher CH₄ pressures, due to the accelerated etching of its carbon precursors. The identification of *in operando* carbon intermediates and the controlling of their evolution have great potential in designing heterogeneous catalysts for the direct conversion of methane. The observed carbon aggregation/etching equilibrium reveals an underlying mechanism in coking prevention and in the fabrication of large-area single-crystal graphene, where the suppression of seeding density and etching up of small grains are required.

KEYWORDS: NAP-XPS, methane, nickel, catalyst, carbon, intermediate, graphene

1. Introduction

Methane (CH₄), as the major component of natural gas, is one of the most important feedstocks^{1,2} for the production of hydrogen,³ carbon monoxide,⁴ methanol,⁵ and higher hydrocarbons.⁶⁻⁸ Intensive research efforts have been devoted to decreasing the activation barrier of the C–H bond,⁹ increasing the product selectivity,⁷ and suppressing the formation of graphite that blocks the reaction sites and deactivates the catalysts.^{10,11} CH₄ can also be used for the synthesis of large-area single-crystal graphene via chemical vapor deposition (CVD) process.¹²⁻¹⁴ Compared with reactive carbon sources like ethylene (C₂H₄),¹⁵⁻¹⁹

acetylene (C_2H_2),²⁰ propane (C_3H_8),²¹ propylene (C_3H_6),²²⁻²⁴ and benzene (C_6H_6)^{19,25}, methane has lower and controllable carbon supply rate due to its tetrahedral structure and noble-gas-like electron configuration.²⁶ Moreover, the hydrogen-rich nature of methane can also make it an etching reagent that reduces the density of seeding sites for the graphene growth.²⁷

For all these catalytical conversions of CH_4 , the in-depth understanding of the processes relies on the atomic-level tracing of the carbon intermediates. However, traditional vacuum-based surface techniques like x-ray/ultraviolet photoemission spectroscopy (XPS/UPS), low energy electron diffraction (LEED), and scanning tunneling microscopy (STM) have encountered some challenges. The first challenge is to make these vacuum-based techniques capable to study the low sticking CH_4 molecules. It is known that for active carbon sources like C_2H_4 , dosage of a few Langmuir would result in adequate carbon coverage for detection by STM or XPS.^{28,29} In other words, a pressure as low as 10^{-8} mbar is sufficient to obtain carbon signal in minute timescales, thus *in operando* experiment could be easily realized at such vacuum level.^{30,31} But for methane, with reported high activation energy (≥ 0.55 eV),^{26,32-34} it takes at least 10^8 seconds to accumulate discernible coverage at 1×10^{-6} mbar, the upper-limit operation pressure of conventional XPS. To observe the dissociation of methane, some auxiliary techniques have been used. For instance, the molecular beam technique could accelerate the gas to a translational energy up to ~ 4 eV.^{35,36} Adding a thermal finger in the vicinity of the sample also significantly increased the sticking probability during gas dosing.^{32,37} High pressure exposure in a separate cell (other than the characterization chamber) was an alternative method.^{32,38} This practice is based on the irreversible trapping (through dissociative adsorption) of those high-energy molecules which exist even at room temperature, according to the Boltzmann distribution. A rough estimation shows that the high-energy portion (over an activation energy of 0.5 eV) is in the order of 10^{-9} at 300 K.

The thermal finger technique confronts the challenge of limited temperature range. It works with a narrow gap (~ 0.5 mm) apart from the sample, and therefore the sample temperature depends extensively on that of the thermal-finger (typically at 500 K and above). Thus, it is not suitable for the lower temperature region. In fact, this missing temperature region is of special research interests to study the carbon clusters before segregation.²⁸ In this aspect, the molecular beam technique has greatly improved, as its sample temperature can be adjusted from 77 to a few hundreds of Kelvins. However, it still confronts the challenge of pressure gap. It is generally known that a gap exists between low pressure ($<10^{-3}$ mbar) and that above millibar, even though the dosages (pressure multiplied by time) are equal.^{39,40} The gap originates mainly from the different molecular behaviors (free molecular flow vs. viscous flow) and the pressure-induced surface reconstruction. The flow behaviors can significantly affect gas temperature distribution. It has been calculated that at the pressure region below 0.01 mbar, no thermal equilibrium could be expected between gas molecule and sample surface due to the large mean free path, and the gas molecules are considered to be “cold molecules” in equilibrium with chamber walls rather than the sample surface.³² But at millibar pressures, gas can be considered as continuous fluid, forming a hot layer near the sample in thermal equilibrium.⁴¹ The pressure-driven reconstruction is caused by the chemical potential of the gas, and will in turn affect the catalytic properties.^{42,43} For instance, at low pressures, volatile phases like Ni_2C disappear upon heating²⁹, and therefore have little influence on the following developments. But at millibar pressure, the total dissociation (carbon supply) increases by at least 6 orders. As a result, observable Ni_2C can remain on the surface. This phase has great impact on the consequent formation of graphene.⁴⁴

Even for the high-pressure cell method (in a separate chamber), challenge still exist as the linkage is missing between the reaction-condition species (at higher pressures and temperatures, referred as *in operando* species) and the observed *in situ* results (after cooling and gas evacuation). Usually the *in operando* species are in dynamic equilibrium with

surrounding reaction gas at elevated temperatures, and will likely evolve during the cooling or evacuation. Therefore, a characterization method that could trace from reaction condition to UHV/RT condition, is necessary to guarantee their uniformity. With such a linkage, other conventional UHV techniques may also tap into the *in operando* species.

The invention of near ambient pressure x-ray photoelectron spectroscopy (NAP-XPS) provides a solution for the above-mentioned challenges: observing low-sticking species (as low as 10^{-9}) *in operando*, and building a bridge to other *in situ* characterizations. The detailed description of the system has been introduced elsewhere.⁴⁵ It extends the operation pressure range (10^{-9} – 10^1 mbar) with an independent freedom in temperature (200–900 K). This range covers typical CVD pressures for graphene growth,^{12,46} and is close to the pressure range in the catalytical methane conversion reactions.^{7,47}

Here we aim to identify the *in operando* carbon species in the CH₄–Ni(111) system with multiple characterizations. Compared to a recent work that employed only NAP-XPS on the CH₄–nickel (foil) system,⁴⁸ we have made improvements in choosing a well-defined Ni(111) single crystal, and in coupling more *in situ* characterizations like UPS, LEED and STM. NAP-XPS was also utilized to trace the surface species during the cooling and evacuation from reaction conditions. Through adjusting the cooling/evacuation parameters, the *in operando* and *in situ* species were kept uniform, and therefore a linkage between them was established. For the identified carbon species, including methine adsorbate (*CH), carbon adatom (Ni₃C or *C₁), aggregated carbon chains/flacks (*C_n), clock-reconstructed Ni₂C, and graphene, their valence bands and atomic structures were explored. The chemical reactivity of the “reactive intermediates”⁴⁹ were verified, which explained the suppression of graphene growth at higher pressures and suggested a possible route to prevent carbon coking.

2. Experimental Section

The ultrahigh vacuum (UHV) system consisted of the lab-based Specs NAP-XPS package with an Al/Mg twin x-ray source,⁴⁵ and a home-built preparation chamber. The

preparation chamber was equipped with an e-beam sample heater (VG Scienta, EBHC), an ion sputtering gun (Omicron ISE 5), a LEED (Omicron SPECTALEED), and a residual gas analyzer (RGA, Microvision Spectra), with a base pressure better than 2×10^{-10} mbar.

The Ni(111) single crystal (99.99%, $\pm 0.5^\circ$), purchased from MaTeck, was welded to a molybdenum plate by tantalum stripes. It was cleaned in the preparation chamber by cycles of Ar^+ sputtering (1.5 kV, 30 μA), and e-beam heating to around 1000 K. After the final cycle, it had a sharp LEED pattern, and very low carbon and oxygen levels (near the detection limit of the NAP-XPS).

High-purity CH_4 gas (Soxal, 99.999%) was used in the experiments. Before feeding, it flew through a LN_2 -trap for further purification.⁵⁰ The purity of feeding gas was checked in the preparation chamber by the RGA. The result showed that after feeding the CH_4 from UHV to 1×10^{-6} mbar (maximum operation pressure of the RGA), the change of partial pressures for $m/e = 18$ (H_2O), 28 (N_2 , CO , and C_2H_4) and 32 (O_2) were all below 1×10^{-12} mbar. Therefore, an impurity level below 1 ppm could be guaranteed.

In the NAP-XPS experiments, the clean Ni(111) sample was positioned near the 300- μm nozzle of the NAP-cell. The focusing parameters were optimized after each sample loading, as the signal was sensitive to both positions of the sample and the nozzle. To minimize the variations in absolute intensities between experiments, the spectra were normalized by the background level (B.E. 274–294 eV) of clean sample in UHV. Core-level spectra of O 1s, C 1s and Ni 2p were measured using the Al $K\alpha$ Source ($h\nu = 1486.61$ eV), with the kinetic energies centering at around 957 eV, 1202 eV and 634 eV, respectively. The pass energy was set at 20 eV, and the full width at half maximum (FWHM) for C 1s was ~ 1.3 eV. The core-level peaks were analyzed by CasaXPS, using the Shirley-type background subtracting. The symmetric peaks were fit using the GL30 line shape (a mixing of 70 Gaussian and 30% Lorentzian), while the asymmetric peak of graphene C 1s peak was fit using the H(0.04,0)GL30 line shape, a hybrid Doniach Sunjic/Gaussian-Lorentzian (product).

The UPS was also carried out in the system. Now the NAP-cell was removed and the sample was loaded in the earthed transfer arm. Helium-I source ($h\nu = 21.2$ eV, VG Microtech 232) was used, and the emission angle was fixed at 48° . The pass energy of the analyzer was set at 2.0 eV. The *in situ* LEED was done after UPS characterization, otherwise the electron-beam bombardment in LEED would change the electronic structure of adsorbates. The STM characterization of the graphene-covered sample was done in a multi-chamber Unisoku USM-1200 low temperature system with a base pressure below 1×10^{-10} mbar. The sample was heated to 400 K to remove the adsorbed gas during sample transfer in air. Then it was cooled down to 77 K by liquid nitrogen and stabilized for a few hours. The electrochemically etched tungsten tip was grounded, and the voltage bias was applied to the sample.

3. Results and Discussion

3.1. *In operando* identification of CH₄ (gas), *C₁ (Ni₃C), *C_n, and clock-reconstructed Ni₂C

Temperature-programmed *in operando* experiments were conducted in the NAP-XPS system. The clean Ni(111) sample was loaded into the NAP-cell at room temperature (RT), and then exposed to CH₄ gas. A pressure of 0.4 mbar was selected, at which both the gas-phase peak became obvious and the total photoelectron signal was not substantially attenuated. The temperature was programmed to increase by 100 K in each step until 900 K. NAP-XPS measurements were carried out after a stabilization period of ~ 1 h at each temperature.

Figure 1. Temperature-programmed NAP-XPS spectra of carbon species on Ni(111) from 300 to 900 K in 0.4 mbar CH₄. Here no graphene formed at 800 and 900 K.

Figure 1 shows the temperature-dependent evolution of carbon species on Ni(111) from 300 to 900 K under 0.4 mbar CH₄. The C 1s peak of gas-phase CH₄ located at around 286 eV (filled in red). The peak position drifted slightly at different temperatures due to the changing of surface work function (WF).⁵¹ Its intensity decreased with rising temperature, as the isobaric expansion reduced the gas density. Other peaks were originated from adsorbed carbon species. Through peak fitting, four types of carbon species were identified. The peak at 283.5 eV (filled in gray) existed only at 300 K, corresponding to the *CH adsorbate on the 3-fold hollow site of Ni(111).^{52,53} The peak at 283.7 eV (filled in dark green) existing at 400–500 K was assigned to the carbon adatom (*C₁ or Ni₃C), which was dehydrogenated from

*CH and remained at the 3-fold hollow site.^{20,54} The peak at 284.5 eV (filled in purple) corresponded to the aggregated carbon (*C_n, n≥2) with varied cluster sizes at 300–700 K.⁵⁵ At higher temperatures (600–800 K), the peak at 283.3 eV (filled in light green) emerged, ascribing to the “clock-reconstructed” surface Ni₂C.^{29,56} At 900 K, no adsorbates was observed except for the gas-phase signal. The coverages of these carbon species were calculated and shown in **Table S1** in the Supporting Information, varied from 0.17 to 0.96 per surface Ni atom.

To further distinguish these *in operando* species (*CH, Ni₃C, *C_n and Ni₂C), and to explore their electronic and atomic structures, *in situ* UPS and LEED were carried out. At each temperature, the experiment started from a clean surface. In **Figure 2**, three samples were first stabilized to 300, 400 and 800 K in UHV, respectively, followed by 0.4 mbar CH₄ exposures for 30 min. They were then cooled to RT in the gas ambient, followed by gas evacuation. The consequent UPS and LEED were both characterized under the UHV environment. The UPS results in the left panels show that clean Ni(111) had a sharp 2-peaked d-band near the Fermi edge (0–3 eV below E_F), being consistent with previous reports.⁵⁷ The peak at 0.1 eV attenuated significantly after CH₄ exposure even at RT. The difference spectra (in green) were obtained by subtracting the spectra of carbon deposited Ni(111) with the attenuated spectra of clean Ni(111).⁵⁸ The middle panels are the corresponding LEED patterns. Besides six (01) spots from Ni(111), the sample after 300 K CH₄ exposure had additional ring-like diffractions at $\sqrt{3} \times \sqrt{3}R30^\circ$ (panel d), and that after 800 K exposure had the characteristic “clock-reconstructed” pattern (panel f). For the sample after 400 K exposure, however, no other diffraction could be observed (panel e), as the randomly distributed *C₁ and *C_n, n≥2 lacked periodicity. In the right panels, the proposed atomic structures of carbon adsorbates after respective treatments were schematically displayed.

Figure 2. UPS (a–c), LEED patterns (d–f), and corresponding schematic drawings (g–i) of *CH, *C_n/Ni₃C and clock-reconstructed Ni₂C species formed on Ni(111) under 0.4 mbar CH₄ ambient at 300, 400 and 800 K, respectively. The difference spectra were obtained from subtracting the CH₄-dosed surface by the attenuated clean Ni(111) spectra. The LEED patterns were taken at the beam energy of 70 eV. In the schematic drawings, the golden/silver, red and black sphere denote surface/subsurface nickel, hydrogen, and carbon atoms, respectively.

The confirmation of the *CH species was based on the integration of fingerprint C 1s binding energy, UPS, and LEED results. In conventional vacuum-based CH₄ exposure using high temperature to activate the molecules, it was difficult to obtain *CH species due to their thermal instability. Reliable observation of *CH species had been made through the molecular beam method on cold substrates (slow heating from 120 K to onwards), combined with the synchrotron-based high resolution XPS.^{52,53} Using NAP-XPS, the RT stable phase of *CH could be maintained. The observed peak at 283.5 eV in **Figure 1** was close to the fingerprint C 1s (283.6 eV) of these literatures,^{47,48} providing preliminary evidence of the *CH species. In **Figure 2 (a)**, the UPS spectrum after CH₄ exposure at 300 K shows a characteristic plateau between 6.0 and 8.0 eV,⁵⁹ originating from the $\sigma_{\text{C-H}}$ orbital.⁶⁰⁻⁶² This feature was unique to all other samples treated at higher temperatures where the carbons had complete dehydrogenated, and could be considered as the evidence of the C–H bond.

The LEED pattern of the *CH-covered surface in **Figure 2 (d)** has a $\sqrt{3} \times \sqrt{3}R30^\circ$ diffraction pattern, consistent to the conclusion that the *CH occupies the 3-fold hollow site of Ni(111), as revealed both theoretically^{26,62,63} and experimentally.⁶⁴ In the **Supporting Information**, the reason for the ring-like diffraction spots was explained, suggesting that it was from the non-perpendicular C–H bonds. According to the normalization of C 1s peak area in **Figure 1**, the coverage of the *CH species was estimated as 0.37 per surface Ni atom at 300 K, in good agreement with the $\sqrt{3} \times \sqrt{3}R30^\circ$ configuration (refer to **Table S1** in the **Supporting Information**). **Figure 2 (g)** is a proposed model for the *CH adsorbates on Ni(111), schematically showing two types of domains that originated from the fcc (with darker adjacent Ni atoms) and the hcp (with lighter adjacent Ni atoms) *CH species.

The dehydrogenation of *CH into carbon adatom (*C₁ or Ni₃C) happened when raising the temperature to 400 K. As their BEs were only 0.2 eV apart in the XPS spectra, they were not differentiated from each other previously.⁵² Additional results from UPS, LEED and O₂ probing test helped to distinguish the *C₁ (Ni₃C) from the *CH. In **Figure 2 (b)**, the plateau-

type electron state at 6–8 eV (from the $\sigma_{\text{C-H}}$ orbital) was replaced by a peak-type state at ~ 7.5 eV, originating from the carbon $\sigma_{2,3\text{v}}$ orbital.⁶⁵ It is reported that the resulting carbon adatom (Ni_3C) retained on the 3-fold hollow site and hence formed a trigonal structure, with the Ni–Ni distance of 2.63 Å and the Ni–C distance of 1.86 Å.^{66,67} Due to the existence of the Ni–C bonding, the adjacent three nickels were pulled out from the Ni layer.⁶⁸ According to **Figure 1**, Ni_3C ($^*\text{C}_1$) was stable at 400–500 K, in rough agreement to the reported value at 373–473 K.⁶⁹ It was less stable than the bulk Ni_3C which started to decompose at temperatures above 673 K.⁷⁰

In **Figure 1**, two routes for forming the carbon clusters ($^*\text{C}_n$, BE at 284.5 eV) could be found. At 300 K where the dominant adsorbate was $^*\text{CH}$, the carbon clusters emerged with a coverage of 0.17 per surface Ni. It was proposed that two $^*\text{CH}$ first coupled to form $\text{HC}^*—^*\text{CH}$, and consequently dehydrogenated to form $^*\text{C}_2$.⁶⁴ At 400–500 K, the widely distributed $^*\text{C}_1$ adatoms can thermally diffuse on the surface and form the carbon clusters.⁵⁵ The later was inferred the major route for the formation of $^*\text{C}_n$, as its coverage rose to 0.65–0.79 at these temperatures. An early work reported the energy barriers of 0.30 eV and 0.40 eV for surface and bulk diffusion of carbon in Ni(111), respectively.⁷¹ The former value is verified both by experiments and calculation, showing that 0.23–0.5 eV is an appropriate barrier for carbon migration on flat nickel surface.^{72,73} But the latter is considered underestimated. A value of ~ 1.0 eV is believed more plausible for the barrier of bulk diffusion.^{74,75} Therefore the bulk diffusion of carbon atoms below 700 K was not a decisive factor for the formation of surface $^*\text{C}_n$ here.⁷⁶

The clock-reconstructed Ni_2C phase acted as a perfect reference for both the atomic structure and the C 1s fingerprint. In **Figure 1**, it existed as the sole carbon species at 800 K, and could be maintained after cooling and evacuation. Its BE was 0.4 eV lower than that of Ni_3C (283.7 eV), consistent with the larger carbon coordination number than that of Ni_3C (4 vs. 3). **Figure 2 (f)** shows the well-known LEED pattern with sharp spots. This structure has

been comprehensively studied by both LEED⁷⁷ and STM⁷⁸⁻⁸⁰. Usually a super cell labelled $\sqrt{39}R16.1^\circ \times \sqrt{39}R16.1^\circ$ or $\sqrt{39}R16.1^\circ \times \sqrt{37}R-34.7^\circ$ is used to facilitate describing the relationship between its near-square unit cell and the Ni(111) substrate. In panel (i), we adapted the latter expression for the schematic drawing. In fact, the key parameters for the Ni₂C unit cell are almost the same in both expressions: (1) it includes two carbon atoms and four nickel atoms; (2) both vectors are about twice of the $\vec{a}$ vector of Ni(111) in length; (3) the angles between the two vectors and the $\vec{a}$ vector are 2.83° and 94.72° respectively; and (4) it has 6 domains from the 3-fold symmetry multiplied by the flip symmetry. The UPS spectra in panel (c) shows that the Ni₂C-covered surface had a merged d-band peak at 0.62 eV, significantly different from the clean and *CH or *C_n covered Ni(111) with double peaks at 0.07 and 1.03 eV. This suggested that the Ni₂C phase was a compound rather than a surface adsorbate. It would be demonstrated later that the Ni₂C phase could transform to graphene, consistent with previous reports.⁸⁰

For the dissociation of methane, one of the most debated values is the activation energy (E_a).^{32,81-83} A wide discrepancy of the E_a can be seen in the Supporting Information. The relationship between the sticking probability at a certain temperature and the activation energy (E_a) is roughly estimated by the formula: $S(T) = e^{-E_a/k_B T}$. The reported large values like 1.31 eV are considered impractical, otherwise the room temperature sticking probability would be as low as $\sim 10^{-22}$, which far deviates the experimental facts. Our NAP-XPS results showed conclusively that the dissociation of methane could happen on clean nickel surface at RT under 0.4 mbar CH₄ ambient within 30 min. Therefore, an activation energy of ~ 0.5 eV could be estimated from these parameters.

The NAP-XPS has unique advantage in estimating the sticking probability at around 10^{-8} – 10^{-10} . In traditional technologies where the gas dosing is carried out at pressures lower than 10^{-4} mbar, the expected exposure time would be hundreds of hours at RT. Heating is a common technique to reduce the experiment time. But due to the long mean free path of the

gas molecules at low pressures, it is difficult to reach thermal equilibrium with the heater via limited collisions. Even though the heater (thermal finger) was placed very close to the sample, the obtained E_a (~ 0.7 eV) was likely overestimated.^{32,84} Interestingly, the measured E_a via NAP gas exposure³⁴ closely matched that from molecular beam exposure,⁸⁵ both at around 0.52 eV which is also close to our estimation. Chen *et al* pointed out that in addition to the translational motion of molecules, the vibrational effects can also decrease the activation energy by ~ 0.15 eV.⁸⁶ Such molecular vibration becomes significant at millibar pressures and above, where the inter-molecular collisions increase by orders of magnitude. As a result of this effect, the sticking probability increases significantly at a pressure above ~ 0.3 mbar.³⁸ It has also been discovered that high pressure is required for the observation of adsorbates in the “kinetically limited dissociative adsorption”.^{85,87,88} According to this model, the gas molecules are first physisorbed to the metal surface, and the incoming molecule fluxes then serve as a “hammer” to cause the dissociation. The existence of these mechanism indicates that in the complex gas-substrate systems, the information (activation barriers, adsorbed species, surface reconstruction & etc.) obtained from NAP-XPS tends to be closer to the real reaction conditions than that from UHV techniques.

3.2. Temperature and pressure factors influencing the evolution: from carbon intermediates to graphene

As aforementioned, the carbon species (*CH, Ni₃C, *C_n and Ni₂C) showed reactivity towards heated CH₄. Previously, we have reported that the *CH species can react with millibar CO₂ gas at 300 K.⁸⁹ In the **Supporting Information**, we also demonstrated that they were reactive towards cold O₂ robing molecules. However, when these intermediates developed into graphene, it became stable and was inert to either the O₂ probing molecules at RT or the CH₄ etching at 900 K. The long-term (>18 months) stability of graphene-protected nickel towards atmosphere passivation has been proved.⁹⁰ In this part, we first characterized

the epitaxially grown graphene on Ni(111) using CH₄ as precursor by NAP-XPS, UPS, LEED and STM. Then we tried to unveil how the pressure, temperature, nucleation centers affect the formation of graphene. In these experiments, the temperature was either increasing or kept constant. Such temperature control excluded the graphene formation from the dissolving-quenching cycles,⁹¹ and the results were mainly related to the surface carbon species. Whereas graphene could be obtained at both 800 and 900 K, in order to get better time resolution and avoid graphene damage due to the bulk diffusion at 928 K,¹⁸ the comparative case study was carried out at 800 K.

3.2.1. Graphene formation on Ni(111) at 900 K, 0.4 mbar CH₄

Figure 3 (a) shows the growth of graphene in a time-resolved NAP-XPS experiment. The sample was first heat to 900 K in UHV, then 0.4 mbar CH₄ gas was introduced ($t = 0$). In the first 24 min, only the gas-phase peak at 286.5 eV (filled in red) was observed. Later at 41 min, two new peaks appeared at 283.3 eV (filled in green, the Ni₂C phase) and at 285.0 eV (filled in blue). The peak at 285.0 corresponded to graphene with strong interaction with nickel.^{24,29,92} It was fitted using the hybrid Doniach Sunjic/Gaussian-Lorentzian line-shape due to its asymmetry.^{93,94} The normalized C 1s peak area of graphene was plotted in panel (b). It grew quickly and reached saturation at around 90 min. For the Ni 2p_{3/2} peak, the enclosed area from 856 to 848 eV attenuated to 87% of its initial value after the graphene coverage. Employing the semi-quantitative formula in estimating the inelastic mean free path (IMFP):

$$\lambda(\text{nm}) = \frac{538 a}{E^2} + 0.41 a^{3/2} (E)^{1/2} \text{ (Eq. 1)}$$

where $a = 0.3567$ nm for graphene, $KE = 634$ eV for Ni 2p_{3/2} photoelectron excited by 1486.61 eV, the calculated λ was 2.2 nm. Using the Ni 2p attenuation of 87%, the thickness of the graphene layer atop was estimated to be ~ 0.31 nm, or about one monolayer.

Figure 3. (a) Time-resolved (TR) NAP-XPS spectra of C 1s, carried out at 900 K under 0.4 mbar CH_4 ; (b) Normalized graphene peak area in the TR experiment; (c) UPS valence band of clean Ni(111), and after graphene formation. Their difference spectrum (in green) was obtained through $\text{Gr-on-Ni(111)} - 0.47 \times \text{Ni(111)}$, here the attenuation factor 0.47 is for fitting the leading edge; (d) Atomic-resolved STM image of the sample after growth of epitaxial graphene, the scale bar represents 1 nm, under a sample bias voltage of 300 mV and a tunneling current of 100 pA; (e) Corresponding LEED pattern after graphene formation, taken at 70 eV;

The valence band structure in panel (c) shows that the second d-band peak of nickel originally at 1.02 eV shifted to 1.27 eV after the formation of graphene. This was a feature of π -d interaction between graphene and metallic nickel.⁶⁵ Although covered with a full layer of graphene (two C atoms per surface Ni atom), the LEED pattern in panel (e) was still sharp. This was different from the blurred diffraction after adsorbing less amount of amorphous *C_n and Ni_3C in **Figure 2** (e), proving that the graphene epitaxially grew on Ni(111). Similar to previous reports, a dim ring was observed whose radius equaled to the (01)-reciprocal vector of Ni(111).^{15,16} This was probably originated from some twisted graphene domains, transformed from Ni_2C via an in-plane mechanism.⁸⁰ The graphene-covered sample was

characterized in low-temperature STM, as shown in panel (d). The hexagonally symmetric honeycomb structure, with a measured lattice vector of $\sim 2.5 \text{ \AA}$, confirming the formation of the single layer graphene.⁹⁵

3.2.2. A case study of how the CH₄ pressure affected the transformation of carbon species into graphene at 800 K

Figure 4 (a) shows the pressure-variant NAP-XPS for C 1s at 800 K. Starting from hot sample (800 K in UHV) followed by instantaneous CH₄ dosing (to 0.4 mbar), the dominant signals were the gas-phase peak (in red) and the Ni₂C (in green) in the first 80 min. Then by reducing the pressure by steps to 0.1 and 0.04 mbar, the gas-phase peak attenuated accordingly, and the graphene peak (in blue) began to increase. Further decreasing the pressure to 2.3×10^{-5} mbar, graphene became dominant, with the peak intensity 10 times higher than that of Ni₂C. Panel (b) records the time-resolved CH₄ pressure and graphene peak intensity. The growth rate was lower at pressures above 0.04 mbar, even though the apparent carbon supply (collision rate, proportional to pressure) was higher. It increased significantly after reducing the pressure to 10^{-3} – 10^{-4} mbar, but fell quickly when further reducing the pressure below 2.3×10^{-5} mbar, due to limited carbon supply. This result implied that at 800 K, the highest graphene growth rate appeared at the CH₄ pressure of $\sim 10^{-3}$ mbar.

Figure 4. (a) Pressure-variant C 1s spectra at 800 K from 0.4 to 7.5×10^{-4} mbar CH₄; (b) Its time-resolved pressure recording and graphene peak area evolution.

Figure 5 compared the graphene growth with different initial surface conditions at the optimized methane pressure of 2×10^{-3} mbar. Three Ni(111) samples were pre-annealed in H₂ at 800 K (green), He at 800 K (red), and CH₄ at 400 K (blue), respectively, all at 2×10^{-3} mbar for 100 min. Their incubation time before the onset of graphene growth varied significantly. For the H₂-treated sample, no graphene was observed in the initial 2 h before its sudden growth. For the He-treated sample, slow graphene growth started after 30 min, but

accelerated at 100 min. For the CH₄-treated sample, a layer of *C_n/Ni₃C at the coverage of ~0.3 per surface Ni atom formed at 400 K. After raising the temperature to 800 K, they quickly transformed into graphene, and the following growth still maintained at a fast rate. All the three samples had close growth rates of ~0.02 C/Ni_{surf.} per min at the fast-growing stage.

Figure 5. Comparison of graphene growth rates at 800 K, 2×10^{-3} mbar CH₄, with variant pre-treatments. Green: pre-annealed in H₂; Red: pre-annealed in He; and Blue: pre-seeded with CH₄ at 400 K to form a layer of *C_n.

The results in **Figure 5** proved that carbon seeds were necessary for the growth of graphene in the CVD process. The annealing in H₂ thoroughly removed the residual surface carbon, therefore, the growth of graphene delayed until its nucleation centers finally formed in a random thermal process (temperature and concentration fluctuation). The temperature of 800 K was found not suitable for seeding, where the *C_n/Ni₃C disappeared and the major stable phase was the clock-reconstructed Ni₂C. Although the transformation of Ni₂C was also a route for graphene growth on Ni(111),⁸⁰ here it played only a minor role as graphene seeds compared to the *C_n/Ni₃C species. This might explain the contradiction that no graphene formed at 900 K in **Figure 1**, starting from a Ni₂C-covered surface; whereas graphene

quickly grew after instant dosing of 0.4 mbar CH_4 to the preheated sample (900 K) in **Figure 3**, where the seeding probably took place during the sudden dosing.

Figure 6 demonstrates how the Ni_3C and $^*\text{C}_n$ species developed at various CH_4 pressures after a temperature jump from 400 to 800 K. All the three samples were first seeded with a $^*\text{C}_n/\text{Ni}_3\text{C}$ layer at 400 K. Then the pressures were adjusted to 0.002, 0.02 and 0.1 mbar, respectively, still at 400 K. After the temperature jump, the carbon species showed different evolution paths. In panel (a), the Ni_3C species disappeared completely after 20 min at 0.1 mbar, or 40 min at 0.02 mbar. But $\sim 1/3$ of them retained and converted to Ni_2C at 0.002 mbar. In panel (b), the evolution of $^*\text{C}_n$ species were also pressure sensitive. At 0.002 mbar, $^*\text{C}_n$ transformed to graphene and quickly grew to a near saturation level (about 5–6 times of the initial $^*\text{C}_n$ concentration). At 0.02 mbar, it had slight increase in the first 10 min, maintained for a few minutes, and quickly fell at 20 min until out of the detection limit. At 0.1 mbar, the $^*\text{C}_n$ kept decreasing, and completely disappeared after 40 min.

Figure 6. The evolution of normalized C 1s peak areas of (a) Ni₃C/Ni₂C and (b) *C_n/Graphene carbon species of the pre-seeded samples, at various CH₄ pressures after a temperature jump from 400 to 800 K at t = 0.

From the results in **Figure 6**, it could be inferred that the etching of carbon seeds by CH₄ was the underlying mechanism for the pressure-sensitive graphene growth. Li *et al* pointed out that CH₄ directly reacting with *CH specie ($\text{CH}_4 + \text{*CH} \rightarrow \text{*CH}_3 + \text{*CH}_2$) can be considered in methane cracking.⁹⁶ Recently, Guo *et al* observed the non-adsorbing methyl ($\cdot\text{CH}_3$) radical generated from CH₄ (g)–catalyst interaction, which played a vital role for the high conversion of CH₄ with low coking.⁷ Here it was inferred that the carbon species (*C₁ and *C_n, with the *n* not very large) could also react with the gas-phase CH₄ via the Eley–Rideal process. Gas-phase product would then release from the surface. In this sense, increasing the CH₄ pressure is a possible way to reduce the density of carbon seeds, which is preferred both in heterogeneous catalysis to suppress coking and in large-area graphene fabrication to inhibit nucleation.

3.3. A brief flow chart of carbon evolution in the CH₄–Ni(111) system

Figure 7 summarizes the evolution of carbon species observed by NAP-XPS in this work. At room temperature, a portion of gas-phase CH₄ molecules could dissociate on Ni(111) at millibar pressure range within hour timescale. As the initial adsorbate *CH₃ dehydrogenates to *CH₂ at ~150 K⁶⁴ followed by even faster dehydrogenation to *CH (–0.6 eV),⁹⁷ the first observed adsorbate here was assigned to *CH, consistent with previous reports.⁹⁸ As the temperature rose, the *CH dehydrogenated to *C₁ adatom, which later developed into *C_n clusters or the “clock-reconstructed” Ni₂C through the surface migration of C and Ni (for Ni₂C). These carbon species showed chemical reactivity towards probing O₂ molecules at 10^{–7} mbar, and could be etched away in millibar pressure CH₄ ambient. These reactive

intermediates have great potential in designing catalysts for carbon conversion reactions. Graphene can also be developed from these carbon intermediates. The discovered relationship between the temperature, the CH₄ pressure and the growth of graphene may benefit its controlling for the synthesis of single-crystal graphene, and the carbon-coking prevention in heterogenous catalysis.

Figure 7. A brief flow chart of the evolution of carbon species observed in this work.

4. Conclusion

We identified a few *in operando* carbon species during the thermal decomposition of CH₄ on Ni(111), and revealed their atomic and electronic structures using NAP-XPS, UPS, LEED and STM. Observable portion of CH₄ molecules dissociated at room temperature and millibar pressures, leaving the *CH species that occupied the 3-fold hollow sites of Ni(111). At 400 K, the *CH further dehydrogenated to *C₁ adatom that still adsorbed on the hollow sites (also labelled as Ni₃C). Surface diffusion of *C₁ resulted in the formation of larger carbon clusters (*C_n). At 600–800 K, a new surface compound appeared, labelled as Ni₂C with the well-known “clock-reconstruction”. All these carbon species were reactive intermediates, and played important roles in heterogeneous catalysis. They can develop to inert graphene at 800–900 K under appropriate pressure and seeding conditions. We proved that high CH₄ pressures ($>10^{-3}$ mbar for the case of 800 K) restrained graphene growth, as the precursor/seeding of graphene (mainly in the form of *C_n) was etched away. This could be applied in the fabrication of large-area single-crystal graphene, because low seeding density is required. It also implies that increasing the reaction pressure in CH₄-involved reactions may reduce the probability of coking on catalysts.

ASSOCIATED CONTENT

Supporting Information

This Supporting Information is available free of charge via the Internet at <http://pubs.acs.org>.

Carbon coverage estimation for Figure 1;

Detailed discussion on LEED patterns of *CH and clock-reconstructed Ni₂C;

O₂ probing test on samples pre-exposed to CH₄ at 300–700 K.

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