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# Dynamics and Mechanism of Carbon Filament Formation during Methane Reforming on Supported Nickel Clusters

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**ABSTRACT:** CH<sub>4</sub>–CO<sub>2</sub> and CH<sub>4</sub>–H<sub>2</sub>O reforming on Ni-based catalysts can lead to the undesired formation of carbonaceous residues. The dynamics of the formation of carbon filaments and encapsulating layers on dispersed Ni nanoparticles (5–11 nm diameter) are determined here using an inertial microbalance to measure mass changes and mass spectrometry to concurrently assess turnover rates under conditions of reforming practice (800–1000 K). The morphology and rate of formation of carbonaceous species were controlled by a ratio of pressures ( $\chi = P_{CH_4}P_{CO}/P_{CO_2}$  or  $\psi = P_{CH_4}P_{H_2}/P_{H_2O}$ ), which are proportional to each other

through the equilibration of water-gas shift) that uniquely determines the thermodynamic activity of carbon at the metal



surface  $((a_{C^*})_s)$  and the thermodynamic driving force for carbon diffusion and filament formation, based on a reaction-transport model derived from the elementary steps that mediate CH<sub>4</sub> reforming. Each sample exhibited three distinct kinetic regimes for carbon formation, which evolved with increasing  $\chi$  values from undetectable carbon deposition (I) to a constant rate of carbon filament growth without detectable changes in  $CH_4$  reforming rates (II) and ultimately to the formation of carbon overlayers with a concurrent decrease in CH<sub>4</sub> reforming and carbon formation rates (III). Rates of filament growth in regime II were proportional to  $\chi$ or  $\psi$  values, consistent with a filament growth mechanism limited by carbon diffusion. Such carbon filaments were similar in diameter to the attached Ni nanoparticles. In regime III, the high prevalent carbon activities led to the simultaneous nucleation of several carbon patches, thus precluding the directional diffusion imposed by a single filament and leading to the encapsulation and loss of accessible surface for CH4 turnovers. Filaments formed in regime II were removed when placed under the conditions of regime I via the microscopic reverse of their formation processes. Threshold carbon activities required for the incipient formation of filaments are higher and filament formation rates are lower (for a given  $\chi$  or  $\psi$ ) on smaller nanoparticles because of the lower stability (higher thermodynamic carbon activity) of filaments with smaller diameters. Carbon deposition rates decreased with increasing temperature (for a given  $\chi$  or  $\psi$ ) because of a corresponding decrease in the lumped kinetic and thermodynamic parameters that relate the surface carbon activity to  $\chi$  or  $\psi$ . The formalism used to describe carbon formation rates, in this study for CH<sub>4</sub> reforming rates far from equilibrium and for carbon formation and removal rates that do not disturb the carbon activity set by CH<sub>4</sub> reforming turnovers at steady-state, also informs the testing of these assumptions while providing also a framework for the rigorous extension of these reaction-diffusion constructs to more practical conditions, for which these assumptions may no longer apply.

# 1. INTRODUCTION

 $CH_4$  reacts with  $CO_2$  or  $H_2O$  to form synthesis gas ( $H_2 + CO$ ), an important intermediate in the production of many valuable fuels and chemicals. Industrial processes predominantly use Ni-based catalysts that tend to form filamentous carbon deposits when using stoichiometric  $CH_4-CO_2$  or  $CH_4-H_2O$  reactant mixtures.<sup>1</sup> Other materials such as noble metals and recently developed bimetallic alloys have demonstrated lower tendencies to form such deposits.<sup>2–5</sup> Such materials, however, have not found widespread use at this time. The formation of carbonaceous residues hinders catalysis by blocking pores, active sites, and even interpellet voids in packed catalyst beds; in extreme cases, these residues lead to catalyst disintegration, elution as fines, and reactor plugging.

 $CO_2/CH_4$  and  $H_2O/CH_4$  ratios significantly larger than unity are used in practice in order to prevent the formation of these carbon residues in strategies that lead to significant recycle and separation costs and energy inefficiencies.<sup>1</sup> The accurate prediction and selection of conditions under which carbon deposition on metal catalysts can be prevented or minimized remain essential in efforts to improve process

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efficiency; this topic has been addressed in several previous studies<sup>6–38</sup> and reviewed by Trimm,<sup>7</sup> Rostrup-Nielsen and Trimm,<sup>8</sup> Baker and Harris,<sup>9</sup> Rodriguez,<sup>10</sup> de Jong and Geus,<sup>11</sup> Liu et al.,<sup>12</sup> Lobo et al.,<sup>13</sup> and Sperle et al.<sup>14</sup> The unique morphology and properties of carbon nanotubes<sup>15,39–41</sup> have driven parallel studies in efforts to optimize their purposeful synthesis by elucidating the pathways required for the formation of single-walled or multiwalled carbon nanotubes on catalytic metal particles.<sup>16–22,42–51</sup>

It is generally accepted that the formation of carbon filaments from hydrocarbons on Ni crystallites proceeds via (a) the dissociative chemisorption of the hydrocarbon on metal surfaces to form carbon atoms, (b) the dissolution of carbon atoms into the metal, (c) the bulk diffusion of the carbon atoms through the metal, and (d) the nucleation of filaments and the precipitation of carbon atoms at the metalfilament interface at the location on the crystallite surface where filament nucleation initially occurred.<sup>13,23-26</sup> The diffusion of carbon atoms through the catalyst particle (step (c)) is typically considered to limit filament growth rates, while the dissolution of carbon atoms into the metal and their deposition at the growing filament are fast quasi-equilibrated processes. The diffusion of carbon through metal particles is driven by gradients in carbon concentration<sup>8,26,27,29,31</sup> or more precisely in carbon chemical potentials and temper-ature.<sup>23,24,28,29</sup> Holstein showed that temperature gradients could not be responsible for filamentous carbon growth.<sup>25</sup>

Holstein<sup>25</sup> and Lund and Yang<sup>30</sup> indicated that the true driving force for diffusion is a gradient in the chemical potential of dissolved carbon ( $\mu_c$ ), defined by

$$\mu_{\rm c} = \mu_{\rm c}^* + RT \ln a_{\rm c} \tag{1}$$

where  $\mu_c^*$  is the chemical potential of the reference state and  $a_c$  is the thermodynamic activity of the carbon dissolved within the metal particle. The chemical potential of carbon is proportional to its thermodynamic activity in dilute solutions of C-atoms within Ni such as those encountered here (<0.01 mol fraction C in Ni)<sup>S2</sup> because activity coefficients become independent of the concentration of the carbon solute. In this limiting case and for isothermal particles, the gradient in thermodynamic activity of dissolved carbon between the part of the Ni surface exposed to gas-phase reactants and that in contact with the growing carbon filament drives the diffusion of carbon through the metal particle toward the filament and determines the formation rates of such filaments.

Most carbon deposition processes of industrial relevance occur during the steady-state catalytic reactions of multicomponent gas mixtures. However, most previous studies measured the dynamics of carbon formation using equilibrated binary mixtures, such as  $\rm CO-\rm CO_2^{31,41,53,54}$  or  $\rm CH_4-\rm H_2^{44,45,53-56}$  For these quasi-equilibrated mixtures, the thermodynamic activity of carbon  $(a_{\rm C})$  is set by the gasphase composition and given by thermodynamic relations<sup>31,55</sup>

2C0 
$$\leftarrow C + CO_2$$
  $(a_c) = \frac{K_{CO}(CO)^2}{(CO_2)}$  (2)

$$CH_4 \quad \xleftarrow{K_{CH_4}} \quad C + 2H_2 \qquad (a_C) = \frac{K_{CH_4}(CH_4)}{(H_2)^2} \qquad (3)$$

Carbon formation rates depend linearly on the carbon activity  $(a_{\rm C})$  for these equilibrated mixtures,<sup>31,55</sup> consistent with a diffusion-limited filament growth mechanism. A few

studies have addressed the formation rates and morphology of carbon filaments during  $CO-H_2-H_2O-CO_2-CH_4$  reactions<sup>14,57–60</sup> but without accurate mechanism-based frameworks, which are required to relate the prevalent carbon activity at catalytic surfaces to the dynamics of filament formation under different reaction conditions. The information available about the effects of Ni crystallite size on growth rates and morphology of carbon deposits remains largely anecdotal.<sup>57,61</sup> Moreover, the effects of H<sub>2</sub> on carbon deposition rates remain contradictory, with some studies<sup>57,58</sup> reporting that H<sub>2</sub> increases carbon formation rates and others<sup>14,60</sup> demonstrating the opposite trend. The effect of H<sub>2</sub> on the thermodynamic carbon activity prevalent during reactions of  $CO-H_2-H_2O-CO_2-CH_4$  mixtures remains largely unexplored at this time.

The mechanistic details of carbon deposition and its dynamics are explored here through measurements of carbon formation rates during steady-state CH4 reforming catalysis under conditions far away from the chemical equilibrium of this reaction on supported Ni-based catalysts with different nanoparticle diameters, as these reforming reactions occur under strict kinetic control. Carbon formation rates are shown to depend solely on  $\chi$  and  $\psi$  ratios of pressures  $(P_{\rm CO}P_{\rm CH_4}/P_{\rm CO_2})$ and  $P_{\rm H_2}P_{\rm CH_4}/P_{\rm H_2O}$ , respectively), which are proportional to each other through the water-gas shift equilibrium constant. These ratios are shown to set the thermodynamic activity of carbon at Ni surfaces via elementary steps previously reported for CH<sub>4</sub>-CO<sub>2</sub> and CH<sub>4</sub>-H<sub>2</sub>O reactions on metal catalysts under similar conditions.<sup>62</sup> These carbon thermodynamic activities are used within a diffusion-reaction framework to relate the dynamics of filament growth and their morphology to the prevalent conditions of reforming catalysis.

The morphology of carbon structures formed during reactions of  $CO-CO_2-H_2$  and  $CO-H_2-H_2O-CO_2-CH_4$  mixtures on Ni catalysts depends on temperature and on the composition of the contacting gaseous mixtures.<sup>37,38,59,63</sup> CO-CO<sub>2</sub> binary mixtures lead to filaments and onion-like carbon structures on Ni, while  $CO-CO_2-H_2$  mixtures form only filamentous carbon,<sup>38</sup> perhaps because H<sub>2</sub> preserves unblocked active surfaces that can continue to supply the C-atoms required to form filaments in such mixtures.  $CO-H_2-H_2O-CO_2-CH_4$  mixtures also tend to form filamentous forms of carbon, although "platelet" carbon structures are also observed at higher O/H ratios in such mixtures.<sup>59</sup> These previous studies fail to provide clear mechanistic connections between the composition of the  $CO-H_2-H_2O-CO_2-CH_4$  mixtures, the rate of their interconversions at surfaces, the surface carbon activity, and the structure of the carbon deposits formed.

The present study addresses such connections. The evidence provided here shows how the nature of the carbon structures (filamentous or encapsulating) is determined by the surface carbon activity, which is related to the reaction environment through the elementary steps of CH<sub>4</sub> reforming catalysis. Such carbon activities are set by the prevalent  $\chi$  (or  $\psi$ ) values. The morphology of the deposited carbon reflects nucleation and growth processes directly related to well-known effects of supersaturation on the nucleation and growth of solid phases.<sup>64</sup>

### 2. EXPERIMENTAL METHODS

Supported Ni catalysts with 7% wt and 15% wt Ni content were prepared by incipient wetness impregnation of MgO powders, prepared for this study (MgO-A) or obtained from commercial sources (MgO-B; Alfa, CAS# 1309-48-4), with aqueous solutions of Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (Alfa, 99.9%). MgO-A powders were prepared by sol-gel methods using supercritical drying.<sup>62</sup> The impregnated powders were treated overnight in stagnant ambient air at 393 K and then in flowing dry air (Airgas, UHP, 1.2 cm<sup>3</sup> g<sup>-1</sup> s<sup>-1</sup>) at 923 K (0.167 K s<sup>-1</sup>) for 5 h. Samples were then treated in H<sub>2</sub> (Airgas, UHP, 50 cm<sup>3</sup> g<sup>-1</sup> s<sup>-1</sup>) by heating to 1123 K (0.167 K s<sup>-1</sup>) and holding for 3 h.

The metal dispersion of fresh Ni catalysts was determined from the uptake of strongly chemisorbed  $H_2$  at 313 K (3–50 kPa) using a Quantasorb chemisorption analyzer (Quantachrome Corporation model 05-10). Samples were treated in H<sub>2</sub> at 873 K for 0.5 h within the adsorption cell before uptake measurements. A backsorption isotherm was measured by repeating this procedure after evacuation for 0.5 h at 313 K. Strongly chemisorbed hydrogen uptakes were obtained from the difference between chemisorption and backsorption uptakes using a 1:1 H/Ni<sub>surf</sub> stoichiometry.<sup>65</sup> The extent of Ni reduction in these samples was measured from temperatureprogrammed reduction (TPR) using a Quantasorb analyzer (Quantachrome Corporation model 05-10), using procedures reported previously,<sup>62</sup> from the amount of H<sub>2</sub> consumed during temperature ramping to 1123 K (at 0.167 K s<sup>-1</sup>) in a flowing 20% H<sub>2</sub>/Ar mixture (6.7 cm<sup>3</sup> g<sup>-1</sup> s<sup>-1</sup>).

Catalyst samples (0.030 g) were treated again within the balance chamber in flowing H<sub>2</sub> at reaction temperature (843-973 K) for 0.5 h before the reaction. Carbon formation rates were measured during CH<sub>4</sub> reforming reactions at 843-973 K using a tapered-element oscillating quartz microbalance (TEOM; Ruprecht and Patashnick, Series 1500 PMA) in a flow-through sample holder that ensured plug-flow hydrodynamics at all inlet CH<sub>4</sub> (50% CH<sub>4</sub>/Ar, Matheson, UHP, certified mixture), CO<sub>2</sub> (50% CO<sub>2</sub>/Ar, Matheson UHP, certified mixture), CO (Matheson, 99.9%), H<sub>2</sub> (Airgas, 99.999%), and H<sub>2</sub>O (>17.9 M $\Omega$  resistivity; introduced by syringe pump, ISCO model 500D) pressures and residence times (and chemical conversion). These TEOM systems measure the mass of samples placed at the tip of a quartz element using changes in its oscillation frequency, thus avoiding the corrections for buoyancy typically required for gravimetric data.

The composition of effluent streams was continuously monitored by on-line mass spectrometry (Leybold Inficon Transpector). Forward CH<sub>4</sub> reforming rates ( $r_f$ ), normalized per initially exposed Ni atom measured from H<sub>2</sub> uptakes, were calculated by correcting measured rates ( $r_n$ ) for approach to equilibrium ( $\eta$ ) using

$$r_{\rm n} = r_{\rm f} (1 - \eta) \tag{4}$$

The approaches to equilibrium for  $CH_4-CO_2$  (eq 5) and  $CH_4-H_2O$  (eq 6) reforming reactions are defined as

$$\eta_{\rm DRM} = \frac{(\rm CO)^2(\rm H_2)^2}{(\rm CH_4)(\rm CO_2)} \times \frac{1}{K_{\rm DRM}}$$
(5)

$$\eta_{\rm SRM} = \frac{(\rm CO)(\rm H_2)^3}{(\rm CH_4)(\rm H_2O)} \times \frac{1}{K_{\rm SRM}}$$
(6)

where  $K_{\text{DRM}}$  and  $K_{\text{SRM}}$  are the equilibrium constants for the respective CH<sub>4</sub> reforming reaction at a given temperature.<sup>66</sup> The absence of interparticle and intraparticle mass transport artifacts was confirmed by turnover rates that were independent of the extent of interparticle and intraparticle dilution with an inert material.<sup>62</sup>

Transmission electron micrographs of fresh and spent catalyst samples were obtained using a JEOL 2010 electron microscope at accelerating voltages of 200 keV. Transmission electron micrograph samples were prepared by crushing powder samples in an agate mortar, suspending the fine powders in isopropanol, placing a drop of the suspension on a porous carbon copper grid, and allowing the liquid to evaporate in ambient air. Micrographs were obtained from regions of the sample that minimized interference with the porous carbon copper grid. Ni crystallites were identified by contrast differences arising from the stronger electron scattering of Ni atoms relative to the Mg and O atoms in the support. Ni crystallite size distributions were measured manually from enlarged prints made from digitized negatives by counting more than 400 crystallites for each sample. Carbon filaments and encapsulating deposits were identified by repeating layered patterns of strong and weak electron scattering, representing the layered structure of such carbon deposits, which are absent from the support material and Ni crystallites. The spacing of these layers and filament diameters were measured from enlarged prints.

# 3. RESULTS AND DISCUSSION

**3.1. Catalyst Characterization.** The size distribution of supported Ni nanoparticles was measured by transmission electron microscopy (TEM). Surface-averaged Ni cluster diameters  $\langle d_s \rangle$  were calculated from<sup>34</sup>

$$\langle d_{\rm s} \rangle = \frac{\sum (n_{\rm i} d_{\rm i}^{3})}{\sum (n_{\rm i} d_{\rm i}^{2})} \tag{7}$$

where  $n_i$  is the number of clusters with diameter  $d_i$ . These values were 5.4, 11.1, and 11.0 nm for 7% wt and 15% wt Ni/ MgO-A and 7% wt Ni/MgO-B, respectively. The respective extents of Ni reduction (from TPR, reported previously for these catalysts)<sup>62</sup> were 28, 46, and 43%. The remaining refractory Ni<sup>2+</sup> species are likely present in a solid solution with the MgO support, the formation of which has been observed at such high temperature treatments.<sup>67</sup> Such compounds are unlikely to catalyze  $CH_4$ - $CO_2$  and  $CH_4$ - $H_2O$  reactions or the formation of carbon deposits. The fractional dispersions of Ni, defined as the number of exposed Ni atoms measured from  $H_2$ chemisorption divided by the number of reduced Ni metal atoms, as determined from reduction measurements, were 0.14, 0.10, and 0.09. These dispersions were also used to estimate average crystallite diameters by assuming spherical Ni particle geometries using<sup>68</sup>

$$D = 1/d \tag{8}$$

where *D* is the fractional dispersion and *d* is the crystallite diameter (in nm). These fractional Ni dispersion values led to average cluster diameters of 6.7, 10.4, and 10.8 nm for 7% and 15% wt Ni/MgO-A and 7% wt Ni/MgO-B samples, respectively, which agree well with TEM-derived  $\langle d_s \rangle$  values. Such agreement also provides additional evidence that the remaining refractory Ni<sup>2+</sup> species are not present within the Ni nanoparticles.

**3.2.** Mathematical Descriptions of Carbon Diffusion Through Ni Nanoparticles and of Carbon Filament Formation. The rate of filament growth on Ni catalysts is limited by the rate of carbon diffusion (normalized by the particle surface area;  $J_{\rm C}$ ) through the Ni particles.<sup>13,23–26</sup> A one-dimensional diffusion model (in z) gives  $J_{\rm C}$  in terms of the

gradient in chemical potential of dissolved carbon, referenced to graphite<sup>25</sup>

$$J_{\rm C} = -\frac{D_{\rm C}c_{\rm C}}{RT}\frac{\mathrm{d}\mu_{\rm C}}{\mathrm{d}z} \tag{9}$$

Here,  $D_C$  is the diffusion coefficient of carbon within Ni,  $c_C$  is the concentration of carbon, *R* is the ideal gas constant, and *T* is the absolute temperature. Substituting the definition of chemical potential (eq 1) into eq 9 yields

$$J_{\rm C} = -\frac{D_{\rm C}}{\gamma_{\rm C}} \frac{\mathrm{d}a_{\rm c}}{\mathrm{d}z} \tag{10}$$

where  $\gamma_{\rm C}$  is the activity coefficient of dissolved carbon within Ni. The activity coefficient is independent of the concentration (and therefore position) for low solute concentrations. Equation 10 can therefore be integrated to give

$$J_{\rm C} = \frac{D_{\rm C}^*}{d_{\rm p}} [(a_{\rm C,Ni})_{\rm s} - (a_{\rm C,Ni})_{\rm fil}]$$
(11)

$$D_{\rm C}^* = \frac{D_{\rm C}}{\gamma_{\rm C}} \tag{12}$$

where  $d_{p}$  is the particle diameter.

Dissolved carbon atoms at the surface—bulk interface are in equilibrium with those at the surfaces.<sup>25,26,30,33</sup> The thermodynamic activity at the free surface  $(a_{C^*})_s$  and at the filament  $(a_{C^*})_{\rm fil}$  can therefore be related to the activity of dissolved carbon at each of these interfaces through a factor  $c^0$  representing the proportionality between the reference states of dissolved carbon (in equilibrium with graphite) and surface carbon (Henry's law constant), such that

$$(a_{\rm C,Ni})_{\rm s} = c^0 (a_{\rm C^*})_{\rm s} \tag{13}$$

$$(a_{C,Ni})_{\rm fil} = c^0 (a_{\rm C^*})_{\rm fil}$$
(14)

Equation 11 can then be written as

$$J_{\rm C} = \frac{D_{\rm C}^* c^0}{d_{\rm p}} [(a_{\rm C^*})_{\rm s} - (a_{\rm C^*})_{\rm fil}]$$
(15)

Figure 1 shows a graphical representation of this diffusion and filament formation process depicted as a one-dimensional process. The carbon diffusion rates that govern filament growth are thus proportional to  $(a_{C^*})_{s}$ , the value of which is set by the elementary steps that mediate  $CH_4-H_2O$  and  $CH_4 CO_2$  reactions at the Ni catalyst surfaces.<sup>62</sup>

**3.3. Mechanism-Based Surface Carbon Activities and Their Implications for Carbon Formation during CH<sub>4</sub> Reforming.** A sequence of elementary steps for CH<sub>4</sub>–CO<sub>2</sub> and CH<sub>4</sub>–H<sub>2</sub>O reactions was previously shown to accurately describe measured reaction rates on Ru,<sup>69</sup> Rh,<sup>70</sup> Ir,<sup>71,72</sup> Pt,<sup>73</sup> and Ni<sup>62</sup> catalysts (Scheme 1). These steps also include implicitly those required for chemical reactions typically denoted as CH<sub>4</sub> decomposition, Boudouard, and water–gas shift. Previous isotopic tracing experiments showed that CH<sub>4</sub> chemical conversion rates were much faster than isotopic cross-exchange rates (CH<sub>4-x</sub>D<sub>x</sub> formation rates) for CH<sub>4</sub>/ CD<sub>4</sub>/CO<sub>2</sub> or CH<sub>4</sub>/CD<sub>4</sub>/H<sub>2</sub>O (1:1:2) mixtures at 823–973 K on all catalysts (Ru, Rh, Ni, Ir, and Pt), reflecting the irreversibility of C–H bond activation (Scheme 1, step 1.1) during CH<sub>4</sub> reforming reactions.<sup>62,69–73</sup> The quasi-equilibrated



**Figure 1.** Carbon diffusion and filament formation model for Ni particles.  $D_{\rm C}^*$  is the diffusivity of carbon in Ni,  $c^0$  is the Henry's law constant relating the surface carbon and dissolved carbon phases,  $d_{\rm p}$  is the diameter of the Ni particle,  $(a_{\rm C^*})_{\rm si}$  is the thermodynamic carbon activity at the free metal surface, and  $(a_{\rm C^*})_{\rm fil}$  is the thermodynamic carbon activity at the metal–filament interface.

Scheme 1. Identity and Reversibility of Elementary Steps for CH<sub>4</sub> Reforming Catalytic Sequences on Ni Catalysts

$$CH_4 + 2 * \underset{k_{-1}}{\overset{k_1}{\longleftarrow}} CH_3 * + H *$$
[1.1]

$$CH_3 * + * \xleftarrow{k_2} CH_2 * + H *$$
[1.2]

$$CH_2 * + * \underbrace{\underset{k_3}{\overset{k_3}{\longleftarrow}} CH * + H * \qquad [1.3]$$

$$CH * + * \stackrel{k_4}{\longleftarrow} C * + H *$$
[1.4]

$$\operatorname{CO}_2 + 2 * \bigoplus^{\operatorname{KS}} \operatorname{CO} * + 0 *$$
 [1.5]

$$C * + O * \stackrel{\underline{k_6}}{\underset{K_7}{\longleftarrow}} CO * + *$$
[1.6]

$$CO * \bigoplus_{K_{i}}^{K_{i}} CO + *$$
 [1.7]

$$H_2 + 2 * \bigoplus^{K_8} 2H *$$
 [1.8]

$$H_2O + 2 * \bigoplus^{KS} OH * + H *$$
[1.9]

$$OH * + * \bigoplus^{K_{10}} O * + H *$$
 [1.10]



nature of CO<sub>2</sub> dissociation (Scheme 1, step 1.5) and CO desorption (Scheme 1, step 1.7) was confirmed by the identical <sup>13</sup>C contents observed in CO and CO<sub>2</sub> molecules during reactions of <sup>13</sup>CO/<sup>12</sup>CO<sub>2</sub>/<sup>12</sup>CH<sub>4</sub> (0.4:1:1) mixtures at 823–973 K on all metal catalysts.<sup>62,69–73</sup> CH<sub>4</sub>/CO<sub>2</sub>/D<sub>2</sub> (1:1:0.2) mixtures led to binomial distributions of deuterium isotopologues of dihydrogen and water at all reactant conversions on these catalysts.<sup>62,69–73</sup> Thus, the recombinative desorption of H-atoms and OH-groups to form H<sub>2</sub> or H<sub>2</sub>O (Scheme 1, steps 1.8–1.10) must also be quasi-equilibrated during CH<sub>4</sub> reforming catalysis. These mechanistic conclusions and the application of the pseudo-steady-state approximation (PSSA) for all surface intermediates give an expression that relates the

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**Figure 2.** CH<sub>4</sub> reforming turnover rate (a), carbon formation rate (per surface Ni) (b), and total carbon accumulated on the Ni surface (c) as functions of time on-stream on 7% wt Ni/MgO-A at  $\chi$  = 1.01 kPa ( $\psi$  = 2.47 kPa; 22.5 kPa CH<sub>4</sub>, 27.5 kPa CO<sub>2</sub> feed) during CH<sub>4</sub>–CO<sub>2</sub> reaction at 873 K (regime I). Reaction conditions were far from CH<sub>4</sub> reforming equilibrium.

prevalent concentration of carbon at surfaces (C\*) during steady-state  $CH_4-H_2O$  and  $CH_4-CO_2$  reactions to the prevalent contacting pressures of reactants and products, as described below.

The application of the PSSA to C\* during  $CH_4-CO_2$  and  $CH_4-H_2O$  reforming under conditions far from equilibrium of this reaction leads to  $(a_{C^*})_s$  values (details in the Supporting Information Section 1.1), given by

$$\frac{(a_{\mathrm{C}}^*)_{\mathrm{s}}}{(\mathrm{L})} = \alpha \chi \frac{(1 + \omega(a_{\mathrm{C}}^*)_{\mathrm{fil}})}{(1 + \omega \alpha \chi(\mathrm{L}))} = \beta \psi \frac{(1 + \omega(a_{\mathrm{C}}^*)_{\mathrm{fil}})}{(1 + \omega \beta \psi(\mathrm{L}))}$$
(16)

$$\alpha = \frac{k_1}{k_6 K_5 K_7} \tag{17}$$

$$\beta = \frac{k_1 K_8}{k_6 K_9 K_{10}}$$
(18)

$$\omega = \frac{D_{\rm C}^* c^0}{d_{\rm p}({\rm L})} \frac{1}{k_{\rm I}({\rm CH}_4)}$$
(19)

Here,  $\chi$  and  $\psi$  represent the  $\frac{(CH_4)(CO)}{(CO_2)}$  and  $\frac{(CH_4)(H_2)}{(H_2O)}$  pressure ratio, respectively, and (L) is the concentration of exposed surface metal atoms. This equation was derived by assuming, as evidenced from experiments, that CH<sub>4</sub> dissociative adsorption (Scheme 1, steps 1.1–1.4) and the reaction of C\*–O\*

(Scheme 1, step 1.6) are irreversible under reaction conditions far from CH<sub>4</sub> reforming equilibrium (except by the extent required by microscopic reversibility) and there are no significant coverages of intermediates during steady-state CH<sub>4</sub> reforming catalysis. The parameters  $\alpha$  and  $\beta$  are proportional to each other through the equilibrium constant for water–gas shift ( $K_{WGS}$ ) at a given temperature because this reaction was equilibrated under all reforming conditions in this study

$$\alpha = K_{\rm WGS}\beta \tag{20}$$

The surface concentration of carbon (C\*) is equivalent to its thermodynamic activity  $(a_{C*})_s$  here. Equation 15 can therefore be rewritten to obtain an expression for the rate of carbon formation (per surface Ni;  $r_C$ )

$$r_{\rm C} = \frac{J_{\rm C}}{({\rm L})} = \frac{D_{\rm C}^* c^0}{d_{\rm p}({\rm L})} \left[ \alpha \chi({\rm L}) \frac{(1 + \omega(a_{\rm C}^*)_{\rm fil})}{(1 + \omega \alpha \chi({\rm L}))} - (a_{\rm C}^*)_{\rm fil} \right]$$
$$= \frac{D_{\rm C}^* c^0}{d_{\rm p}({\rm L})} \left[ \beta \psi({\rm L}) \frac{(1 + \omega(a_{\rm C}^*)_{\rm fil})}{(1 + \omega \beta \psi({\rm L}))} - (a_{\rm C}^*)_{\rm fil} \right]$$
(21)

An additional assumption, relaxed later for experiments where it is inaccurate, that the rates of carbon transport into the Ni–C solid solution are much smaller than the rates of C\* formation from  $CH_4$  decomposition (Scheme 1, steps 1.1–1.4)



**Figure 3.** Transmission electron micrographs of carbon morphology after CH<sub>4</sub>-CO<sub>2</sub> reaction on 7% wt Ni/MgO-A at 873 K and (a)  $\chi$  = 1.01 kPa ( $\psi$  = 2.47 kPa), (b)  $\chi$  = 2.16 kPa ( $\psi$  = 5.29 kPa), and (c)  $\chi$  = 9.7 kPa ( $\psi$  = 23.8 kPa).

10 nm

and C\* removal by reaction between C\* and O\* (Scheme 1, step 1.6) leads to

$$r_{\rm C} = \frac{J_{\rm C}}{({\rm L})} = \frac{D_{\rm C}^* c^0}{d_{\rm p}({\rm L})} [\alpha \chi({\rm L}) - (a_{\rm C}^*)_{\rm fil}]$$
$$= \frac{D_{\rm C}^* c^0}{d_{\rm p}({\rm L})} [\beta \psi({\rm L}) - (a_{\rm C}^*)_{\rm fil}]$$
(22)

The mechanism-based model represented by eqs 21 and 22 thus relates the carbon diffusion and filament formation rate to the prevalent gas-phase composition under steady-state conditions away from chemical equilibrium of  $CH_4$  reforming reactions. When reforming turnover rates are much larger than filament growth rates, it leads to values of the latter that are single-valued functions of  $\chi$  (or  $\psi$ ) (eq 22).

**3.4.** Measured Effects of  $\chi$  and  $\psi$  on Carbon Deposition Rates. Carbon formation rates were measured at different inlet CH<sub>4</sub>, CO<sub>2</sub>, CO, H<sub>2</sub>, and H<sub>2</sub>O concentrations and residence times, resulting in a broad range of  $\chi$  and  $\psi$  values (0–10 and 0–24 kPa, respectively) during catalytic reactions of CH<sub>4</sub>–CO<sub>2</sub> and CH<sub>4</sub>–H<sub>2</sub>O reforming. These  $\chi$  and  $\psi$  ratios are calculated from the mean pressures for all chemical species along the reactor.

Figure 2 shows  $CH_4-CO_2$  turnover rates (normalized per initially exposed Ni atom), carbon formation rates (at near the detection limit), and the cumulative amount of carbon formed

on 7% Ni/MgO-A as a function of the time elapsed since its initial contact with the reacting stream for a  $\chi$  value of 1.01 kPa ( $\psi = 2.47$  kPa; 22.5 kPa CH<sub>4</sub>, 27.5 kPa CO<sub>2</sub> feed) at 873 K. Carbon formation rates were nearly undetectable (<0.05 C Ni<sub>surf</sub> s<sup>-1</sup>; Figure 2b) because the prevalent surface carbon activity ( $a_{C^*}$ )<sub>s</sub> was insufficient to nucleate carbon filaments. CH<sub>4</sub>-CO<sub>2</sub> turnover rates did not change with time (Figure 2a) because the ( $a_{C^*}$ )<sub>s</sub> value did not lead to kinetically detectable C\* coverages on Ni surfaces, consistent with the small amounts of carbon deposited on Ni particles, as observed in TEM images of this sample (Figure 3a). Such behavior is characteristic of CH<sub>4</sub>-CO<sub>2</sub> and CH<sub>4</sub>-H<sub>2</sub>O reactions on this catalyst at  $\chi$  values below 1.1 kPa (or  $\psi$  < 2.7 kPa; 873 K); this range of values defines what is denoted here as regime I.

Figure 4 shows  $CH_4-CO_2$  turnover rates (normalized per initially exposed Ni atom), carbon deposition rates, and the cumulative amount of carbon deposited as a function of the time elapsed on 7% Ni/MgO-A since its initial contact with the  $CH_4-CO_2$  stream at  $\chi$  values of 2.16 kPa ( $\psi = 5.29$  kPa; 25 kPa  $CH_4$ , 15 kPa  $CO_2$  feed) and 3.74 kPa ( $\psi = 9.16$  kPa; 25 kPa  $CH_4$ , 10 kPa  $CO_2$  feed) at 873 K.  $CH_4$  reforming turnover rates remained essentially constant with time (Figure 4a), even after the deposition of carbon quantities corresponding to very large C/Ni<sub>surf</sub> ratios (~800; Figure 4c). Such large extents of carbon deposition are consistent with the presence of filamentous carbon structures affixed to nearly all nanoparticles, as evident in TEM images of samples exposed to



**Figure 4.** CH<sub>4</sub> reforming turnover rate (a), carbon formation rate (per surface Ni) (b), and total carbon accumulated on the Ni surface (c) as functions of time on-stream on 7% wt Ni/MgO-A at  $\chi = 2.16$  kPa ( $\psi = 5.29$  kPa; 25 kPa CH<sub>4</sub>, 15 kPa CO<sub>2</sub> feed) and 3.74 kPa ( $\psi = 9.16$  kPa; 25 kPa CH<sub>4</sub>, 10 kPa CO<sub>2</sub> feed) during CH<sub>4</sub>–CO<sub>2</sub> reaction at 873 K (regime II). Reaction conditions were far from CH<sub>4</sub> reforming equilibrium. Dotted lines were added to guide the eye.

these environments (Figure 3b). The rate of carbon formation (Figure 4b) shows an initial increase upon contact with the reacting mixture, consistent with an induction period associated with the stochastic assembly of the number of Catoms required to nucleate the filamentous carbon phase. This process becomes more probable as the activity of the carbon species at the surface of Ni nanoparticles increases with increasing  $\chi$  or  $\psi$  values.<sup>9,56</sup> Consequently, larger values of  $\chi$  or  $\psi$  (and of carbon activity) lead to shorter induction periods (Figure 4b). Carbon deposition rates ultimately reached a near constant value with time. These nearly constant carbon deposition and CH<sub>4</sub> turnover rates indicate that Ni surfaces remain accessible for C-H activation events (Scheme 1, step 1.1), in spite of the prevalence of affixed filamentous carbon structures, and that C\* surface coverages do not change with time. C\* species formed from CH<sub>4</sub> are removed via reactions with either H\* (Scheme 1, step 1.4) or O\* (Scheme 1, step 1.6) or via diffusion through the particle and deposition at the carbon filament. The low steady-state C\* coverages (and  $(a_{C^*})_s$  values) here require that the rates of removal be sufficient to maintain such low coverages even as the activity of C\* increases with increasing  $\chi$  values between 1.1 and 4.2 kPa ( $\psi$  = 2.7–10.3 kPa; 873 K), a range of carbon activity that we denote here as regime II.

Figure 5 shows  $CH_4$ - $CO_2$  turnover rates (normalized per initially exposed Ni atom), rates of formation of carbon

filaments, and the total amount of carbon deposited on 7% Ni/ MgO-A as a function of the time elapsed since the initial contact with the CH<sub>4</sub>–CO<sub>2</sub> stream for a  $\chi$  value of 5.3 kPa ( $\psi$ = 13 kPa; 873 K; 25 kPa CH<sub>4</sub>, 5 kPa CO<sub>2</sub> feed). CH<sub>4</sub> reforming rates decreased monotonically with time (Figure 5a), while carbon formation rates (Figure 5b) showed a brief induction period (100 s), during which rates initially increased as carbon supersaturation and nucleation processes occurred, followed by a relatively constant carbon deposition rate and ultimately a gradual decrease in rate with time. At these high  $\chi$ and  $\psi$  values, the concomitant high carbon activity leads to the simultaneous incipient nucleation of filament precursors at several locations on a given nanoparticle and to their ultimate coalescence to form carbon layer structures that block active surfaces for C-H activation reactions (Figure 3c). These processes lead to a concurrent decrease in CH4 reforming and carbon formation rates with time for such  $\chi$  and  $\psi$  values (Figure 5a and 5b, respectively). This behavior was observed on 7% Ni/MgO-A samples at  $\chi$  values above 4.2 kPa ( $\psi$  > 10.3 kPa; 873 K), which is denoted here as regime III.

Carbon formation rates increased monotonically with increasing  $\chi$  and  $\psi$  values in regimes II and III during steady-state catalytic reactions of CH<sub>4</sub>-CO<sub>2</sub> and CH<sub>4</sub>-H<sub>2</sub>O. Figure 6 shows steady-state carbon formation rates at 873 K as a function of  $\chi$  and  $\psi$  ratios on 7% Ni/MgO-A. At the intermediate values of  $\chi$  (or  $\psi$ ) corresponding to regime II,

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**Figure 5.** CH<sub>4</sub> reforming turnover rate (a), carbon formation rate (per surface Ni) (b), and carbon accumulated on the Ni surface (c) as functions of time on-stream on 7% wt Ni/MgO-A at  $\chi = 5.3$  kPa ( $\psi = 13$  kPa; 25 kPa CH<sub>4</sub>, 5 kPa CO<sub>2</sub> feed) during CH<sub>4</sub>-CO<sub>2</sub> reaction at 873 K (regime III). Reaction conditions were far from CH<sub>4</sub> reforming equilibrium.



Figure 6. (a) Carbon formation rates vs  $\chi$  ( $P_{CO}P_{CH_4}/P_{CO_2}$ ) or  $\psi$  ( $P_{H_2}P_{CH_4}/P_{H_2O}$ ) on 7% wt Ni/MgO-A at 873 K with a magnified view (b) of carbon removal (regime IV).  $P_{CO}P_{CH_4}/P_{CO_2}$  or  $P_{H_2}P_{CH_4}/P_{H_2O}$  ratios were changed by varying inlet CH<sub>4</sub>, CO<sub>2</sub>, CO, H<sub>2</sub>, or H<sub>2</sub>O partial pressures and/or space velocity during CH<sub>4</sub>/CO<sub>2</sub> and CH<sub>4</sub>/H<sub>2</sub>O reactions. ( $\blacklozenge$ ) CH<sub>4</sub>/CO<sub>2</sub> reaction, ( $\bigstar$ ) CH<sub>4</sub>/H<sub>2</sub>O reaction, and ( $\diamondsuit$ ) CH<sub>4</sub>/CO<sub>2</sub> reaction with addition of H<sub>2</sub>. Dashed lines were drawn to guide the eye and determined by linear best-fit methods.

steady-state carbon formation rates are proportional to  $\chi$  or  $\psi$  values and reflect rates predicted by the functional form of eq 22 for diffusion-limited filament growth.

The linear dependence of carbon formation rates on  $\chi$  (or  $\psi$ ) in regime II can be used to obtain lumped parameters

associated with the slope  $\left(\frac{D_{C}^*c^0}{d_p}\alpha\right)$  and *y*-intercept  $\left(\frac{D_{C}^*c^0}{d_p(L)}(a_{C^*})_{\rm fil}\right)$ (eq 22). This  $\left(\frac{D_{C}^*c^0}{d_p(L)}(a_{C^*})_{\rm fil}\right)$  term represents the rate of carbon transport (per surface Ni) from the filament to a bare Ni surface. The product of  $\omega$   $\left(\frac{D_{C}^*c^0}{d_p(L)}\frac{1}{k_1(CH_4)}; \text{ eq } 19\right)$  and  $(a_{C^*})_{\rm fil}$  in the numerator of eqs 16 and 21 therefore represents the ratio of this rate to that of carbon formation from CH<sub>4</sub> decomposition on sparsely covered Ni nanoparticle surfaces  $(k_1(CH_4); \text{ Scheme 1, step 1.1})$ . These two rates were 0.41  $\pm$  0.04 and 4.7  $\pm$  0.1 C Ni<sub>surf</sub><sup>-1</sup> s<sup>-1</sup>, respectively, for  $\chi$  (or  $\psi$ ) values in regime II ( $\chi = 1.1-4.2$  kPa,  $\psi = 2.7-10.3$  kPa; 25 kPa CH<sub>4</sub>; 873 K); such values lead to  $\omega(a_{C^*})_{\rm fil}$  values between 0.08 and 0.1. These small values influence only slightly the (1 +  $\omega(a_{C^*})_{\rm fil}$ ) term in the numerator of eqs 16 and 21, consistent with the single-valued dependence on  $\chi$  (or  $\psi$ ) observed in regime II (Figure 6a).

The  $\omega \alpha \chi(L)$  term in the denominator of eqs 16 and 21 represents the ratio of the rate of carbon diffusion from the Ni surface  $\left(\frac{D_{C}^{*c^{0}}}{d_{p}}\alpha\chi\right)$ , under conditions where such rates are insufficient to perturb the surface carbon activity  $(a_{C^*})_{st}$  to that of C-H activation events ( $k_1$ (CH<sub>4</sub>); Scheme 1, step 1.1). The linear trend in regime II ( $\chi = 1.1-4.2$  kPa,  $\psi = 2.7-10.3$  kPa; 873 K; Figure 6a) suggests that carbon transport rates in this regime are insufficient to perturb  $(a_{C^*})_s$  and therefore obey the functional form of eq 22, allowing  $\left(\frac{D_{c}^{*c^{0}}}{d_{p}}\alpha\chi\right)$  to be extracted from these data (<1.6 C Ni<sub>surf</sub><sup>-1</sup> s<sup>-1</sup>). CH<sub>4</sub> turnover rates were between 4.6 and 4.8 moles (g-atom-Ni<sub>surf</sub> s)<sup>-1</sup> ( $k_1$ (CH<sub>4</sub>); Scheme 1, step 1.1; 25 kPa CH<sub>4</sub>) for these conditions. These rates lead to  $\omega \alpha \chi(L)$  values below 0.34, which lead, in turn, to small (but measurable) effects on  $(1 + \omega \alpha \chi(L))$  in the denominator of eqs 16 and 21 and to an expectation of some curvature in the trends of carbon formation rates with  $\chi$  at the higher values of  $\chi$  in regime II. The  $(1 + \omega \alpha \chi(L))$  term, however, is partially offset by the  $(1 + \omega(a_{C^*})_{fl})$  term (1.08– (1.1) in the numerator (eqs 16 and 21), which causes the linear trends to persist throughout regime II. These considerations illustrate the caution required in applying the model described by eq 22 as carbon transport rates become similar to the rates of carbon formation (Scheme 1, step 1.1-1.4) or removal (Scheme 1, step 1.6), as in the case of regime III described below.

At even higher values of  $\chi$  (or  $\psi$ ) (regime III;  $\chi > 4.2$  kPa,  $\psi > 10.3$  kPa; 873 K, 25 kPa CH<sub>4</sub>), carbon formation rates, defined here as the maximum (and nearly constant) rates observed with time, do not increase linearly with the carbon activity. The carbon deposition rates in regime III ( $\chi > 4.2$  kPa,  $\psi > 10.3$  kPa; 873 K) are below those predicted by extending the linear trends from regime II (Figure 6a). This reflects, in part, the kinetically detectable encapsulation of Ni nanoparticles by carbon adlayers, as shown by CH<sub>4</sub> reforming turnover rates that decreased with time (Figure 5a). This trend also reflects the decrease in C\* activity ( $a_{C*}$ )<sub>s</sub> caused by the high rates of C\* removal by diffusion (1.6–2.0 C Ni<sub>suff</sub><sup>-1</sup> s<sup>-1</sup>, Figure 6a) prevalent in regime III. This effect is captured by the  $\omega \alpha \chi$ (L) term in the denominator of eqs 16 and 21, which represents the rate of carbon diffusion away from

unaffected by these diffusion processes, to the rate of CH<sub>4</sub> turnover on a bare surface ( $k_1$ (CH<sub>4</sub>); Scheme 1, step 1.1). The  $\left(\frac{D_{C}^* c^0}{d_p} \alpha \chi\right)$  values can be estimated by extrapolating the linear trends from regime II (Figure 6a), while the value of  $k_1$ (CH<sub>4</sub>) is given by CH<sub>4</sub> turnover rates (4.5–4.8 moles (g-atom-Ni<sub>surf</sub> s)<sup>-1</sup>; 25 kPa CH<sub>4</sub>; Figure 5a), leading to  $\omega \alpha \chi$ (L) values between 0.4 and 0.8, which lead, in turn, to lower carbon formation rates, as evident from eq 21. Thus, the assumptions inherent in the derivation of eq 22 are accurate only when the rates of carbon formation from CH<sub>4</sub> decomposition and removal by reaction between C\* and O\* are much higher than the rates of carbon transport into the Ni–C solid solution,

conditions that are met in regimes I and II in this study. 3.5. Measured Effects of  $\chi$  and  $\psi$  on Carbon Removal Rates. Previous studies have indicated that carbon removal processes occur when exposing Ni- or Fe-based catalysts to  $H_2O$  or  $H_2$  environments.<sup>35,36</sup> The reversibility of filament formation processes was examined here using low CH<sub>4</sub> pressures (and small  $\chi$  values) ( $\chi$  < 1.1 kPa,  $\psi$  < 2.7 kPa; 2.5 kPa CH<sub>4</sub>; 873 K) on 7% Ni/MgO-A samples containing carbon filaments previously formed in regime II ( $\gamma = 2.16$  kPa,  $\psi$  = 5.29 kPa; 25 kPa CH<sub>4</sub>). These conditions were expected to consume such filaments via the reverse processes, as indicated by the form of eq 22, and are denoted as regime IV. Gas compositions leading to  $\chi$  values below 0.07 kPa (or  $\psi < 0.17$ kPa; 2.5 kPa CH<sub>4</sub>) at 873 K (after filament growth in regime II;  $\chi = 2.16$  kPa,  $\psi = 5.29$  kPa) led to the removal of carbon at rates (Figure 6b) that are linearly dependent on  $\chi$  (and  $\psi$ ) but do not align with the linear trends in regime II (Figure 6a), as would have been expected from eq 22.

These results indicate that the low CH<sub>4</sub> pressure required to consume carbon filaments in regime IV leads to carbon diffusion rates from the filament that increase C\* coverages over those present during steady-state catalysis in the absence of such filaments, thus requiring the functional form of eq 21 to accurately describe carbon removal rates. Equation 21 allows estimates of the group of terms associated with the yintercept  $\left(\frac{D_{Ce}^{*,0}}{d_{n}(L)}(a_{C*})_{\text{fil}}\right)$ , whose magnitude represents the rate of carbon diffusion from the filament to a bare Ni surface (0.47  $\pm$  0.02 C Ni<sub>surf</sub><sup>-1</sup> s<sup>-1</sup>). This value is nearly identical to that obtained from the data in regime II (0.41  $\pm$  0.04 C Ni<sub>surf</sub><sup>-1</sup> s<sup>-1</sup>; Section 3.4), as expected from carbon filament activities that are insensitive to the composition of the gas phase, and is similar to the CH4 turnover rate expected at the CH4 pressure used in regime IV ( $k_1$ (CH<sub>4</sub>); Scheme 1, step 1.1; 0.48 C  $Ni_{surf}^{-1} s^{-1}$ ). These rates lead to a  $(1 + \omega(a_{C^*})_{fl})$  value of 2 in the numerator of eqs 16 and 21 and consequently an expectation of a two-fold larger slope in regime IV than in regime II. The observed slope for regime IV ( $6.4 \pm 0.5$ ; Figure 6b) is 16-fold higher in regime IV than that in regime II (0.4  $\pm$ 0.03; Figure 6a). Such a quantitative disagreement between the expected and observed slope may be caused by the formation of carbon patches that block active sites formed during the He purge that was used after the formation of the carbon filaments

The value of  $\omega \alpha \chi(L)$  was estimated to be smaller than 0.07 under all conditions in regime IV by extrapolating the linear trends from regime II, described by the functional form of eq

and before the carbon removal experiments.

the Ni surface  $\left(\frac{D_c^{\kappa}c^0}{d_p}\alpha\chi\right)$ , when the surface carbon activity is

22, to determine the value of  $\left(\frac{D_c^*c^0}{d_p}\alpha\chi\right)$ ; these small values of

 $\omega \alpha \chi(L)$  in the denominator of eqs 16 and 21 allow it to be neglected. Carbon removal rates in regime IV ( $\chi < 1.1$  kPa,  $\psi < 2.7$  kPa; 2.5 kPa CH<sub>4</sub>) therefore do not reflect the linear trends predicted by the functional form of eq 22 but instead reflect an increase in the surface carbon activity caused by the diffusion of carbon from the filament to the free metal surface, which results in lower carbon removal rates than those predicted by extrapolating trends from regime II.

3.6. Electron Microscopy Evidence for the Morphology of Carbon Structures for Different Carbon Thermodynamic Activities. The morphologies of carbon deposits formed on Ni catalysts during  $CH_4-CO_2$  and  $CH_4-H_2O$  reforming catalysis were determined by inspection of TEM images of samples exposed to conditions leading to regimes I, II, and III. The nature of the carbon structures (filamentous or encapsulating) was determined by the surface carbon activity ( $a_{C^*}$ )<sub>s</sub>, which led to distinct forms of carbon in regimes II and III and to the absence of detectable carbon structures in regime I (Section 3.4).

TEM images of 7% wt Ni/MgO-A catalysts in regime I (Figure 3a) do not show visible evidence of carbon deposits ( $\chi$  = 1.01 kPa,  $\psi$  = 2.47 kPa, 873 K), consistent with CH<sub>4</sub> reforming rates that remained constant during contact with reacting mixtures (Figure 2a) and with the small mass changes observed during steady-state reforming under these conditions (Figure 2c). The absence of carbon filaments shows that the carbon activities ( $a_{C*}$ )<sub>s</sub> prevalent in regime I are too low to allow the widespread nucleation and growth of carbon filaments.

TEM images of 7% wt Ni/MgO-A samples in regime II ( $\chi$  = 2.16 kPa,  $\psi$  = 5.29 kPa; 873 K; Figure 3b) predominantly show multiwalled carbon filaments similar in diameter to the Ni nanoparticles affixed to their ends. These carbon filaments showed "fishbone"-like structures, with carbon layers angled relative to the axis of growth but parallel to the crystallite surface. Such an ordered alignment of the carbon layers with the facets of the Ni particle on which they nucleate suggests that carbon atoms are systematically added to the filament; each carbon layer is completed before it is pushed away from the Ni surface and assembly of the next carbon layer begins. The interlayer spacing of approximately 0.35 nm at the filament walls (Figure 7) is very similar to that expected for graphitic structures (0.34 nm) that are essentially free of residual H-atoms.<sup>18</sup>



**Figure 7.** Transmission electron micrograph showing the structure of the carbon filament and interlayer spacing of graphite layers on 7% wt Ni/MgO-A after CH<sub>4</sub>-CO<sub>2</sub> reaction at 873 K and  $\chi$  = 2.16 kPa ( $\psi$  = 5.29 kPa).

Each filament formed in regime II contains a Ni nanoparticle affixed at one end and a part of each nanoparticle seemingly devoid of carbon deposits. Nanoparticles affixed at filament tips exhibit a "pear-shaped" nature (Figures 3b and 7), which may reflect the significant restructuring required in order to accommodate the epitaxial growth of graphite-type layers that have been proposed to grow preferentially on Ni(111) and Ni(311) facets;<sup>74-76</sup> restructuring thus acts to preserve the other facets, such as the Ni(100) and Ni(110) surfaces that have been proposed to be favored for C-H activation.<sup>11,43,77</sup> Metal nanoparticles can exhibit liquid-like properties at reforming temperatures, <sup>78,79</sup> thus enabling the detachment of the nanoparticle from the support and the adoption of these particle-filament arrangements. The clean surfaces, which may consist of (100) or (110) facets that are less likely to form epitaxial carbon layers,<sup>11,43,77</sup> can therefore continue to activate  $\hat{C}H_4$ , leading to  $CH_4$  reforming and carbon formation rates that remain essentially unchanged with time in regime II (Figure 4a; Section 3.4), even as the extensive formation of filaments occurs (Figure 4b,c; Section 3.4). The restructuring and reorienting of the metal crystallites due to interactions with hydrocarbons and subsequent filament growth are also conducive to the directional diffusion of carbon from the free metal surface to the carbon filament required to prevent the formation of encapsulating carbon adlayers, as reported in previous studies.<sup>43,63,76,80-83</sup>

At 873 K and under conditions of regime III ( $\chi > 4.24$  kPa;  $\psi$  > 10.4 kPa), TEM images show that CH<sub>4</sub> reforming on 7% wt Ni/MgO-A causes the extensive encapsulation of Ni nanoparticles by onion-like carbon layers (Figure 3c). Such structural motifs reflect the high carbon activity resulting from CH<sub>4</sub> reforming elementary steps under the conditions that lead to such large  $\chi$  values. The resulting carbon supersaturation within Ni nanoparticles leads to the simultaneous nucleation of carbon patches as potential precursors to filament growth. These multiple carbon sinks lead, in turn, to a disruption of the unidirectional carbon activity gradient otherwise imposed by the presence of a single filament as the unique carbon sink. TEM images in regime III also show that Ni nanoparticles lack the "pear-shaped" character of those affixed to a filament (Figure 3c vs Figure 3b). The formation of these encapsulating carbon structures causes a monotonic change in the fraction of the Ni nanoparticle surfaces that remain accessible for the activation of the C-H bonds in the step that limits CH<sub>4</sub> reforming rates and which form C\* as products and, in doing so, sets the C\* coverages that drive carbon diffusion and the rate of carbon deposition. Consequently, reforming and carbon deposition rates decrease monotonically with time in regime III (Figure 6a,b;  $\chi = 9.7$  kPa,  $\psi = 23.8$  kPa; Section 3.4). After complete encapsulation, Ni surfaces become inaccessible and cannot form active O\* or H\* species from gaseous reactants. As a result, exposure of these coated nanoparticles to low values of  $\chi$  or  $\psi$  ( $\chi$  < 1.1 kPa,  $\psi$  < 2.7 kPa; regime IV), which led to the removal of carbon from nanoparticles with affixed carbon filaments formed under the conditions of regime II (Figure 6b; Section 3.5), did not lead to the removal of these carbon overlayers.

**3.7. Effects of CH<sub>4</sub> Reforming Reaction Temperature on Carbon Formation Rates.** Carbon formation rates during CH<sub>4</sub>-CO<sub>2</sub> and CH<sub>4</sub>-H<sub>2</sub>O reforming reactions were also measured on 7% wt Ni/MgO-A at different temperatures (843-973 K) and  $\chi$  (and  $\psi$ ) values in regime II, where carbon formation rates are strictly proportional to such  $\chi$  (and  $\psi$ )



**Figure 8.** Carbon formation rates vs  $\chi$  ( $P_{CO}P_{CH_4}/P_{CO_2}$ ) on 7% wt Ni/MgO-A during CH<sub>4</sub>-CO<sub>2</sub> (open symbol) or CH<sub>4</sub>-H<sub>2</sub>O reactions (solid symbol) ( $\square$  843 K,  $\triangle \blacktriangle$  873 K,  $\bigcirc \spadesuit$  893 K,  $\diamondsuit \clubsuit$  973 K). Dashed lines determined by linear best fit models.

values (Section 3.4). The data in Figure 8 show that carbon formation rates decreased with increasing temperature at each  $\chi$  or  $\psi$  value. These temperature effects on carbon formation rates reflect the respective consequences of temperature for terms that account for the slope  $\left(\frac{D_{c}^{*}c^{0}}{d_{p}}\alpha\right)$  and y-intercept  $\left(\frac{D_{c}^{*}c^{0}}{d_{p}(L)}(a_{C^{*}})_{fil}\right)$  in the functional form of eq 22.

 $10^{3}/T$  (K<sup>-1</sup>) **Figure 9.** Arrhenius plot of  $\frac{D_{C}^{*}c^{0}}{d_{p}}\alpha$ . The carbon diffusivity in Ni  $D_{C}^{*}$ , Henry's Law constant  $c^{0}$ , and the group of kinetic and thermodynamic parameters  $\alpha$  are expected to show temperature dependences. The dashed line was obtained through linear regression and reflects an effective energy barrier of  $-10 \pm 2$  kJ mol<sup>-1</sup>.

Figure 9 shows  $\left(\frac{D_c^*c^0}{d_p}\alpha\right)$  values as a function of inverse temperature; all terms except the particle diameter  $(d_p)$  are expected to exhibit Arrhenius-like dependences. The data in Figure 9 give an effective energy barrier of  $-10 \pm 2$  kJ mol<sup>-1</sup> for  $\left(\frac{D_c^*c^0}{d_p}\alpha\right)$ , which reflects the combined temperature effects on the diffusivity of carbon in Ni  $(D_c^*)$ , its Henry's law

constant ( $c^0$ ), and the grouping of rate and equilibrium constants contained in  $\alpha$  ( $k_1/k_6K_5K_7$ , eq 17; Scheme 1).

The activation energies and enthalpies for each of these terms can be obtained from the literature and used to evaluate the value reported here. Massaro and Petersen previously measured the diffusivity of carbon in Ni  $(D_c^*)$  using acetylene decomposition between 623 and 973 K and reported an activation energy barrier of 83  $\pm$  5 kJ mol<sup>-1.84</sup> Lander et al. measured the temperature dependence for the solubility of carbon in Ni, which is reflected in the Henry's law constant ( $c^0$ ), and reported a dissolution enthalpy of -40 ± 1 kJ mol<sup>-1.85</sup> The parameter  $\alpha$  ( $k_1/k_6K_5K_7$ ; eq 17) includes the rate constants for C-H activation ( $k_1$ ; Scheme 1, step 1.1) and for C\*-O\* recombination ( $k_6$ , Scheme 1, step 1.6) and the equilibrium constants for  $CO_2$  dissociative adsorption ( $K_5$ , Scheme 1, step 1.5) and molecular desorption of CO  $(K_7,$ Scheme 1, step 1.7). The temperature dependence of  $k_1$  on these Ni-based catalysts was previously found to be  $105 \pm 3 \text{ kJ}$ mol<sup>-1.62</sup> Snoeck et al. studied the gasification of carbon filaments on Ni-based catalysts using CO2 at 773-848 K and used a mechanism-based rate equation to obtain  $k_6$ ,  $K_5$ , and  $K_7$ values.<sup>86</sup> They reported an activation energy of  $244 \pm 68 \text{ kJ}$  mol<sup>-1</sup> for  $k_6$  along with the enthalpies associated with  $K_5$  $(-104 \pm 85 \text{ kJ mol}^{-1})$  and  $K_7 (100 \pm 61 \text{ kJ mol}^{-1})$ .<sup>86</sup> The effective energy barrier calculated from the literature for

 $\left(\frac{D_{Cc}^{r,0}}{d_p}\alpha\right)$ , after rigorously propagating the respective uncertainties in the individual parameters, is therefore  $-12 \pm 126$  kJ

mol<sup>-1</sup>. This value is in agreement with that observed in this study ( $-10 \pm 2$  kJ mol<sup>-1</sup>), although more precise measurements of the parameters  $k_6$ ,  $K_5$ , and  $K_7$  are needed to conclusively demonstrate this.

Figure 8 shows that  $\left(\frac{D_{\rm C}^{*c^0}}{d_{\rm p}({\rm L})}(a_{\rm C}^*)_{\rm fil}\right)$  values, reflected in the absolute value of the *y*-intercept in the carbon formation rates, increase with temperature. Figure 10 shows these  $\left(\frac{D_{\rm C}^{*c^0}}{d_{\rm p}({\rm L})}(a_{\rm C}^*)_{\rm fil}\right)$  values in a logarithmic scale as a function of inverse temperature, in which the slope corresponds to an effective energy barrier of 95  $\pm$  22 kJ mol<sup>-1</sup>.

This value can also be compared with literature values for the individual parameters in this term. The  $d_p$  and (L) terms are independent of temperature. The enthalpy of formation for carbon filaments was previously measured by de Bokx et al. (44  $\pm$  4 kJ mol<sup>-1</sup>)<sup>54</sup> and accounts for the Arrhenius-like dependence of the  $(a_{C^*})_{fil}$  term, which when combined with the temperature dependences of  $D_C^*$  and  $c^0$  (83  $\pm$  5 and 40  $\pm$  1 kJ mol<sup>-1</sup>, respectively; discussed above) gives an effective barrier of 79  $\pm$  6 kJ mol<sup>-1</sup> for  $\left(\frac{D_C^*c^0}{d_p(L)}(a_{C^*})_{fil}\right)$ , in reasonable agreement with the value determined in the present study (95  $\pm$  22 kJ mol<sup>-1</sup>).

These data show that carbon formation rates decrease with increasing temperature, even though the diffusivity term  $(D_c^*c^0)$  increases because the coefficients that relate  $\chi$  to  $(a_{C^*})_s$  ( $\alpha$ ; eq 17) show a compensating opposite trend, leading to similar values of  $\left(\frac{D_c^*c^0}{d_p}\alpha\right)$  at different temperatures, as evident from the similar slopes in the data shown in Figure 8. The parameters reflected in the absolute value of the *y*-intercept  $\left(\frac{D_c^*c^0}{d_p(L)}(a_{C^*})_{\rm fil}\right)$  become larger with increasing temperature. This



**Figure 10.** Arrhenius plot of  $\frac{D_{C}^{*}c^{0}}{d_{p}(L)}(a_{C^{*}})_{\rm fil}$ . The carbon diffusivity in Ni  $D_{C}^{*}$ , Henry's Law constant  $c^{0}$ , and the carbon filament activity  $(a_{C^{*}})_{\rm fil}$  are expected to show temperature dependences. The dashed line was obtained through linear regression and reflects an effective energy barrier of 95 ± 22 kJ mol<sup>-1</sup>.

trend reflects the temperature effects on the filament activity  $(a_{C^*})_{\rm fil}$ , which compensates for the increase in  $(D_{\rm C}^*c^0)$  values with increasing temperature. These combined temperature dependences for the parameters that define the  $\left(\frac{D_{\rm C}^*c^0}{d_{\rm p}}\alpha\right)$  and  $\left(\frac{D_{\rm C}^*c^0}{d_{\rm p}({\rm L})}(a_{\rm C^*})_{\rm fil}\right)$  terms lead to the observed lower carbon formation rates at higher temperatures for each given value of  $\chi$  (Figure 8). The effects of temperature on  $\left(\frac{D_{\rm C}^*c^0}{d_{\rm p}}\alpha\right)$  and  $\left(\frac{D_{\rm C}^*c^0}{d_{\rm p}({\rm L})}(a_{\rm C^*})_{\rm fil}\right)$  also

lead to a shift in the *x*-intercepts of the curves in Figure 8 toward higher values of  $\chi$  as temperature increases. These intercepts represent the threshold value of  $\chi$  ( $\chi_{min}$ ) required for the incipient growth of carbon filaments and the point at which  $\alpha\chi(L)$  is equal to the activity of the filament ( $a_{C^*}$ )<sub>fil</sub>. Higher

reaction temperatures therefore broaden the range of  $\chi$  values that preclude the detectable formation of carbon deposits, as observed in TEM images or mass changes during reforming catalysis (regime I; Section 3.4 and 3.6) and enable the use of H<sub>2</sub>O/CH<sub>4</sub> ratios closer to unity in practice, thereby improving process efficiencies.

3.8. Effect of Ni Nanoparticle Diameter on Carbon Morphology and Filament Formation Rates. TEM images of carbon filaments formed on 7% wt Ni/MgO-B (11.0 nm mean diameter, Figure 11a) and 15% wt Ni/MgO-A (11.1 nm particles, Figure 11b) after exposure to  $CH_4$ -CO<sub>2</sub> reaction conditions in regime II (873 K;  $\gamma = 2.6$  kPa,  $\psi = 6.4$ kPa) were used to compare Ni crystallite diameters to those of the carbon filament structures affixed to their ends for two different materials with similar mean nanoparticle size. In all cases, the diameters of the carbon filaments were similar to those of the Ni nanoparticles to which they were attached. Filaments associated with larger particles in the size distribution typically exhibited thicker walls (Figure 3b vs Figure 11), in agreement with previous reports 42,50,51 and consistent with the larger carbon nucleating [Ni(111)] and Ni(311)] facets prevalent on larger crystallites.

The role of Ni particle size on the dynamics of carbon deposition was investigated by comparing carbon deposition rates on 7% wt Ni/MgO-A (5.4 nm particles) with those on 7% wt Ni/MgO-B and 15% wt Ni/MgO-A (11.0 and 11.1 nm particles, respectively) at  $\chi$  (and  $\psi$ ) values that led to proportional increases in carbon formation rates (873 K; regime II, Section 3.4). Carbon deposition rates were nearly identical on 7% wt Ni/MgO-B and 15% wt Ni/MgO-A (Figure 12), in spite of their different MgO supports. Carbon deposition rates were larger on 7% wt Ni/MgO-B and 15% wt Ni/MgO-A (11.0 and 11.1 nm particles, respectively) than those on 7% wt Ni/MgO-A samples with smaller Ni particles (5.4 nm) at each given value of  $\chi$  (or  $\psi$ ) (Figure 12). These trends with diameter are opposite to those reported previously, which attributed these trends to the longer diffusion paths in larger Ni crystallites.<sup>46–48,87</sup> These previous studies, however, measured carbon filament growth rates on larger catalyst



Figure 11. Transmission electron micrograph of carbon morphology after  $CH_4$ - $CO_2$  reaction on (a) 7% wt Ni/MgO-B and (b) 15% wt Ni/MgO-A at 873 K and  $\chi = 2.60$  kPa.



**Figure 12.** Carbon formation rates vs  $\chi$  ( $P_{CO}P_{CH_4}/P_{CO_2}$ ) or  $\psi$  ( $P_{H_2}P_{CH_4}/P_{H_2O}$ ) on Ni/MgO at 873 K during CH<sub>4</sub>-CO<sub>2</sub> (open symbol) or CH<sub>4</sub>-H<sub>2</sub>O reaction (solid symbol) ( $\bigcirc 0^{\circ}$  7% wt Ni/MgO-A with 5.4 average nm Ni particles,  $\triangle 15\%$  wt Ni/MgO-A with 11.1 nm average Ni particles, and  $\diamondsuit 0^{\circ}$  7% wt Ni/MgO-B with 11.0 average nm Ni particles). Lines determined by linear best-fit models.

particles (15–140 nm), where the diffusion length may be the dominant factor for these trends in carbon filament growth rates. The Ni crystallite diameter, however, affects terms other than this path length, specifically the rate and equilibrium constants that determine the value of  $\alpha$  ( $k_1/k_6K_5K_7$ ; eq 17) and the activity of the carbon filament ( $a_{C^*}$ )<sub>fil</sub>. Such effects were probed by examining the expected effects of nanoparticle diameter particle size on the parameters included in the  $\left(\frac{D_{CC}^{*,0}}{d_p}\alpha\right)$  and  $\left(\frac{D_{CC}^{*,0}}{d_p(L)}(a_{C^*})_{fil}\right)$  values reflected by the slope and *y*-intercept, respectively, of the data in Figure 12.

intercept, respectively, of the data in Figure 12. The  $\left(\frac{D_c^*c^0}{d_p}\alpha\right)$  values for 5.4 nm (7% wt Ni/MgO-A; 0.39 ±

0.03) and 11 nm (7% wt Ni/MgO-B and 15% wt Ni/MgO-A;  $0.40 \pm 0.02$ ) nanoparticles were nearly identical, in spite of the particle diameter  $(d_p)$  that differed by a factor of 2. The diffusivity of carbon  $(D_c^*)$  and Henry's law constant  $(c^0)$  do not vary with particle size, suggesting that  $\alpha$  must be two-fold larger on the larger particles to offset the longer diffusion length. This  $\alpha$  term  $(k_1/k_6K_5K_7; eq 17)$  contains rate constants for C-H activation ( $k_1$ ; Scheme 1, step 1.1) and C\*-O\* recombination ( $k_6$ , Scheme 1, step 1.6) and equilibrium constants for  $CO_2$  dissociation ( $K_5$ , Scheme 1, step 1.5) and CO desorption ( $K_7$ , Scheme 1, step 1.7). CH<sub>4</sub> reforming turnover rates on these 11 nm nanoparticles (7% wt Ni/MgO-B and 15% wt Ni/MgO-A) were 1.3 times smaller than those on the 5.4 nm particles (7% wt Ni/MgO-A) at 873 K,<sup>6</sup> indicative of the difference in the values of  $k_1$ . Such differences reflect the lower average coordination at surfaces of smaller Ni crystallites,<sup>62</sup> which leads to lower C-H activation barriers.<sup>88</sup> The remaining parameters in  $\alpha$  ( $k_6K_5K_7$ ) must therefore be 2.6 times larger on 5.4 nm particles (7% wt Ni/MgO-A) than those on 11 nm particles (7% wt Ni/MgO-B and 15% wt Ni/ MgO-A) for  $\alpha$  to be two-fold larger on the larger particles, as suggested by the nearly identical  $\left(\frac{D_c^* c^0}{d_p}\alpha\right)$  values for 5.4 and 11 nm nanoparticles. The values of  $k_6$ ,  $K_5$ , and  $K_7$  cannot be

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determined from CH<sub>4</sub> reforming rates because the respective steps are not kinetically relevant, thus rendering their sensitivity to nanoparticle diameters inaccessible from experiments. Energy estimates from density functional theory (DFT) for  $k_6$  and  $K_7$  on extended Rh surfaces have shown that stepped Rh(211) surfaces give lower activation barriers for C\*-O\* recombination ( $k_{6i}$ ; ~130 vs ~185 kJ mol<sup>-1</sup>) and more endothermic CO molecular desorption events ( $K_{7i}$ ; ~177 vs ~160 kJ mol<sup>-1</sup>) than close-packed Rh(111) surfaces,<sup>89</sup> which become more prevalent with increasing nanoparticle diameter. The smaller  $k_6$  values (and likely  $K_5$  values because more coordinatively saturated surfaces tend to exhibit lower molecular binding energies)<sup>88</sup> on larger particles may compensate, at least in part, for the smaller  $k_1$  values and the larger diffusion lengths ( $d_p$ ).

The  $\left(\frac{D_{Cc}^{*0}}{d_{p}}(a_{C}^{*})_{\text{fil}}\right)$  term that accounts for the *y*-intercept for the data in Figure 12 contains terms that also depend on nanoparticle size. The data indicate that  $\left(\frac{D_{Cc}^{*0}}{d_{p}}(a_{C}^{*})_{\text{fil}}\right)$  is 5.7 ± 4.3 times larger on the smaller (5.4 nm; 7% wt Ni/MgO-A;  $-0.4 \pm 0.1$ ) than that on the larger (11 nm; 7% wt Ni/MgO-B and 15% wt Ni/MgO-A;  $-0.07 \pm 0.05$ ) Ni particles. The carbon diffusivity ( $D_{C}^{*}$ ) and solubility constant ( $c^{0}$ ) are not likely to depend on size. Consequently, the larger  $\left(\frac{D_{Cc}^{*0}}{d_{p}}(a_{C}^{*})_{\text{fil}}\right)$ 

values on smaller Ni nanoparticles must reflect the combined effects of a shorter diffusion path and a larger filament carbon activity for the smaller particles.

The diameters of the carbon filaments resembled those of the attached Ni particles (Figures 3b and 11). Larger diameter filaments show less structural distortion of the sp<sup>2</sup> geometry required for stable graphite layers<sup>90</sup> and are therefore thermodynamically more stable.<sup>47</sup> This change in carbon filament activity ( $a_{C^*}$ )<sub>fil</sub> is reflected in the shift in the threshold value of  $\chi$  ( $\chi_{min}$ ) required for carbon formation from 1.1 ± 0.3 to 0.2 ± 0.1 kPa for 5.4 nm (7% wt Ni/MgO-A) and 11 nm particles (7% wt Ni/MgO-B and 15% wt Ni/MgO-A), respectively. These data indicate that the activity of carbon filaments on 5.4 nm particles is 5.5 ± 3.0 larger than that on 11 nm particles, a value comparable to that derived from the *y*-intercept (2.8 ± 2.1).

The effects of particle size on 
$$\left(\frac{D_{C}^{*o}}{d_{p}}\alpha\right)$$
 and  $\left(\frac{D_{C}^{*o}}{d_{p}}(a_{C}^{*})_{\mathrm{fil}}\right)$ 

values lead to a shift in  $\chi_{min}$  required for the formation of carbon filaments toward higher values of  $\chi$  with decreasing nanoparticle size. The synthesis and stabilization of small Ni particles therefore represent a potentially effective strategy in broadening the range of  $\chi$  values that ensure the absence of detectable carbon deposits. Such strategies enable the use of H<sub>2</sub>O/CH<sub>4</sub> ratios closer to unity for CH<sub>4</sub> reforming reactions in practice, thereby improving process efficiencies.

**3.9.** Implications of Approach to  $CH_4$  Reforming Equilibrium for Carbon Formation Rates. The mechanism-based model described in Section 3.3 (eq 22) and used to describe measured filament formation rates in Sections 3.4–3.8 applies only when  $CH_4$  decomposition (Scheme 1, steps 1.1–1.4) or  $C^*-O^*$  recombination (Scheme 1, step 1.6) steps are irreversible and  $CH_4$  reforming reactions are far from equilibrium.

In this section, we extend these treatments to the general case in which these steps and the overall  $CH_4$  reforming

reaction approach equilibrium, as defined by their respective approach to equilibrium values. The approach to the equilibrium parameter ( $\eta$ ) relates the forward ( $r_{\rm f}$ ) and reverse ( $r_{\rm r}$ ) rate of a given reaction by

$$\eta = \frac{r_{\rm r}}{r_{\rm f}} \tag{23}$$

Such formalisms are used here to derive an expression for the activity of surface carbon species in general, irrespective of the prevalent  $\eta$  value.

The catalytic sequence in Scheme 1 can be divided into two half-reactions, one including all the steps required to form C\* and H<sub>2</sub> from CH<sub>4</sub> (reaction A) (Scheme 1, steps 1.1–1.4, 1.8) and the other involving the steps that remove C\* via reactions with O\* derived from CO<sub>2</sub> to form CO (reaction B) (Scheme 1, steps 1.5–1.7) or from H<sub>2</sub>O to form H<sub>2</sub> and CO (reaction B') (Scheme 1, steps 1.6–1.10). The approaches to equilibrium ( $\eta$ ) for reactions A and B (or B') are defined respectively as

$$\eta_{\rm A} = \frac{({\rm H}_2)^2 (a_{\rm C}^*)_{\rm s}}{({\rm L})({\rm CH}_4) K_{\rm A}}$$
(24)

$$\eta_{\rm B} = \eta_{\rm B'} = \frac{(\rm CO)^2(L)}{(\rm CO_2)(a_{\rm C}^*)_{\rm s}K_{\rm B}} = \frac{(\rm H_2)(\rm CO)(L)}{(\rm H_2O)(a_{\rm C}^*)_{\rm s}K_{\rm B'}}$$
(25)

Here,  $K_{A}$ ,  $K_{B}$ , and  $K_{B'}$  are the equilibrium constants for their respective half-reactions.  $K_{B}$  and  $K_{B'}$  are also related to each other by the equilibrium constant for the water-gas shift reaction ( $K_{WGS}$ ) because this reaction was found to be equilibrated under all experimental conditions

$$K_{\rm B}K_{\rm WGS} = K_{\rm B'} \tag{26}$$

The approaches to equilibrium for half-reactions A and B are also related to the overall approach to equilibrium parameters for  $CH_4-CO_2$  ( $\eta_{DRM}$ ) and  $CH_4-H_2O$  ( $\eta_{SRM}$ ) reactions

$$\eta_{\rm A}\eta_{\rm B} = \eta_{\rm A}\eta_{\rm B'} = \eta_{\rm DRM} = \eta_{\rm SRM} \tag{27}$$

The approach to equilibrium values for half-reactions A ( $\eta_A$ , eq 24) and B (or B';  $\eta_{B'}$ , eq 25) can be estimated for the conditions used here using data available in the literature.  $K_A$  and  $K_B$  were previously reported for carbon filament growth on Ni-based catalysts using CH<sub>4</sub>-H<sub>2</sub> and CO<sub>2</sub>-CO mixtures (650-1000 K) to set the surface carbon activity (0.9 ± 0.3 and 0.16 ± 0.03, respectively);<sup>54</sup> the activity of the carbon filaments (10 nm diameter;  $(a_C)_{fil,10nm}$ ) formed under these conditions can also be derived from these data (1.8 ± 1, referenced to graphite).<sup>54</sup> The activity of carbon filaments  $(a_C)_{fil}$  is represented by the threshold value of  $\chi$  required to form such carbon deposits ( $\chi_{min}$ ; Sections 3.7 and 3.8). The carbon activity  $(a_C)_s$  can therefore be calculated for a given value of  $\chi$  using

$$\frac{(a_{\rm C})_{\rm s}}{(a_{\rm C})_{\rm fil,10nm}} = \frac{c^0 \alpha \chi({\rm L})}{c^0 \alpha \chi_{\rm min,10nm}({\rm L})} = \frac{\chi}{\chi_{\rm min,10nm}}$$
(28)

Here, we approximate  $\chi_{\min,10nm}$  as the value of  $\chi$  required to nucleate filaments of similar diameter (11 nm) on Ni nanoparticles (0.2 ± 0.1 kPa; Section 3.8). This treatment of the data leads to values of  $\eta_A$  and  $\eta_B$  that are less than 0.04 and 0.001, respectively, calculated at the reactor exit. These values of  $\eta_A$  and  $\eta_B$  correspond with forward rates of CH<sub>4</sub> decomposition (reaction A) and C\*–O\* recombination (reaction B, or B') that are at least 25 and 1000 times faster throughout the  $CH_4$  reforming reactor, respectively, indicating that both reactions are irreversible under the conditions of this study, thus corroborating the assumptions used to derive the models described by eqs 21 and 22.

The mechanism-based model that leads to eq 22 requires that half-reactions A and B (or B') be irreversible, a condition met by the data reported in this study but met only near the inlet region in practical  $CH_4$  reforming reactors. An expression for the surface carbon activity  $(a_{C^*})_s$  that is valid under all  $CH_4$ reforming conditions can be derived by including the approach to equilibrium for each of the half-reactions (details in the Supporting Information Section 1.2)

$$\frac{(a_{\rm C}^*)_{\rm s}}{(\rm L)} = \alpha \chi \frac{(1-\eta_{\rm A})}{(1-\eta_{\rm B})} = \alpha \chi \frac{(1+\eta_{\rm B}^*)}{(1+\eta_{\rm A}^*)}$$
(29)

$$\eta_{\rm A}^* = \frac{({\rm H}_2)^2 \alpha \chi}{({\rm CH}_4) K_{\rm A}}$$
(30)

$$\eta_{\rm B}^* = \eta_{\rm B'}^* = \frac{(\rm CO)^2}{(\rm CO_2)\alpha\chi K_{\rm B}} = \frac{(\rm H_2)(\rm CO)}{(\rm H_2O)\alpha\chi K_{\rm B'}}$$
(31)

The terms  $\eta_A^*$  and  $\eta_B^*$  (or  $\eta_{B'}^*$ ) are related to the approach to equilibrium for  $CH_4-CO_2$  ( $\eta_{DRM}$ ) and  $CH_4-H_2O$  ( $\eta_{SRM}$ ) reactions by

$$\eta_{\rm A}^* \eta_{\rm B}^* = \eta_{\rm A}^* \eta_{\rm B'}^* = \eta_{\rm SRM} = \eta_{\rm DRM}$$
(32)

Equation 29 was derived by assuming that the rate of diffusion of carbon is much smaller than the forward rates of reactions A and B (or B') and that there are no significant coverages of intermediates during steady-state  $CH_4$  reforming catalysis, an assumption that will be relaxed later in this section.

Equation 29 indicates that surface carbon activities decrease as reaction A approaches equilibrium (while reaction B remains far from equilibrium;  $\eta_A \rightarrow 1$ ). The quasi-equilibration of reaction A before reaction B leads to  $\eta_A^*$  values significantly greater than unity, allowing eq 29 to be simplified to

$$\frac{(a_{\rm C}^*)_{\rm s}}{(\rm L)} = \frac{(\rm CH_4)K_{\rm A}}{(\rm H_2)^2}$$
(33)

Conversely, when reaction B approaches equilibrium before reaction A ( $\eta_{\rm B} \rightarrow 1$ ), the surface carbon activity increases. When reaction B achieves equilibrium before reaction A,  $\eta_{\rm B}^*$  becomes significantly greater than unity, and eq 29 can be simplified to

$$\frac{(a_{\rm C^*})_{\rm s}}{(\rm L)} = \frac{K_{\rm B}({\rm CO})^2}{({\rm CO}_2)}$$
(34)

Equations 33 and 34 are, in fact, the same as eqs 2 and 3, which describe the reactions of quasi-equilibrated binary mixtures of CO–CO<sub>2</sub> or CH<sub>4</sub>–H<sub>2</sub>, respectively. Thus, the quasi-equilibration of either half-reaction A or B, depending on which reaction reaches equilibrium more quickly, sets the surface carbon activity  $(a_{C^*})_s$  as CH<sub>4</sub> reforming approaches equilibrium. The estimated maximum values of  $\eta_A$  and  $\eta_B$  for this study (0.04 and 0.001, respectively) indicate that the CH<sub>4</sub> decomposition half-reaction (reaction A; Scheme 1, steps 1.1–1.4) reaches equilibrium first under the conditions of this study. This is because the water–gas shift reaction favors the

products (H<sub>2</sub> and CO<sub>2</sub>) at these temperatures, causing a subsequent increase in  $\eta_A$  (eq 24) and decrease in  $\eta_B$  (eq 25).

Equation 29 was derived by assuming that there are no significant coverages of intermediates during steady-state  $CH_4$  reforming catalysis. This assumption can be relaxed to give an expression for the surface carbon activity that is applicable even as C\* coverages become significant (details in the Supporting Information Section 1.2)

$$\frac{(a_{C^*})_s}{(L)} = \alpha \chi \frac{(1+\eta_B^*)}{\left(1+\frac{(CO)^2}{(CO_2)K_B}+\alpha \chi+\eta_A^*\right)} \\
= \beta \psi \frac{(1+\eta_{B'}^*)}{\left(1+\frac{(CO)(H_2)}{(H_2O)K_{B'}}+\beta \psi+\eta_A^*\right)}$$
(35)

Equation 35 is able to describe and predict surface carbon activities under a wide range of  $CH_4$  reforming reaction conditions, including those that may be encountered in practice. These derivations thus show that the mechanistic conclusions that lead to expressions for surface carbon activities and carbon formation rates under conditions far from CH<sub>4</sub> reforming equilibrium are general and provide a mathematical framework for the rigorous extension of the reaction-diffusion constructs under more practical conditions, including those corresponding with more moderate CH<sub>4</sub> reforming conversions and even equilibrium conditions for this reaction. The data reported and the kinetic parameters derived here are specific for Ni-based catalysts, but the mathematical framework is general for the analysis of other reactants and catalysts and demonstrates the requirement for the accurate details of catalytic mechanisms in describing the formation of chemisorbed carbon and its various solid forms during catalysis.

### 4. CONCLUSIONS

CH<sub>4</sub>-CO<sub>2</sub> and CH<sub>4</sub>-H<sub>2</sub>O reactions on supported Ni catalysts tend to form carbon deposits that are detrimental to the catalytic process at stoichiometric reactant ratios. The dynamics of carbon formation on dispersed Ni nanoparticles of varying diameters (5-11 nm) were measured during steadystate CH<sub>4</sub> reforming reactions (843-973 K) in this study to understand the conditions under which these residues form. Carbon formation rates and morphologies (filamentous or encapsulating) were solely determined by the pressure ratio  $P_{\rm CH_4}P_{\rm CO}/P_{\rm CO_7}$  ( $\chi$ ) (or  $P_{\rm CH_4}P_{\rm H_7}/P_{\rm H_7O}$  ( $\psi$ )), which sets the thermodynamic carbon activity at the metal surface  $(a_{C^*})_s$  via the elementary steps that mediate CH4 reforming under conditions far from equilibrium of this reaction. Carbon formation rates were proportional to  $\chi$  (and  $\psi$ ) under conditions leading to the formation of carbon filaments but without concurrent decreases in CH4 reforming and carbon formation rates, consistent with a filament growth mechanism limited by carbon diffusion. Higher values of  $\chi$  and  $\psi$  (and values of  $(a_{C^*})_s$  led to the simultaneous incipient nucleation of multiple carbon patches, ultimately leading to the encapsulation of Ni nanoparticles by carbon adlayers and loss of accessible surface for CH4 turnovers. Carbon deposition rates decreased with increasing temperature because of the corresponding decrease in the value of the lumped kinetic and thermodynamic parameter that relates  $\chi$  to  $(a_{C^*})_{s}$ . Carbon formation rates also decreased with decreasing Ni particle size

because of the lower stability and concomitant increase in activity of the smaller diameter carbon filaments that formed on smaller Ni particles. The synthesis and stabilization of small Ni particles at high temperatures thus present a potentially effective strategy in bringing  $H_2O/CH_4$  ratios closer to those required by stoichiometry while ensuring the absence of detectable carbon deposits.

The results from this study are consistent with previously proposed bulk diffusion mechanisms for filament growth and expand on previous carbon formation studies by relating thermodynamic carbon activities to prevalent gas-phase compositions during the steady-state catalysis of multicomponent CH<sub>4</sub> reforming mixtures. The study provides insights into the kinetic and thermodynamic parameters underlying the deposition and removal of carbon and provides guidance for avoiding carbon filament formation under conditions away from CH<sub>4</sub> reforming equilibrium. Carbon formation rates are accurately described by a mechanism-based reaction-transport model and demonstrate the need for accurate details of the catalytic mechanisms in describing the formation of chemisorbed carbon and its various solid forms during catalysis. Such mechanism-based relations are rigorous and general in their ability to relate surface carbon activities to prevalent gas-phase compositions and can therefore be extended, with additional parameters, to CH<sub>4</sub> reforming reactions that approach equilibrium, as in the case of reactions in practice.

# ASSOCIATED CONTENT

### **Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcc.0c05590.

Expression for  $(a_{C^*})_s$  derived from the CH<sub>4</sub>-H<sub>2</sub>O and CH<sub>4</sub>-CO<sub>2</sub> reforming mechanism under conditions far from equilibrium. Expression for  $(a_{C^*})_s$  derived from the CH<sub>4</sub>-H<sub>2</sub>O and CH<sub>4</sub>-CO<sub>2</sub> reforming mechanism under conditions approaching CH<sub>4</sub> equilibrium when carbon formation rates are small (PDF)

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#### Notes

The authors declare no competing financial interest.

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