Influence of Mo on the Fe:Mo:C nano-catalyst thermodynamics for single-walled carbon nanotube growth

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We explore the role of Mo in Fe:Mo nanocatalyst thermodynamics for low-temperature chemical vapor deposition growth of single walled carbon nanotubes (SWCNTs). By using the size-pressure approximation and ab initio modeling, we prove that for both Fe-rich (≈ 80% Fe or more) and Mo-rich (≈ 50% Mo or more) Fe:Mo clusters, the presence of carbon in the cluster causes nucleation of Mo2C. This enhances the activity of the particle since it releases Fe, which is initially bound in a stable Fe:Mo phase, so that it can catalyze SWCNT growth. Furthermore, the presence of small concentrations of Mo reduce the lower size limit of low-temperature steady-state growth from ≈0.5nm for pure Fe nanoparticles to ≈ 0.52nm. Our ab initio-thermodynamic modeling explains experimental results and establishes a new direction to search for better catalysts.

Critical factors for the efficient growth of single walled carbon nanotubes (SWCNTs) via catalytic chemical vapor deposition (CCVD)4,23 are the compositions of the interacting species (feedstock, catalyst, support)4,5,6,7,8,9,10, the preparation of the catalysts, and the synthesis conditions11,12,13,14,15,16,17,18. Efficient catalysts must have long active lifetimes (with respect to feedstock dissociation and nanotube growth), high selectivity and be less prone to contamination19,20,21,22,23. Common factors that lead to reduction in catalytic activity are deactivation (i.e. chemical poisoning or coating with carbon), thermal sintering (e.g. caused by highly exothermic reactions on the clusters surface)24,14,14,24 with insufficient heat transfer25,26 and solid-state reactions (nucleation of inactive phases in the cluster)22,23,25.

Metal alloy catalysts, such as Fe:Co, Co:Mo and Fe:Mo, improve the growth of CNTs from Al2O3 substrates, because the presence of more than one metal species can significantly enhance the activity of a catalyst20,27,29,30,31, and can prevent catalyst particle aggregation20,31,32,33. In the case of Fe:Mo nanoparticles supported on Al2O3 substrates, the enhanced catalyst activity has been shown to be larger than the linear combination of the individual Fe/Al2O3 and Mo/Al2O3 activities20,27,28. This is explained in terms of substantial inter-metallic interaction between Mo, Fe and C20,35,36 which is congruent with previously observed solid-state reactions between these elements. In fact, the addition of Mo in mechanical alloying of powder Fe and C mixtures25 promotes solid state reactions even at low Mo concentrations by forming ternary phases, such as the (Fe,Mo)23C6 type carbide28.

The way in which carbon interacts with transition metals depends on the metal species. Fe and Co belong to the “carbon dissolution-precipitation mechanism” group, whereas relatively large fractions of carbon dissolve into the cluster before stable carbides are formed, while Mo belongs to the “carbide formation-decomposition” group where carbide formation occurs rapidly at low carbon concentrations30. These mechanisms are governed by the interplay between solubility of C in the metal matrix (interstitial and/or substitutional defects) and the ease of metal carbide formation. Although relating C solubility and catalytic ability of metal catalysts is not simple (factors like temperature, diffusion, kinetics and particle size have to be considered22,23), metals which form carbides can be efficient catalysts as long as they offer sufficient carbon solubility, even if the formation of the carbides interferes with the SWCNT growth, as is the case of Fe22,23. Co can dissolve a relatively large fraction of carbon C and does not form stable ordered carbides, whereas Mo has limited C solubility and forms several stable carbides (even at low temperature). Similarly to Co, Fe can dissolve a relatively large fraction of C (at least in the γ phase), but concomitantly it forms carbides at temperatures relevant to SWCNT growth (Fe₃C)25,36. Nucleation of Fe₃C and subsequent loss of C solubility30 can be used to identify the thermodynamic lower limit for the CVD growth of very thin SWCNTs from Fe nanoparticles22,23. Thus, for efficient CVD growth from Fe, Mo, Fe:Mo and Co:Mo clusters, the particles must be small (dispersed) and metallic (preserved from carbidization). In fact, active catalyst species in Co:Mo catalysis are also small metallic species32,33 with Mo added to limit particle aggregation by forming molybdate species which are later reduced to give small metallic Co:Mo nanoparticles. It has been shown that disruption of the Co-Mo interactions leads to a lower SWCNT growth efficiency40.

The use of alloys instead of pure metals provides additional degrees of freedom, such as fractions of the metal species, which has chemical and thermodynamic advan-
tages. The chemical advantages arise since the fractions of constituent species can be tailored to enhance catalytic performance that can be measured by the yield and quality of nanotubes\textsuperscript{22,33,34}. It has been found that low Fe:Mo ratios are favorable for growing SWCNTs (on Al\textsubscript{2}O\textsubscript{3} substrates) since the presence, after activation, of the phase Fe\textsubscript{3}(MoO\textsubscript{4})\textsubscript{3} can lead to the formation of small metallic clusters\textsuperscript{32} (the best compromise between catalytic activity and SWCNT selectivity was found to be Fe\textsubscript{3.5}Mo\textsubscript{1.5}O\textsubscript{12}, Ref\textsuperscript{35}). High fractions of Fe in Fe:Mo lead to formation of larger particles during the reduction step which are inactive for SWCNT growth, unless precautions are taken to avoid excessive sintering\textsuperscript{20} (no formation of molybdate species has been reported when using CH\textsubscript{4} feedstock with Fe:Mo catalysts\textsuperscript{20} and hence the chemical role of Mo in Fe:Mo is different from that in Co:Mo). The thermodynamic advantages are revealed when considering the vapor-liquid-solid model (VLS), which is the most probable mechanism for CNT growth\textsuperscript{12,20,41}. The metal nanoparticles are very efficient catalysts when they are in the liquid or viscous states\textsuperscript{22}, probably because one has considerable carbon bulk-diffusion in this phase (compared to surface or sub-surface diffusion). Generally, unless stable intermetallic compounds form, alloying metals reduce the melting point below those of the constituents\textsuperscript{35,36}. This happens, for instance, with the addition of small fractions of Mo to Fe. Hence, to enhance the yield and quality of nanotubes, one can tailor the composition of the catalyst particle to move its liquidus line below the synthesis temperature\textsuperscript{20}. However, identifying the perfect alloy composition is non trivial. In fact, the presence of more than two metallic species allows for the possibility of different carbon pollution mechanisms by allowing thermodynamic promotion of ternary carbides. So far, due to the very complex interplay between competing phases at the nano-scale (even for pure Fe particles\textsuperscript{22,23}), the search for the proper catalyst composition has been empirical\textsuperscript{20,32,33,34,40}.

In the present manuscript we address the interaction between C and Mo:Fe nanoparticles. We use thermodynamic and quantum mechanical results to discuss the complexity of Fe- (~80% Fe or more) and Mo-rich (~50% Mo or more) Fe:Mo catalysts, previously addressed phenomenologically. The results are useful for the development of efficient catalysts for nanotube and graphene growth.

**Methods.** Investigating the behavior of C in Fe:Mo nanoparticles requires an understanding of the interplay of the various phases of the Fe-Mo-C system at the nanoscale. Determining the thermodynamic stability of different phases in nanoparticles of different sizes with \textit{ab initio} calculations is complicated and computationally expensive. In Ref\textsuperscript{22,23} we have developed a simple model, called the “size-pressure approximation”, which allows one to estimate the phase diagram at the nanoscale starting from bulk calculations under pressure.

The \textit{size-pressure approximation}. Surface curvature and superficial dangling bonds on nanoparticles are responsible for internal stress fields which modify the atomic bond lengths. For spherical clusters, the phenomenon can be modeled with the Young-Laplace equation $\Delta P = 2\gamma/R$ where the parameter $\gamma$ (surface tension for liquid particles) can be calculated with \textit{ab initio} methods. As a first approximation, where all surface effects that are not included in the curvature are neglected, the study of phase diagrams for spherical particles can be mapped onto the study of phase diagrams for bulk systems under the same pressure that is produced by the curvature. It is important to mention that $\gamma$ is not a real surface tension but an \textit{ab initio} fitting parameter describing size-induced stress in nanoparticles. In our case, it can be assumed that $\gamma$ is independent of the fraction of Mo (since the best Fe:Mo catalysts are Fe-rich) and C (since the amount of C in the catalytically active particle state is limited\textsuperscript{10,20}). Figure 2 of Ref\textsuperscript{22} shows the implementation of the “size-pressure approximation” for Fe nanoparticles. The idea is simple. Two interpolations are involved: “pressure versus distortion” and “distortion versus curvature” are coupled to obtain a relation “pressure versus curvature” (where curvature is $1/R$). In more details, the left hand side of Figure 2 of Ref\textsuperscript{22} shows the average distortion of the bond length inside the cluster $\Delta d_{nn} = d_{nn}^0 - d_{nn}$ for a variety of spherical bcc particles as a function of the inverse radius ($1/R$). The right hand side shows the compression of the bond length as a function of the hydrostatic pressure for the bulk system. Combining the two sets of data yields:

$$P \cdot R = 2.46 \text{ GPa} \cdot \text{nm} \quad (\gamma = 1.23 \text{J/m}^2).$$

Equation (1) is used to deduce the Fe-Mo-C phase diagram of nanoparticles of radius $R$ from \textit{ab initio} calculations of the bulk material under pressure $P$. The parameter $\gamma$ compares well with the experimental values of the surface tension of bulk Fe at the melting point $\sim 1.85$ J/m\textsuperscript{2} and $\sim 1.90$ J/m\textsuperscript{2}. For a detailed explanation of the “size-pressure approximation” see Ref\textsuperscript{22}.

The assumption of $\gamma$ being independent of the Mo concentration is justified at zero (and low) temperature because molybdenum tends to segregate inside the particle, so that it can not affect the chemistry and the bonding states at the surface (see the section “surface energies” near the end of the manuscript). At high temperature, Mo would eventually populate the surface and modify $\gamma$. To a first approximation, by linearly interpolating between the experimental values of the surface tension for Fe (1.85 J/m\textsuperscript{2}) and Mo (2.08 J/m\textsuperscript{2}) (i.e., Vegard’s law), and assuming that the parameter $\gamma$ follows the same trend, we would obtain a $\sim 3\%$ increase for $\gamma$ at the optimal composition Fe\textsubscript{x}Mo\textsubscript{y} of the catalyst (see below). Thus, all the estimated radii and diameters deduced from equation (1) might be overestimated of few percent at high temperature (energies and pressures are not affected by
thermodynamics and activity. 

Quantum mechanical calculations. Simulations are performed with VASP, using projector augmented waves (PAW) and exchange-correlation functionals as parameterized by Perdew, Burke and Ernzerhof (PBE) for the generalized gradient approximation (GGA). Simulations are carried out with spin polarization, at zero temperature, and without zero-point motion. All structures are fully relaxed. Numerical convergence to within about 2 meV/atom is ensured by enforcing a high energy cut-off (500 eV) and dense k-meshes. The hydrostatic pressure estimated from the pressure-size model is implemented as Pulay stress. Ternary phase diagrams are calculated using bcc-Mo, bcc-Fe and SWCNTs as references (pure-Fe phase is taken to be bcc because our simulations are aimed at the low temperature regime of catalytic growth). The reference SWCNTs have the same diameter of the particle to minimize the curvature-strain energy. In fact, CVD experiments of SWCNT growth from small (~0.6-2.1 nm) particles indicate that the diameter of the nanotube is similar to the diameter of the catalyst particle from which it grows. In some experiments where the growth mechanism is thought to be root-growth, the ratio of the catalyst particle diameter to SWCNT diameter is ~1.0, whereas in experiments involving pre-made floating catalyst particles this ratio is ~1.6. Formation energies are calculated with respect to decomposition into the nearby stable elements or phases, depending the position in the ternary phase diagram as described later.

Competing phases. Pure elements (bcc-Fe, bcc-Mo and SWCNT-C) are included in the calculation in their most stable low temperature configurations. Other phases are included if they are stable in the temperature range used in CVD growth of SWCNTs or if they have been reported experimentally during or after the growth. Thus, we include the binaries Mo2C, Fe2Mo and Fe3C. In addition, since our Fe-rich Mo:Fe experiments were performed with compositions close to Fe2Mo, we include a random phase Fe3Mo generated with the special quasi-random structure formalism (SQS). Bulk ternary carbides, which have been widely investigated due to their importance in alloys and steel, can be considered as derivatives of binary structures with extra C atoms in the interstices of the basic metal alloy structures. Three possible ternary phases have been reported for bulk Fe-Mo-C and they are referred as τ1 (M6C), τ2 (M3C) and τ3 (M23C6) (M is the metal species). For simplicity, we follow the same nomenclature. τ1 is the well-known M6C phase, which has been observed experimentally as Fe2Mo2C and Fe3Mo1C structures (η carbides). Both of these structures are fcc, but have different lattice spacings. Our calculations show that the most stable variant τ1 is Fe4Mo2C, and we denote it as τ1 henceforth. τ2 is the Fe2MoC phase, which has an orthorhombic symmetry distinct from that of Fe3C. We consider Fe21Mo23C44 as the third τ3 fcc phase. We use the Cr23C6 as the prototype structure where Fe and Mo substitute for Cr. Although M23C6 type phases do not appear in the stable C-Fe or C-Mo systems, they have been reported in ternary C-Fe-Mo systems and also appear as transitional products in solid state reactions. Time-temperature precipitation diagrams of low-C steels have identified τ2-M3C, τ3-M23C6 and τ1-M6C as low-temperature, metastable and stable carbides, respectively. Furthermore, τ2-M3C carbides precipitate quickly due to carbon-diffusion controlled reaction while τ3-M23C6 carbides precipitate due to substitutional-diffusion controlled reactions. Moreover, τ1-M6C carbides precipitate that the most stable variant τ1 is Fe4Mo2C, and we denote it as τ1 henceforth. τ2 is the Fe2MoC phase, which has an orthorhombic symmetry distinct from that of Fe3C. We consider Fe21Mo23C44 as the third τ3 fcc phase. We use the Cr23C6 as the prototype structure where Fe and Mo substitute for Cr. Although M23C6 type phases do not appear in the stable C-Fe or C-Mo systems, they have been reported in ternary C-Fe-Mo systems and also appear as transitional products in solid state reactions. Time-temperature precipitation diagrams of low-C steels have identified τ2-M3C, τ3-M23C6 and τ1-M6C as low-temperature, metastable and stable carbides, respectively. Furthermore, τ2-M3C carbides precipitate quickly due to carbon-diffusion controlled reaction while τ3-M23C6 carbides precipitate due to substitutional-diffusion controlled reactions. The latter phenomenon, requiring high temperature, longer times and producing metastable phases is not expected to enhance the catalytic deactivation of the nanoparticle. In summary, as long as the presence of carbon does not lead to excessive formation of M3C (Fe3C and τ2-Fe3MoC), the catalyst should remain catalytically active for SWCNT growth.

Results. A structure at a given composition is considered stable (at zero temperature and without zero-point motion) if it has the lowest formation energy of all structures at this composition and, if on the ternary phase diagram, it lies below the convex hull of tie planes connecting all the other stable structures. Phases lying above the convex hull and with small positive formation energies may be favored at higher temperatures due to configurational and vibrational entropy contributions.

We generate the convex hulls with the qconvex package. By projecting the 3D facets onto the 2D plane we obtain the graphs shown in Figure 1 where the panels (a),(b),(c) and (d) represent the phase diagrams at zero temperature of nanoparticles of radii R ∼ ∞, 1.23, 0.62, 0.41 nm, calculated at P = 0, 2, 4, and 6 GPa, respectively. Stable and unstable phases are shown as black squares and red dots, respectively. The solid green lines, connecting the stable phases are the projected edges of the 3D convex hull “facets”. The numbers 1…8 in panels (c) and (d) indicate the boundary phases’ crossings of our test cases, and are discussed below. Table I shows the formation energies of the various competing phases calculated with respect decomposition into the appropriate stable components (reported in the “refs.” lines).

In each panel of Figure 1 the two dotted lines connecting Fe3Mo and FeMo to SWCNT denote the introduction of carbon into the system. Fe3Mo has been reported to be an effective catalyst composition, while FeMo represents a hypothetical Fe:Mo particle with a Mo content larger than 33%. This Mo-rich nanoparti-
The ternary phase diagram for Fe-Mo-C nanoparticles of $R \sim \infty$, 1.23, 0.62, 0.41 nm. Notations are explained in the text.

Table I: Formation energies (meV/atom) for binary and ternary phases for nanocatalysts of different sizes: Fe$_3$C, Mo$_2$C, Fe$_2$Mo, $\tau_1$, $\tau_2$, and $\tau_3$, calculated with respect to the reference species shown in the table.

| Phases       | (meV/at.) |
|--------------|-----------|
| Fe$_3$C      | 48.7      |
| (refs.)      | Fe$_3$C   |
| Fe$_2$Mo     | -2.0      |
| (refs.)      | Fe$_2$Mo  |
| Mo$_2$C      | -113.7    |
| (refs.)      | Mo$_2$C   |
| $\tau_1$     | 46.8      |
| (refs.)      | Fe$_2$Mo  |
| $\tau_2$     | 451.7     |
| (refs.)      | Mo$_2$C   |
| $\tau_3$     | 61.4      |
| (refs.)      | Fe$_2$Mo  |

FIG. 1: (color online). Ternary phase diagram for Fe-Mo-C nanoparticles of $R \sim \infty$, 1.23, 0.62, 0.41 nm. Notations are explained in the text.

The size of the particles have been calculated with the interpolation shown in Figure 2 of Ref.22,23. We investigate a very small particle with $N_{atoms} \sim 40$, which may be able to support SWCNT growth, to explore size-induced stabilization trends. As seen from the zero temperature phase diagrams in Figure 1 and the energies in Table I, Mo$_2$C and Fe$_2$Mo are stable for bulk materials as well as nanoparticles, while Fe$_3$C and $\tau_3$ are stable only for small nanoparticles of radius $R \sim 0.41$ nm ($E_f[Fe_3C] \leq 0$ for $R < 0.58$ nm$^{22,23}$). $\tau_1$ and $\tau_2$ are always unstable.

Fe$_4$Mo particles. The most obvious advantage that a Fe$_4$Mo particle has over a pure Fe particle is that the [Fe$_4$/Mo$_1$]$_{1-x}$-$C_x$ line does not intersect any carbide (Fe$_3$C, $\tau_3$, $\tau_2$). This implies that, at least at low temperatures, there is a surplus of unbounded metal (probably even at high temperatures since the line is far from all of the competing stable phases). This is illustrated in Figure 2 which shows the fractional evolution of species as one progresses along the [Fe$_4$/Mo$_1$]$_{1-x}$-$C_x$ line in Figure 1.

Large Fe$_4$Mo particles ($R \geq 0.62$ nm). When a large Fe$_4$Mo particle ($R \geq 0.62$ nm in Figure 2(a)) is exposed to carbon feedstock, the Mo$_2$C phase nucleates by dissociating Fe$_2$Mo. This is seen for concentrations between $0 < x_c \lesssim 0.09$. The vertical dashed line “1” in the figure indicates the boundary crossing of the [Fe$_4$/Mo$_1$]$_{1-x}$-$C_x$ pollution path with the Fe$\rightarrow$Mo$_2$C edge, as shown in Figure 1(c). Nucleation of Mo$_2$C has two consequences:

| R (nm) | $\infty$ | 1.23 | 0.62 | 0.41 |
|--------|----------|------|------|------|
| P (GPa)| 0        | 2    | 4    | 6    |
| N (#)  | $\infty$ | ~600 | ~150 | ~40  |

TABLE I: Formation energies (meV/atom) for binary and ternary phases for nanocatalysts of different sizes: Fe$_3$C, Mo$_2$C, Fe$_2$Mo, $\tau_1$, $\tau_2$, and $\tau_3$, calculated with respect to the reference species shown in the table.
it consumes carbon atoms that are added to the particle by bonding them to molybdenum, and it releases free-Fe which is beneficial for the catalytic activity of the cluster (the Fe fraction increases with C concentration in the range 0 < x_c ≤ 0.09). In addition, while forming Mo2C, carbon does not produce SWCNTs. In fact, we need to saturate the particle in C and enter the region Fe-Mo2C-SWCNT of the phase diagram in Figure 1(c) before free carbon is available. Hence, the fraction of C is non-zero only after x_c ~ 0.09 in Figure 2(a). For x_c ≤ 0.09 the free Fe is expected to be on the particle surface since the fraction of free-Fe is larger than that of Mo2C and, as presented later, surface energy calculations show that free-Fe resides at the surface of the particle whereas the Mo (Mo2C) parties found near particle core. To conclude, steady state growth of SWCNTs is possible from large Fe3Mo particles since free, catalytically active Fe is present, even for x_c ≥ 0.09.

Small Fe4Mo particles (R < 0.41 nm). Similarly to the large Fe3Mo particle, initial exposure of the small Fe4Mo cluster (R < 0.41 nm) to carbon feedstock promotes Mo2C nucleation by dissociating Fe3Mo and releasing free Fe. However, for x_c ≥ 0.09 the scenario is different. In fact, while the fraction of free Fe increases between 0 < x_c ≤ 0.09 (left of line “4” in Figure 2(b)), it reduces to zero between 0.09 ≤ x_c ≤ 0.23 (points “4” and “5” of Figure 1(d)). Concomitantly, the carbide τ3 nucleates by bonding carbon atoms that are added to the particle and hence eliminating the amount of free Fe that was released during the growth of Mo2C. Similarly to Fe-C particles, with the carbide Fe3C, the nucleation of τ3 is clearly detrimental for SWCNT growth. In fact, the lack of simultaneous presence of free-Fe and excess C causes the particle to be catalytically inactive. However, the different formation energies of τ3 and Fe3C lead to different size thresholds between the two regimes (growth/no-growth). In Refs. 22,23 we estimated that the minimum radius needed for a low-temperature Fe particle to be active is R_{min}^Fe ~ 0.58 nm. For the Fe4Mo case, by interpolating the energies of τ3 reported in Table I by determining P at which E[τ3(P)] = 0, and by using the size/pressure approximation relation (1), we obtain R_{min}^{Fe_{4}Mo} ~ 0.52 nm. The reduced size advantage R_{min}^{Fe_{4}Mo} < R_{min}^{Fe} agrees with experimental results that show that nanotubes, grown from Fe-rich FeMo catalysts are thinner than those grown from pure Fe particles. 23 As pointed out before,22,23 the presence of R_{min}^{Fe_{4}Mo} defines three possible thermodynamic scenarios: steady-state-, limited- and no-growth for R > R_{min}^{Fe_{4}Mo}, R ∼ R_{min}^{Fe_{4}Mo} and R < R_{min}^{Fe_{4}Mo}, respectively. It is worth mentioning that as long as the concentration of Mo in a Fe-rich FeMo clusters is chosen to be slightly larger than that of τ3 we obtain R_{min}^{Fe_{4}Mo} < R_{min}^{Fe}.

FeMo test particles. To address the poor growth capability of Mo-rich FeMo catalysts (low yield of SWCNTs at high temperature)22 we repeated the above analysis with an equiconcentration FeMo particle. For simplicity, we choose to avoid dealing with the Mo5.1Fe0.9 phase reported at low temperature23 because, as our results show, its presence does not affect the pollution mechanism discussion.

Large FeMo particles (R ≥ 0.62 nm). Contrary to Fe3Mo particles, large FeMo clusters contain ample amounts of molybdenum capable of nucleating Mo2C. Irrespective of whether Mo5.1Fe0.9 is included in the discussion, both free-Fe and an excess of C are present for x_c ≥ 0.20 (line “3” in Figure 2a and phase boundary “3” in Figure 1(c)). Hence, the growth SWCNTs is possible for x_c ≥ 0.20. However, since the fraction of Fe considerably smaller than that of Mo2C, the activity of
the whole FeMo particle is drastically smaller than that of the Fe₄Mo catalyst. Thus, although it is possible to growth SWCNTs from large FeMo clusters, the expected yield is low and the synthesis temperature needs to be high (to overcome the reduced fraction of catalytically active free-Fe), as experimentally reported. Thermodynamically, an excess of C and a amount of free-Fe for \( x_\tau \geq 0.20 \) guarantees the existence of steady-state growth of SWCNTs (albeit slow and inefficient).

Small FeMo particles (\( R \leq 0.41 \) nm). Small FeMo particles are similar to small Fe₄Mo clusters. Nucleation of \( \tau_3 \) and the absence of free-Fe and excess C means that the particle is catalytically inactive. The minimum cluster radius, \( R_{\text{FeMo}}^{\text{min}} \), is the same as \( R_{\text{FeMo}}^{\text{min}} \), because this quantity is determined by the stabilization of the same \( \tau_3 \) phase. Thus, there are three possible thermodynamic scenarios that are similar to the previous case, i.e., low-yield steady-state-, low-yield limited- and no-growth for \( R > R_{\text{FeMo}}^{\text{min}} \), \( R \sim R_{\text{FeMo}}^{\text{min}} \) and \( R < R_{\text{FeMo}}^{\text{min}} \), respectively. The analysis can be extended to different fractions of Fe and Mo and the results are summarized in Table II.

**Surface energies.** The chemical species that are found on the surface of a Fe:Mo cluster with coexisting Fe, and Fe₂Mo phases is the species that has the lowest surface energy per unit area, \( \gamma \). This quantity can be obtained from the relation

\[
\gamma = \frac{|E_n - nE_B|}{2A},
\]

where \( E_n \) is the total energy of a \( n \)-layer slab, \( E_B \) is the total energy of a single bulk layer, and \( A \) is the surface of the unit cell (the factor two accounts for the creation of two surfaces). For bcc Fe, we construct slabs with the lowest surface energy (1 1 0) termination. Surface termination for the ordered Fe₂Mo phase has not been reported in experiments or in theoretical works. By using the package AFLLOW, which performs high-throughput simultaneous optimization of planar density (high) and number of broken bonds (low), we find that the closed packed (0 0 4) plane of Fe₂Mo has the lowest energy. We obtain \( \gamma_{\text{Fe}}(110) = 2.44 \) J/m² and \( \gamma_{\text{Fe₂Mo}}(004) = 3.12 \) J/m². The relation \( \gamma_{\text{Fe}} < \gamma_{\text{Fe₂Mo}} \) indicates that Mo will not be at the cluster surface. Thus, in Fe-rich Fe:Mo nanocatalysts, Fe covers as much surface area as possible, and the aforementioned nucleation of Mo₂C caused by C pollution is advantageous for the activity of the particle, by releasing free-Fe on the surface.

**Conclusions.** In this paper we discuss the role of Mo in the thermodynamic properties of Fe:Mo nanocatalysts by using the size-pressure approximation and \textit{ab initio} modeling. We show that for both Fe-rich (~80% Fe or more) and Mo-rich (~50% Mo or more) Fe:Mo clusters, the presence of carbon causes nucleation of Mo₂C which enhances the activity of the particle by releasing free-Fe. With respect to pure Fe-catalysts, the addition
of Mo (up to small concentrations) decreases the size of the smallest catalyst needed for low-temperature CVD steady-state growth to $R_{\text{Fe}: \text{Mo}} \sim 0.52$ nm.

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