Combining Vibrational Spectroscopies with Quantum Chemical Calculations for Molecular-Level Understanding of Reaction Mechanisms on Catalytic Surfaces

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Heterogeneous catalysis is a critical component in the improvement of existing technologies and development of new solutions in the area of clean energy and sustainability. Combining vibrational spectroscopies with quantum chemical calculations can provide molecular-level information on the structure of catalytic surfaces and reaction pathways. As an initial step, comparison between experimental and computational vibrational spectra can be used for identification of adsorption modes for reactants and products and also for determination of the nature of stable surface species under reaction conditions. In subsequent steps, quantum chemical models calibrated based on stable reaction species on appropriately selected surfaces can be used for evaluation of multiple reaction pathways, identification of transient reaction intermediates, and development of reaction mechanisms for incorporation into kinetic models and description of observable reaction rates. This methodology is illustrated with two spectroscopic techniques: infrared and high resolution electron energy loss spectroscopies and two catalytic systems: Fischer-Tropsch synthesis over Co/TiO2 catalysts and hydrocarbon reactivity on catalytic Pt-Sn alloys.
Advantages of Combining Vibrational Spectroscopies with Quantum Chemical Calculations

Heterogeneous catalysis is a critical component in the improvement of existing technologies and development of new solutions in the area of clean energy and sustainability. This chapter illustrates challenges and advances in catalytic technologies with two examples: (1) Fischer-Tropsch synthesis for the production of synthetic fuels over Co/TiO₂ catalysts and (2) characterization of hydrocarbon adsorption and reactivity on Pt-Sn catalysts for upgrading biomass-derived feedstocks.

These examples highlight advantages of combining experimental vibrational spectroscopies and quantum chemical calculation using density functional theory (DFT) for molecular-level understanding of reaction mechanisms on catalytic surfaces. The advantages of such an integrated experimental-theoretical approach can be grouped into two main areas. The first area is related to assignment of experimental vibrational peaks. Vibrational spectra of surfaces and adsorbates are usually complex and difficult to interpret. Assignments of vibrational bands have previously relied almost exclusively on referencing to model surfaces or model adsorbates. For example, model organometallic cluster compounds have been used for the interpretation of vibrational bands for hydrocarbons adsorbed on metal and metal oxide surfaces. Similarly, adsorption of, for example, halogen-containing model hydrocarbons, which are expected to adsorb by splitting the halogen fragment, have been used for interpretation of vibrational spectra of different types of hydrocarbon surface species. Use of reference surfaces and adsorbates requires significant experimental efforts and often does not provide sufficient accuracy for unambiguous interpretation of vibrational spectra in catalysis research.

DFT calculations are particularly useful for the interpretation of experimental spectra of surfaces and adsorbates because they can be used to generate simulated vibrational modes for comparison with experimental measurements. Different hypotheses on the structure and geometry of surfaces and adsorbates can be tested computationally. Calculations can provide information not only on the positions of vibrational bands but also estimates of their intensities for infrared and Raman measurements. An additional advantage compared to experimental referencing is the information on the energetic stability of different evaluated surfaces and adsorbates, which can also be obtained with DFT calculations. The information on relative stability provides additional guidance for discrimination between different options for assignments of experimental vibrational peaks. The challenge of using calculated frequencies, however, is that they usually require an adjustment based on an empirically obtained scaling factor or correction. It is, therefore, important to augment vibrational spectroscopic results with additional experimental catalyst characterization for validation of DFT models, as illustrated by the examples in this chapter.

The second area where the combination of vibrational spectroscopy with DFT calculations is particularly useful is in identification of reaction intermediates and development of reaction mechanisms. In purely spectroscopic studies, an assumption is usually made that the surface species observed under reaction
conditions are the actual reaction intermediates because no other information on the reaction mechanism is typically available. Such assumptions, however, are frequently incorrect since the surface species that are easiest to detect at reaction conditions are likely to be spectators, which are the most stable and unreactive and, therefore, represent a dead end in one of the reaction pathways. A classical example is ethylidyne C-CH\textsubscript{3} species that dominate vibrational spectra under reaction conditions in ethylene and acetylene hydrogenation, ethane hydrogenolysis, and other transformations of C\textsubscript{2} hydrocarbons on metal surfaces. When initially identified spectroscopically under reaction conditions, ethylidyne C-CH\textsubscript{3} was proposed to be a reactive intermediate, only later to be shown to be the most stable and, therefore, the least reactive C\textsubscript{2} hydrocarbon species (1–7).

The experimental information about detectable stable surface species is, nevertheless, extremely valuable for the development of DFT reaction models. This information is needed as a reference for the selection of model surfaces (size and chemical composition of a cluster or unit cell, type of the surface termination, total number of surface layers and number of relaxed layers, etc.) and computational parameters (choice of a functional and a basis set, integration grid, convergence criteria, etc.). Without such experimental calibration, computational models are usually highly speculative.

Spectroscopic studies, therefore, can provide critical information required for the development of realistic surface models by identifying adsorption modes for reactants and products and also by determining the nature of stable surface species under reaction conditions. In turn, computational models calibrated based on stable reaction species on appropriately selected surfaces can be used to evaluate multiple reaction pathways and identify transient reaction intermediates, which would be difficult to observe experimentally.

Examples in this chapter illustrate advantages of combining quantum chemical calculations with two vibrational spectroscopies: infrared (IR) spectroscopy and high resolution electron energy loss spectroscopy (HREELS). The IR spectroscopic study illustrates identification of the composition and structure of a catalytic surface based on modeling of vibrational spectra for an adsorbed reactant molecule. The HREELS study illustrates identification of hydrocarbon adsorption modes and catalytic activity of surface sites based on modeling of vibrational spectra that change due to temperature-dependent evolution of adsorbates.

**Initial State of Cobalt Catalytic Nanoparticles Under Fischer-Tropsch Reaction Conditions**

**Significance and Challenges of Fischer-Tropsch Catalysis**

Fischer-Tropsch (F-T) synthesis is a commercial process for converting synthesis gas (or syngas – a mixture of carbon monoxide and hydrogen) into a mixture of hydrocarbons, which can be used as liquid transportation fuels or feedstocks for the chemical industry:

\[ \text{CO} + \text{H}_2 \rightarrow \text{Hydrocarbons} + \text{H}_2\text{O} \quad (1) \]
Syngas can be produced from multiple traditional sources, such as crude oil, coal, and natural gas, and also from alternative sources: for example, from renewable biomass or even municipal solid waste. There is currently renewed interest in F-T technology, and there are multiple ongoing research activities in F-T catalysis and process development due to efforts in diversifying the energy supply and switching to alternative and sustainable feedstocks.

Compared to direct upgrading of biomass into bio-fuels, the syngas option offers greater flexibility for types of products that can be produced: from light olefins as a feedstock for the chemical industry to a wide range of fuels: from liquefied petroleum gas to gasoline, jet fuel and diesel. The syngas processing route also avoids the need to remove oxygen for increasing the caloric value of bio-fuels and, in general, affords greater control over the properties of the final product, allowing, for example, to produce fuels in compliance with existing specifications.

A common challenge in integrating F-T catalysis into new biomass conversion technologies is that the processing needs to be performed at a relatively small scale at the location of biomass collection. Transportation of large volumes of biomass is usually prohibitively expensive. As a result, small-scale, preferably mobile, F-T catalysis units need to be developed. An additional challenge for biomass conversion is a variable H/C and, correspondingly, H₂/CO ratio of feedstocks due to natural variability in biomass properties.

These new challenges are compounded by the limitations of the traditional F-T catalysts, which are usually Co and Fe nanoparticles supported on metal oxides (8). Specific issues related to inefficiencies of current catalysts with respect to their activity, selectivity and stability are outlined below.

Since most F-T reactions are exothermic, it is preferable to operate the chemistry at lower temperatures in order to shift the thermodynamic equilibrium to reaction products and, thus, increase the yield. In addition, lower temperatures suppress formation of methane – an undesirable byproduct. The choice of moderate reactor temperatures of about 500-620 K, however, leads to reaction rates that are low compared to traditional hydrocarbon conversion processes: usually less than 0.5 g hydrocarbon/(g catalyst h) (9), and, as a result, development of new more active catalysts is desirable for improving process economics (8–10).

The product distribution of F-T synthesis is usually described with an Anderson-Schulz-Flory (ASF) distribution or, more accurately, with an overlap of two separate ASF distributions (10). The parameters of these distributions depend on the catalyst composition, with some catalyst formulations being more efficient in reducing the formation of undesirable methane and maximizing formation of targeted higher hydrocarbons (9–11). Typical selectivities for C₅-C₁₂ (gasoline) and C₁₃-C₁₈ (diesel) fractions are 20-40 and 5-15 wt%, respectively. Further improvements in catalyst selectivity are, certainly, desirable.

Catalyst deactivation with time on stream is usually attributed to coking, chemical poisoning, for example with sulfur, and changes in the active phase through oxidation or metal particle agglomeration (8, 9, 12). A typical catalyst lifetime is about 6 months. As the catalyst deactivates, the process temperature is usually increased, resulting in even lower selectivities. More stable formulations can, reportedly, be obtained, for example, by incorporating noble-metal promoters, Ru, Re or Pt, that can increase hydrogenation of coke precursors and improve
reducibility of the active Co or Fe phases (9, 13–15). The stability issue is especially significant for Fe-based catalysts (8).

Since most reactions in F-T synthesis are highly exothermic, engineering solutions for efficient management of heat and mass transfer limitations contribute to process improvements. For example, there are studies on new reactor configurations where a catalyst is deposited on the walls of a monolith, serving as a heat exchanger and allowing for better heat management (16). Advances in reactor design bring the overall process performance closer to intrinsic catalytic kinetics and make catalysis research even more significant. There is, thus, general agreement that catalyst development is crucial for improvements in F-T technology (8, 9, 11, 12, 17–23). F-T catalysis research, however, remains mostly a trial and error exercise because of insufficient understanding of the reaction mechanism and properties of catalytic surfaces.

There are currently three main reaction mechanism schemes: (1) Carbide mechanism where the chain growth proceeds through C or CH$_x$ species (24–26), which is also referred to as “CH$_2$ insertion” based on the CH$_x$ species most often cited as the likely intermediate; (2) CO insertion mechanism where the chain is propagated by CO addition with subsequent hydrogenation (10, 27–30); and (3) propagation through oxygenated intermediates other than CO, for example, through formates (17, 19, 21, 31–33).

The uncertainty of the reaction mechanism is compounded by a lack of understanding of dynamic changes of the catalytic surface under reaction conditions. Depending on the feed composition, reaction temperature and pressure, and time on stream, supported Co and Fe catalytic nanoparticles may change their surface composition from metallic to different oxide and carbide phases. Although most researchers acknowledge the importance of such dynamic catalytic surface changes under reaction conditions, none of the current reaction mechanisms incorporates this complexity. This omission is mostly due to the difficulty of catalyst surface characterization under reaction conditions and a disconnect between experimental and computational studies.

The study presented in this section closely integrates IR spectroscopic measurements with DFT calculations for identification of surface changes for Co/TiO$_2$ catalysts under F-T reaction conditions and for selection of appropriate catalytic surface models. The developed surface models can be incorporated into improved reaction mechanisms and kinetic models, which are essential for optimization of operating conditions and process control systems with existing catalysts and for development of new catalyst formulations.

**Experimental and Computational Details**

Two Co/TiO$_2$ samples were prepared using different preparation methods: one by incipient wetness impregnation with a Co loading of 14.6 wt% and another by homogeneous deposition precipitation with a Co loading of 9.9 wt%. The samples were prepared similarly to those reported previously in studies of Co-Mn/TiO$_2$ catalysts (34, 35). The two samples were calcined at 673 K and then reduced at either 573 or 623 K for 2 h, generating a total of 4 samples differentiated by two preparation methods and two reduction temperatures. The size of supported Co
nanoparticles was estimated at 2.5-3.2 nm using transmission electron microscopy (TEM).

The samples were tested under F-T reaction conditions in a flow reactor with simultaneous collection of vibrational spectra using Diffuse Reflectance Infrared Fourier Transform (DRIFT) spectroscopy. In addition, the samples were characterized with CO adsorption at room temperature using DRIFT spectra as a function of He purging time.

DFT calculations were performed using the DMol³ code in Materials Studio 4.0 software by Accelrys Software, Inc (36). The calculations employed the generalized gradient approximation (GGA) using the Perdew-Wang (PW-91) functional. The basis set used a double-numerical basis with polarization (DNP) (37). Tightly bound core electrons were represented with semicore pseudopotentials (38). Reciprocal-space integration over the Brillouin zone was approximated through k-point sampling with a separation of 0.5 nm⁻¹ using the Monkhorst-Pack grid: (3×3×1). Convergence with respect to the number of k-points was tested by increasing their number for representative structures. The density mixing fraction of 0.1 with Direct Inversion in the Iterative Subspace (DIIS) and orbital occupancy with smearing of 0.04 Ha were used. The DMol³ code employs real space cutoffs of the basis set to reduce computational cost. These cutoff distances were set at 0.41 nm for all atoms.

All surfaces were modeled with periodic slabs with a separation of 3 nm in the c direction. Surfaces were generated from Co and CoO bulk structures using optimized lattice constants: \(a=b=0.2640\) nm, \(c=0.4295\) nm for Co (experimental 0.2507 and 0.4069 nm) and \(a=b=c=0.4328\) nm for CoO (experimental 0.4267 nm). Metallic surfaces were constructed using 4 layers of either a 2×2 super cell with a total of 16 atoms or a 2×3 super cell with a total of 24 atoms. Oxide surfaces of CoO(100) and CoO(111) were modeled using 4 layers of 2×2 super cells with a total of 16 Co and 16 O atoms. All surface layers were optimized with Co during geometry optimizations, simulating surface relaxation upon adsorption. Adsorption energies were calculated at 0 K without zero-energy corrections using as a reference the sum of energies for the appropriate clean surface and CO calculated separately.

Vibrational frequencies for adsorbed CO were obtained from the mass-weighted Hessian (second derivative) matrix (39). Evaluation of the Hessian matrix was performed using two-point numerical differentiation of analytical gradients (36). A step size of 0.01 Bohr was used for the numerical differentiation using the finite difference method. For molecular systems, the size of the Hessian matrix is \(3N\times3N\), where \(N\) is the number of atoms. For periodic systems, however, the computational cost is higher. In order to reduce the computational cost of frequency calculations, the so-called “partial Hessian” approach was used. This approach is particularly well suited for use with the finite difference method. The vibration of adsorbed CO is localized compared to low-frequency motions of surface Co atoms and, therefore, the frequency of the CO vibration depends mostly on the motions of the C and O atoms. Consequently, a good estimate can be obtained with the finite difference approach using only the atoms of the adsorbate. Studies of other adsorption systems have shown that the partial Hessian approximation yields vibrational frequencies within a few
wavenumbers of the corresponding exact calculations (40–42). The reported calculated vibrational frequencies were uniformly scaled with a single empirical factor of 1.0756 based on referencing to the experimental frequency of 2020 cm\(^{-1}\) for CO adsorbed on metallic Co in static adsorption experiments at room temperature.

**Results and Discussion**

Catalyst samples prior to reaction testing were analyzed by temperature-programmed reduction (TPR) in H\(_2/\)Ar flow from room temperature to 873 K at a rate of 10 K/min. Two H\(_2\) consumption peaks were detected. The first one at 533-553 K for the transition from Co\(_3\)O\(_4\) to CoO and the second one at 698-733 K for the transition to metallic Co. These TPR results show that Co may not be fully reduced (may not be fully metallic due to presence of Co(II) oxide) after reduction at our chosen reduction temperatures of 573 and 623 K and during F-T reaction testing at 493 K. Previous studies with Co-Mn/TiO\(_2\) showed that larger Co\(_2\)O\(_3\) clusters redisperse and form smaller metallic Co nanoparticles on reduction (34, 35).

The conclusion that Co nanoparticles on the fresh catalyst may not be fully reduced is supported by X-ray photoelectron spectroscopic (XPS) results. XPS measurements were performed after reduction and consequent passivation with CO\(_2\) at 423 K. All XPS spectra exhibited Co 2p\(_{3/2}\) and Co 2p\(_{1/2}\) peaks at 781.1–781.2 eV and 796.5–796.8 eV, respectively, and an energy separation between the Co 2p\(_{3/2}\) and Co 2p\(_{1/2}\) peaks of around 15.5–15.8 eV, indicating the presence of a CoO-like phase.

The IR spectra for the Co/TiO\(_2\) catalyst prepared by incipient wetness and pre-reduced at 623 K under F-T reactions conditions at 493 K as a function of time on stream are shown in Figure 1. The feed gas hourly space velocity (GHSV) was kept at 3010 h\(^{-1}\) with the CO/H\(_2\) feed molar ratio of 0.5. Consumption of reactants and formation of products was monitored using a gas chromatograph. The initial strong rovibrational band for gas-phase CO centered at 2143 cm\(^{-1}\) at 22 min of time on stream significantly reduces as the reaction progresses, and CO adsorbed on the catalyst surface is observed at 98 min on stream. The band for atop-bonded (linear) CO is usually located at about 2010-2060 cm\(^{-1}\).

Interestingly, two distinct atop CO peaks are observed in Figure 1: one peak at ~2056 and another at ~2010 cm\(^{-1}\). The same two peaks for adsorbed CO were observed under reaction conditions for the three other evaluated Co/TiO\(_2\) catalyst samples obtained with different preparation procedures. Furthermore, these two bands (at ~2050 and ~2020 cm\(^{-1}\)) were also observed in separate CO adsorption experiments without hydrogen at room temperature (additional IR spectra are not shown for brevity).

These two bands can be attributed to CO adsorbed on Co nanoparticles and not on the TiO\(_2\) support because similar double-feature IR bands were previously reported for Co catalysts on different supports: for Co/SiO\(_2\) (22, 43–45) and Co/Al\(_2\)O\(_3\) (19, 46, 47). In the study on the effects of water addition on the performance of Co/SiO\(_2\) catalysts, the apparent intensity ratio of the bands at 2056 and 2010 cm\(^{-1}\) changes with the partial pressure of added water and corresponding changes in
catalyst activity and selectivity, demonstrating the importance of dynamic catalyst surface changes (44). Although the two atop CO bands were reported in multiple previous studies, their assignments are conflicting and mostly speculative. For example, they were assigned to vertical and angled CO on metallic Co sites, CO adsorbed on a single metallic Co atom with and without co-adsorbed H on the same atom, CO adsorbed on metallic Co and partially charged Coδ+, or simply labeled as CO on Co Type 1 and Co Type 2 sites (11, 12, 45–47).

Figure 1. In-situ IR spectra of a Co/TiO₂ catalyst (pre-reduced at 623 K) under F-T reaction conditions as a function of time on stream. Feed GHSV 3010 h⁻¹, 1 atm, CO/H₂ mol feed ratio of 0.5, 493 K. (see color insert)
In order to explain the origin of the two atop-bonded CO species observed in IR experiments, DFT calculations were used to develop catalyst surface models and test different assignments by evaluating CO adsorption energies and vibrational frequencies on different surface sites. First, the hypothesis that CO adsorbs on different Co metallic sites was evaluated. CO adsorption on a flat Co(001) surface (Figure 2a) (48) was compared to that on step sites of Co(102) (Figure 2b) (24, 48) and on Co(001) with 2 top atom rows removed (Figure 2c) (24, 25). The results in Table 1 for calculated adsorption energies and normal vibrational modes show that the estimated frequency for CO on step sites is within several wavenumbers from that for CO on the flat Co sites. In addition, higher adsorption energies for CO on step sites compared to that on the flat Co(001) are inconsistent with a more rapid decrease of the peak at 2056 cm\(^{-1}\) on He purging in CO adsorption experiments at room temperature. The DFT calculations, therefore, suggest that atop-bonded CO on different metallic Co sites (flat and step surfaces) have similar frequencies and, thus, the two atop-bonded CO peaks cannot be explained by the morphology of Co particles. In addition, if one of the experimentally observable bands was indeed associated with CO on steps or other coordinatively unsaturated sites (defects), then the intensity of such a band should correlate with a number of defects and exhibit a trend with the size of Co nanoparticles. The absence of such a trend in previous studies is consistent with our conclusion that the morphology of metallic Co particles cannot explain the two experimentally observed atop-bonded CO peaks.

Since the calculation results in Table 1 suggest that CO species adsorbed on different metallic Co sites are spectroscopically indistinguishable, the same conclusion applies to CO species adsorbed at different angles to the surface on Co metallic sites, for example on steps or defects. The computational results, therefore, also do not support the hypothesis that the two spectroscopic peaks can be explained by vertical and angled CO species. The hypothesis of hydrogen co-adsorption was not evaluated computationally because the same two atop-bonded CO peaks were observed in our CO adsorption experiments in the absence of hydrogen.

The second hypothesis, which was evaluated computationally, attributed the two different adsorption sites to metallic Co and metallic Co on top of Co oxide. An arrangement of a metallic Co layer on top of CoO would generate partially charged Co\(^{5+}\) surface atoms. For this evaluation, the adsorption of CO on metallic Co was compared to that on surfaces with 2 layers (Figure 2d) and then with 1 layer of metallic Co on top of CoO(100) oxide surface (Figure 2e) as representations of materials with a metallic shell surface over an oxide core. The CO frequency results in Table 1 for these shell structures (entries d and e) indicate that even a single layer of metallic Co on top of an oxide structure would adsorb CO similarly to purely metallic Co: the CO frequency is predicted to be the same within 2 cm\(^{-1}\). In addition, a shell metal model would not be able to explain the experimentally observed decrease in the concentration of three-fold and bridge-bonded CO associated with the dominance of the atop-bonded peak at 2056 cm\(^{-1}\) in our CO adsorption measurements at room temperature.
The experimentally observed decrease in the coverage of three-fold and bridge-bonded CO could be explained if the atop-bonded CO at 2056 cm\(^{-1}\) were associated with Co atoms surrounded by oxygen atoms on the surface, eliminating Co three-fold sites and reducing the number of Co bridge sites. Accordingly, the third hypothesis assumed that the band at 2056 cm\(^{-1}\) may be associated with CO surrounded by adsorbed oxygen as neighboring surface species. Surface oxygen can be present due to, for example, bulk oxygen diffusion from a partially reduced core of Co particles. The hypothesis of surface oxygen was tested by evaluating CO adsorption on the metallic Co(001) surfaces with a variable concentration of adsorbed oxygen: 1/6, 1/3 and 1/2 of monolayer atomically adsorbed oxygen (Figures 2f-h). The results in Table 1 indicate that the calculated CO frequency is significantly affected by oxygen coverage. The band is shifted to higher values by 10, 19 and 58 cm\(^{-1}\) for, respectively, 1/6, 1/3, and 1/2 ML oxygen coverage. These results suggest that the CO peak in the presence of surface oxygen would be broad, and that its position would change significantly with oxygen coverage caused, for example, by different reduction temperatures. Since this is not observed experimentally and the positions of the two CO peaks are fairly constant, this suggests that oxygen on the surface is not simply adsorbed at a variable coverage but is a part of a well-defined Co phase.

Figure 2. Models of metallic and Co oxide surfaces used in DFT calculations for interpretation of IR spectra for CO adsorption on Co/TiO\(_2\) in Figure 1. Only two top layers are shown for each model for clarity. DFT results for CO adsorption are presented in Table 1. (see color insert)
Table 1. DFT Calculation Results for Adsorption Energies and Vibrational Frequencies for Atop-Bonded CO on Different Metallic Cobalt and Cobalt Oxide Surfaces*

<table>
<thead>
<tr>
<th>Model surface</th>
<th>-ΔE ads, kJ/mol</th>
<th>Calculated frequency, cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>a. Co(001) flat surface</td>
<td>143</td>
<td>2020</td>
</tr>
<tr>
<td>b. Co(102) step surface 1/6 ML coverage</td>
<td>160</td>
<td>2018</td>
</tr>
<tr>
<td>c. Co(001) step surface (2 rows removed) 1/6 ML coverage</td>
<td>167</td>
<td>2020</td>
</tr>
<tr>
<td>d. Two layers of Co on top of CoO(100) flat surface</td>
<td>161</td>
<td>2020</td>
</tr>
<tr>
<td>e. One layer of Co on top of CoO(100) flat surface</td>
<td>176</td>
<td>2018</td>
</tr>
<tr>
<td>f. Co(001) flat surface 1/6 ML coverage by oxygen atoms</td>
<td>140</td>
<td>2030</td>
</tr>
<tr>
<td>g. Co(001) flat surface 1/6 ML coverage by oxygen atoms</td>
<td>135</td>
<td>2039</td>
</tr>
<tr>
<td>h. Co(001) flat surface 1/6 ML coverage by oxygen atoms</td>
<td>128</td>
<td>2078</td>
</tr>
<tr>
<td>i. CoO(111) flat surface</td>
<td>132</td>
<td>2040</td>
</tr>
<tr>
<td>j. CoO(100) flat surface</td>
<td>133</td>
<td>2043</td>
</tr>
</tbody>
</table>

* 1/4 ML CO coverage unless otherwise noted. Model surfaces with the same letter labels as the entries in Table 1 are shown in Figure 2.

The final hypothesis assumed that the two CO peaks can be attributed to adsorption on metallic Co and CoO oxide since TPR and XPS measurements suggest that both of these phases are present. Two CoO surfaces, CoO(111) and Co(100) shown in, correspondingly, Figures 2i and 2j, were evaluated and compared to metallic Co(001). The CoO(100) surface was found to be more energetically stable than CoO(111). The CO frequency on CoO(100) is calculated to be at 2043 cm⁻¹ (Table 1), in good agreement with the experimental peak at 2056 cm⁻¹. This peak for CO on CoO is predicted to be at a higher wavenumber than that for CO on the flat metallic Co(001) at 2020 cm⁻¹, which is also in good agreement with the second experimental band at 2010 cm⁻¹ in Figure 1. For comparison, a previous DFT study for CO adsorption on Co(001) reported a frequency of 2017 cm⁻¹ (49). In addition, the calculated adsorption energy for CO on CoO is lower than that on metallic Co by about 10 kJ/mol (Table 1) and, therefore, the former can be expected to desorb preferentially on He purge, again in agreement with our experimental observations. Moreover, the adsorption of CO on CoO explains the decrease in intensity of CO adsorbed on three-fold and bridge Co sites when the 2056 cm⁻¹ band dominates the spectra in CO adsorption experiments at room temperature. The CoO(100) surface (Figure 2g) has atop Co sites, a reduced number of bridge bonding sites and no three-fold Co sites due to neighboring lattice oxygen.
Atop-bonded CO on Co$^{+2}$ sites of CoO is sometimes assigned to an IR peak at $\sim$2143 cm$^{-1}$, which was not observed in our studies. Such an assignment, however, is based on limited evidence because CO adsorption on Co oxides, compared to metallic Co, has not been well studied. For example, this assignment, as a tentative interpretation, was made based on an apparent correlation between the intensity of the IR peak at 2143 cm$^{-1}$ and XRD measurements for Co/SiO$_2$ samples at different extents of Co oxidation (50). Since XRD measurements do not provide information about the surface composition, such a correlation is not reliable. In addition, in IR measurements of CO adsorption on Co sites in CoO-MgO samples (51–53), the dominant peaks were at $\sim$2028 and $\sim$2076 cm$^{-1}$, in agreement with the results in Figure 1. Furthermore, the same peaks were observed with CoO-MoO$_3$ samples at 77 K and room temperature, indicating that CO adsorbs predominantly on metallic Co and CoO sites, and not on Co carbides, because CO decomposition and formation of Co carbide phases at 77 K can be expected to be minimal.

In summary, a combination of DFT calculations with IR spectroscopic results provided a molecular-level understanding of the initial surface structure of Co/TiO$_2$ catalysts. Evaluation of multiple possible Co surfaces (metallic Co with flat and step sites, metallic Co with surface oxygen at different coverage values, cobalt oxide, and metallic cobalt layers on top of cobalt oxide) with DFT calculations suggests that only metallic Co and a Co oxide surface similar to Co(II) oxide are consistent with the IR measurements and additional catalyst characterization with TPR and XPS measurements. The assignment of one of the IR bands to CO adsorbed on a Co oxide phase can be specifically tested in future experiments. If this assignment is confirmed, calibrations of IR peak intensities will make it possible to evaluate the ratio of the two Co phases (metallic and oxidized) under reaction conditions and analyze its effects on the catalyst activity, selectivity, and stability. Additional studies can also evaluate the effects of the formation of Co carbides on the catalyst surface due to decomposition of CO under reaction conditions. Understanding of such dynamic surface changes is critical for optimization of reaction conditions for current catalysts and development of improved catalyst formulations.

**Adsorption and Reactivity of Acetylene on Platinum-Tin Surface Alloys**

**Platinum Bimetallic Nanoparticles as Catalysts of Choice for Upgrading Biomass-Derived Oils to Fuels and Chemicals**

Biomass conversion to transportation fuels and chemical feedstocks remains an area of high profile and intensive research (54–62). Triglycerides from vegetable oils, animal fats or algae can be used directly as a component of diesel fuel or upgraded by esterification (60, 63–65). Conversion technologies for other types of biomass (lignocellulosic feedstocks) can be classified into three main types: (1) gasification to produce synthesis gas for further processing using Fischer-Tropsch synthesis, (2) pyrolysis or liquefaction to produce bio-oil, and (3) hydrolysis for the production of aqueous sugars and lignin. These technologies have different efficiencies, depending on the nature of the biomass source (e.g.,

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wood, corn stover, crop residues, sugar cane, grasses, or aquatic plants). The first two technologies, gasification and production of bio-oil, offer greater flexibility and robustness with respect to the type of biomass than the third route, hydrolysis (59). Although the first route offers the greatest flexibility (practically all biomass types can be gasified), gasification has a major disadvantage: all the existing carbon-hydrogen bonds in the biomass need to be broken in the production of synthesis gas in order to be reassembled later using a capital and energy-intensive Fischer-Tropsch synthesis. This breaking and reassembling of chemical bonds is inherently inefficient.

The inefficiency of breaking all carbon-hydrogen bonds is avoided in the second route: production of bio-oil. Since it is a potentially more efficient technology, bio-oil production and conversion to fuels and chemicals are actively studied as a sustainable and environmentally friendly technology for obtaining transportation fuels and feedstocks for the chemical industry. Bio-oils can be produced by two methods: pyrolysis and liquefaction. In pyrolysis, biomass is heated in the absence of air, forming a gaseous product, which then condenses as bio-oil with yields of up to 80 wt% (55, 56, 61). A number of pyrolysis technologies have been commercialized. In contrast to simple pyrolysis, liquefaction is usually performed at elevated pressures (50-200 atm) in a controlled atmosphere, for example, in the presence of hydrogen and a catalyst, and longer reactor residence times in order to obtain bio-oil with better properties, mostly with lower oxygen content (55–58).

Bio-oils produced by pyrolysis typically contain about 40-45 wt% oxygen and 25-30 wt% water. Bio-oils obtained by liquefaction typically have 15 wt% oxygen and 5 wt% water (55–58). Bio-oils are usually hydrophilic and cannot be used directly as a component of petroleum-based transportation fuels. As a result, all bio-oils, including the higher quality bio-oils obtained from liquefaction, have to be upgraded in order to reduce the concentration of oxygenates (oxygen-containing hydrocarbons) and water. A high oxygen concentration makes bio-oils (a) acidic and corrosive, (b) unstable with respect to polymerization and other reactions during storage, (c) too viscous for use as a fuel component, and (d) less energetically valuable per unit weight than petroleum-derived hydrocarbons. Although there are efficient processes for the production of bio-oils, there are significant challenges in the development of efficient bio-oil upgrading technologies.

Direct upgrading of bio-oils is currently dominated by technologies adapted from petroleum refining: (1) oxygen removal and hydrogenation with catalysts traditionally used for desulfurization of petroleum products and (2) cracking and oxygen removal with catalysts traditionally used for cracking of heavier petroleum fractions to produce gasoline and diesel fractions. Bio-oils can also be converted to hydrogen or synthesis gas using steam reforming for further conversion using Fischer-Tropsch synthesis (66–69).

Oxygen removal in the presence of hydrogen (hydrodeoxygenation) is usually performed at 573-873 K at a hydrogen pressure above 100 atm over sulfided Co-Mo or Ni-Mo supported catalysts (56, 59, 70–72). These catalysts have been developed for sulfur and nitrogen removal in the petroleum refining industry, and they are not optimized for bio-oil upgrading. Insufficient activities and low
hydrogen efficiencies have prompted introduction of a two-stage process (73, 74). The other major disadvantage of Co-Mo and Ni-Mo catalysts is that they are most active in the sulfided form, which needs to be maintained by a sulfur supply in the feed, such as H2S addition. Utilization of sulfides presents a significant environmental hazard. Furthermore, process operation at high hydrogen pressures is expensive and requires a source of hydrogen, which for sustainability reasons should be obtained from renewable sources, and therefore, requires additional processing (59, 71). Hydrogen efficiency and catalyst stability are also issues that require improvement (70). As a result, there are intensive research efforts aimed at replacing sulfided catalysts with supported metals such as Pt (71, 75).

Bio-oil upgrading with zeolite catalysts is typically performed at atmospheric pressure and 623-773 K. The most common zeolite is ZSM-5, which is adapted from fluid catalytic cracking (FCC) in petroleum refining. Cracking over zeolites reduces oxygen content and improves thermal stability. The products include hydrocarbons (aromatic and aliphatic), water-soluble organics, water, oil-soluble organics, gases (CO2, CO, light alkanes) and coke. Similarly to hydrodeoxygenation over Co-Mo and Ni-Mo sulfides, these catalysts are not tailored for bio-oil upgrading and, therefore, the amount of coke produced can be significant, up to 40 wt%, and the yield of the organic liquid fraction is small at 15-35 wt% (55, 56). As an alternative to cracking over zeolites, hydrotreating over Pt/ZSM-5 catalysts has been recently evaluated (76).

Since upgrading of bio-oils over sulfided Co-Mo or Ni-Mo and over zeolites is not sufficiently effective, significant research efforts are directed at identifying more efficient new technologies. The following promising chemistries have been recently reported that utilize Pt and Pt bimetallic catalysts: (a) aqueous-phase reforming to CO2 and high-purity H2, (b) generation of high purity synthesis gas (mixture of CO and H2), and (c) hydrogenolysis for simultaneous cracking and oxygen removal. In addition, glycerol has been evaluated for use in direct alcohol fuel cells by utilizing Pt catalysts (77).

Aqueous-phase reforming for production of high purity hydrogen was initially reported for a number of oxygenated hydrocarbons over Pt/Al2O3 catalysts in 2002 (78–80). A similar chemistry was later proposed for production of light alkanes from biomass-derived feedstocks over Pt/SiO2-Al2O3 (81). Addition of Sn to Pt/Al2O3 has been found to improve catalyst performance (82). Catalyst and process development has relied primarily on kinetic studies and high-throughput (trial and error) screening (83, 84). For example, more than 130 bimetallic Pt and Pd-based formulations were screened for aqueous-phase reforming (APR) of ethylene glycol, and Pt-Ni and Pt-Co bimetallics were identified as promising leads (84). The increased activity of the alloys was proposed to be linked to lower adsorption energies of the reaction products, CO and H2. In contrast, surface science studies of oxygenates on Pt(111) and Ni/Pt(111) bimetallic surfaces were used to propose that the reforming activity was correlated with the d-band center of the surfaces (62, 85).

Empirical studies on the effects of the Pt particle size, catalyst composition and supports demonstrate the potential for optimization of the catalyst formulation and process conditions (86–89). For example, larger Pt nanoparticles were linked to a selectivity change towards hydrodeoxygenation rather than formation of H2.
and CO₂ based on kinetic studies (90). As another example, a Pt-Re catalytic system was reported to be more selective than pure Pt (91). Similarly to these examples, most of the recent studies on promising pure Pt and Pt bimetallic catalysts, such as Pt-Sn, rely on trial and error methodology for the selection of the catalyst and process variables (92–94). Development of molecular models for the adsorption and reactivity of hydrocarbons on platinum bimetallic nanoparticles will provide guidance for the identification of the most preferable technologies for bio-oil upgrading (e.g., aqueous or gas-phase reforming, one or two-stage hydrodeoxxygenation), efficient catalyst formulations for these preferable technologies and, moreover, optimized reaction conditions for the preferable catalysts.

The study in this section illustrates a synergistic combination of HREELS spectroscopic measurements and DFT calculations with vibrational analyses for the development of a molecular-level understanding of acetylene adsorption and reactivity on catalytic surfaces of Pt and Pt-Sn alloys. The developed methodology can be extended from acetylene to other hydrocarbons, particularly to model compounds that represent derivatives from the three main components of bio-oils: (1) hemicellulose (e.g., formic and acetic acids, methanol and ethanol, acetone and formaldehyde), (2) cellulose (e.g., glucose and fructose), and (3) lignin (e.g., phenol, 2-methoxyphenol and isoegenol). The methodology can, similarly, be extended to adsorption and reactivity studies on other bimetallic surfaces.

**Experimental and Computational Details**

Acetylene adsorption was studied with HREELS and temperature programmed desorption (TPD) in ultrahigh vacuum (UHV) at 90-1000 K on two ordered Pt surface alloys with different Sn concentrations: Pt₃Sn/Pt(111) and Pt₂Sn/Pt(111).

The (2×2) Sn/Pt(111) surface alloy (Pt₃Sn) was prepared by evaporating 0.7 ML Sn onto the Pt(111) surface and subsequently annealing to 1000 K for 10 s. The (√3×√3)R30° Sn/Pt(111) surface (Pt₂Sn) was prepared by evaporating 1.0 ML Sn on the Pt(111) surface and annealing to 850 K for 10 s. The 2-D order of both surfaces was observed by low energy electron diffraction (LEED). The coverage of Sn in the topmost surface layer was θSn=0.25 for the (2×2) Sn/Pt(111) alloy and θSn=0.33 for the (√3×√3)R30° Sn/Pt(111) alloy, corresponding to the (111) plane of Pt₂Sn and Pt₃Sn surface layers, respectively.

HREELS spectra were collected with the sample initially at 90 K with a typical resolution of 50 cm⁻¹ and incident beam energy of 4.5 eV. All TPD measurements were made using the QMS ionizer in line-of-sight with the sample surface and a linear heating rate of 3 K/s. The crystal was positioned 1 mm away from the entrance aperture of the QMS shield to reduce contributions to the spectra from the crystal back and edges (95). Two highly transparent, fine, grounded screens were in place to eliminate possible damage to the adsorbed layer from low energy electrons emitted by the QMS ionizer region (96).

Gradient-corrected periodic DFT calculations were performed with the DMOl³ code in Materials Studio 4.0 software by Accelrys Software, Inc.

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The calculations used the DNP basis set and the GGA RPBE functional. Tightly bound core electrons were represented with semicore pseudopotentials. Reciprocal-space integration over the Brillouin zone was approximated through \( k \)-point sampling with a separation of 0.5 nm\(^{-1} \) using the Monkhorst-Pack grid: \((2\times2\times1)\). Convergence with respect to the number of \( k \)-points was tested by increasing their number for representative structures. The density mixing fraction of 0.1 with DIIS and orbital occupancy with smearing of 0.005 Ha were used. The orbital cutoff distance was set at 0.41 nm for all atoms.

All surfaces were modeled using infinite slabs constructed with periodic unit cells, similarly to our previous studies for ethylene oxide and cyclohexanone adsorption (97, 98). The optimized Pt lattice constant of 0.4028 nm was used to generate the surface from the bulk crystal with a vacuum spacing between the slabs in the \( c \) direction of 3 nm. An infinite slab with a \( 4\times4\times4 \) unit cell with a total of 64 Pt atoms (Figure 3a) was used to model the Pt(111) surface. The Pt\( _3\)Sn/Pt(111) surface was constructed using a \( 4\times4\times4 \) unit cell of Pt(111) and then substituting 4 out of 16 surface Pt atoms by Sn in the appropriate positions (Figure 3b). The Pt\( _2\)Sn/Pt(111) surface was constructed using a \( 3\times3\times4 \) unit cell of Pt(111) and then substituting 3 out of 9 surface Pt atoms by Sn in the appropriate positions (Figure 3c).

**Figure 3.** Unit cells of periodic infinite surface models for Pt and Pt-Sn: side view (left) and top view of the first layer (right). (see color insert)
All surface layers were optimized with acetylene during geometry optimizations, simulating surface relaxation upon adsorption. Adsorption energies were calculated at 0 K without zero-energy corrections using as a reference the sum of energies for the appropriate clean surface and acetylene calculated separately. Frequency calculations were performed with a partial Hessian for the adsorbed hydrocarbon species. Calculated frequencies are reported without adjustments.

Results and Discussion

HREELS spectra for acetylene adsorption on the Pt$_3$Sn alloy at the dosing temperature of 90 K exhibit a single carbon-carbon bond stretching, $v_{CC}$, peak at 1601 cm$^{-1}$ (spectrum is not shown for brevity). This peak can be assigned to acetylene species $\pi$-bonded to a single Pt atom because acetylene is expected to adsorb initially without bond breaking at low temperatures. The corresponding peak at 1635 cm$^{-1}$ for the Pt$_2$Sn alloy in the spectrum collected at 200 K in Figure 4 can also be assigned to $\pi$-bonded acetylene.

The calculated carbon-carbon bond stretching frequencies for different acetylene adsorption modes and C-CH$_2$ vinylidene species on Pt(111) and the two Pt-Sn alloys are summarized in Table 2. The calculated frequencies for $\pi$-bonded acetylene are significantly different from the experimentally observed values. The calculated frequencies at 1817-1830 cm$^{-1}$ in Table 2 are close to that of gas-phase acetylene at 1974 cm$^{-1}$ and overestimate the experimental values by about 200 cm$^{-1}$. In contrast, for strongly bound acetylene species, calculated and experimental frequencies are in good agreement without any adjustments or corrections. For example, the calculated $v_{CC}$ of 1351 cm$^{-1}$ (Table 2) for the most stable acetylene configuration on Pt(111) in a di-$\sigma$/$\pi$-bonded mode (Figure 5a) is close to the reported experimental value of ~1310 cm$^{-1}$ (99, 100).

The value of $v_{CC}$ for di-$\sigma$/$\pi$-bonded acetylene on the Pt$_3$Sn surface is calculated to be at 1326 cm$^{-1}$, similar to that on Pt(111). Since there are no experimental peaks that are close to this value in Figure 4, we can conclude that di-$\sigma$/$\pi$-bonded acetylene does not form on this Pt-Sn alloy. DFT calculations suggest that this is due to relative destabilization of this adsorption mode compared to other configurations caused by the presence of surface Sn atoms. The di-$\sigma$/$\pi$-bonded acetylene is not observed on the Pt$_2$Sn alloy because there are no three-fold Pt sites due to the arrangement of Sn atoms on the surface (Figure 3c). In addition, DFT calculations suggest that adsorption on 2Pt-Sn sites or, more broadly, on any Sn sites for both alloys is less energetically favorable than adsorption on Pt-only sites.

On annealing from 90 to 200 K, $\pi$-bonded acetylene on the alloys transforms to a more stable di-$\sigma$-bonded configuration ($v_{CC}$ peak at 1495 cm$^{-1}$ for the Pt$_2$Sn alloy in Figure 4). The calculated frequency of 1476 cm$^{-1}$ in Table 2 is in good agreement with the experimental value. On the Pt$_3$Sn surface, the calculated frequency is similar at 1460 cm$^{-1}$. The experimental peak for Pt$_3$Sn in Figure 4, however, is observed at a significantly lower value of 1417 cm$^{-1}$, which indicates the presence of different hydrocarbon species. This peak can be assigned to vinylidene, C-CH$_2$,
species that form upon acetylene isomerization ($v_{CC}$ calculated at 1445 cm$^{-1}$ in Table 2).

DFT calculated reaction energies for acetylene isomerization to C-CH$_2$ are summarized in Figures 5d-f. These results suggest that it is energetically preferable for acetylene to transform into C-CH$_2$ on the Pt(111) and Pt$_3$Sn surfaces where C-CH$_2$ species can be di-$\sigma$/\pi-bonded to three-fold Pt sites in the $\mu_3$-$\eta^2$ configuration (Figures 5d and e). In contrast, on the Pt$_2$Sn alloy in the absence of three-fold Pt sites, C-CH$_2$ species are predicted to be di-$\sigma$-bonded to a bridge Pt-Pt site ($\mu_2$-$\eta^1$ configuration, Figure 5f) and, therefore, to be less stable. As a result, the isomerization of acetylene to C-CH$_2$ on Pt$_2$Sn is estimated to become endothermic at $+13$ kJ/mol and, therefore, less favorable. This energetic difference provides a preliminary explanation of why di-$\sigma$-bonded acetylene is observed on Pt$_2$Sn while C-CH$_2$ vinylidene is observed on Pt$_3$Sn. Additional DFT calculations can evaluate transition states and provide further insight on the geometric and energetic requirements for acetylene isomerization.

Figure 4. HREELS spectra for acetylene on Pt-Sn alloys at 200 K and DFT computational models of stable adsorbates with vibrational modes that match experimental frequencies. (see color insert)
Figure 5. DFT computational models of acetylene CH-CH (a-c), vinylidene C-CH₂ (d-f) and acetylene dimer C₄H₄ (g-i) on Pt(111) (a, d, g), Pt₃Sn (b, e, h) and Pt₂Sn (c, f, i). Reaction energies are shown for the transformation of adsorbed acetylene to C-CH₂ and C₄H₄. (see color insert)

Table 2. DFT Calculation Results for the Carbon-Carbon Bond Stretching Vibrational Mode, ν_{CC}, of Acetylene and Vinylidene Species Adsorbed on Different surfaces, cm⁻¹

<table>
<thead>
<tr>
<th>Surface species / Surface</th>
<th>Pt(111)</th>
<th>Pt₃Sn/Pt(111)</th>
<th>Pt₂Sn/Pt(111)</th>
</tr>
</thead>
<tbody>
<tr>
<td>di-σ/π CH-CH</td>
<td>1351</td>
<td>1326</td>
<td>N/A</td>
</tr>
<tr>
<td>di-σ CH-CH</td>
<td>1426</td>
<td>1460</td>
<td>1476</td>
</tr>
<tr>
<td>π CH-CH</td>
<td>1830</td>
<td>1825</td>
<td>1817</td>
</tr>
<tr>
<td>C-CH₂</td>
<td>1460</td>
<td>1445</td>
<td>1535</td>
</tr>
</tbody>
</table>
In acetylene TPD spectra for the alloys, C4 hydrocarbons and benzene are detected, indicating that in addition to isomerization and dehydrogenation, acetylene can produce dimers and trimers. The amount of produced C4 and C6 hydrocarbons is larger over the Pt2Sn alloy with a higher Sn concentration. In contrast, no coupling products are observed in the absence of Sn on Pt(111) where adsorbed acetylene on annealing decomposes to carbon and hydrogen in line with our previously reported study (101). In another study in the presence of gas-phase hydrogen, the activity of the Pt2Sn alloy for dimerization and trimerization was found to be 4-5 times higher than that over Pt(111) (102). The origin of this reactivity difference was evaluated by comparing the energetics of acetylene coupling to produce C4H4 surface-bound dimer species on Pt(111) and the two alloys (Figures 5g-i). The calculation results summarized in Figure 5 suggest that while the coupling reaction is estimated to be thermoneutral at -1 kJ/mol on Pt(111), it is predicted to become exothermic and, therefore, energetically favorable in the presence of Sn. Increasing the Sn concentration makes the reaction more favorable from -62 kJ/mol for Pt2Sn to -87 kJ/mol for Pt2Sn. The Sn content, however, has to be at an optimal level for activity enhancement since the reaction proceeds only on Pt sites, and Sn atoms only modify the energetics of Pt sites and their geometric arrangements.

In summary, this study identifies the adsorption modes of acetylene on Pt-Sn surface alloys. The results demonstrate that the presence of Sn changes preferential hydrocarbon adsorption sites, decreases stability of adsorbed species and favors associative reactions, thus, enabling formation of C4 hydrocarbons and benzene. The developed experimental-theoretical approach can be applied to studying the adsorption and reactivity of other hydrocarbons, e.g., biomass-derived hydrocarbons, on promising Pt and Pt bimetallic catalytic surfaces. The same methodology can be extended to other bimetallic materials.

Acknowledgments

Infrared spectra under Fischer-Tropsch reaction conditions were collected by Emiel de Smit under supervision of Prof. Bert Weckhuysen, Utrecht University, Netherlands. The research on Fischer-Tropsch catalysis in Prof. Bert Weckhuysen’s group was partially funded by the Dutch government grant NRSC-C 2009-2013. The HREELS spectra for acetylene adsorption on Pt-Sn alloys were collected by Haibo Zhao and interpreted by Xiaofang Yang under supervision of Prof. Bruce Koel, Princeton University. The work on Pt-Sn alloys in Prof. Bruce Koel’s group was partially supported by the National Science Foundation under grant CHE-1129417. DFT calculations were performed by Jie Gao under supervision of Prof. Simon Podkolzin, Stevens Institute of Technology. Prof. Simon Podkolzin’s research was partially supported by the National Science Foundation under grant OISE-1157600. Additional funding for Prof. Simon Podkolzin’s research was provided by Stevens Institute of Technology.
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