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In Situ Methods for Identifying Reactive Surface Intermediates during Hydrogenolysis Reactions: C–O Bond Cleavage on Nanoparticles of Nickel and Nickel Phosphides

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Supporting Information

ABSTRACT: Identifying individual reactive intermediates within the "zoo" of organometallic species that form on catalytic surfaces during reactions is a long-standing challenge in heterogeneous catalysis. Here, we identify distinct reactive intermediates, all of which exist at low coverages, that lead to distinguishable reaction pathways during the hydrogenolysis of 2-methyltetrahydrofuran (MTHF) on Ni, Ni₁₂P₅, and Ni₂P catalysts by combining advanced spectroscopic methods with quantum chemical calculations. Each of these reactive complexes cleaves specific C-O bonds, gives rise to unique products, and exhibits different apparent activation barriers for ring opening. The spectral features of the reactive



intermediates are extracted by collecting in situ infrared spectra while sinusoidally modulating the H₂ pressure during MTHF hydrogenolysis and applying phase-sensitive detection (PSD), which suppresses the features of inactive surface species. The combined spectra of all reactive species are deconvoluted using singular-value decomposition techniques that yield spectra and changes in surface coverage for each set of kinetically differentiable species. These deconvoluted spectra are consistent with predicted spectral features for the reactive surface intermediates implicated by detailed kinetic measurements and DFT calculations. Notably, these methods give direct evidence for several anticipated differences in the coordination and composition of reactive MTHF-derived species. The compositions of the most abundant reactive intermediate (MARI) on Ni, Ni₁₂P₅, and Ni₂P nanoparticles during the C–O bond rupture of MTHF are identical; however, MARI changes orientation from Ni₃(μ^3 - $C_{5}H_{10}O$) to $Ni_{3}(\eta^{5}-C_{5}H_{10}O)$ (i.e., lies more parallel with the catalyst surface) with increasing phosphorus content. The shift in binding configuration with phosphorus content suggests that the decrease in steric hindrance to rupture the ³C-O bond is the fundamental cause of increased selectivity toward ³C-O bond rupture. Previous kinetic measurements and DFT calculations indicate that C-O bond rupture occurs on Ni ensembles on Ni, Ni12P5, and Ni2P catalysts; however, the addition of more electronegative phosphorus atoms that withdraw a small charge from Ni ensembles results in differences in the binding configuration, activation enthalpy, and selectivity. The results from this in situ spectroscopic methodology support previous proposals that the manipulation of the electronic structure of metal ensembles by the introduction of phosphorus provides strategies for designing catalysts for the selective cleavage of hindered C-X bonds and demonstrate the utility of this approach in identifying individual reactive species within the zoo.

1. INTRODUCTION

Identifying reactive intermediates over heterogeneous catalysts has challenged the field for decades because the "surface organometallic zoo" of species (i.e., a collection of organic intermediates bound to metal surfaces that may or may not be involved in a given reaction) exists during catalysis on solid surfaces.¹⁻³ The heterogeneous catalysis community has employed a number of techniques and methods to deconvolute the zoo to determine the identity and structure of intermediates that form during reactions. Bent³ discusses methods and applications of surface vacuum techniques to mimic surface

intermediates that form on heterogeneous catalysts but acknowledges the disconnect between the model systems (i.e., single crystals in vacuum) and nanoparticles and porous materials at atmospheric or higher pressure. Burwell⁴ reviews other spectroscopic and kinetic strategies for deconvoluting the zoo during reactions of hydrocarbons over metal surfaces (e.g., hydrogenolysis and hydrogenation) through isotopic labeling, vibrational spectroscopy, nuclear magnetic resonance spectros-

Received: June 11, 2019 Published: September 26, 2019 Scheme 1. Previously Proposed Mechanism for the Competitive C–O Bond Rupture Pathways (Unhindered ${}^{2}C$ –O and Hindered ${}^{3}C$ –O) That Form Distinguishable Product Pools from the Quasi-equilibrated Reactant Pool of MTHF (C₅H₁₀O) and MF (C₅H₆O) over Ni, Ni₁₂P₅, and Ni₂P Surfaces^{*a*}



^aElementary steps include adsorption (Ads), dehydrogenation (C-H_{act}), C-O bond rupture (C-O_{act}), and subsequent hydrogenation and desorption (not depicted). Images illustrate the composition of intermediates and bonds to the surface but are not intended to suggest the specific orientation of intermediates to the surface. Calculated free energies for Ni, N₁₂P₅, and Ni₂P surfaces are reported in the Supporting Information (Figures S1–S3). The compositions of these complexes are described below each structure. \rightleftharpoons enclosed in a circle indicates quasi-equilibrated steps, \rightarrow with a carrot symbol in the center of the line indicates kinetically relevant steps, \rightleftharpoons indicates reversible steps, and \rightarrow indicates a dative bond to the surface.

copy, and X-ray absorbance spectroscopy. However, distinguishing the relevant reactive intermediates even in simple reactions has proven challenging. For example, studies of ethylene hydrogenation, a prototypical hydrocarbon conversion, suggest that ethyl, ⁵ di- σ , and π -bonded ethylene^{5,6} and ethylidyne^{6,7} coexist on catalyst surfaces, but combinations of kinetic and spectroscopic measurements on Pd–Al₂O₃ suggest that ethylidyne is a spectating species. As such, ethylidyne features appear in all forms of spectroscopic measurements, in situ, operando, or otherwise; however, ethylidyne is not directly involved in the elementary steps responsible for hydrogenation.⁷ Similar circumstances in other catalytic reactions frequently lead to discrepancies among spectroscopic, kinetic, and computational investigations of catalysis.

These discrepancies present increasingly difficult challenges as the reactants become larger and more complex and when the number of potential reaction pathways increases. These barriers are particularly significant for reactions of larger hydrocarbons or oxygenates which possess large numbers of overlapping features of similar groups (e.g., C-H or C-C stretches) that reflect contributions of all distinct reactive and spectating species present; the similarities among these features often impede attempts to detect and distinguish reactive complexes among the zoos that form during C-C bond coupling in alkanols and alkanals⁸⁻¹¹ or the hydrogenolysis¹²⁻¹ ⁴ of petroleum or lignin derivatives. In the case of hydrogenolysis reactions of alkanes over transition metals,^{15–19} rapid hydrogentransfer steps drastically increase the number of species present on catalyst surfaces (i.e., deeply dehydrogenated and nearly saturated analogues of each skeletal isomer coexist), where many of the detected species may not react on the time scale of the catalytic cycle. Methods for in situ spectroscopy that overcome these challenges, in combination with kinetic measurements and computational catalysis tools, would provide important information on the identity, composition, and orientation of kinetically relevant reactive intermediates, provide a deeper understanding of surface reactions and their mechanisms, and help to reveal critical catalytic properties of materials that govern rates and selectivities.

The hydrogenolysis of C-O bonds in 2-methyltetrahydrofuran (MTHF) over SiO₂-supported Ni, Ni₁₂P₅, and Ni_2P catalysts described previously²⁰ presents all of the challenges (vide supra) for establishing the taxonomy of the surface organometallic zoo. Kinetic studies demonstrate that Ni, Ni₁₂P₅, and Ni₂P catalyze two parallel pathways: rupture of the hindered and unhindered C–O bonds (tertiary $({}^{3}C-O)$ and secondary $(^{2}C-O)$, respectively, where ^{*x*}C indicates that C is bound to x non-H atoms) to form primary or secondary alcohols and aldehydes (Scheme 1).^{20,21} The addition of phosphorus to Ni increases the selectivity toward cleaving the ${}^{3}C-O$ bond in MTHF by decreasing the relative activation enthalpy barrier (ΔH^{\ddagger}) of ³C–O bond rupture to that of ²C–O bond rupture;²⁰ however, without direct spectroscopic evidence, it is not clear if the addition of phosphorus influences the binding configurations of intermediates and thus ΔH^{\ddagger} because rate measurements occur on heterogeneous supported nanoparticles while DFT calculations use single crystal surfaces. Scheme 1 illustrates the numerous reactive intermediates that may exist on the catalyst surface, including adsorbed MTHF and sequentially dehydrogenated intermediates that lead to kinetically relevant C-O bond rupture, as calculated by DFT (Figures S1-S3 for Ni, Ni₁₂P₅, and Ni₂P, respectively) and detailed in previous work.²⁰ Each of these reactive intermediates has a unique stability (given by the binding free energy G) and energy barrier to form, which results in differences in surface coverage for each intermediate and rate constants for each elementary step. Additionally, the rapid, quasi-equilibrated H-transfer steps result in a pool of intermediates with compositions between MTHF and 2-methylfuran (MF) that do not lead directly to C-O bond rupture. These species (and species adsorbed on the SiO₂ support) are spectators, which are defined as complexes that can contribute to in situ steady-state spectra but that are not directly involved in catalysis and therefore cannot be responsible for the differences in the measured rates and selectivities for C-O bond rupture over Ni, Ni12P5, and Ni2P. All of the species present during the reaction (i.e., reactants, products, spectators, and reactive intermediates) contain similar functional groups and thus vibrational modes (e.g., ν (CH₃), ν (CH₂), and ν (CH)),

which makes the composition and structure of individual species difficult to distinguish if spectra reflect multiple species. While the hydrogenolysis of MTHF is a relevant model reaction for the hydrodeoxygenation of biomass-derived species in its own right, this specific combination of chemistry and catalysts provides a fitting testbed for in situ experimental strategies to characterize surface organometallic zoos. Vibrational spectroscopy, such as infrared spectroscopy, coupled with a methodology that removes spectator species and isolates individual reactive intermediates is required to discern differences in the coordination of reactive intermediates across catalyst surfaces that may lead to measured differences in selectivity.

Simple spectroscopic techniques and data processing methods allow one to isolate and identify reactive intermediates that form in situ under relevant catalytic conditions. Modulation excitation spectroscopy (MES) coupled with phase-sensitive detection (PSD), introduced by Baurecht et al.²² and highlighted by Urakwa et al.,²³ selectively detects species that respond to periodic stimulations, such as changes in reactant concentrations. PSD converts the time-resolved spectra obtained during MES to phase-resolved spectra that contain the combined spectral features of all multiple reactive intermediates that respond to the periodic stimulation. Differences among the free energies of activation for elementary steps for the interconversion of reactive intermediates (e.g., shown in Scheme 1) can be used to discern smaller pools of intermediates, which are distinguished by the phase shift between the stimulus and their response. Individual sets of reactive intermediates, therefore, can be identified by both their spectral and kinetic characteristics that are extracted from phase-resolved spectra; however, we are not aware of previous reports that use this strategy to investigate reactive surface intermediates on supported catalysts. A quantitative interpretation of phaseresolved spectra requires additional methods that rely on singular value decomposition approaches to isolate individual species (i.e., the spectra and corresponding concentrations) from the phase-resolved spectra, particularly when spectra contain overlapping features from multiple intermediates, a known challenge in spectroscopy.²⁴ Together, these methods provide a framework to deconvolute the surface organometallic zoo by inferring the composition and coordination of reactive intermediates during complex reactions under relevant operating conditions.

Here, we demonstrate that the combination of these spectroscopic methods and density functional theory (DFT) provides compelling evidence for the composition and binding orientation of individual reactive intermediates for C-O bond hydrogenolysis of MTHF over Ni, Ni₁₂P₅, and Ni₂P surfaces. Spectra isolated from MES experiments that utilize sinusoidal hydrogen concentration ([H₂]) transients, PSD, and singularvalue decomposition methods agree closely with predicted vibrational spectra for DFT-optimized structures of reactive surface species. Although studies have used MES and PSD to analyze intermediates over heterogeneous catalysts,²⁵⁻²⁹ the addition of singular value decomposition methods to deconvolute phase-resolved spectra is necessary to distinguish differences in reactive intermediates with similar vibrational modes and structures. These methods reveal distinct vibrational spectra for reactive species implicated in ³C–O and ²C–O bond rupture that exist at low surface coverages and which are not distinguishable from steady-state measurements. Both the vibrational features and the phase shift of these species are consistent with expectations from DFT calculations. Spectra of the MARI, which experimental and theoretical kinetics indicate is adsorbed MTHF over Ni, Ni₁₂P₅, and Ni₂P surfaces,²⁰ reveal changes in binding orientation from Ni(μ^3 -C₅H₁₀O) to Ni₃(η^5 -C₅H₁₀O) with increasing atomic ratio of P/Ni. The change in binding configuration with the P/Ni ratio suggests that the electron-deficient Ni^{δ+} draws the furan ring closer to the surface and decreases the steric hindrance of the methyl group to the ³C-O bond. Measured differences in selectivities toward ³C-O bond rupture and ΔH^{\ddagger} over Ni, Ni₁₂P₅, and Ni₂P²⁰ increase with increasing proximity of the ³C-O bond in the MARI to the surfaces. This study highlights the benefits of combining MES, PSD, and singular value decomposition methods to analyze individual reactive intermediates and provides a guide to design catalysts that can selectively cleave hindered C-O bonds.

2. EXPERIMENTAL AND THEORETICAL METHODS

2.1. Catalyst Synthesis and Characterization. Nickel phosphide catalysts (Ni_xP_y) supported on high-surface-area silica (SiO_2) were prepared using strong electrostatic adsorption (SEA),³⁰ which involved adding the nickel precursor $(Ni(NO_3)_2 \cdot (H_2O)_6)$ to DI water, followed by adding an NH₄OH aqueous solution to the precursor solution to form an aqueous [Ni(NH₃)₆]²⁺ complex.³⁰ High surface area SiO₂ (SiO₂, Sigma-Aldrich, Davisil grade 646, 35-60 mesh, pore volume 1.15 cm³ g⁻¹) was added to the aqueous solution and stirred. Vacuum filtration separated the solids from the liquid, after which the solids were rinsed with 2 L of DI water and then dried in stagnant air for 48 h at 333 K. Subsequently, the dried solids were heated at 0.05 K s^{-1} to 773 K and held for 5 h in flowing dry air (8.3 cm³ s⁻¹, Airgas, Ultra Zero). Samples were then cooled in He (Airgas, 99.99%) to 323 K and then heated at 0.05 K s^{-1} to 963 K and held for 2 h in flowing 10% H₂/He (8.3 cm³ s⁻¹) Airgas, 99.999%) with the intent to reduce the Ni to its metallic state. Finally, samples were cooled to ambient temperature in He and then passivated in a flowing mixture of 20% dry air and 80% He $(8.3 \text{ cm}^3 \text{ s}^{-1})$ for 3 h. A sample of Ni-SiO₂ was set aside (1.9 wt %) while the remaining Ni-SiO₂ was impregnated with 0.14 M phosphorous acid solution (Sigma-Aldrich, H₃PO₃ solution \geq 50%) in 0.1 cm³ aliquots to achieve molar Ni/P ratios of 2:1 and 1:1 for Ni₁₂P₅ and Ni₂P catalysts, respectively. These samples were dried and then treated with the same oxidizing, reducing, and passivating heat treatments as those used to synthesize Ni-SiO₂.

Nanoparticle diameters were measured using transmission electron microscopy (TEM). The diameters of more than 300 particles were counted from the TEM images obtained to calculate surface-areanormalized average nanoparticle diameters $\langle d_{\text{TEM}} \rangle$ for each sample,

$$\langle d_{\rm TEM} \rangle = \frac{\sum_i n_i d_i^3}{\sum_i n_i d_i^2} \tag{1}$$

where n_i is the number of clusters with diameter d_i . The crystallographic structures of Ni_xP_y-SiO₂ materials were determined using powder X-ray diffraction (XRD) as shown previously²⁰ and agree closely with published results for Ni₁₂P₅ and Ni₂P powders.³¹ Sample images, cluster size distributions, and diffraction patterns were described previously.²⁰

Temperature programmed reduction (TPR) was performed on dried Ni and Ni_xP_y samples in order to confirm that the Ni and Ni_xP_y materials were reduced by the thermal treatments in H₂/He mixtures. The samples were heated to 773 K and held for 6 h in flowing dry air with the intent to fully oxidize the samples. Samples were then cooled to 303 K, after which the sample was heated to 1073 at 0.05 K s⁻¹ while the H₂ consumption and H₂O production were monitored as a function of sample temperature using a quadrupole mass spectrometer. Previous work²⁰ shows reduction profiles that indicate the formation of a nickel phosphide phase as opposed to separate nickel and phosphide phases because the Ni_xP_y reduction profiles are not a linear combination of the Ni(NO₃)₂ and H₃PO₃ reduction profiles but the presence of Ni decreases the reduction temperature of the phosphite group.

2.2. In Situ Infrared Spectroscopy. Reactive intermediates formed during the hydrogenolysis of 2-methyltetrahydrofuran

(MTHF, Sigma-Aldrich, \geq 99.5%) over self-supporting pellets of Ni, Ni₁₂P₅, and Ni₂P catalysts (35 ± 5 mg) were observed using in situ transmission Fourier transform infrared (FTIR) spectroscopy using a custom-made transmission cell, previously described,⁸ with a spectrometer (Bruker, TENSOR 37) equipped with a liquid-N₂-cooled HgCdTe detector. MTHF was introduced using a syringe pump (KD Scientific, Legato 110) in a crossflow configuration with the primary gas flow (H₂ and He) controlled by mass flow controllers (Alicat). Transfer lines were heated to 323 K to rapidly vaporize the liquid reactant. Prior to acquiring spectra, the catalyst was pretreated in situ to 673 K and held for 1 h in flowing H₂ at ambient pressure. All spectra acquisition was performed using Bruker Corporation's OPUS Spectroscopy Software 7.0.129.

2.2.1. Steady State in Situ Spectroscopic Measurements. The background IR spectra for steady-state measurements were collected under a flow of 15 kPa He and 86 kPa H₂ at the respective temperature of the steady-state measurement (473–573 K) following in situ pretreatment. Steady-state measurements were obtained during flows of MTHF (5 kPa), H₂ (81 kPa), and He (15 kPa). Following each steady-state measurement, the catalyst surface was reactivated by heating to 673 K in flowing H₂ and soaking at 673 K for 0.5 h. Spectra at subsequent temperatures were recorded after cooling to the desired temperature and obtaining a new background IR spectrum. Spectra were collected at a resolution of 1 cm⁻¹ and averaged over 128 scans for both the initial background and measured steady-state conditions.

Reference spectra of gas-phase molecules in flowing He (MTHF; MF, Aldrich Chemistry, 99%; 2-propanol, Macron Fine Chemicals, ACS grade; and tetrahydrofuran, Macron Fine Chemicals, ACS grade) were recorded with a background spectrum of 101 kPa He in the absence of any catalyst pellet. Spectra were collected at a resolution of 1 cm⁻¹ and averaged over 128 scans for both the initial background and measured steady-state conditions detailed in Figure S7.

2.2.2. Modulation Excitation Spectroscopy. The background IR spectra for steady-state measurements were collected under a flow of 101 kPa He at 543 K following the in situ pretreatment in H₂ (673 K, 0.5 h). Modulation experiments were obtained under a constant flow rate of MTHF (10 μ L min⁻¹ MTHF) and reactant gases (0.3 cm³ s⁻¹, He and H₂). Gas flow rates were controlled using LabVIEW to change the flow rates of H₂ and He in sinusoidal functions 180° out of phase with each other at periods ranging from 4 to 1200 s such that the H₂ pressure ranged from 2.5 to 84 kPa. Spectra were collected at a resolution of 1 cm⁻¹ for both the initial background and modulation conditions.

Figure 1a displays an example time-resolved spectra during MES experiments that modulate $[H_2]$ from 2.5 to 84 kPa over a 1200 s period (i.e., $[H_2](\psi = 0^\circ) = 43.25$ kPa, $[H_2](\psi = 90^\circ) = 84$ kPa, $[H_2](\psi = 180^\circ) = 43.25$ kPa, and $[H_2](\psi = 270^\circ) = 2.5$ kPa). The MTHF pressure ([MTHF]) is set to 12 kPa to establish MTHF-derived intermediates as the MARI based on previous rate measurements.²⁰ Time-resolved spectra collected over the duration of the experiment (100–2000 spectra over 0.1–2 h) were resampled and averaged to a single period prior to additional spectral processing using MATLAB (Figure 1b).

2.3. Spectral Processing. Phase sensitive detection²² removes spectral features that do not oscillate at the stimulated frequency of $[H_2]$, shown in Figure 1b, which is selected to be comparable to steady-state turnover rates measured under similar conditions. The remaining features reflect changes in the coverage, coordination, and composition of surface species that are induced by the changes in $[H_2]$. These transformations are obtained by processing spectra acquired in the time domain using the follow equation:

$$A_n(\varphi_n^{\text{PSD}}) = \frac{2}{T} \int_0^T A(t) \sin(n\omega t + \varphi_n^{\text{PSD}}) \,\mathrm{d}t \tag{2}$$

Here, A(t) and $A_n(\varphi_n^{\text{PSD}})$ are the time- and phase-domain responses of the measured species (i.e., the time- and phase-resolved spectral intensities), respectively, T is the length of the period for the $[\text{H}_2]$ modulation (4–1200 s), ω is the demodulation index (set n equal to 1, i.e., the fundamental frequency, in all instances here), and φ_n^{PSD} is the user-defined phase demodulation angle. PSD was applied to the



Figure 1. In situ infrared spectra (a) obtained as a function of time during the reaction of MTHF over 10 nm $Ni_{12}P_5$ with H_2 pressure modulated over a period of 1200 s (12 kPa MTHF, 2.5–84 kPa H_2 , 543 K). (b) Resampled phase-resolved spectra for a single period calculated from the transient spectra in (a).

resampled time-resolved spectra using the resample function in MATLAB, which interpolates the data and averages to a single period at a uniform sampling rate. The absorbance in the phase-resolved spectra indicates the deviation from average values following the PSD rather than the absolute intensity of a recorded spectrum, which is a function of the coverage of species, not the deviation from the average coverage. MATLAB code used to resample and perform phase demodulation is included in the Supporting Information

The multivariate curve resolution-alternating least-squares (MCR-ALS) algorithm recovers the changes in absorbance with phase angle (or time) and the isolated spectrum of each kinetically distinguishable pool of species from the three-dimensional matrix of data (i.e., the phase-resolved spectra),^{24,32–35} such as the spectra in Figure 1b. In this application, a singular value decomposition (SVD) algorithm was used following principal component analysis to assess the appropriate number of components (e.g., independent species) that fully describe the phase-resolved spectra: two species for 4 nm Ni and three species for 10 nm Ni12P5 and 12 nm Ni2P. Phase-resolved spectra were truncated prior to the application of MCR-ALS to include only the region of overlapping C-H stretching modes (2700-3100 cm⁻¹). Initial estimates were generated using the evolving factor analysis method provided in the MATLAB graphical user interface.³³ Spectra were constrained to yield only positive values because the background spectrum of the pretreated catalyst did not contain any vibrational features within this range $(2700-3100 \text{ cm}^{-1})$ that could be lost as a result of the reaction conditions. The MCR-ALS algorithm iteratively optimized the initial estimates for each spectrum and coverage until the convergence criterion (10^{-6}) was achieved. Spectra recorded over the same catalyst with different period lengths of [H₂] modulation reveal the same set of isolated spectra; thus, only one data set (i.e., data from one representative period length) is shown in Section 3 and the Supporting Information for each catalyst.

The subsequent analysis of the isolated spectra and coverage changes obtained from MCR-ALS (e.g., baseline correction and data smoothing) was performed using OriginPro. Spectra isolated from the phase-resolved spectra using MCR-ALS were deconvoluted to the individual peaks that represent specific vibrational modes. Individual Lorentzian peaks were constrained to positive values with a common baseline equal to 0 and fit to a convergence criterion of 10^{-9} . The number of individual peaks was determined by the number of distinct C–H stretching modes within MTHF (e.g., $\nu_a(CH_3)$, $\nu_a(CH_2)$, $\nu_s(CH_3)$, $\nu_s(CH_2)$, and $\nu(CH)$). Additional peaks were added on the basis of the analysis of the gas-phase MTHF spectrum, which required more than the individual peaks that reflect the five fundamental C–H vibrations (i.e., $\nu_a(CH_3)$, $\nu_a(CH_2)$, $\nu_s(CH_3)$, $\nu_s(CH_2)$, and $\nu(CH)$ modes) to accurately describe the spectral features as detailed in the Supporting Information (Figure S4). Peak assignments for each isolated spectrum were based on comparisons with measured reference gas-phase MTHF, MF, 2-propanol, and tetrahydrofuran, previously reported spectra,^{36–39} and DFT-predicted vibrations.

2.4. Computational Methods. Periodic plane-wave density functional theory (DFT) calculations were performed using the Vienna ab initio simulation package (VASP).⁴⁰⁻⁴³ Plane waves were constructed using projector augmented-wave (PAW) potentials with an energy cutoff of 396 eV.^{44,45} The Perdew–Burke–Ernzerhof (PBE) form of the generalized gradient approximation (GGA) was used to determine exchange and correlation energies for bulk and surface formation calculations,⁴⁶ and the revised PBE functional (RPBE)^{47,48} was used for adsorption, reaction, and activation energy calculations as described in more detail elsewhere.²⁰ Additional calculations were performed using dispersion-corrected functionals such as optB88vdW, ^{49,50} optB86b-vdW, ^{51,52} RPBE-D3BJ, ^{53,54} and vdW-DF2.^{49,55} The close-packed (111) surface was used for Ni, and the (001) surface was used for both Ni12P5 and N2P because it has the lowest surface formation energy, although vibrational features of species adsorbed on other facets may contribute to the experimental FTIR spectra. Calculations were not run spin-polarized except for the Ni catalyst because Ni₂P and Ni₁₂P₅ catalysts were previously shown not to have spin-polarized electronic structures.²⁰ Frequency calculations were performed on gas-phase molecules and all optimized adsorbed species using the harmonic oscillator approximation. The vibrational frequencies were calculated from the Hessian matrix, which was constructed using the finite difference method with two displacements in each Cartesian coordinate. All catalyst atoms were constrained during these frequency calculations, and dipole corrections were applied to slab models. Charge analysis was carried out using QUAMBO.⁵⁶ Further details of the computational methods were presented in our previous work.²

3. RESULTS AND DISCUSSION

3.1. Ambiguous Steady-State Spectra over Ni, Ni₁₂P₅, and Ni₂P Catalysts. Figure 2a shows in situ infrared (IR) spectra under reaction conditions where MTHF is the MARI, based on previous experiments and calculations detailed in previous works²⁰ (12 kPa MTHF, 43.3 kPa H₂, and 543 K). The in situ spectra are nearly identical for Ni, Ni₂P, Ni₁₂P₅, and pure SiO₂; however, large differences in measured turnover rates, selectivities, and ΔH^{\ddagger} for MTHF conversion on these materials suggest that the underlying potential energy surfaces and thus the relative stabilities and structures of reactive intermediates are distinct on these three catalysts. As such, Figure 2a may reflect contributions from a single most abundant (but not necessarily reactive) surface intermediate or a combination of spectating and reactive intermediates. The slight differences in the intensities of various C-H vibrational modes (2850-3000 cm⁻¹) corresponding to methyl, methylene, and methyne stretches (Figure 2b) indicate either a difference in the coordination of the intermediates or a difference in the coverage of the various intermediates present on the catalyst surface. The spectra of MTHF over Ni, Ni12P5, and Ni2P show a lower relative intensity (i.e., negative absorbance difference) of features between 2972 and 2850 cm⁻¹ in comparison to SiO_{24} which is consistent with either the partial screening of certain C-H stretching modes parallel to the surface by dipole reflections within the Ni, Ni12P5, and Ni2P nanoparticles or



Figure 2. (a) In situ infrared spectra obtained during steady-state reactions of MTHF and H_2 over SiO₂ (green) and SiO₂-supported catalysts including 4 nm Ni (black), 10 nm Ni₁₂P₅ (red), and 12 nm Ni₂P (blue) (12 kPa MTHF, 43 kPa H₂, 46 kPa He, and 543 K). Spectra are normalized to give an absorbance of unity at ~2975 cm⁻¹. (b) Difference between the normalized spectra of 4 nm Ni (black), 10 nm Ni₁₂P₅ (red), and 12 nm Ni₂P (blue) with SiO₂. Ratio of maximum intensities at ~2975 cm⁻¹ for spectra over Ni, Ni₁₂P₅, and Ni₂P relative to that for SiO₂ are shown in Table S1.

changes in the compositions of the intermediates (i.e., loss of C-H bonds from dehydrogenation steps over the Ni, $Ni_{12}P_{5}$, and Ni₂P surfaces). Table S1 lists the raw intensity of recorded spectra normalized by mass, which indicates the ratio of absorbance over Ni, Ni₁₂P₅, and Ni₂P catalysts with SiO₂ ranging between 1.25 and 2. The negative absorbance difference (Figure 2b) relative to SiO₂ suggests that measured features over Ni, Ni₁₂P₅, and Ni₂P catalysts result from MTHF-derived species bound to Ni, Ni₁₂P₅, and Ni₂P surfaces or species desorbed from Ni, Ni₁₂P₅, or Ni₂P and bound to SiO₂. The differences among Ni, Ni₁₂P₅, and Ni₂P demonstrate that these spectra contain contributions from species bound to the surfaces of Ni, Ni₁₂P₅, or Ni₂P because the gas-phase compositions (i.e., MTHF, MF, and other partially dehydrogenated species) of these experiments are identical because H-transfer is quasi-equilibrated on all three catalysts.²⁰ Furthermore, the spectra over Ni, Ni₁₂P₅, and Ni₂P would be identical if the spectra reflected species bound only to the SiO₂. However, the slight differences in the steady-state spectra over Ni, Ni₁₂P₅, and Ni₂P do not explain the underlying relationship between surface properties (i.e., coordination of intermediates) and the previously reported 50-fold increase in selectivity toward ³C-O bond rupture over Ni₂P relative to Ni²⁰ because the composition, coverages, and reactivity of the intermediates that contribute to these spectra are uncertain.

The free energy of the reactive species that cleave ${}^{3}C-O$ and ${}^{2}C-O$ bonds in MTHF on Ni, Ni₁₂P₅, and Ni₂P differs, 20 which

suggests that the individual contributions of the species on these surfaces may be deconvoluted by comparing steady-state spectra obtained at different temperatures. However, the dominant coordination modes of species with a given composition should also vary with temperature, as noted in previous works that observe the rotation of C₆-hydrocarbons from hexylidyne in all trans to gauche-trans-trans configurations over Pt^{38,57} and Ru⁵⁸ with increased temperature, which can complicate this approach. Spectra obtained at steady state as a function of temperature (400–600 K, Figure S6) over SiO₂-supported 4 nm Ni, 10 nm Ni₁₂P₅, and 12 nm Ni₂P clusters reveal significant changes with increasing temperature in spectral features attributed to the C-H stretching. Nevertheless, it is difficult to differentiate which changes in the resultant spectra are caused by changes in the coverage and coordination of the reactive intermediates and those that reflect features of unreactive surface intermediates. Increasing temperature results in lower coverages and higher relative ratios of dehydrogenated species (e.g., MF) to saturated species, which are expected trends.

The different activation enthalpies (ΔH^{\ddagger}) for ²C–O bond rupture and ³C-O bond rupture in MTHF cause the hydrogenolysis selectivities to depend strongly on temperature, and specifically, selectivities toward ³C-O bond rupture (i.e., primary alcohols and aldehydes) increase with increasing temperature over Ni surfaces but decrease with increasing temperature over Ni12P5 and Ni2P surfaces as discussed previously.²⁰ As a result, differences in temperature likely change the ratio of coverage for the reactive intermediates for ${}^{3}C-O$ relative to that for ${}^{2}C-O$ bond rupture. Once again, the features for the MARI and for the low-coverage reactive intermediates cannot be distinguished from each other or from spectator species. Consequently, analyses of steady-state spectra acquired at distinct temperatures or across a series of materials cannot be used reliably to determine changes in the coordination or coverage of reactive intermediates. Other approaches are necessary to suppress contributions from all spectator species and to isolate spectral features corresponding to reactive intermediates that turnover at time scales relevant to C–O bond rupture, as determined by steady-state turnover rate measurements.²⁰ The following section employs techniques to observe the composition, orientation, and relative coverages of reactive intermediates bound to Ni, Ni₁₂P₅, and Ni₂P during C-O bond rupture reactions of MTHF by probing time scales similar to the measured turnover rates.

3.2. Identifying Reactive Intermediates by Modulating the H₂ Pressure over Ni₁₂P₅. H₂ modulation combined with PSD identifies spectral features of intermediates whose concentrations respond to H₂ and can distinguish species whose formation and consumption reflect different sets of rate constants because these lead to distinct phase shifts between the stimulus and the response (Figure 1b). Here, several distinct spectra are isolated from phase-resolved spectra over Ni, Ni₁₂P₅, and Ni₂P (Figure 1b for Ni₁₂P₅; phase-resolved spectra not shown for Ni and Ni₂P). More than one species must contribute to the phase-resolved spectra shown in Figure 1b because the spectral features do not all oscillate in phase with one another. Normalized spectra in Figure S9 also illustrate the contribution of multiple species within the phase-resolved spectra because the spectral features are all slightly different when normalized by the absorbance at 2976 cm⁻¹. The presence of more than one species within the phase-resolved spectra indicates the need for further deconvolution using SVD. Together, PSD and SVD methods remove contributions of species that do not respond to

changes in $[H_2]$ (e.g., spectator species) and isolate each species by their different transient responses to the changes in $[H_2]$.

Figure 3 displays the three isolated spectra corresponding to reactive intermediates leading to the two transition states ($^{2}C-$



Figure 3. Spectra of independent reactive intermediates (solid black lines) ($C_5H_{10}O^*$, a; $C_5H_9O^*_{2C-O}$, b; and $C_5H_9O^*_{3C-O}$, c) extracted from phase-domain spectra over Ni₁₂P₅–SiO₂, 2.5–84 kPa H₂ modulated at a period of 1200 s, 12 kPa MTHF, and 543 K using MCR-ALS. Spectral fit to Lorentzian distributions that indicate individual C–H stretches ($\nu_a(CH_3)$, green; $\nu_s(CH_3)$, light green; $\nu_a(CH_2)$, blue; $\nu_{ap}(CH_2)$, teal; $\nu_s(CH_2)$, light blue; $\nu(CH)$ of ³C, red; and $\nu(CH)$ of ²C, pink) which form the cumulative spectra (transparent line). Phase shifts (ψ) related to the changes in coverage are relative to the changing [H₂] ($\psi_0 = 0^\circ$). DFT-predicted intermediates optimized using the RPBE functional (inset) that are consistent with assigned species based on spectral features (O, red; C, black; H, white; P, orange; and Ni, green). Measured and predicted peak centers listed in Table 1.

 O^{\ddagger} and ${}^{3}C-O^{\ddagger}$) obtained from experiments with the modulation of [H₂] on Ni₁₂P₅ (2.5-84 kPa H₂, 12 kPa MTHF, 1200 s period, 543 K). The application of multivariate curve resolution-alternating least squares (MCR-ALS) isolates these three spectra and determines their concentration (i.e., coverage) profiles from phase-resolved spectra, each of which is independent from other two spectra and coverages. Linear combinations of the three isolated spectra shown in Figure 3 fully reproduce the phase-resolved spectra for modulations in $[H_2]$ at all measured period lengths (4–1200 s). Comparison with MES experiments over SiO₂ (Figure S15) confirms that these isolated species are bound to the Ni12P5 surface, not SiO₂. The remaining reactive intermediates that lead to C–O bond rupture not depicted by these spectra either have insignificant coverage relative to these three species or their coverage as a function of changing $[H_2]$ is indistinguishable from these three intermediates at the measured period lengths (4-1200 s). We describe the precise intermediates that each of these spectra reflect (vide infra). Analogous experiments and analysis completed over Ni and Ni₂P reveal unique spectra discussed further in Section 3.3.

The ν (C–H) modes represented in the spectra of Figure 3 can be deconvoluted to determine the identity and coordination of the three kinetically distinct reactive intermediates that exist on Ni₁₂P₅, each of which possesses a unique phase shift (ψ) relative to the [H₂] stimulus: 0° (Figure 3a), 185° (Figure 3b), and 237° (Figure 3c). Figure 4 illustrates these respective phase



Figure 4. Experimental (solid line, filled symbols) and simulated (dashed line, open symbols) deviations from the average coverage of reactive intermediates ($C_5H_{10}O^*$, brown **■**; $C_5H_9O^*_{2C-O}$, purple **▲**; $C_5H_9O^*_{3C-O}$, orange **●**; $C_5H_8O^*$, pink **V**) during the modulation of H₂ pressure (1200 s period, 2.5–84 kPa, 12 kPa MTHF, and 543 K). The differential equations and estimated rate constants used to calculate the stimulated coverages are detailed in the Supporting Information, Section S4.

shifts. The structure, composition, and orientation of the reactive intermediates corresponding to each spectrum are determined by the analysis of the asymmetric and symmetric C– H stretching modes of the methyl, methylene, and methyne groups following the peak-fitting procedures described in the SI (Section S2) and comparison to spectra predicted from DFT.

The first isolated species (Figure 3c, $\psi = 237^{\circ}$) possesses features resembling $\nu_a(CH_3)$, $\nu_a(CH_2)$, $\nu_s(CH_3)$, and $\nu_s(CH_2)$ modes (Table 1); however, this spectrum lacks absorbance features at wavenumbers that correspond to $\nu(CH)$ modes (\sim 2900 cm⁻¹, red and pink). Peak assignments are based on measured gas-phase spectra of tetrahydrofuran (lacks methyne and methyl groups, Figure S6b), 2-propanol (lacks methylene groups, Figure S6c), and MF (lacks methylene groups, Figure S6a), and MTHF (Figures S5) in conjunction with previously reported peak assignments.^{36–39,59} The absence of ν (CH) \approx 2900 cm⁻¹ suggests that the ³C atom dehydrogenates and bonds directly to the surface. This is consistent with the proposed mechanism for cleaving C-O bonds in MTHF over Ni₁₂P₅ surfaces²⁰ (Scheme 1), which indicates that the C atoms of the C–O bond that ruptures must be fully dehydrogenated prior to cleavage. Therefore, the intermediate leading to ³C-O bond rupture (i.e., $C_5H_9O_{3C-O}^*$) does not contain the H atom of the methyne group present in the gas phase. Consequently, the absence of the methyne stretch in Figure 3c suggests that this spectrum reflects $C_5H_9O_{3C-O}^*$ as depicted in the inset image, and ultimately leads to primary alcohols and aldehydes.

The second isolated species (Figure 3b, $\psi = 185^{\circ}$) shows two distinct features centered at 2926 and 2904 cm⁻¹, which reflect the presence of two unique ν (CH) modes. The feature at 2904 cm⁻³ resembles the methyne group at the ³C of gas-phase MTHF, which suggests that this bond remains intact. The second feature at 2926 cm⁻¹ is clearly distinguishable and may correspond to the methyne group that forms following the removal of a single H atom from the ${}^{2}C$ of the ${}^{2}C$ –O bond to form $C_5H_9O_{2C-O}^*$. This suggests that the spectrum of Figure 3b reflects the intermediate that subsequently cleaves the ²C-O bond, depicted in the inset of Figure 3b, and ultimately forms secondary alcohols and ketones. While the composition of this intermediate $(C_5H_9O_{2C-O}^*)$ matches that of the species that cleaves the ${}^{3}C-O$ bond (C₅H₉O ${}^{*}_{3C-O}$, Figure 3c inset), the two intermediates are distinguished by their coordination to the surface and the consequences this has on ring-opening selectivity.

The third isolated species (Figure 3a, $\psi = 0^{\circ}$) contains a significantly greater ratio of the intensity of the perturbed asymmetric methylene stretch ($\nu_{ap}(CH_2)$) (2942 cm⁻¹) to that of the unperturbed asymmetric methylene stretch ($\nu_{2}(CH_{2})$) (2962 and 2976 cm⁻¹) features in comparison to $C_5H_9O^*_{3C-O}$ (Figure 3c) and $C_5H_9O_{2C-O}^*$ (Figure 3b), indicating that a greater fraction of the methylene groups are perturbed by the surface (i.e., the furan ring is more parallel to the surface, as shown in the inset of Figure 3a). The fractional changes in the coverage of each reactive intermediate caused by the modulation of $[H_2]$ reflect the values of rate constants for the elementary steps involved and the participation of hydrogen in these steps, which offer additional characteristics to differentiate each reactive intermediate (Figure 4). Solving a set of differential equations derived from the previously proposed mechanism²⁰ reveals the simulated relative changes in coverage as a result of [H₂] for each intermediate leading from adsorbed MTHF $(C_5H_{10}O^*)$ to ²C-O and ³C-O bond rupture as detailed in Scheme 1. Modeling the modulation of $[H_2]$ within MATLAB and solving the set of ordinary differential equations (Section S4) over 30 periods provide the parameters for the simulated coverage for each reactive intermediate. Initial parameters (e.g., average coverage for reactive intermediates) were optimized to ensure that the average coverage for each intermediate was constant throughout the 30 periods of modulation. Section S4

Table 1. Binding Conf	igurations and Vibrational	Modes for Reactive Int	termediates Measured ov	ver 10 nm Ni ₁₂ P ₅ (1	12 kPa MTHF,
2.5-84 kPa H ₂) and I	Predicted over Ni ₁₂ P ₅ (001) at 543 K			

	wavenumber (cm^{-1})						
	Ni ₄ (η^{5} -C ₅ H ₁₀ O*), $\psi = 0^{\circ}$		$Ni_2(\mu^2-C_5H_9O^*)$	$()_{2C-O}, \psi = 185^{\circ}$	$Ni_2(\mu^2 - C_5H_9O^*)_{3C-O}, \psi = 237^\circ$		
mode	measured ^a	predicted ^b	measured ^a	predicted ^b	measured ^a	predicted ^b	
$\nu_{\rm a}({\rm CH_3})^c$		3002	2996	3014			
	2991	2999	2986	3006	2996	3024	
$\nu_{\rm a}({\rm CH_3})$ and $\nu_{\rm a}({\rm CH_2})^d$	2976	2996			2961		
$ u_{\rm a}({\rm CH_2}) $	2962	2980	2975	2990	2986	3003	
			2963		2976		
$\nu_{\rm ap}({\rm CH_2})^e$	2942	2971	2942	2954	2937	2981	
ν (CH) ^f	2923	2751	2926	2899			
ν (CH)			2904	2889			
$\nu_{\rm s}({\rm CH}_3)^g$	2888	2879	2880	2888	2891	2846	
				2884			
$\nu_{\rm s}({\rm CH}_3)$ and $\nu_{\rm s}({\rm CH}_2)^h$		2876					
$\nu_{\rm s}({ m CH_2})$	2863	2876	2858	2848	2864	2906	
		2836					

^{*a*}Peak assignments are based on recorded spectra of gas-phase MTHF, THF, MF, and isopropanol (Figure S6) and the literature. ^{*b*}Predicted vibrations were calculated using the RPBE functional. The asymmetric vibrations were corrected by 0.985, and the symmetric vibrations were corrected by 0.967. Figure S10 shows the parity between the measured and predicted vibrational modes for gas-phase MTHF and the reactive intermediates with the scaling corrections. DFT-predicted frequencies using other functionals (optB88-vdW, optB86b-vdW, RPBE-D3BJ, and vdW-DF2) are shown in Tables S2–S4. ^{*c*}Asymmetric methyl stretch. ^{*d*}Asymmetric methylene stretch. ^{*s*}Perturbed asymmetric methylene stretch frequencies for three different gas-phase molecules (furan, methane, and methanol) and how including vdW interactions shifts these frequencies by similar magnitudes.

provides additional details regarding the differential equations and rate constants derived from the energy barriers predicted through DFT calculations²⁰ used for these simulations. These simulations predict that C₅H₁₀O* exhibits the greatest change in coverage (i.e., greatest amplitude) relative to the other reactive intermediates and exhibits a phase shift of 0°. Experimentally, the species with $\psi = 0^{\circ}$ (Figure 3a, reflected by the brown line in Figure 4) has the greatest change in coverage relative to the other isolated species (>2.5 times) under these modulation conditions. Additionally, a comparison of the isolated spectra with spectra obtained at steady state (Figure S11) indicates that the third species (Figure 3a) is most similar in spectral features with the steady-state spectra, which suggests that the third species is a dominant surface intermediate. Together, the spectral features, the relative changes in coverage, and phase shifts suggest that the species depicted in Figure 3a corresponds to $C_5H_{10}O^*$ and has a greater surface coverage than either of the other two reactive intermediates (i.e., the MARI).

The measured phase shifts for the species shown in Figure 4 indicate that three species display differentiable kinetic responses to the changes in $[H_2]$. Scheme 1 indicates, however, that the coverage of a greater number of intermediates should respond to changes in $[H_2]$. The appearance of only three distinct species from the phase-resolved spectra suggests either that the kinetic responses of two or more species are indistinguishable because of similarities in the barriers for formation and consumption or that the changes in coverage with modulation in $[H_2]$ are not detectable. First, the dehydrogenation of MTHF to MF occurs at rates significantly greater than C-O bond rupture, and as a result, all intermediates within this pool may change in unison with the coverage of $C_5H_{10}O^*$. Notably, the reaction conditions and equilibrium constant for the dehydrogenation of MTHF to MF favor higher concentrations of MTHF relative to MF (78:1 MTHF/MF), which suggests that the coverage of deeply dehydrogenated surface

species should also be much lower than for $C_5H_{10}O^*$. Therefore, species within this pool that rapidly converts between MTHF and MF may not significantly contribute to the isolated spectrum in Figure 3a and do not have distinguishable phase shifts such that the SVD methods resolve their distinct spectra. Second, the proposed mechanism includes two dehydrogenation steps prior to ${}^{2}C-O$ bond rupture (Scheme 1); however, only one of these intermediates is resolved $(C_5H_9O_{2C-O}^*)$ Figure 3b). $C_5H_8O^*$ displays a distinct kinetic response in the simulated coverages shown in Figure 4 (dashed pink line); however, it is also the least responsive to the $[H_2]$ changes relative to the other reactive intermediates (i.e., smallest deviation from average coverage). This suggests that our experimental setup and spectral processing cannot detect the small changes in the coverage of $C_5H_8O^*$, which likely exists at low coverages.

The measured change in coverage for $C_5H_9O_{2C-O}^*$ is 185° phase shifted from the MARI, the simulated phase shift is 178°, the measured change in coverage for $C_5H_9O_{3C-O}^*$ is 237° phase shifted, and the simulated phase shift is 337°. The difference in measured phase shifts and amplitudes for $C_5H_9O_{2C-O}^*$ and $C_5H_9O_{3C-O}^*$ from the simulated values may result from undesirable hydrodynamics within the transmission cell that alters the specific modulation conditions (e.g., reducing the amplitude of $[H_2]$ changes) or may indicate that the energy barriers predicted by DFT surfaces differ slightly on the supported Ni₁₂P₅ nanoparticles. Ideally, these methods in addition to the frequency response⁶⁰⁻⁶⁵ could be used to back calculate the rate constants for elementary steps experimentally to improve DFT models; however, this is outside the scope of this work.

The inset images in Figure 3 (enlarged in Figure 5e–g) depict the DFT-optimized structures whose vibrational modes are consistent with the respective spectra (Table 1). The vibrational modes of $C_5H_9O^*_{3C-O}$ bound to the 4-fold Ni hollow as $Ni_2(\mu^2$ -



Figure 5. DFT-predicted structures of the reactive intermediates $(C_5H_{10}O^*, C_5H_9O^*_{2C-O}, C_5H_8O^*, and C_5H_9O^*_{3C-O})$ on Ni (a–d), Ni₁₂P₅ (e–h), and Ni₂P (i–l) using the RPBE functional. The ν (CH) modes are shown in red (³C–H) and pink (²C–H). The ³C and ²C atoms are labeled in yellow. Top views can be found in the Supporting Information (Figure S12).

 C_5H_9O) (Figure 5f) indicate the loss of the $\nu(CH)$ that is present in $C_5H_{10}O^*$ (2923 cm⁻¹) (Figure 5e), which is consistent with the loss of the measured vibration at 2923 cm⁻¹ present in Figure 3. DFT-optimized structures (Figure 5g) and predicted vibrations (Table 1) indicate that two distinguishable vibrational modes for the methyne stretches at ²C and the ^{3}C exist in C5H9O*2C-0 (2904 and 2926 cm $^{-1}$, respectively). The spectrum of $C_5H_9O^*_{2C-O}$ (Figure 3b) also reflects the presence of a second methyne vibration. Figure 5g highlights these two distinguishable methyne groups at 2904 cm^{-1} (red) and 2926 cm⁻¹ (pink). The MARI (Figure 5e) binds to the 4fold Ni hollow of Ni₁₂P₅(001) as Ni₄(η^5 -C₅H₁₀O), which brings all of the methylene groups into close proximity to the surface. An observed increase in the ratio of $\nu_{ap}(CH_2)$ (2942 cm⁻¹) to ν_{a} (CH₂) (2962 and 2976 cm⁻¹) of the MARI spectrum (Figure 3c) matches the coordination of the DFT-optimized structure of $Ni_4(\eta^5-C_5H_{10}O)$. The single methyne group at ³C (2923 cm⁻¹) is highlighted in red. DFT calculations predict distinguishable vibrations for the different methylene groups because they have slightly different electronic properties (e.g., C4 and C3), which the deconvolution of individual peaks following the application of MES, PSD, and MCR-ALS captures. The consistency between the isolated spectra and DFT-predicted structures and measured and calculated vibrational modes confirms that

the combination of MES, PSD, and MCR-ALS reveals spectra of individual reactive intermediates over 10 nm Ni₁₂P₅. The DFTpredicted structures of all reactive intermediates over Ni, Ni₁₂P₅, and Ni₂P are shown in Figure 5. The RPBE functional used here neglects dispersive interactions; therefore, these intermediates were reoptimized using other functionals that account for dispersive interactions and van der Waals forces such as optB88vdW,^{49,50} optB86b-vdW,^{51,52} RPBE-D3BJ,^{53,54} and vdW-DF2.^{49,55} The inclusion of these interactions did not alter the structures shown in Figure 5 significantly as shown in Figures S17-S20, although the vibrational frequencies for each mode were shifted by similar magnitudes (by $\sim 10-50$ cm⁻¹, Tables S2–S4) compared to the RPBE-calculated frequencies while the positions of features with respect to each other remain generally constant, as also shown for three different gas-phase molecules (furan, methane, and methanol) in Tables S5–S7.

The compositions of reactive intermediates that lead to ${}^{3}C-O$ and ${}^{2}C-O$ bond rupture within MTHF over Ni, Ni₁₂P₅, and Ni₂P surfaces remain constant across all three catalysts and also over wide ranges of reactant pressures and temperatures, as shown by measured rates that show constant dependencies on the pressures of H₂, MTHF, and CO and the implications of DFT calculations.²⁰ As such, modulation experiments of [H₂] should reveal spectra of these same reactive intermediates over

Ni and Ni₂P catalysts. However, differences in the precise orientation of these intermediates with respect to the surfaces of Ni, $Ni_{12}P_5$, and Ni_2P may give insight into the reasons for large changes in the C–O bond rupture selectivities between these catalysts.

3.3. Coordination of Reactive Intermediates over Ni, $Ni_{12}P_5$, and Ni_2P . Similar $[H_2]$ modulation experiments performed on 12 nm Ni₂P and 4 nm Ni isolate the spectra of reactive intermediates (Figures S13 and S14, respectively) that show distinct spectral features and therefore imply that the reactive intermediates bind to these surfaces with orientations that differ from those on 10 nm Ni₁₂P₅. We employ the same logic to identify reactive intermediates over Ni and Ni₂P as described in detail for $Ni_{12}P_5$ in Section 3.2 (e.g., comparing the relative intensities of $\nu_{ap}(CH_2)$ and $\nu_a(CH_2)$, changes in coverage, and DFT-predicted vibrations and structures). On 12 nm Ni₂P nanoparticles, this analysis reveals three distinct reactive intermediates that include the MARI (C₅H₁₀O*) and species that likely lead to ²C-O rupture (C₅H₉O*_{2C-O}) and ³C-O rupture (C₅H₉O*_{3C-O}). In contrast, 4 nm Ni nanoparticles stabilize only species that appear to be the MARI $(C_5H_{10}O^*)$ and a partially dehydrogenated intermediate that likely cleaves ${}^{2}C-O$ bonds (C₅H₉O $*_{2C-O}$). Spectra that reflect species with the same composition over these three surfaces (Ni, Ni₁₂P₅₁ and Ni₂P) display significant differences that relate to different orientations of the furanic ring. For example, spectra that reflect C5H9O*2C-0 over 10 nm Ni12P5 and 12 nm Ni2P show a significantly greater intensity of $\nu_{\rm ap}({\rm CH_2})$ with an increased red shift for $\nu_{ap}(CH_2)$ relative to the analogous spectrum over 4 nm Ni (2942 and 2948 compared to 2965 cm⁻¹ respectively). Additionally, the peak center related to $\nu_a(CH_3)$ gradually red shifts from \sim 3000 to 2976 cm⁻¹ as the P to Ni ratio decreases. These spectral differences suggest that the methylene groups of C5H9O*2C-O are drawn much closer to the surface while the methyl group interacts less with the surface over Ni₁₂P₅ and Ni₂P relative to Ni, which is reflected in the DFT-optimized structures in Figure 5. The spectra of $C_5H_9O_{3C-O}^*$ bound to Ni₁₂P₅ and Ni₂P are similar, with nearly all of the peak centers within 4 cm^{-1} . The absence of an isolated spectrum on Ni that resembles $(C_5H_9O_{3C-O}^*)$ i.e., clearly lacking a methyne stretch) is not surprising because ${}^{3}C-O$ bond rupture rates are at least an order of magnitude lower than ²C–O bond rupture rates.²⁰ Consequently, the spectroscopic characterization of reactive species on Ni, Ni₁₂P₅, and Ni₂P presented here is qualitatively consistent with observations that the addition of P to Ni increases the propensity to cleave the ${}^{3}C-O$ bond during catalytic MTHF hydrogenolysis. C-O bonds rupture within reactive intermediates that form by dehydrogenation of the MARI on Ni, Ni₁₂P₅, and Ni₂P. While the composition of the MARI appears to be the same across these catalysts ($C_5H_{10}O^*$, as shown by DFT and rate measurements),²⁰ the coordination of the MARI to the ensembles of Ni atoms that comprise the active site differs. Figure 6 displays the spectra of the MARI on Ni, Ni₁₂P₅, and Ni₂P as determined by the spectral features and the relative changes in coverage (Figures 4, S13d, and S14c) as discussed in Section 3.2 and Supporting Information, Section S4. Comparisons of the spectra for these MARI show that the ratios of peak areas of $\hat{\nu}_{ap}(CH_2)$ (~2940 cm¹) to $\nu_a(CH_2)$ $(\sim 2960 \text{ cm}^{-1})$ increase with increasing P/Ni atomic ratio, which suggests that the addition of P increases the strength of the dative interaction between methylene groups and the surface. Additionally, the relative intensity of ν (CH) (~2900 cm⁻¹) to $\nu(CH_2)$ and $\nu(CH_3)$ (2990–2940 and 2880–2850 cm⁻¹,



Figure 6. Spectra of the most abundant reactive intermediates $(C_5H_{10}O^*)$, black solid line) extracted from phase domain spectra over (a) 12 nm Ni₂P-SiO₂, (b) Ni₁₂P₅-SiO₂ (reproduced from Figure 3a), and (c) 4 nm Ni-SiO₂ at 12 kPa MTHF and 543 K obtained during MES of the H₂ pressure modulated between 2.5 and 84 kPa and isolated using MCR–ALS. Spectra were fit to Lorentzian distributions that indicate individual C–H stretches (ν_a (CH₃), green; ν_s (CH₃), light green; ν_a (CH₂), blue; ν_{ap} (CH₂), teal; ν_s (CH₂), light blue; ν (CH) of ³C, red; and ν (CH) of ²C, pink), which form the cumulative spectra (brown, transparent line). DFT-predicted intermediates optimized using the RPBE functional (inset) that are consistent with assigned species based on spectral features (O, red; C, black; H, white; P, orange; and Ni, green). Measured peak centers are listed in Table 2. All species isolated over Ni₂P and Ni shown in Figures S13 and S14, respectively.

Table 2. Vibrational Modes for Reactive Intermediates Measured over 10 nm Ni₁₂P₅, 12 nm Ni₂P, and 4 nm Ni (12 kPa MTHF, 2.5–84 kPa H₂, 543 K)

	wavenumber (cm ⁻¹)								
	(C ₅ H ₁₀ O*)			$(C_{5}H_{9}O^{*})_{2C-O}$			$(C_{5}H_{9}O^{*})_{3C-O}$		
mode ^a	Ni ₂ P	Ni ₁₂ P ₅	Ni	Ni ₂ P	Ni ₁₂ P ₅	Ni	Ni ₂ P	Ni ₁₂ P ₅	Ni
$\nu_{\rm a}({\rm CH_3})^b$	3026		2988	3024	2996	2995			
	2993	2991	2976	2997	2986	2985	2996	2996	
$ u_{\rm a}({\rm CH}_3) \text{ and } \nu_{\rm a}({\rm CH}_2)^c $	2974	2976	2966	2975	2975	2976	2962	2961	
$\nu_{\rm a}({\rm CH_2})$	2956	2962	2956	2965	2963		2986	2986	
							2976	2976	
$ u_{\rm ap}({\rm CH}_2)^d$	2935	2942	2939	2948	2942	2965	2934	2937	
$\nu(CH)^e$				2930	2926	2940			
$\nu(CH)$	2904	2923	2918	2909	2904	2914			
$\nu_{\rm s}({\rm CH}_3)^f$	2885	2888	2883	2894	2880	2881	2881	2891	
$\nu_{\rm s}({\rm CH}_2)^{\rm g}$	2866	2863	2863	2871	2858	2855	2853	2864	

^{*a*}Peak assignments are based on recorded spectra of gas-phase MTHF, THF, MF, and isopropanol (Figure S6); the literature; and predicted vibrations. ^{*b*}Asymmetric methyl stretch. ^{*c*}Asymmetric methylene stretch. ^{*d*}Perturbed asymmetric methylene stretch. ^{*e*}Methyne stretch. ^{*f*}Symmetric methyl stretch.

respectively) features increases with increasing P/Ni ratio, which indicates that the methyne stretch of $C_5H_{10}O^*$ is more parallel to the Ni surface than to the Ni₁₂P₅ and Ni₂P surfaces. Together, these changes in spectral features with P/Ni ratio suggest that the MARI exists as a Ni(μ^3 - $C_5H_{10}O$) structure on Ni but more closely resembles Ni₃(η^5 - $C_5H_{10}O$) as the P/Ni increases, which is consistent with DFT-optimized structures on these surfaces (Figures 6, insets).

The orientation of the MARI may be a descriptor for selectivity toward ³C-O and ²C-O bond rupture because $C_5H_{10}O^*$ is the common reactive intermediate for the two C–O bond rupture pathways. Kinetic studies describe the mechanism in which adsorbed MTHF sequentially dehydrogenates at ³C or ²C prior to ³C-O or ²C-O bond rupture.²⁰ Manipulating the P/Ni ratio changes the absolute free energies (Figures S1-S3) and enthalpies²⁰ of reactive intermediates and adsorbates. Measured and predicted ΔH^{\ddagger} for ³C–O bond rupture decrease relative to those for ²C–O bond rupture within MTHF with an increasing P/Ni ratio, which results in higher selectivities for ³C-O bond rupture on Ni₂P compared to that on Ni.²⁰ Numerous works have studied the effects of steric hindrance on the selectivity of rupturing hindered and unhindered C-C and C–O bonds. 12,15,36,66 The selectivity of 2 C– 2 C bonds relative to ${}^{2}C-{}^{3}C$ bonds (where ^{*x*}C indicates a C atom bound to *x* non-H atoms) during the hydrogenolysis of methylcyclopentane increases with the Pt particle size, which may result from the steric hindrance of several adsorbates that inhibit the flat-lying coordination required to bind ³C to the surface.⁶⁶ DFT calculations indicate that ³C-O bond rupture over Rh is energetically unfavorable relative to ²C-O bond rupture in MTHF by 30 kJ mol⁻¹ and suggest that steric hindrance prevents the initial dehydrogenation of the ³C atom.¹² These previous works and data reported here suggest that the coordination of reactive intermediates strongly impacts the accessibility of hindered bonds to the catalyst surface, thus influencing the selectivity.

Ensembles of Ni atoms catalyze both types of C–O bond rupture on Ni, Ni₁₂P₅, and Ni₂P surfaces,²⁰ yet the electronic structure of the Ni atoms within these ensembles differs because the addition of electronegative P withdraws charge from Ni, and these changes are likely responsible for the differences in coordination between $C_5H_{10}O^*$ and the surface among the

three catalysts. The charge analysis using QUAMBO⁵⁶ for these three catalysts shows that average Ni charge increases from 0 e⁻ on Ni(111) to +0.188 e^- on Ni₁₂P₅(001) and +0.246 e^- on $Ni_2P(001)$, consistent with the increase in selectivity toward $^{3}C-O$ cleavage with an increasing P/Ni ratio. Furthermore, $^{2}C-$ O bond activation withdraws more e^{-'}s from the Ni atoms on the surface than ${}^{3}C-O$ activation because the ${}^{2}C$ atom is more negatively charged than the ³C atom in the reactants (Figures S21–S24). Given that Ni atoms are more positively charged in the Ni_rP_v materials, it is likely that the enhanced e⁻ withdrawal for ${}^{2}C-O$ deselects this pathway over the reduced e⁻ withdrawal for ${}^{3}C-O$ activation. This higher selectivity of Ni_xP_y toward ${}^{3}C-$ O activation could also be attributed to structural effects where the phosphorus atoms break up Ni ensembles and increase Ni-Ni distances (average Ni-Ni distances: ~2.5 Å for Ni, 2.5-2.9 Å for Ni₁₂P₅, and 2.7–3.7 for Ni₂P). Increased Lewis acidity in mixed metal phosphides (FeMoP,^{67,68} RuMoP,⁶⁷ and NiMoP⁶⁷) during the hydrodeoxygenation of phenol increases the selectivity for direct deoxygenation to benzene rather than ring hydrogenation followed by deoxygenation. These works suggest that the coordination of the phenyl group to the NiMoP surface significantly decreases the selectivity toward the direct deoxygenation pathway (20%) relative to FeMoP and RuMoP (90 and 45%, respectively), which exhibit tilted phenyl rings with the O pointing toward the surface based on DFT-predicted structures and measured selectivities.^{67,68} Falicov and Somorjai⁶⁹ discuss the relationship between the catalytic activity and electronic structure of metal surfaces, where the electronic structure may be manipulated by the presence of different neighboring atoms (e.g., combinations of Cu and Ni) or surface morphology (e.g., stepped or kinked sites). For example, kinked Pt(10,8,7) shows higher rates relative to Pt(100), Pt(111), and Pt(13,11) for the hydrogenolysis of isobutane, which contains only hindered C–C bonds.⁶⁹ Similarly, calculated ΔG^{\ddagger} for hindered C-C bond cleavage in methylcyclopentane is lower over (211) relative to (111) surfaces for Pt, Pd, Rh, and Ir.⁷⁰ The d band of these unsaturated atoms of the stepped surfaces⁶⁹ is less filled as in Lewis acidic ensembles of Ni^{δ^+} presented on the surface of $Ni_{12}P_5$ and $Ni_2P.^{50,52,71}$ These e⁻-deficient metal ensembles may attract e⁻-rich furan and cycloalkane rings and thus help to reduce barriers to cleave hindered C-O or C-C bonds relative to an e⁻-rich continuous surfaces.

4. CONCLUSIONS

Here, we combine in situ infrared spectroscopy with mathematical methods and DFT to deconvolute the surface organometallic zoo of reactive intermediates that exist during the hydrogenolysis of a model oxygenate and to better understand the origins of the differences in selectivity toward hindered and unhindered C–O bonds within MTHF across Ni, $Ni_{12}P_5$, and Ni_2P catalysts. These results indicate that the selectivity patterns toward primary and secondary alcohols and aldehydes result from significant differences in the coordination of the reactive intermediates and the proximity of the C–O bonds to the surface in the MARI.

Although in situ spectra acquired at steady state are not helpful in answering these questions, the combination of MES, PSD, and statistical approaches (MCR-ALS) reveals spectra of reactive intermediates that are consistent with DFT-optimized structures and predicted vibrations. Differences in intrinsic energy barriers yield distinguishable temporal responses to changes in $[H_2]$ for reactive intermediates such that the deconvolution methods isolate the spectrum of three reactive intermediates over 10 nm Ni12P5. The different time-dependent behavior of each reactive intermediate provides information regarding the distinct sets of rate constants (that reflect unique intrinsic activation free energies for each step). Comparisons of peak centers and relative amplitudes of specific C-H vibrations in isolated spectra over 10 nm Ni₁₂P₅ and 12 nm Ni₂P depict $C_5H_{10}O^*$, $C_5H_9O^*_{2C-O}$, and $C_5H_9O^*_{3C-O}$, and spectra on 4 nm Ni reflect only C₅H₁₀O* and C₅H₉O*_{2C-O}. The absence of $C_5H_9O_{3C-O}^*$ over Ni indicates a lower relative coverage than on Ni₁₂P₅ and Ni₂P and is consistent with the previously reported lower selectivity toward ³C-O bond rupture on Ni relative to that on Ni₁₂P₅ and Ni₂P.

Spectra of the most abundant reactive intermediates (MARI) were determined by the greatest change in coverage with [H₂], as indicated by calculated coverages of reactive intermediates. Spectra of MARI ($C_5H_{10}O^*$) display an increase in $\nu_{CH2,ap}(C-$ H) relative to $\nu_{CH2,a}(C-H)$ with increasing P/Ni, which suggests that the presence of P increases the stability of the furanic ring near the catalyst surface by removing some charge from the Ni atoms that catalyze C-O bond rupture. The proximity of the ring, and thus the methyne group in MTHF, to the catalyst surface may remove the steric hindrance of the methyl group and reduce enthalpic barriers for subsequent steps leading to ³C–O bond rupture relative to ²C–O bond rupture on Ni12P5 and Ni2P surfaces relative to Ni. The different orientations of the MARI may be the fundamental cause of the increase in the selectivity of hindered ³C-O bond rupture with increasing P/Ni ratio.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.9b06112.

Reaction coordinate diagrams, reference gas phase spectra, steady-state spectra at multiple temperatures, predicted vibrational modes, calculations for simulated coverages, time-resolved spectra over SiO_2 , DFT-predicted structures, and isolated spectra and deviations in coverage over Ni and Ni₂P (PDF)

MATLAB phase-sensitive detection code (PDF)

DFT structures (ZIP)

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The authors declare no competing financial interest.

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