Mechanisms and Active Sites for C–O Bond Rupture within 2-Methyltetrahydrofuran over Ni, Ni$_{12}$P$_{5}$, and Ni$_2$P Catalysts

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**ABSTRACT:** Nickel phosphide catalysts (Ni$_12$P$_5$ and Ni$_2$P) preferentially cleave sterically hindered 3C–O bonds over unhindered 2C–O bonds and Ni$_2$P is up to 50 times more selective toward 3C–O bond cleavage than Ni. Here, we combine kinetic measurements, in situ infrared spectroscopy, and density functional theory (DFT) calculations to describe the mechanism for C–O bond rupture over Ni, Ni$_{12}$P$_5$, and Ni$_2$P catalysts. Steady-state rate measurements and DFT calculations of C–O bond rupture within 2-methyltetrahydrofuran (MTHF) show that quasi-equilibrated MTHF adsorption and dehydrogenation steps precede kinetically relevant C–O bond rupture at these conditions (1–50 kPa MTHF; 0.1–6 MPa H$_2$; 543 K). Rates for 3C–O and 2C–O bond rupture are inhibited by H$_2$, and the ratio of these rates increases with [H$_2$]$^{1/2}$, suggesting that the composition of the reactive intermediates for 3C–O and 2C–O rupture differs by one H atom. Site-blocking CO$_x$, NH$_x$, and H$^+$ inhibit rates without altering the ratio of 3C–O to 2C–O bond rupture, indicating that these C–O bond rupture precursors and transition states bind to identical active sites. DFT-based predictions suggest that these sites are exposed ensembles of 3 Ni atoms on Ni(111) and Ni$_2$P(001) and 4 Ni atoms on Ni$_{12}$P$_5$(001) and that the incorporation of P disrupts extended Ni ensembles and alters the reactivity of the Ni. Increasing the phosphorus to nickel ratio (P:Ni) decreases measured and DFT-predicted activation enthalpies ($\Delta H^\ddagger$) for 3C–O bond rupture relative to that of 2C–O bond rupture. Selectivity differences between specific C–O bonds within MTHF reflect differences in the H content of reactive intermediates, activation enthalpy barriers, and P:Ni of Ni, Ni$_{12}$P$_5$, and Ni$_2$P nanoparticles.

**KEYWORDS:** nickel phosphide, reaction mechanism, hydrogenolysis, kinetics, 2-methyltetrahydrofuran, active site, DFT

1. INTRODUCTION

Abundant amounts of unused, inedible biomass (e.g., corn stover, wood clippings) could be used as feedstocks for platform chemicals (e.g., benzene, $\alpha$-\omega-diols) that are traditionally synthesized from petroleum feeds, without competing with food sources. Their high lignin content renders them difficult to process through microbial decomposition; however, pyrolysis can depolymerize lignin into mixtures of smaller oxygenates (i.e., bio-oil). Conversion of oxygenates (e.g., alcohols, ketones, furans, pyrans, and aromatics) into higher value chemicals (e.g., benzene, and $\alpha$-\omega-diols) requires cleavage of C–O bonds at select locations within these species to minimize hydrogen consumption and increase yield to high-value chemicals. Yet, the selective rupture of specific C–O bonds without complete deoxygenation or competing C–C bond cleavage remains a challenge.

Metal phosphides (MPs) are promising catalysts for selective C–O bond rupture. These materials were originally studied as catalysts for hydrodesulfurization and hydrodenitrogenation of fuels in response to increasingly stringent regulations on SO$_x$ and NO$_x$ emissions. MPs selectively cleave C–(O,N,S) bonds over C–C bonds in comparison to transition metals, metal sulfides, and metal nitrides. Previous studies have reported that selectivities and rates for C–O bond rupture change with the metal identity and metal to phosphorus ratio (i.e., phase), formation of bimetallic phosphides, and variations in the support. The reactivity of MPs for hydrogenolysis of C–O bonds in various oxygenates (e.g., anisole, guaiacol, guaiacol, 2-methyltetrahydrofuran (MTHF), dibenzofuran, and methyl laurate) indicate that Ni$_2$P is the most reactive of the MPs studied (Ni$_2$P, Ni$_{12}$P$_5$, Ni$_{25}$P$_{17}$, NiMo$_2$P$_3$, NiMo$_3$P$_4$, Fe$_3$P, NiFe$_2$P, Co$_2$P, and W$_8$).
While studies have shown Ni$_2$P has high selectivity and reactivity toward C−O bond rupture products, the mechanism toward specific C−O bond rupture (e.g., either at sterically hindered or unhindered positions) and the structure and functions of the active site remain unclear. The kinetics of MTHF over Ni$_2$P have been studied by analysis of rate data with a model derived for a mechanism considering multiple reactive intermediates for total deoxygenation; however, models that specifically describe the rupture of each of the two C−O bonds have not been proposed previously. The heterogeneous surface of Ni$_2$P presents multiple potential active sites each of which may cleave hindered and unhindered C−O bonds; however, the identity of the active site (or sites) for these competing pathways has not been determined on these complex surfaces. Consequently, the relationship between MP properties and C−O bond cleavage selectivity is largely unclear.

In this study, we analyze two parallel mechanisms for C−O bond rupture in MTHF over supported Ni$_2$P, Ni$_{12}$P$_5$, and Ni catalysts using kinetic analysis, in situ spectroscopy, and density functional theory (DFT) calculations to identify the composition of the reactive intermediates and the active sites that bind them. Steady-state rate measurements obtained as a function of MTHF pressure ([MTHF], 1−50 kPa) and H$_2$ pressure ([H$_2$], 0.1−6 MPa) at 543 K show that adsorption and MTHF dehydrogenation steps are quasi-equilibrated, that the kinetically relevant step involves partially dehydrogenated intermediates, and that the active sites for this reaction on Ni, Ni$_{12}$P$_5$, and Ni$_2$P are largely covered by a mixture of MTHF-derived intermediates, CO*, and H*. DFT calculations confirm that C−O bond cleavage occurs after C−H bond activation of the carbon atom on Ni$_2$P, Ni$_{12}$P$_5$, and Ni$_2$P surfaces. Thus, the mechanism for rupturing C−O bonds of MTHF strongly resembles those for C−C bond rupture in alkanes and cycloalkanes as well as C−O bond rupture in cyclic ethers and alcohols on transition metal surfaces. Rates of unhindered (2C−O) and hindered (3C−O) bond rupture are similarly inhibited by CO and NH$_3$ on Ni, Ni$_{12}$P$_5$, and Ni$_2$P catalysts, which suggests that both reactions occur at the same active site and that this active site also binds CO* and NH$_3$*. The H$_2$ dependencies of 2C−O and 3C−O bond rupture rates differ by [H$_2$]$^{1/2}$ on Ni, Ni$_{12}$P$_5$, and Ni$_2$P nanoparticles, which suggests that the transition state for 3C−O bond cleavage has one more H atom than that for 2C−O bond cleavage. Thus, both C−O ruptures occur after the complete dehydrogenation of the C atom involved. Measured and predicted activation enthalpies indicate lower activation enthalpies for 3C−O relative to 2C−O bond rupture with increased phosphorus to nickel ratios (P:Ni), which results in higher selectivity toward 3C−O bond rupture over Ni$_{12}$P$_5$ and Ni$_2$P surfaces. Understanding the underlying reasons for these differences in reactivity and developing P-modified catalysts to selectively cleave hindered C−O (or other carbon bonds) within hydrodeoxygenation reaction networks would be desirable for the production of linear alcohols or diols from renewable biomass-derived feedstocks and for the production of normal alkanes during ring-opening catalysis and reforming of petrochemicals.

2. RESULTS AND DISCUSSION

2.1. Selectivity for C−O Bond Cleavage. Figure 1 displays product selectivities for the reaction of MTHF with H$_2$ on SiO$_2$-supported 19 nm Ni$_{12}$P$_5$ nanoparticles as a function of conversion, which was controlled by varying the residence time of the reactant mixture (5 kPa MTHF, 1.0 MPa H$_2$, 543 K). Pentanal and 2-penten-4-one are the sole primary products of this reaction as shown by their nonzero selectivities (60% and 20%, respectively) as the conversion approaches zero (Figure 1a). The selectivities for all other products approach zero at short residence times (Figure 1b and 1c), which indicates that they are formed by secondary reactions. Pentanal and 2-penten-4-one form following rupture of the C−O and the C−O bonds, respectively, concurrent with C−H rupture and formation (Scheme 1). Figure 1b shows the secondary products that react at short residence times (i.e., at conversions below 0.3%) to form tertiary products. Secondary products, such as 1-pentanol, 2-penten-4-ol, 2-pentanone, and 2-pentanol, form by subsequent hydrogenation of pentanal and 2-penten-4-one (i.e., the primary products), whereas 1-butene and n-butane likely form by decarbonylation of pentanal and subsequent hydrogen transfer steps as indicated by formation of 1-butene and n-butane (gray diamonds), 1-pentanol (blue open squares), n-pentane (green solid pentagons), 2-penten-4-ol (red solid right-facing triangles), 2-pentanone (purple solid down-facing triangles), 2-pentanol (orange open right-facing triangles), 1-butene (black open squares), and n-pentane (gray diamonds). The H$_2$ dependencies of 3C−O and 2C−O bond rupture products are shown in Supporting Information (Figure S1).
of CO in nearly equimolar quantities (e.g., 23 ± 1 C-% selectivity to n-butane and 6 ± 1 C-% selectivity to CO at 1.2% conversion). Water forms from dehydrating 1-pentanol and 2-pentanol but is not indicated in Figure 1 because it lacks carbon. Figure S1 shows that selectivity patterns for hydrogenolysis on 5 nm Ni12P5 are similar to that on 19 nm Ni12P5, while 12 nm Ni12P5 is highly selective toward pentane (80 C-%) and 4 nm Ni produces significantly less 3C−O bond rupture products (e.g., n-butane and 1-pentanol). Pentane forms from the dehydration of 1- and 2-pentanol and, therefore, is not attributed to either pathway in calculations for turnover rates. Selectivities toward unsubstituted cyclic ethers (i.e., tetrahydropyran and furan) or aliphatic ethers (e.g., diethyl ether and methyl propyl ether) are insignificantly different (i.e., < 0.1%) at the conditions of this study (473−575 K, 5 kPa MTHF, 1 MPa H2, 5 kPa MTHF, 543 K) over SiO2-supported Ni, Ni12P5, and Ni2P nanoparticles (Figures S3a and S4), which demonstrates Ni12P5 predominantly cleaves C−O bonds (as opposed to C−C bonds) in primary reactions of MTHF. The lack of C−C cleavage in MTHF and the subsequent decarbonylation of pentanal is additional evidence that decarbonylation reactions occur via mechanisms distinct from C−C hydrogenolysis, as previously reported on Ir.35

Measured turnover rates for 3C−O bond rupture (r3C−O) and 3C−O bond rupture (r3C−O) (i.e., the consumption rate of MTHF to form 2-pentene-4-one and subsequent 3C−O bond rupture products, and pentanal and subsequent 3C−O bond rupture products, respectively) decrease with increasing conversion to an extent much greater than expected based on depletion of the reactant (e.g., 40% decrease at less than 4% conversion) as demonstrated on 5 nm Ni12P5 (Figures S3a and S4; 0−5 kPa CO, 5 kPa MTHF, 1 MPa H2, 543 K). These results suggest that a reaction product inhibits C−O bond rupture. CO is formed by decarbonylation of aldehyde products27−30 (Figure 1, Scheme 1) and binds strongly to the catalyst surface, as shown in situ FTIR measurements that reflect significant coverages of CO* on SiO2-supported Ni12P5 during reactions of H2 and preadsorbed MTHF at 523 K.28 Rates for C−O bond rupture are less affected by conversion as CO is cofed (0−5 kPa CO, Figure S3b), because the pressure of CO becomes a weak function of conversion. These data (Figure S3) indicate that r3C−O and r3C−O remain nearly constant over the range of differential MTHF conversion (at values < 10%) at CO pressures ([CO]) equal to or greater than 1 kPa CO and indicate that water formed from dehydrating alcohols (<0.05 kPa) is not responsible for product inhibition. Consequently, rate measurements made in the remainder of this paper were obtained (unless otherwise noted) with at least 1 kPa CO cofed.

Controlling C−O bond hydrogenolysis selectivity within MTHF and other oxygenates provides catalytic routes to produce value-added chemicals, such as cleaving hindered C−O bonds to produce α,ω-functionalized alcohols and aldehydes from 2-hydroxymethyl-tetrahydrofuran.5 The ratio of the rate of r3C−O to r3C−O can be defined as follows

\[
\chi = \frac{r_{3C-O}}{r_{3C-C}}
\]

such that large values of \(\chi\) demonstrate a preference for cleaving 3C−O bonds. Values of \(\chi\) depend weakly on conversion in the absence of cofed CO (Figure 2, 1 MPa H2, 5 kPa MTHF, 543 K).

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2.2. Effects of Reactant Pressures on C–O Bond Rupture Rates on Ni, Ni₁₂P₅, and Ni₂P Catalysts. C–H bonds can break and form rapidly at reaction conditions that favor C–O and C–C bond rupture in alkanes and alcohols as shown previously,²⁵,³³,³⁵ and this also occurs here through the dehydrogenation of MTHF to 2-methylfuran (MF) illustrated in Scheme 1. The approach to equilibrium (η) for the dehydrogenation of MTHF is defined as follows

\[
\eta = \frac{[\text{H}_2]^{2} \cdot \text{[MF]}}{K_{\text{DH}} \cdot \text{[MTHF]}}
\]

(2)

where \(K_{\text{DH}}\) is the equilibrium constant for dehydrogenation. Figure S5 shows that η is nearly unity and does not depend on residence time or reactant conversion on all catalysts (1–50 kPa MTHF, 250–500 kPa H₂, 1–2.5 kPa CO, 543 K), which indicates that MTHF dehydrogenation is quasi-equilibrated at all conditions of this study. By extension, we assume that partially dehydrogenated surface and gaseous intermediates derived from MTHF exist within a quasi-equilibrated pool of intermediates derived from MTHF on Ni, Ni₁₂P₅, and Ni₂P catalysts being most sensitive to \([\text{CO}]\) (Figure S7) obtained during reactions of MTHF with H₂ over Ni, Ni₁₂P₅, and Ni₂P catalysts (5 kPa MTHF, 81 kPa H₂, 543 K) show a combination of spectral features between 3000 and 2700 cm⁻¹ attributed to asymmetric and symmetric ν(CH₃) modes.³⁶–⁴¹ These ν(CH₃) modes correspond only to surface intermediates derived from MTHF on Ni, Ni₁₂P₅, and Ni₂P as the intensities of surface intermediates on SiO₂ are negligible, and the gas-phase contributions of MTHF have been subtracted. CO formed by decarboxylation of reaction intermediates bind to Ni₁₂P₅ and Ni surfaces at these conditions, as shown by distinct absorbance features at 2035 cm⁻¹ on Ni₁₂P₅ and in the range of 1710–2025 cm⁻¹ on Ni that correspond to reported frequencies for CO bound to Ni ensembles on Ni₁₂P₅ and Ni surfaces,²⁸,³⁴ respectively, and which shows that CO formed by decarboxylation of reaction intermediates produces CO partial pressures that are sufficiently high to compete with MTHF-derived species for active sites. Additional spectra of adsorbed CO over Ni are shown in the Supporting Information (Figure S8). The lack of an obvious absorbance feature for ν(CO) on 12 nm Ni₂P indicates that CO* exists at much lower coverages on the Ni₂P surface relative to the Ni and Ni₁₂P₅ surfaces at these conditions, which is consistent with binding energies for CO* on Ru(0001) that decrease as the ratio of atomic phosphorus to ruthenium increases.⁴⁴ The coexistence of CO* and MTHF-derived surface intermediates (Figure S7) is consistent with product inhibition from CO (Figures S3 and S4), the form of the rate dependence on [MTHF] (Figure 3), and previous spectroscopic observations of coadsorbed MTHF and CO formed in situ over NiP₅ nanoparticles.²⁸

Both r₂C–O and r₃C–O decrease upon cofeeding increasing [CO] over all Ni, Ni₁₂P₅, and Ni₂P nanoparticles (Figure 4, 5 kPa MTHF, 0.25–1 MPa H₂, 543 K), which confirms that the CO* binds to active sites for ³C–O and ²C–O bond rupture. The degree of CO inhibition on C–O bond rupture rates decreases with increasing molar ratio of P to Ni, with Ni catalysts being most sensitive to [CO] (r₂C–O ~ [CO]⁻¹), while Ni₁₂P₅ (both 5 and 19 nm) is less so (r₂C–O ~ [CO]⁻¹), and Ni₂P is nearly unaffected (r₂C–O ~ [CO]⁻⁰), which agrees with the relative sizes of CO* features within in situ FTIR spectra (Figure S7). Thus, CO (produced either in situ or cofed) adsorbs to active sites for C–O bond rupture in competition with MTHF-derived intermediates and binds less strongly to Ni₁₂P₅ surfaces than to either Ni₂P or Ni surfaces. The lower proclivity for CO to bind to and inhibit reactions on phosphorus-modified Ni catalysts resembles similar trends shown by studies of temperature-programmed desorption of CO from phosphorus-modified Ni(100) surfaces.⁴⁵ These investigations demonstrated that the sticking coefficient of CO decreases with increasing P coverage, because the presence of electronegative P atoms decreased the extent of back-donation from the Ni atoms to the adsorbed CO.⁴⁵ The resistance of NiP₅ surfaces to CO poisoning expands the benefits of Ni₁₂P₅ and Ni₂P as hydrogenolysis catalysts. On all catalysts, CO inhibits both ³C–O and ²C–O bond rupture to the same extent.

Figure 3. Changes in rates of consumption of the MTHF-MF reactant pool to form pentanal and subsequent ³C–O bond rupture products (open symbols) and 2-penten-4-one and subsequent ²C–O bond rupture products (solid symbols) indicated in Scheme 1 as functions of MTHF pressure in the presence of CO over 4 nm Ni (black diamonds, 2.5 kPa CO, 500 kPa H₂), 5 nm Ni₁₂P₅ (green triangles, 1 kPa CO, 250 kPa H₂), 19 nm Ni₁₂P₅ (red squares, 2.5 kPa CO, 500 kPa H₂), and 12 nm Ni₂P (blue triangles, 2.5 kPa CO, 500 kPa H₂) at 543 K. Trend lines reflect fits to an inhibited, unimolecular, Langmuir–Hinshelwood expression (Section S1). Figure S6 displays these data as total turnover rates and selectivities.
values that increase with a half-order dependence on \([\text{H}_2]\) (i.e., decrease with \([\text{H}_2]\) structure.

χ ∼ SiO2.28 Yet neither of these publications report turnover rates for 2C rupture shows an inverse half-order dependence (i.e., χ ∼ 0) and Ni at moderate H2 pressures (<0.75 MPa \([\text{H}_2]\)) but rates are more inhibited by \([\text{H}_2]\) \((r_{2C-O} \sim [\text{H}_2]^{-3/2})\) and \(r_{3C-O} \sim [\text{H}_2]^{-1/2}\) at higher pressures. Differences in the degree of H2 inhibition toward 2C−O and 3C−O bond rupture leads to χ values that increase with a half-order dependence on \([\text{H}_2]\) (i.e., χ ∼ \([\text{H}_2]^{1/2}\)). Hydrodeoxygenation rates for MTHF are reported to increase with \([\text{H}_2]\) for Ni3P on USY at 573 K27 and decrease with \([\text{H}_2]\) \((r \sim [\text{H}_2]^{-1/2})\) for Ni3P supported on SiO2.28 Yet neither of these publications report turnover rates for 2C−O and 3C−O bond rupture specifically. Related investigations of C−C bond rupture rates in hydrocarbons32−34 and C−O bond rupture in oxygenates35 on transition metal catalysts have shown that C−C or C−O bonds cleave in dehydrogenated species, which cause \(r_{\text{C-C}}\) and \(r_{\text{C-O}}\) to depend on \([\text{H}_2]\) in ways that reflect the total number of H atoms removed from the reactant and the catalyst surface in quasi-equilibrated steps preceding C−C or C−O bond rupture. The independence of χ as CO* coverage changes (Figure 4), however, indicates that 2C=O and 3C=O bond rupture occurs on identical sites, which shows that the effect of \([\text{H}_2]\) on χ values must originate from differences in the content of their transition states instead of differences in the extent (Figure 4), suggesting that both reactions occur at the same active site regardless of the surface composition or structure.

Measured \(r_{2C-O}\) and \(r_{3C-O}\) values decrease with increasing \([\text{H}_2]\) on Ni, Ni12P5, and Ni3P catalysts (Figure 5). On Ni12P5 and Ni, 2C−O bond rupture shows an inverse first-order dependence in \([\text{H}_2]\) (i.e., \(r_{2C-O} \sim [\text{H}_2]^{-1}\)), while 3C−O bond rupture shows an inverse half-order dependence (i.e., \(r_{3C-O} \sim [\text{H}_2]^{-1/2}\)). H2 kinetics for Ni3P are similar to those on Ni12P5 and Ni at moderate H2 pressures (<0.75 MPa \([\text{H}_2]\)), but rates are more inhibited by \([\text{H}_2]\) \((r_{2C-O} \sim [\text{H}_2]^{-3/2})\) and \(r_{3C-O} \sim [\text{H}_2]^{-1/2}\) at higher pressures.

The observed surface species and effects on \([\text{H}_2]\), \([\text{MTHF}]\), and [CO] suggest that C−O bond rupture occurs in oxygenate intermediates following quasi-equilibrated C−H bond cleavage.

2.3. Proposed Elementary Steps and Derived Rate Expression. Scheme 2 shows a series of elementary steps that lead to C−O bond rupture within MTHF on Ni, Ni12P5, and Ni3P catalysts. These steps and their assumed reversibilities lead to rate equations that are consistent with the rate measurements shown in Figures 3, 4, and 5 and with the quasi-equilibrated adsorption and dehydrogenation of MTHF (i.e., \(\eta \rightarrow 1\) in eq 2, Figure S5). Dissociative adsorption of H2 to form H* (Step 2.0), molecular adsorption of MTHF (Step 2.1), and sequential dehydrogenation of the C atoms of the cleaved 2C−O and 3C−O bonds (Steps 2.2a, 2.3a, and 2.2b) are assumed to be quasi-equilibrated based on the observed quasi-equilibrated nature of MTHF dehydrogenation (Figure S5). The adsorption of CO (Step 2.6) is assumed to be quasi-equilibrated as effects of CO pressure on rates are fully reversible. The ruptures of 2C−O (Step 2.4a) and 3C−O (Step 2.3b) bonds are both sole kinetically relevant steps for the two pathways shown in Scheme 2, and the C atoms of these bonds are assumed to be fully dehydrogenated prior to C−O cleavage, based on the observed dependence of rates on the amount of displaced H*.
Scheme 2. Proposed Elementary Steps for ²C−O (2.1-2.5a) and ³C−O (2.1-2.4b) Bond Rupture in MTHF on Ni₂P, Ni₁₂P₅, and Ni Nanoparticles

[Figure 5] A series of steps follow the kinetically relevant steps (2.4a and 2.3b) to form the primary products, 2-pentene-4-one and pentanal, indicated in Figure 1. This mechanism provides physical understanding of C−O bond rupture, and the rate constants, both measured and calculated using DFT, provide additional insights and corroboration of this mechanism.

Intrinsic activation enthalpies (ΔH_{act}) and reaction enthalpies (ΔH_{rxn}) for C−O cleavage pathways within Scheme 2 and others were calculated using DFT to validate the proposed mechanisms and to estimate apparent activation enthalpies (ΔH^‡) for C−O bond rupture for comparisons to experimentally determined ΔH^‡ values (shown in section 2.5). Gaseous MTHF can adsorb and react with an unoccupied site on the NiₓP(001) surface to undergo ²C−O bond cleavage (H_{act} = 140 kJ mol⁻¹) or ³C−O bond cleavage (H_{act} = 139 kJ mol⁻¹) (Figure 6); however, these barriers are much greater than those to dehydrogenate the ²C (H_{act} = 85 kJ mol⁻¹) or ³C atoms (H_{act} = 111 kJ mol⁻¹). Similarly, the barrier to remove the second H atom from the ²C atom (H_{act} = 71 kJ mol⁻¹) is lower than that for ²C−O activation (H_{act} = 105 kJ mol⁻¹) of that intermediate. The number and lengths of the bonds that each calculated transition-state forms to the surface indicate that fully dehydrogenated intermediates are more strongly bound to the surface than partially dehydrogenated intermediates (Figure S11). Reverse barriers for C−H activation are lower than the forward barriers for C−O cleavage, consistent with quasi-equilibrated C−H cleavage. Comparisons between the barriers for C−H and C−O cleavage confirm that C atoms are fully dehydrogenated in a series of quasi-equilibrated steps prior to C−O bond rupture, which supports the mechanism proposed in Scheme 2 and the composition of the reactive intermediates inferred from kinetic data (section 2.2).

The activation enthalpy barriers relative to a bare NiₓP(001) surface (ΔH^‡) increase as MTHF is dehydrogenated (from 144 to 162 to 182 kJ mol⁻¹ for ²C−O cleavage and from 143 to 148 kJ mol⁻¹ for ³C−O cleavage), indicating that it is enthalpically easier to activate C−O bonds in less dehydrogenated intermediates. These transition states, however, differ in the number of quasi-equilibrated C−H activations that precede them, and each C−H activation in this series results in the formation of ¹/₂H₂(g) because H₂ dissociation and reformation occur at rates much greater than C−O activation (i.e., Step 2.0 is quasi-equilibrated, as indicated by the equilibration between MTHF and MF at all conditions, Figure S5). Enthalpy barriers for C−O cleavage do not reflect the entropy gain upon dehydrogenation and subsequent H₂(g) formation, and these entropic effects will favor C−O cleavage in extensively dehydrogenated intermediates. Free-energy barriers (ΔG^‡) that appropriately account for entropy at relevant temperatures (543 K) show that C−O bond rupture in intermediates with fully dehydrogenated C atoms have the lowest ΔG^‡ values for both ²C−O and ³C−O cleavage (Figure 6).
which suggests that C–O cleavage occurs after complete dehydrogenation of the C atom, consistent with Scheme 2. The enthalpic preference for C–H cleavage over C–O cleavage, the entropic effects associated with dehydrogenation, and the preferential C–O cleavage following complete dehydrogenation of the C atom is also shown by DFT calculations on the Ni12P5 and Ni surfaces (Figures 7 and S12, respectively).

Scheme 2 indicates that rates of C–O bond rupture ($r_{C-O}^C$ and $r_{C-O}^O$) are proportional to the concentration of the MTHF-derived reactive intermediates specific to each C–O bond rupture pathway

$$r_{C-O} = k_{C-O} \cdot [C_4H_{8+m}O^*]$$

(3)

Here, $m$ is the number of C and O atoms the $^2$C is bound to prior to $^2$C–O bond rupture (i.e., 2 or 3) and $k_{C-O}$ is the intrinsic rate constant for $^2$C–O bond rupture in $C_4H_{8+m}O^*$ intermediates derived from MTHF by quasi-equilibrated dehydrogenation steps (e.g., $^2$C–O bonds cleave in $C_4H_4O^*$, which is formed by removing 2 H atoms from the $^2$C atom). A rate expression for $^2$C–O bond rupture in MTHF-derived intermediates is derived by applying the pseudo-steady-state hypothesis to [$C_4H_6mO^*$] and treating adsorption and dehydrogenation steps as quasi-equilibrated as prescribed by Scheme 2

$$r_{C-O} = k_{C-O} \cdot [K_{CH}] \cdot [MTHF] \cdot [K_O[H_2]]^{1/2} \cdot [C_4H_{8+m}O^*]$$

(4a)

$$r_{C-O} = k_{C-O} \cdot [K_{CH}] \cdot [MTHF] \cdot [K_O[H_2]]^{1/2} \cdot [C_4H_{8+m}O^*]$$

(4b)

where rate ($k$) and equilibrium ($K$) constants are defined in Scheme 2 and $[C_4H_{8+m}O^*]$ is the concentration of unoccupied sites for $^2$C–O bond rupture.

An expression for $[C_4H_{8+m}O^*]$ is obtained by invoking a site balance for all potential surface species and applying the quasi-equilibrium assumptions as before

$$[L] = [\ast] + \sum_{i=0}^{n=4} \left( \prod_{j=1}^{i} K_{CH,j} \right) \cdot [H_2]^{-(i/2)} \cdot [K_{MTHF}]^{1/2} \cdot [C_4H_{8+m}O^*]$$

(5)

Here, $\prod_{j=1}^{i} K_{CH,j}$ is the product of equilibrium constants for each sequential dehydrogenated MTHF-derived species and CO$^*$ as most abundant surface intermediates (MASI). The enthalpy differences between adsorbed MTHF ($C_4H_{10+O^*}$) and the partially dehydrogenated species ($C_4H_{10+O^*}$) that form via quasi-equilibrated C–H bond rupture (Figures 6 and 7) suggest that the coverage of $C_4H_{10+O^*}$ (i.e., $K_{CH}[MTHF]$) will be much greater than those of all dehydrogenated MTHF-derived species. This conclusion is also supported by reaction orders in [H$_2$] for $r_{SC-O}$ and $r_{2C-O}$ that are constant from 1 to 4 MPa H$_2$ on Ni and from 0.125 to 6 MPa H$_2$ on Ni$_{12}$P$_5$ nanoparticles (Figure 5), which suggests that the H content and coverage of all MASI do not change in response to a near 50-fold increase in [H$_2$]. The decrease of the $r_{SC-O}$ and $r_{2C-O}$ dependence on [H$_2$] by one-half order at [H$_2$] greater than 0.75 MPa over 12 nm Ni$_{12}$P$_5$ clusters (Figure 5) indicates that H$^*$ becomes the MASI at such conditions. These assertions on the nature of the MASI, along with eqs 4a, 4b, and 5, yield complete rate expressions for $^2$C–O bond rupture in terms of gas-phase species

$$r_{C-O} = \frac{k_{C-O} \cdot [K_{CH}] \cdot [MTHF] \cdot [K_O[H_2]]}{(1 + K_{CH} \cdot [MTHF] + [K_O[H_2]]^{1/2} + [K_{CO}[CO]])}$$

(6a)
The derived rate expressions account for the effects of [MTHF] (Figure 3), [H₂] (Figure 5), and [CO] (Figures 4, S3, and S4) on \( \Delta^\circ \)O bond rupture rates during MTHF hydrodeoxygenation. The rate expressions in eqs 6a and 6b describe rates on all measured materials as shown by the comparison of measured turnover rates over a wide range of conditions (Figures 3–5) and predicted rates obtained by regression of rate constants for each material (Figure S13).

These experimental and computational results show that \( \text{O} \) bond rupture occurs in \( \text{C}_6\text{H}_{10}\text{O}^* \) and \( \text{C}_6\text{H}_{10}\text{O}^* \) species, respectively, following quasi-equilibrated dehydrogenation of the \( \text{C} \) atom on surfaces covered by a mixture of CO*, \( \text{C}_6\text{H}_{10}\text{O}^* \), and H*. Measurements and calculations described in section 2.4 further probe the chemical nature and the structure of the active sites for \( \text{C} \)–\( \text{O} \) bond rupture.

### 2.4. Identity and Chemical Nature of C–O Bond Rupture Active Sites

Figure 8 shows potential binding sites on Ni(111), Ni₁₂P₃(001), and Ni₃P(001) surfaces (Figure 5). The increase in H* coverage on Ni₃P may be facilitated by the relatively low CO* coverages on that surface (compared to Ni or Ni₁₂P₃). In comparison, transition-state structures on the Ni₂P₃(001) surface bind to the two different 4-fold Ni hollows at the center and corners of the unit cell (Figure 8, M₄a and M₄b). \( \text{C} \)–\( \text{O} \) and \( \text{C} \)–\( \text{O} \) bonds rupture occur preferentially on the M₄b site, and \( \text{C} \)–\( \text{O} \) bond rupture is 24 kJ mol⁻¹ enthalpically more favorable than \( \text{C} \)–\( \text{O} \) bond rupture (Figure 7), inconsistent with the measured enthalpy differences discussed in section 2.5; however, the M₄b site is also the preferred adsorption site for CO* on Ni₂P₃(001) surface and has a significantly greater \( Q_{CO} \) relative to M₄a (Q_{CO} of 204 and 69 kJ mol⁻¹, respectively). The large values of \( Q_{CO} \) on M₄b sites suggest that CO* binds to those sites irreversibly, leaving M₄a sites to catalyze both pathways and leading to DFT-predicted \( \Delta H^\circ \) values for \( \text{C} \)–\( \text{O} \) bond rupture pathways (Figure 7, blue) that are more consistent with the measured values, discussed in section 2.5. CO* bound irreversibly to M₄a sites had little effect on the reactivity of M₄b sites, as shown by CO* cleavage calculations with a spectating CO* on M₄b (Figure S14).

DFT calculations predict \( Q_{CO} \) to be much larger than MTHF on all three surfaces (Table S3), which is consistent with the observation that even at low [CO] CO significantly inhibits \( \text{C} \)–\( \text{O} \) cleavage, as described in section 2.1. However, the small values of \( Q_{MTHF} \) are not consistent with the observed sublinear dependence of \( r_{\text{C} \rightarrow \text{O}} \) on [MTHF] (Figure 3) or the spectroscopic evidence for the coexistence of \( \text{C}_6\text{H}_{10}\text{O}^* \) and CO* during catalysis (Figure S7). Notably, the revised Perdue–Burke–Ernzerhof (RPBE) functional used here underestimates \( Q \) of physisorbed species, such as MTHF, because it does not account for attractive van der Waals

\[
\frac{r_{\text{C} \rightarrow \text{O}}}{[L]} = \frac{k_{\text{b}}K_{\text{ads}} K_{\text{r}} [\text{MTHF}] (K_{\text{r}} [\text{H}_2])^{1/2}}{(1 + K_{\text{r}}[\text{MTHF}] + (K_{\text{r}} [\text{H}_2])^{1/2} + K_{\text{CO}} [\text{CO}])}
\]

(6b)

\[
\Delta^\circ \text{H}^\circ = 133, 118, 94, 90, 182, 178
\]

\[
\Delta^\circ \text{S}^\circ = -56, -101, -74, 85, -71, 85
\]

\[
\Delta^\circ \text{G}^\circ = 163, 63, 134, 44, 212, 132
\]
interactions. Incorporating these interactions through empirical descriptions (DFT-D3) or by using exchange-correlation functionals that explicitly include van der Waals terms (e.g., optB88-vD, optB86-vD, vdW-DF2) increase Q_{MTHF} on Ni, Ni_{12}P, and Ni_{2}P surfaces by more than 30 kJ mol^{-1} (Table S3). Employing vdW-based methods may more accurately predict MTHF adsorption (i.e., positive heats of adsorption) while simultaneously overpredicting binding energies for chemisorbed species such as H^{+} and CO^{+}.\textsuperscript{48} Dispersive forces are not included in calculations for energy and enthalpy barriers of elementary steps discussed in section 2.3, because they overpredict binding energies for chemisorbed species. Comparisons between enthalpy and energy barriers for elementary steps in the absence of dispersive forces are still relevant, while the absolute values have an offset from underestimated binding energy of MTHF.

Direct observation of adsorbates provides additional information about the chemical nature (i.e., metallic and acidic) of the catalyst surface. Measured vibrational frequencies for adsorbed CO (Figure S7) show a red shift in ν(CO) from 2142 cm\(^{-1}\) in the gas phase to 2035 cm\(^{-1}\) on 10 nm Ni_{12}P and 2025, 1909, 1833, and 1710 cm\(^{-1}\) on 4 nm Ni, which reflects electron back-donation that weakens the C–O bond. The red shift in ν(CO) over Ni is more significant than that for Ni_{12}P, and is consistent with previous spectroscopic studies of adsorbed CO on Ni, Ni_{12}P, and Ni_{2}P surfaces,\textsuperscript{47} which suggests a lesser extent of electron back-donation into the C–O bond on Ni_{12}P and Ni_{2}P relative to Ni. Previous DFT calculations indicate a small transfer of charge from Ni to P (0.06 e\textsuperscript{-}) in Ni_{12}P,\textsuperscript{46} producing Lewis acid sites (i.e., Ni\textsuperscript{4+}) that decrease the extent of electron back-donation from Ni atoms to the C–O bond relative to Ni atoms in Ni nanoparticles while still retaining the metallic properties demonstrated by adsorbed CO.

Prior publications have implicated Brønsted\textsuperscript{16,18,19,51,49} or Lewis\textsuperscript{15,16,19,49} acid sites formed upon introduction of P atoms in reactions that cleave C–O bonds within oxygenates in the presence of H\(_{2}\) yet it is not clear that these sites activate C–O bond rupture. In situ FTIR spectra obtained while cofeeding pyridine (C\(_{5}\)H\(_{5}\)N) with MTHF and H\(_{2}\) (Figure S15; 1 kPa MTHF, 80 kPa H\(_{2}\), 15 kPa He, 543 K) show only present on 12 nm Ni_{2}P. Features of adsorbed C\(_{5}\)H\(_{5}\)N are absent in the absence of dispersive forces are still relevant, while the absolute values have an offset from underestimated binding energy of MTHF.

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Figure 10 shows that both r\textsubscript{2C–O} and r\textsubscript{3C–O} decrease in proportion to NH\(_{3}\) pressure ([NH\(_{3}\)]; r\textsubscript{C–O} ∝ [NH\(_{3}\)]\textsuperscript{-1}) when NH\(_{3}\) is introduced with the reactants (5–350 kPa NH\(_{3}\), 5 kPa MTHF, 0.25 MPa H\(_{2}\), 543 K), which indicates that the ensemble of Ni atoms that facilitate C–O bond rupture on Ni\(_{12}P\) and Ni\(_{2}P\) can be occupied and inhibited by the adsorption of a single NH\(_{3}\) molecule at the atop position of one Ni atom (M\(_{1}\)) within the active ensemble (M\(_{0}\) or M\(_{4}\)) on Ni\(_{2}P\) and Ni\(_{12}P\) surfaces, respectively (Table S2). Site requirements for all adsorbates (H\(^{+}\), CO\(^{+}\), NH\(_{3}\)^{+}, and C\(_{2}\)H\(_{4}\)O\(^{+}\) are identical between each C–O bond rupture pathway on Ni\(_{12}P\) and Ni\(_{2}P\), which is consistent with the assumption that C–O bond rupture occurs through a single-
Table 1. Measured and Predicted Activation Enthalpies (kJ mol⁻¹) for ²C–O and ³C–O Bond Rupture Pathways on C₅H₁₀O*-Covered Ni, Ni₁₂P₅, and Ni₂P Surfaces (ΔHCHOOO⁻) and Their Differences (ΔΔHSC–SC⁻⁻)

<table>
<thead>
<tr>
<th>catalyst</th>
<th>C₅H₁₀O* (ΔHCHOOO⁻)</th>
<th>C₅H₁₀O* (ΔHCHOOO⁻)</th>
<th>C₅H₁₀O* (ΔHCHOOO⁻)</th>
<th>C₅H₁₀O* (ΔHCHOOO⁻)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>measured</td>
<td>predicted</td>
<td>measured</td>
<td>predicted</td>
</tr>
<tr>
<td>12 nm NiP⁺</td>
<td>193 ± 9</td>
<td>170 ± 9</td>
<td>178 ± 9</td>
<td>144 ± 9</td>
</tr>
<tr>
<td>19 nm Ni₁₂P₅⁺</td>
<td>180 ± 5</td>
<td>155 ± 5</td>
<td>90 ± 9</td>
<td>79 ± 9</td>
</tr>
<tr>
<td>5 nm Ni₂P⁺</td>
<td>144 ± 12</td>
<td>134 ± 12</td>
<td>90 ± 9</td>
<td>79 ± 9</td>
</tr>
<tr>
<td>4 nm Ni⁺</td>
<td>119 ± 8</td>
<td>130 ± 4</td>
<td>118 ± 16</td>
<td>166 ± 11</td>
</tr>
</tbody>
</table>

*aMeasured values extracted from Figures 11 and S18. *bPredicted values over Ni(111), Ni₁₂P₅(001), and Ni₂P(001) at 543 K. *cMeasured at 0.125 MPa H₂. *dMeasured at 1 MPa H₂.

The site mechanism as described by eqs 6a and 6b, NH₃ also inhibits C–O bond rupture rates proportionally over Ni nanoparticles, which do not have Lewis or Brønsted acid sites present based on in situ measurements with pyridine (Figure S15); therefore, the spectroscopic and kinetic evidence alone cannot show that the active site for C–O bond rupture on Ni₁₂P₅ and Ni₂P is acidic. Differences in selectivity during C–O bond rupture reactions have previously been attributed to adjustments in acid site concentration by manipulating metal to phosphorus ratio¹⁸ or operating in the presence of mineral⁵⁵ or solid⁵⁶,⁵⁷ acids. Here, measured values for γ are independent of [NH₃] on Ni, Ni₁₂P₅, and Ni₂P catalysts, which indicates that the addition of P atoms adjusts the electronic structure of the Ni atoms rather than creating a second type of active site. A single active site for both C–O bond rupture pathways is consistent with predicted transition states for "C–O bond rupture, H*, CO*, and NH₂* all exclusively bound to Ni atoms instead of P atoms (Figure 9 and Table S3). The following section uses quantitative comparisons of measured activation enthalpies under different surface coverages and DFT-derived activation barriers to infer mechanistic details of C–O bond rupture pathways in MTHF.

2.5 Comparisons of Activation Enthalpies for C–O Bond Rupture on Ni, Ni₁₂P₅, and Ni₂P Nanoparticles with Different Surface Coverages. Experimental and computational results show agreement for the proposed mechanism for "C–O bond rupture within MTHF over Ni, Ni₁₂P₅, and Ni₂P nanoparticles at active sites comprised of Ni ensembles; however, the trends in selectivities and active site properties can be understood in greater detail by analysis of the changes to measured activation enthalpies that result from differences in the MASI present during catalysis. Kinetic measurements indicate that elementary steps leading to C–O bond rupture (Scheme 2, 2.1–2.3a and 2.1–2.2b) are quasi-equilibrated. Transition-state theory (TST) provides a hypothetical equilibrium between a transition-state complex and the preceding reactive intermediate (e.g., C₅H₁₀O* and C₅H₁₀O*⁻). These combined equilibria can be expressed as

\[ C₅H₁₀O* + \text{H}_2 \rightleftharpoons \frac{m}{2} \text{H}_2 + mC₅H₁₀O*⁻ \]  

where \( K_{\text{eq},\text{c–o}} \) is the equilibrium constant for forming the "C–O bond rupture transition state ("C₅H₁₀O*⁻) and a stoichiometric amount of gas-phase H₂ from MTHF and a bare surface. The full rate expression can be expressed in terms of the pressures of gas phase species and \( K_{\text{eq},\text{c–o}} \) using the conventions of TST and the quasi-equilibrated nature of eq 7 to find

\[ \frac{p_{\text{C–O}}}{[L]} = \frac{k_T}{h} K_{\text{c–o}}^{\text{a}} \text{[MTHF][H}_2]^{(2–m/2)} \]  

This expression describes reactions on a predominantly bare surface (i.e., * as MASI) but can be modified to describe reactions occurring on CO*-*, H*-*, or C₅H₁₀O*-covered surfaces as shown in the Supporting Information (Section S2).

Table 1 displays both the experimental and the computational results for ΔH° for a C₅H₁₀O*-covered surface. Experimental values for \( K_{\text{c–o}}^{\text{a}} \) and subsequently ΔH° are determined from measured turnover rates for ³C–O and ²C–O bond rupture as functions of inverse temperature over Ni, Ni₁₂P₅, and Ni₂P nanoparticles (Figures 11 and S18, 5 kPa MTHF, 0.125–1 MPa H₂; 473–583 K).

Figure 11. Transition-state equilibrium constants (\( K^\circ \)) for ²C–O (red circles) and ³C–O (blue triangles) bond rupture pathways as a function of inverse temperature on silica-supported 12 nm Ni₅P (5 kPa MTHF, half filled, 0.125 MPa H₂; filled, 1 MPa H₂).
Rates measured across the Ni₅, Ni₁₂P₅, and Ni₅P nanoparticles at the same conditions (e.g., Figure S1, 1 MPa H₂, 5 kPa MTHF, and 543 K) indicate that the turnover rates for C–O bond rupture over Ni₁₂P₅ are greater than those over Ni₅P; however, the reaction conditions (e.g., T, [CO]) strongly influence relative rates. Comparisons with previous studies that show greater turnover frequencies occur over the more metal-rich phases of phosphides including C–O bond rupture of guaiacol over Ni₁₂P₅ compared to Ni₅P at differential conversion¹⁸ and furan over SiO₂-supported Ru₅P and Ru₁₂P,¹² but direct comparison of materials needs to account for all reaction conditions. The decrease in C–O bond rupture rates with increasing P:Ni ratio under conditions with a C₅H₁₀O* surface (Figure S1, 1 MPa H₂, 5 kPa MTHF, and 543 K) is also consistent with the increase in measured ΔH‡ with increasing P:Ni on C₅H₁₀O* surfaces and greater predicted ΔH‡ over Ni₅P(001) compared with Ni₁₂P₅(001) (Table 1). While absolute values for ΔH‡ deviate between experimental and computational results, the difference in activation enthalpies between the ²C–O and the ³C–O bond rupture pathways (ΔΔH₂C–3C*) is consistent for the Ni₁₂P₅ and Ni₅P materials (Table 1). Positive values for ΔΔH₂C–3C* indicate ³C–O bond rupture is more enthalpically favorable over ²C–O bond rupture, and ΔΔH₂C–3C* increases with P: Ni ratio, similar to χ (Figure 2). These systematic increases in ΔΔH₂C–3C* and χ values with the P: Ni ratio may result from differences in binding modes and orientation of intermediates over Ni, Ni₁₂P₅, and Ni₅P surfaces, as suggested by the predicted transition-state structures (Figure 9). We are currently conducting in situ infrared spectroscopy to determine the differences between the binding modes of MTHF-derived adsorbates on Ni, Ni₁₂P₅, and Ni₅P surfaces.

Previous studies on transition metal surfaces show that trends in the binding energies of hydrocarbons, alcohols, thiols, and amino acids can be related to the adsorption energies of chemisorbed fragments such as CH₂*, OH*, SH*, and NH₂*.⁵⁸ As shown in Figure 9, C–O bond cleavage transition states interact with the catalyst surfaces through the C and O atoms of the cleaved bond. These transition states can be represented by a simpler model, in which the C and O atoms are constrained to their transition-state positions and all substituents bound to these C and O atoms are replaced with H atoms (i.e., coadsorbed CH₂* and OH* replace the ²C–O and coadsorbed CH₂* and OH* replace the ³C–O⁻). Alternatively, the pair of fragments that represents each transition state can be relaxed and their enthalpies calculated at their most stable binding sites. Figure 12 shows that either method for calculation provides differences in adsorption enthalpies between coadsorbed CH₂* and OH* and coadsorbed CH₂* and OH* (ΔΔH₂C–3C*) that are negative for Ni (indicating favorable ²C–O bond cleavage) and positive for Ni₁₂P₅ and Ni₅P (indicating favorable ³C–O bond cleavage). Qualitatively, these comparisons of these values for simple analogues for the more complex C–O bond cleavage transition states show that calculations for the stable binding modes of CH₄* and OH* can provide estimates for the values of ΔΔH₂C–3C* that capture the preference for a given metal or metal phosphide to cleave hindered or unhindered C–O bonds in MTHF (and likely other oxygenates) shown in the full transition-state models (Figure 12). Therefore, the binding energies of simple adsorbates (CH₂* and OH*) can be calculated to rapidly screen C–O cleavage selectivity on complex catalytic surfaces (such as \( \frac{\Delta \Delta H}{3C-O} \) and \( \frac{\Delta \Delta S}{3C-O} \) for all \(^{22}C-O\) cleavage transition states (Figure 9 and S11) on Ni(111), Ni(100), Ni₅P(001), and Ni₁₂P₅(001)). Calculated \( \Delta \Delta G^\ddagger \) values predict that \(^{22}C-O\) selectivity (\( \chi = 0.2 \), at 1 MPa H₂) is lower on M₅₆ sites of Ni₁₂P₅(001) than on the

**Figure 12.** DFT-predicted differences in activation enthalpies (ΔΔH₂C–3C*) (black) and differences in adsorption enthalpies for CH₂* and OH* coadsorbed in binding modes that match the transition state (red) and CH₄* and OH* coadsorbed in their most stable binding sites (blue) (\( \chi = 1 \) for \(^{22}C-O\) and 2 for \(^{32}C-O\)).

**Figure 13.** DFT-predicted ratios of \(^{22}C-O\) to \(^{32}C-O\) bond rupture rates (\( \chi \)) on Ni(111) (black dashed line), Ni(100) (black solid line), Ni₁₂P₅(001) (red dashed line), and Ni₅P(001) (blue dashed line) surfaces, and measured values of \( \chi \) as a function of H₂ pressure for 4 nm Ni (black solid diamonds), 12 nm Ni₁₂P₅ (blue solid triangles), 5 nm Ni₁₂P₅ (green solid right-facing triangles), and 19 nm Ni₅P (red solid squares) at 5 kPa MTHF and 543 K. Values calculated using eqs 1 and 9 with DFT-derived values of ΔH‡ and ΔS‡ for all \(^{22}C-O\) cleavage transition states (Figure 9 and S11) on Ni(111), Ni(100), Ni₁₂P₅(001), and Ni₅P(001).
Ni,P(001) surface, which agrees with differences in measured \( \chi \) values in Figure 13. Predicted values of \( \Delta H_{\text{C-O}} \) (Table 1) and \( \chi \) (Figure 13) over Ni are significantly different from the measured values of each, which may result from C–O bond rupture occurring on sites other than the (111) or (100) surfaces (e.g., corner or edge sites). Overall, the trends in predicted C–O bond rupture selectivities are consistent with the trends in measured values of \( \chi \) (Figure 13) and measured \( \Delta H_{\text{C-O}} \) (Table 1): the selectivity toward 3C–O bond rupture increases with increased ratios of P:Ni.

Measured \( \Delta H^r \) values that differ between lower and higher reaction temperatures (Figure 11) reflect differences between the MASIs that exist under these conditions. The value of \( \Delta H^r \) increases from 23 to 193 kJ mol\(^{-1}\) for 2C–O bond rupture and from 18 to 170 kJ mol\(^{-1}\) for 3C–O bond rupture over 12 nm Ni,P (Figure 11 and Table S4) as the temperature increases above 543 K and the \( [H_2] \) decreases from 1 to 0.125 MPa. This increase in \( \Delta H^r \) values combined with changes in the dependence of rates on \([H_2]\) suggests that the MASIs change from \( H^* \) to \( C_2H_4O^* \). The increase in \( \Delta H^r \) is consistent also with values for Q\(_{\text{MTHF}}\) that are predicted to be greater than that of Q\(_{\text{H2}}\) over Ni,P(001) when dispersion forces are included (Table S3). Upon introducing CO (5 kPa) with the reactants over Ni,P and Ni nanoparticles (Figure S18), values for \( \Delta H^r \) for both C–O bond rupture pathways increase as the result of a change from \( C_2H_4O^* \) to CO* as the MASI. The changes in \( \Delta H^r \) with temperature and rate dependence with \([H_2]\) and [MTHF] over Ni, Ni,P, and Ni,P nanoparticles occur at the same temperature or pressures for both C–O bond rupture pathways, which suggests adsorbates (H*, \( C_2H_4O^* \), and CO*) possess the same binding energy for both 2C–O and 3C–O bond rupture active sites. Collectively, these observations suggest that the same site catalyzes both C–O bond rupture pathways on each of these catalysts.

Differences in \( \Delta H^r \) values that result from differences in MASIs should be equivalent for 2C–O and 3C–O bond rupture if a single site catalyzes both pathways as demonstrated by 12 nm Ni,P and 4 nm Ni (Table S5). Neither 5 nor 19 nm Ni,P nanoparticles show equivalent changes in \( \Delta H^r \) for 2C–O and 3C–O bond rupture as the MASIs transitions from \( C_2H_4O^* \) to CO*. This may reflect a difference between the interactions between CO* and the 2C–O and 3C–O transition states, as demonstrated for CO hydrogenation over Ru.\(^{62}\) However, additional studies over Ni,P nanoparticles with narrower size distributions need to confirm this hypothesis. While Ni,P nanoparticles do not show equivalent changes in \( \Delta H^r \) values between 2C–O and 3C–O bond rupture with the MASIs transitions, the consistency between measured and predicted transition-state composition, C–O bond rupture mechanism, active site chemical nature, and selectivity provides strong evidence that the same ensembles of Ni atoms catalyze both 2C–O and 3C–O bond rupture on Ni, Ni,P, and Ni,P catalysts.

3. CONCLUSIONS

Turnover rates for the hydrogenolysis of 2C–O and 3C–O bonds within MTHF were measured as a function of MTHF, H\(_2\), and CO pressure over SiO\(_2\)-supported Ni, Ni,P, and Ni,P catalysts. These kinetic data were combined with DFT calculations on the low-energy surfaces of these catalysts to determine the reaction mechanism and the nature of the active sites for C–O bond cleavage on metal phosphide catalysts. H\(_2\) pressure inhibits 3C–O and 2C–O bond cleavage rates to different extents, and the degree of H\(_2\) inhibition suggests that the transition states for these pathways have lost 1 or 2 H atoms from gas-phase MTHF, respectively. Consequently, the ratio of 2C–O to 3C–O bond rupture rates increases with H\(_2\) pressure across Ni, Ni,P, and Ni,P catalysts. Predicted enthalpy barriers for C–O and C–H bond rupture within MTHF intermediates over Ni, Ni,P, and Ni,P surfaces indicate “C–H bond rupture is at least \( \sim 30 \) kJ mol\(^{-1}\) more favorable than “C–O bond rupture until the “C is fully dehydrogenated. Thus, MTHF undergoes quasi-equilibrated dehydrogenation steps that remove all hydrogen atoms from “C before the kinetically relevant “C–O bond rupture, which is consistent with quasi-equilibrium between MTHF, MF, and H\(_2\) as well as the measured effect of H\(_2\) pressure on rates.

Site requirements are identical for 2C–O and 3C–O bond rupture across Ni, Ni,P, and Ni,P catalysts as shown by constant C–O cleavage ratios over wide ranges of the pressures for CO, NH\(_3\), and MTHF. Comparisons of predicted adsorption energies for intermediates and measured differences in activation enthalpies of H\(_2\), CO\(_2\), and C\(_2\)H\(_4\)O-covered surfaces indicate both C–O bond rupture pathways are catalyzed by ensembles of 3–4 Ni atoms on Ni, Ni,P, and Ni,P catalysts. This conclusion indicates that Brensted acid sites formed by the incomplete reduction of P–OH groups are not catalytically relevant for the elementary steps described here. Measured and predicted activation enthalpies are lower for 3C–O bond rupture relative to 2C–O bond rupture (by \( \sim 34 \) kJ mol\(^{-1}\)) over Ni,P and Ni,P surfaces, which is consistent with the observation that the preference to selectively cleave 3C–O bonds over 2C–O bonds increases along with the P:Ni ratio of the catalyst. DFT predictions for Ni-terminated Ni,P(001) and Ni,P(001) surfaces reproduce these selectivity patterns, whereas P-terminated structures do not, which further indicates that ensembles of Ni atoms exposed on supported Ni,P and Ni,P nanoparticles are the active sites and surfaces. Furthermore, DFT calculations of CH\(_2\) and OH\(_2\) adsorption energies qualitatively predict C–O bond rupture selectivities on Ni, Ni,P, and Ni,P catalyst surfaces and suggest strategies for the rapid evaluation of complex catalysts for selective C–O cleavage.

The proposed mechanism, active site characteristics, and calculated energy and enthalpy barriers demonstrate that the temperature, H\(_2\) pressure, and P:Ni ratio of the catalyst ultimately control the turnover rates and selectivity between C–O bond rupture within oxygenates. Ni,P nanoparticles show greater resistance to CO poisoning than do Ni and Ni,P nanoparticles no matter whether the CO comes from the decarbonylation of aldehydes or is intentionally introduced. Ni,P catalysts also form significantly more fully deoxygenated products, which may be less desirable depending on the intended application of the product stream as fuels or high-value chemicals. Future studies inspecting the implementation of Ni,P and Ni,P catalysts for selective hydrogenolysis of oxygenates will need to balance the decrease in C–O bond rupture rates and increase in selectivity toward hindered C–O bond rupture with increasing P:Ni ratio while also considering additional functional groups present within bio-oil.

4. MATERIALS, METHODS, AND CHARACTERIZATION

4.1. Synthesis and Characterization of Supported Nickel and Nickel Phosphide Catalysts. 4.1.1. Synthesis of Silica Supported Nickel and Nickel Phosphide Nanoparticles. Nickel phosphide catalysts supported on high surface...
Table 2. Catalyst Composition and Nanoparticle Dispersion

<table>
<thead>
<tr>
<th>catalyst</th>
<th>(d_{\text{TEM}}) (nm)</th>
<th>mol % Ni</th>
<th>mol % P</th>
<th>mmol (\text{CO}_{\text{ads}})/mol Ni</th>
<th>mmol (\text{CO}_{\text{ads}})/gcat</th>
<th>Ni dispersion(^a) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Ni}_2\text{P})</td>
<td>12 ± 3</td>
<td>1.94</td>
<td>1.94</td>
<td>24</td>
<td>8</td>
<td>7.3</td>
</tr>
<tr>
<td>(\text{Ni}_{12}\text{P}_5)</td>
<td>19 ± 7</td>
<td>2.03</td>
<td>0.58</td>
<td>10</td>
<td>3.5</td>
<td>4.1</td>
</tr>
<tr>
<td>(\text{Ni}_3\text{P}_2)</td>
<td>10 ± 3</td>
<td>1.95</td>
<td>0.58</td>
<td>111</td>
<td>31</td>
<td>44.6</td>
</tr>
<tr>
<td>(\text{Ni}_{12}\text{P}_5)</td>
<td>5 ± 1</td>
<td>1.67</td>
<td>0.58</td>
<td>25</td>
<td>8.1</td>
<td>7.4</td>
</tr>
<tr>
<td>Ni</td>
<td>4 ± 1</td>
<td>1.96</td>
<td>0.00</td>
<td>25</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^a\)Surface area normalized average nanoparticle diameter determined from >300 nanoparticles. \(^b\)Elemental composition of samples determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) following digestion in strong acid solutions. \(^c\)CO uptake determined by adsorption isotherms at 298 K following a reductive treatment in 50 cm\(^3\) min\(^{-1}\) \(\text{H}_2\) at 673 K for 1 h and subsequent vacuum annealing at 673 K for 1 h. \(^d\)Ni dispersion calculated from CO uptake and the calculated preferred binding orientation for CO as 3- or 4-fold Ni hollows as described in the Supporting Information Table S3.

Production of CO was followed using a quadrupole mass spectrometer as a function of sample temperature using the QMS. Figure S26 shows reduction profiles indicating the formation of a nickel phosphide phase as opposed to separate nickel and phosphide phases, because the \(\text{Ni}_{12}\text{P}_3\) and \(\text{Ni}_2\text{P}\) reduction profiles are not a linear combination of the \(\text{Ni(NO}_3\text{)}_2\) and \(\text{H}_3\text{PO}_4\) reduction profiles, rather the presence of Ni decreases the reduction temperature of the phosphite group.

4.1.4. In Situ Fourier Transform Infrared Spectroscopy. Reactive intermediates and basic probe molecules (i.e., pyridine) formed or adsorbed during hydrolysis of 2-methyltetrahydrofuran (MTHF) over self-supporting pellets of \(\text{Ni}_2\text{P}\) and \(\text{Ni}_2\text{P}\) catalysts were observed using in situ transmission Fourier transform infrared (FTIR) spectroscopy using a custom-made transmission cell as previously described.\(^{65}\) Liquid reactants (MTHF and pyridine) were introduced using a syringe pump in a crossflow configuration with the primary gas flow (\(\text{H}_2\) and \(\text{He}\)) controlled by mass flow controllers. Prior to acquiring spectra, the catalyst was pretreated in situ to 673 K in flowing \(\text{H}_2\) at ambient pressure. Steady state measurements were obtained while flowing MTHF, \(\text{H}_2\), and He prior to introducing pyridine. The subsequent spectra analysis (e.g., subtraction of the gas-phase contribution, baseline correction, and data smoothing) was performed using OriginLab’s OriginPro software, as detailed in the Supporting Information Section S3.1.5.

4.2. Catalytic Rate Measurements. Rate and selectivity measurements were conducted in a packed bed reactor heated with a three-zone electrically heated furnace and pressurized (0.1–6.0 MPa) with a dome-loaded back-pressure regulator, which was controlled by an electronic pressure regulator. The reactor pressure was monitored upstream and downstream of the catalyst bed. Comparisons of these measurements showed that the pressure drop across the catalyst bed was less than 1% of the total pressure. Gas flow rates (\(\text{H}_2\), \(\text{CO}\), and \(\text{NH}_3\)) were controlled using mass flow controllers. The flow rates of liquids including MTHF and 2-methylfuran (MF) were controlled using a stainless steel syringe pump. All transfer lines downstream of the liquid inlet were heated to avoid condensation of the products or reactants.

Catalysts were pretreated in situ by heating to 673 K flowing \(\text{H}_2\) prior to all catalytic measurements. The effluent of the reactor was characterized using online gas chromatography equipped with a flame ionization detector and thermal conductivity detector. A complete list of these standards and calculations for sensitivity factors is shown in the Supporting Information (Section S3). Conversions were calculated on a...
carbon basis on the amount of carbon that appears in the products. The carbon and oxygen balance closes within ±10%. Turnover rates are normalized by the number of CO adsorption sites determined through chemisorption experiments described in section 4.1.2. Data reported as a function of conversion, reactant pressure, and temperature follow an initial break-in period (Figure S27), and turnover rates are corrected for the number of active sites lost over time, as described in the Supporting Information (Section S3.2.1).

4.3. Computational Methods. 4.3.1. Nickel and Nickel Phosphide Lattice Parameters and Surface Formation Energies. Periodic plane-wave density functional theory (DFT) calculations were performed using the Vienna ab initio simulation package (VASP). Plane waves were constructed using projector augmented-wave (PAW) potentials with an energy cutoff of 396 eV. 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, which should give a more accurate estimation of lattice parameters. Wave functions were converged to within 10−8 eV, and forces were computed using a fast Fourier transform (FFT) grid; the maximum force on each atom was converged to <0.01 eV Å−1. The unit cells of bulk Ni (space group Fm3m), NiP (space group P62m), and Ni12P5 (space group I4/m) were built based on crystallographic data, and the lattice parameters were then optimized using DFT. The optimized bulk lattice parameters for Ni (a = b = c = 3.52 Å), NiP (a = b = 5.87 Å and c = 3.37 Å) and Ni12P5 (a = b = 8.63 Å, c = 5.07 Å) were consistent with previous DFT studies and in close agreement with the measured values a = b = c = 3.52 Å, a = b = 5.86 Å and c = 3.38 Å, and a = b = 8.65 Å, and c = 5.07 Å. Further details of the bulk calculations are presented in the Supporting Information (Section S3.3). All Ni calculations were run spin polarized because of its ferromagnetic properties. Calculations showed less than 10−8 eV energy difference between spin- and nonspin-polarized calculations for Ni12P5(001) and Ni2P(001) calculations, consistent with previous DFT studies, so all calculations of Ni12P5(001) and Ni2P(001) surfaces were done without spin polarization. The closed-packed Ni(111) surface has the lowest surface formation energy (1008 kJ mol−1 nm−2) compared to Ni(100) (1142 kJ mol−1 nm−2) and Ni(110) (1211 kJ mol−1 nm−2), as well established for transition metals. For NiP and Ni12P5 surfaces, there is an alternation of planes in the z direction that have different Ni and P composition; scanning tunneling microscope (STM) images confirm the existence of two different terminations on NiP(001) single crystals. Our DFT calculations indicate that the Ni-rich terminations in NiP(001) and Ni12P5(001) have the lowest surface formation energies (823 kJ mol−1 nm−2 and 963 kJ mol−1 nm−2, respectively) (Figure S29). Thus, the Ni(111), Ni12P5(001), and NiP(001) surfaces were used, although the kinetic relevance of other surfaces cannot be eliminated. These surfaces were modeled with k-point meshes of 4 × 4 × 1 and 5 × 5 × 1 for Ni(111), Ni12P5(001), and NiP(001) surfaces, and the energies changed by less than 10−6 eV if larger k-point meshes were used, as further detailed in the SI (Section S3.3.2, Figures S28–30).

4.3.2. Energy Barrier Calculations. The revised Perdew–Burke–Ernzerhof (RPBE) functional was used for calculations of adsorption, reaction, and activation energies because it exhibits better performance in predicting adsorption energies in metal surfaces. Additional calculations (discussed in sections 2.3 and 2.4) were performed using optB88-vdW, optB86b-vdW, RPBE-D3BJ, and vdW-DF2 functionals which attempt to include dispersion interactions such as van der Waals forces. Wave functions were converged to within 10−6 eV, and structures were relaxed until all forces on unconstrained atoms were <0.05 eV Å−1. Gaseous species were modeled within 16 × 16 × 16 Å unit cells of vacuum. The Ni(111) catalyst surface was modeled as a 3 × 3 closed-packed periodic lattice with four layers in the orthogonal direction and a 10 Å vacuum between slabs; the bottom two layers were fixed in their bulk positions and the top two layers relaxed. After geometric convergence, a single-point calculation with a (8 × 8 × 1) k-point mesh was performed to determine the electronic energy. The NiP(001) and Ni12P5(001) surfaces shown in Figures 8 and S31 were modeled with two repeating units and a 10 Å vacuum in the z direction. The bottom repeat units (two atomic layers for NiP and four atomic layers for Ni12P5), Figure S31b and S31c) were fixed in their bulk positions, while all other atoms were relaxed.

Transition-state structures were obtained for each elementary reaction by using the nudged elastic band (NEB) method and the dimer method. The NEB method was carried out using 16 images, and wave functions were converged to within 10−6 eV. The maximum force on each atom was converged to <0.5 eV Å−1. These protocols provided an estimate of the reaction path and starting points for the structure and the reactive mode for each transition state. The dimer algorithm was then used with wave functions converged to within 10−6 eV, and the maximum force on each atom was converged to <0.05 eV Å−1.

Frequency calculations were performed on all optimized adsorbed species (all catalyst atoms were fixed) to estimate enthalpies (H) and free energies (G) for all reactants, products, and transition states at 543 K. For gaseous molecules, translational and rotational enthalpies and free energies were also computed from statistical mechanics. DFT-derived intrinsic enthalpy and free energy barriers (ΔH‡ and ΔG‡ respectively) and reaction energies (ΔHrxn or ΔGrxn) denote differences between a transition state or the product and the precursor reactant for that elementary step. Overall barriers (ΔH‡ and ΔG‡) are defined as the enthalpy or free energy of forming the partially dehydrogenated transition state [C2H10(10−2/2)O*] and a stoichiometric amount of gas-phase H2 from gas-phase MTHF (C5H10O) and a bare surface

\[ C_5H_{10}O(g) + \rightarrow [C_2H_{10}(10\rightarrow2/2)O^{\ast}] + \lambda H_2(g) \] (10)

\[ \Delta H^\ddagger = H^\ddagger + \lambda H_{H_2} - H_{MTHF} - H_g \] (11)

\[ \Delta G^\ddagger = G^\ddagger + \lambda G_{H_2} - G_{MTHF} - G_g \] (12)

Further details of the computational methods and equations for zero-point vibrational energies (ZPE), H‡ rot and G‡ rot from vibrational frequencies and H‡ trans, G‡ trans, and G‡ rot for gas-phase molecules are reported in the SI (Section S3.3.2).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.7b04403.
XRD diffractograms, CO adsorption isotherms, temperature-programmed reduction profiles, FTIR spectra, TEM images and nanoparticle size distributions, product selectivity distributions, approach to equilibrium, measured rate parity plot, predicted transition-state structures, free energy reaction coordinate diagrams, k-point mesh, deactivation profiles, and error propagation analysis (PDF)

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**Notes**

The authors declare no competing financial interest.

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