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## Compositional dependence of hydrodeoxygenation pathway selectivity for $\text{Ni}_{2-x}\text{Rh}_x\text{P}$ nanoparticle catalysts†

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Transition-metal phosphides (TMPs) are promising materials for biomass conversion processes, where their metal–acid bifunctionality provides active sites for the necessary variety of catalytic reactions (e.g., hydrogenation, hydrogenolysis, decarbonylation, and dehydration). Aiming to understand the catalytic performance of ternary TMP catalysts for the hydrodeoxygenation (HDO) reaction of biomass-derived oxygenates, a synthetic protocol was developed herein to prepare a series of ternary  $\text{Ni}_{2-x}\text{Rh}_x\text{P}$  nanoparticles (NPs), incorporating Rh into a parent  $\text{Ni}_2\text{P}$  template. This solution synthesis method allowed for a series of NPs to be prepared having precisely controlled compositions with similar morphology and crystalline structure. Detailed characterization of this series of  $\text{Ni}_{2-x}\text{Rh}_x\text{P}$  ( $x \leq 1$ ) NPs revealed that Rh substituted into the parent hexagonal crystal lattice of  $\text{Ni}_2\text{P}$  with concomitant expansion of the lattice. The influence of composition on the catalytic performance of silica-supported  $\text{Ni}_{2-x}\text{Rh}_x\text{P}$  ( $x = 0$  to 0.8, and cubic  $\text{Rh}_2\text{P}$ ) NPs was investigated through the HDO reaction of *m*-cresol. Whereas  $\text{Rh}_2\text{P}$  was more selective for direct deoxygenation relative to  $\text{Ni}_2\text{P}$ , increasing concentrations of Rh in  $\text{Ni}_{2-x}\text{Rh}_x\text{P}$  resulted in a decreased selectivity to direct deoxygenation products (i.e., toluene, benzene, xylene), and an associated increased selectivity to hydrogenation products (i.e., methylcyclohexene). Through *in situ* high energy X-ray diffraction and density functional theory modeling, we identified  $\text{OH}^*$  adsorption energy and surface-P sp-band center as effective descriptors for the observed shift in selectivities across this series of TMPs. Furthermore, the calculated electronic-structure changes were found to exert greater influence over the observed product selectivity than the subtle geometric changes associated with lattice expansion. Identification of this structure–function relationship demonstrates that the controlled synthesis of TMPs enables an understanding of composition-dependent selectivity for the HDO reaction of phenolic molecules and this approach could be extended to other ternary TMP compositions for diverse catalytic applications.

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## Introduction

Transition-metal phosphides (TMPs) are exceptional catalysts for a variety of biomass upgrading reactions, such as

hydrogenation, hydrogenolysis, decarbonylation, and dehydration, due to their metal–acid bifunctionality.<sup>1–4</sup> TMPs also exhibit hydrotreating activities similar to, or better than, both traditional transition-metal sulfide-based materials and their

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PDFs, RMC simulation fits, summary of structural parameters from RMC simulations, RMC models and associated bond angle distributions, catalytic performance data from guaiacol and *m*-cresol HDO, HYD and DDO pathway selectivities, DFT-calculated and experimental lattice parameters, average d-band center for surface-metal atoms *versus* average sp-band center for surface-P atoms, adsorption energetics for  $\text{OH}^*$  with lattice constant. See DOI: <https://doi.org/10.1039/d3ta02071a>

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parent metals, and can activate hydrogen at low pressures and moderate temperatures.<sup>5–7</sup> Tunable reaction rates and product selectivities have been demonstrated through compositional control of the metal identity and phosphorus-to-metal ratio.<sup>3,8</sup> Among the synthetically accessible binary TMPs (*e.g.*,  $M_yP$ , where  $M$  represents a single metal),  $Ni_2P$  nanoparticles (NPs) have shown promise for the hydrodeoxygenation (HDO) reaction of oxygenated compounds derived from biomass.<sup>9,10</sup>

The selective HDO of phenolic molecules to deoxygenated aromatic and cyclic compounds is a key step in the production of renewable chemicals and fuels from biomass, but achieving control over the selectivity requires understanding and control over the catalytic active sites.<sup>11</sup> For example, two pathways are typically observed in the HDO of phenolics: (i) direct deoxygenation (DDO) to produce an aromatic product (*e.g.*, phenol to benzene), and (ii) hydrogenation (HYD) followed by dehydration and hydrogenation to produce a cycloalkane (*e.g.*, phenol to cyclohexane).<sup>12–15</sup> Coplanar (parallel) orientation of the aromatic ring was proposed to drive selectivity toward HYD products due to the proximity of the ring to adsorbed  $H^*$  species ( $*$  denotes an adsorbed species) at the metallic sites, while nonplanar orientation (perpendicular/tilted) promoted DDO selectivity through interaction of the phenolic OH group (Ph–OH) with the Lewis acid surface sites.<sup>16–19</sup> The adsorbate orientation can be influenced by the surface electronic structure, often described by metal Lewis acidity, that can be modulated through changes in catalyst composition.<sup>20</sup> Stronger Lewis acidity has been correlated with more favourable interaction of the Ph–OH group with Lewis acid sites on the catalyst surface leading to increased DDO selectivity.<sup>20</sup> One approach to control HDO pathway selectivity is through the alloying of binary metal phosphides with another metal to form ternary TMPs (*e.g.*,  $M_xM'_yP_z$ , where  $M'$  represents a second metal).<sup>21,22</sup> These more complex compositions were shown to modulate both the electronic and geometric properties of the parent binary TMP, leading to increased HDO reaction rates and composition-dependent selectivity.<sup>13,20</sup> Recently, the HDO reaction for a variety of biomass-derived model compounds (*e.g.*, phenol, guaiacol, furfural) was investigated over ternary TMPs containing Mo, Fe, Ni, and Co.<sup>13,20,23</sup> One noteworthy result was that the addition of Fe to parent  $Mo_2P$  NPs increased the Lewis acidity and promoted increased activity and selectivity toward benzene from phenol through effective C–O bond cleavage.<sup>20</sup>

Considering the added complexity of ternary TMPs, approaches have been developed to provide a high level of synthetic control to establish structure–function relationships that govern HDO pathway selectivity on TMP catalysts. Traditional synthesis methods for TMPs *via* impregnation of metal and phosphorus salts on high surface area metal-oxide supports followed by high temperature reduction can lead to broad particle size distributions, overreduction of metal salts to metal NPs, non-uniform phosphorus incorporation, and excess phosphate species that do not participate in TMP formation.<sup>24,25</sup> Solution synthesis routes, on the other hand, can enable control over composition, particle morphology, and crystal structure,<sup>22,26–32</sup> providing model systems to understand the role of the second metal. Our group has previously established

solution synthesis approaches to obtain  $Ni_2P$ ,  $Rh_2P$ , and a variety of alloyed  $Ni_2-xRh_xP$  NPs *via* the thermolysis of low-valent metal triphenylphosphine complexes.<sup>33,34</sup> The parent  $Ni_2P$  and  $Rh_2P$  NPs prepared through this route were evaluated in the guaiacol HDO reaction,<sup>35,36</sup> with  $Rh_2P/SiO_2$  producing higher yields of the deoxygenated products anisole and benzene due to more effective activation of the Ph–OH bond compared to  $Ni_2P/SiO_2$  which yielded primarily phenol.<sup>37</sup>

Herein, the composition-dependent performance of a ternary  $Ni_{2-x}Rh_xP$  NP series was evaluated as a low precious-metal alternative to binary  $Rh_2P$  for the generation of deoxygenated products from phenolic molecules. The  $Ni_{2-x}Rh_xP$  NPs ( $x = 0.2, 0.4, 0.6, 0.8, 1.0$ ) were synthesized in a two-step solution synthesis approach *via* the thermal decomposition of molecular precursors to maintain uniform morphology and crystal structure across the series. The NPs were characterized by X-ray diffraction (XRD), scanning transmission electron microscopy (STEM), and pair distribution function analysis (PDF) of *in situ* high energy (HE)-XRD patterns. These data revealed that Rh substituted into Ni sites of the hexagonal  $Ni_2P$  crystal structure while maintaining the bulk structure with only a slight loss of metal–phosphorus bonds in the presence of  $H_2$  at 350 °C. Density functional theory (DFT) calculations showed that the increasing concentration of Rh in  $Ni_{2-x}Rh_xP$  was compensated by a decreasing negative charge at the P atom, whereas the charge of Ni and Rh remained constant. Composition-dependent selectivity in the *m*-cresol HDO reaction was observed, where increasing concentrations of Rh promoted HYD selectivity (up to 72% with  $Ni_{1.4}Rh_{0.6}P$ ), in contrast to the binary  $Rh_2P$  catalyst which promoted DDO selectivity (90%). DFT calculations demonstrated that increasing Rh content ( $x$ ) substituted in the  $Ni_{2-x}Rh_xP(0001)$  surface resulted in weakened  $OH^*$  adsorption energetics across the series, providing a good descriptor for the experimentally observed decrease in DDO and increase in HYD selectivity with increasing Rh concentration. The surface-P sp-band center was identified as an effective electronic structure descriptor for the  $OH^*$  binding energy, and thus DDO selectivity. The composition-dependent understanding developed herein demonstrates that the catalytic performance of ternary TMPs is not easily represented by a linear combination of two parent materials, but instead, is intimately related to the crystal structure and electronic structure that dictate surface–substrate interactions.

## Experimental methods

### Catalyst synthesis

A two-step synthesis route was employed to prepare  $Ni_{2-x}Rh_xP$  ( $x = 0.2, 0.4, 0.6, 0.8, 1$ ) NPs, as described previously.<sup>33</sup> First, amorphous Ni–P NPs were prepared by rapidly heating  $Ni(CO)_2(PPh_3)_2$  (0.639 g, 1.0 mmol) and  $PPh_3$  (1.05 g, 4.0 mmol) in dried oleylamine (OAm, 6.5 mL) and dried 1-octadecene (ODE, 6.5 mL) to 250 °C and holding for 15 min before cooling to ambient temperature. After the addition of 0–0.50 molar equivalents of solid  $RhCl(CO)(PPh_3)_2$  at ambient temperature under  $N_2$ , the reaction vessel was purged with  $N_2$  through



a needle inserted through the septum for 2 min. Then, the reaction mixture was heated rapidly to 300 °C under N<sub>2</sub> and held at this temperature for 1 h before removing the heat source and allowing the flask to cool to ambient temperature. The reaction mixture was then transferred to a centrifuge tube with the aid of approximately 0.1 mL chloroform. The NPs were flocculated with the addition of 15 mL of 2-propanol and separated *via* centrifugation at 10 000 rpm for 10 min. The NPs were again redispersed in 0.1 mL chloroform and flocculated with 30 mL 2-propanol before recovering by centrifugation.

Ni<sub>2</sub>P NPs were prepared, as described previously,<sup>33,34</sup> by heating a mixture of Ni(CO)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (0.639 g, 1.0 mmol), PPh<sub>3</sub> (1.049 g, 4.0 mmol), dried OAm (6.5 mL), and dried ODE (6.5 mL) rapidly to 300 °C and holding at this temperature for 1 h before the heat source was removed and the reaction mixture allowed to cool to ambient temperature. Similarly, Rh<sub>2</sub>P was prepared by heating a mixture of RhCl(CO)(PPh<sub>3</sub>)<sub>2</sub> (0.691 g, 1.0 mmol), OAm (4.9 mL), and ODE (8.0 mL) rapidly to 300 °C and holding for 1 h before the heat source was removed and the reaction mixture allowed to cool to ambient temperature. The NPs were purified, as described above.

All NPs were supported at approximately 5 wt% Ni<sub>2-x</sub>Rh<sub>x</sub>P loading on SiO<sub>2</sub>. After recovery, the purified NPs were redispersed in 10 mL chloroform. In a separate Erlenmeyer flask containing a 25 mm long stir bar, SiO<sub>2</sub> was dispersed in chloroform (10 mL g<sup>-1</sup> SiO<sub>2</sub>) and sonicated for 5 min. The SiO<sub>2</sub> mixture was stirred at 400 rpm and the NP suspension was added dropwise. The combined mixture was sonicated again for 5 min and left to stir overnight at ambient temperature. The supported NPs were collected by centrifugation at 10 000 rpm for 5 min and dried under flowing N<sub>2</sub>, before being stored in an N<sub>2</sub>-filled glovebox. Additional information about the materials and purity used is provided in the ESI.†

## Characterization

The metal and phosphorus loadings of both unsupported and SiO<sub>2</sub>-supported NPs were determined using inductively coupled plasma optical emission spectroscopy (ICP-OES) at Galbraith Laboratories (Knoxville, TN). Scanning transmission electron microscopy (STEM) imaging was performed on an aberration-corrected Nion Co. Ultra-STEM 100 operated at 100 kV and a JEOL 2200FS STEM/TEM instrument equipped with a CEOS GmbH (Heidelberg, Ger) corrector on the illuminating lenses to determine the NP morphology. The AMAG 5C mode was used to achieve a probe with a nominal 150 pA current and associated resolution of a nominal 0.07 nm. The presence and distribution of Ni, Rh, and P in the NPs were confirmed by utilizing energy dispersive X-ray spectroscopy (EDS) analysis and acquiring spectrum images with a Bruker-AXS silicon-drift detector system (SDD) on the JEOL 2200FS STEM/TEM microscope. Powder XRD data were collected using a Rigaku Ultima IV diffractometer with a Cu K $\alpha$  source (40 kV, 44 mA). Diffraction patterns were collected in the 2 $\theta$  range of 20–100° at a scan rate of 4° min<sup>-1</sup> on both unsupported and SiO<sub>2</sub>-supported NPs. Theoretical diffraction patterns were simulated at room temperature to aid phase identification. *In situ* high energy XRD

(HE-XRD) experiments were performed at the 6-ID-D beamline of the Advanced Photon Source (APS) at Argonne National Laboratory. HE-XRD patterns were collected at room temperature, 350 °C in 5% H<sub>2</sub>/Ar, and at 350 °C in guaiacol-saturated 5% H<sub>2</sub>/Ar. Catalytic site densities of the SiO<sub>2</sub>-supported Ni<sub>2-x</sub>Rh<sub>x</sub>P NPs were determined by H<sub>2</sub> chemisorption. Volumetric chemisorption experiments were performed using a Quantachrome Instruments Autosorb-1C gas sorption instrument. Additional details about sample preparation and data processing for each characterization technique is available in the ESI.†

## Catalyst evaluation

Catalytic performance was evaluated in a tubular fixed-bed reactor at 350 ± 1 °C and 0.50 ± 0.03 MPa. The reactor tube was 7.62 mm diameter with 20 mL total volume (Autoclave Engineers). The catalyst bed consisted of 0.2–0.5 g of catalyst diluted with 177–250  $\mu$ m diameter particles of silicon carbide to a volume of 4 mL. The catalyst bed was loaded into the reactor tube with the remaining reactor volume packed with crushed quartz. Approximately 2 mL of fine-crushed quartz (150–250  $\mu$ m) was packed above and below the catalyst bed, and the remaining reactor volume (~12 mL) was packed with coarse-crushed quartz (300–425  $\mu$ m). The loaded reactor tube was positioned within the isothermal region of the furnace. The temperature of the isothermal zone was measured with a 4-point thermocouple inserted into the center of the catalyst bed. For catalyst evaluation in the guaiacol HDO reaction, the reactor was co-fed with a 95% H<sub>2</sub>/5% Ar mixture and guaiacol at a molar ratio of 12 : 1 (*i.e.*, twice the stoichiometric amount of H<sub>2</sub> required to reduce guaiacol to cyclohexane, water, and methane). For catalyst evaluation in the *m*-cresol HDO reaction, the reactor was co-fed with a 95% H<sub>2</sub>/5% Ar mixture and *m*-cresol at a molar ratio of 8 : 1 (*i.e.*, twice the stoichiometric amount of H<sub>2</sub> required to reduce *m*-cresol to methylcyclohexane and water). An Eldex Optos 1 LMP HPLC pump was used to feed guaiacol or *m*-cresol into the reactor at a rate corresponding to the desired weight hourly space velocity (2–5 h<sup>-1</sup>), which is the ratio of the mass flow rate of reactant to the catalyst mass per hour. The guaiacol or *m*-cresol was vaporized immediately upstream of the reactor in heated stainless-steel tubing at 250 °C and mixed with the 95% H<sub>2</sub>/Ar mixture.

The reactor effluent was fractionated into liquid and gas phases in a condenser operated at 30 °C and samples of each phase were quantified with two different gas chromatography (GC) instruments. The uncondensed reactor effluent was sampled immediately downstream of the condensable trap and analyzed with an on-line Agilent Technologies 7890B gas chromatograph modified by Wasson ECE Instrumentation, Inc. The condensed samples were identified and quantified with an Agilent Technologies 7890A GC equipped with a flame ionization detector (FID) and mass spectrometer (MS). In all cases, the mass balance and carbon balance, based on measured inlet and outlet flowrates were over 90%. The equations used to calculate conversion, selectivity, and site time yield (STY) are presented in the ESI.†

## Computational methods

Density functional theory (DFT) calculations were implemented through the Vienna *Ab initio* Simulation Package (VASP).<sup>38,39</sup>



Exchange–correlation effects were captured through the spin-polarized generalized gradient approximation (GGA) using the Perdew–Burke–Ernzerhof (PBE) exchange–correlation functional.<sup>40</sup> Electron-ion interactions were described using projector augmented-wave (PAW) potentials with valence wavefunctions expanded through a plane-wave basis set with a cutoff energy of 500 eV.<sup>41,42</sup> Dispersion corrections were included through the D3 method by Grimme *et al.*<sup>43</sup>

Density functional theory (DFT) calculations were performed on bulk and surface  $\text{Ni}_{2-x}\text{Rh}_x\text{P}$  models with  $x$  values ranging from 0 to 0.83, in increments of 0.17, since phase separation was observed experimentally for  $x \geq 1$ . The preferred sites for Rh substitution into the bulk unit cell were determined for each value of  $x$ . Because the primitive bulk  $\text{Ni}_2\text{P}$  unit cell contains six metal sites, the bulk unit cell was doubled in the  $x$  direction to simulate all compositions. The DFT-calculated lattice parameters for bulk  $\text{Ni}_{2-x}\text{Rh}_x\text{P}$  are summarized in Table S13,† showing good agreement with the experimental lattice parameters for parent  $\text{Ni}_2\text{P}$  and  $\text{Rh}_2\text{P}$ .  $\text{Ni}_{2-x}\text{Rh}_x\text{P}$  surfaces were modeled as the (0001) facet, due to the prevalence of this facet in previous  $\text{Ni}_2\text{P}$  Wulff particle constructions over a range of P chemical potentials ( $\mu_{\text{P}}$ ).<sup>44</sup> The (0001) surface involves repeating  $\text{Ni}_3\text{P}_2$  and  $\text{Ni}_3\text{P}$  layers, resulting in two possible bulk terminations. Under P-poor conditions, previous work by He and coworkers found that the  $\text{Ni}_3\text{P}$ -terminated  $\text{Ni}_2\text{P}$ (0001) surface was thermodynamically favoured;<sup>44</sup> therefore, this termination was simulated given the absence of a P-source in the reactor feed (*i.e.*, P-poor conditions) during catalyst evaluation. A vacuum layer at least 10 Å thick was employed to separate successive slabs in the  $z$  direction. For each surface, a 4-layer slab model was simulated in which all adsorbates and the top half of the slab model could freely relax, while the bottom half was fixed in its bulk-truncated position. The position of Rh atoms in the periodic slabs was optimized using a  $(1 \times 1)$  unit cell, and the optimal  $\text{Ni}_{2-x}\text{Rh}_x\text{P}$ (0001) surfaces ( $x = 0, 0.17, 0.33, 0.50, 0.67$ , and  $0.83$ ) are illustrated in Fig. 3. Adsorption of  $\text{OH}^*$  on  $\text{Ni}_3\text{P}$ -terminated  $\text{Ni}_{2-x}\text{Rh}_x\text{P}$ (0001) was studied using a  $(1 \times 1)$  surface unit cell. Due to its large size, adsorption of *m*-cresol\* on  $\text{Ni}_{2-x}\text{Rh}_x\text{P}$ (0001) was studied using a  $(3 \times 3)$  surface unit cell, with Rh occupying the preferred substitution site for the corresponding  $(1 \times 1)$  surfaces. A four-layer  $\text{Rh}_2\text{P}$ (100) surface was also studied based on the cubic Wulff shape of  $\text{Rh}_2\text{P}$  particles;<sup>45</sup> a  $(4 \times 4)$  surface unit cell was studied for all surface intermediates. For  $\text{Rh}_2\text{P}$ (100), a P-terminated surface was evaluated due to its stability relative to the Rh-terminated surface across a wide range of  $\mu_{\text{P}}$ <sup>45</sup> (refer to ESI† for details).

## Results and discussion

### Synthesis and characterization of $\text{Ni}_{2-x}\text{Rh}_x\text{P}$ ( $x = 0, 0.2, 0.4, 0.6, 0.8, 1.0$ ) nanoparticles

Ternary  $\text{Ni}_{2-x}\text{Rh}_x\text{P}$  NPs were synthesized using a two-step approach beginning with the formation of amorphous Ni–P NPs by thermolysis of the molecular precursor  $\text{Ni}(\text{CO})_2(\text{PPh}_3)_2$  in a mixture of oleylamine and 1-octadecene at 250 °C, according to our previously published procedure.<sup>33,34</sup> After cooling the reaction mixture to ambient temperature, 0.10–0.50

molar equivalents of the second molecular precursor,  $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$ , were added to target specific stoichiometric ratios of  $\text{Ni}_{2-x}\text{Rh}_x\text{P}$  ( $x = 0.2–1.0$ ). The reaction was then heated to 300 °C for 1 h to promote decomposition of the Rh precursor, incorporation of Rh into the pre-formed amorphous Ni–P NPs, and phosphidation of the NPs. Particle formation was monitored by removing aliquots of the reaction mixture for XRD analysis while heating to the reaction temperature, and at several time points during the 1 h hold at 300 °C in the case of  $\text{Ni}_{1.6}\text{Rh}_{0.4}\text{P}$  NP synthesis (Fig. S1†). At 275 °C, the particles were amorphous, as indicated by the lack of reflections in the XRD pattern. Small crystalline particles (crystallite size of  $\sim 1$  nm determined by Scherrer analysis of the (111) reflection) with the hexagonal  $\text{Ni}_2\text{P}$  structure were observed by XRD analysis of an aliquot taken after the reaction mixture reached 300 °C, with increased crystallite size observed after 60 min at 300 °C (10.1 nm). Binary hexagonal  $\text{Ni}_2\text{P}$  ( $x = 0$ ) and cubic  $\text{Rh}_2\text{P}$  ( $x = 2.0$ ) NPs were prepared similarly to our previous report for comparison to the ternary series of  $\text{Ni}_{2-x}\text{Rh}_x\text{P}$  NPs.<sup>34</sup>

The Ni, Rh, and P composition of the as-prepared  $\text{Ni}_{2-x}\text{Rh}_x\text{P}$ ,  $\text{Ni}_2\text{P}$ , and  $\text{Rh}_2\text{P}$  NPs was determined using inductively coupled plasma optical emission spectroscopy (ICP-OES), and measured  $x$  values were in close agreement with the targeted  $x$  values (Table 1). The  $\text{Ni}_{2-x}\text{Rh}_x\text{P}$  NPs contained excess P compared to the expected total metal-to-phosphorus (M/P) ratio of 2.0 but maintained similar M/P ratios of 1.6–1.8 throughout the series (Table 1). The excess P may include residual P-containing organic species (*e.g.*, surface ligands) on the NPs, as observed in our previous reports.<sup>33,34</sup>

XRD was performed to identify the crystal phase and crystallite size (Fig. 1a) of the synthesized NPs. The diffraction pattern of the parent  $\text{Ni}_2\text{P}$  NPs matches that of the hexagonal  $\text{Ni}_2\text{P}$  phase. The hexagonal crystal structure was maintained in the ternary compositions for  $x$  between 0.2 and 0.8. However, the (111) reflection systematically shifted from  $40.8^\circ$  to  $40.0^\circ$  with increasing Rh concentration (Fig. 1a and Table S1†), suggesting lattice expansion with the incorporation of Rh into the parent  $\text{Ni}_2\text{P}$  material. The computed  $\text{Ni}_2\text{P}$  diffraction pattern has two superlattice diffraction peaks at  $30.4^\circ$  and  $32.0^\circ$  corresponding to the (211) and (101) planes, respectively, which decreased in intensity with increasing Rh incorporation, indicating increased atomic disorder.<sup>48,49</sup> At  $x = 1$ , the appearance of reflections at  $32.7^\circ$  and  $47.3^\circ$  indicated that the cubic  $\text{Rh}_2\text{P}$  phase was present in addition to the hexagonal  $\text{Ni}_2\text{P}$  phase (Fig. 1a). Scherrer analysis performed on the (111) reflection demonstrated that the crystallite sizes for the phase-pure ternary materials with  $x$  of 0.2–0.8 (8.9–9.9 nm) were of comparable size to the parent  $\text{Ni}_2\text{P}$  NPs (9.8 nm) (Table 1).

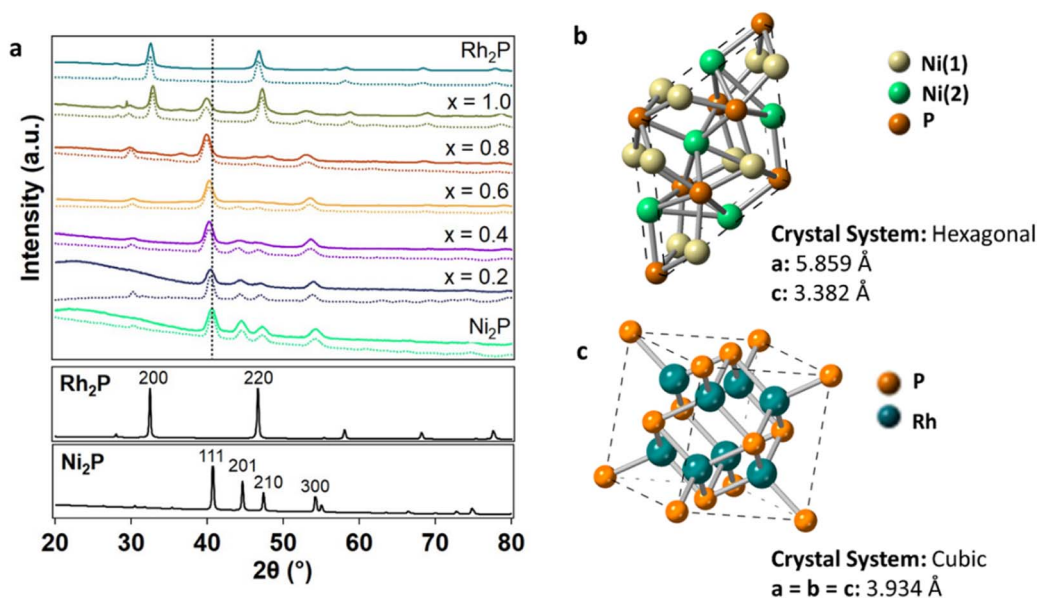
In the hexagonal  $\text{Ni}_2\text{P}$  crystal structure, Ni atoms are located in two distinct sites, denoted as Ni(1) and Ni(2), that differ based on their local environment (Fig. 1b).<sup>26,46</sup> Ni(1) is defined as a near-tetrahedral Ni site with four Ni–P bonds at an average bond distance of 2.24 Å and eight distant Ni neighbours at 2.64 Å. Ni(2) is defined as a square pyramidal Ni site with five P neighbours at 2.43 Å and six Ni neighbours at 2.65 Å.  $\text{Rh}_2\text{P}$  has a cubic crystal structure with one distinct Rh site (Fig. 1c). Previously, preferential site occupancy at Ni(2) over Ni(1) sites





**Table 1** Elemental composition determined by ICP-OES and particle size data from TEM and XRD analysis of unsupported  $\text{Ni}_{2-x}\text{Rh}_x\text{P}$  NPs

Target $x$	Measured $x$	mol% Ni	mol% Rh	mol% P	(Ni + Rh)/P molar ratio	Particle size by TEM (nm)	Volume average particle size by TEM (nm)	Crystallite size by XRD (nm)
0	—	64.5	0	35.5	1.7	$10.9 \pm 0.4$	$11.1 \pm 0.7$	9.8
0.2	0.21	59.3	7.3	33.4	1.6	$9.2 \pm 0.3$	$9.7 \pm 0.6$	8.9
0.4	0.43	54.4	14.8	30.8	1.8	$10.0 \pm 0.5$	$10.5 \pm 0.8$	9.9
0.6	0.65	47.2	22.8	30.0	1.8	$10.2 \pm 0.4$	$10.8 \pm 0.7$	9.1
0.8	0.82	41.0	28.7	30.3	1.8	$9.5 \pm 0.3$	$10.1 \pm 0.6$	9.4
1.0	0.99	35.3	34.8	29.8	1.8	$11.1 \pm 0.4$	$11.8 \pm 0.7$	11.2
2.0	—	0	66.1	33.9	1.6	$10.4 \pm 0.7$	$10.7 \pm 0.9$	13.6

**Fig. 1** (a) XRD patterns of  $\text{Ni}_{2-x}\text{Rh}_x\text{P}$  NPs ( $x = 0, 0.2, 0.4, 0.6, 0.8, 1.0, 2.0$ ) with simulated patterns (dashed lines) from Rietveld refinement and the  $\text{Ni}_2\text{P}$  (111) reflection highlighted (vertical black dashed line). The corresponding bulk  $\text{Ni}_2\text{P}$  (mp-21167)<sup>46</sup> and  $\text{Rh}_2\text{P}$  (mp-2732)<sup>47</sup> simulated patterns are provided below. (b) Hexagonal  $\text{Ni}_2\text{P}$  structure with  $\text{Ni}(1)$  and  $\text{Ni}(2)$  sites denoted<sup>46</sup> and (c) cubic  $\text{Rh}_2\text{P}$  structure.<sup>47</sup>

was observed with the incorporation of Fe atoms.<sup>21</sup> Here, substitution of Rh at specific Ni sites in  $\text{Ni}_2\text{P}$  was quantified by simulating the diffraction patterns of the  $\text{Ni}_{2-x}\text{Rh}_x\text{P}$  NPs using Rietveld refinement in the MAUD crystal structure software (Table 2).<sup>50</sup> The simulations (Fig. 1a, dashed lines) accounted for the specific crystallite sizes determined from Scherrer analysis of each XRD pattern and the measured metal concentrations determined by ICP-OES analysis. Rh was determined to preferentially substitute into the square pyramidal  $\text{Ni}(2)$  sites at 67%, 63%, 64%, and 53% for  $x$  equal to 0.2, 0.4, 0.6, and 0.8, respectively. At higher concentrations, Rh increasingly populated the near-tetrahedral  $\text{Ni}(1)$  sites with 33%, 37%, 36%, and 47% occupancy at  $x$  equal to 0.2, 0.4, 0.6, and 0.8, respectively. This is consistent with literature reports that demonstrated higher concentrations of heterometals leading to increased substitution at the tetrahedral  $\text{Ni}(1)$  site.<sup>51</sup> For  $x$  less than 0.8, substitution of Rh atoms into the  $\text{Ni}_2\text{P}$  lattice resulted in slight lattice parameter expansion in both  $a$  and  $c$  (Table 2 and Fig. S2†), consistent with that observed for the preferential substitution of Ni by Fe.<sup>15,21</sup> The Rietveld refinement performed

here also revealed phase separation in materials with  $x$  of 0.8 and 1. For  $x$  equal to 0.8, minimal phase separation was observed ( $\sim 3$  vol%); however, for  $x$  equal to 1, more extensive phase separation (50 vol%) was observed, as was apparent in the XRD pattern (Fig. 1a). Phase separation into the hexagonal  $\text{Ni}_2\text{P}$  and cubic  $\text{Rh}_2\text{P}$  phases was also observed in a recent report by Brock, *et al.* for  $\text{Ni}_{2-x}\text{Rh}_x\text{P}$  NPs with  $x \geq 1.5$ , where it was determined that Rh incorporation reached a maximum of  $x$  equal to 1.25 without separation using a single-step synthesis method.<sup>52,53</sup>

To identify the distribution of Ni, Rh, and P within the NPs, scanning transmission electron microscopy (STEM) coupled with energy dispersive X-ray spectroscopy (EDS) was performed. Exemplary STEM images and associated analysis is provided in Fig. 2 for  $\text{Ni}_{1.6}\text{Rh}_{0.4}\text{P}$ . This analysis was also performed for all compositions of  $x$  between 0.2 and 1.0 (Fig. S3–S6†), and co-location of Rh and Ni atoms within the NPs of each composition was confirmed (Fig. 2d–h, S3–S6d–h†). The bright field (BF) STEM image (Fig. 2a, S3–S6a†) indicated that the particles are uniform in size and shape. Average particle diameters for



**Table 2** Lattice constants and atom percent occupancy of Rh in Ni(1) and Ni(2) sites for  $\text{Ni}_{2-x}\text{Rh}_x\text{P}$  NPs

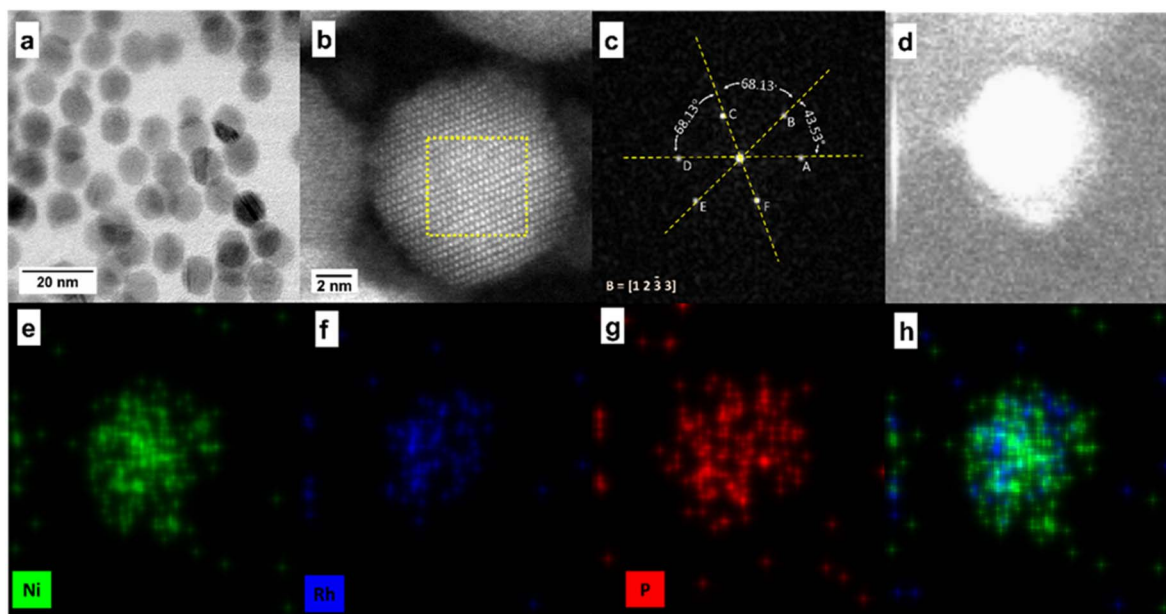
$x$	$a$ (Å)	$c$ (Å)	Rh in Ni(1) (at%)	Rh in Ni(2) (at%)
0	5.86	3.38	—	—
0.2	5.93	3.41	33	67
0.4	5.94	3.43	37	63
0.6	5.97	3.45	36	64
0.8 <sup>a</sup>	6.00	3.46	47	53
1.0 <sup>b</sup>	5.94	3.43	—	—
2.0	5.05	5.05	—	—

<sup>a</sup> Fit with 3 vol% cubic phase. <sup>b</sup> Fit with 50 vol% cubic phase.

compositions with  $x \leq 1$  were between 9.2 and 11.1 nm (Table 1 and Fig. S7†), which were comparable or slightly larger than the crystallite sizes calculated from the Scherrer analysis of the (111) reflection in the XRD patterns of the  $\text{Ni}_{2-x}\text{Rh}_x\text{P}$  NPs. There was no obvious trend in particle size observed with addition of Rh. The average particle diameter for the  $\text{Rh}_2\text{P}$  NPs (10.4 nm) was smaller than that determined by Scherrer analysis of the XRD pattern (13.6 nm), possibly due to the higher polydispersity of the NPs (standard deviation of 0.7 nm). High resolution (HR) high-angle annular dark-field (HAADF)-STEM (Fig. 2b, S3–S6b†) indicated that the  $\text{Ni}_{2-x}\text{Rh}_x\text{P}$  NPs were highly crystalline. Fast Fourier transform (FFT) analysis of individual particles showed that the  $\text{Ni}_{1.6}\text{Rh}_{0.4}\text{P}$  composition had the same hexagonal crystal structure as the parent  $\text{Ni}_2\text{P}$  (Table S2†). For all  $\text{Ni}_{2-x}\text{Rh}_x\text{P}$  NPs with  $x \leq 1$ , the FFT patterns were indexed to the hexagonal  $\text{Ni}_2\text{P}$  phase (Fig. 2c, S3–S6c, Tables S3–S6†), consistent with the phase determined by XRD (Fig. 1a).

The phase-pure  $\text{Ni}_{2-x}\text{Rh}_x\text{P}$  NPs ( $x \leq 0.8$ ) were supported on  $\text{SiO}_2$  with a target loading of 5 wt% NPs (see ESI† for additional

experimental details) and further structural characterization was performed. XRD analysis confirmed that the crystal phase did not change upon supporting (Fig. S8†), and ICP-OES analysis confirmed that the molar ratios of Ni, Rh, and P atoms were maintained (Table S7†). High energy (HE)-XRD coupled with atomic pair distribution function (PDF) analysis was performed on as-prepared  $\text{Ni}_2\text{P}/\text{SiO}_2$ ,  $\text{Rh}_2\text{P}/\text{SiO}_2$ , and  $\text{Ni}_{1.6}\text{Rh}_{0.4}\text{P}/\text{SiO}_2$  to understand the local arrangement of metal atoms in the NPs.  $\text{Ni}_{1.6}\text{Rh}_{0.4}\text{P}/\text{SiO}_2$  was selected as a representative ternary TMP material because 20 mol% provides a high enough Rh concentration to detect structural changes associated with Rh incorporation while maintaining phase homogeneity, as determined by standard XRD analysis (Fig. 1a). The diffraction patterns observed in both laboratory- and HE-XRD (Fig. S9†) align in  $Q$ -space, indicating that the structures of each sample are consistent with bulk  $\text{Ni}_2\text{P}$ , bulk  $\text{Rh}_2\text{P}$ , and Rh-containing  $\text{Ni}_2\text{P}$ , respectively. PDF analysis was performed on the HE-XRD patterns (Fig. S10 and S11†) and the first shell average coordination numbers (CNs) (*i.e.*, first nearest neighbor) and bond distances were calculated using the reverse Monte Carlo (RMC) method (Fig. S12–S15 and Table S8†). This analysis revealed that  $\text{Ni}_2\text{P}/\text{SiO}_2$  was found to have 2.4 Ni–P bonds at 2.30 Å and 3.4 Ni–Ni bonds at 2.63 Å.  $\text{Rh}_2\text{P}/\text{SiO}_2$  had 2.7 Rh–P bonds at 2.40 Å and 3.0 Rh–Rh bonds at 2.70 Å. The bond distances and CNs of both  $\text{Ni}_2\text{P}/\text{SiO}_2$  and  $\text{Rh}_2\text{P}/\text{SiO}_2$  were consistent with those expected for the respective binary TMP phases.<sup>46,47</sup>  $\text{Ni}_{1.6}\text{Rh}_{0.4}\text{P}/\text{SiO}_2$  had 2.2 Ni–P bonds at 2.35 Å and 2.3 Rh–P bonds at 2.42 Å, in addition to 3.1 Ni–Ni bonds at 2.65 Å, 0.4 Ni–Rh bonds at 2.69 Å, 1.5 Rh–Ni bonds at 2.69 Å, and 2.1 Rh–Rh bonds at 2.69 Å. The incorporation of Rh led to bond distance elongation in the Ni–P and Ni–Ni scattering pairs in  $\text{Ni}_{1.6}\text{Rh}_{0.4}\text{P}/\text{SiO}_2$  relative to  $\text{Ni}_2\text{P}/\text{SiO}_2$ , consistent with the lattice parameter expansion observed by standard XRD (Fig. 1a).



**Fig. 2** (a) Bright field STEM image of  $\text{Ni}_{1.6}\text{Rh}_{0.4}\text{P}$  NPs, (b) high resolution HAADF-STEM image with the corresponding (c) FFT oriented along the [1233] direction, (d) HAADF-STEM image on a different particle for EDS analysis, and associated EDS elemental maps for (e) Ni, (f) Rh, (g) P, and (h) Ni and Rh overlaid.



With this detailed understanding of the as-prepared TMP catalyst structures,  $\text{Ni}_2\text{P}/\text{SiO}_2$ ,  $\text{Rh}_2\text{P}/\text{SiO}_2$ , and  $\text{Ni}_{1.6}\text{Rh}_{0.4}\text{P}/\text{SiO}_2$  were evaluated by *in situ* HE-XRD in  $\text{H}_2$  and a representative phenolic probe molecule (guaiacol) at 350 °C to understand the structure of the NPs under reaction conditions. During treatment in  $\text{H}_2$ , increased atomic disorder (Fig. S11†) and the loss of local Ni–P (CN = 2.0) and/or local Rh–P (CN = 2.1) coordination is concomitant with an increase in Ni–Ni (CN = 3.4) and/or Rh–Ni (CN = 1.5) coordination in the second coordination sphere for all materials, while all bond distances remained unchanged (Table S8†). The Ni–P, Ni–Ni, and Ni–Rh coordination numbers were within 11% of the as-synthesized values, suggesting that the overall hexagonal crystal structure was maintained. For  $\text{Ni}_2\text{P}/\text{SiO}_2$ , increased atomic disorder in  $\text{H}_2$  was also observed in the bond angle distributions (Fig. S16†) derived from RMC models, where an increase in the average Ni–P–Ni bond angle in  $\text{H}_2$  corresponded to an increase of the full width at half maximum (FWHM) of each feature (*i.e.*, peak broadening) (Table S9†). Increased disorder was also observed in  $\text{Ni}_{1.6}\text{Rh}_{0.4}\text{P}/\text{SiO}_2$  relative to  $\text{Ni}_2\text{P}/\text{SiO}_2$  (Fig. S17 and Table S9†). It is important to note that the differences in CNs are a result of the increased disorder in the system and not due to a loss of P atoms, as the stoichiometry was maintained for each RMC simulation. No further structural changes were observed upon subsequent exposure to guaiacol, suggesting that the  $\text{H}_2$ -treated structure is relevant for understanding the composition-dependent performance described below.

### Electronic structure of $\text{Ni}_{2-x}\text{Rh}_x\text{P}$ nanoparticles

Models were developed for  $\text{Ni}_{2-x}\text{Rh}_x\text{P}$  NPs ( $x = 0.2$  to  $0.8$ ) by determining the most energetically favourable configuration of Rh sites in a  $\text{Ni}_2\text{P}$  surface. The lattice parameter of each theoretically determined composition was consistent with that obtained experimentally by XRD (Table S13 and Fig. S2†). DFT calculations, using Bader charge analysis, were performed on bulk  $\text{Ni}_{2-x}\text{Rh}_x\text{P}$  to understand the charge distribution between Ni, Rh, and P atoms with increasing  $x$  (Table 3). This analysis was performed for  $x$  ranging from 0 to 0.83, as distinct phase separation was observed experimentally at  $x$  equal to 1. The Bader charge for both Ni ( $+0.25$  to  $+0.27e^-$ ) and Rh ( $+0.11$  to  $+0.14e^-$ ) in bulk  $\text{Ni}_{2-x}\text{Rh}_x\text{P}$  remained relatively constant across the  $x$  range. The bulk P charge, however, became less negative

with increasing Rh concentration to compensate for the substitution of more positively charged Ni atoms with less positively charged Rh atoms, increasing from  $-0.55$  to  $-0.41e^-$  for  $x$  increasing from 0 to 0.83.

A similar analysis was performed to evaluate charge transfer in  $\text{Ni}_{2-x}\text{Rh}_x\text{P}$  surfaces. The (0001) surface is often used in computational studies of  $\text{Ni}_2\text{P}$  catalysis,<sup>54–56</sup> due to its low surface energy relative to other  $\text{Ni}_2\text{P}$  facets and its presence in Wulff particle constructions over a range of P chemical potentials ( $\mu_{\text{P}}$ ).<sup>44</sup> The  $\text{Ni}_3\text{P}$ -terminated (0001) surface was considered for this analysis based on work by He *et al.* demonstrating that this mixed surface termination is thermodynamically favoured under P-poor conditions, which is representative of the HDO reaction environment.<sup>44</sup> Likewise, for cubic  $\text{Rh}_2\text{P}$ , a P-terminated (100) surface was evaluated due to its stability across a wide range of  $\mu_{\text{P}}$ .<sup>45</sup> The preferred locations for Rh substitution into  $\text{Ni}_{2-x}\text{Rh}_x\text{P}$ (0001) slab models were calculated for  $x$  ranging from 0.17 to 0.83 (Fig. 3). The incorporation of higher Rh concentrations led to varying degrees of Rh substitution into the first and third layers of  $\text{Ni}_{2-x}\text{Rh}_x\text{P}$ (0001). The electronic structure of the individual atoms and average values for the metal sites in the topmost layer for each  $\text{Ni}_{2-x}\text{Rh}_x\text{P}$ (0001) surface was evaluated using Bader charge analyses. As observed for bulk  $\text{Ni}_{2-x}\text{Rh}_x\text{P}$ , the surface-Ni and surface-Rh charges remained relatively constant (Table 4), while the introduction of Rh into the surface layer resulted in a less-negative charge for surface-P, increasing from  $-0.47e^-$  ( $x = 0$ ) to  $-0.32e^-$  ( $x = 0.83$ ). However, considering the average surface metal ( $M_{\text{avg}}$ ) charge based on the composition of the topmost surface layer (Fig. 3), the addition of Rh to the surface layer resulted in a decrease in the  $M_{\text{avg}}$  charge from  $+0.25e^-$  (*i.e.*,  $Q_{\text{Ni}}$ ) at  $x = 0$  and 0.17, to  $+0.18e^-$  (*i.e.*,  $(2Q_{\text{Ni}} + Q_{\text{Rh}})/3$ ) at  $x = 0.33$ , 0.50, and 0.67, and to  $+0.10e^-$  (*i.e.*,  $(Q_{\text{Ni}} + 2Q_{\text{Rh}})/3$ ) at  $x = 0.83$ . Previous studies on TMP-catalyzed HDO used Bader charge analysis as a proxy for Lewis acidity, suggesting that systems with greater positive charges for surface-metal atoms have stronger Lewis acidities and promote increased DDO selectivity.<sup>13,20</sup> In the  $\text{Ni}_{2-x}\text{Rh}_x\text{P}$  series, the surface-P charge became less negative with increasing  $x$  while the charge of Ni and Rh surface atoms did not change. Instead, addition of Rh to the surface layer resulted in a decrease to  $M_{\text{avg}}$  charge (Table 4). In contrast, Hicks *et al.* reported increasing average positive charge on the metal atoms (Fe and Mo) and decreasing average negative charge on the P atoms in the  $\text{Fe}_x\text{Mo}_{2-x}\text{P}$  system with increasing Fe.<sup>20</sup> They postulated that electronegativity (EN) differences were a primary driving force for the observed charge transfer between M, M', and P atoms. Less electronegative metals, like Fe (EN = 1.64) and Mo (EN = 1.30), may have a greater propensity for charge transfer at different molar ratios in  $\text{Fe}_x\text{Mo}_{2-x}\text{P}$  due to the larger EN difference relative to P (EN = 2.06).<sup>20</sup> Conversely, Ni (EN = 1.75) and Rh (EN = 2.28) have EN values closer to that of P, which may limit charge transfer. The lower EN of Ni relative to Rh also accounts for the greater charge transfer between Ni and P atoms in  $\text{Ni}_2\text{P}$  compared to Rh and P atoms in  $\text{Rh}_2\text{P}$ .

The metal sp- and d-band centers, as well as the P sp-band centers, were also evaluated to further explore the influence of

**Table 3** Bader charge ( $Q$ ) averaged over Ni, Rh, and P atoms in bulk  $\text{Ni}_2\text{P}$  ( $x = 0$ ),  $\text{Ni}_{2-x}\text{Rh}_x\text{P}$  ( $x = 0.17$ – $0.83$ ), and  $\text{Rh}_2\text{P}$  ( $x = 2$ ). The notation '—' indicates that atom type is not present

$x$	$Q (e^-)$		
	Ni	Rh	P
0	+0.27	—	−0.55
0.17	+0.27	+0.13	−0.52
0.33	+0.27	+0.13	−0.49
0.50	+0.26	+0.13	−0.46
0.67	+0.26	+0.14	−0.44
0.83	+0.25	+0.14	−0.41
2	—	+0.11	−0.22





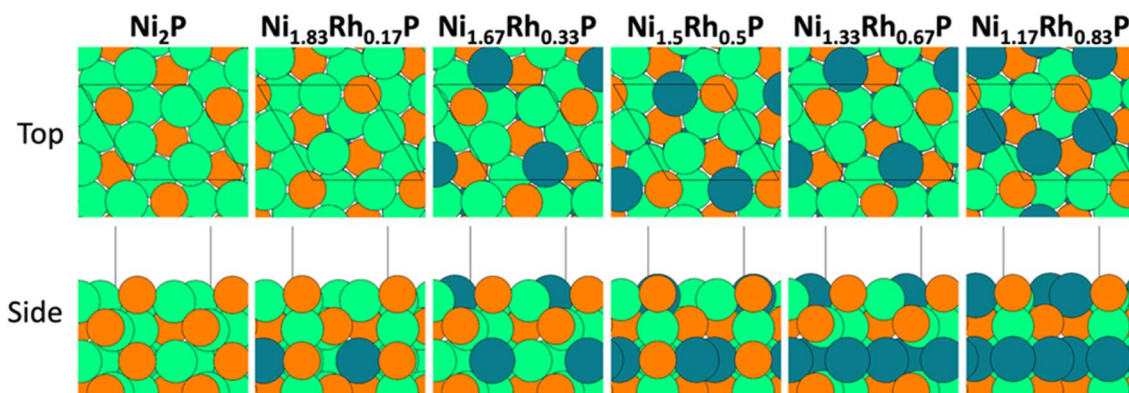


Fig. 3 Top and side views of the  $(1 \times 1)$   $\text{Ni}_3\text{P}$ -terminated  $\text{Ni}_{2-x}\text{Rh}_x\text{P}(0001)$  surface ( $x = 0, 0.17, 0.33, 0.50, 0.67$ , and  $0.83$ ). Black lines denote the surface unit cell. Atom colors: orange – P, green – Ni, teal – Rh.

Rh substitution on the electronic structure of  $\text{Ni}_{2-x}\text{Rh}_x\text{P}$  NPs. The d-band center has been established as a descriptor for both metal reactivity<sup>57</sup> and adsorption strength of key surface intermediates, while the sp-band center has shown promise as a descriptor for multi-component materials.<sup>58</sup> The calculated average d- and sp-band centers of the Ni, Rh, M, and P atoms in the  $\text{Ni}_{2-x}\text{Rh}_x\text{P}(0001)$  surface are reported in Table 4. Similar to the average metal surface charge, while the d-band centers for Ni and Rh surface atoms do not change appreciably with increasing  $x$ , the average d-band values for the surface-metal ensemble decrease as Rh incorporates into the surface layer.

### Hydrodeoxygenation of phenolic lignin model compounds

The hydrogen ( $\text{H}^*$ ) binding site densities on the  $\text{Ni}_{2-x}\text{Rh}_x\text{P}$  catalysts were determined by  $\text{H}_2$  chemisorption. When normalized to the metal content on a molar basis, the  $\text{H}^*$  binding site density remained relatively unchanged at 0.010–0.014  $\text{mol}_{\text{H}^*}/\text{mol}_{\text{M}}$  across the  $\text{Ni}_{2-x}\text{Rh}_x\text{P}$  series (Table 5) despite changing Rh concentration, and in contrast to a 3–4 $\times$  increase in  $\text{H}^*$  binding site density observed for  $\text{Rh}_2\text{P}$  (0.040  $\text{mol}_{\text{H}^*}/\text{mol}_{\text{M}}$ ). These values are lower than the ideal values of *ca.* 0.1  $\text{mol}_{\text{H}^*}/\text{mol}_{\text{M}}$  based on a geometric model of 10 nm NPs, where inaccessible sites may be due to a combination of residual ligand decomposition products, lost NP surface area from interaction with the support surface, and the inherent

differences in metal phosphide  $\text{H}_2$  activation compared to that of traditional metals. No trend with Rh content was observed, and therefore, any observed changes in catalytic activity and/or selectivity are not likely due to increased or decreased number of available catalytic sites as a function of Rh content. Indeed, the site-time yield values (STY, calculated as in eqn (4) in the ESI†) from the *m*-cresol HDO reaction were comparable across the  $\text{Ni}_{2-x}\text{Rh}_x\text{P}$  series (0.064–0.097  $\text{s}^{-1}$ ) and displayed no trend with  $\text{H}^*$  binding site density.

The catalytic performance of  $\text{SiO}_2$ -supported  $\text{Ni}_{2-x}\text{Rh}_x\text{P}$  NPs was evaluated in the HDO reaction of phenolic model compounds. Guaiacol was initially selected as a probe molecule based on our previous study.<sup>35</sup> However, initial evaluation of the catalysts in a packed-bed reactor ( $\text{H}_2/\text{guaiacol} = 12 : 1$ , 350 °C, 0.5 MPa) yielded *ca.* 15% conversion, and only minor changes in product selectivity were observed between  $\text{Ni}_2\text{P}/\text{SiO}_2$  and  $\text{Ni}_{1.6}\text{Rh}_{0.4}\text{P}/\text{SiO}_2$ , with both favouring phenol at 42–48% (Table S10†), indicating that demethoxylation of guaiacol to phenol was the primary transformation occurring at low conversion. Therefore, *m*-cresol was selected as a model compound to understand how changes in  $\text{Ni}_{2-x}\text{Rh}_x\text{P}$  composition impacts the selectivity to fully deoxygenated products. HDO of *m*-cresol over the  $\text{SiO}_2$ -supported materials was evaluated under similar conditions to our previous reports ( $\text{H}_2/\text{m-cresol} = 8 : 1$ , 350 °C, 0.5 MPa)<sup>35,59,60</sup> with an *m*-cresol weight-hourly space velocity (WHSV) of 10  $\text{h}^{-1}$ .

Table 4 Bader charge ( $Q$ , in  $e^-$ ), d-band center ( $E_d$ , eV), and sp-band center ( $E_{\text{sp}}$ , eV) averaged over Ni, Rh, total M, and P atoms in the surface layer of  $\text{Ni}_3\text{P}$ -terminated  $\text{Ni}_{2-x}\text{Rh}_x\text{P}(0001)$  ( $x = 0, 0.17, 0.33, 0.50, 0.67, 0.83$ ) and P-terminated  $\text{Rh}_2\text{P}(100)$  ( $x = 2.0$ ). The notation ‘—’ indicates that atom type is not present

$x$	Ni			Rh			$M_{\text{avg}}$			P	
	$Q (e^-)$	$E_d (\text{eV})$	$E_{\text{sp}} (\text{eV})$	$Q (e^-)$	$E_d (\text{eV})$	$E_{\text{sp}} (\text{eV})$	$Q (e^-)$	$E_d (\text{eV})$	$E_{\text{sp}} (\text{eV})$	$Q (e^-)$	$E_{\text{sp}} (\text{eV})$
0	+0.25	−1.33	+0.07	—	—	—	+0.25	−1.33	+0.07	−0.47	−3.08
0.17	+0.25	−1.35	+0.06	—	—	—	+0.25	−1.35	+0.06	−0.47	−3.11
0.33	+0.25	−1.36	+0.07	+0.03	−1.60	+0.22	+0.18	−1.44	+0.12	−0.40	−3.21
0.50	+0.25	−1.37	+0.09	+0.03	−1.61	+0.25	+0.18	−1.45	+0.14	−0.40	−3.23
0.67	+0.25	−1.38	+0.12	+0.03	−1.61	+0.28	+0.18	−1.46	+0.17	−0.40	−3.24
0.83	+0.24	−1.35	+0.20	+0.03	−1.56	+0.31	+0.10	−1.49	+0.27	−0.32	−3.26
2.00	—	—	—	+0.10	−2.07	−0.35	+0.10	−2.07	−0.35	−0.12	−2.92





Table 5 H<sub>2</sub> chemisorption and STY data for Ni<sub>2-x</sub>Rh<sub>x</sub>P/SiO<sub>2</sub> NPs

	H <sub>2</sub> chemisorption μmol <sub>H<sub>2</sub></sub> /g <sub>cat</sub>	H <sub>2</sub> chemisorption mol <sub>H<sub>2</sub></sub> /mol <sub>M</sub>	<i>m</i> -cresol HDO STY (s <sup>-1</sup> )
<i>x</i> = 0	6.8	0.012	0.068
<i>x</i> = 0.2	7.4	0.012	0.083
<i>x</i> = 0.4	7.1	0.014	0.064
<i>x</i> = 0.6	6.0	0.011	0.096
<i>x</i> = 0.8	5.3	0.010	0.097
<i>x</i> = 2.0	14.3	0.040	0.038

The model compound *m*-cresol enables a comparative study of reaction pathway selectivity for C–O bond scission to produce toluene (DDO pathway) *versus* ring hydrogenation (HYD pathway) to produce methylcyclohexane, methylcyclohexanol, and subsequently, methylcyclohexene and methylcyclohexane after dehydration and further hydrogenation (Fig. 4a).<sup>9,12</sup> The pathway selectivity to HYD and DDO products across the SiO<sub>2</sub>-supported Ni<sub>2-x</sub>Rh<sub>x</sub>P NP series were compared to those for binary Ni<sub>2</sub>P/SiO<sub>2</sub> and Rh<sub>2</sub>P/SiO<sub>2</sub> at *m*-cresol conversions less than 15% (Fig. 4b, Tables S11 and S12†) using grouped product analysis. Across the Ni<sub>2-x</sub>Rh<sub>x</sub>P NP series, a minor portion of the total products (4.99–13.6%) were light hydrocarbons (*e.g.*, C<sub>1</sub>–C<sub>5</sub> paraffins) likely formed by cracking reactions. No trend was observed in the selectivity to these light hydrocarbons, and they were excluded from our analysis of pathway selectivity (Table S11†). The major products observed over the Ni<sub>2-x</sub>Rh<sub>x</sub>P NP series were methylcyclohexanone (33.9–40.4%), toluene (21.2–33.7%), and methylcyclohexene (7.99–17.9%), with minor products including methylcyclohexanol (2.3–7.6%),

methylcyclohexane (1.6–2.8%), and benzene/xylenes (<1% each). HYD selectivity was determined by the sum of carbon selectivities to methylcyclohexanone, methylcyclohexanol, methylcyclohexene, and methylcyclohexane. DDO selectivity was determined by the sum of carbon selectivities to toluene, benzene, and xylenes, where benzene and xylenes are formed through methyl transfer reactions. Rh<sub>2</sub>P/SiO<sub>2</sub> was highly selective toward DDO products (90%), consistent with previous observations for guaiacol and phenol HDO reactions.<sup>35,37</sup> On the other hand, Ni<sub>2</sub>P/SiO<sub>2</sub> slightly favoured HYD (54%) over DDO (46%). We anticipated that incorporation of Rh into the Ni<sub>2-x</sub>-Rh<sub>x</sub>P NP series would invoke Rh<sub>2</sub>P-like selectivity, leading to enhanced DDO selectivity. However, the introduction of Rh instead increased the HYD pathway selectivity from 58% for Ni<sub>1.8</sub>Rh<sub>0.2</sub>P/SiO<sub>2</sub> to 66% for Ni<sub>1.6</sub>Rh<sub>0.4</sub>P/SiO<sub>2</sub> to 72% for Ni<sub>1.4</sub>Rh<sub>0.6</sub>P/SiO<sub>2</sub> (Fig. 4b and Table S12†), with a corresponding decrease in DDO selectivity. A modest decrease in HYD selectivity to 63% was observed for Ni<sub>1.2</sub>Rh<sub>0.8</sub>P/SiO<sub>2</sub>, attributed to the small degree of phase separation to Rh<sub>2</sub>P occurring in that composition (3 vol%, determined by Rietveld refinement). These data suggest that the TMPs cannot be treated simply as a linear combination of the performance of their parent metal phosphides.

### Hydrodeoxygenation selectivity descriptors

DFT calculations were employed to understand the unanticipated selectivity trends for *m*-cresol HDO on the Ni<sub>2-x</sub>Rh<sub>x</sub>P NP series in the context of developing computationally tractable descriptors. Previous studies have proposed distinct descriptors for DDO *versus* HYD selectivity in phenol HDO chemistry, including: Bader charge as a metric for change in Lewis acidity from charge transfer between M, M', and P,<sup>4,20,62</sup> the energy difference between the phenolic reactant adsorption in parallel *versus* perpendicular/tilted binding modes,<sup>23,63</sup> the Ph–OH bond distance in the adsorbed phenolic compound,<sup>64–66</sup> and the binding energy of OH\*.<sup>66</sup> In assessing correlations between possible descriptors and the experimentally measured *m*-cresol HDO selectivity, the descriptor values on the simulated TMP compositions were compared with the measured selectivity on the most similar Ni<sub>2-x</sub>Rh<sub>x</sub>P composition (*e.g.*, DFT calculated properties for *x* equal to 0.17 were compared to experimental data for *x* equal to 0.2). Due to some phase separation, the measured DDO selectivity for Ni<sub>1.2</sub>Rh<sub>0.8</sub>P may be affected by contributions from the cubic Rh<sub>2</sub>P phase (Fig. 4b). Therefore, *x* equal to 0.8 was not considered in analyses aiming to understand selectivity trends across the TMPs.

As described above, there was not an appreciable change in surface-Ni or -Rh charge across the Ni<sub>2-x</sub>Rh<sub>x</sub>P series (Table 4), indicating that individual surface-metal charge is not a good descriptor for the observed selectivity changes at varying *x* for this Ni<sub>2-x</sub>Rh<sub>x</sub>P series. The *m*-cresol\* adsorption geometry was evaluated on Ni<sub>3</sub>P-terminated Ni<sub>2-x</sub>Rh<sub>x</sub>P(0001) and P-terminated Rh<sub>2</sub>P(100) surfaces. The results, presented in Fig. S18,† indicate that *m*-cresol\* preferentially adsorbs in a parallel orientation (par.) *versus* a perpendicular/tilted orientation (perp./tilt) on all surfaces by a range of *ca.* 0.5 eV to 0.7 eV.

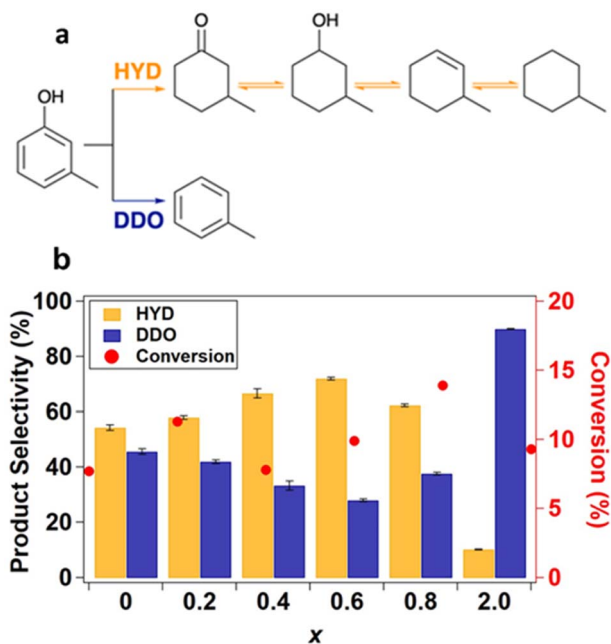


Fig. 4 (a) *m*-cresol HDO reaction pathways.<sup>61</sup> (b) Pathway selectivity in *m*-cresol HDO at 350 °C, 0.5 MPa, WHSV 10 h<sup>-1</sup> in an 8 : 1 molar feed ratio of H<sub>2</sub> : *m*-cresol with data averaged over 290 to 460 minutes time-on-stream.



The difference in binding energy between the parallel and perpendicular adsorption geometries of *m*-cresol\* was not well-correlated to the observed HDO selectivity. The Ph-OH bond distance in the preferred parallel adsorption configuration did not vary significantly or systematically across the TMP series (Fig. S18†) and is thus also not an effective *m*-cresol HDO selectivity descriptor for this series of TMP catalysts.

For the DDO of phenolic molecules, the thermodynamics associated with Ph-OH bond scission depend on the adsorption energy of OH\*, with stronger OH\* binding generally making the elementary step more exothermic. Previous work has also implicated the OH\* binding energy as a descriptor for phenol DDO selectivity on Ni-based single-atom surface alloys;<sup>66</sup> therefore, OH\* was evaluated as a descriptor for the observed DDO *versus* HYD selectivity in the Ni<sub>2-x</sub>Rh<sub>x</sub>P NP series. The most-stable adsorption sites for OH\* binding are provided in Fig. 5 for the Ni<sub>3</sub>P-terminated Ni<sub>2-x</sub>Rh<sub>x</sub>P(0001) and P-terminated Rh<sub>2</sub>P(100) surfaces. The OH\* binding energy was observed to decrease with incorporation of additional Rh atoms into the surface layer of Ni<sub>3</sub>P-terminated Ni<sub>2-x</sub>Rh<sub>x</sub>P(0001), ranging from -3.44 eV for Ni<sub>2</sub>P(0001) to -3.10 eV for Ni<sub>1.17</sub>Rh<sub>0.83</sub>P(0001). On P-terminated Rh<sub>2</sub>P(100), OH\* binds stronger with a binding energy of -3.73 eV. When the DDO selectivities are plotted against the OH\* binding energies across the TMP series, a strong correlation is observed ( $R^2 = 0.96$ ; Fig. 6a). Notably, OH\* binds to surface-metal hollow sites on Ni<sub>2-x</sub>Rh<sub>x</sub>P(0001) and to surface-P atoms on P-terminated Rh<sub>2</sub>P(100). Thus, the average surface-Rh d-band center is not able to describe the OH\* binding energy on P-terminated Rh<sub>2</sub>P(100) because the Rh sites are in the second layer (*i.e.*,

subsurface) and are blocked by surface-P. However, the average surface-metal d-band center is well-correlated with the average surface-P sp-band center for Ni<sub>3</sub>P-terminated Ni<sub>2-x</sub>Rh<sub>x</sub>P(0001) (Fig. 6b), and as a result, modulation in the OH\* binding strength was observed to be a strong function of the average sp-band center of surface-P atoms ( $R^2 = 0.98$ ; Fig. 6c) across the entire series of these binary and ternary TMP catalysts. In summary, OH\* binding energy is well-described by the sp-band center of surface-P atoms, because P atoms are present in the

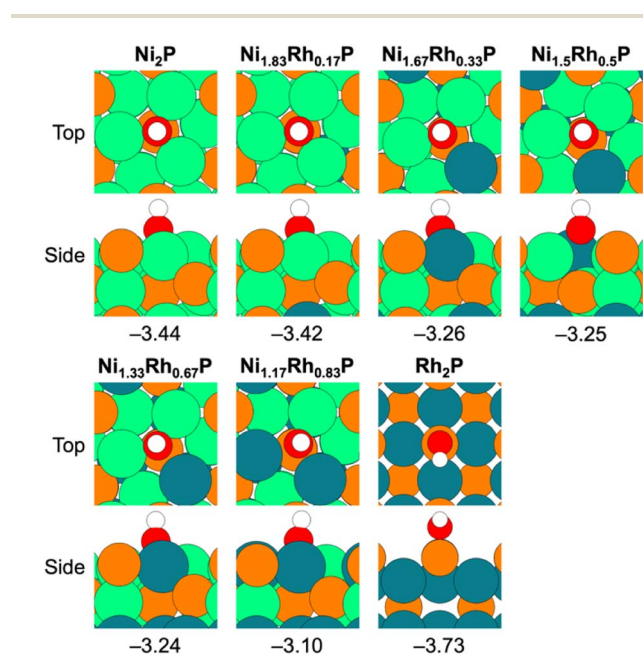


Fig. 5 Top and side views for OH\* adsorption on Ni<sub>3</sub>P-terminated Ni<sub>2-x</sub>Rh<sub>x</sub>P(0001) ( $x = 0, 0.17, 0.33, 0.5, 0.67, 0.83$ ) and P-terminated Rh<sub>2</sub>P(100) ( $x = 2.0$ ). Adsorption energies, in eV, are provided below each snapshot. Atom colors: orange – P, green – Ni, teal – Rh, white – H, red – O.

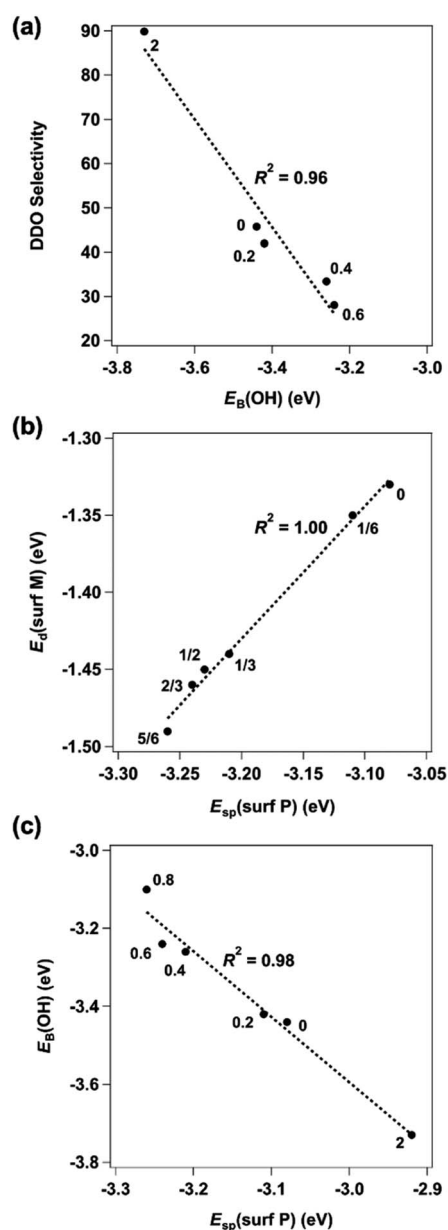


Fig. 6 (a) Experimental DDO selectivity *versus* OH\* binding energy ( $E_B(\text{OH})$ , in eV). (b) Average d-band center for surface-metal atoms ( $E_d(\text{surf M})$ , in eV) *versus* average sp-band center for surface-P atoms ( $E_{sp}(\text{surf P})$ , in eV) for Ni<sub>3</sub>P-terminated Ni<sub>2-x</sub>Rh<sub>x</sub>P(0001) ( $x = 0, 0.2, 0.4, 0.6, 0.8$ ) and P-terminated Rh<sub>2</sub>P(100) ( $x = 2.0$ ). Data labels correspond to  $x$ . Linear fits are marked by the dashed black line alongside the corresponding  $R^2$  value.



surface layer of the studied parent  $\text{Ni}_2\text{P}$ , parent  $\text{Rh}_2\text{P}$ , and ternary  $\text{Ni}_{2-x}\text{Rh}_x\text{P}$  surface models. As a result, both  $\text{OH}^*$  binding energy and sp-band center of surface-P atoms may provide computationally tractable descriptors for *m*-cresol HDO pathway selectivity on TMPs containing P in the surface layer, including TMPs with varying  $\text{OH}^*$  binding sites (*i.e.*, M or P) as found here.

Given that the charge on the individual Ni and Rh surface sites does not change with varying  $x$ , the DFT calculations indicated that it is the formation of Ni–Rh surface ensembles that leads to the modulation of both the  $\text{OH}^*$  adsorption energy and average surface-P sp-band center, and thereby the observed selectivity changes. To assess whether geometric effects (*i.e.*, lattice expansion) from Rh incorporation might also affect the observed DDO *versus* HYD selectivity, the  $\text{OH}^*$  adsorption energy was evaluated on  $\text{Ni}_3\text{P}$ -terminated  $\text{Ni}_2\text{P}(0001)$  with the lattice systematically expanded to match the lattice constants corresponding to each studied  $x$  value for bulk  $\text{Ni}_{2-x}\text{Rh}_x\text{P}$  (Table S13†). These results, presented in Table S14,† indicate that the lattice expansion resulting from increased incorporation of Rh resulted in only negligible weakening of the  $\text{OH}^*$  binding energy, with values ranging from  $-3.44$  eV to  $-3.38$  eV for  $\text{Ni}_2\text{P}(0001)$  with lattice parameters representative of  $x$  equal to 0 and 0.83, respectively. Therefore, the calculated  $\text{OH}^*$  binding energies on  $\text{Ni}_{2-x}\text{Rh}_x\text{P}(0001)$  are primarily influenced by the formation of the Ni–Rh surface-ensembles arising from Rh substitution into the surface layer of  $\text{Ni}_{2-x}\text{Rh}_x\text{P}(0001)$ .

Previous reports attributed composition-dependent HDO selectivity to either the addition of a metal modifier site that perturbs the adsorption geometry or ligand effects modifying the electronic structure of the parent metal site in the ternary TMP.<sup>15,20,64</sup> Though both geometric and electronic consequences occur with varying  $x$  values in the  $\text{Ni}_{2-x}\text{Rh}_x\text{P}$  system, DFT analysis suggests a minimal geometric influence on the HYD *versus* DDO selectivity in the *m*-cresol HDO reaction (Table S14†). Concomitant electronic-structure changes were imposed with increasing  $x$  leading to weaker  $\text{OH}^*$  binding energies at the surface-metal ensemble sites, promoting the formation of HYD products over DDO products. To identify a robust descriptor of catalyst performance, the sp-band center of surface-P atoms was calculated to include the electronic contribution of P atoms, which is not necessarily encompassed in oxophilicity and electronegativity arguments. Although oxophilicity and electronegativity arguments can describe the phenolic molecule HDO pathway selectivity for some ternary TMP systems,<sup>13,17</sup> they do not provide universal descriptors for the rational design of novel ternary TMP catalysts, as evidenced by the results for this  $\text{Ni}_{2-x}\text{Rh}_x\text{P}$  NP series. Oxophilicity lacks universality as a descriptor because it describes discrete metal properties, and not necessarily how the metal atoms interact with P atoms in an ordered structure, which can change depending on the crystal structure. We demonstrated that the  $\text{OH}^*$  adsorption energy provides a promising computationally tractable descriptor for the HYD/DDO selectivity on TMP surfaces with varying composition, crystal structure, and surface termination.

In this report,  $\text{OH}^*$  adsorption energy trends well with the catalytic performance observed across the hexagonal  $\text{Ni}_{2-x}\text{Rh}_x\text{P}$

and cubic  $\text{Rh}_2\text{P}$  NPs. Further, this study showed that incorporating varying concentrations of Rh into a parent  $\text{Ni}_2\text{P}$  framework did not invoke  $\text{Rh}_2\text{P}$ -like catalytic properties, highlighting that crystal structure and surface termination are interwoven in ternary TMPs and play important roles in the resultant catalytic selectivity.

## Conclusions

A two-step solution synthesis approach was employed to access well-defined ternary  $\text{Ni}_{2-x}\text{Rh}_x\text{P}$  NPs with consistent crystal structure and particle morphology across a range of compositions. Through extensive characterization, the addition of Rh was observed to result in preferential Ni(2) site substitution in binary  $\text{Ni}_2\text{P}$ . For all compositions of  $\text{Ni}_{2-x}\text{Rh}_x\text{P}$  ( $x \leq 1$ ), Ni and Rh atoms were co-located in a single particle with uniform distribution of both elements. Lattice parameter expansion was observed with increasing Rh concentration. At high Rh concentrations ( $x \geq 0.8$ ), phase separation to hexagonal and cubic phases associated with parent  $\text{Ni}_2\text{P}$  and  $\text{Rh}_2\text{P}$ , respectively, was observed. The  $\text{H}_2$ -pretreated catalyst exhibited an 11% loss in the number of Ni–P bonds with a corresponding increase in metal–metal bonding but maintained a coordination number ratio (Ni–P/Ni–M) consistent with the hexagonal crystal structure observed in the XRD patterns. Subsequent structural changes were not observed after guaiacol exposure at  $350^\circ\text{C}$ , suggesting that the  $\text{H}_2$ -treated structure is relevant for understanding performance in phenolic molecule HDO reactions. The catalytic performance of  $\text{Ni}_{2-x}\text{Rh}_x\text{P}$  NPs was assessed *via m*-cresol HDO and composition-dependent selectivity was observed. Binary  $\text{Ni}_2\text{P}$  had comparable selectivity to HYD and DDO, while binary  $\text{Rh}_2\text{P}$  favoured DDO. Increasing Rh concentration in  $\text{Ni}_{2-x}\text{Rh}_x\text{P}$  NPs promoted HYD selectivity until  $x$  equal to 0.6, but minor phase separation at  $x$  equal to 0.8 likely resulted in the slight increase in DDO selectivity. The composition-dependent understanding developed here demonstrates that the catalytic performance of ternary TMPs is not easily represented by a linear combination of the parent materials.

We sought to identify a robust descriptor to explain composition-dependent performance of the  $\text{Ni}_{2-x}\text{Rh}_x\text{P}$  series through DFT calculations. Although the Bader charge analysis is often used as a proxy for Lewis acidity, suggesting that systems with greater positive charges for surface-metal atoms have stronger Lewis acidities and promote increased DDO selectivity, the charge of surface-metal atoms in  $\text{Ni}_{2-x}\text{Rh}_x\text{P}$  remained relatively unchanged and could not describe the observed changes in catalyst performance in this series. DFT calculations revealed that the decreased DDO selectivity with increasing  $x$  is described by the  $\text{OH}^*$  adsorption energy, as Rh incorporation into the  $\text{Ni}_3\text{P}$ -terminated  $\text{Ni}_{2-x}\text{Rh}_x\text{P}(0001)$  surface resulted in weaker  $\text{OH}^*$  adsorption. Modulation in the  $\text{OH}^*$  binding strength was a strong function of the average sp-band center of surface-P atoms across all evaluated TMPs, regardless of the specific  $\text{OH}^*$  binding site. These studies highlight that (1) the surface-metal and -P atoms in TMPs, not the bulk structures, must be investigated to understand



catalytically relevant sites, and (2) the heterogeneity of surface sites in TMPs makes it challenging to find a single descriptor encompassing the role of material composition, crystal structure, and surface termination. The OH\* binding energy is a promising descriptor for both the reactivity of hexagonal Ni<sub>2</sub>P and cubic Rh<sub>2</sub>P crystal structures during *m*-cresol HDO and could serve as a general descriptor for novel ternary TMP formulations. Electronic structure descriptors, such as the P sp-band center or the metal d-band center, can also serve as effective HDO selectivity descriptors but their utility is dependent on the presence of each species (*i.e.*, P or M) in the TMP surface. Future work should continue to evaluate these descriptors as general/universal descriptors for DDO *versus* HYD pathway selectivity in phenolic molecule HDO. Further analysis of the electronic structure of TMPs should also rely on developing fundamental structure–function relationships for catalytically relevant surfaces, rather than solely on the bulk material properties. More broadly, this work highlights the necessity of precisely defined structures to deconvolute geometric and electronic effects, especially in complex reactions, such as phenolic HDO, and the approach undertaken in this work is extensible to a wider set of materials to aid the development of structure–function relationships for rational catalyst design.

## Author contributions

Nicole J. LiBretto: conceptualization, methodology, investigation, formal analysis, data curation, validation, writing – original draft, writing – review & editing; Sean A. Tacey: conceptualization, methodology, software, investigation, formal analysis, writing – review & editing, visualization; Muhammad Zubair: methodology, software, formal analysis, data curation, writing – review & editing, visualization; Tuong V. Bui: investigation, writing – review & editing; Kinga A. Unocic: investigation, visualization, writing – review & editing; Frederick G. Baddour: conceptualization, formal analysis, writing – review & editing; Michael B. Griffin: resources, investigation, writing – review & editing; Joshua A. Schaidle: conceptualization, supervision, funding acquisition; Carrie A. Farberow: conceptualization, supervision, methodology, writing – review & editing; Daniel A. Ruddy: conceptualization, supervision, formal analysis, writing – review & editing; Nicholas M. Bedford: methodology, investigation, resources, supervision, writing – review & editing, project administration; Susan E. Habas: conceptualization, investigation, supervision, writing – review & editing, funding acquisition.

## Conflicts of interest

There are no conflicts of interest to declare.

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## Notes and references

- 1 S. Kim, E. E. Kwon, Y. T. Kim, S. Jung, H. J. Kim, G. W. Huber and J. Lee, Recent advances in hydrodeoxygenation of biomass-derived oxygenates over heterogeneous catalysts, *Green Chem.*, 2019, **21**, 3715–3743.
- 2 X. Lan, R. Pestman, E. J. M. Hensen and T. Weber, Furfural hydrodeoxygenation (HDO) over silica-supported metal phosphides – The influence of metal–phosphorus stoichiometry on catalytic properties, *J. Catal.*, 2021, **403**, 181–193.
- 3 S. T. Oyama, T. Gott, H. Zhao and Y.-K. Lee, Transition metal phosphide hydroprocessing catalysts: A review, *Catal. Today*, 2009, **143**, 94–107.
- 4 V. Jain, Y. Bonita, A. Brown, A. Taconi, J. C. Hicks and N. Rai, Mechanistic insights into hydrodeoxygenation of phenol on bimetallic phosphide catalysts, *Catal. Sci. Technol.*, 2018, **8**, 4083–4096.
- 5 S. Boullosa-Eiras, *et al.*, Potential for metal-carbide, -nitride, and -phosphide as future hydrotreating (HT) catalysts for processing of bio-oils, in *Catalysis*, ed. Spivey J. J. and Han Y.-F., Dooley K. M., RSC, 2014, vol. 26, pp. 29–71.
- 6 R. Prins and M. E. Bussell, Metal phosphides: preparation, characterization and catalytic reactivity, *Catal. Lett.*, 2012, **142**, 1413–1436.





- 7 H. Y. Zhao, D. Li, P. Bui and S. T. Oyama, Hydrodeoxygenation of guaiacol as model compound for pyrolysis oil on transition metal phosphide hydroprocessing catalysts, *Appl. Catal., A*, 2011, **391**, 305–310.
- 8 L. Song and S. Zhang, A versatile route to synthesizing bulk and supported nickel phosphides by thermal treatment of a mechanical mixing of nickel chloride and sodium hypophosphite, *Powder Technol.*, 2011, **208**, 713–716.
- 9 V. O. O. Gonçalves, P. M. de Souza, V. T. da Silva, F. B. Noronha and F. Richard, Kinetics of the hydrodeoxygenation of cresol isomers over Ni<sub>2</sub>P/SiO<sub>2</sub>: Proposals of nature of deoxygenation active sites based on an experimental study, *Appl. Catal., B*, 2017, **205**, 357–367.
- 10 A. Berenguer, J. A. Bennet, J. Hunns, I. Moreno, J. M. Coronado, A. F. Lee, P. Pizarro, K. Wilson and D. P. Serrano, Catalytic hydrodeoxygenation of m-cresol over Ni<sub>2</sub>P/hierarchical ZSM-5, *Catal. Today*, 2018, **304**, 72–79.
- 11 X. Wu, Q. Ge and X. Zhu, Vapor phase hydrodeoxygenation of phenolic compounds on group 10 metal-based catalysts: reaction mechanism and product selectivity control, *Catal. Today*, 2021, **365**, 143–161.
- 12 D. A. Ruddy, J. A. Schaidle, J. R. Ferrell, J. Wang, L. Moens and J. E. Hensley, Recent advances in heterogeneous catalysts for bio-oil upgrading via “*ex situ* catalytic fast pyrolysis”: catalyst development through the study of model compounds, *Green Chem.*, 2014, **16**, 454–490.
- 13 Y. Bonita and J. C. Hicks, Periodic trends from metal substitution in bimetallic Mo-based phosphides for hydrodeoxygenation and hydrogenation reactions, *J. Phys. Chem. C*, 2018, **122**, 13322–13332.
- 14 L. Nie and D. E. Resasco, Kinetics and mechanism of m-cresol hydrodeoxygenation on a Pt/SiO<sub>2</sub> catalyst, *J. Catal.*, 2014, **317**, 22–29.
- 15 L. Nie, P. de Souza, F. B. Noronha, W. An, T. Sooknoi and D. E. Resasco, Selective conversion of m-cresol to toluene over bimetallic Ni–Fe catalysts, *J. Mol. Catal. A: Chem.*, 2014, **388**, 47–55.
- 16 A. M. Robinson, L. Mark, M. J. Rasmussen, J. E. Hensley and J. W. Medlin, Surface chemistry of aromatic reactants on Pt- and Mo-modified Pt catalysts, *J. Phys. Chem. C*, 2016, **120**(47), 26824–26833.
- 17 G. Held, Adsorption and dissociation of benzene on bimetallic surfaces—the influence of surface geometry and electronic structure, *J. Phys.: Condens. Matter*, 2003, **15**, R1501–R1516.
- 18 S. J. Jenkins, Aromatic adsorption on metals via first-principles density functional theory, *Proc. R. Soc. A*, 2009, **465**, 2949–2976.
- 19 J. Zhong, J. Chen and L. Chen, Selective hydrogenation of phenol and related derivatives, *Catal. Sci. Technol.*, 2014, **4**, 3555–3569.
- 20 D. J. Rensel, J. Kim, V. Jain, Y. Bonita, N. Rai and J. C. Hicks, Composition-directed Fe<sub>x</sub>Mo<sub>2–x</sub>P bimetallic catalysts for hydrodeoxygenation reactions, *Catal. Sci. Technol.*, 2017, **7**, 1857–1867.
- 21 A. Hitihami-Mudiyanselage, M. P. Arachchige, T. Seda, G. Lawes and S. L. Brock, Synthesis and characterization of discrete Fe<sub>x</sub>Ni<sub>2–x</sub>P nanocrystals (0 < x < 2): compositional effects on magnetic properties, *Chem. Mater.*, 2015, **27**, 6592–6600.
- 22 D. R. Liyanage, S. J. Danforth, Y. Liu, M. E. Bussell and S. L. Brock, Simultaneous control of composition, size, and morphology in discrete Ni<sub>2–x</sub>CoxP nanoparticles, *Chem. Mater.*, 2015, **27**, 4349–4357.
- 23 Y. He and S. Laursen, The surface and catalytic chemistry of the first row transition metal phosphides in deoxygenation, *Catal. Sci. Technol.*, 2018, **8**, 5302–5314.
- 24 D. Li, H. Baydoun, B. Kulikowski and S. L. Brock, Boosting the catalytic performance of iron phosphide nanorods for the oxygen evolution reaction by incorporation of manganese, *Chem. Mater.*, 2017, **29**, 3048–3054.
- 25 A. Parra-Puerto, K. L. Ng, K. Fahy, A. E. Goode, M. P. Ryan and A. Kucernak, Supported transition metal phosphides: Activity survey for HER, ORR, OER, and corrosion resistance in acid and alkaline electrolytes, *ACS Catal.*, 2019, **9**, 11515–11529.
- 26 S. J. Danforth, D. R. Liyanage, A. Hitihami-Mudiyanselage, B. Illic, S. L. Brock and M. E. Bussell, Probing hydrodesulfurization over bimetallic phosphides using monodisperse Ni<sub>2–x</sub>M<sub>x</sub>P nanoparticles encapsulated in mesoporous silica, *Surf. Sci.*, 2016, **648**, 126–135.
- 27 T. Su’a, M. N. Poli and S. L. Brock, Homogeneous nanoparticles of multimetallic phosphides via precursor tuning: Ternary and quaternary M<sub>2</sub>P phases (M = Fe, Co, Ni), *ACS Nanosci. Au*, 2022, **2**, 503–519.
- 28 S. Carenco, D. Portehault, C. Boissière, N. Mézailles and C. Sanchez, Nanoscaled metal borides and phosphides: Recent developments and perspectives, *Chem. Rev.*, 2013, **113**, 7981–8065.
- 29 A. E. Henkes, Y. Vasquez and R. E. Schaak, Converting metals into phosphides: A general strategy for the synthesis of metal phosphide nanocrystals, *J. Am. Chem. Soc.*, 2007, **129**, 1896–1897.
- 30 S. Carenco, Y. Hu, I. Florea, O. Ersen, C. Boissiere, N. Mezeilles and C. Sanchez, Metal-dependent interplay between crystallization and phosphorus diffusion during the synthesis of metal phosphide nanoparticles, *Chem. Mater.*, 2012, **24**, 4134–4145.
- 31 M. E. Mundy, D. Ung, N. L. Lai, E. P. Jahrman, G. T. Seidler and B. M. Cossairt, Aminophosphines as versatile precursors for the synthesis of metal phosphide nanocrystals, *Chem. Mater.*, 2018, **30**, 5373–5379.
- 32 F. D’Accrescio, E. Schrader, C. Sassoye, M. Selmane, R. F. Andre, S. Lamaison, D. Wakerley, M. Fontecave, V. Mougel, G. LeCorre, H. Grutzmacher, C. Sanchez and S. Carenco, A single molecular stoichiometric P-source for phase-selective synthesis of crystalline and amorphous iron phosphide nanocatalysts, *ChemNanoMat*, 2020, **6**, 1208–1219.
- 33 C. A. Downes, K. Van Allsburg, S. Tacey, K. A. Unocic, F. G. Baddour, D. A. Ruddy, N. J. LiBretto, M. M. O’Connor, C. A. Farberow, J. A. Schaidle and



- S. E. Habas, Controlled synthesis of transition metal phosphide nanoparticles to establish composition-dependent trends in electrocatalytic activity, *Chem. Mater.*, 2022, **34**(14), 6255–6267.
- 34 S. E. Habas, F. G. Baddour, D. A. Ruddy, C. P. Nash, J. Wang, M. Pan, J. E. Hensley and J. A. Schaidle, A facile molecular precursor route to metal phosphide nanoparticles and their evaluation as hydrodeoxygenation catalysts, *Chem. Mater.*, 2015, **27**, 7580–7592.
- 35 M. B. Griffin, F. G. Baddour, S. E. Habas, D. A. Ruddy and J. A. Schaidle, Evaluation of silica-supported metal and metal phosphide nanoparticle catalysts for the hydrodeoxygenation of guaiacol under *ex situ* catalytic fast pyrolysis conditions, *Top. Catal.*, 2016, **59**, 124–137.
- 36 M. B. Griffin, F. G. Baddour, S. E. Habas, C. P. Nash, D. A. Ruddy and J. A. Schaidle, An investigation into support cooperativity for the deoxygenation of guaiacol over nanoparticle Ni and Rh<sub>2</sub>P, *Catal. Sci. Technol.*, 2017, **7**, 2954–2966.
- 37 Y. Kanda, T. Chiba, R. Aranai, T. Yasuzawa, R. Ueno, T. Tayao, K. Kato, Y. Obora, K.-i. Shimizu and Y. Uemichi, Catalytic activity of rhodium phosphide for selective hydrodeoxygenation of phenol, *Chem. Lett.*, 2019, **48**, 471–474.
- 38 G. Kresse and J. Furthmüller, Efficient iterative schemes for *ab initio* total-energy calculations using a plane-wave basis set, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1996, **54**, 11169–11186.
- 39 G. Kresse and J. Furthmüller, Efficiency of *ab initio* total energy calculations for metals and semiconductors using a plane-wave basis set, *Comput. Mater. Sci.*, 1996, **6**, 15–50.
- 40 J. P. Perdew, K. Burke and M. Ernzerhof, Generalized gradient approximation made simple, *Phys. Rev. Lett.*, 1996, **77**, 3865–3868.
- 41 P. E. Blöchl, Projector augmented-wave method, *Phys. Rev.*, 1994, **50**, 17953–17979.
- 42 G. Kresse and D. Joubert, From ultrasoft pseudopotentials to the projector augmented-wave method, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1999, **59**, 1758–1775.
- 43 S. Grimme, J. Antony, S. Ehrlich and H. Krieg, A consistent and accurate *ab initio* parametrization of density functional dispersion correction (DFT-D) for the 94 elements H–Pu, *J. Chem. Phys.*, 2010, **132**, 154104.
- 44 J. He, Á. Morales-García, O. Bludský and P. Nachtigall, The surface stability and equilibrium crystal morphology of Ni<sub>2</sub>P nanoparticles and nanowires from an *ab initio* atomistic thermodynamic approach, *CrystEngComm*, 2016, **18**, 3808–3818.
- 45 H. Duan, D. Li, Y. Tang, Y. He, S. Ji, R. Wang, H. Lv, P. P. Lopes, A. P. Paulikas, H. Li, S. X. Mao, C. Wang, N. M. Markovic, J. Li, V. R. Stamenkovic and Y. Li, High-performance Rh<sub>2</sub>P electrocatalyst for efficient water splitting, *J. Am. Chem. Soc.*, 2017, **139**, 5494–5502.
- 46 K. Persson, *Materials Data on Ni<sub>2</sub>P (SG:189) by Materials Project*, 2014.
- 47 K. Persson, *Materials Data on Rh<sub>2</sub>P (SG:225) by Materials Project*, 2014.
- 48 D. Kim, C. Xie, N. Becknell, Y. Yu, M. Karamad, K. Chan, E. J. Crumlin, J. K. Korskov and P. Yang, Electrochemical activation of CO<sub>2</sub> through atomic ordering transformations of AuCu nanoparticles, *J. Am. Chem. Soc.*, 2017, **139**, 8329–8336.
- 49 J. J. Choi, C. R. Bealing, K. J. Hughes, E. Zhang, D.-M. Smilgies, R. G. Hennig, J. R. Engstrom and T. Hanrath, Controlling nanocrystal superlattice symmetry and shape-anisotropic interactions through variable ligand surface coverage, *J. Am. Chem. Soc.*, 2011, **133**, 3131–3138.
- 50 L. Lutterotti and M. Bortolotti, Object-oriented programming and fast computation techniques in Maud, a program for powder diffraction analysis written in Java, *Compcomm. Newslett.*, 2003, **1**, 43–50.
- 51 P. E. R. Blanchard, A. P. Grosvenor, R. G. Cavell and A. Mar, Effects of metal substitution in transition-metal phosphides (Ni<sub>1-x</sub>M<sub>x</sub>)<sub>2</sub>P (M = Cr, Fe, Co) studied by X-ray photoelectron and absorption spectroscopy, *J. Mater. Chem.*, 2009, **19**, 6015–6022.
- 52 D. R. Liyanage, D. Li, Q. B. Cheek, H. Baydoun and S. L. Brock, Synthesis and oxygen evolution reaction (OER) catalytic performance of Ni<sub>2-x</sub>Ru<sub>x</sub>P nanocrystals: enhancing activity by dilution of the noble metal, *J. Mater. Chem. A*, 2017, **5**, 17609–17618.
- 53 T. N. Batugedara and S. L. Brock, Role of noble- and base-metal speciation and surface segregation in Ni<sub>2-x</sub>Rh<sub>x</sub>P nanocrystals on electrocatalytic water splitting reactions in alkaline media, *Chem. Mater.*, 2022, **34**, 4414–4427.
- 54 C. Wei, R. R. Rao, J. Peng, B. Huang, I. E. L. Stephens, M. Risch, Z. J. Xu and Y. Shao-Horn, Recommended practices and benchmark activity for hydrogen and oxygen electrocatalysis in water splitting and fuel cells, *Adv. Mater.*, 2019, **31**, 1806296.
- 55 R. B. Wexler, J. M. P. Martinez and A. M. Rappe, Active role of phosphorus in the hydrogen evolving activity of nickel phosphide (0001) surfaces, *ACS Catal.*, 2017, **7**, 7718–7725.
- 56 L. Partanen, M. Hakala and K. Laasonen, Hydrogen adsorption trends on various metal-doped Ni<sub>2</sub>P surfaces for optimal catalyst design, *Phys. Chem. Chem. Phys.*, 2018, **21**, 184–191.
- 57 J. K. Nørskov, F. Abild-Pedersen, F. Studt and T. Bligaard, Density functional theory in surface chemistry and catalysis, *Proc. Natl. Acad. Sci. U. S. A.*, 2011, **108**, 937–943.
- 58 R. Michalsky, Y.-J. Zhang, A. J. Medford and A. A. Peterson, Departures from the adsorption energy scaling relations for metal carbide catalysts, *J. Phys. Chem. C*, 2014, **118**, 13026–13034.
- 59 F. G. Baddour, V. A. Witte, C. P. Nash, M. B. Griffin, D. A. Ruddy and J. A. Schaidle, Late-transition-metal-modified β-Mo<sub>2</sub>C catalysts for enhanced hydrogenation during guaiacol deoxygenation, *ACS Sustainable Chem. Eng.*, 2017, **5**, 11433–11439.
- 60 M. B. Griffin, G. A. Ferguson, D. A. Ruddy, M. J. Bidy, G. T. Beckham and J. A. Schaidle, Role of the support and reaction conditions on the vapor-phase deoxygenation of m-cresol over Pt/C and Pt/TiO<sub>2</sub>, *Catalysts*, 2016, **6**(4), 2715–2727.



- 61 W. Jin, L. Pastor-Perez, D. Shen, A. Sepulveda-Escribano, A. Gu and T. R. Reina, Catalytic upgrading of biomass model compounds: novel approaches and lessons learnt from traditional hydrodeoxygenation – a review, *ChemCatChem*, 2019, **11**, 924–960.
- 62 H. He, S. Xia and D. Luo, Sn-assisted nickel synergistically catalyzes the direct cleavage of C–O bond in lignin-derived m-cresol: theoretical and experimental analysis, *J. Catal.*, 2022, **410**, 180–193.
- 63 Y. He and S. Laursen, Trends in the surface and catalytic chemistry of transition-metal ceramics in the deoxygenation of a woody biomass pyrolysis model compound, *ACS Catal.*, 2017, **7**, 3169–3180.
- 64 X. Liu, W. An, C. H. Turner and D. E. Resasco, Hydrodeoxygenation of m-cresol over bimetallic NiFe alloys: kinetics and thermodynamics insight into reaction mechanism, *J. Catal.*, 2018, **359**, 272–286.
- 65 X. Liu, W. An, Y. Wang, C. H. Turner and D. E. Resasco, Hydrodeoxygenation of guaiacol over bimetallic Fe-alloyed (Ni, Pt) surfaces: reaction mechanism, transition-state scaling relations and descriptor for predicting C–O bond scission reactivity, *Catal. Sci. Technol.*, 2018, **8**, 2146–2158.
- 66 J. Zhou, W. An, Z. Wang and X. Jia, Hydrodeoxygenation of phenol over Ni-based bimetallic single-atom surface alloys: mechanism, kinetics and descriptor, *Catal. Sci. Technol.*, 2019, **9**, 4314–4326.

