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# Bimetallic Ru–Ni Catalyzed Aqueous-Phase Guaiacol Hydrogenolysis at Low H<sub>2</sub> Pressures

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ABSTRACT: Aqueous phase hydrogenolysis of renewable biomass at low H<sub>2</sub> pressures is an attractive route to selectively produce renewable fuels and valuable chemicals. Here, we showed that the dispersive Ru and Ni nanoparticles (NPs) on HZSM-5 with an optimum H. radical transfer catalyzed a rapid rate (152 mmol $\cdot$ g<sup>-1</sup>·h<sup>-1</sup>) in hydrogenolysis of C–O bonds in lignin-derived guaiacol at 240 °C and 2 bar H, pressure in water. The co-impregnated individual Ru and Ni nanoparticles (NPs) on HZSM-5 were highly dispersed and did not present an alloy structure, but the individual Ru and Ni NPs were in a close proximity. The guaiacol hydrogenolysis rates were proportional to the amounts of the adjacent RuO<sub>2</sub> and NiO NPs on the calcined samples, suggesting the closely contacted Ru and Ni NPs on HZSM-5 are the active sites. In the water phase at low H<sub>2</sub> pressures, Ru dissociated the hydrogen molecules to H· radicals (H·), and then such radicals were transferred to adjacent Ni atoms for activating the capability of inert Ni centers. The adjustment of the H. transfer length between Ru and Ni NPs led to shorter H. transfer lengths, which resulted in activities as high as 118 mmol·g<sup>-1</sup>·h<sup>-1</sup>. The transferring and anchoring of H· radicals was considered to be achieved by the Si-OH groups and their defects on HZSM-5, as demonstrated by temperature programmed desorption of hydrogen coupled with mass spectroscopy (TPD/H<sub>2</sub>-MS) experiment. To further shorten the H. transfer length over uniformly formed Ru and Ni nanoparticles, the isolated Ni islands were removed through the incorporation of a Ru precursor that initially occupied the Brönsted acid sites on HZSM-5. By fully activating the two metals in the aqueous phase via an H. transfer mechanism at low H<sub>2</sub> pressures, the rational design of bimetallic Ru-Ni catalysts provides a promising approach for achieving substantially high rates in selective hydrogenolysis steps.

**Keywords**: Bimetallic Ru–Ni, XAFS, H· Radical Transfer, Aqueous-Phase Hydrogenolysis, Lignin.

#### INTRODUCTION

The hydrogenolysis of C–O bonds represents an important reaction for the conversion of biomass that has ACS Paragon F attracted the attention of biomass conversion researchers<sup>1</sup>. Water is found in biomass with large amounts and is also produced as a result of oxygen removal reactions. Thus, selective hydrogenolysis of biomass is most likely carried out in water.

With regard to the aqueous-phase lignin conversion, Ru has been reported to be a proper hydrogenolysis metal showing medium activity and high selectivity for converting of lignin and its model compounds<sup>2-4</sup>. Ru/C showed higher hydrogenolysis selectivity than Pd/C and Pt/C for hydrogenolysis of lignin dimers ( $\beta$ -O-4 linkage) to arenes in the aqueous phase<sup>2</sup>. The Ru–WO<sub>x</sub> bifunctional catalyst displayed high catalytic activities for the hydrogenolysis of lignin derived phenols and phenyl ethers to arenes<sup>3</sup>. A porous Ru/Nb<sub>2</sub>O<sub>5</sub> catalyst enabled the selective production of arenes via direct hydrodeoxygenation of organosolv lignin<sup>4</sup>. A number of mechanisms have been proposed to explain the high activity of Ru in the hydrothermal biomass conversion processes. Akpa et al. showed that the interaction of water molecules with hydroxylbutyl intermediates considerably decreased the energy barriers for the hydrogenation of 2-butanone over a Ru(0001) surface, thereby increasing the reaction rates in water<sup>5</sup>. Additionally, Gallezot et al. demonstrated that water molecules co-adsorbed on Ru(0001) could lower the energy barriers, while the dissociation of water could result in larger hydrogen concentrations on the Ru(0001) surface. Thus, both effects would increase the hydrogenation rates of carbonyl groups<sup>6</sup>.

Low  $H_2$  pressures have been found to favor the selective aqueous-phase hydrogenolysis of biomass feedstock. We have previously reported that the weaker adsorbed  $H_2$  species on the Ru surface surrounding the benzene rings will be fast desorbed as the temperature increases, while the  $H_2$  species nearby the oxygen atoms are strongly adsorbed due to the induction by the oxygen atom of the  $\beta$ -O-4 model compound (contributing to 45–62% C–O linkages in lignin), and thus are retained on the Ru surface even with a rising temperature. This resulted in selective cleavage of C-O bonds and thus, achieves very high aromatic hydrocarbons selectivity<sup>7</sup>. However, low H<sub>2</sub> pressures will partially lower hydrogenolysis capability of Ru in water.

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Bimetallic Ru-Ni materials may modify the electronic and structural properties of the surface, which may highly accelerate the hydrogenolysis rates of C-O bond cleavage. In some cases it has been reported that unsupported core-shell RuNi nanoparticles (NPs) allowed the formation of smaller particle sizes as compared to Ni<sup>8</sup>, or the addition of Ru to Ni enhanced the interaction between both metals while weakening the interaction of Ni with Al-SBA-15<sup>9</sup>. Herein, in this work, we report that the optimization of the H- radical transfer length and the full activation of the two metals (Ru and Ni) can maximize the selectivity and activity for the cleavage of C-O bond of bio-molecule guaiacol in the aqueous phase and at low hydrogen pressures. Extensive characterization was used to explore the intrinsic Ru and Ni structure and interactions between Ru and Ni, as well as the structure-activity relationship. Based on these understandings, we eventualthe optimum bimetallic ly synthesized Ru-Ni<sub>modified</sub>/HZSM-5 catalyst for the selective hydrogenolysis reactions on guaiacol in water.

#### **RESULTS AND DISCUSSION**

Bimetallic RuNi/HZSM-5 Catalyzed Aqueous-phase Guaiacol Hydrogenolysis at a Low H<sub>2</sub> Pressure. Guaiacol, a lignin-derived model compound, was selected as the feedstock for the selective aqueous-phase hydrogenolysis reaction to phenol over Ru-M, Ru, and Ni based HZSM-5 catalysts. Mild conditions (240  $^{\circ}$ C, 2 bar H<sub>2</sub>) were selected to ensure high hydrogenolysis rates and to avoid the hydrogenation of the aromatic benzene rings<sup>10</sup>. We summarized the gained rates for gas-phase and liquid phase hydrogenolysis of guaiacol to benzene in literature and in our work (Tables S1 and S2), and by comparison Ru/HZSM-5 was shown to be a particularly active hydrothermally-stable hydrogenolysis catalyst in the aqueous phase. The Ru/HZSM-5 catalyst showed a hydrogenolysis rate of 32 mmol·g<sup>-1</sup>·h<sup>-1</sup> and a 90% phenol selectivity, which represents the highest catalytic rate reported to date for guaiacol hydrogenolysis."

A series of 5 wt%Ru–5 wt%M (M = Pd, Pt, Co, Cu, Fe, and Ni) bimetallic catalysts supported on HZSM-5 (prepared by the co-impregnation method) were tested towards the model reaction guaiacol hydrogenolysis in the aqueous phase (Fig. 1). The carbon balance in the liquid phase exceeded 92% in the tested cases. The addition of noble metals (i.e., Pd and Pt) to Ru/HZSM-5 resulted in slightly lower hydrogenolysis rates, although the phenol selectivity remained nearly unchanged (85-93%). Transition base metals (i.e., Fe, Co, Cu, and Ni) were subsequently added to the Ru/HZSM-5 catalysts. RuNi/HZSM-5 showed the highest activity (118 mmol·g<sup>-1</sup>·h<sup>-1</sup>, 4 times higher than that of Ru/HZSM-5) among the catalysts tested and a selectivity towards phenol similar to that of Ru/HZSM-5 (89%) within 1 h, although Ni/HZSM-5 only attained a low rate of 3.2 mmol  $g^{-1}$  h<sup>-1</sup>. When compared to

Ru/HZSM-5, RuCo/HZSM-5 showed a slightly higher hydrogenolysis rate (ca. 40  $\text{mmol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ ), while RuCu/HZSM-5 and RuFe/HZSM-5 exhibited lower rates (18 and 24 mmol·g<sup>-1</sup>·h<sup>-1</sup>, respectively). The stability of the active bimetallic RuNi/HZSM-5 catalyst was subsequently examined by conducting four consecutive catalytic runs (Fig. S1). The conversion and the phenol selectivity remained at around 72 and 90%, respectively, for the four consecutive runs, thereby indicating that the RuNi/HZSM-5 catalyst was robust. As revealed by TEM images (Fig. S2), the bimetallic Ru and Ni NPs were slightly sintered after the four consecutive runs, while N<sub>2</sub> adsorption measurements revealed a minimal loss of surface areas in the recycled catalysts (Table S<sub>3</sub>). These data demonstrated that RuNi/HZSM-5 was reusable. In a next step, we focused on understanding the role of RuNi/HZSM-5 in enhancing the hydrogenolysis rates during the aqueous-phase reaction at low H<sub>2</sub> pressures.



**Figure 1.** Selective hydrogenolysis of guaiacol to phenol over Ru–M, Ru-, and Ni- based HZSM-5 catalysts. The left axis shows the hydrogenolysis rate on guaiacol, while the right axis shows the selectivity towards phenol. General conditions: guaiacol (1.0 g), 5 wt% Ru-5 wt% M/HZSM-5 or 5 wt% Ru/HZSM-5 (0.03 g), H<sub>2</sub>O (100 mL), 240 °C, 2 bar H<sub>2</sub>, 1 h, and stirring at 650 rpm.

Determination of the distribution and structure of bimetallic Ru-Ni nanoparticles. The RuNi/HZSM-5 catalyst (5%Ru-5%Ni/HZSM-5) was extensively characterized by X-ray diffraction (XRD), high-resolution transmission electron microscopy (HR-TEM), scanning transmission electron microscopy coupled with high-angle annular dark field (STEM-HAADF), TEM coupled with electron energy loss spectroscopy (TEM-EELS), X-ray absorption fine structure spectroscopy (XAFS), and density functional theory (DFT) calculations. As shown in XRD patterns (Fig. 2a), no diffraction peaks ascribed to Ru were observed for 5%Ru/HZSM-5 because of the high dispersion of the metal, while diffraction peaks ascribed to face centered cubic phases (fcc)-structured Ni (111) were observed for 5%Ni/HZSM-5. Unlike the monometallic catalysts, no Ru- or Ni-related diffraction peaks in XRD patterns were identified for the RuNi/HZSM-5 catalysts. The absence of diffraction peaks corresponding to Ru in the bimetallic catalyst may indicate the presence of highly dispersed Ru NPs. The absence of diffraction peaks ascribed to Ni (111) in the RuNi/HZSM-5 catalyst was result-

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**Figure 2.** (a) XRD patterns of 5%Ru/HZSM-5, 5%Ni/HZSM-5, and 5%Ru-5%Ni/HZSM-5. A series of characterizations for RuNi/HZSM-5 sample (Figs. 2b–h); (b) HAADF image and particle distributions, (c) HRTEM image, (d) HRTEM image, (e) HAADF image, (f) HAADF-mapping, (g) HAADF-mapping with higher magnification, (h) EELS line scan. (i) FT-EXAFS spectra at the Ni K-edge and Ru K-edge of Ni, Ru–Ni and Ru NPs on HZSM-5.

Table 1. Curve-fitting results of 5%Ni/HZSM-5, 5%Ru/HZSM-5, and 5%Ru-5%Ni/HZSM-5.

| Sample                                                                        | Edge      |       | Shell   |       | Ν     | R/Å    |       | $\Delta \sigma_2/\text{Å}_2$ |
|-------------------------------------------------------------------------------|-----------|-------|---------|-------|-------|--------|-------|------------------------------|
| Ni/HZSM-5                                                                     | Ni K-edge |       | Ni-Ni   |       | 7.250 | 2.4858 |       | 0.00604                      |
| RuNi/HZSM-5                                                                   | Ni K-edge |       | Ni-Ni   | :     | 2.472 | 2.4751 |       | 0.00523                      |
|                                                                               | Ru K-edge |       | Ru-Ru   | -     | 3.948 | 2.6574 |       | 0.00318                      |
| Ru/HZSM-5                                                                     | Ru K-edge |       | Ru-Ru   |       | 3.972 | 2.6544 |       | 0.00325                      |
| *N: Coordination number, R: distance, $\Delta \sigma_2$ : Debye-Waller factor |           |       |         |       |       |        |       |                              |
| Table 2. The formation energy of Ru-Ni alloy calculated from DFT.             |           |       |         |       |       |        |       |                              |
| Alloy (Ru : Ni, mass ratio)                                                   |           | 5:0.5 | 5 : 1.5 | 5:2.5 | 5:3.5 | 5:4.5  | 5:5   | 5 : 12.5                     |
| Formation energy (ev/atom)                                                    |           | 0.032 | 0.057   | 0.054 | 0.044 | 0.042  | 0.045 | 0.028                        |

ed from the weak crystallization of Ni NPs, thereby imply ing that the bimetallic NPs maybe well dispersed, with Ru promoting the dispersion of Ni NPs.

representative HAADF-STEM image of Α RuNi/HZSM-5 (Fig. 2b) revealed that the bimetallic NPs were uniformly dispersed throughout the HZSM-5 support (average diameter: ca. 4.5 nm), in line with the XRD results. HRTEM observations on RuNi/HZSM-5 revealed the presence of separate Ru (101) and Ni (111) NPs over HZSM-5, with interlayer spacings of 0.26 and 0.23 nm, respectively (Figs. 2c-2d), thereby indicating that individual Ru and Ni NPs are present on the HZSM-5 surface. To figure out the intrinsic structures of the bimetallic RuNi/HZSM-5 catalyst in a larger region (300 nm and 100 nm), the STEM-EELS and STEM-mapping measurements were performed (Figs. 2e-2h). The STEM-Mapping results (Figs. 2e-2g) clearly showed that Ru and Ni NPs were uniformly and separately distributed in the tested region, especially with the higher magnitude image (Fig. 2g). A small domain with Ni-rich particles (green region, Fig. 2g) may form the Ni islands, and this information is highly agreed with the following catalyst characterization of TPR-H<sub>2</sub> profiles. The EELS line scan (Fig. 2h) demonstrated the uniform distribution of Ru and Ni elements in the region of 30 nm. Thus, EELS mapping and line scan, XRD,

and HRTEM results consistently confirmed the uniformly distribution of individual Ru and Ni NPs on HZSM-5.

X-ray absorption fine structure (XAFS) measurement was conducted on RuNi/HZSM-5 for the Ru and Ni Kedges. Fig. 2i shows the first shell fitting results (with k<sup>3</sup> weight, and the fitting results in k-space are presented in Figs. S<sub>3</sub>a to S<sub>3</sub>d), and the gained parameters are provided in Table 1. The coordination numbers for the Ni-Ni contributions in the first shell of Ni/HZSM-5 and RuNi/HZSM-5 were 7.250 and 2.472 (see Table 1). The smaller Ni-Ni coordination number of RuNi/HZSM-5 reflected the smaller size of Ni particles compared to that on Ni/HZSM-5. The nearly identical coordination numbers for the Ru-Ru contributions in the first shell of Ru/HZSM-5 (3.972) and RuNi/HZSM-5 (3.948) suggested comparable Ru particle sizes on these two samples. The Ni-Ni interatomic distances were both 2.48 Å on Ni/HZSM-5 and RuNi/HZSM-5, respectively, which is in good agreement with that of fcc Ni metal (2.49 Å). The same Ru-Ru bond distances (ca. 2.65 Å) were detected for the Ru k-edge in the Ru based samples. It was noted that the Ru-Ni bond (at around 2.54 Å)<sup>12</sup> was not observed. According to these results, RuNi alloy NPs were not formed, which was consistent with the HRTEM results. Moreover, DFT calculations (Table 2) indicated that the formation energies of RuNi alloys at varying atomic ratios (i.e., 5/0.5–5/12.5) were in the 0.028–0.057 eV/atom range. These positive values confirmed that a RuNi alloy phase was hardly formed. These results were in agreement with previous analyses indicating that Ni and Ru are essentially immiscible at equilibrium in virtue of a positive enthalpy of formation<sup>13</sup>. Thus, the synthesis of RuNi alloys was hindered at mild conditions. Based on these combined results, we concluded that the individual Ru and Ni NPs were highly dispersed on HZSM-5, and RuNi alloy phases were not formed.

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Interaction of Ru and Ni NPs on HZSM-5. We subsequently explored the interaction between Ru and Ni NPs on HZSM-5. Temperature programmed reduction of hydrogen (TPR-H<sub>2</sub>) was used to assess the interaction between the metals and the support as well as the interactions between the two metals. The monometallic Ru catalyst exhibited a strong reduction peak with a maximum at 143 °C (Fig. 3a) that was assigned to the reduction of RuO<sup>14</sup>. The second minor peak observed at lower temperatures (66°C) was likely ascribed to the reduction of small amounts of the Ru precursor (i.e., RuCl<sub>3</sub>·3H<sub>2</sub>O)<sup>15</sup>. In contrast, the monometallic Ni catalyst exhibited two reduction peaks at 321 and 450 °C that can be attributed to the reduction of NiO species showing different interaction strengths with HZSM-5<sup>16</sup>. The bimetallic RuNi catalyst exhibited three reduction peaks at 207, 310, and 409 °C, which corresponded to "RuO<sub>2</sub>-NiO", "NiO-1", and "NiO-2" species, respectively. The "RuO2-NiO" species referred to the individual RuO2 and NiO nanoparticles in a close proximity, while "NiO-1" and "NiO-2" represented NiO species interacting with HZSM-5. Remarkably, the reduction temperature for "RuO<sub>2</sub>-NiO" species (207 °C) lied between RuO<sub>2</sub> (143 °C) and NiO (321 and 450 °C) species in the monometallic catalysts. The lower reduction temperature of the "RuO2-NiO" species than "NiO" species can be explained by a mechanism involving an initial H<sub>2</sub> dissociation over Ru NPs to form H· radical species that are subsequently transferred to adjacent Ni atoms to facilitate the reduction of NiO17. The presence of new "RuO<sub>2</sub>-NiO" species also suggested a strong interaction between Ru and Ni NPs.

Infrared (IR) spectroscopy of adsorbed CO was used to identify the states of bimetallic NPs. Ru/HZSM-5 showed three main bands at 2017, 2080, and 2134  $\text{cm}^{-1}$  (Fig. 3b), assigned to linear-adsorbed CO on metallic Ru<sup> $\circ$ </sup>, Ru<sup> $\delta$ +-</sup> (CO), as well as  $Ru^{\delta_+}$ -(CO)<sub>n</sub> species located inside the HZSM-5 pores, respectively<sup>18</sup>. Ni/HZSM-5 showed a band at 2055 cm<sup>-1</sup> that was assigned to linearly adsorbed CO on Ni<sup>0.18</sup> The bimetallic RuNi/HZSM-5 catalyst showed four bands at 2023, 2049, 2082, and 2145 cm<sup>-1</sup> ascribed to linearly adsorbed CO on Ru<sup>°</sup>, Ni<sup>°</sup>, and Ru<sup> $\delta_+$ </sup>-(CO), and Ru<sup> $\delta_+$ </sup>- $(CO)_n$  species, respectively<sup>19</sup>. No additional COadsorption peaks were observed for RuNi/HZSM-5 as compared to Ru/HZSM-5 and Ni/HZSM-5, probably ruling out the possibility of Ru-Ni alloy phase. In addition, even after incorporating of Ni atoms, the CO adsorption intensity on RuNi/HZSM-5 was almost unchanged compared to Ru/HZSM-5, suggesting well dispersed Ru and Ni NPs on the surface of RuNi/HZSM-5. It is worth noting

that the CO adsorption peak over the Ni<sup>o</sup> species in the RuNi/HZSM-5 sample shifted to lower wavenumbers (2049 cm<sup>-1</sup>) as compared to Ni/HZSM-5 (2055 cm<sup>-1</sup>), while the three peaks ascribed to Ru species in RuNi/HZSM-5 (2023, 2082, and 2145 cm<sup>-1</sup>) shifted to higher wavenumbers as compared to Ru/HZSM-5 (2017, 2080 and 2134 cm<sup>-1</sup>). The red- and blue-shifts of the Ni-CO and Ru-CO signals, respectively, suggested that electrons were transferred from Ru to Ni atoms, thereby further confirming a close interaction between both metals, which were in line with the TPR-H<sub>2</sub> results.



**Figure 3.** The characterizations of Ru/HZSM-5, Ni/HZSM-5, and RuNi/HZSM-5 catalysts by (a) TPR-H<sub>2</sub> profiles and (b) FT-IR spectra of adsorbed CO at ambient temperature. XPS spectra of (c) Ru 3d spectral region in Ru/HZSM-5 and RuNi/HZSM-5, and (d) Ni 2p spectral region in Ni/HZSM-5 and RuNi/HZSM-5. **Black curve** (RuNi/HZSM-5), **Red curve** (Ru/HZSM-5), and **Blue curve** (Ni/HZSM-5).

X-ray photoelectron spectroscopy (XPS) measurements were carried out to assess the chemical states of Ru and Ni in the Ru/HZSM-5, Ni/HZSM-5, and RuNi/HZSM-

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5 samples (Figs. 3c-d). The main peak at 284.8 eV in the Ru 3d spectra (Fig. 3c) was attributed to a strong C1s signal from carbon<sup>20</sup>. The Ru peaks in Ru/HZSM-5 (red curve) at binding energies (BEs) of 280.4 and 285.7 eV were assigned to Ru(o) 3d<sub>5/2</sub> and Ru(o) 3d<sub>3/2</sub>, respectively<sup>20</sup>. Ru remained in the metallic Ru(o) state for RuNi/HZSM-5 (black curve) after Ni addition, although the BE of the  $Ru(o) 3d_{5/2}$  and  $Ru(o) 3d_{3/2}$  bands increased by 0.2 eV. Fig. 3d shows the Ni 2p<sub>3/2</sub> spectra of Ni/HZSM-5 and RuNi/HZSM-5. In the case of Ni/HZSM-5 (blue curve), the peak at 852.9 eV (satellite peak at 858.8 eV) was ascribed to Ni(o) species, while the peak at 855.5 eV was assigned to Ni in an oxidized state (NiO) originated via surface oxidation of Ni(o) NPs in air<sup>21</sup>. In the case of RuNi/HZSM-5, the BEs of the Ni 2p3/2 spectra decreased to 852.5 and 858.4 eV, while the band associated to NiO species remained unchanged as compared to Ni/HZSM-5. The increased binding energy of Ru(o) species and decreased binding energy of Ni(o) species, respectively, further supported that electrons were transferred from Ru to Ni atoms, in line with the results from IR spectra of CO adsorption (Fig. 3b). This electron transfer between Ru and Ni resulted in electron-deficient Ru and electronenriched Ni atoms, thereby increasing the strength of the interaction between Ni and Ru NPs.

**Determination of the active site on RuNi/HZSM-5.** According to the TPR-H<sub>2</sub> profile (Fig. 3a), the calcined RuNi/HZSM-5 catalyst contained "RuO<sub>2</sub>-NiO", "NiO-1", and "NiO-2" species corresponding to interacting RuO<sub>2</sub>-NiO NPs, weakly interacting NiO-HZSM-5, and strongly interacting NiO-HZSM-5 entities, respectively. To determine the actual active site of RuNi/HZSM-5, the hydrogen reduction temperatures and the Ni/Ru ratios were varied to investigate the relationship between the nature of the active sites and their catalytic performances.

To separately reduce the "RuO<sub>2</sub>-NiO", "NiO-1", and "NiO-2" species, the calcined RuNi/HZSM-5 catalysts were reduced at varying temperatures (i.e., 180, 240, 350, 435, and 800 °C, Fig. 4a). Then the as-received RuNi/HZSM-5 samples were tested in the aqueous-phase guaiacol hydrogenolysis reaction at 240 °C and 2 bar H, (Fig. 4b). RuNi/HZSM-5 showed different guaiacol hydrogenolysis rates (25, 102, 82, 53, and 36 mmol $\cdot$ g<sup>-1</sup>·h<sup>-1</sup>) depending on the reduction temperatures (180, 240, 350, 435, and 800 °C, respectively). The maximum hydrogenolysis rate (102 mmol·g<sup>-1</sup>·h<sup>-1</sup>) was achieved after reduction of RuNi/HZSM-5 at 240 °C, with exclusive interacted Ru and Ni NPs after reduction of "RuO<sub>2</sub>-NiO" species. Above 240 °C, the hydrogenolysis rates decreased gradually with temperature increase, probably due to the presence of Ni/HZSM-5 species at higher reduction temperatures. These results may indicate that closely contacted individual RuO, and NiO particles (labeled as "RuO,-NiO" species) on HZSM-5 rather than "RuO<sub>2</sub>" or "NiO" were the main precursors for generating active sites of interacted Ru and Ni NPs for the hydrogenolysis of guaiacol. In addition, the reduced Ni islands on HZSM-5 at higher reduction temperatures may impede the hydrogenolysis capability of interacted Ru and Ni NPs from "RuO<sub>2</sub>-NiO" species. But this evidence is not sufficient, since the hightemperature reduction process may change the resulted particle sizes of Ru and Ni NPs on HZSM-5, and then alter the corresponding catalytic activities.



**Figure 4.** (a) TPR-H<sub>2</sub> profile of calcined 5%Ru-5%Ni/HZSM-5. (b) Hydrogenolysis rates of guaiacol to phenol over 5%Ru-5%Ni/HZSM-5 reduced at different temperatures. (c) TPR-H<sub>2</sub> profile of calcined 5%Rux%Ni/HZSM-5 with varying Ni contents. (d) Guaiacol hydrogenolysis rates to phenol and normalized TPR-H<sub>2</sub> areas for 5%Ru-x%Ni/HZSM-5 samples with varying Ni contents. General conditions: guaiacol (1.0 g), RuNi/HZSM-5 catalyst (0.03 g), H<sub>2</sub>O (100 mL), 240 °C, 2 bar H<sub>2</sub>, 1 h, and stirring at 650 rpm.

Subsequently, the relation of guaiacol hydrogenolysis and Ru/Ni ratios was explored. The Ni/Ru ratios were varied by adjusting the Ni content (0, 0.5, 1, 2, 3, 5 and 7.5 wt%) at a constant Ru content of 5 wt%. As shown in the TPR- $H_2$  profiles (Fig. 4c), the temperatures and peak areas for reducing "RuO<sub>2</sub>-NiO" species gradually increased with the increasing Ni contents. The higher reduction temperatures from 140 to 220 °C with Ni contents of 0-3 wt% (at 5 wt% Ru loading) suggested stronger Ru and Ni interaction, which may be resulted from closer distance of RuO<sub>2</sub> and NiO species. This is in line with the results from XPS spectra and IR spectra of adsorbed CO. On the 5%Ru-5%Ni/HZSM-5 sample, isolated Ni island species (reduction temperatures from 220 to 435 °C) appeared and the reduction temperatures for "RuO<sub>2</sub>-NiO" species kept stable, indicating that the atom numbers for interacted Ru and Ni NPs reached an equilibrium value. Continuously increasing the Ni content to 7.5 wt%, the reduction peaks at 243 °C appeared between reduction peaks for interacted "RuO<sub>2</sub>-NiO" and isolated NiO species, suggesting that additional NiO NPs may partially cover RuO<sub>2</sub>-NiO species.



**Figure 5.** The speculated formation process of x%Ru-5%Ni/HZSM-5 (x=0-7.5) catalysts with varying Ni contents at a Ru loading of 5 wt%.

As shown in TPR-H<sub>2</sub> profile at Fig. 4d, the consumed H<sub>2</sub> were proportional to the concentrations of the RuO<sub>2</sub> and NiO precursors on HZSM-5. Below the Ni contents at 3 wt% on RuNi/HZSM-5 samples, the consumed H<sub>2</sub> were quantitatively resulted from the concentrations of "RuO<sub>2</sub>-NiO" species. Within the higher Ni contents of 5-7 wt% on RuNi/HZSM-5 samples, the consumed H<sub>2</sub> included the hydrogen-reduction of RuO<sub>2</sub>-NiO and surplus NiO species.



**Figure 6.** (a) FT-IR spectra of adsorbed CO on 5%Ru-x%Ni/HZSM-5 with varying Ni contents at ambient temperature. (b) Normalized areas of CO adsorption for Ru<sup> $\delta$ +</sup>-(CO) species in IR spectra on 5%Ru-x%Ni/HZSM-5 samples with varying Ni contents.

The x%Ru-5%Ni/HZSM-5 (x=0-7.5) samples were tested for guaiacol hydrogenolysis at the identical conditions (Fig. 4d). Within Ni contents of 0-3 wt%, the guaiacol hydrogenolysis rates were proportional to the concentrations of the "RuO<sub>2</sub>-NiO" species, further suggesting that the reduced interacted Ru and Ni NPs may be the active sites. However, such hydrogenolysis rates were lowered with 5%-7.5% Ni contents on RuNi/HZSM-5 samples, probably due to the presence of isolated NiO islands and covered  $RuO_2$ -NiO species by NiO on their calcined samples, as shown in TPR-H<sub>2</sub> profiles at Fig. 4c. Thus, based on the above understandings, we speculate the formation process of x%Ru-5%Ni/HZSM-5 (x=o-7.5) samples at Fig. 5.

The hydrogenolysis activities can be influenced by the accessible Ru atoms on the tested reduced RuNi/HZSM-5 samples, apart from the amounts of closely interacted Ru and Ni species. To figure it out, we explored the accessibility of Ru atoms by IR spectroscopy of adsorbed CO with 5%Ru- x%Ni/HZSM-5 (x=0-7.5) samples (Fig. 6a), and the deconvolution of the corresponding species was provided in Fig. S4. The peak at 2134 cm<sup>-1</sup> assigning to  $Ru^{\delta+}$ -(CO) species gradually decreased from 5%Ru/HZSM-5 to 5%Ru-7.5%Ni/HZSM-5 as Ni contents increased. In line with it, the plotted integrated areas of the  $Ru^{\delta_+}$ -(CO) species band was displayed as a function of Ru/Ni ratios in Fig. 6b, showing that the accessible Ru atoms were decreasing with increased Ni contents. This gained information concerning on the accessible Ru atoms (Fig. 6b) was not consistent with the activity changes in Fig. 4d (black line), further confirming that the closely contacted Ru and Ni NPs on HZSM-5 are the active sites.

Understanding the H<sup>+</sup> transfer on Ru and Ni NPs on HZSM-5 for aqueous phase guaiacol hydrogenolysis. The RuO<sub>2</sub>, RuO<sub>2</sub>–NiO, and NiO surface species are present on the calcined RuNi/HZSM-5 catalyst. We prepared three RuNi/HZSM-5 samples (i.e., T-1, T-2, and T-3) having different Ru–Ni distances in an attempt to investigate the influence of the Ru–Ni distance on the reaction rates (Fig. 7a). RuNi/HZSM-5 (T-1) was synthesized by separately pressing the impregnated Ru/HZSM-5 and Ni/HZSM-5 powders and subsequent physical mixture of the pressed samples. RuNi/HZSM-5 (T-2) was prepared by initially mixing the Ru/HZSM-5 and Ni/HZSM-5 followed by pressing. RuNi/HZSM-5 (T-3) was prepared by pressing the co-impregnated RuNi/HZSM-5 catalyst.

Subsequently, TPR-H<sub>2</sub> technique was used to assess the degree of interaction between Ru and Ni centers (Fig. 7b). The TPR profile of RuNi/HZSM-5 (T-1) revealed the presence of separate RuO<sub>2</sub> (reduction peaks at 140 °C) and NiO (reduction peaks at 330 and 460 °C) particles on the support, demonstrating no apparent interaction between them. The reduction temperature at 197 °C on RuNi/HZSM-5 (T-2) was relatively lower than 207 °C for the interacting RuO<sub>2</sub>-NiO species on RuNi/HZSM-5 (T-3), but was much higher than the reduction temperature of RuO<sub>2</sub> on T-1 (140 °C), indicating a much stronger interaction between RuO2 and NiO NPs on T-2. The order for the strength of interaction between RuO, and NiO NPs on T-1, T-2 and T-3 was: T-3 > T-2 >T-1. Therefore, it can be concluded that the hydrogen transfer distance between Ru and Ni centers followed the trend: T-3 < T-2 < T-1, indicating that the reduction temperature of NiO was strongly influenced by the length of the hydrogen transfer process.

Apart from the characterization of  $TPR-H_2$  profiles, the Ru and Ni interaction was also detected by the EELS lines of three RuNi/HZSM-5 samples of T-1, T-2, and T-3

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(Fig. 7c). The average distances between Ru and Ni particles determined by EELS are defined to be the adjacent distances between Ru-rich and Ni-rich centers, as indicated from Fig. 7c. On T-1, the average distance of Ru and Ni particles as detected by the SEM-EELS was around 150-180  $\mu$ m. On the T-2 and T-3 samples, the average distances of Ru and Ni atoms were ca. 50-100 nm and 3.3 nm, respectively, as analyzed by the STEM-EELS measurements. The trend in Ru- and Ni- particle distance among T-1, T-2, and T-3 (T-3 < T-2 < T-1) shown from EELS results are highly consistent with that from TPR-H<sub>2</sub> profiles in Fig. 7b.



Three approaches for constructing Figure 7. (a) RuNi/HZSM-5 (T-1), RuNi/HZSM-5 (T-2), and RuNi/HZSM-5 (T-3) samples. (b) TPR profiles of (T-1), RuNi/HZSM-5 (T-2), RuNi/HZSM-5 and RuNi/HZSM-5 (T-3) samples. (c) The average distances between Ni and Ru particles detected by the EELS measurements on T-1, T-2 and T-3, (d) A schematic representation of the reduction of NiO and catalytic properties of

catalysts with different Ru and Ni distance.

The guaiacol hydrogenolysis activities were evaluated on the T-1, T-2, and T-3 samples at optimal conditions  $(240 \,^{\circ}\text{C} \text{ and } 2 \text{ bar H}_2)$  in aqueous phase. The hydrogenolysis rates increased as follows: 46 mmol·g<sup>-1</sup>·h<sup>-1</sup> (T-1), 60 mmol·g<sup>-1</sup>·h<sup>-1</sup> (T-2), and 118 mmol·g<sup>-1</sup>·h<sup>-1</sup> (T-3). The closer distance between Ru and Ni is, the higher hydrogenolysis activity attained, as shown in Fig. 7d. These results strongly indicated that the hydrogenolysis capacity of RuNi was also particularly determined by the length of the hydrogen transfer process.

Based on the above results, we formulated a reaction mechanism for the hydrogenolysis of C-O bonds over RuNi centers in the aqueous phase at low hydrogen pressures. The Ni NPs showed a very low activity (3.2 mmol·g<sup>-1</sup>·h<sup>-1</sup>) because of their relative poor hydrogen dissociation ability and the low concentration of H<sub>2</sub> in water. However, the addition of Ru to Ni dramatically enhanced the hydrogenolysis rates to 118 mmol·g<sup>-1</sup>·h<sup>-1</sup>. As shown in Fig. 8, in the co-impregnated bimetallic RuNi/HZSM-5 catalyst, it is speculated that Ru can fast dissociate lowconcentrated hydrogen in water to form H. radicals that are rapidly transferred to the adjacent Ni atoms, thereby activating these inert Ni centers at low hydrogen pressure. Thus, the hydrogenolysis capability was greatly influenced by the distance between Ru and Ni (i.e., the length of the hydrogen radical transfer process).



**Figure 8.** The supposed schematics of the C–O hydrogenolysis mechanisms of guaiacol over Ni/HZSM-5 and RuNi/HZSM-5.

Next, we try to explore how the HZSM-5 support acts as a holder to store and transfer the H- radicals between Ru and Ni NPs by the TPD-H<sub>2</sub> coupled with MS measurement. First we investigated the stability of HZSM-5 as a function of temperature, we observed that at round 400 °C the Brönsted acid site (BAS) of HZSM-5 was dehydrated to generate water, as evidenced by the appearance of H<sub>2</sub>O signal on the MS detector (Fig. S<sub>5</sub>). In addition, in our previous work we also observed structural changes of HZSM-5 during regeneration by air-calcination and hydrogen-reduction process.<sup>22</sup> The acid site concentrations changed in the following trend: (i) the LAS increased and the BAS decreased, (ii) the sum of BAS and LAS (ca. 90 µmol/g) was nearly unchanged. Therefore, there are structural changes to HZSM-5 during calcination in flow air, i.e., above 450 °C, the dehydration of BAS formed Lewis acid sites. In fact, this gained former result highly agrees with our conclusion in this work on the loss of BAS of HZSM-5 at around 400 °C as shown from the TPD-MS (Fig. S5). Meanwhile, the produced H<sub>2</sub>O would release H<sub>2</sub> due to the recombination of H protons (derived from H<sub>2</sub>O) during the mass-spectrometric detection, which would seriously affect the detection of H<sub>2</sub> signal, and thus, we set the desorption temperature lower than 300 °C. Fig. 9a displayed TPD/H<sub>2</sub>-MS profiles of HZSM-5, RuNi/HZSM-5, and physically mixed RuNi/HZSM-5 and HZSM-5 samples. It showed that no hydrogen was adsorbed on the HZSM-5. But it was surprisingly noted that a significantly increased concentration on desorbed H<sub>2</sub> signal was observed on the physically mixed sample compared to RuNi/HZSM-5. It is suggested that the additional HZSM-5 may act as an H-



**Figure 9.** (a) The H<sub>2</sub>-TPD-MS profiles of HZSM-5, RuNi/HZSM-5, and physical mixture of RuNi/HZSM-5 and HZSM-5. (b) The speculated mechanism of transfer and reservoir of H species on RuNi/HZSM-5.

radical acceptor and transferor, after H<sub>2</sub> dissociation on Ru and Ni NPs. Therefore, hydrogen spillover occurs on the physical mixture of RuNi/HZSM-5 and HZSM-5. It was also observed that the maximum H<sub>2</sub> desorption temperature on physically mixed RuNi/HZSM-5 and HZSM-5 (130 °C) was much lower than that on RuNi/HZSM-5 (150 °C). This demonstrates a much weaker interaction of adsorbed H atoms on HZSM-5 compared to adsorbed H atoms on interacted Ru and Ni NPs. With the increasing amount of the HZSM-5 mixed into RuNi/HZSM-5 powder, the desorption curve on RuNi/HZSM-5 and 4 HZSM-5 can be clearly fitted into two peaks (Fig. S6), with one appearing at 76 °C and another appearing at 118 °C. They were assigned to the desorbed H atoms on HZSM-5 and desorbed H atoms on Ru and Ni NPs, respectively. This result is fitted with the statement of Prins<sup>23</sup> that the Hspillover species are strongly bonded to a metal particle and only moderately to a non-reducible support. Based on this recognition, the desorption temperature for H· on HZSM-5 would be much lower than that on interacted Ru and Ni NPs, and this is proved by our experimental results (Fig. 9a).

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It has been reported that defects on non-reducible oxides by high temperature treatment may anchor H atoms.<sup>24</sup> In line with it, Choi et al.<sup>24</sup> reported that surface hydroxyls, presumably Brönsted acids, are proved as a main mediator for migration of H atoms on the surface of HZSM-5. As shown in Fig. 9b, we depicted that the surface defects of Si-OH groups and the intact Si-OH groups including the Brönsted acids on HZSM-5 acted as an excellent holder to anchor and transfer the H· radicals. In addition, it is reported that H. radical spillover on nonreducible aluminum oxides is mediated by three coordinated centers and restricted to relative short distances from one metal to another metal.<sup>25</sup> This also suggests that the distance between the Ru and Ni centers may greatly influence the transfer of H. radicals, thus affecting the hydrogen spillover process. This is also evidenced by our designed experiments, when exploring the relationship between varying Ru and Ni distances and the corresponding hydrogenolysis activities, as displayed at Fig. 7. Therefore, the close interaction of Ru–Ni NPs can greatly increase the reaction rates by fully activating the capacity of metals via optimum H· transfer for the hydrogenolysis reaction at low hydrogen concentrations.

Blocking the inactive isolated Ni/HZSM-5 species on RuNi/HZSM-5 to form uniform interacted Ru and Ni NPs with shorted H. transfer distance. Abundant isolated Ni/HZSM-5 species were observed in the coimpregnated RuNi/HZSM-5 sample as evidenced by the reduction temperature peaks at 321 and 425 °C in the TPR-H, profile (Fig. 3a). The isolated Ni/HZSM-5 catalyst showed poor activity towards the hydrogenolysis of guaiacol (3.2 mmol·g<sup>-1</sup>·h<sup>-1</sup>) at 2 bar H<sub>2</sub> in water. On one hand, the presence of Ni islands hindered the formation of active interacted Ru and Ni NPs, or partially covered active interacted Ru and Ni NPs (Fig. 10a), which would lower their hydrogenolysis activity as confirmed from the results in Fig. 4d. On the other hand, the presence of Ni island would lengthen the H. transfer distance on Ru and Ni NPs. In order to block the presence of these inactive, isolated Ni species (RuNi/HZSM-5, Fig. 10a) while simultaneously maximizing the number of RuNi sites with shorter H. transfer distance, we used an improved synthesis method. In this method, the Ru precursor was firstly introduced over the HZSM-5 support after which the Ni precursor was incorporated. The catalyst was finally aircalcined and hydrogen-reduced in order to generate the active catalyst (Ru-Ni<sub>modified</sub>/HZSM-5, 5 wt% Ru-5 wt% Ni, Fig. 10b). The Ru-Ni<sub>modified</sub>/HZSM-5 catalyst showed guaiacol hydrogenolysis rates of 152 mmol·g<sup>-1</sup>·h<sup>-1</sup> (versus 118  $mmol \cdot g^{-1} \cdot h^{-1}$  for RuNi/HZSM-5).

We speculated that the initial incorporation of the Ru salt would favor ion-exchange between Ru ions and H<sup>+</sup> on HZSM-5, and the subsequent introduction of Ni ions would result in well-dispersed interacted Ru and Ni NPs on Ru-Ni<sub>modified</sub>/HZSM-5. The absence of Ni islands and the presence of abundant Ru-Ni active sites on the improved sample with shorted H· transfer distance would be responsible for the much higher C<sub>aromatic</sub>-O hydrogenolysis rates.

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#### **ACS Catalysis**



**Figure 10.** Formation mechanism and accelerated rates of guaiacol hydrogenolysis at 240 °C and 2 bar  $H_2$  with (a) RuNi/HZSM-5, (b) modified Ru-Ni/HZSM-5. Characterization of RuNi/HZSM-5 and modified Ru-Ni/HZSM-5 samples by (c) IR of pyridine adsorption, (d) TPR- $H_2$ , and (e) IR of adsorbed CO at ambient temperature.

To confirm our hypothesis, we conducted a series of characterizations on the catalyst samples. The sizes of interacted Ru and Ni NPs on Ru-Ni<sub>modified</sub>/HZSM-5 (d =  $4.5 \pm 0.8$  nm) were comparable to those on RuNi/HZSM-5  $(d = 4.5 \pm 1.2 \text{ nm})$ , as shown on TEM images (Fig. S7), eliminating their influence on the reaction. The acid sites of the samples were studied by analyzing the IR spectra of pyridine adsorption (Fig. 10c). The BAS on Ni/HZSM-5 (0.005 mmol·g<sup>-1</sup>) were almost completely occupied by Ni ions as compared to HZSM-5 (BAS: 0.175 mmol·g<sup>-1</sup>), while Ru/HZSM-5 showed a significantly higher concentration of BAS (0.020 mmol·g<sup>-1</sup>). These results indicated that the Ni ions have significantly stronger proton-exchange capacities compared to Ru ions. In line with this hypothesis, we confirmed the presence of RuO<sub>2</sub>-NiO and isolated NiO islands species on the co-impregnated RuNi/HZSM-5 catalyst by TPR-H<sub>2</sub> profile (i.e., reduction peaks from 207 °C, 310 °C, and 409 °C, respectively). In contrast, Ru@Ni/HZSM-5 did not exhibit the reduction peaks corresponding to isolated Ni/HZSM-5 (Fig. 10d). The presence of isolated Ni species was also demonstrated by the IR spectra of CO adsorption on RuNi/HZSM-5 (i.e., distinguishing peak of Ni<sup>o</sup> species at 2049 cm<sup>-1</sup>, Fig. 10e), while this peak was basically absent for Ru-Ni<sub>modified</sub>/HZSM-5. All these results suggest that more uniform RuNi NPs with shorted H· transfer distances are formed by this improved way, and thus, achieve much higher C-O bond hydrogenolysis rates.

#### **CONCLUSIONS**

By means of a new route involving H- radical transfer mechanism in aqueous phase, we remarkably enhanced the C-O cleavage rates on lignin-derived guaiacol using a bimetallic RuNi catalyst. In-depth XRD, HR-TEM, STEM-HAADF, STEM-EELS, XAFS, and DFT calculations characterization confirmed that the co-impregnated individual Ru and Ni NPs were highly dispersed and strongly interacted with each other, although alloyed phases were not formed. The closely contacted Ru and Ni NPs on HZSM-5 were subsequently proven to be the active sites. The dissociated H· radicals on Ru atoms were readily transferred to the adjacent inert Ni sites as a result of the interacting electronic structures of Ru and Ni particles, as evidenced by TPR-H<sub>2</sub>, IR spectra of CO adsorption, and XPS analyses. We observed a relationship between the H· radical transfer length on Ru and Ni NPs and the C-O bond cleavage activity. That is the increased hydrogenolysis rates upon shortening the H. transfer length. The structure design of

the catalyst allowed it to be more sensitive to lower  $H_2$  concentrations in water. The H· radicals transferring and anchoring was realized by the Si-OH groups and defects of HZSM-5, as demonstrated by TPD/H<sub>2</sub>-MS experiments. To further shorten the H· transfer length over uniformly formed Ru and Ni nanoparticles, Ni islands were blocked by initially occupying the BAS of HZSM-5 by ion-exchanged Ru ions, thereby maximizing the guaiacol hydrogenolysis rates. The new catalytic system involving H· radical transfer in aqueous phase reactions provides a promising approach for selective hydrogenolysis of biomass molecules over multi-functional catalysts.

#### ASSOCIATED CONTENT

#### Supporting Information

Catalyst recycling data, TPD-MS profile of HZSM-5, EXAFS raw data, the deconvolution of FT-IR spectra of adsorbed CO, TPD-MS profile of HZSM-5, TEM images of RuNi/HZSM-5 samples. This material is available free of charge via the Internet at <u>http://pubs.acs.org</u>.

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59 60 The authors declare no competing financial interest.

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