to produce benzyl alcohols and bioaromatics via the reductive lignin depolymerization process over Fe/H-style ultrastable Y (HUSY), Ni/HUSY, and Ni–Fe/HUSY catalysts using HCOOK/ETHOH in air. Synergy effect between HCOOK and the catalysts improved the depolymerization process, resulting in a higher bio-oil recovery. HCOOK does not act solely as an in situ hydrogen source; it also interacts with lignin to enable its initial depolymerization via a base-catalyzed mechanism to low-molecular-weight fragments, and in tandem with the catalyst, the hydrogenolysis rate of the depolymerized lignin monomers was enhanced. Fe/HUSY displayed an excellent activity for the catalytic reductive step in contrast to Ni/HUSY and Ni–Fe/HUSY by facilitating methoxy group removal via hydrogenolysis, thereby contributing to the yield and stabilization of the low-molecular-weight aromatics [diethyl ether (DEE)-soluble products]. Fe/HUSY gave the highest DEE product yield of >99 wt % and a total benzyl alcohol yield of 16 wt % with a total selectivity of 47 wt % (60 wt % for aromatic alcohols). Fe/HUSY was reused for the lignin depolymerization reaction without much loss of its initial activity, giving 13 wt % yield of benzyl alcohols with a selectivity of 58 wt % (77 wt % for aromatic alcohols).

**INTRODUCTION**

The utilization of lignocellulosic biomass as an alternative and sustainable resource for production of fuels, chemicals, and materials is progressively being regarded as a promising strategy to contribute to net emission reduction of greenhouse gases. Lignin is one of the most abundant aromatic resources in nature and accounts for about one-third of the organic carbon on earth; it mainly consists of three phenylpropyl alcohols—p-coumaryl alcohol (H), coniferyl alcohol (G), and sinapyl alcohol (S)—connected by carbon—ether (mostly β-O-4) and carbon—carbon such as β−5, β−β, and 5−5 bonds. The composition and the proportion of the lignin subunits vary considerably between different plant species, as well as the linkage types in the polymer and the quantity of methoxy groups present on the aromatic ring. These differences play an important role during lignin isolation from biomass. As such, organosolv lignin can be obtained through the pretreatment of lignocellulose by certain solvents such as ethanol, methanol, acetic acid, formic acid, or mixed organic solvents with water. Organosolv lignin is known to have a good solubility in polar organic solvents in comparison to other technical lignins (e.g., kraft and soda lignins). It is a sulfur-free lignin and has high purity and relatively lower molecular weight compared with other technical lignins and so has a higher catalytic conversion potential to valuable chemicals and products.

Over the past few decades, numerous lignin depolymerization methodologies including thermochemical, catalytic, and oxidative approaches have been studied for converting lignin...
into bioaromatics. However, recent research priorities have been on the development of cheap transition-metal heterogeneous catalysts for the hydrogenolysis process during the depolymerization process to reduce operating costs. Traditionally, heterogeneous acid catalysts, especially zeolites, have been successfully used in industrial processes including catalytic cracking, dealkylation, dehydration, and isomerization due to their low cost, high surface area, and excellent acid catalytic performance. Mesoporous/microporous zeolites with high Brønsted acid sites are reported to be highly effective for dealkylation and de-etherification reactions during lignin conversion processes. Ma et al. reported that using zeolite catalysts with different acidities and pore sizes in catalytic fast pyrolysis greatly impacted the lignin conversion to bioaromatics. As recently demonstrated by Wannmoe et al., H-style ultrastable Y (HUSY) catalyst with a Si/Al molar ratio of 5 and large pore size outperformed other HUSY type, H-BEA, and proton-exchanged Zeolite Socony Mobil-5 catalysts with higher Si/Al ratios to produce the highest yield of bioaromatics from organosolv lignin. Zhai et al. made great effort in depolymerizing organosolv birch lignin in methanol using bimetallic Ni–Fe catalysts supported on activated carbon to enhance the selectivity and yield of aromatic monomers. Song et al. showed that native lignin in birchwood was effectively depolymerized in alcohol over Ni-based catalysts [on supports such as Santa Barbara amorphous-15 (SBA-15)] into bioaromatics. This and other studies indicated that the use of an external gaseous H₂ source may not be necessary. This and other studies indicated that the use of an external gaseous H₂ source may not be necessary. This and other studies indicated that the use of an external gaseous H₂ source may not be necessary. However, despite all of these research, key challenges still exist in developing commercial viable technologies using technical lignins (such as organosolv lignin) because of low product yield as a consequence of reduced proportion of β-O-4 bonds and an increase in the proportion of condensed carbon–carbon bonds. Furthermore, the use of organic solvents, high catalyst loading, and catalyst stability in organic solvents still pose problems. We have considered some of these issues, and with the aim to improve the overall process economics, we have targeted the production of two groups of compound classes, namely, benzyl alcohols and bioaromatics (di- and polyaromatics). The former are used for higher-value applications in the fine chemical and pharmaceutical industries and will therefore lead to increased revenue, while the latter have potential for the production of bioresins.

In this study, mono- and bimetallic Ni and Fe supported on HUSY zeolite catalysts were investigated in ethanol and ethanol–water mixtures. Ethanol was selected as a solvent because it acts as a capping agent and formaldehyde scavenger, thereby suppressing char formation. In addition, a comparison between the oxide and metallic forms was performed and a depolymerization reaction was conducted in the presence of H₂ gas and using HCOOK as a hydrogen donor for the in situ conversion of aromatic aldehydes to aromatic alcohols. Simultaneously, the effect of the catalyst structure and catalyst reusability was also determined. The structures of the catalysts were investigated by several techniques, i.e., X-ray powder diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and X-ray photoelectron spectroscopy (XPS). The efficiency of lignin depolymerization was determined by gas chromatography–mass spectrometry (GC–MS), while the types of gases produced with the different solvents were measured by GC-thermal conductivity detector (TCD).

### RESULTS AND DISCUSSION

**Catalyst Characterization.** Table 1 shows the main physical properties of the synthesized catalysts. It can be seen that the Brunauer–Emmett–Teller (BET) surface area and total pore volume decreased with metal addition to the support as a result of the metal covering the zeolite support as well as partially blocking the pore channels’ mouth. The total acidity increased in the order Fe < HUSY < Ni–Fe < Ni. Two different types of acidic sites (Table S1) were distinguished—the weak acidic sites (signal maxima at 100–106 °C) and the strong acidic sites (signal maxima at 386–585 °C). The weaker sites are predominant in the Ni–Fe/HUSY (17.58 mmol g⁻¹) catalyst, but the stronger sites are present in the Ni/HUSY (2.67 mmol g⁻¹) catalyst. Figure 1 shows the XRD patterns for the support and metal-impregnated samples at the specific range of 2θ = 40–80°.

![Graph showing XRD patterns](image)

**Figure 1.** XRD patterns of fresh catalyst samples: (a) HUSY zeolite, (b) 10% Ni/HUSY, (c) 10% Fe/HUSY, and (d) 5% Ni–5% Fe/HUSY.

### Table 1. Physical Properties of Synthesized Catalysts

| catalyst     | S, BET (m² g⁻¹) | total pore volume (cm³ g⁻¹) | mean pore diameter (nm) | total acidity* (mmol g⁻¹) | mean metal crystallite size (nm) |
|--------------|----------------|-----------------------------|-------------------------|--------------------------|---------------------------------|
| HUSY         | 536            | 0.56                        | 2.93                    | 17.34                    | 21.8                            |
| 10% Ni/HUSY  | 432            | 0.49                        | 2.92                    | 19.45                    | 23.2                            |
| 10% Fe/HUSY  | 402            | 0.45                        | 3.07                    | 12.54                    | 25.8                            |
| 5% Ni–5% Fe/HUSY | 340            | 0.41                        | 2.95                    | 18.20                    | 21.9                            |

*Total acidity is the sum of high- and low-temperature peaks of acid sites’ concentration.
Figure 2. SEM images and elemental mapping of the fresh catalysts: (a, b) 10% Ni/HUSY, (d, e) 10% Fe/HUSY, and (g, i) 5% Ni–5% Fe/HUSY, and TEM images of the fresh catalysts: (c) 10% Ni/HUSY and (f) 10% Fe/HUSY.

Figure 3. HR-XPS spectra; (A) Ni 2p spectra for catalyst samples: (a) 10% Ni/HUSY and (b) 5% Ni–5% Fe/HUSY; (B) Fe 2P spectra for catalyst samples: (a) 10% Fe/HUSY and (b) 5% Ni–5% Fe/HUSY; (C) O 1s spectra for catalyst samples: (a) 10% Ni/HUSY, (b) 10% Fe/HUSY, and (c) 5% Ni–5% Fe/HUSY.
Table 2. Lignin Conversion (%) and Product Yield (wt %) under Different Conditions with and without Metal Oxide Catalysts

| entry | catalyst | solvent            | catalyst-to-lignin ratio (w/w) | time (h) | lignin conversion (%) | DEE-soluble products | acetone-soluble products | char          |
|-------|----------|--------------------|--------------------------------|----------|-----------------------|----------------------|-------------------------|---------------|
| 1     | blank    | ETOH/H2O (50:50)   |                                | 2        | 86.94                 | 60.21                | 4.79                    | 8.27          |
| 2     | HUSY     | ETOH/H2O (50:50)   | 0.1:1                          | 2        | 93.18                 | 76.35                | 4.77                    | 2.05          |
| 3     | Ni/HUSY  | ETOH/H2O (50:50)   | 0.1:1                          | 2        | 95.43                 | 76.42                | 3.39                    | 1.18          |
| 4     | Fe/HUSY  | ETOH/H2O (50:50)   | 0.1:1                          | 2        | 95.17                 | 89.36                | 4.49                    | <1            |
| 5     | Ni–Fe/HUSY | ETOH/H2O (50:50) | 0.1:1                          | 2        | 96.05                 | 81.58                | 3.95                    | <1            |
| 6     | Fe/HUSY  | ETOH/H2O (50:50)   | 0.3:1                          | 2        | 95.55                 | 92.18                | 4.45                    | <1            |
| 7     | Fe/HUSY  | ETOH/H2O (50:50)   | 0.3:1                          | 2        | 63.30                 | 41.73                | 16.43                   | 20.27         |
| 8     | Fe/HUSY  | ETOH/H2O (50:50)   | 0.5:1                          | 2        | 97.79                 | 91.85                | 2.21                    | <1            |
| 9     | Fe/HUSY  | ETOH/H2O (50:50)   | 1:1                            | 2        | 97.61                 | 88.00                | 2.39                    | 4.29          |
| 10    | Fe/HUSY  | ETOH/H2O (25:75)   | 0.3:1                          | 2        | 90.57                 | 72.27                | 5.15                    | 6.94          |
| 11    | Fe/HUSY  | ETOH/H2O (75:25)   | 0.3:1                          | 2        | 91.10                 | 93.42                | 1.96                    | 6.94          |
| 12    | Fe/HUSY  | ETOH               | 0.3:1                          | 2        | 91.84                 | 98.80                | 3.19                    | 6.97          |
| 13    | Fe/HUSY  | ETOH               | 0.3:1                          | 0.5      | 78.22                 | 66.04                | 20.59                   | 1.19          |
| 14    | Fe/HUSY  | ETOH               | 0.3:1                          | 1        | 93.63                 | 87.86                | 3.23                    | 3.14          |
| 15    | Fe/HUSY  | ETOH               | 0.3:1                          | 4        | 93.60                 | >99                   | 1.68                    | 4.72          |
| 16    | Fe/HUSY' | MeOH               | 0.3:1                          | 4        | 82.98                 | 63.18                | 16.55                   | 0.47          |

“All reaction conditions unless stated otherwise: 350 °C, HCOOK (7.45 mmol) in air. *Without HCOOK. †See Tables S9 for further details of product composition of the DEE-soluble fractions.

The unique diﬀraction peaks (2θ = 10–38°) of the HUSY support are shown in Figure S1 and correspond to a single crystalline phase with the faujasite framework. For the metal catalysts, the characteristic peaks of NiO and Fe2O3 (hematite) were detected without any substantial transformation of the peak position, indicating the existence of these oxides within the HUSY matrix (Figure 1). However, for the 5% Ni−5% Fe/HUSY bimetallic catalyst, the unit crystal size of Fe2O3 is higher than that of the corresponding monometallic catalyst—an indication of possible NiO particles' inclusion in the crystal lattice of Fe2O3.

The micrographs from the scanning electron microscopy (SEM) of Ni, Fe, and Ni−Fe catalysts with corresponding EDS elemental mappings of Ni and Fe are depicted in Figure 2. The results reveal that Ni and Fe species are well distributed on the zeolite surface with a uniform dispersion, which is in good agreement with the mean metal crystallite size as calculated from XRD patterns (Table 1). High-resolution transmission electron microscopy images of fresh 10% Ni/HUSY and 10% Fe/HUSY are also presented in Figure 2c,f. The HUSY zeolite support is light gray, and oxides of Ni and Fe are shown as dark particles. The NiO particles (inset of Figure 2c) are well defined as cubes, whereas the Fe2O3 particles (inset of Figure 2f) are less uniform and appear in clusters of spherical particles.

The chemical states of monometallic Ni, Fe, and bimetallic Ni−Fe catalysts were also confirmed by X-ray photoelectron spectroscopy (XPS) measurements. The high-resolution XPS (HR-XPS) results of Ni 2p, Fe 2p, and O 1s are presented in Figure 3A–C, respectively. All spectra were first calibrated using the C 1s peak at 284.8 eV and subtracted by a Shirley background. In Figure 3A, the binding energies of Ni 2p3/2 (856.2 and 853.9 eV) and Ni 2p1/2 (871.2 and 873.9 eV) peaks indicate the characteristic peak of NiO. In addition, both Ni 2p3/2 (861.4 eV) and Ni 2p1/2 (880.4 eV) peaks are also attributed to Ni(OH)2. These peaks also clearly appear in the bimetallic Ni−Fe/HUSY sample although no strong diffraction peaks were found in XRD patterns. As shown in Figure 3B, two main peaks belonging to Fe 2p3/2 (710.3 eV) and Fe 2p1/2 (724.4 eV) appear in the spectra of the monometallic Fe/HUSY and bimetallic Ni−Fe/HUSY samples. These characteristics were related to Fe3+ in α-Fe2O3 and the results are consistent with the XRD results. The XPS results of O 1s of the monometallic and bimetallic catalyst samples are shown in Figure 3C, where three-band peaks are observed as previously reported in the literature. The first highest peak at 531.7 eV is associated with oxygen atoms in Si–O−M (Si–O−Al) bonds, and the right shoulder peak at $529.0\,\text{eV}$ was assigned to $M$–O–M bonds. The O 1s signal at 533.3 eV could be assigned to hydroxyl oxygen species or oxygen in SiO2 impurity.

**Catalytic Activities toward Lignin Depolymerization.** Based on our previous work on organosolv lignin conversion to monoaromatics over the HUSY zeolite catalyst, it was decided that the metal-doped HUSY zeolite should be investigated to determine the catalytic effect of metal addition to zeolite on lignin depolymerization in ETOH/H2O (50/50 vol %) at 350 °C for 2 h in the presence of air. More importantly, the effect of the addition of HCOOK on the catalyst properties and stability as well as the presence of a hydrogen source was also examined. The product yields [diethyl ether (DEE)-soluble, acetone soluble, and char] and lignin conversion for the catalyzed and uncatalyzed reactions are summarized in Table 2, entries 1–5. Compared with the uncatalyzed reaction, the metal-supported HUSY catalysts show higher lignin conversion and DEE-soluble product yields but lower acetone-soluble product yield and char content. There were also differences in the product yields between Fe and the Ni supported catalysts. These results indicate that the nature of the metal supported on the zeolite, i.e., physical and chemical characteristics, plays important roles in product yields. Among these metal oxides, the Fe/HUSY catalyst showed the highest DEE product yield (89.4 wt %), while the lowest DEE product yield was obtained with the monometallic Ni (76.4 wt %). It is well known that Ni has been widely used as a catalyst in steam reforming and gasification reactions.
The results from Lu’s study showed that Ni supported on MgO was a more effective catalyst for biomass gasification compared with Fe/MgO catalysts, producing more H₂ and CO₂ gases. The metals Ni and Fe have different catalytic effects on the water–gas shift reaction (CO + H₂O → CO₂ + H₂); therefore, a concomitant gasification reaction of the DEE-soluble on the Ni/HUSY catalyst could promote some of the products into volatile compounds and gases (i.e., H₂ and CO₂).

Chen et al. reported that the pore size could also affect lignin depolymerization performance. In this work, addition of Fe produces a larger pore size than addition of Ni to the zeolite, which probably contributed to enabling the high yield of lower molecular fragments through steric constraints that can hinder the interactions between the intermediate fragmented lignin species and/or result in further decomposition into smaller-molecular-weight compounds inside the pore channel. In addition, Fe/HUSY has the highest mean metal crystal size and so provides the largest surface coverage for the depolymerization process.

Table 2, entry 7, shows that without the use of HCOOK and increasing three times the amount of the catalyst, the DEE-soluble fraction obtained was very low, whereas the char formed was 20 wt, %, over 2× higher than the blank where no catalyst was used. On the contrary, the presence of HCOOK and a similar catalyst loading (Table 2, entry 6) significantly improved the yield of the DEE-soluble fraction. This clearly suggests that the mechanism of lignin depolymerization and subsequent stabilization of the fragmented lignin intermediates is to a greater extent achieved by formate-mediated reaction steps. Product selectivity as determined by GC–MS for the DEE fractions and the total monomer yields are then summarized in Figure 4, where the main product compound groups have been classified as nonaromatics, alkylphenolics, oxygenates, cyclic, aromatics, oxygenated polyaromatics, and others (see detailed composition in Table S3). It is important to remark that in all experiments conducted in this study (Table 3, except entry 7), it was established that mono-oxygenated compounds syringol (1), vanillic acid (2), (alkyl)benzyl alcohol (3), 3-phenylpropanol (4), 2-hydroxy-6-methoxycatechol (5), benzoic acid (6), and 5′-hydroxy-2′,3′,4′-trimethylacetophenone (8) were obtained as the major compounds for the oxygenate group, while 2,3,5,6-tetramethylphenol (7) was the main compound of the alkyl phenol group. In the case where no HCOOK was added during reaction (Table 3, entry 7), compounds such as phenol, products 1 and 2, and other methoxylated phenol derivatives were the dominant products obtained, an indication of the effectiveness of the use of HCOOK to enhance demethoxylation through hydrogenolysis. More importantly, HCOOK catalyzed the conversion of the aldehydes to benzyl alcohols as was observed by Baidossi et al. A higher selectivity toward product 3 was obtained with Ni/HUSY and Fe/HUSY compared with the bimetallic catalyst. However, the yields of products 4 and 5 were similar in all conditions except for the Ni/HUSY catalyst. A small amount of 6 was produced when the Fe/HUSY catalyst was used. These results indicate that metal-based Lewis acid catalysts such as Ni and Fe promote alkylation reaction in the presence of alcohol as a solvent. However, Fe/HUSY shows a higher activity in compound 6 when the reaction was conducted under air. This is probably due to Lewis acid-catalyzed transformation of alcohols to acids on the Fe³⁺ sites of the Fe/HUSY catalyst, particularly alcohol oxidation reactions where benzyl alcohol is oxidized to acetoephone, benzaldehyde, and benzoic acid. The yield of total monomeric oxygenates reached a maximum of 7.33 wt % using Fe/HUSY. Previous studies demonstrated that significant deoxygenation and monomer formation were achieved with Ni/ZSM-5, Ni/Al-SBA-15, and Ni-SBA-15. Hence, in this study, the metal-supported HUSY catalysts showed lower deoxygenation and monomer yield because of lower surface area and lower pore size compared with the mesoporous catalysts and differences in reaction conditions used.

In conclusion, our results therefore indicate that the Fe/HUSY catalyst is more suitable for the reductive depolymerization of lignin into small-molecular-weight compounds, i.e., benzyl alcohols, under the conditions tested. Besides, it produced the highest amounts of cyclic and aromatic compounds and, hence, was selected for further studies.

**Effect of Reactant Gas on Lignin Depolymerization.**

The lignin depolymerization reaction was investigated in the presence of air and hydrogen environments. The main product fractions obtained after the reaction with their corresponding lignin conversions are shown in Table 4, entries 1–7. It can be observed that when hydrogen was present, higher yields of the DEE product (95.0–98.8 wt %) and char (3.0–7.5 wt %) are produced as compared with when the reaction was conducted under air. Char formation tended to occur with the addition of hydrogen gas, which may be ascribed to the combined effects of activated adsorption of hydrogen on the metal sites and the total number of acidic sites of the catalysts during the hydrodeoxygenation (HDO) reaction of phenolic compounds. A relative decrease in the acetone-soluble fraction was observed, except for the reaction where a physical mixture of Ni/HUSY and Fe/HUSY was used. This result can be explained as interactions between Ni and Fe species (as evidenced by XRD and XPS data, Figures 1 and 3, respectively) when impregnated in the same HUSY support, synergistically influenced product yield, and selectivity.

**Figure 4.** Total monomer yields (wt %) in oxygenates and selectivity (%) of composition of the DEE-soluble products in terms of nonaromatics, alkylphenolics, oxygenates, cyclic compounds (including more than one-ring structures), aromatics (including more than one-ring structures), oxygenated polyaromatics, and others based on total peak area from GC–MS at 350 °C with and without catalysts and using air as the gas reactant (Table 2, entries 1–5). See Table S2 for further details of selectivity of composition of the DEE-soluble products.
5). Gaseous products on all of the catalysts tested were similar; H₂ and CO₂ were the two main gases analyzed by the GC (Figure S2).

As shown in Figure 6, the depolymerization reaction of lignin, carried out with Ni/HUSY under a hydrogen environment, has the highest selectivity for the aromatics and the total monoaromatics in the oxygenates group category. More so, Table 3 entry 19 showed that the maximum yield of benzyl alcohol (product 3), 10.43 wt %, was obtained with Ni/HUSY even though both Ni/HUSY and Fe/HUSY produced similar yields out of all of the monomeric compounds combined together (16.88 and 16.32 wt %). The Ni/HUSY catalyst, under a hydrogen atmosphere, also selectively produced 2-cyclohexen-1-ylidene that belongs to the cyclic group. Ni/HUSY is a common bifunctional hydrodeoxygenation catalyst with both active metal and acid sites of the support. However, the in situ formation of high-molecular-weight products, such as naphthalenes and anthracenes (Table S3), via the polymerization of intermediates of phenolic compounds during breakup of the active ArO−CH₃ bond 44 negatively impacted the hydrodeoxygenation reaction, promoting char formation. The compounds 2H-pyran-2-one, tetrahydro-4-methyl essentially disappeared, but the oxygenated polyaromatic group remained the same for the Ni/HUSY catalyst. The selectivity toward nonaromatic compounds was lower with Fe/HUSY but that of the alkyl phenols was higher in contrast to the Ni/HUSY catalyst.

Table 3. Main Monomer (Oxygenate Group) Yield Obtained after the Depolymerization of Eucalyptus Lignin (EUL) at 350 °C Using Different Conditions with and without a Transition-Metal Catalyst  

| entry | monomer yield (wt %) | total yields (wt %) |
|-------|----------------------|---------------------|
|       | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |       |
| 1a    | 1.24 | 0.85 | 3.55 | n.d. | 5.64 |
| 2a    | 1.95 | 0.76 | 3.57 | n.d. | 6.28 |
| 3a    | 2.52 | 1.41 | 3.37 | n.d. | 7.30 |
| 4a    | 2.52 | 0.88 | 3.32 | 0.61 | 7.33 |
| 5a    | 0.72 | 0.66 | 3.26 | 1.03 | 5.67 |
| 6a    | 2.35 | 1.62 | 2.93 | 1.59 | 8.49 |
| 7a    | 3.98 | 0.87 |       |       | 5.13 |
| 8a    | 2.65 | 1.69 | 3.20 | n.d. | 7.54 |
| 9a    | 1.10 | 1.54 | 2.56 | n.d. | 5.20 |
| 10a   | 0.77 | 0.49 | 2.25 | 1.28 | 4.79 |
| 11a   | 2.66 | 1.76 | 2.59 | 1.49 | 8.50 |
| 12a   | 4.28 | 1.95 | 1.19 | 1.35 | 8.77 |
| 13a   | 1.07 | 0.98 | n.d. | 1.60 | 3.65 |
| 14a   | 1.22 | 1.02 | n.d. | 1.61 | 3.85 |
| 15a   | 15.56 | 2.28 | n.d. | n.d. | 17.84 |
| 16a   | 9.56 | 0.96 | 3.66 | n.d. | 14.12 |
| 17a   | 8.11 | 0.75 | 3.79 | n.d. | 12.65 |
| 18a   | 9.58 | 0.88 | 3.52 | n.d. | 13.98 |
| 19a   | 10.43 | 3.20 | 3.25 | n.d. | 16.88 |
| 20a   | 9.99 | 3.29 | 3.04 | n.d. | 16.32 |
| 21a   | 9.30 | 3.08 | 2.49 | n.d. | 14.87 |
| 22a   | 8.71 | 2.87 | 2.26 | n.d. | 13.84 |
| 23a   | 1.62 | 0.17 |       |       | 1.79 |
| 24a   | 13.42 | 3.94 | n.d. | n.d. | 17.36 |

aFrom Table 2, entries 1–15. bFrom Table 4, entries 1–7. cFrom Table S10, entries 1–2.
HUSY catalyst. Compared with the metal-oxide-based catalysts (Table 3, entries 3−5), the reduced catalysts (Table 3, entries 16−22) significantly increased product 3 concentration (i.e., benzyl alcohols) up to 10.43 wt %. These results imply that the depolymerization of lignin in ETOH/H2O mixtures under a reducing reaction environment promoted the removal of methoxy groups by hydrogenolysis along with C-alkylation.

Effect of Reaction Time and Ethanol Content on Product Type and Yield. As shown in Table 3, the highest values of monoaromatics were obtained when the reaction was conducted in the presence of an external hydrogen source. Thus, we decided to investigate whether increasing the reaction time and using ETOH alone as the solvent over the Fe/HUSY catalyst would be an alternative means to produce high values of monoaromatics without the use of an expensive external hydrogen source. Prior to investigating the use of ETOH alone as a solvent, we examined different ETOH/H2O ratios to identify the role water played as a cosolvent in the depolymerization process. The results indicated that the highest selectivity of monoaromatics and cyclic compounds can be achieved with the ETOH solvent alone, with a reduced number of compounds formed, i.e., better selectivity (Figure S3 and Table S5).

Figure 5. Total monomer yields (wt %) in oxygenates and selectivity (%) of composition of the DEE-soluble products in terms of nonaromatics, alkylphenolics, oxygenates, cyclic compounds (including more than one-ring structures), aromatics (including more than one-ring structures), oxygenated polyaromatics, and others based on total peak area from GC−MS at 350 °C for 2 h with 10 wt % catalyst loading of different reduced metal catalysts in ETOH/H2O (50:50 vol %) with and without the addition of hydrogen (Table 4, entries 1−7). See Table S4 for further details of selectivity of composition of the DEE-soluble products.

Table 4. Lignin Conversion and Product Yield Obtained Using Different Reduced Metal Catalysts with and without Addition of Hydrogen

| entry | catalyst | solvent | catalyst-to-lignin ratio (w/w) | time (h) | type of gas | lignin conversion (%) | DEE-soluble products® | acetone-soluble products | char |
|-------|----------|---------|-------------------------------|---------|-----------|----------------------|-----------------------|-------------------------|------|
| 1     | Ni/HUSY  | ETOH/H2O (50:50) | 0.1:1 | 2 | air | 95.58 | 77.87 | 4.31 | <1 |
| 2     | Fe/HUSY  | ETOH/H2O (50:50) | 0.1:1 | 2 | air | 94.22 | 83.56 | 5.78 | <1 |
| 3     | Ni−Fe/HUSY | ETOH/H2O (50:50) | 0.1:1 | 2 | air | 95.05 | 87.10 | 4.95 | <1 |
| 4     | Ni/HUSY  | ETOH/H2O (50:50) | 0.1:1 | 2 | H2 | 94.24 | 95.02 | 2.74 | 3.02 |
| 5     | Fe/HUSY  | ETOH/H2O (50:50) | 0.1:1 | 2 | H2 | 94.51 | 96.74 | 2.34 | 3.15 |
| 6     | Ni−Fe/HUSY | ETOH/H2O (50:50) | 0.1:1 | 2 | H2 | 93.85 | 96.52 | 1.83 | 4.22 |
| 7     | Ni−Fe/HUSY | (physical mixture) | ETOH/H2O (50:50) | 0.1:1 | 2 | H2 | 87.89 | 98.84 | 4.55 | 7.46 |

All reaction conditions: 350 °C, HCOOK (7.45 mmol), atmospheric pressure of H2 or air. See Table S4 for further details of product composition of the DEE-soluble fractions.

Figure 6. Total monomer yields (wt %) in oxygenates and selectivity (%) of composition of the DEE-soluble products in terms of nonaromatics, alkylphenolics, oxygenates, cyclic compounds (including more than one-ring structures), aromatics (including more than one-ring structures), oxygenated polyaromatics, and others based on total peak area from GC−MS at 350 °C with varying reaction times over Fe/HUSY with 30% catalyst loading in ETOH (Table 2, entries 12−15). See Table S9 for further details of selectivity of composition of the DEE-soluble products.
...tion and may have degraded to selectively produce 2,3-dihydrofuran derivatives. 3^P NMR also (Figure S5 and Table S7) showed that the 4→O→5 linkage of lignin disappeared after reaction. The spirodienone structure in the oxygenated polyaromatic group was undetected when the ethanol content was greater than 50% by volume. The condensation products were mainly diaromatic components such as biphenyl-2-yl-methanol and naphthol with molecular weights higher than 200 g mol\(^{-1}\). These oxygenated products may be formed via either oligomerization of the monomeric products or cyclization of the hexyl-alkylated aromatics.

Entries 4, 6, 8, and 9 of Table 2 show the lignin conversion and product yields obtained at different Fe/HUSY-to-lignin ratios from 0.1 to 1 by weight. Lignin conversion increased with the catalyst loading amount to reach a maximum of about 98 wt % conversion at a 1:1 lignin/catalyst ratio. Similarly, DEE-soluble products increased to a maximum yield of about 92 wt %; however, it declined with further increment in the catalyst loading. This is because of the accelerated decomposition of HCOOK, generating molecular hydrogen that subsequently reacts rapidly to stabilize the depolymerized lignin fragments before repolymerization to heavier molecular fractions, accounting for the progressive reduction of the acetone product and char yields. Meanwhile, hydrogenolysis and deoxygenation of lignin toward monoaromatic and oligomeric products were also favored as catalyst loading increased, thus accounting for the increased proportion of the total monomer yield in the oxygenates (Figure S6 and Table S8). However, the noticeable decline of DEE products (Table 2, entries 4, 6, 8, and 9) and monomer yield (Figure S6) after the catalyst/lignin ratio of 0.3:1 is indicative of the consecutive conversion of the low-molecular-weight (LMW) fractions into gaseous compounds.

The effect of reaction time on the lignin conversion and product yields in the presence of Fe/HUSY with 30% catalyst loading using ETOH alone as the solvent was therefore studied (Table 2, entries 12–15). From the analysis of results, the reaction time was also an important factor in both DEE and acetone product yields. DEE product yield increased with reaction time, while there was a corresponding decrease in the acetone fraction. This result is in good agreement with that of Limarta et al., whose studies also observed a similar trend during the lignin depolymerization process in supercritical ETOH. Significant amounts of char were formed at a moderate reaction time (2 h) and then decreased as the reaction time progressed. The reason for this is not known but may be related to the modification of the catalyst with reaction time, as when using methanol as the solvent, the product yield as well as lignin conversion is lower than those of ETOH as the solvent. A large amount of acetone-soluble product was formed (16.6 wt %), which was consistent with previous reports in which depolymerization in methanol (Table 2, entry 16) produced higher-molecular-weight compounds, implying that lignin depolymerization conducted under ETOH is more effective in suppressing repolymerization reactions than methanol.

Figure 6 shows the time versus selectivity plot for the main groups of compounds. It also shows the progressive yield of the monoaromatics from 0.5 to 4 h. The selectivity of the nonaromatics (i.e., the fatty acids, endogenous to lignin, and fatty acid esters) did not change at 1 h but significantly did thereafter corresponding to the increase in the monoaromatic content. The selectivity for the oxygenates also decreased but not as sharply as that of the nonaromatics. The selectivity of the cyclic, aromatics, and oxygenated polyaromatics increased with reaction time. It is probable that the decrease in the selectivity of the nonaromatics during depolymerization could be due to their catalytic decomposition to hydrocarbons. The formation of the latter would then enhance deoxygenation and consequently increase the formation of nonaromatics. The product mixtures obtained after hydrothermal treatment of lignin with ETOH/HCOOK in Fe/HUSY for 2 and 4 h (Table 2, entries 12 and 15) were further analyzed by the electrospray ionization mass spectrometry (ESI-MS) technique (Figure S7). The result showed that the intensities of lower-molecular-weight compounds obtained for 4 h were higher than those obtained at 2 h, confirming that increasing the reaction time increases the formation of the monoaromatics, under the conditions used in this work.

The main monomeric products obtained with ETOH with increasing reaction time were determined, and the results are presented in Table 3, entries 12–15. Compound 3 significantly increased with time, while there was a gradual increase in yield with 4. Compound 6, however, decreased with time. The yield of compound 5 reached a maximum at 2 h and decreased thereafter. A value of 17.84 wt % was obtained for the monomeric products with Fe/HUSY under an air atmosphere at 4 h, a value slightly higher than that obtained with Ni/HUSY (16.88 wt %) and Fe/HUSY (16.32 wt %) in the presence of hydrogen after 2 h. Also, the benzyl alcohol (3) yield was in the order 6 wt % [Fe/HUSY (in air)] > 10.4 wt % [Fe/HUSY (in H\(_2\))] > 10 wt % [Ni/HUSY (in H\(_2\))] as well. As such, the combined use of HCOOK and ETOH provided enough hydrogen in situ and hydrocarbons for the depolymerization process, thus eliminating the need for an external hydrogen source.

From the above experimental results, the possible pathway for the formation of these monomeric products is via the reaction mechanism that involves the base-catalyzed formation of a reactive quinone methide—enol ether intermediate since the lignin depolymerization reaction was performed in an alkaline condition (starting pH = 11). The depolymerized fragment, especially the enol ethers, then undergoes a catalytic reductive step with the in situ hydrogen generated from HCOOK via the decomposition of formate ions. The hydrogen reductive step of the fragmented lignin species via processing such as hydrogenolysis and/or hydrodeoxygenation on the catalyst, accompanied by an increase in the degree of demethoxylation and deoxygenation, thus generates stable monomeric and dimeric compounds as well. In addition, solvent-aided catalytic conversion cannot be excluded as alkylation of the depolymerized fragments with ethanol may also occur through either O-alkylation of phenolic intermediates or C-alkylation of the aromatic rings.

**Study of Spent Fe/HUSY.** To test the stability of the catalyst, the spent catalyst was recycled and reused for the depolymerization reaction under similar experimental conditions (ETOH/H\(_2\)O, 50:50 vol % at 2 h in HCOOK) as the fresh catalyst. The DEE-soluble fraction yield was 83.01 wt % at 88.17 wt % lignin conversion, corresponding to approximately 10 wt % decrease in the catalytic activity (Table S10). However, the yield of the monomeric oxygenates significantly reduced by about 30 wt % (Figure S8). This decline of the catalytic activity is expected since during depolymerization of lignin over acidic zeolite catalysts, a large number of aromatic compounds are formed, where some of these eventually react
to form char, which influence catalyst performance when it is recycled. A repeat experiment with the spent Fe/HUSY catalyst and HCOOK/ETOH was carried out but at a longer time of 4 h. Table S10 shows that the lignin conversion was 97.5 wt % and the DEE-soluble fraction was >99 wt %. Table S11 shows that the selectivity for the total benzyl alcohols was 58 wt % (77 wt % for total aromatic alcohols) and the yield was ~13 wt % (Table 3, entry 24). These results are comparable to those obtained with fresh Fe/HUSY, although with higher selectivity. Unfortunately, further recycling experiments could not be conducted because of significant catalyst loss during recovery and the coverage of the catalytic sites with carbon and ash.

As mentioned earlier, using HCOOK during reaction not only produces in situ hydrogen but also suppresses char formation. To gain an insight into the changes that occurred on the catalyst surface, HR-XPS analysis was conducted on the fresh and spent Fe/HUSY catalysts. The characterization results are summarized in Figure 7a–d. The C 1s peak dramatically increased after depolymerization of lignin for the spent catalyst compared with the fresh one, indicating that highly dehydrogenated carbonaceous species were formed. A comparison of the Fe 2p spectra for fresh and spent Fe/HUSY catalysts, irrespective of the differences in the electron binding energy, shows that the electronic state significantly affected the structure of the shake-up peaks (satellites) and that particular important changes took place in the yellow region (Figure 7b,d) of the Fe 2p3/2 species (Fe3+). We observed that the surface atomic concentration of Fe decreased from 3.6 to 0.8%, whereas that of carbon increased by almost 4-fold from 11.9 to 45.2%. Hence, this suggests carbonaceous species covering the surface of the catalyst.

XRD of the spent Fe/HUSY catalyst was carried out to probe its structural integrity after the depolymerization process. The XRD (Figure 8) spectra obtained for the spent catalyst were significantly different when compared with the fresh catalyst. The peak intensity of the spent catalyst was greatly attenuated (Figure 8b), and after the second cycle of reusing the spent catalyst (Figure 8c), no observable difference was noticed in peak intensity. This structural change has arisen due to desilication of the fresh catalyst, which may have led to a partial collapse of the zeolite framework.55 Also, it may be due to the fact that deposited carbon (confirmed by XPS) on the catalyst surface is amorphous in nature.

**CONCLUSIONS**

This work has demonstrated that lignin can be depolymerized in a HCOOK/ETOH reaction system utilizing a HUSY zeolite-based catalyst. The process is highly selective for organosolv lignin conversion into the high-value benzyl alcohols and bioaromatics, utilizing HCOOK as the hydrogen donor for the catalytic reductive step. Moreover, HCOOK not only was able to facilitate the fragmentation of lignin into low-molecular-weight fractions but also hinders the fragmented
species from condensation into heavier compounds. Thermo-
catalytic reduction of lignin considerably increased the
depolymerization rate of lignin as well as the hydrogenolysis of
the lightweight compounds. Fe/HUSY demonstrated
promising performance in the subsequent hydrogenolysis of
the fragmented lignin species into monomeric aromatics,
especially in the conversion of aldehydes into benzyl alcohol.
To a lesser extent, complimentary reactions on the catalyst
such as hydrodeoxygenation (HDO) and alklylation
contribute to increased oil yield and stabilization of the aromatic
monomers. Fe/HUSY exhibited good catalytic performance,
which could be ascribed to its acidity and structural and
geometrical configurations. Product selectivity and yield can be
tuned depending on the type of metal site on the HUSY
support; however, process conditions such as alcohol/water
ratio, type of alcohol, catalyst concentration, gaseous environ-
ment, and reaction time have considerable effects as well. The spent Fe/HUSY can be reused, and its catalytic behavior for the
depolymerization reaction was found to be close to that of the
fresh one in terms of the yield toward benzyl alcohol, which stabilized at 13 wt % yield corresponding to 77 wt %
selectivity of aromatic alcohols. Thus, the implementation of a
transition-metal-based catalyst in combination with an environ-
mental-friendly hydrogen source represents an economically
feasible approach to lignin valorization.

## EXPERIMENTAL SECTION

### Chemicals and Materials.
Eucalyptus wood chips were obtained from The Siam Forestry Co., Ltd. in Kanjanaburi province, Thailand. They were air-dried at 70 °C overnight and then cut with Retsch SM 200 (Hann, Germany) to an average particle size of 0.5 mm in diameter. Eucalyptus lignin (EUL) was fractionated from the biomass according to a procedure described in detail in a previous publication. In summary, 10% (v/v) eucalyptus wood particles were pulsed in a 79% (v/v) ternary mixture of ethyl acetate/ETOH/H2O (32:25:43) with 21% (v/v) formic acid at 164 °C for 45 min with the initial pressure of 20 bar N2. The EUL was then recovered from the organic solvent by separation, filtration, evaporation, and drying at 105 °C.

Commercial HUSY (Si/Al molar ratio = S) zeolite catalyst was purchased from Tosoh, Japan. The aromatic monomers that were used for product quantification are benzoic acid, benzyl alcohol, 4-methylbenzyl alcohol, 2-methylbenzyl alcohol, 4-ethylbenzyl alcohol, 3-phenylpropyl alcohol, and 2-
hydroxy-6-methoxyacetophenone, which were purchased from Sigma-Aldrich. Nickel(II) nitrate hexahydrate [Ni(NO3)2·6H2O] was purchased from Univar, Australia, and iron(III) nitrate nanohydrate [Fe(NO3)3·9H2O] was obtained from Ajax Finechem, Australia. All chemicals and reagents were used as received.

The composition of EUL (Tables S6, S7, S12, and S13 and Figures S4, S5, S9, and S10) was analyzed using the standard Klason lignin method, pyrolosis gas chromatography—mass spectrometry (Py-GC/MS), gel permeation chromatography (GPC), 2D heteronuclear single quantum coherence (HSQC), and phosphorous (31P) NMR. The amounts of Klason lignin, acid soluble lignin, total carbohydrate contents, and ash are 89.9, 2.7, 5.4, and 1.0 wt %, respectively. Py-GC/MS was used to analyze the EUL substructures in which H, G, and S contents are 1.5, 29.6, and 68.9%, respectively.

### Catalyst Preparation and Characterization.
The catalysts were prepared by means of incipient wetness
impregnation. To prepare the catalyst precursor, the calculated amount of the required metal salt content [i.e., Ni(NO3)2·6H2O or Fe(NO3)3·9H2O] was dissolved in deionized water. The aqueous solution was then impregnated on HUSY by continuous stirring at 60 °C followed by microwave-drying. The sample was calcined in air at 400 °C for 4 h at a heating rate of 10 °C min⁻¹ to obtain the metal oxide form. The catalysts that were prepared contained 10 wt % Fe, 10 wt % Ni, and 5 wt % Fe and 5 wt % Ni for the bimetallic catalyst. The catalysts were labeled as 10% Ni/HUSY, 10% Fe/HUSY, and 5% Ni—5% Fe/HUSY. Catalyst reduction was also conducted by reacting at 400 °C for 5 h in 5 vol % H2/Ar atmospheres.

N2 adsorption—desorption isotherms were obtained at liquid
N2 temperature (−196 °C) using BELSORP-max Micro-
tracBEL equipment (Japan). Prior to each measurement, the samples were degassed at 200 °C overnight on a vacuum line. The specific surface area and pore properties of the catalysts were calculated by the Brunauer—Emmett—Teller (BET) technique. The pore size distribution curve was determined using the Barrett—Joyner—Halenda model on the adsorption isotherm curve.

The total acidity of the fresh solid catalysts was analyzed by temperature-programmed desorption (TPD) with ammonia. The catalysts were performed in BEL-CAT-A-200, a chemisorption apparatus consisting of a gas mixing unit, a U-

tube quartz microreactor with a thermocouple, and a thermal
conductivity detector (TCD). Then, 50 mg of the sample was pretreated in He flow (50 mL min⁻¹) at 500 °C for 1 h and then exposed to 5 vol % NH3/He at room temperature for 30 min. TPD was carried out at a heating rate of 10 °C min⁻¹ in a flow of He (50 mL min⁻¹), and NH3 was desorbed and monitored by a TCD detector.

X-ray powder diffraction (XRD) spectra of fresh and spent solid catalysts were collected using a PANAnalytical X’Pert Pro diffractometer operating in Bragg—Brentano geometry with a cobalt source at 40 kV and 40 mA at step size of 0.016° in the range of 4—90°. Incident optics included 0.05 rad Soller slits, a 0.5° fixed divergence slit, a 2° fixed antiscatter slit, and a 15
mm mask. Receiving optics before the X’Celerator detector included 0.05 rad Soller slits, a 5.0 mm fixed antiscatter slit, and an iron Kβ filter. The samples were spun during data collection. Phase identification was performed using PDF4+ and ICSD databases in X’Pert Highscore Plus (v4.5, PANalytical) and Jade (v4.1.0, Materials Data Inc.).

The morphology and elemental composition of the catalysts were analyzed by a scanning electron microscope (JEOL 7001F FESEM) at an accelerating voltage of 15 kV connected with an Oxford X-Max 80 mm² SDD EDS detector using chemical standards for semiquantification. The chemical states of elements in the fresh and spent catalysts were analyzed by an X-ray photoelectron spectroscopy (Kratos Analytical, U.K.). High-resolution X-ray photoelectron spectroscopy (HR-XPS) was also employed to determine the information on the chemical composition and oxidation state of the fresh and spent metal oxide catalysts. Atomic contents (%) were calculated using CasaXPS version 2.3.19 software (Manchester, U.K.). Peak fitting of the high-resolution data was also carried out using CasaXPS software.

Transmission electron microscopy (TEM) micrographs were taken on the fresh Fe/HUSY and Ni/HUSY catalysts as they both showed better catalytic activities than the bimetallic catalyst from the initial screening tests. The TEM
The microscope used was a JEOL JEM2100 transmission electron microscope operated at an accelerating voltage of 200 kV. Images were acquired on a TVIPS XF416 camera, and spectra were acquired with an Oxford X-Max energy-dispersive X-ray spectrometer.

**Catalytic Lignin Depolymerization.** For the depolymerization reaction, a mixture of lignocellulosic material and ETOH/H₂O [1.75% (w/v)] was transferred to a 25 mL stainless steel high-pressure reactor (Parr Reactor 4740, Parr Instrument, Moline, IL) with and without a catalyst. A known amount of HCOOK (7.43 mmol) was then added to the reactor. The reactor was heated in a sand bath at different reaction conditions depending on the experimental requirement. At the end of the reaction time, the reactor was rapidly quenched in a water bath to stop further reaction. A standard workup procedure for separating the products from the reaction mixture is shown in Figure 9.

Briefly, the content in the reactor was decanted into a container, and the reactor was washed with distilled water to recover any residue. The pH of the mixture was then adjusted to 2.0 using 1 M HCl to precipitate the solid from the liquid phase and retain the soluble phenols in the latter phase. The acidified mixture was then filtered with No. 52 Whatman filter paper. The liquid was extracted with diethyl ether (DEE) to recover low-molecular-weight (LMW) products (i.e., phenolic monomers and oligomers). The DEE was also used to recover other LMW compounds in the water fraction. The combined DEE-soluble fraction was mixed with Na₂SO₄ to remove residual water, filtered, and then evaporated to recover the phenolic monomers and oligomers. The DEE-insoluble fraction was dissolved in acetone, and the solid (i.e., catalyst and char) was separated by filtration. The acetone-soluble fraction was evaporated to obtain the heavy-molecular-weight products. Then, products were dried under vacuum at 45 °C overnight. All fractions were expressed on a dry basis. Experiments were conducted in duplicate.

**Product Characterization.** Phenolic products in the DEE-soluble fraction were identified and quantified using a GC–MS system (Agilent J&W GC columns 6890 app Hephaestus) equipped with an Agilent HP-5MS capillary column (30 m × 0.25 mm × 0.25 μm; Agilent). The temperature program of the oven was set at 90 °C for 10 min; then, it was ramped up to 300 °C at a rate of 4 °C min⁻¹ and kept at this temperature for 5 min. Wiley library-HP G1035A and NIST library of mass spectra and subsets-HP G1033A were used for the identification of products released (a criterion quality value ≥80% was used). Calibration standards were prepared for the quantification of the main phenolic monomers.

The yields of phenolic monomers, DEE-soluble product, acetone-soluble product, char, and lignin conversion were calculated using the following equations

\[
\text{phenolic monomers yield in DEE-soluble (wt %)} = \frac{\text{weight of phenolic monomers (g)}}{\text{weight of initial lignin (g)}} \times 100
\]

\[
\text{DEE-soluble product yield (wt %)} = \frac{\text{weight of DEE-soluble fraction (g)}}{\text{weight of initial lignin (g)}} \times 100
\]

\[
\text{acetone-soluble product yield (wt %)} = \frac{\text{weight of acetone-soluble fraction (g)}}{\text{weight of initial lignin (g)}} \times 100
\]

\[
\text{char yield (wt %)} = \frac{\text{weight of acetone-insoluble fraction (g)} - \text{weight of catalyst}}{\text{weight of initial lignin (g)}} \times 100
\]

\[
\text{lignin conversion (%)} = 100 - (\text{acetone-soluble product + char yield})
\]

**Product Gas Analysis.** Gas compounds were identified via a gas chromatograph (Shimadzu GC-2014, Japan). The mixture gas products were satisfactorily separated by the use.

Figure 9. Workup procedure for product separation after liquefaction.
of a 50/80 ShimCarbon ST column (2 m × 2 mm I.D., Agilent). The outlet of the gas chromatograph column was directly connected to both the thermal conductivity detector (TCD) and the flame ionization detector. Gas analysis was conducted for the experiments that involved the use of the reduced catalysts.

**Nuclear Magnetic Resonance (NMR).** Two-dimensional (2D) heteronuclear single quantum coherence (HSQC) was used to analyze the products. The sample was prepared by dissolving 25–30 mg of materials in 0.75 mL of dimethyl sulfoxide-d$_6$ (DMSO-d$_6$). The $^1$H and $^{13}$C correlation 2D HSQC spectra were recorded at room temperature using a 600 MHz spectrometer (Agilent) equipped with a cooled 5 mm TCI Cryoprobe (cold $^1$H and $^{13}$C channels). The spectrometer frequency of 600 MHz was used for $^1$H and 150 MHz in the case of $^{13}$C dimensions detection. A total of 1024 complex points were collected for the $^1$H dimension with a 1.5 s recycle delay. A total of 64 transients at 256 time increments were recorded for the $^{13}$C dimension. The central solvent (DMSO-$_d$6) peak was used as an internal chemical shift reference point ($\delta_C/\delta_H$ 39.5/2.49). The spectra were acquired using an adiabatic HSQC pulse program (Bruker standard pulse sequence "hsqcetgpsi2") under the following conditions: spectra were acquired from 10 to 0 ppm in F2 ($^1$H) using 200 ms, and an interscan delay of 1 s, and from 165 to 0 ppm in F1 ($^{13}$C) using 256 increments of 32 scans with a total acquisition time of 2 h 40 min. $^1$J$_{CH}$ used was 145. The spectral widths of $^1$H and $^{13}$C dimensions were 5 and 20 kHz, respectively. The processing used a shifted squared sine bell Gaussian apodization in $^1$H and $^{13}$C. HSQC data processing and plots were carried out using ACD/NMR processing software, with automatic phase and baseline correction.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b02413.

XRD patterns of fresh catalyst samples; representative GC-TCD chromatogram of the gas compositions produced after depolymerization over reduced mono- and bimetallic supported on HUSY; total monomer yields (wt %) in oxygenates and selectivity (%) of composition of the DEE-soluble products under various conditions; 2D HSQC of the parent EUL lignin obtained after fractionation; hydroxyl groups of structural units detected by $^{31}$P NMR; ESI-MS analysis of the DEE-soluble products after depolymerization; Py-GC/MS chromatograms of eucalyptus organosolv lignin after supercritical pretreatment using carbon dioxide and ethanol–water as co-solvents. XRD patterns of fresh catalyst samples; representative GC-TCD chromatogram of the gas compositions produced after depolymerization over reduced mono- and bimetallic supported on HUSY; total monomer yields (wt %) in oxygenates and selectivity (%) of composition of the DEE-soluble products under various conditions; 2D HSQC of the parent EUL lignin obtained after fractionation; hydroxyl groups of structural units detected by $^{31}$P NMR; ESI-MS analysis of the DEE-soluble products after depolymerization; Py-GC/MS chromatograms of eucalyptus organosolv lignin after supercritical pretreatment using carbon dioxide and ethanol–water as co-solvents. The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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