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One-Pot Process for Hydrodeoxygenation of Lignin to Alkanes Using Ru-based Bimetallic and Bifunctional Catalysts Supported on Zeolite Y

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The synthesis of high-efficiency and low-cost catalysts for hydrodeoxygenation (HDO) of waste lignin into advanced biofuels is crucial for enhancing current biorefinery processes. Inexpensive transition metals, including Fe, Ni, Cu, Zn, were severally co-loaded with Ru on HY zeolite to form bimetallic and bifunctional catalysts. These catalysts were subsequently tested for HDO conversion of softwood lignin and several lignin model compounds. Results indicated that the inexpensive earth abundant metals could modulate the hydrogenolysis activity of Ru and decrease the yield of low molecular weight gaseous products. Among these catalysts, Ru-Cu/HY showed the best HDO performance, giving the highest selectivity to hydrocarbon products. The improved catalytic performance of Ru-Cu/HY was probably due to the following three factors: (1) high total and strong acid sites, (2) good dispersion of metal species and limited segregation, (3) high adsorption capacity for polar fractions, including hydroxyl groups and ether bonds. Moreover, all the bifunctional catalysts were proven to be superior over the combination catalysts of Ru/Al_2O_3 and HY zeolite.

Introduction

Lignin is one of the three major components in lignocellulosic biomass, and it is also the only large-volume renewable resource for aromatic compounds. Lignin has a higher C/O ratio and energy density than the other two biomass components, namely cellulose and hemicellulose (carbohydrates).^[1] Compared with carbohydrates, lignin is very heterogeneous, consisting mainly of three different phenylpropanoid units linked by various C-O-C and C-C bonds. Given its three-dimensional, highly branched

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chemical structure, lignin is recalcitrant to conversion, especially selective, under either thermal, catalytic, or biological conditions. The difficulty in lignin valorization thus significantly reduces biorefinery product slates in commercial production. As a matter of fact, most of the current biorefinery processes, such as bioethanol production, only focus on the utilization of cellulose and hemicellulose. The large amount of residual lignin is treated as waste or as low value-added solid fuel.^[2] Therefore, better utilization of lignin for the production of value-added chemicals or advanced biofuels will contribute to the economics of modern lignocellulosic biorefineries. Increased attention has been focused in recent years on lignin valorization, with various processes attempted.^[3] However, the selective conversion of lignin to well-defined products is still a nascent endeavor.^[4]

Hydrodeoxygenation (HDO) conversion of lignin, in which lignin is depolymerized and deoxygenated using hydrogen over catalysts, is regarded as one of the most promising ways to transform lignin into value-added aromatics or fuel range hydrocarbons.^[5] However, to make this process industrially viable, several challenges, especially the development of highly effective catalysts with low cost, should be addressed. Sulfided CoMo and NiMo-based catalysts that are traditionally developed for removal of sulfur and nitrogen in the industrial hydrotreating of petrochemical feedstocks were introduced into lignin HDO conversion.[1b] However, these catalysts showed several intractable problems, such as sulfur contamination of the products (the catalyst needs H₂S for stabilility), rapid deactivation of the catalysts during reaction because of sulfur deprivation, and easy catalyst poisoning by the water generated in the reaction.^[6] Noble metals as catalysts, typically including Pt,^[7] Pd,^[8]Re,^[9]Rh,^[10] or Ru^[11] loaded on various supports, have also been used, showing high catalytic activities towards hydrogenolysis and hydrogenation reactions.^[12] Among these noble metals, Ru is the least expensive and exhibits superior HDO performance in an aqueous phase.[11c]Arjan Kloekhorst et al. recently performed a catalyst screening study on the catalytic hydrotreatment of Alcell lignin, and found that the best results for conversion in high yields of lignin to bio-oil were obtained from supported Ru catalysts.[11d]

Ru-based bimetallic catalysts or bifunctional catalysts were also prepared with the aim to increase and fine-tune the HDO catalytic activity towards lignin conversion, as well as to further reduce catalyst costs. In this respect, unsupported bimetallic RuNi nanoparticles were successfully synthesized by Yan's group, and were tested for the conversion of lignin model compounds. The results suggest that the catalytic activity of Ru_{0.15}Ni_{0.85} nanoparticles was found to be superior when compared to singlecomponent catalysts.^[13]Bimetallic catalysts, which usually show different electronic and chemical properties from their parent metals, have gained considerable academic and commercial

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interest since the 1960s, due to their enhanced performances of selectivity, activity, and stability in various reactions.^[14] The electronic environment of the metals in bimetallic catalysts can be changed by the formation of heteroatom bonds, which can lead to modifications of the electronic structure of metals through ligandbinding effects.^[15] Also, the formation of heterogeneous metal-metal bonds in bimetallic catalysts can cause changes in orbital overlap, resulting in the strain effects that can alter the geometry of the bimetallic structures.^[16] Both the electronic structure and the surface geometry of a catalytic material greatly affect its catalysts, it is possible to synthesize the desired catalyst with unique catalytic activities for a specific reaction. Despite the great potential of bimetallic catalysts, the design and usage of them for lignin conversion are still in their infancy.

Acidic zeolites, well-established heterogeneous catalysts, have been successfully used in commercial industries including catalytic cracking, isomerization, and alkylation reactions.[17] Zeolites with suitable Si/Al ratios (acidity) and pore structures were shown to be effective heterogeneous catalysts in lignin deconstruction.^[11h,18] Zeolites are also widely used as support materials for transition and/or noble metals, constituting most bifunctional catalysts. The electronic interactions of the supported metal particles with the highly charged environment of zeolites makes these metal particles stable, and results in superior catalytic activity compared to conventional aluminum or silicon oxide supported catalysts.^[19] Bifunctional ruthenium catalysts supported on various zeolites have been synthesized by several groups for the HDO conversion of lignin model compounds^[11h] or lignin-derived bio-oil.[11e] Literature reports indicate that these catalysts are highly effective at removing oxygen-containing groups and saturating the aromatic rings. Very recently, we have reported that the combination of a Ru-based catalyst with an acidiczeolite formed a reliable catalytic system capable of selectively convertina lignin jet fuel to range hydrocarbons.^[3b]Encouraged by these papers, we were interested in using earth-abundant metals, including Fe, Ni, Cu, Zn, to partially replace the noble metal Ru, resulting in the synthesis of bimetallic catalysts that were supported on HY zeolite for lignin HDO conversion. HY zeolite was chosen in our currentstudy because it possesses high concentrations of active acid sites that were crucial for the lignin hydrolysis and hydrodeoxygenation activities.

Results and Discussion

Hydrodeoxygenation of guaiacol over Ru-based bifunctional catalysts supported on HY zeolite

Our previous studies indicated that the combination of noble metal catalyst (Ru/Al_2O_3) in the presence of acidic zeolite (HY) had a high hydrodeoxygenation (HDO) activity on lignin conversion.^[3b] A catalytic process which could produce jet fuel-range hydrocarbons from lignin was demonstrated. In order to integrate the noble metal catalyst and the acidic zeolite in one catalyst, as well as to increase the efficiency of noble metal utilization. bifunctional catalysts with bimetals Ru-M/HY (M= Fe.

Ni, Cu, Zn) were prepared and tested for lignin model compounds and softwood lignin HDO conversion in this study. Both Ru and inexpensive metal (M) loading were 2.5 wt% in all of the investigated bimetallic catalysts, while the Ru loading was 5 wt% when it was loaded alone.

Initially, the prepared catalysts were tested in the HDO of guaiacol, a typical lignin model compound, at 250°C with 4 MPa H₂ for 2 h in an aqueous phase. Guaiacol was used as a model compound since it has three characteristic C-O bonds that are commonly encountered in lignin, namely C_{methyl}-OAr, C_{aryl}-OMe and C_{aryl}-OH, with their respective bond dissociation enthalpies (BDE) of 262-276, 409-421, and 466 kJ mol⁻¹.^[21]

Although guaiacol conversion was more than 90 wt% over all of the investigated catalysts. Table 1 shows that relatively higher lignin conversions had been obtained over bimetallic catalysts than that over Ru/HY, especially, when Ru-Cu/HY or Ru-Zn/HY were used, where almost all of the guaiacol was converted. This result indicates that the bimetallic catalysts possess higher HDO activities than Ru/HY. Table 1 shows 8 kinds of products that were obtained from HDO of guaiacol over the investigated catalysts. Catechol, phenol, and benzene were usually observed as products in quaiacol HDO reaction.^[21] However, none of these compounds were detected in our research, indicating the high hydrogenation activity of the prepared catalysts, which can achieve full aromatic ring saturation reaction. Products of p1~p4 contain oxvgen functional groups, among which cyclohexanone(p1) and cyclohexanol (p2) are the common intermediates that can be typically found in guaiacol HDO reactions. An non-negligible amount of p3 and p4, which were probably isomerized from p1 and p2, respectively, were formed over all of the investigated catalysts, with slightly higher selectivities over bimetallic catalysts than that over Ru/HY. Products of p5~p7 are hydrocarbons. Cyclohexane (p5) was derived by the complete HDO of guaiacol, while p6 and p7 were derived from dimerization and ring-opening reactions, respectively. Table 1 shows that the investigated bimetallic catalysts can generate higher yields of cyclohexane than that found with the monometallic catalyst. The highest yield of cyclohexane (~45%) was obtained by Ru-Cu/HY catalysis. The total yield of hydrocarbon products was approximately 62% over Ru-Cu/HY catalyst, indicating the higher HDO catalytic activity of this bimetallic catalyst.

Different properties of bimetallic catalysts from those of the corresponding monometallic catalysts, including the enhancement of hydrogenation activities, have been observed by previous researchers.^[14] According to their results, the enhancements of hydrogenation activities on the bimetallic surfaces have been correlated to the modification of the electronic properties due to the formation of subsurface bimetallic structures.^[22]To facilitate the hydrogenation reaction, one hypothesis is that an effective catalyst should bond relatively weakly to the reactants to keep the carbon-carbon and carbonhydrogen bonds intact.^[14] Hammer and Nørskov have shown that the binding strength of molecules on transition metals is dependent on the electronic structure of the surface, by using the surface d-band center with respect to the Fermi level to describe the surface electronic property.^[23] Chen et al. have summarized

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experimental and theoretical studies that identify a nearly linear relationship between the binding energies and the surface *d*-band center for many adsorbates on a wide range of bimetallic

Table 1. Hydrodeoxygenation of guaiacol over Ru/HY and Ru-M/HY (M=Fe, Ni, Cu, Zn) catalysts.[a]

 $(f)^{OH} \rightarrow (f)^{OH} + (f)^{OH}$

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		Guaiacol	Cyclohexanone	Cyclohexanol	Clopentane carbaldehyde	Cyclopenty methanol	l Cyclohexar	ne Dimers	Ring-open Products	Gases		
_	Cataluat	Conversion			Hydrocarbon							
	Catalyst	(wt%)		1	2	3	4	5	6	7	8	Yield (p5~p7)
_	Ru/HY	91	27	7.5 [^]	18.1 3	3.5	7.9	18.5	6.3	8.2	10.0	30.0
	Ru-Fe/HY	96	22	2.8 ^	11.0 6	6.1	3.8	29.9	3.2	10.9	7.3	42.2
	Ru-Ni/HY	95	2'	1.0 ^	11.6 5	5.1 1	1.3	28.4	3.4	10.8	8.4	40.5
	Ru-Cu/HY	>99	13	3.1	8.1 3	3.9	3.1 ·	44.8	9.5	8.1	4.4	62.4
	Ru-Zn/HY	>99	17	7.2	9.0 5	5.8 1	0.2 3	32.6	8.2	10.9	6.1	51.7

^[a] Reaction conditions: water, 30 mL; catalyst, 100 mg; guaiacol, 100 mg; hydrogen pressure, 4 MPa; reaction temperature, 250°C; reaction time 2 h.

surfaces.^[24] In the hydrogenation reaction, the shifts in the surface *d*-band center on the bimetallic surfaces affect the binding energy of both atomic and molecular adsorbates on the catalysts. Some of the bimetallic surfaces formed from 3d transition metals (including Fe, Ni, Cu, Zn) and noble metals (such as Ru, Pt, Pd) with shifts of the *d*-band center closer to the Fermi level have been demonstrated to be more weakly bonded to reactants than the parent metals (Ru, Pt, Pd).^[24] Thus, compared with Ru/HY, the enhanced HDO activity of the prepared bimetallic catalysts in thisstudy could be attributed to the formation of the bimetallic structures with modified electronic properties.

The HDO conversion of lignin and lignin model compounds include various kinds of reactions, such as hydrogenation, hydrogenolysis, dehydration, dimerization and isomerization reactions. Ru has been shown to be the most active catalyst for hydrogenolysis; however, it is well known to have high rates of C-C bond cleavage^[25], which leads to excessive production of lowmolecular products (C1~C4 gaseous products, Table 1 p8). The selectivities of gas products were lower over the investigated bimetallic catalysts, indicating 3d transition metals (M) in catalysts of Ru-M/HY (M=Ni, Fe, Cu, Zn) could modulate the hydrogenolysis activity of Ru and improve the HDO behavior, which then results in higher selectivity to high carbon number hydrocarbon products (C>5). Moreover, it is noteworthy that when Cu was used to combine with Ru, the lowest yield of gas products was achieved. Meanwhile, high selectivities to p5 (cyclohexane) and p6 (dimers) were obtained, suggesting Cu in Ru-Cu/HY could obviously decrease the hydrogenolysis activity of Ru while maintain high hydrodeoxygenation activity.



As mentioned above, no aromatic products were detected in the process, indicating all the synthesized catalysts have high hydrogenation activity towards completely saturating the aromatic rings. Based on the obtained products, we proposed a reaction pathway of guaiacol hydrodeoxygenation conversion over acidic zeolite HY supported Ru and bimetallic Ru-M catalysts, and this is depicted in Scheme 1.

It has been reported that the aromatic ring of guaiacol can be fully hydrogenated over acid-catalyst supported precious metal catalysts when heated from room temperature to ~108°C.[26] Thus, the first step of guaiacol HDO reaction in our studies probably involved the addition of 3 moles of hydrogen to the aromatic ring to generate a product of 2-methoxycyclohexanol. After that, 2methoxycyclohexanol could be converted to cyclohexan-1,2-diol via the hydrogenolysis of Cmethyl-O bond. The produced cyclohexan-1,2-diol can undergo further dehydration reactions to form cyclohex-1-en-1-ol which could easily isomerize to yield cyclohexanone. Cyclohexanone was an important intermediate in the process, the selectivity of which was higher than other oxygen-containing intermediates. Hydrogenation of the aromatic ring in guaiacol (with 2-methoxycyclohexanol product), followed by a demethoxylation and/or dehydroxylation pathway (with cyclohexanone/cyclohexanol and cyclohexane products) have been proposed in the HDO of guaiacol on Rh-based catalysts.^[27]To verify this, the guaiacol HDO reaction time was reduced to 1 h, and both 2-methoxycyclohexanol and cyclohexan-1,2-diol were detected, indicating the pathway for cyclohexanone formation in our study is in agreement with the literature. However, this result is different from other reports which have shown that cyclohexanone was obtained directly from phenol during guaiacol HDO reactions when Cu, Fe or Pt-Fe based catalysts were used.^[21] Cyclohexanone was not stable in our reaction. Catalysis with acidic HY zeolite or oxides could isomerize cyclohexanone to form cyclopentanecarbaldehyde (p3), or hydrogenated to produce cyclohexanol (p2). Cyclohexanol can undergo further dehydration reactions over acidic HY zeolite or oxides to generate cyclohexene which could be facilely hydrogenated to the main product of cyclohexane. It is worth noting that though а significant amount of cyclopentanecarbaldehyde (p3) and cyclopentylmethanol (p4) were detected in the reaction, the HDO products from them, such as cyclopentane and its derivatives, were not found. This may be

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due to the instability of these products which were prone to go over-hydrogenolysis reaction toform low molecular weight products. Some dimers and ring-openproducts were also detected in the products, indicating that the dimerization and ringopen reactions occurred during HDO.



^[a] Reaction conditions: water, 30 mL; catalyst, 100 mg; Lignin model compound, 100 mg; hydrogen pressure, 4 MPa; reaction temperature, 250°C; reaction time 2 h.

Hydrodeoxygenation of other lignin model compounds over Ru based bifunctional catalysts supported on HY zeolite

In order to further evaluate the HDO reactivity of the prepared bimetallic catalysts, Ru-Cu/HY was selected as a representative catalyst for the HDO of additional lignin model compounds, including diphenyl ether (**DPE**), (benzyloxy)benzene (**BB**) and benzofuran (**BF**).

DPE is usually chosen as the model compound of 4-O-5 linkages in lignin for investigating the aryl-O-aryl bond cleavage chemistry.^[28] The 4–O–5 bond is reported as the strongest ether bond in lignin with the bond dissociation energy (BDE) as high as314 kJ mol^{-1.[29]} The cleavage of an aryl-O-aryl bond usually requires harsh conditions. Without catalysts, DPE has been reported to be unreactive in water at temperatures below 500°C.^[30] this study, DPE conversion In was approximately83% after reaction at 250°C for 2 h, suggesting the high HDO reactivity of Ru-Cu/HY catalyst. BB and BF are used to represent the α -O-4 and β -5 structures in lignin, respectively. The HDO results of the model substrates indicate that both of them could be converted at high yields. Cyclohexane was found to be the main product when DPE and BB were used as reactants. However, the prevailing HDO product from BF was found to be octahydrobenzofuran, with the intramolecular ether bond remaining intact. A small amount of dimer products (dicyclohexylmethane) was detected in the HDO products of BB and BF, suggesting the dimerization reactions can occur after the cleavage of ether bonds during the reaction. Results indicated that much less isomerization prouducts were generated from these model compounds than those from guaiacol, probably because the phenolic hydroxyl group and methoxyl group can increase the electron density of the aromatic ring and thus increase the isomerization reactivity of guaiacol.

Hydrodeoxygenation of softwood lignin over Ru based bifunctional catalysts supported on HY zeolite

Soft wood lignin isolated from flowthrough reactor was used to test the catalytic HDO activity of the prepared catalysts. In a typical reaction, 100 mg pine wood lignin, 100 mg bifunctional catalyst were dispersed in 30 ml DI water and reacted at 250°C under 4 MPa hydrogen for 4 h. After reaction, the products of the reaction were extracted by using 30 mL ethyl acetate and analyzed by using GC and GC-MS. The HDO results are depicted in Figure 1.



Figure 1. Hydrodeoxygenation of soft wood lignin over various bimetal-HY catalysts. Reaction conditions: water, 30 mL; bifunctional catalyst, 100 mg, [or 5 wt.% Ru/Al2O3 (300 mg) + HY (300 mg), optimized loarding]; lignin, 100 mg; hydrogen pressure, 4 MPa; reaction temperature, 250°C; reaction time 4 h.

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Figure 2.GC-MS chromatogram of lignin conversion over Ru-Cu/HY catalysis.

The conversion of softwood lignin and the yield of detectable products were very low when there was no catalyst in the control reaction. Adding the prepared catalysts, the lignin conversion and HDO product yields increased significantly. Lignin conversion was found in the same level over all five of the catalysts. Hydrocarbon selectivities were a little higher over Ru-Cu/HY catalysis than over the others, possibly because the activation energy for hydrogen bulk diffusion over Cu was much smaller than that over other metals.^[32]

The detected product slate for the catalysts tested was similar, with cyclohexane derived alkanesin jet-fuel or diesel range as the majority of the products, as depicted in Figure 2. Small fractions of oxy-compounds and ring-opening products were also detected. The total yields of the detected hydrocarbon products were approximately 26 wt% to 32 wt%, which were higher than that found over the combination catalysis of Ru/Al₂O₃ and HY zeolite (22 wt%), indicating the integration of metals with acidic zeolite can increase the catalytic selectivity of hydrocarbons from lignin HDO. The superior catalytic activity of Ru-M/HY over that of combination catalyst could be attributed to the so-called intimacy criterion.^[31] In metal-acid bifunctional catalysts, the proximity of metal sites to acid sites is crucial for their catalytic capability.^[32] Large distances between metal and acid sites always lead to low diffusivity of reaction intermediates, giving rise to gas and coke products via secondary reactions.^[31-33] Thus, for the two functional sites, the closer the better. Obviously, in bifunctional catalysts of Ru-M/HY, the distances between metal and acid sites are much smaller than that in the combination catalysts of Ru/Al₂O₃ with HY zeolite.

Structural characterization of Ru-based bifunctional catalysts supported on HY zeolite

In order to make clear why bimetallic catalysts of Ru-M/HY (M= Fe, Ni, Cu, Zn), especially Ru-Cu/HY, exhibited better catalytic performance than Ru/HY in the HDO conversion of lignin models and softwood lignin, some essential characterizations were carried out to reveal the physical and chemical properties of these catalysts. Table 3 lists the surface area values, pore volumes, and average pore diameters of HY zeolite and the synthesized bifunctional catalysts. The BET surface area of HY is 724 m²/g, while the BET surface area of all the five supported catalysts is approximately 600 m²/g. The impregnation of Ru, or bimetals into HY zeolite, caused some reduction in pore volume and pore diameter. This phenomenon is common in supported catalysts. In spite of the decrease of the BET surface area and the closure of some of pores by active metals, all of these materials still have sufficiently high surface area values for catalytic purposes.

Typical nitrogen adsorption/desorption isotherms of the prepared catalysts are shown in Figure S1. Isotherms showing similar type IV curves and porosities were obtained for all the synthesized catalysts, indicating that pore structures of these materials were mesoporous with narrow pore size distributions.

Results obtained from the BET test and nitrogen adsorption/desorption tests suggest that all the prepared supported catalysts have relative high surface area values and keep the typical mesoporous structure of HY zeolites. The physical porosity of these catalysts are similar, indicating the differences in their catalytic activity are not from changes in physical properties of HY zeolite but from other influences.

Table 3. Physical properties of HY zeolite and the synthesized catalysts.								
Catalyst	BET surface area (m²/g)	Pore volume (cm³/g)	Average pore diameter (nm)					
HY	724	0.40	2.48					
Ru/HY	608.52	0.37	2.46					
Ru-Fe/HY	598.54	0.36	2.44					
Ru-Ni/HY	591.13	0.34	2.29					
Ru-Cu/HY	587.92	0.37	2.51					
Ru-Zn/HY	604.53	0.38	2.46					
Table 4 Acid properties of the prepared catalysts.								
Catalyst	Ru/HY Ru-Zn/HY	Ru-Cu/HY Ru-Ni/H	IY Ru-Fe/HY					

The conversion of lignin and the selectivity of products might strongly depend on the acid properties of the catalyst.^[34] Thus, NH₃-TPD measurements were carried out to determine the relationship between the activity of the catalyst and the number of acid sites. Table 4 lists the uptakes of NH₃ per gram of catalysts, which can reflect the number of acid sites in these catalysts. The acidity of the prepared bifunctional catalysts is mainly derived from the acidic HY zeolite support. The impregnation of different metals in the support may result in different acid properties in the catalysts. As shown in Table 4 there are some slight differences in the number of acid sites in these catalysts. If we rank them by NH₃ uptake we have two sets. Ru/HY and Ru-Zn/HY showed lower uptake compared to Ru-Cu/HY, Ru-Ni/HY, and Ru-Fe/HY, indicating the total number of acid sites in the last three catalysts

0.123

0.122

0.130

Total mL

(NH₃/g cat.)

0.089

0.099

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are slightly higher than that inRu/HY and Ru-Zn/HY. The higher catalytic activity of Ru-Cu/HYin lignin HDO conversion may have some relationship with its higher number of acid sites. Figure 3 shows the NH₃-TPD profiles of the prepared catalysts. The profiles of NH₃ desorbed from the catalysts can be representative of the acid strength distribution on the catalysts. NH₃ adsorbed on stronger acid sites could be desorbed at higher temperatures than that on weaker acid sites. Deconvolution of the traces shows essentially two peaks: one at approximately 220°C and the other at approximately 300°C. Desorption of later peaks (higher temperature) indicate stronger acid sites on the catalyst. The ratio between the second to the first peak was found to be larger in the Ru-Zn/HY, Ru-Cu/HY, and Ru-Ni/HY cases, and since Ru-Cu/HY and Ru-Ni/HY were found to be higher in NH₃ uptake, they may associate with the stronger acid sites preferentially.



Figure 3.NH₃-TPD curves of the synthesized bifunctional

The phase and phase composition of the prepared catalysts were determined by XRD, as shown in Figure 4. The XRD patterns of all the prepared bifunctional catalysts in the range of 2θ =10° to 2θ =33° are similar, with a majority of the peaks in this range being assigned to the typical FAU structure of HY zeolite^[35], indicating that the impregnation of metals in the support has no obvious effect on the parent zeolite structure. After impregnation, calcination, and reduction, metal species as well as their oxides might exist within the HY zeolite structure. The presence of formed reduced metals and metal oxides was not obvious from XRD patterns as compared with the signals of HY zeolite. This result is in accordance with previous investigations which have revealed that the diffraction signals of metal and metal oxide particles could not easily be observed upon incorporation into the zeolite structure when the metal loading was low,[35a,36] or the metal oxides might be present as non-crystalline phases.[36] Besides, good dispersion of metal species and limited segregation of the related oxide particles could also obscure the metal and metal oxides species from being observed with XRD.^[37]

Although the XRD signals of metal and metal oxides within the bimetallic catalysts are not as intense as that of HY support, they are evident enough to show the existence of different metals and metal oxides in different synthesized catalysts, as shown in Figure 4 (2θ =33° to 2θ =50°). The existence of these bimetallic particles in the prepared catalysts was further verified by energy-dispersive

X-ray spectroscopy, as dipicted in Figure S2. Moreover, the XRD reflections indicate indirectly a synergistic effect of a second metal in bimetallic Ru–M (M= Fe, Ni, Cu, Zn) catalysts. The addition of a second metal has definitely changed the morphology and the crystalline nature of the Ru present in the HY zeolite, as evidenced from Figure 4. Also, the relative intensity of the peaks such as 2θ =43.8° was reduced when compared to the pure Ru-supported catalyst, indicating the well-dispersed nature of the bimetallic catalysts. These reflections indicate that the addition of a second metal to Ru would have enabled Ru to form much smaller particles that are mixed with the second metal after the hydrogen reduction.



Figure 4. XRD patterns for the synthesized bifunctional catalysts.

As indicated by the XRD, a part of the 3d transition metals within the bimetallic catalysts were not totally reduced, with some remaining metal oxides present in the acidic support of HY zeolite. Both the acidic HY zeolite and the metal oxides can catalyze reactions that eliminate some of the oxygenated functionalities while building up the C–C chain.^[38] For instance, ketonization, oligomerization, and transalkylation of methoxy groups, catalyzed by acids and oxides, maximize the fraction of carbon that is ultimately retained in the liquid product.^[38] Moreover, Montassier and co-authors suggest that Cu metal has a higher adsorption capacity for polar fractions (including hydroxyl group and ether bonds) due to its electrophilicity, and this adsorption leads to a weakening of the O-H and C-O bond. This propensity for adsorbing polar fractions might be enhancedwhen Cu associated with noble metals or metals with a lower *d* orbital electron

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occupancy, which can accept electrons from Cu, lead to an increase in the Cu atom's electrophilicity,^[25] This phenomenon can possibly account for the higher HDO reactivity of Ru-Cu/HY catalyst than the other catalysts.

The morphology and microstructure of the synthesized bifunctional catalysts were investigated by STEM, as shown in Figure 5. The average metal particle size for the monometallic catalyst of Ru/HY is about 10~15 nm (Figure 5, a) which is larger than that supported on other materials reported in previous studies.^[11g,22,25] Ru metal particles tend to form compact clusters with diameters of approximately 50 nm (Figure 5, b).We have found that bimetallic nanoparticles have smaller average sizes



Figure 5.HAADF-STEM images of the prepared zeolite supported Ru-based catalysts. (a-b) Ru/HY, (c) Ru-Fe/HY, (d) Ru-Ni/ HY, (e) Ru-Cu/ HY, (f) Ru-Zn/HY.

and narrower size distribution as compared with those of monometallic Ru nanoparticles. The metal particle sizes are about 2~5 nm, 3~6 nm, 6~8 nm, and 8~10 nm for Ru-Cu/HY, Ru-Ni/ HY, Ru-Fe/HY, and Ru-Zn/HY catalysts, respectively. Bimetallic clusters are found, however with much smaller diameters. Moreover, the morphology of these bimetallic clusters is quite different from that of ruthenium monometallic particles. For example, the bimetallic Ru-Cu clusters are rather loose (Figure. 5, e), probabaly due to that ruthenium and copper are immiscible in the bulk.^[24]The different size and morphology of

monometallic Ru particles with bimetallic clusters indicate the existence of strong synergetic effects between Ru and the investigated inexpensive earth abundant transition metals, which can prevent Ru from serious self-aggregation. It is well known that the catalytic activity of a supported metal catalyst is highly dependent on the metal particle/cluster size and metal particle/cluster morphology.^[39] Metal particles/clusters with small size or incompact structure have large fractions of the atoms exposed on the surface to reactants, resulting in high/unique catalytic activities. The Ru–Cu bimetallic nanoparticles on HY are in a good dispersion without serious aggregation. The STEM results are quite consistent with the XRD characterization of these catalysts.

All of the aforementioned factors (e.g., large surface area/small particle size, high total and strong acid sites, and bimetallic nanoparticles with high dispersion) could contribute to change/improve the activity of the bimetallic catalysts for the hydrodeoxygenation conversion of lignin and its model compounds.

X-ray Photoelectron Spectroscopy (XPS) was performed on the Ru-based bimetallic catalysts. XPS is a surface sensitive technique which has a nominal sampling depth of ~4 nm. High energy resolution photoemission spectra of the Ru3d_{5/2}, Ru3d_{3/2} and C1s regions are shown in Figure S3.. The Binding Energy (BE) of the Ru 3d_{5/2} line after charge correction referencing the AI 2p line at 74.7 eV is 279.9 ±0.2 eV. This is consistant with Ruº or bimetalic Ru as reported in the literature.^[40, 41] The Ru 3d_{3/2} component should be about 4.2 eV higher binding energy which overlaps the C 1s lines. High energy resolution photoemission spectra of the Fe $2p_{3/2}$, Ni 2p, Cu 2p, and Zn $2p_{3/2}$ regions from catalysts Ru-Fe-HY, Ru-Ni/HY, Ru-Cu/HY and Ru-Zn/HY respectively are shown in Figure S4. The BE of the Fe 2p_{3/2} line from Ru-Fe/HY is 711.8 eV consistant with Fe^{+3 [41]} The BE of the Ni 2p_{3/2} line for Ru-Ni/HY is 456.7 eV, consistant with Ni^{+3 [41]}. The BE for the Cu 2p_{3/2} line is 933.6 eV and the shake-up lines at ~942 eV is consistant with Cu^{+2.[41]} For Ru-Zn/HY the BE for the Zn 2p_{3/2} line is 1022.9 eV.

Conclusions

Bifunctional catalysts Ru/HY and Ru-M/HY (M= Fe, Ni, Cu, Zn) were synthesized and evaluated on HDO conversion of softwood lignin as well as several lignin model compounds. Results obtained from guaiacol HDO conversion indicate that all the bimetallic catalysts, especially Ru-Cu/HY, exhibited better HDO catalytic activities (regarding guaiacol conversion and hydrocarbon yield) as compared with Ru/HY. The combination of a 3d transition metal (Fe, Ni, Cu, Zn) with Ru can modulate the hydrogenolysis activity of Ru and help to prevent the hydrocarbon products from being over-hydrogenolysis to form gaseous products. Results from conversion of other lignin model compounds and softwood lignin also revealed the high HDO catalytic activity of the prepared bimetallic catalysts. The yield of hydrocarbon products over the synthesized bifunctional catalysts was higher than that over the combination mixing catalyst of Ru/Al₂O₃ and HY zeolite, which could be probably ascribed to the

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intimacy criterion. These catalysts were characterized by BET, NH₃-TPD, XRD, and STEM to study the structure-catalytic activity relationship. Results revealed that Ru-Cu/HY has both higher acid volume and larger ratio of stronger acid sites as compared to other prepared bifunctional catalysts. XRD test indicated that the impregnation of metals in the HY support has little effect on the parent zeolite structure. Moreover, XRD and STEM results suggested that the addition of a second metal to Ru enabled Ru to form smaller size particles. The morphology of the bimetallic clusters was found to be quite different (smaller average size and narrow size distribution) from that of monometallic particles as indicated by STEM. Further study on the alloying effect of ruthenium metal with Fe, Ni, Cu, and Zn is in progress.

Experimental section

Materials: Ruthenium (III) chloride hydrate (RuCl₃·xH₂O, Ru content 37 wt%), anhydrous zinc (II) chloride (ZnCl₂, Zn content 48.02 wt%), anhydrous cuprous (II) chloride (CuCl₂, Cu content 47.28 wt%), nickel (II) chloride hydrate (NiCl₂·6H₂O, 98% purity, Ni content 24.71 wt%) and ferric (III) chloride hydrate (FeCl₃·6H₂O, 98% purity, Fe content 20.67 wt%) were purchased from Fisher Scientific. Guaiacol, diphenyl ether, benzofuran and (benzyloxy)benzene were purchased fromSigma-Aldrich. Lignin was isolated from Lodgepole Pine sawdust using flowthroughpretreatment. Zeolite HY (CBV 400) was purchased from Zeolyst International.

Lignin isolation and purification: Softwood samples containing 0.5 g dry weight mass were loaded into flowthrough tubular reactors with 20.5 ml working volumes and stainless steel porous frits. The flowthrough reactors were then connected to an HPLC pump and a fluidized sand bath system (model SBL-2D, Omega engineering, Inc., CT). 0.05% (w/w) sulfuric acid at room temperature was pumped through the reactor to purge the entrained air. Then, the reactors were pressurized to a set pressure of 300 psi-700 psi. The loaded biomass was completely wetted by this procedure. The reactors were heated to 250°C by plunging the pre-heating coil and reactors into a 4-kW fluidized sand bath. The temperature of the sand bath was set to 15°C higher than the target reaction temperature. The flow rate was set at 25 mL/min. After 8 min of pretreatment, the reactors were cooled immediately by immersion in cold water. At this flow rate, the average temperature of the dilute sulfuric acid in the reactor tubes was measured at the target temperature. The liquid collected through the pretreatment was centrifuged at 1000 rpm, and the flowthrough lignin precipitate was washed with DI water by centrifuging at 1000 rpm. The precipitated lignin sample was freeze-dried and stored at room temperature for further use.

Catalyst preparation: Monometallic catalyst of Ru/HY with a Ru loading of 5 wt% and bimetallic Ru-M/HY (M=Fe, Ni, Cu, Zn) catalysts with each metal loading of 2.5 wt% were prepared by using a conventional incipient wetness impregnation procedure with aqueous solutions of the metals salts.^{11h} The resultant

suspension was stirred for 24 h at room temperature followed by evaporation of the excess water at 55°C. The obtained solids were dried at 120 °C and calcined at 550 °C for 4 h with a ramp up of temperature of 10 °C /min under air sparging. The catalysts were reduced at 250 °C for 2 h under 2 MPa H₂ before use.

Catalyst characterization: The catalytic materials synthesized in this work were characterized by X-ray diffraction (XRD), scanning transmission electron microscopy (STEM), N₂ physisorption using the Brunauer-Emmett-Teller (BET), and NH₃ temperature programmed desorption (TPD). X-ray diffraction (XRD) patterns were taken with a Bruker D8 Venture diffractometer equipped with Cu tube operated at 40 W (40 kV, 1 mA). High-angle annular dark-field (HAADF) scanning transmission electron microscopy (STEM) images were taken on a probe-corrected FEI Titan 80-300 S/TEM operating at 300 kV.

X-Ray Photoelectron Spectroscopy was perfromed using a Physical Electronics Quantera Scanning X-ray Microprobe. This system uses a focused monochromatic Al K α X-ray (1486.7 eV) source for excitation and a spherical section analyzer. The instrument has a 32 element multichannel detection system. The X-ray beam is incident normal to the sample and the photoelectron detector is at 45° off-normal. High energy resolution spectra were collected using a pass-energy of 69.0 eV with a step size of 0.125 eV. For the Ag 3d_{5/2} line, these conditions produced a FWHM of 1.0 ± 0.1 eV. The binding energy scale is calibrated using the Cu 2p_{3/2} feature at 932.62 ± 0.05 eV and Au 4f_{7/2} at 83.96 ± 0.05 eV. Spectra have been charge corrected to the Al 2p line at 74.7 eV.^[42]

N₂ physisorption analysis for determination of surface area and mesopore size was carried out using a Micromeritics ASAP2020 volumetric analyzer at liquid nitrogen temperature (77 K). The surface area was calculated by Brunauer-Emmett-Teller (BET) equation from the adsorption data obtained at P/P₀ values between 0.05 and 0.2. The average mesopore size was determined from the adsorption branch of the isotherm using the Barrett-Joyner-Halenda (BJH) algorithm. NH₃ temperatureprogrammed desorption (NH₃-TPD) measurements were performed in a quartz tube reactor equipped with a thermal conductivity detector (TCD). The samples (~50 mg) were degassed in a cell under pure He gas flow (50 mL/min) at 700°C for 2 h (ramping rate = 10 °C /min) to remove the possible Si-OH groups that can potentially decompose by dehydration and formation of water. Then, the samples were treated with the O₂ flowing (10 mL/min) for 1 h, purged with pure He for 15 min, and treated with H₂ flow (10 mL/min) for 1 h. The samples were cooled down to ambient temperature in the cell under pure He flow and exposed to NH₃ gas for 20 min. After adsorption of NH₃ gas, the samples were purged with pure He flow for 30 min, and subsequently the cell was heated to 700°C for NH3 the TPD measurements. The desorbed NH₃ molecules were monitored using a thermal conductivity detector (TCD) upon increase of temperature of the samples.

Catalytic hydrodeoxygenation (HDO) reactions: In a typical reaction, lignin or lignin model compound (100 mg), water (30 mL) and catalyst (100 mg) were added to a Parr reactor (reactor

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volume= 100 mL). The reactor was sealed and purged with H₂three times, and then pressurized with 4 MPa H₂ (room temperature). The reactions were carried out at 250 °C for 2 or 4 h. After each reaction, the reactor was cooled to room temperature to quench the reaction by immersing in a cold water bath. *n*-decane (5 μ L) was added to the reaction solution and used as an internal standard for hydrocarbons calibrations. Ethyl acetate (30 mL) was used to extract the products from the reaction solution. After centrifugation at a speed of 10000 rpm for 10 min, the extract was separated and analyzed by GC and GC-MS. The aqueous phase was filtered to recover the solids which were made up of unreacted lignin, catalyst, and char. The solids were washed with DI water and then ethanol (each for three times). After that, the washed solids were dried at 105 °C for 24 h and weighed.

Lignin deconstruction products analysis: The organic solvent extracted samples (1 μ L) were injected into a stream of He (carrier gas) flowing at 0.6 mL min⁻¹ into a DB-5 (30 m length × 250 µm I.D. × 0.25 µm film thickness, J&W Scientific) capillary column fitted in an Agilent Technologies 7890A GC system set in the splitless mode. The GC oven was programmed to reach 45°C and soak for 2 min; then ramp up at the rate of 15°C per min until the temperature reached 200°C and held at this temperature for 1 min, after which the temperature was raised at the rate of 5°C/min until the temperature reached 280°C, where it was held at the final temperature for 7 min. Eluting compounds were detected with an MS (Agilent Technologies 5975C) inert XL EI/CI MSD with a triple axis detector, and compared using NIST libraries. Shimadzu TOC-V Analyzer was used to quantify the total organic carbon of the lignin and residue solids (including catalyst and residue lignin). The effective carbon number (ECN) approach can be used for calculating relative response factors in cases where pure standard materials are not available for detector calibration.²⁰ Lignin conversion, the mass yield of each product and its selectivity were calculated as follows:



For the conversion of lignin:

Conversion= Carbon content in original lignin-carbon content in residue solid Carbon content in original lignin

$$Yieldx (wt\%) = \frac{\frac{Mass n_decane}{142} \times \frac{areax/ECNx}{area n_decane/10} \times MWx}{Mass lignin}$$

Total product yield= $\sum_{x=1}^{25}$ Yieldx

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Keywords: Lignin • bimetallic catalyst • bifunctional catalysts •hydrodeoxygenation • biofuel • jet fuel

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Entry for the Table of Contents

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Lignin to advanced bio-fuels: High yields (26 wt% to 32 wt%) of alkanes in jet fuel or diesel range have been directly produced from aqueous phase hydrodeoxygenation (HDO) conversion of softwood lignin by the catalysis of Ru-based bimetallic catalysts supported on zeolite Y. These bimetallic and bifunctionalcatalysts showed high efficiency as compared with the combination catalysts of Ru/Al₂O₃ and HY zeolite.



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Page No. – Page No. Hydrodeoxygenation of Lignin to liquid alkanes on Ru-based Bimetallic CatalystsSupported on Zeolite Y

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