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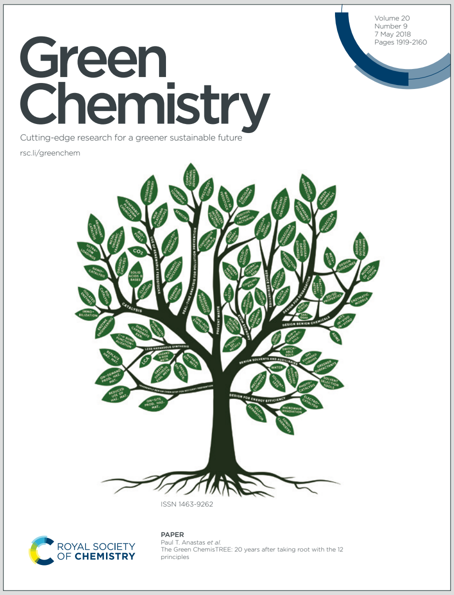

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ARTICLE

Cleavage of Lignin C-O Bonds over a Heterogeneous Rhenium Catalyst through Hydrogen Transfer Reactions

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Hydrogenolysis is one of the most popular strategies applied in depolymerization of lignin for the production of aromatic chemicals. Currently, such strategy is mainly conducted under high hydrogen pressure, which are either at the risk of safety or not sustainable and economical. Herein, we report that heterogeneous rhenium oxide supported on active carbon (ReO_x/AC) exhibits excellent activity in selective cleavage of lignin C-O bonds in isopropanol. High yields of monophenols (up to 99.0 %) from various lignin model compounds and aromatic liquid oil (>50%) from lignin feedstock were obtained respectively under mild condition in the absence of H_2. Characterization of the catalyst by X-ray absorption fine structure, X-ray photoelectron spectroscopy and H_2-temperature-programed reduction suggests that the activity of ReO_x/AC can be attributed to the presence of $Re^{IV\text{-}VI}$. The interaction between the surface oxygens groups of active carbon and rhenium oxide could also play an important role for the cleavage of C-O bonds. Notably, ReO_x/AC-catalyzed C-O bond cleavage pathway beyond typical deoxydehydration mechanism was disclosed. More importantly, 2D-HSQC-NMR and GPC characterization showed that ReO_x/AC exhibited high activity not only in β-O-4 cleavage, but also in deconstruction of more resistant linkages of β-5 and β-β in lignin without destroying the aromatic ring. This study paves the way towards the development of rhenium-based catalyst for the reductive valorization of realistic lignin material in a controlled through hydrogen transfer pathway.

1. Introduction

In light of the accelerating depletion of fossil fuels and increasing demand for energy, lignocellulose, the most abundant biomass, is generally regarded to be a sustainable feedstock for energy, chemicals and biofuels.[1] As one of the major components of lignocellulose, lignin is by far the only largest renewable source that supply aromatic chemicals owing to its high abundance and inherent aromatic structure.[2] Thus, the effective depolymerization of lignin into aromatics would greatly improve the economics of the overall biorefinery process.[3] Currently, both heterogeneous and homogeneous catalytic processes for reductive or oxidative lignin depolymerization strategies have been developed.[4] However, in most cases, high pressure (3-5 MPa) of molecular hydrogen or oxygen atmosphere is required for lignin depolymerization at high temperatures (> 250 °C), and low conversions in conjunction with broad product distributions are usually obtained.[5] One major challenge reflects in the selective cleaving of the aryl C-O linkages between primary aromatic units whilst avoiding side reactions such as over-hydrogenation and over-oxidation under low-severity condition. In this aspect, several breakthroughs have recently been achieved. For instance, Luterbacher and co-workers reported that the diol protection reagents such as formaldehyde can stabilize α,γ-diol group of lignin and hence promote high-selective monomer production.[6] Wang et al. reported solar energy-driven conversion of native lignin at room temperature.[7] Acidolysis using trifilic acid or formic acid is also confirmed to be a promising route to obtain aromatic monomers from lignin.[8] Very recently, the lignin-first strategy also shows promise in depolymerization of lignin to afford high yield of aromatic chemicals without pretreatment of lignocellulose.[9] Despite of these progress, in many biorefinery processes, including paper industry, great amount of lignin is generated as a waste stream. Development of a new catalytic system for the depolymerization of lignin to aromatic chemicals in an efficient way is still desirable.

Rhenium (Re) is a group 7 transition metal that is less electronegative than typical transition metals such as ruthenium, rhodium, and palladium. The wide range of oxidation states of Re suggests the potential for the discovery of new reactivity features of Re in chemical reactions.[10] Recently, it has emerged as a promising metal in the field of biomass conversion. It has been found to promote the deoxydehydration of polyols and alcohols to olefins owing to its specific ability to form diolate through the coordination of diol with Re species.[11] This is of interest because lignin contains a large number of hydroxyl groups whilst rhenium has outstanding capacity to remove the hydroxyl via deoxydehydration reaction.[12] Therefore, Kühn and co-workers

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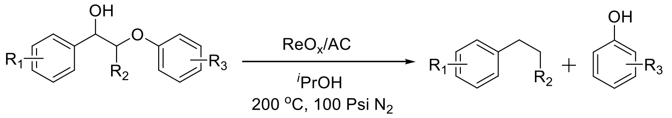
first reported the Re(VII) complex CH_3ReO_3 (MTO)-catalyzed cleavage of β-O-4 compounds in the absence of redox species.[13] Furthermore, the depolymerization of lignin over Re_2O_7 through hydrogenation has been demonstrated by our own group.[14] More recently, we found that ReO_x/AC can catalyze hydrogenolysis of lignin α-O-4 model compounds under 3 MPa H_2 atmosphere.[15] However, this catalytic system exhibited much poorer performance with regard to the conversion of β-O-4 model compounds, the most abundant linkage in native lignin.[4] On the other hand, hydrogen itself is a clean energy, and hydrogenolysis of lignin with H_2 at high temperature and high pressure needs special equipment, which increases the cost and may cause safety issues. Therefore, new catalytic system for the cleavage of β-O-4 linkages in lignin without H_2 is highly desirable. Compared with hydrogenation reactions involving H_2, transfer hydrogenation by using hydrogen-donating solvent such as alcohols is safer and easier to handle.[16-17] In the present work, selective cleavage of C-O bonds in β-O-4 model compounds (Scheme 1) and lignin over ReO_x/AC without H_2 was demonstrated in isopropanol through hydrogen transfer mechanism. High yields of aromatics (up to 99%) from model compounds and liquid oils (>50%) from isolated lignin were obtained respectively in isopropanol. The reaction pathway and active species were extensively studied as well.



Scheme 1. Depolymerization of lignin catalyzed by ReO_x/AC through hydrogen transfer reactions

2. Experimental

General procedure for ReO_x/AC catalyzed lignin model compounds: The catalytic reaction was performed in a Parr autoclave (Parr, 75 mL). Typically, the model compound (0.41 mmol), catalyst (1.6 mol% Re), the standard mesitylene (18 mg) and isopropanol (15 mL) were placed to the autoclave (Parr, 75 mL) and flushed by N_2 for several times. The reaction vessel was conducted at 200 °C with 100 psi N_2 and stirred (800 rpm) for 3 h. After reaction, the gases were collected and the liquid phase was analyzed by gas chromatography with a flame ionization detector (GC-FID) employing the mesitylene as an internal standard (HP-5 column, 30 m × 0.32 mm × 0.25 μm).

General procedure for conversion of lignin feedstocks: The catalytic conversion of lignin feedstocks was carried out in a Parr autoclave (75 mL). Typically, lignin (100 mg), ReO_x/AC (1.6 mol% Re), and the solvent isopropanol (15 mL) were placed to the Parr autoclave, followed by stirring at 800 rpm. When the reaction was finished, the gases were collected and analyzed, and the residue solid was washed with isopropanol, and then dried at 50 °C in preparation for two-dimensional heteronuclear single quantum coherence nuclear magnetic resonance (2D-HSQC-NMR) characterization. The liquid was vacuumed at 30 °C to afford a liquid oil. Noting that lignin does not dissolve in ethyl acetate, ethyl acetate was added (3×15 mL) in the oil to extract the low molecular aromatic products. The extraction liquid was collected, then evaporated at 30 °C to remove solvent, affording a 54.0% yield of oil products from organosolv poplar lignin (OPL) and a 50.2% yield from organosolv wheat lignin (OWL). The liquid oil constants volume of 2 mL with isopropanol, and the monomeric products were quantified by the internal standard method (standard: mesitylene) using GC-FID (HP-5 column, 30 m × 0.32 mm × 0.25 μm). The molecular weight distributions of the liquid oils were determined by matrix assisted laser desorption/ionization time-of-flight MS (MALDI-TOF-MS). The oil yields were calculated according to the equation:

Oil yield（wt%）=(the weight of produced oily product)/(the weight of original lignin)×100%

Catalyst preparation: The MO_x/AC (AC, NORIT, M = Re, W, V, Mo) catalysts were prepared by impregnating the AC with an aqueous solution of NH_4ReO_4, $(NH_4)_6H_2W_{12}O_{40}\cdot H_2O$, $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ and NH_4VO_3. After drying at 110 °C for 12h, the MO_x/AC was calcined in nitrogen at 500 °C for 3 h. The loading amount Re, W, Mo and V was 1.18%, 0.72%, 0.63%, 0.40%, respectively, which is determined by ICP-AES.

3. Results and Discussion

3.1 Optimization of the reaction conditions

β-O-4 is the most frequent linkage in almost all types of lignin, and the chemical reactivity of this bond results in the considerable resistance of lignin to chemical digestion.[4] 2-(2-methoxyphenoxy)-1-phenyl ethanol (**1**), a common lignin β-O-4 dimeric model compound, was initially studied to explore the activity of the catalysts in isopropanol. First, the activity of ReO_x/AC was compared to other active carbon-supported metal oxides, including WO_x, MoO_x, and VO_x (entries 1-5), and ReO_x/AC displayed a substantially higher catalytic activity than others, giving 83.0% yield of guaiacol and 81.6% yield of ethylbenzene (entry 1). In sharp contrast, an experiment using solely AC as the catalyst led to lower conversion and different selectivity, providing 1-isopropoxy-2-phenoxyethyl benzene as the main product, which was also detected in literature.[18,9c] However, this catalyst provided very poor yields of ethylbenzene and guaiacol (Table 1, entry 15, for details regarding the products, see Figure S2). This is mainly attributed to acidic catalysis, because the surface of AC has numerous acidic functional groups due to nitric acidic treatment before use, as demonstrated by X-ray photoelectron spectroscopy (XPS) (Figure S4 and Table S1). With these results in hand, we conducted subsequent reactions using ReO_x/AC as the catalyst to optimize the reaction conditions. Table 1 shows that decreasing amount of Re led to incomplete C-O bond cleavage (entries 1, 7 and 8). As an example, reducing the catalyst amount to 0.1 mol% Re afforded a decreased yield of **2** (75.8%) and a much lower yield of **3** (53.5%) (entry 8). Interestingly, styrene (**4**) was obtained in a yield of 13.8% in this experiment. In the case of MeOH as solvent, despite relatively high conversion was also achieved, the total yield of **3** and **4** (54.7%) was lower than that using ^{i}PrOH as solvent (entry 10 vs entry 1). Moreover, using THF as solvent under H_2 atmosphere gave much poorer performance (entry 11) than that in ^{i}PrOH. These results suggested that ReO_x/AC exhibited high catalytic activity

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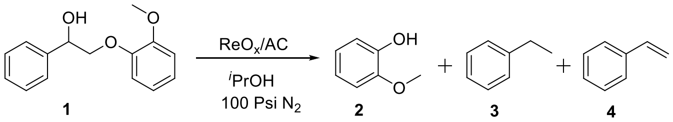
Table 1. Results of the ReO_x/AC-catalyzed C-O bonds cleavage of lignin model compound **1** under different reaction conditions.[a]



Entry	Cat.	Metal amount [mol%]	Solvent	Temp. (°C)	t (h)	Conv. (%)[b]	Yield (%)[b]			
							2	**3**	**4**	**3 + 4**
1	ReO_x/AC	1.6	^{i}PrOH	200	3	99.9	83.0	81.6	0	81.6
2	WO_x/AC	1.0	^{i}PrOH	200	3	99.9	63.4	69.0	0	69.0
3	WO_x/AC	1.6	^{i}PrOH	200	3	99.9	69.9	76.9	0	76.9
4	MoO_x/AC	1.6	^{i}PrOH	200	3	99.9	59.6	70.0	0	70.0
5	VO_x/AC	1.9	^{i}PrOH	200	3	99.9	79.4	72.9	0	72.9
6	ReO_x/AC	1.6	^{i}PrOH	200	6	99.9	84.1	82.1	0	82.1
7	ReO_x/AC	0.9	^{i}PrOH	200	3	99.9	76.2	76.4	0	76.4
8	ReO_x/AC	0.1	^{i}PrOH	200	3	90.0	75.8	53.5	13.8	68.4
9	ReO_x/AC	1.6	^{i}PrOH	200	1	89.3	44.1	44.1	20.7	64.8
10	ReO_x/AC	1.6	MeOH	200	3	95.3	93.6	7.9	46.8	54.7
11[c]	ReO_x/AC	1.6	THF	200	3	53.7	34.5	10.3	19.4	29.7
12	ReO_x/AC	1.6	^{i}PrOH	120	3	0.8	0	0	0.6	0.6
13	ReO_x/AC	1.6	^{i}PrOH	150	3	37.0	25.8	5.5	14.4	19.9
14	ReO_x/AC	1.6	^{i}PrOH	180	3	80.3	63.2	43.6	14.1	57.7
15	AC	0	^{i}PrOH	200	6	69.3	29.4	2.5	28.9	31.4
16	--	0	^{i}PrOH	200	6	0	0	0	0	0

[a]Reaction conditions: **1** (100 mg), isopropanol (15 mL), MO_x/AC (M = Re, W, Mo, V) and mesitylene (18 mg) were added to a stainless-steel autoclave (Parr, 75 mL) with an initial N_2 pressure of 100 psi; [b]Conversions and yields were determined by GC-FID with mesitylene as an internal standard; [c]100 psi H_2 was the initial pressures.

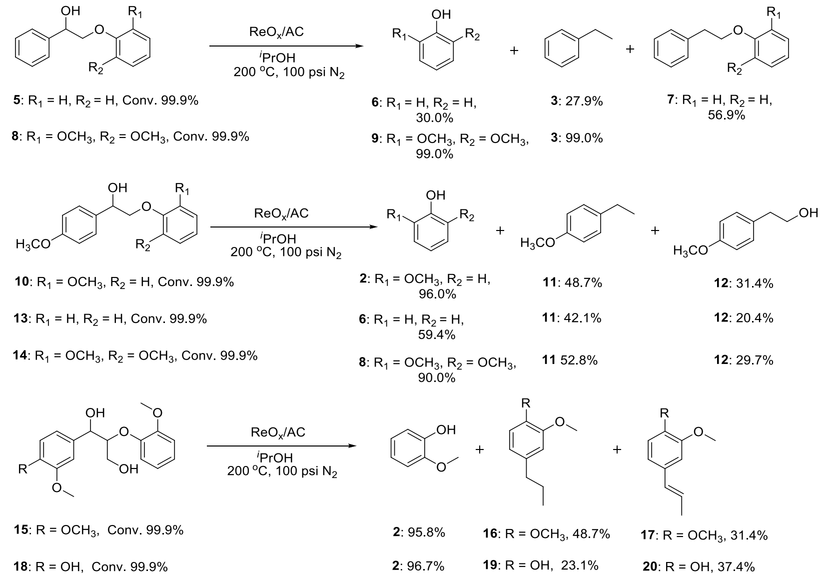
in isopropanol system. A shorter reaction time and lower reaction temperature also tended to produce styrene (entries 9, 12-14). We therefore propose that ethylbenzene might be generated from styrene via deep-hydrogenation, which will be further discussed along with the time course experiments below. In all trials, the catalytic activity and the selectivity for the desired products were greatly affected by the reaction temperature. For instance, low temperature of 120 °C almost gave no conversion, while a higher temperature of 180 °C significantly increased the reaction rate (entries 12-14), and 200 °C was the optimized reaction temperature (entry 1). Moreover, a blank experiment failed to convert compound **1** (entry 16). Additional, acetone and H_2 were found in the catalytic reaction, suggesting that isopropanol serves as in-situ hydrogen sources (Figure S5-S6).

3.2 Expanding the substrate scope

To generalize this protocol, the conversion of a series of lignin model compounds with different functional groups were investigated (Scheme 2). After the reaction, the substrates were almost completely consumed, whilst the yields of the aromatics varied. Electron-donating methoxyl group substitution on the aryl ring (compounds **8**, **10**, **14** and **15**) led to high yields of the target products, while the substrates without substitution on the o-terminus aryl ring (compounds **5** and **13**) gave relatively lower yields of C-O cleavage products. In particular, compound **5** provided the lowest performance in C-O bond cleavage; instead, 1-phenethoxybenzene (**7**) with a yield up to 56.9 % was obtained, suggesting that the rate of hydrogenation is superior to hydrogenolysis reaction. Hence the substitution pattern of the ring plays an important role in determining the products distribution. It is interesting to note that **12** was one of the major products from the conversions of **10**, **13** and **14**, implying that hydrolysis reaction occurred as well, which was different from the reactions of **1**, **5** and **8**. Noting that the substrates (**10**, **13** and **14**) had additional methoxy group on the C-terminus aryl ring compared to compounds **1**, **5** and **8**, this major difference in structure may induce the different reaction pathway. In addition, there was a possibility that **11** might be produced from **12**, however, catalytic experiment under the same conditions suggested that the reaction did not occur when conversion of **12**. Thus compound **12** is a final product for the conversion of **10**, **13** and **14**. Moreover, highly substituted substrates **15** and **18** also worked well under the same conditions, affording the corresponding C-O bond cleavage product guaiacol in 95.8% and 96.7% yields, respectively, along with **16** (48.7%), **19** (23.1%), **17** (31.4%) and **20** (37.4%). Based on all above results, one can conclude that ReO_x/AC promotes the cleavage of various β-O-4 linkages with different functional groups in isopropanol in the absence of hydrogen atmosphere.

3.3 Probing the active species

To ascertain the nature of the active species, characterization of the catalyst was conducted. XPS provided the binding energy (BE) values of the surface Re 4f7/2 orbitals in ReO_x/AC before and after reaction (Figure 1). As references for BE of Re_2O_7 (Re^{VII}) and ReO_3 (Re^{VI}) locate at 46.7 eV and 44.5 eV, respectively,[19] one can conclude that the BE of 45.8 eV for the fresh catalyst corresponds to Re^{VI-VII} species. The X-ray absorption near-edge structure (XANES) results in Figure 2 confirmed this hypothesis. that of ReO_4^-, and the valence of Re was 6.7 according to the Re-L3 edge XANES white line area (Figure S7).[11c] This result is likely attributed to partial reduction of rhenium oxide by carbon during the thermal treatment under N_2.[20] Another possible reason is an interaction between rhenium oxide and surface oxygen groups of the carbonaceous materials through electronic perturbation/chemisorption.[21-22] Such an interaction could modify the electronic density of the Re species and thus increase the activity of the ReO_x/AC to a greater extent than physical mixing of rhenium oxide and AC, which is supported by the following experiments. When a mixture of AC and Re_2O_7 was applied to the conversion of substrate **1**, products **2**, **3** and **4** were obtained in yields of 33.3%, 20.6% and 8.8% (Table S2, entry 3), respectively, which were much lower than that obtained from ReO_x/AC. This result, in combination with the data generated over AC (Table 1, entry 12) and Re_2O_7 alone (Table S2, entry 2), demonstrates a clear synergistic effect between AC and the Re species. Furthermore, the recycling experiment associated with incomplete conversions for lignin model compounds was also performed. The result showed that the catalyst can be recycled for five times with a slight loss in activity (Figure S8) due to leaching of Re species into the surrounding solution according to ICP-AES results (1.18 wt% Re in fresh catalyst vs 0.94 wt% in used catalyst, and 0.17% Re in the reaction solution after reaction). It was also found that ethylbenzene yield dropped fast whereas styrene yield increased in recycle runs, suggesting lower hydrogenation activity of the catalyst in recycle runs. Similar trend was observed when recycle experiment was performed using organsolv lignin as the substrate. For instance, the yield of 2,6-dimethoxy-4-propylphenol and 2-methoxy-4-propylphyenol decreased in the second run, however the yields of 2,6-dimethoxy-4-(prop-1-enyl) phenol and 2-mehtoxy-4-(prop-1-enyl)phenol increased. These results indicated that the ability of hydrogenation of the catalyst become weaker probably due to the leaching of Re species during the reaction and carbon deposition on the surface of the catalyst.[23] Noting that the products distribution shift from propyl chain to propenyl chain in recycle runs (Fig S8B), the acid catalysed pathway producing the propenyl chain is less affected by the above two factors. It was also found that in the last two recycle runs (R4 and R5), the yields of aromatic monomers slightly increased, which might be caused by the depolymerization of the residue in last experiment, since both the lignin residue and the catalyst are in solid state and cannot be separated each other. These results arise a question that this material might actually function as a homogeneous catalysis through the leaching of Re into the solvent. To address this point and confirm that it is heterogeneous catalysis, several control experiments were carried out. First, a hot filtration after removal of the solid catalyst was performed, followed by attempted conversion of an additional quantity of substrate **1** under the same condition as in Table 1, entry 1. The results showed that no reaction occurred in the filtrate. In addition, a hot filtration followed by the addition of fresh AC and additional substrate after removal of the catalyst was performed, leading to a 7.9% yield of **2** without any of product **3**. Comparative experiments with different oxorhenium compounds such as NH_4ReO_4, Re_2O_7, ReO_3 and ReO_2 also showed extremely low conversions (<11.0%) (Table S3). These above results indicated that the active Re species were present on the carbon support. H_2-temperature-programed reduction (TPR) also gave an evidence on this hypothesis. H_2-TPR profiles of ReO_x/AC, pure AC and a physical mixture of



Scheme 2. C-O bonds cleavage of various lignin model compounds catalyzed by ReO_x/AC.

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Re_2O_7 and AC are presented in Figure 3. The broad signals above 400 °C can be assigned to the partial reduction of AC,[22] both AC and the mixture of Re_2O_7 and AC have such signals. In addition, the mixture sample generated a sharp signal at 278 °C. It should be noted that two weak, broad signals at 260 °C and 355 °C appeared in H_2-TPR profile of ReO_x/AC sample, both signals can be assigned to the reduction of the surface oxide. The reduction temperature of ReO_x/AC was significantly lower than that of the physical mixture sample, indicating that ReO_x/AC is more readily reduced and thus there is an interaction between AC and rhenium oxide. XPS characterization showed that the reactivity of the catalysts correlated with the valence of the Re species. After reaction, ReO_x/AC displayed four signals at BEs of 45.8, 43.5, 41.8 and 41.0 eV. Since the Re 4f7/2 peak of ReO_2 (Re^{IV}) appears at 42.5 eV while 44.5 eV is assigned to ReO_3 (Re^{VI}),[24] it is reasonable to assign the 43.5 eV peak to Re^{V}, which was the richest Re species in the catalyst (46.7%; Table S4) according to semi-quantitative analysis. The peaks at 41.8 and 41.0 eV, accounting for 10.7% and 7.2%, respectively, are assigned to species Re^{III} and Re^{II}. According to the white-line area of the Re-L3 edge XANES data, the estimated average valence was 5.6 (Figure S5). Noting that the Re valence of the fresh catalyst was estimated 6.7, these results provided us a key information that ReO_x/AC catalyst can be reduced by H_2 (generated *in situ* from isopropanol) to form different low valence Re species. While these new species are not stable and are liable to be oxidized back to higher valence forms when exposing to air even for a short time (Figure S9). Previously, Kühn and co-workers reported that methdioxorhenium (V) complex, formed via reduction of methtrioxorhenium (VII) acted the active specie for cleavage of C-O bond in lignin model compounds.[13] Tomishige reported that Re^{IV}/Re^{VI} species of the heterogeneous catalysts ReO_x-Pd/CeO_2 are the active sites in the deoxydehydration reaction.[11a, 11c] Based on the above XPS and EXAFS results accumulated and published results,[11c, 13, 15, 25] it is reasonable to propose that Re^{IV-VI} is the active species that responsible for C-O bond activation.

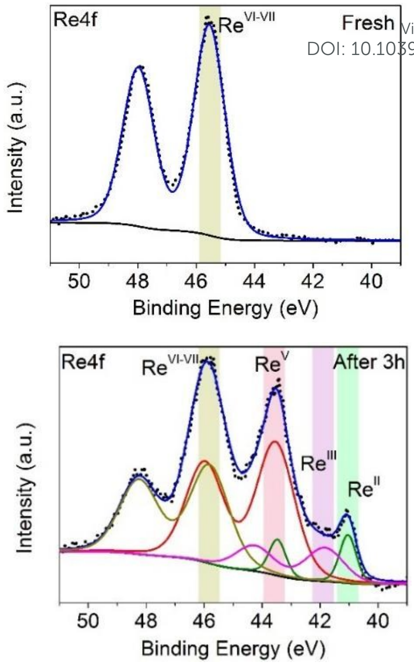

Figure 1. Re 4f XPS patterns of ReO_x/AC before and after reaction.

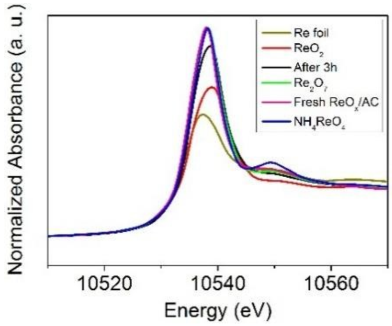

Figure 2. Re L3 edge XANES spectroscopy.

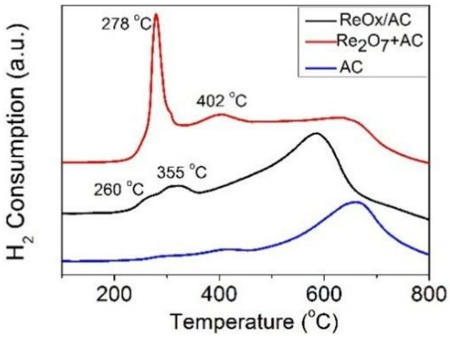

Figure 3. H_2-TPR data of various catalysts.

3.4 Exploring the catalytic reaction pathway

Monitoring the time course of the conversion of 2-(2-Methoxyphenoxy)-1-phenyl ethanol in Figure 4 showed that the concentrations of 2-(2-methoxyphenoxy)-1-phenylethanone and (E)- and (Z)- 1-methoxy-2-(styryloxy)benzene isomers were firstly increased, then quickly decreased after 1 h. In parallel, C-O bond cleavage products increased with increasing the reaction time, indicating that dehydrogenation product (2-(2-methoxyphenoxy)-1-phenylethanone) and dehydration product ((E)- and (Z)- 1-methoxy-2-(styryloxy)benzene) might be the plausible intermediates. Hence, two reaction pathways (dehydrogenation and dehydration) probably exist in this transformation. To verify this hypothesis, the following control experiments were carried out. When the conversion of (E)-1-methoxy-2-(styryloxy)benzene (**21**) was catalyzed by ReO_x/AC under the same conditions (Scheme 3, equation (1)), products **3** and **6** were obtained in yields of 71.1% and 65.3%, respectively, via a cascade hydrolysis, isomerization and hydrogenolysis reactions (Route 1 in Scheme 4). If 2-phenoxy-1-phenylethanone (**22**) was used as the substrate, the deoxygenation product **7** (47.1% yield) along with **3** (38.3% yield) and **6** (20.2% yield) were generated (Scheme 3, equation (2)). Taken these two comparative reactions and the above time course experiments together, one can suppose that in the transformation of compound **1**, both the dehydration species (E)- and (Z)- 1-methoxy-2-(styryloxy)benzene and dehydrogenation product 2-(2-methoxyphenoxy)-1-

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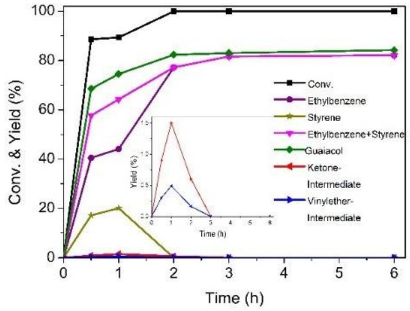
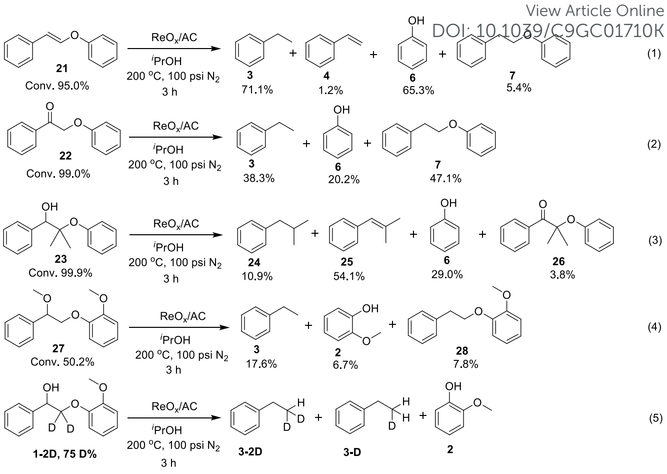


Figure 4. Time course experiment catalyzed by ReO$_x$/AC in the transformation of the compound 1. Reaction conditions: lignin model compound 1 (100 mg, 0.41 mmol), ReO$_x$/AC (1.6 mol% Re), and internal standard mesitylene (18 mg) in isopropanol (15 mL) with N$_2$ (100 psi) at 200 °C. Conversion and yields were determined with GC-FID by an internal standard method.



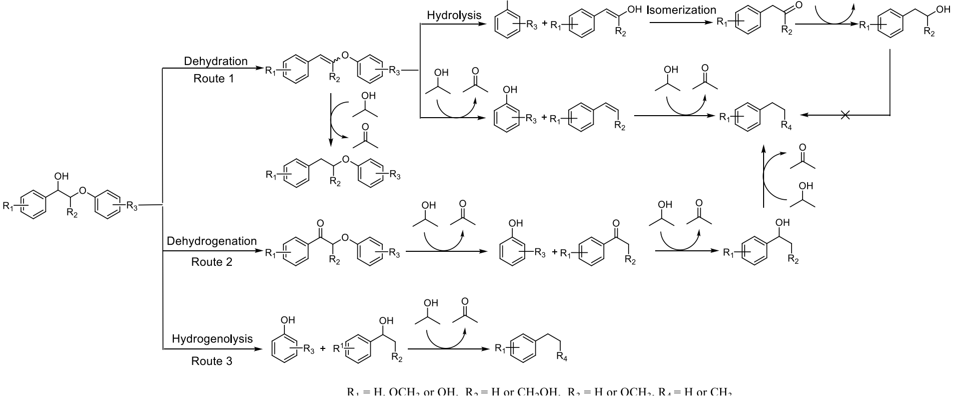
Scheme 3. Control experiments used to determine the reaction pathway.

phenylethanone were reactive intermediates. Furthermore, after comparison the products distributions of two control reactions (Scheme 3, equations (1) and (2)), one can easily acknowledge that the corresponding vinyl ether should be the major intermediate in the transformation of compound **1**, and the reaction starting from dehydration is preferred. The acidity of the catalyst (originated from acidic groups of the AC surface) may play an important role in catalyzing the dehydration reaction and subsequent C-O cleavage to afford styrene and guaiacol according to Table 1, entry 15).

To obtain additional information with regarding to the hydrogenolysis process and to clarify the role of different functional groups in β-O-4 aryl ethers, several comparative reactions with various substrates were conducted. Substrate **23**, in which the C$_\beta$ position is blocked by two methyl groups such that it cannot undergo dehydration, was synthesized for conversion over ReO$_x$/AC under the same conditions (equation (3)). Hydrogenolysis products **24**, **25** and **6** were obtained in yields of 10.9%, 54.1% and 29.0%, respectively. Furthermore, substrate **27**, without OH group in the C$_\alpha$ position (in contrast to substrate 1), is unable to undergo dehydrogenation, giving a small amount of the hydrogenolysis products ethylbenzene and guaiacol (equation (4)). The above two reactions, including the results in Figure 4, confirm that the presence of a hydrogen in the C$_\alpha$ or C$_\beta$ position is not necessary for the cleavage of β-O-4 aryl ethers, and that a hydrogenolysis reaction occurs during the transformation (Route 3 in Scheme 4). The isotopically-labeling experiment further supports that both route 1 (dehydration) and route 3 (hydrogenolysis) occurred since both hydrogenolysis product 3-2D and dehydration product 3-D were detected (equation (5) and Figure S12). Therefore, we propose a reaction pathway that proceeds through three routes (dehydration, dehydrogenation and hydrogenolysis), as summarized in Scheme 4.

3.5 Depolymerization of organosolv lignins catalyzed by ReO$_x$/AC

Based on the results obtained in model compounds conversion, two organosolv lignins were extracted from wheat straw and poplar.[26] Fourier transform infrared spectroscopy (FTIR) characterization indicated that the isolated organosolv poplar lignin (OPL) and organosolv wheat lignin (OWL) both had a basic lignin skeleton (Figure S13and Table S6). The relative ratios of the main linkages were semiquantitative determined by 2D-HSQC NMR (Figure S14).[27]



R$_1$ = H, OCH$_3$ or OH, R$_2$ = H or CH$_2$OH, R$_3$ = H or OCH$_3$, R$_4$ = H or CH$_3$

Scheme 4. Proposed reaction pathways for ReO$_x$/AC-catalysed in lignin β-O-4 model compounds.

Catalytic depolymerization of the two lignins over ReO$_x$/AC in isopropanol in the absence of H$_2$ provided three products: oil, solid residue and trace CO$_2$. In the case of OPL, an oil yield of 54.0 wt% and a monomer yield of 11.4 wt% were obtained, while OWL provided an oil yield of 50.2 wt% with a monomer yield of 5.3 wt% (Table 2). GC-MS analysis confirmed the absence of cycloalkanes in the oil products, indicating that the catalyst was highly selective in activating the C-O bond linkages in lignin without destroying aromatic rings. As the grass lignin OWL

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Table 2. Catalytic hydrogenolysis of two lignins over ReO$_x$/AC.[a]

Lignin	**A** : **B** : **C**	**S** : **G** : **H**		M$_w$[g mol^{-1}][d]		Oil	Monomer	Monomers	Residual
	[%][b]	before[b]	After[c]	before	after	[wt%]	[wt%][e]	in oil [%]	[wt%]
OPL	74.3:2.8:12.9	63.6:36.4:0	68.6:31.7:0	1707	710	54.0	11.4	21.1	30.2
OWL	48.7:28.2:23.1	28.6:57.6:13.8	30.9:61.7:7.4	2403	618	50.2	5.3	10.6	26.7

[a]Reaction conditions: lignin (100 mg), ReO$_x$/AC (1.6 mol% Re), ^{i}PrOH (15 mL), T = 200 °C, P = 100 psi N$_2$, t = 8 h. [b]Determined by 2D HSQC NMR characterization of isolated lignin. [c]Determined by 2D HSQC NMR characterization of oil products. [d]Determined by gel permeation chromatograph (GPC) after acetylation. [e] Identified with GC-MS and quantified with GC-FID by an internal standard.

provided a lower oil yield, particularly a lower yield of monomers from OWL than that from OPL, indicating that hardwood lignin OPL was easier to be deconstructed than grass lignin OWL. Three facts may cause the results: 1) The β-O-4 (**A**) proportion of OPL (74.3%) was higher than that of OWL (48.7%), which is in agreement with Bouxin and co-workers report that the yield and the nature of monomeric products were largely dependent on the proportion of β-O-4 linkage.[26a] 2) OWL has higher molecular weight (see GPC results, Table S7) and more stubborn C-C linkages such as phenylcoumaran (**B**, β-5, 28.2%) and resinol (**C**, β-β, 23.1%) as determined by 2D HSQC NMR analysis (Figure S12-4). 3) As reported by Sels and co-workers, lignin rich in **S**-units more readily undergoes depolymerization due to more methoxy group.[9d] In our study, OPL had a higher proportion of **S** units (63.6%) compared with OWL (28.6%), representing another reason why OPL underwent depolymerization to a greater extent than OWL.

Careful analysis of the 2D HSQC NMR spectra of the lignin feedstocks and lignin oils provided additional information of the depolymerization behaviours. In the linkage region of the OPL oil spectrum, the signals of **B**$_\alpha$ (δ_C/δ_H 87.21/5.59 ppm) and **B**$_\beta$ (δ_C/δ_H 53.30/3.59 ppm) related to phenylcoumaran linkages (β-5) are much weaker compared with those of the original OPL sample (Figure S14-3). However, **A** signal related to β-O-4 linkage greatly decreased, whereas the **C**$_\alpha$ (δ_C/δ_H 84.89/4.71 ppm), **C**$_\beta$ (δ_C/δ_H 53.80/3.06 ppm) and **C**$_\gamma$ (δ_C/δ_H 71.07/4.22 ppm, δ_C/δ_H 71.07/3.88 ppm) signals from resinol linkages (β-β) were almost unchanged. These results indicate that β-O-4 and β-5 linkages were converted or modified to some extent over ReO$_x$/AC. With regard to OWL transformation, the 2D-HSQC-NMR spectra of the lignin oil shows that the peaks related to **A**, **B** and **C** linkages clearly decreased, suggesting that β-O-4, β-5 and β-β linkages were probably converted or modified. Integration of the peak areas (linkages/100 C9 units) provided us an estimation of the differences in interunit linkages composition (Figure S16), which led to the same conclusion.

The oily products were identified and quantified by GC-MS and the detailed distributions of phenolic monomers are collected in Table S8. Following the reactions of both the OPL and OWL, major phenolic compounds such as guaiacylpropane (1.9% for OPL, 0.8% for OWL) and 4-propylsyringol (6.5% for OPL, 1.1% for OWL), which are attributed to guaiacyl (**G**) and syringyl (**S**) units, were obtained. Other monomers, including methyl 3-(4-hydroxyphenyl)propanoate (0.4%) and ethyl 3-(4-hydroxyphenyl)acrylate (0.2%) were derived from p-coumarate (***p*CA**) units, while methyl 3-(4-hydroxy-3-methoxyphenyl)acrylate (0.5%) originated from ferulate (**FA**) units. The **S**: **G**: **H** (coumaryl) ratios of the monomers in the lignin oils were similar to those in the original lignins (Table 2).

The overall monomer yields in the oils suggest that these oils contained high boiling point products which cannot be detected by GC-MS. Thus, both GPC and MALDI-TOF-MS analysis of the oil products were performed. The GPC results of the oils showed a significant decrease in the molecular weight compared with that of the original lignin samples (Table S7), suggesting that the two lignins underwent depolymerization. This outcome is supported by the MALDI-TOF-MS data, which show numerous products in the m/z range of 100 to 700 and 150 to 750 for OPL and OWL, respectively (Figure S17). Noting that the molecular weights of typical **S**, **G** and **H** units such as syringylpropane (168 g mol^{-1}), guaiacylethanol (210 g mol^{-1}) and 4-propylphenol (136 g mol^{-1}) are in the range of 100-300 g mol^{-1}, the products obtained from the OPL and OWL evidently contain monomers, dimers, trimers and tetramers, with the first three as the dominant compounds.

4. Conclusions

This work demonstrated the cleavage of various lignin β-O-4 model compounds and realistic lignin materials to give aromatic compounds over ReO$_x$/AC catalyst in isopropanol solvent through hydrogen-transfer pathway. High yields of monophenols (up to 99.0%) were obtained from the model compounds, and significant amounts of aromatic oils (50.2%-54.0%) along with a 6.5% yield of 4-propylsyringol resulted from the lignin feedstock. Characterization of the catalyst and a study of the associated reaction mechanism showed a clear synergistic effect between Re species and the AC, with Re^{IV-VI} being the primary active species. A reaction pathway involving

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β-O-4 cleavage was proposed, in which isopropanol serves as a hydrogen donor. These results suggest the potential application of Re-based catalysts for the conversion of biomass.

Conflicts of interest

There are no conflicts to declare.

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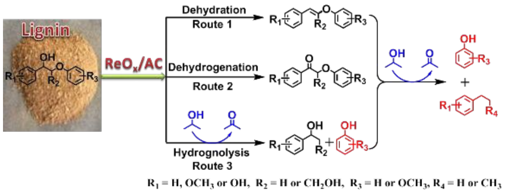

One sentence abstract: ReO_x/AC exhibits high catalytic activity and selectivity for the C-O bond cleavage of lignin *via* hydrogen transfer reactions in isopropanol.