Title: Highly Efficient Cleavage of Ether Bonds in Lignin Models via Transfer Hydrogenolysis over Dual-Functional Ru/Montmorillonite

Authors: Zhimin Xue, Haitao Yu, Jing He, Yibin Zhang, Xue Lan, Rundong Liu, Luyao Zhang, and Tiancheng Mu

This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: ChemSusChem 10.1002/cssc.202000978

Link to VoR: https://doi.org/10.1002/cssc.202000978
Abstract: Cleavage of ether bonds is the crucial but challenging step for lignin valorization. To efficiently realize this transformation significantly relays on the development of robust catalysts or catalytic systems. Herein, montmorillonite (MMT)-supported Ru (denoted as Ru/MMT) was fabricated as a dual-functional heterogeneous catalyst to cleave various types of ether bonds via transfer hydrogenolysis without using any additional acids or bases. It was found that the prepared Ru/MMT could efficiently catalyze the cleavage of various lignin models and lignin-derived phenols, and cyclohexanes (fuels) and cyclohexanols (key intermediates) were the main products. The synergistic effect between electron-enriched Ru and the acidic sites on MMT contributed to the excellent performance of Ru/MMT. Systematic studies revealed that the reaction was conducted through two possible reaction pathways, including the direct cleavage of ether bonds and the formation of intermediates with one hydrogenated benzene ring, for all the examined types of ether bonds, i.e., 4-O-5, α-O-4, and β-O-4.

Introduction

To alleviate excessive reliance on the diminishing fossil resources (i.e., coal, petroleum, and natural gas), utilization of renewable and abundantly available lignocellulose has been recognized as a promising alternative way to produce the essential fuels and chemicals.[1] In this regard, transformation of lignin (the major component of lignocellulose) and its derived chemicals has gained increasing interest in recent years.[2] Generally, the cleavage of ether bonds is the critical step to convert lignin (including lignin derivatives hereafter) into renewable fuels and valuable chemicals owing to the abundant existence of various ether bonds in lignin.[3,4]

Of the developed strategies (i.e., oxidation, hydrogenolysis, and hydrosis) to cleave the ether bonds in lignin, hydrogenolysis has attracted significant attention owing to its high atom-economy.[4] The hydrogenolytic cleavage process often involves the use of high-pressure H2,[5] which would result in the great potential risk especially when the reactions are conducted under high temperature. To avoid the use of high-pressure H2, catalytic transfer hydrogenolysis (CTH) using alcohols as the alternative hydrogen resources has been recognized as a highly important lignin-first biorefinery approach for the reductive catalytic fractionation of lignocellulosic biomass.[6] For the hydrogenolytic cleavage of the ether bonds in lignin/lignin models, several catalytic systems have been constructed up to date. For example, employing isopropanol as the hydrogen resource, the ether bonds in several lignin model compounds could be cleaved over supported metals (i.e., Ru, Pd, Pt, ReOx)[7] or bimetallic Pd/Ni.[8] Meanwhile, Cu-based catalysts could catalyze CTH of lignin and its model compounds using methanol as the hydrogen resource.[10] Furthermore, the CTH process could directly cleave the ether bonds in lignin to form small-molecular compounds over αmolybdenum carbide[11] or RANEY® Ni.[12] More interestingly, the alcoholic groups in lignin could be directly used as the hydrogen resource to convert lignin and its model compounds.[13] In spite of these important achievements, robust catalysts are still highly desired for transfer hydrogenolytic cleavage of the ether bonds in lignin or its typical models.

Fabrication of efficient catalysts using naturally occurring materials is the important content of green chemistry. Montmorillonite (MMT), a type of naturally abundant clay, is a two-dimensional silicate material, which is used in many fields due to its interlayer structure and exchange ability.[14] More importantly, the acidic sites in MMT could potentially promote the hydrogenolytic cleavage of the other bonds. Therefore, MMT-supported metals could be highly promising catalysts for transfer hydrogenolytic cleavage of the ether bonds in lignin.

Consider the unique property of MMT, herein, we prepared MMT-supported Ru nanoparticles (denoted as Ru/MMT) as a dual-functional heterogeneous catalyst to cleave
the ether bonds in various lignin derivatives with cyclohexanes (fuels) and cyclohexanols (key raw materials and intermediates) as the target products via transfer hydrogenolysis. It was observed that the prepared Ru/MMT possessed excellent activity for the titled reaction without using any additional additives (homogeneous acids or bases), and various cyclohexanes and cyclohexanols could be successfully achieved.

Results and Discussion

Fabrication and characterization of Ru/MMT

The desired Ru/MMT was fabricated through a two-step process, including ion exchange of Ru\(^{2+}\) with the interlayer cations in MMT and subsequent reduction of the above Ru\(^{2+}\)-exchanged MMT in H\(_2\)/Ar at 300 °C, and the detailed route was described in the experimental section. As examined by SEM technique (Figure 1A), Ru nanoparticles were successfully supported on the MMT with an average size of 1.8 nm without any aggregation (Figure 1B). Elemental distribution mapping (Figure S1) indicated that the Ru element was dispersed uniformly in Ru/MMT. Meanwhile, Ru/MMT had similar XRD pattern with the MMT (Figure 1C), suggesting that supporting Ru particles did not change the structure of MMT, and there was no obvious peaks for Ru particles in the XRD pattern of Ru/MMT, implying the high dispersion of Ru particles without aggregation, which was consistent with the TEM result (Figure 1A). Furthermore, XPS spectra indicated most of the exchanged Ru\(^{2+}\) ions were reduced to Ru\(^{0}\) (Figure 1D). Additionally, the content of Ru element was 3.46 wt% determined by ICP-AES (VISTA-MPX).

Catalyst screening for the transfer hydrogenolytic cleavage of diphenyl ether

Diphenyl ether was initially employed as a model reactant to evaluate the catalytic performance of the prepared Ru/MMT using isopropanol as the hydrogen resource at 150 °C (Table 1). There was no reaction occurring in the absence of any catalyst (Table 1, entry 1) or using MMT as the catalyst (Table 1, entry 2). To our delight, the Ru/MMT could completely convert the diphenyl ether to form cyclohexane and cyclohexanol (Table 1, entry 3), indicating the key role of Ru\(^{0}\) to cleave the ether bond in diphenyl ether. In comparison, Ru/SiO\(_2\) and Ru/TiO\(_2\) was prepared to catalyze the transfer hydrogenolytic cleavage of diphenyl ether. Although Ru/SiO\(_2\) and Ru/TiO\(_2\) showed moderate activity for the reaction (Table 1, entries 4 and 5), the generated products (cyclohexane, benzene, cyclohexanol, and phenol) were complicated. Additionally, it was observed that diphenyl ether could be converted over commercial Ru/C (Table 1, entry 6), but the activity of Ru/C was still lower than the Ru/MMT. These results verified that the prepared Ru/MMT was a superior heterogeneous catalyst for transfer hydrogenolytic cleavage of diphenyl ether, and the reasons for the excellent performance of Ru/MMT would be discussed in the following sections. In another aspect, ethanol was examined as the hydrogen resource for the reaction. Unfortunately, the conversion of diphenyl ether was very low even at 180 °C (Table 1, entries 7 and 8) due to the much higher reduction potential of ethanol than isopropanol, which was consistent with some earlier works.\(^{11,17}\)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Conversion (%)(c)</th>
<th>Yield of products (%)(^{d,e})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>None</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>MMT</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>Ru/MMT</td>
<td>100</td>
<td>53.7</td>
</tr>
<tr>
<td>4</td>
<td>Ru/SiO(_2)</td>
<td>44.7</td>
<td>5.8</td>
</tr>
<tr>
<td>5</td>
<td>Ru/TiO(_2)</td>
<td>63.2</td>
<td>2.6</td>
</tr>
<tr>
<td>6</td>
<td>Ru/C</td>
<td>86.9</td>
<td>4.3</td>
</tr>
<tr>
<td>7</td>
<td>Ru/MMT</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>8</td>
<td>Ru/MMT</td>
<td>1.9</td>
<td>0.7</td>
</tr>
</tbody>
</table>

[a] Reaction conditions: diphenyl ether, 1 mmol; isopropanol, 5.0 g; reaction temperature, 150 °C; reaction time, 6 h; the catalyst amount, 100 mg (3.5 mol% of Ru). [b] The conversions and yields were achieved by GC using n-dodecane as the internal standard, and the yields were based on the amount of C6 ring. [c] The amount of Ru/SiO\(_2\) (4.85 wt% Ru), Ru/TiO\(_2\) (4.73 wt% Ru), and Ru/C (5 wt% Ru) were 71.73, 69 mg, respectively. [d] Ethanol (5.0 g) was used to replace isopropanol. [e] Reaction temperature was 180 °C.

Optimization of reaction conditions for transfer hydrogenolytic cleavage of diphenyl ether

Generally, reaction temperatures have significant impact on the reaction efficiency. As shown in Figure 2A, the conversion of diphenyl ether increased with the increasing of reaction temperatures from 120 to 160 °C, and the reaction could be completed at 150 °C. Meanwhile, the product distribution also changed with the change of reaction temperature. For example, at 120 °C, four main products, i.e., cyclohexane, benzene, cyclohexanol, and phenol, were obtained with the yields of 10.2, 11.4, 18.4, and 2.1%, respectively. With the increase of reaction temperatures, benzene and phenol would disappear at 140 °C. Additionally, at all the examined temperatures, cyclohexyl phenyl ether was detected as the reaction intermediate, and its amount decreased with the increasing reaction temperature. On the basis of the above results, we chose 150 °C as the optimal temperature for subsequent experiments.
Furthermore, the influence of the catalyst usage on the reaction efficiency was examined (Figure 2B). It was found that the conversion of diphenyl ether increased with the increase of catalyst amounts from 20 to 100 mg (0.7 to 3.5 mol% Ru), and diphenyl ether could be completely transformed into cyclohexane and cyclohexanol with a catalyst usage of 100 mg (3.5 mol% Ru). Meanwhile, small amounts of benzene and phenol would be detected with a low catalyst usage (20 and 40 mg), and they disappeared with the high catalyst usage (> 40 mg) because the catalytic activity of Ru/MMT was enhanced with more catalyst.

Reaction time was another important parameter to affect the product distribution. As shown in Figure 2C, the conversion of diphenyl ether steadily increased with the prolonging reaction time, and the reaction was completed in 6 h. Meanwhile, same tendency was observed for the yields of cyclohexane and cyclohexanol. Additionally, cyclohexyl phenyl ether was observed in the whole reaction process, and nearly all of it was converted with a reaction time of 6 h.

Heterogeneity and reusability of Ru/MMT

The heterogeneous nature of Ru/MMT in the catalytic process was evaluated by a control experiment, in which the Ru/MMT was removed when the reaction was carried out at 150 °C for 2 h, and then the reaction continued to be conducted for another 6 h without the existence of Ru/MMT. Obviously, no further conversion of diphenyl ether occurred (Figure 3A), and the distribution of products was also unchanged (Figure S2), implying that Ru/MMT was a heterogeneous catalyst under the reaction conditions. Meanwhile, based on the result of ICP, the concentration of Ru in the reaction mixture was extremely low (< 1.0 ppm), indicating the negligible leaching of Ru species into the reaction solutions.

In another aspect, the reusability of Ru/MMT was determined in the reaction process to convert diphenyl ether (Figure 3B). It was observed that the conversion of diphenyl ether and the distribution of products showed no significant change after Ru/MMT was reused for eight cycles. As characterized by TEM (Figure S3), the morphology of the Ru/MMT and the size distribution of Ru particles showed no obvious change after Ru/MMT was reused for eight catalytic cycles. These above results suggested the good stability of Ru/MMT under the employed reaction conditions.

Scope of the lignin-based derivatives

Encouraged by the above-achieved excellent results, Ru/MMT was attempted to catalyze the transfer hydrogenolytic cleavage of different types of ether bonds in lignin, including 4-O-5, α-O-4, and β-O-4 (Table 2). First, the compounds containing the 4-O-5 ether bond (i.e., diphenyl ether, 4,4′-dimethyl diphenyl ether, and 4,4′-dihydroxy diphenyl ether) could be efficiently converted into the corresponding cyclohexanes and cyclohexanols over Ru/MMT (Table 2, entries 1-3) although the 4-O-5 type has been considered as the most stubborn ether bond. Thereinto, a higher temperature (160 °C) was needed for the complete conversion of 4,4′-dimethyl diphenyl ether (Table 2, entry 3). Second, the β-O-4 ether bond, the most abundant linkage in lignin, could also be successfully cleaved over Ru/MMT (Table 2, entries 4-7). For example, the β-O-4 ether bond in phenethyl phenyl ether could be fully cleaved to form ethylbenzene and cyclohexanol as the main products (Table 2, entry 4). 2-Phenoxyacetophenone and α-phenethyl alcohol phenyl ether, two typical models containing β-O-4 ether bond, could also be converted to generate the corresponding chemicals, but the reaction temperature should be increased to 180 °C with a reaction time of 12 h (Table 2, entries 5 and 6). More interestingly, the compound containing the methoxy ortho-substituted β-O-4 (2-(2-methoxyphenoxy)-1-phenylethanol), which could be completely converted at 160 °C with a reaction time of 12 h, possessed higher reactivity (Table 2, entry 7) because ortho-substituted methoxy group could assist the cleavage of β-ether bond. Third, the α-O-4 ether bond (e.g., benzyl phenyl ether and 4-benzyloxyphenol) could also be cleaved over Ru/MMT at 160 °C with a reaction time of 6 h (Table 2, entries 8 and 9).
Table 2. Transfer hydrogenolytic cleavage of various ether bonds in lignin models over Ru/MMT.[4]

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Temperature (°C)</th>
<th>Conversion (%)[^b]</th>
<th>Yield of products (%)[^c]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td><img src="image1.png" alt="Substrate 1" /></td>
<td>150</td>
<td>100</td>
<td><img src="image2.png" alt="Yield 1" /></td>
</tr>
<tr>
<td>2</td>
<td><img src="image3.png" alt="Substrate 2" /></td>
<td>160</td>
<td>99</td>
<td><img src="image4.png" alt="Yield 2" /></td>
</tr>
<tr>
<td>3</td>
<td><img src="image5.png" alt="Substrate 3" /></td>
<td>150</td>
<td>97</td>
<td><img src="image6.png" alt="Yield 3" /></td>
</tr>
<tr>
<td>4</td>
<td><img src="image7.png" alt="Substrate 4" /></td>
<td>150</td>
<td>100</td>
<td><img src="image8.png" alt="Yield 4" /></td>
</tr>
<tr>
<td>5[^c]</td>
<td><img src="image9.png" alt="Substrate 5" /></td>
<td>180</td>
<td>99</td>
<td><img src="image10.png" alt="Yield 5" /></td>
</tr>
<tr>
<td>6[^c]</td>
<td><img src="image11.png" alt="Substrate 6" /></td>
<td>180</td>
<td>99</td>
<td><img src="image12.png" alt="Yield 6" /></td>
</tr>
<tr>
<td>7[^c]</td>
<td><img src="image13.png" alt="Substrate 7" /></td>
<td>160</td>
<td>99</td>
<td><img src="image14.png" alt="Yield 7" /></td>
</tr>
<tr>
<td>8</td>
<td><img src="image15.png" alt="Substrate 8" /></td>
<td>160</td>
<td>100</td>
<td><img src="image16.png" alt="Yield 8" /></td>
</tr>
<tr>
<td>9</td>
<td><img src="image17.png" alt="Substrate 9" /></td>
<td>160</td>
<td>100</td>
<td><img src="image18.png" alt="Yield 9" /></td>
</tr>
</tbody>
</table>

[^a]: Reaction conditions: substrate, 1 mmol; isopropanol, 5.0 g; Ru/MMT, 100 mg (3.5 mol% of Ru); reaction time, 6 h.  
[^b]: The conversions and yields were achieved by GC using n-dodecane as the internal standard, and the yields were based on the amount of C6 ring.  
[^c]: The reaction time was 12 h.
As well-known, lignin bio-oil contains many phenols, in which the benzene ring was generally substituted by methoxy group. Therefore, the possibility of transfer hydrogenolytic cleavage of Ar-O-CH₃ in various phenols over Ru/MMT was examined (Table 3). Initially, phenol was easily transformed into cyclohexanol with small amount of cyclohexane at 120 °C with a reaction time of 6 h (Table 3, entry 1). In contrast, phenyl methyl ether needed a much higher temperature (170 °C) to achieve a complete conversion (Table 3, entry 2) with the methoxycyclohexane yield of 16.5%, and its yield was still 11.9% even when the reaction time was prolonged to 12 h, indicating the difficulty to completely cleave this type of ether bonds (cyclohexyl-O-CH₃). Subsequently, the reactivity of various substituted phenols was detected. Both guaiacol (with one ortho-substituted methoxy group) and 4-methoxyphenol (with one para-substituted methoxy group) could be completely converted at 150 °C with a reaction time of 6 h (Table 3, entries 3 and 4). The difference for these two substrates was that the amount of the methoxy-substituted products from guaiacol (Table 3, entry 3) was much lower than that from 4-methoxyphenol (Table 3, entry 4), indicating that the ortho-substituted substrate was more reactive, which was consistent with the above finding in cleavage of the 4-O-5 and β-O-4 ether bonds. However, when there were two ortho-substituted methoxy groups (2,6-dimethoxyphenol), the reactivity would be significantly decreased owing to the steric hindrance effect (Table 3, entry 5). Even at 180 °C, too much methoxy-substituted products were obtained although the substrate was completely converted. To our surprise, eugenol could also be converted into the corresponding propyl-substituted products (Table 3, entry 6) with a reaction temperature of 180 °C.

All these above results in Tables 2 and 3 indicated the superior activity of Ru/MMT in the cleavage of various ether bonds in lignin models and the conversion of various methoxy-substituted phenols via transfer hydrogenolysis.

Table 3. Transfer hydrogenation of phenols in various lignin bio-oil over Ru/MMT.\[^a\]

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Temperature (°C)</th>
<th>Conversion (%)[^b]</th>
<th>Yield of products (%)[^b]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td>120</td>
<td>100</td>
<td>3.9 95.3</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>170</td>
<td>99</td>
<td>55.9 26.1 16.5</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>150</td>
<td>100</td>
<td>77.8 7.1 3.6 8.2 2.2</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>150</td>
<td>98</td>
<td>65.9 4.4 9.2 14.3 3.9</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td>180</td>
<td>85</td>
<td>8.9 4.1</td>
</tr>
<tr>
<td>6</td>
<td></td>
<td>180</td>
<td>93</td>
<td>70.2 6.7 5.1 9.4</td>
</tr>
</tbody>
</table>

\[^a\] Reaction conditions: substrate, 1 mmol; isopropanol, 5.0 g; Ru/MMT, 100 mg (3.5 mol% of Ru); reaction time, 6 h. \[^b\] The conversions and yields were achieved by GC using n-dodecane as the internal standard, and the yields were based on the amount of C6 ring.
Reasons for the excellent performance of Ru/MMT

As shown in Table 1, Ru/MMT possessed better performance than commercial Ru/C for the reaction involving diphenyl ether as the reactant (Table 1, entry 3 vs. 6). Moreover, it was observed that the difference in catalytic activity between Ru/MMT and Ru/C would be enhanced when more functional groups were contained in the reactants. For example, 4,4'-dihydroxy diphenyl ether could be completely converted over Ru/MMT at 150 °C with a reaction time of 6 h (Table S1, entry 1), while the conversion was only 46.8% over Ru/C even at 180 °C with a reaction time of 24 h (Table S1, entry 2). More importantly, the ether bond in phenethyl phenyl ether could be fully cleaved over Ru/MMT at 150 °C (Table S1, entry 3), while almost no reaction was detected over Ru/C even at 180 °C (Table S1, entry 4). These results strongly indicated that Ru/MMT was a highly superior catalyst for the transfer hydrogenolytic cleavage of the ether bonds in comparison with Ru/C.

Two reasons possibly resulted in the much better performance of Ru/MMT than Ru/C. First, the property of Ru particles played a key role for the reaction. As determined by XPS (Figure 4), the binding energy of Ru 3p of Ru in Ru/MMT (484.5 eV and 462.3 eV) was lower than that in Ru/C (485.6 eV and 463.4 eV), suggesting the generation of electron-enriched Ru in Ru/MMT.[18] Electron-enriched Ru was beneficial for the formation of active H (from isopropanol) for the transfer hydrogenolysis. Second, the acidic sites could interact with the O of the ether bonds (Scheme S1),[19] benefiting their cleavage. Therefore, the acidity of Ru/MMT and Ru/C was determined by NH3-TPD method. The results clearly suggested that the acidity of Ru/MMT (0.25 mmol/g) was much higher than Ru/C (0.05 mmol/g), and thus there were more acidic sites in Ru/MMT to interact with the ether bonds, which resulted in the excellent performance of Ru/MMT. On the basis of the above discussions, the synergistic effect between the electron-enriched Ru and the stronger acidity significantly contributed to the excellent performance of Ru/MMT for the transfer hydrogenolytic cleavage of the ether bonds.

![Figure 4. XPS spectra of Ru 3p in Ru/MMT (A) and Ru/C (B).](image-url)

Discussions on reaction pathway

It is a highly important aspect to explore the reaction pathway for the cleavage of different types of ether bonds.

First, diphenyl ether was selected as the model compound to study the pathway to cleave the 4-O-5 ether bond. As described in Figure 2C, the yield of cyclohexyl phenyl ether was increased first and then decreased with the prolonging reaction time, and no dicyclohexyl ether was generated in the whole reaction process, implying cyclohexyl phenyl ether was the reaction intermediate. The C-O bond in the cyclohexyl phenyl ether would be cleaved to generate cyclohexane and phenol (not detected because of its rapid-conversion rate at 150 °C owing to the lower bonding energy of the C(sp3)-O bond compared to the C(sp2)-O bond[7c-20] in another aspect, benzene would be detected at lower reaction temperature (Figure 2A), indicating the occurrence of the direct cleavage of the C-O bond in diphenyl ether. More importantly, the yield of benzene was higher than that of cyclohexane, while almost no benzene could be generated through the former pathways. Therefore, the cleavage of the 4-O-5 ether bond proceeded through two reaction pathways (Scheme 1A), and we deduced that the later pathway was major. In addition, the final yield of cyclohexane was slightly higher than that of cyclohexanol because cyclohexanol could be further converted into cyclohexane under the reaction conditions.

Second, phenethyl phenyl ether was employed to investigate the reaction pathway of the cleavage of β-O-4 ether bonds. In the reaction process, there were no 2-phenylethanol and 2-cyclohexylethanol yielded, and [2-(cyclohexyloxy)ethyl]benzene and (2-cyclohexylethoxy)benzene can be detected. Meanwhile, the yield of cyclohexane, which should be generated from cyclohexanol conversion, was very low. At a lower reaction temperature, the yield of ethylbenzene was much higher than that of ethylcyclohexane (Table S2). From these results, we could deduce that the cleavage of the β-O-4 ether bond in phenethyl phenyl ether occurred through the direct cleavage of phenethyl phenyl ether or the formation of [2-(cyclohexyloxy)ethyl]benzene and (2-cyclohexylethoxy)benzene as the reaction intermediates (Scheme 1B).

Third, the reaction pathway to cleave the α-O-4 ether bonds was studied using benzyl phenyl ether as the model reactant. In the reaction process, four main products, i.e., cyclohexanol, cyclohexane, toluene, and methylcyclohexane, were achieved. Meanwhile, [(cyclohexyloxy)methyl]benzene and (cyclohexylmethoxy)benzene were detected, and their yields increased first and then decreased until disappeared. Moreover, the amount of cyclohexane was much lower than cyclohexanol because cyclohexane was generated from the conversion of cyclohexanol rather than the cleavage of the α-O-4 ether bond. Additionally, small amount of benzyl alcohol and cyclohexanemethanol could be generated. From these results, we could deduce that the cleavage of the α-O-4 ether bond in benzyl phenyl ether mainly occurred through the direct cleavage of phenethyl phenyl ether or the formation of [(cyclohexyloxy)methyl]benzene and (cyclohexylmethoxy)benzene as the reaction intermediates (Scheme 1C). In addition, small amount of side pathways also occurred via the formation of benzyl alcohol and cyclohexanemethanol (Scheme S2).

From above discussions, it was obvious that the direct cleavage of the ether bonds and the formation of intermediates with one hydrogenated benzene ring was the dominant pathway for the three types of ether bonds contained in the examined three model compounds. However, the reaction pathway would be highly different when more functional groups (e.g., methoxy and phenolic hydroxyl) were involved. Therefore, more work should be done for substrates with more complex structures.
Conclusion

In conclusion, Ru/MMT was successfully fabricated via simple ion exchange of Ru$^3+$ with the interlayer cations of MMT and subsequent reduction of the exchanged Ru$^3+$. The prepared Ru/MMT could efficiently cleave various lignin derivatives containing different types of ether bonds (i.e., 4-O-5, α-O-4, β-O-4, and Ar-O-Me) by transfer hydrogenolysis using isopropanol as the hydrogen resource, and various corresponding cyclohexanes and cyclohexanols could be achieved. Detailed investigations indicated that the excellent performance of Ru/MMT was resulted from the cooperation of electron-enriched Ru and the acidic sites on MMT. Systematic studies revealed that two possible reaction pathways, including the direct cleavage of ether bonds and the formation of intermediates with one hydrogenated benzene ring, occurred for all the examined types of ether bonds, i.e., 4-O-5, α-O-4, and β-O-4. We believe that transfer hydrogenolytic reaction is an efficient strategy to cleave the ether bonds in lignin derivatives, and Ru/MMT has great potential applications in this important transformation for lignin valorization.

Experimental Section

Fabrication of Ru/MMT

To prepare Ru/MMT, Ru$^3+$-exchanged MMT should firstly be prepared. In a typical route, MMT (20.0 g) was dispersed in water (800 mL). Subsequently, aqueous solution of RuCl$_3$ (50 mL containing ca. 1.8 g RuCl$_3$) was added into the above dispersion of MMT. The mixture was stirred for about 48 h at room temperature. Finally, Ru$^3+$-exchanged MMT was achieved through filtration and freeze drying. Ru/MMT could be successfully obtained by the reduction of Ru$^3+$-exchanged MMT using H$_2$/Ar mixture (The volume ratio of H$_2$/Ar was 5/100.) at 300 °C for 5 h.

Transfer hydrogenolytic cleavage reactions

In a typical experiment, substrate (1 mmol), desired amount of catalyst, and isopropanol (5.0 g) were charged into a stainless reactor of 22 mL with a magnetic stirrer. After being sealed, the reaction mixture was stirred at a desired temperature for the desired time. After the reaction, the products were analyzed quantitatively using n-dodecane as the internal standard by gas chromatography (GC, Agilent 7890 equipped with an FID detector). The yields were obtained on the basis of the amount of C6 ring in the used substrates.

Reusability of the Ru/MMT
To examine the reusability of Ru/MMT, Ru/MMT was recovered by centrifugation after each cycle, and washed with ethanol (4×5 mL). After drying under vacuum at 50 °C overnight, the catalyst was reused for the next catalytic cycle.

Acknowledgements (optional)

The authors thank the National Natural Science Foundation of China (21873012, 21773307) for financial support.

Keywords: Biomass conversion • transfer hydrogenolysis • cleavage of ether bonds • lignin derivatives • synergistic effect


Montmorillonite (MMT) supported Ru particles (denoted as Ru/MMT) was fabricated as a dual-functional heterogeneous catalyst to cleave various types of ether bonds via transfer hydrogenolysis. Without employing any additional acids or bases, various types of ether bonds in lignin derivatives could be efficiently cleaved over Ru/MMT. The synergistic effect between electron-enriched Ru and the acidic sites on MMT contributed to the excellent performance of Ru/MMT.