Journal Name RSCPublishing

ARTICLE

Selective Hydrogenolysis of Phenols and Phenyl Ethers to Arenes though Direct C-O Cleavage over Ruthenium-Tungsten Bifunctional Catalysts

Cite this: DOI: 10.1039/x0xx00000x

Yao-Bing Huang,[a,b] Long Yan,[a] Meng-Yuan Chen,[a] Qing-Xiang Guo,[a] Yao Fu[a,]*

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

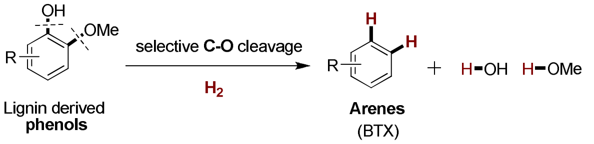
www.rsc.org/

Direct hydrogenolysis of the aromatic C_{sp2}-O bonds in both phenols and phenyl ethers to form arene selectively is a core enabling technology that can expand greatly the scope of chemical manufacture from biomass. However, conventional hydrogenolysis of phenols typically led to aromatic ring saturation instead of the cleavage of the C_{sp2}-O bonds. Herein, we report a recyclable Ru-WO_x bifunctional catalyst that showed high catalytic activities for the hydrogenolysis of a wide scope of phenols and phenyl ethers, including dimeric lignin model compounds and the primitive phenols separated from pyrolysis lignin, to form arenes selectively in water. Preliminary mechanistic studies supported that the reactions occurred via a direct cleavage of the C_{sp2}-O bonds and the concerted effects of the hydrogenating Ru sites and the Lewis acidic W sites is the key to such unusual reactivity.

1 Introduction

Lignin, a three-dimensional amorphous network of cross-linked phenylpropane units connected by C-O and C-C bonds, has been considered as a renewable bioresource for the sustainable production of aromatic chemicals from nature.[1] To achieve this goal, much effort have been devoted to the development of new strategies to the depolymerization of lignin and further upgrade of them into fuels or chemicals.[2] Selective C-O bond cleavage and deoxygenation are the key topics of these conversions. However, due to the high bond dissociation energies of C-O bonds in aryl ethers (aryl-O-alkyl, aryl-O-aryl) and phenols (Ar-OH, Ar-OMe),[3] both of the two steps required harsh reaction conditions and suffered from poor product selectivities. Recently, several promising catalyts were developed for the cleavage of C-O bonds in dimeric lignin model compounds (with β-O-4, α-O-4 and 4-O-5 ether linkages) based on Ni,[4] Fe,[5] Ru,[6] Pd,[7] Ir,[8] V,[9] and others,[10] which constituted the important progresses toward the goal of lignin depolymerization. At the same time, the depolymerized phenols were further upgraded into fuels or chemicals such as alkanes and cyclohexanols.[11] However, most of the upgrading procedures are the reductive systems and always led to the aromatic ring hydrogenation products which greatly limited the application area of phenols. Therefore, selective cleaving C-O bonds in phenols while preserving their aromatic rings remains a main challenge for the valorization of lignin, especially for the production of arenes such as BTX (benzenes, toluenes and xylenes) (eq 1).

To address the above problems, several groups reported different catalysts based on Mo or W for the direct hydrogenolysis of phenols but required harsh conditions.[12] Recently, Rinaldi et al. reported an impressing work on the dehydroxylation of phenols into arenes through hydrogenation-dehydration-dehydrogenation processes over Raney Ni and zeolites catalysts which brought a new route for the production of arenes from phenols.[13] Despite of these advances, efficient systems for the selective hydrogenolysis of C_{Ar}-O bonds in phenols are still desirable.



(1)

To selectively cleave the C_{Ar}-O bonds on aromatic ring, a chelated agent was always necessary to chelate with O atom and weaken the C_{Ar}-O bond which would then be easier to be cleaved under reductive conditions, as reported in many organic synthesis.[14] Thus, a bifunctional catalyst with both hydrogenating and oxophilic sites would be ideal candidate for the hydrogenolysis reactions. Examples of such kind of catalysts were the Rh-ReO_x/SiO_2 and Pd/C+$Hf(OTf)_4$ that showed remarkable performances in the cleavage of C-O bonds in alkyl ethers.[15] High-valence metals with strong Lewis acidity would be good choices as the source of oxophilic sites. Among the candidates, tungsten based catalysts were reported as a Lewis acidic metal and exhibited good activities toward the hydrogenolysis reactions.[16] Herein, we reported a highly efficient heterogeneous catalyst based on ruthenium-tungsten for the selective hydrogenolysis of C_{Ar}-O bonds in phenols under hydrogen atmosphere in aqueous media. The catalysts were characterized and used in the hydrogenolysis of the phenols and dimeric lignin model compounds. Lastly, the catalyst was applied to the hydrogenolysis of phenolic mixture extracted from bio-oil, yielding a mixture of arenes.

2 Experimental

2.1 General

Phenols and Ruthenium (III) chloride (TCI) were purchased from TCI. Benzyl bromide, (2-Bromoethyl)benzene, Di-p-tolyl ether and Ammonium tungstate oxide hydrate were supplied by Alfa Aesar. SiO_2-Al_2O_3 (SiO_2 72.0 wt%, Al_2O_3 25.2 wt%, mainly amorphous) and other supports were supplied by Saint-Gobain NorPro Company. The other reagents or solvents were purchased from Sinopharm Chemical Reagent Co., Ltd.

2.2 Preparation of phenyl ethers and primitive lignin-derived phenols.

The phenyl ethers with β-O-4 and α-O-4 linkage were prepared according to the previous reported methods.[4a] A dry flask equipped with a reflux condenser, argon inlet and magnetic stir bar, was charged with the anhydrous potassium carbonate (20 mmol), then air was excluded with argon. Phenol (10 mmol), acetone (30 ml) and a benzyl bromide (10 mmol) were added and the reaction mixture was refluxed for 3 h. After cooled down, the solids were filtered. The filtrate was evaporated and dissolved in methylene chloride (50 ml). 5% KOH aqueous solution (25ml) and brine (50 ml) were used to wash the organic phase, and the organic layer was dried over anhydrous Na_2SO_4. The solution was evaporated and the crude product was purified by flash column chromatography. For β-O-4, change benzyl bromide to the corresponding (2-Bromoethyl)benzene, the preparation method was the same as the α-O-4 model compound. The 4-O-5 dimer was purchased from the chemical companies.

The bio-oil was obtained from our laboratory by flash pyrolysis of rice husk at about 550-600 °C.[17] The primitive lignin-derived phenols separated from bio-oil were obtained by a modified glycerol-assisted distillation technology: 10 g of glycerin was added to 100 g of bio-oil, and the mixture was distilled. The first distillate (about 60 g) was collected under 120 °C. The second distillate, mainly consisting of phenol, was collected at 120 °C under vacuum condition (0.1 atm), and about 10 g was obtained. The mixture was then washed by $KHCO_3$ aq. for times. The organic layer was then extracted by hexane for at least 5 times. The organic pahse was collected and dried over anhydrous Na_2SO_4. After that, the phenols used in the hydrogenolysis reaction were obtained as a light yellow liquid.

2.3 Preparation of the catalysts

Preparation of 5Ru-30W/SiAl catalyst: 2 g of SiAl (Aladdin) was firstly impregnated with the solution containing 0.416 g of Ruthenium (III) chloride and 1.224 g of Ammonium metatungstate (AMT), then the mixture was vigorously stirred for 12 h, dried at 493 K for 12 h. The resulted gray powder was then reduced in a H_2 flow: from RT to 723 K at 10 K/min, and then to 1073 K at 1 K/min and holding at that temperature for 1 h. Prior to exposure to air, the catalysts were passivated in a flow of 2 % O_2/N_2 for 0.5 h at room temperature. The black sample is denoted as 5%Ru-30%WO_x/SiAl. The Ru/SiAl, WO_x/SiAl, and other catalysts were prepared in the same procedures with Ru-WO_x/SiAl.

2.4 Characterization of the catalysts

Micromeritics ASAP 2020 analyzer (Tristar II 3020M) was used to measure nitrogen adsorption/desorption isotherms. The catalyst surface area was determined through the Barrett-Emmet-Taller (BET) method. X-ray power diffraction (XRD) patterns of the catalysts were measured on an X'pert (PAN alytical) diffractometer at 40 kV and 40 mA. Transmission electron microscopy (TEM) microphotographs were acquired on a JEOL-2010 electron microscope. Scanning electron microscopy (SEM) microphotographs were performed using a SIRION 200 electron microscope. Scanning transmission electron microscopy (STEM) microphotographs and element mapping were performed on a JEM-2100F electron microscope. A Thermo Scientific Escalab 250-X-ray photoelectron spectrometer was used for X-ray photoelectron spectra (XPS) analysis.

2.5 Catalytic performances

Phenol 1.0 mmol, catalyst Ru-WO_x/SiAl 120 mg were placed in a 25 ml Parr reactor equipped with a magnetic stirrer, 12 ml H_2O solvent were added to the reactor. After purging the reactor with hydrogen several times to remove the air, the reactor was charged with the desired H_2 pressure and heated to the reaction temperature. The mixture was vigorously stirred for several hours and quickly cooled to room temperature. The mixture was added the internal standard, exampled and analyzed by gas chromatograph equipped with a TR-65MS or a TR-5MS capillary column to determine the product yield.

3 Results and discussion

3.1 Characterization of the catalysts

Figure 1a shows the XRD analysis of the Ru-WO_x/SiAl catalyst. The weak diffraction peaks present in 40.3 and 43.4 can be assigned to the W(110) and Ru(101) planes, respectively. The present of the broad peak around 20-30 indicates that the structure of the SiAl support were changed by the incorporation of metals, which was confirmed by the XRD analysis of Ru/SiAl and WO_x/SiAl catalysts (Figure S3). The weak diffraction of the peak intensity suggests that the two metal particles were well dispersed on the supports.

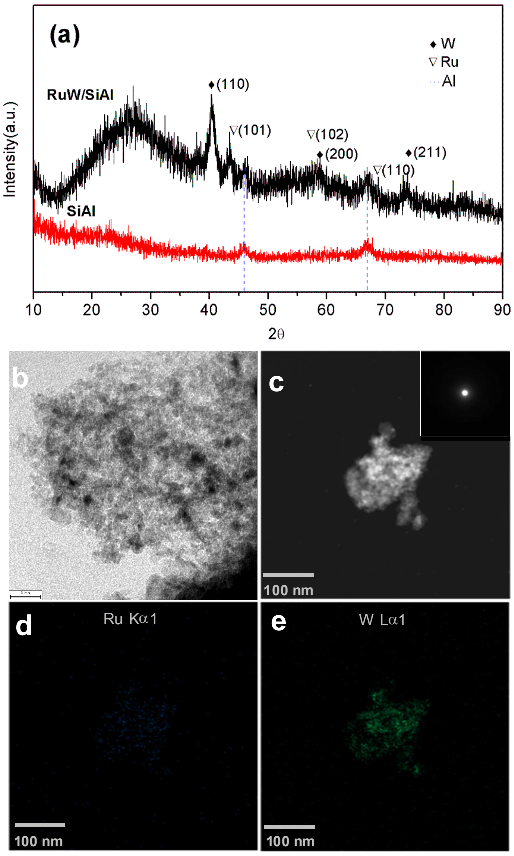


Figure 1. (a) XRD spectra of Ru-WO$_x$/SiAl and SiAl. (b) TEM image. (c) STEM image. Elemental mappings of (d) Ru and (e) W of the Ru-WO$_x$/SiAl catalyst. Inset in (c) was the fast Fourier transformation of the image.

This characteristic was further confirmed by the STEM spectra and the corresponding elemental mapping analysis of the Ru and W particles (Figure 1b-1e). X-ray photoelectron spectroscopy (XPS) was employed to investigate the oxidative states of the metal particles (Figure 2). The Ru particles of the catalyst presented a doublet corresponding Ru 3d$_{5/2}$ and 3d$_{3/2}$. The Ru 3d$_{5/2}$ peak at 280.8 eV is attributed toRu^0, higher than the reported metallic Ru (280.0), which may be attributed to the strong interaction of Ru particles with the other oxides that made the Ru surface electron-deficient and increased the binding energy.[18] Another Ru 3d$_{5/2}$ peak at 282.4 eV is related to the RuO$_2$. The Ru^0 formed as the major phase and took about 71% of total Ru particles.

Furthermore, the W XPS analysis revealed that W particles existed mainly in the oxidation states. The W 4f$_{7/2}$ binding energies of 36.0, 34.6, 32.8 and 31.7 were attributed to the W^{6+}, W^{5+}, W^{4+} and W^0, respectively. Combined with the previous XRD analysis, we speculated that some of the W metal has been doped into the supports, forming the composite oxides that are reluctant to be reduced even at higher reduction temperature. BET analysis of the catalyst revealed that the introduction of metal particles reduced the BET surface area from 429.5 m^{2}g^{-1} to 202.5 m^{2}g^{-1}, and enlarged the pore sizes (table S1, figure S1-2).

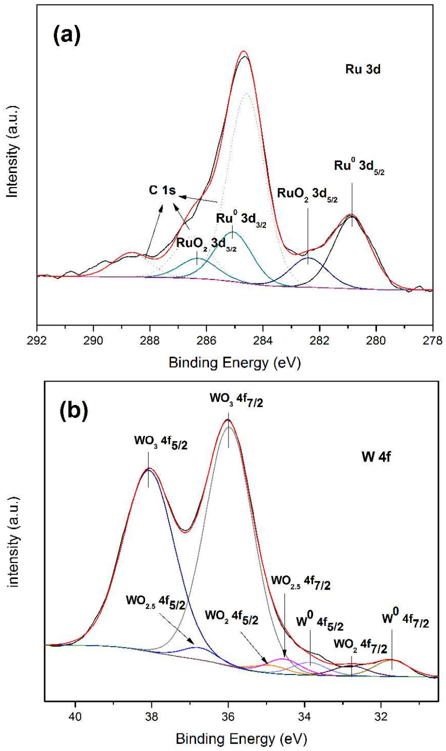
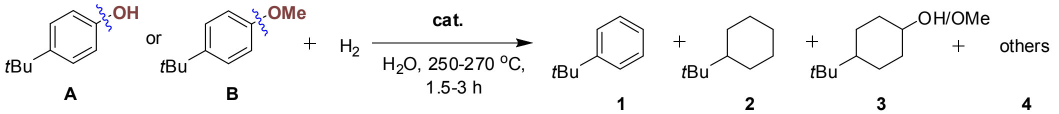


Figure 2. (a) XPS spectra of the Ru in Ru-W/SiAl catalyst. (b) XPS spectra of the W in Ru-WO$_x$/SiAl catalyst.

3.2 Hydrogenolysis of the model phenols

The activities of Ru-WO$_x$/SiAl for the hydrogenolysis of C$_{Ar}$-OH and C$_{Ar}$-OMe bonds in phenols were investigated. For this purpose, *p-tert*-butylphenol (**A**) and *4-tert*-butylanisole (**B**) were chosen as the model compounds. GC-MS analysis of the reaction mixture revealed that the products were *tert*-butylbenzene (**1**), *tert*-cyclohexane (**2**), ring hydrogenation products (*p-tert*-butyl cycloheanol/*1-tert*-butyl-4-methoxycyclohexane (**3**)) and the others (isomerized alkanes or small unknow products (**4**)) (table 1). Among the selected supports, the catalysts with SiAl support (5Ru-30WO$_x$/SiAl) showed superior activity in the hydrogenolysis reaction and reached higher selectivity (81%) of the arene product **1** at full conversion of **A** under 270 °C, 2.0 Mpa H$_2$ for 2 h (table 1, entries 1-3). The ring hydrogenation product **2** was the main by products (10%) and about 8% of the carbon was lost during the reaction. Several catalysts with different ratios of Ru/W were also prepared and evaluated for the hydrogenolysis reaction (Table 1, entries 4-6). When the W loading was gradually reduced, both the reaction conversion and the arene selectivity decreased while the undesired alkane selectivity increased, which may be caused by the lack of Lewis acidic sites necessary for the direct hydrogenolysis of the C$_{sp2}$-O bond. In addition, when the Ru loading was reduced, the selectivities of the products remained unchanged, albeit with a lower conversion (88%). The above results indicated that both of the two metal sites were necessary for the efficient hydrogenolysis of the C-O bonds, achieving higher products yields.

Table 1. Optimization of the reaction conditions for the hydrogenolysis of phenols or ethers.



entry	Substrate	Catalyst	H_2 (Mpa)	T (°C)	Time (h)	Con.(%)[a]	Selectivity[a]			
							1	**2**	**3**	**4**[d]
1	**A**	5Ru-30WO_x/ZrO_2	2.0	270	2	27	65	20	2	13
2	**A**	5Ru-30WO_x/ TiO_2	2.0	270	2	40	60	25	1	14
3	**A**	5Ru-30WO_x/SiAl	2.0	270	2	100	81	10	1	8
4	**A**	5Ru-15WO_x/SiAl	2.0	270	2	95	72	15	3	10
5	**A**	5Ru-5WO_x/SiAl	2.0	270	2	78	63	22	4	11
6	**A**	2.5Ru-30WO_x/SiAl	2.0	270	2	88	82	10	1	7
7[b]	**A**	5Ru-30WO_x/SiAl	2.0	270	2	70	77	13	1	9
8	**A**	5Ru/SiAl	2.0	270	2	72	10	62	8	16
9	**A**	30WO_x/SiAl	2.0	270	2	1	-	-	-	-
10[c]	**A**	5Ru/SiAl+30WO_x/SiAl	2.0	270	2	61	21	66	6	5
11	**A**	5Ru-30WO_x/SiO_2	2.0	270	2	34	80	10	1	9
12	**A**	5Ru-30WO_x/Al_2O_3	2.0	270	2	65	79	9	1	11
13	**B**	5Ru-30WO_x/SiAl	2.0	270	2	89	89	5	-	6
14	**B**	5Ru-30WO_x/SiAl	2.2/1.8/1.6	270	2	99/78/60	86/92/93	7/3/2	-/-/-	7/5/5

Conditions: substrate 1.0 mmol, catalyst 120 mg, H_2O 12ml. [a] Determined by GC and GC-MS analysis. [b] The catalyst was recovered by the filtration from the reaction mixture and washed by H_2O for at least 3 times. [c] The two catalysts were all 120 mg. [d] Other products included isomerization alkanes and unknown small molecules.

After the reaction, the catalysts can be recycled and maintained a good selectivity, but the reaction conversion decreased to 70% (table 1, entry 7). It was probably caused by the loss of catalyst during the recycle procedure. Besides, the leaching of the W particles was also noticed since the reaction solution became blue after the reaction, which was in accordance with the previous work.[16b] Thus, future work will be focused on the design of more robust catalyst to solve this problem.

To figure out the catalytic role of Ru, W metals and the in the hydrogenolysis reaction, Ru/SiAl and W/SiAl were prepared and tested in the model reaction (table 1, entries 10-11). When Ru/SiAl was used, the selectivity of **1** was only 10%. A lot of over hydrogenated products **2** and **3** were detected with high selectivities (52% and 13%). This was in accordance with the previous work that Ru-only catalysts showed good activity in the hydrodeoxygenation (HDO) reactions, especially in the upgrade of phenolic compounds to alkanes.[11] No reaction was observed when W/SiAl was used which may be caused by the weak hydrogenating ability of W particles. Mechanically mixing the two catalysts for the hydrogenolysis reaction led to a mixture of the ring hydrogenation products, similar selectivity to the Ru/SiAl catalyzed reaction (table 1, entry 12). This result suggested that intimate contact between the Ru and W components created in the co-impregnation was necessary to impose adjacent hydrogenating and Lewis acidic bifunctional sites where the O atoms could be chelated and easily cleaved by the adjacent hydrogenating sites.

To explore the role of the supports in the hydrogenolysis, SiO_2 and Al_2O_3 supported catalysts were prepared and tested. Compared to the SiAl supported catalyst, both of the catalysts gave the similar product selectivitis, howerer, SiO_2 supported catalysts gave much lower conversion (34%) while Al_2O_3 supported catalysts gave moderate conversion (65%). Previous work on the adsorption of phenols on the oxides revealed that phenols could easily adsorbed on the surface of Al_2O_3 by chemisorption model, forming the corresponding phenates Al···OPh species, while phenols interacted with SiO_2 via H-bonding.[19] From these results, we speculated that Al_2O_3 was more helpful than SiO_2 in the absorption or coordination of the oxygen-containing groups which stabilized the molecule on the catalyst and help the activation of the C-O bond when Ru-WO_x particles catalyzed the hydrogenolysis reaction. However, due to the instability of Al_2O_3 in hydrothermal condition, serious structure collapse of the Al_2O_3 supported catalyst was observed after the reaction. Instead, the addition of silica to alumina supports appeared as a good alternative, providing a more hydrothermal stable catalyst, which may be the main reason for the excellent performances of the Ru-W/SiAl catalyst in the current system.

After successfully cleaving the C_{Ar}-OH bond, we applied the optimized condition for the hydrogenolysis of the C_{Ar}-OMe bond in 4-tert-butylanisole **B**. The selectivity of **1** was 89%, **2** was 5% and few isomerized alkanes, at 89% conversion of **B** (table 1, entry 13). With higher H_2 pressure (2.2 Mpa), **B** was fully converted but with a slight decrease in the selectivity of **1** (86%). Noteworthy, lower H_2 pressure (1.8 and 1.6 Mpa) led to a decrease in the reaction conversion but achieved higher selectivities of **1** (92% and 93%, respectively) which made this catalytic system more practical when being designed into continuous systems in the industrial application (table 1, entry 14).

3.3 Effect of the reaction temperature

To evaluate the influence of reaction temperature on the hydrogenolysis reaction, the model reaction was carried out at different reaction temperature. Figure 3 shows the catalytic performances of the Ru-WO_x catalysts at different reaction temperatures. When the reaction was carried out at lower temperature (260 °C and 250 °C), the conversion of **A** decreased sharply (85% and 51%), however, the selectivities of the products were almost unchanged. The reaction achieved a maximum arene yield of 81% at 270 °C. Further increasing the reaction temperature to 280 °C led to a slight decrease of the arene selectivity, and more side products (small molecules or gases) cannot be identified. The above results revealed that proper reaction temperature could accelerate the hydrogenolysis reaction by increasing the reaction rate and minimize the over reduction of the generated arenes and the carbon loss.

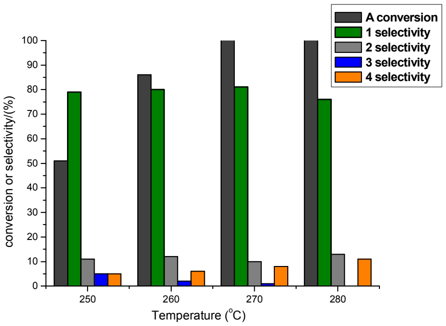


Figure 3 Effect of the reaction temperature. Reaction condition: ^{t}Bu-PhOH 1.0mmol, Ru-WO_x/SiAl 120 mg, H_2 2.0 Mpa, H_2O 12 ml, 2h.

3.4 Effect of the reaction pressure

Apart from the reaction temperature, the H_2 pressure was another key parameter for the hydrogenolysis of phenols. Figure 4 shows the product distribution of the reaction under different H_2 pressures. When at lower H_2 pressures (1.6 Mpa), the conversion of A was 73%, but the arene product 1 reached a highest selectivity of 88% while that of alkane product 2 was only 6%. Further increasing the H_2 pressures to 1.8-2.2 Mpa resulted in an increase of reaction conversion. The selectivity of 1 gradually decreased while 2 increased. The generated arenes was easily hydrogenated into the alkanes in the presence of metal site. The reaction reached a maximum yield of 1 under 2.0 Mpa H_2 pressures with a full conversion of **A**.

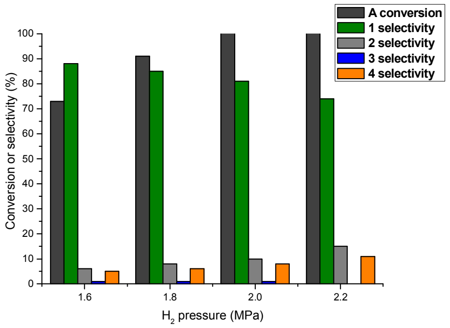


Figure 4 Effect of the H_2 pressure. Reaction condition: ^{t}Bu-PhOH 1.0mmol, Ru-WO_x/SiAl 120 mg, H_2O 12 ml, 270°C, 2h.

3.5 Reaction mechanism

To gain preliminary insights into the reaction mechanism, the model reaction with **A** as the substrate was conducted at optimized condition and tracked by GC and GC-MS (figure 5 and figure S5). According to the results, **A** was gradually converted into the arene product **1** with the time. The ring hydrogenation product **2** generated when the reaction started but in a negligible level, however, it gradually increased as the reaction proceeded. When the reaction finished, the arene product reached the highest yield, however, it would then decreased when the reaction time was extended while the cycloalkane product **2** increased. This may be attributed to the further ring hydrogenation of the arene product, yielding cycloalkane. In addition, previous work showed that phenol could be dehydrated into arene through the cyclohexanol intermediate[13], the direct hydrogenolysis of *p*-*tert*-butyl cyclohexanol was also conducted, yielding the major cycloalkane product **2** and trace amout of the arene product **1** which excluded the hydrogenation-dehydration-dehydrogenation mechanism (scheme S2). Thus, a possible mechanism was proposed, that was: phenols were firstly absorbed on the surface of the catalyst and then the O atoms were chelated with the oxophilic sites (Lewis sites from W and the supports), the C-O bonds were then activated. After that, the cleavage of C-O bonds took place assisted by the hydrogenating sites on Ru particles. Although the direct evidence about was not gained, the current results may play a guide role in the design of effective catalysts for the hydrogenolysis of C-O bonds in phenols in the near future.

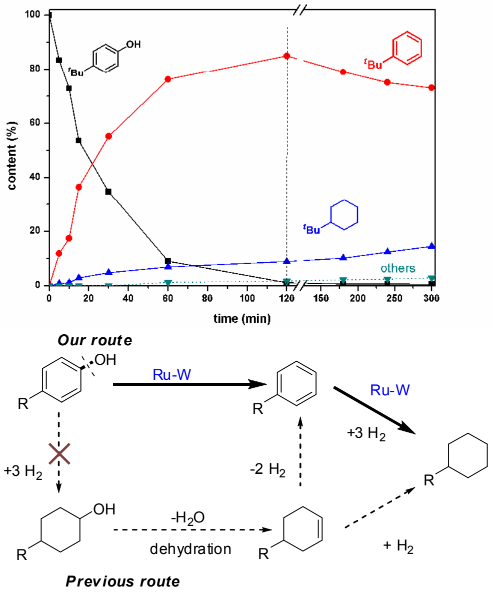
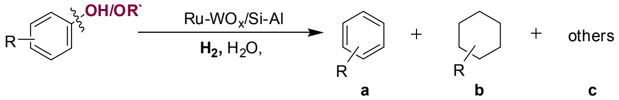
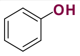
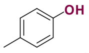
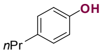
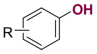
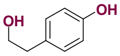
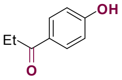
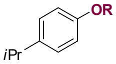
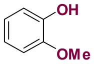
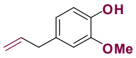
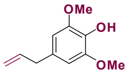


Figure 5. (a) Product distributions as functions of time. Conditions: ^{t}Bu-PhOH 1.0mmol, Ru-WO_x/SiAl 120 mg, H_2 2.0 Mpa, H_2O 12 ml, 270 °C. (b) Possible reaction mechanism.

Table 2. Hydrogenolysis of different phenols.



Substrate		Conditions T(°C)/P(MPa)/t(h)	Conv.^{a} (%)	Yield (%)^a		
				a	b	c
1		220/1.0/1.5	100	77	10	13
2		220/1.0/1.5	100	83	7	10
3		270/1.8/2.0	100	82	6	12
4	 R=*p*-*i*Pr	270/1.8/2.0	100	83	8	9
5	R=*m*- *i*Pr		100	81	10	9
6	R=*o*-*i*Pr		90	70	14	6
7		220/1.0/1.5	95	85	7	8
8		270/1.8/2.0	100	87	4	9
9	 R=-Me	270/2.2/3.0	100	90	6	6
10	R=-Et		97	82	5	8
11	R=-*n*Bu		84	70	5	9
12		250/1.6/1.5	100	79	9	12
13		270/2.2/3.0	100	85	5	10
14		270/2.2/4.0	86	68	7	11

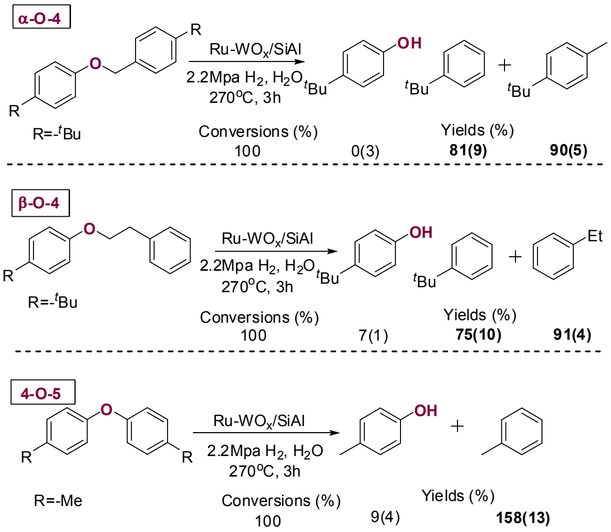
Reaction condition: phenol 1.0 mmol, Ru-WO$_x$/SiAl 120 mg, H_2O 12 mL. ^{a} Deterimed by GC and GC-MS analysis. All the oxygen-containing groups or alkenyl group were converted to the corresponding hydrocarbons. Others were mainly the loss of the carbon and trace isomerization products.

3.6 Hydrogenolysis of other phenols

To explore the scope of the application of the Ru-WO$_x$/SiAl catalyst, we further investigated the hydrogenolysis of other phenols with different substitution that are commonly used or present in the phenolic mixture depolymerized from lignin, as listed in table 2. The reaction conditions were slightly changed depending on the reactivity nature of different phenols. For phenol, p-methylphenol and 4-(2-hydroxyethyl)phenol, the reaction proceeded at a relatively milder condition and achieved good yields of arenes (table 2, entries 1, 2, 7). The alkyl C-O bond in the substrate of entry 7 was also cleaved in the reaction and the corresponding alkyl benzene was obtained. The influence of the substitution on different position of the aromatic ring was also examined (table 2, entries 4-6). The phenols with isopropyl group on the para- and meta-positions showed comparable reactivity toward the hydrogenolysis reaction, resulting in similar yields of arene. However, the ortho-substituted 2-isopropylphenol gave an inferior yield, implying that steric hindrance increase the difficulty for the hydrogenolysis reaction. When phenols with an acyl group, it was also converted to the corresponding alkyl group due to its high reactivity compared to C_{Ar}-O bonds (table 2, entry 8). Besides, the Ru-WO$_x$/SiAl catalyst showed high activities towards the hydrogenolysis of aromatic ethers such as Ar-OMe, Ar-OEt and Ar-O^{n}Bu (table 2, entries 9-11). The reaction conversion and the arene yield decreased with the growth of the carbon atoms in the alkyl chain. At last, three representative phenols derived from lignin with both -hydroxyl and -methoxy group were also investigated. For guaiacol, the reaction was donducted at 250 °C, 1.6 Mpa H_2 for 1.5 h, the benzene yield was 79% with 9% of cyclohexane. For 4-allyl-2-methoxyphenol and 4-allyl-2, 6-dimethoxyphenol, higher H_2 pressure and longer reaction time were required to make the maximum conversion of the phenols and achieved the highest yield of arene products.

3.7 Hydrogenolysis of dimeric phenyl ethers

Then, we investigated the hydrogenolysis of dimeric lignin model compounds with α-O-4, β-O-4 and 4-O-5 ether linkages, which had attracted considerable attentions over the past few years. In contrast to the previous work that the cleavage of these linkages yielded the corresponding arenes and phenols[4-10], the main products in our systems were mainly arenes, the generated phenols were further converted into arenes by the hydrogenolysis of the -hydroxyl group. The reaction were conducted at 270°C, 2.2 Mpa H_2 for 3 h, and achieved a moderate to good yields of the corresponding arenes (~80%) at full conversions of the dimeric model compounds (scheme 1).



Scheme 1. Hydrogenolysis of dimeric lignin model compounds. Conditions: substrate 1.0 mmol, Ru-WO$_x$/SiAl 120mg, 2.2 Mpa H_2, 12 ml H_2O, 270 °C, 3 h. Deterimined by GC analysis. The number in parentheses were the ring hydrogenation products

3.8 Hydrogenolysis of primitive phenols from bio-oil

Lastly, we applied the methodology to the conversion of the real primitive phenols separated from bio-oil. The bio-oil was prepared by flash pyrolysis of rich husk and then distilled by the glycerol-assisted distillation technology as reported in our laboratory[17]. The distillate was then washed with $KHCO_3$, extracted with *n*-hexane and concertrated. The resulted mixture was analyzed by GC-MS and GC. Phenols took about 72 wt % of the result mixture, while the other 28 wt% of the mixture cannot be identified (Figure S4 and Table S2). Hydrogenolysis of these primitive phenols over Ru-WO_x/SiAl catalyst formed a mixture of arenes and saturated alkanes, together with some unreacted phenols. Quantitative analysis of the resulted mixture by GC revealed that a yield of 36 wt% of the final products could be detected. Among these products, arenes took about 75 wt%, alkanes 10 wt% and the remained phenols and other by products 15 wt% (Table 3 and Table S3). Overall, these results further demonstrated that the Ru-W type catalysts were promising candidates for the selective cleavage of phenols derived from lignin to yield arenes.

Table 3 Hyrogenolysis of the Primitive phenols extracted from pyrolysis lignin.

Primitive phenol 100.0 mg			
Identified phenols	72 wt%	Unknow mixture	28 wt%
Detected products after reaction 36.2 (mg)			
Benzene	6.1	cyclohexane	1.0
Toluene	7.0	Methylcyclohexane	0.9
Ethylbenzene	10.2	Ethylcyclohexane	1.1
Propylbenzene	4.0	Propylcyclohexane	0.7
Total arenes	75 wt%	Total alkanes	10 wt%
Unknow products and remained phenols 15 wt%			

4 Conclusions

In conclusion, we have demonstrated a highly active catalytic system based on bimetallic Ru-W catalysts for the selective cleavage of C_{Ar}-O bonds in phenols. The -hydroxyl and -methoxyl groups on the aromatic ring could be easily removed to yield the corresponding arenes with high selectivity under hydrogen atmosphere. Researches on the catalysts revealed that synergism between the Ru particles and W particles was the key to the hydrogenolysis reactions. Besides, the catalyst also showed excellent activities in the hydrogenolysis of various phenolic compounds with different functionalities and three dimeric lignin model compounds with α-O-4, β-O-4 and 4-O-5 ether linkages. Finally, the Ru-W catalyst was applied to the hydrogenolysis of the phenols separated from the real bio-oil, yielding arenes in high selectivities. These promising results open a new route for the valorization of phenols derived lignin which would greatly extend the application areas of lignin. Detailed studies of the reaction mechanism are still underway.

Acknowledgements

This work was supported by the 973 Program (2012CB215306), NSFC (21325208, 21172209, 21272050), CAS (KJCX2-EW-J02), SRFDP (20123402130008), FRFCU and PCSIRT.

Notes and references

[a] Collaborative Innovation Center of Chemistry for Energy Materials, CAS Key Laboratory of Urban Pollutant Conversion, Anhui Province Key Laboratory of Biomass Clean Energy, Department of Chemistry, University of Science and Technology of China, Hefei 230026 (China)
[b] College of Chemical Engineering, Nanjing Forestry University, Nanjing 210037 (china)

† Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/c000000x/

(1) J. Zakzeski, P. C. A. Bruijnincx, A. L. Jongerius, B. M. Weckhuysen, *Chem. Rev.* 2010, **110**, 3552.

(2) (a) A. oledano, L. Serrano, A. M. Balu, R. Luque, A. Pineda, J. Labidi, *ChemSusChem* 2013, **6**, 529. (b) Q. Song, F. Wang, J. Cai, Y. Wang, J. Zhang, W. Yu, J. Xu, *Energy Environ. Sci.*, 2013, **6**, 994.

(3) E. Furimsky, *Appl. Catal.,* 2000, **199**, 147.

(4) (a) A. G. Sergeev, J. F. Hartwig, *Science* 2011, **332**, 439. (b) J. He, C. Zhao, J. A. Lercher, *J. Am. Chem. Soc.* 2012, **134**, 20768. (c) A. G. Sergeev, J. D. Webb, J. F. Hartwig, *J. Am. Chem. Soc.* 2012, **134**, 20226. (d) V. Molinari, C. Giordano, M. Antonietti, D. Esposito, *J. Am. Chem. Soc.* 2014, **136**, 1758.

(5) Y. Ren, M. Yan, J. Wang, Z. C. Zhang, K. Yao, *Angew. Chem. Int. Ed.* 2013, **52**, 12674.

(6) J. M. Nichols, L. M. Bishop, R. G. Bergman, J. A. Ellman, *J. Am. Chem. Soc.* 2010, **132**, 12554.

(7) (a) T. H. Parsell, B. C. Owen, I. Klein, T. M. Jarrell, C. L. Marcum, L. J. Haupert, L. M. Amundson, H. I. Kenttämaa, F. Ribeiro, J. T. Miller, M. M. Abu-Omar, *Chem. Sci.* 2013, **4**, 806. (b) M. V. Galkin, J. S. M. Samec, *ChemSusChem*, 2014, **7**, 2154.

(8) (a) J. D. Nguyen, B. S. Matsuura, C. R. J. Stephenson, *J. Am. Chem. Soc.* 2014, **136**, 1218. (b) M. C. Haibach, N. Lease, A. S. Goldman, *Angew. Chem. Int. Ed.,* 2014, **53**, 10160.

(9) (a) S. Son, F. D. Toste, *Angew. Chem. Int. Ed.* 2010, **49**, 3791. (b) S. K. Hanson, R. Wu, L. A. "Pete" Silks, *Angew. Chem. Int. Ed.* 2012, **51**, 3410.

(10) (a) A. Fedorov, A. A. Toutov, N. A. Swisher, R. H. Grubbs, *Chem. Sci.* 2013, **4**, 1640. (b) A. Rahimi, A. Azarpira, H. Kim, J. Ralph, S. S. Stahl, *J. Am. Chem. Soc.* 2013, **135**, 6415. (c) M. Chatterjee, T. Ishizaka, A. Suzuki, H. Kawanami, *Chem. Commun.*, 2013, **49**, 4567.

(11) (a) C. Zhao, Y. Kou, A. A. Lemonidou, X. Li, J. A. Lercher, *Angew. Chem. Int. Ed.* 2009, **48**, 3987. (b) Y. Nakagawa, M. Ishikawa, M. Tamura, K. Tomishige, *Green Chem.* 2014, **16**, 2197.

(12) (a) J. Chang, T. Danuthai, S. Dewiyanti, C. Wang, A. Borgna, *Chemcatchem* 2013, **5**, 3041. (b) A. L. Jongerius, R. W. Gosselink, J. Dijkstra, J. H. Bitter, P. C. A. Bruijnincx, B. M. Weckhuysen, *ChemCatChem* 2013, **5***,* 2964.

(13) Y. Wang, R. Rinaldi, *Angew. Chem. Int. Ed.* 2013, **52**, 11499.

(14) (a) P. Álvarez-Bercedo, R. Martin, *J. Am. Chem. Soc.* 2010, **132**, 17352. (b) M. Tobisu, K. Yamakawa, T. Shimasaki, N. Chatani, *Chem. Commun.*, 2011, **47**, 2946.

(15) (a) M. Chia, Y. J. Pagan-Torres, D. Hibbitts, Q. Tan, H. N. Pham, A. K. Datye, M. Neurock, R. J. Davis, J. A. Dumesic, *J. Am. Chem. Soc.* 2011, **133**, 12675. (b) A. C. Atesin, N. A. Ray, P. C. Stair, T. J. Marks, *J. Am. Chem. Soc.* 2012, **134**, 14682.

(16) (a) Y. B. Huang, M. Y. Chen, L. Yan, Q. X. Guo, Y. Fu, *ChemSusChem* 2014, **7**, 1068. (b) A. Wang, T. Zhang, *Acc. Chem. Res.* 2013, **46**, 1377.
(17) J. Guo, R. Ruan, Y. Zhang, *Ind. Eng. Chem. Res.* 2012, **51**, 6599.
(18) P. Zhang, T. Wu, T. Jiang, W. Wang, H. Liu, H. Fan, Z. Zhang, B. Han, *Green Chem.*, 2013, **15**, 152.
(19) A. Popov, E. Kondratieva, J. M. Goupil, L. Mariey, P. Bazin, J. P. Gilson, A. Travert, F. Mauge, *J. Phys. Chem. C* 2010, **114**, 15661.