HYDRODEOXYGENATION OF LIGNIN-DERIVED AROMATICS OVER BI-FUNCTIONAL RUMOOx/C UNDER MILD CONDITION

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ABSTRACT

Bifunctional ruthenium and molybdenum oxide nanoparticles supported on activated carbon were designed and empolyed in hydrodeoxygenation (HDO) of lignin-derived aromatics for lignin depolymerization products upgrading. The typical model phenolic monomers and dimers could be efficiently converted to hydrocarbons over RuMoOx/C under mild conditions in decalin, i.e. at 160℃ and 30 bar H_2. When HDO reaction was executed with real lignin-derived aromatics at 280℃ and 30 bar H_2, the total yield of hydrocarbons and cyclohexanol/ether were 56.93% and 18.99%. The main hydrocarbons were cyclohexane and alkyl-substituted cyclohexane. Characterization results revealed that the nanoparticles of ruthenium and molybdenum oxide species highly dispersed on activated carbon, while the presence of Ru active site and MoO_x on activated carbon were crucial for the remarkable hydrogenolysis/ hydrodenation and deoxygenation activity, respectively. The hydrodeoxygenation pathway of diphenyl ether as a model compound catalyzed by optimized RuMoOx/C was discussed and the structure-activity relationship in hydrodeoxygenation was proposed.

Keywords: Hydrodeoxygenation, lignin model compound, model dimer, Lignin-derived aromatics, $RuMo_xO/C$ catalyst

1. INTRODUCTION

Lignin, as the only renewable aromatic polymer, is showing its significant utilization potential. One efficient approach is catalytic degradation of lignin to produce valuable aromatics, such as alkyl-substituted phenols, guaiacols and syringols by various approaches[1]. These monomer aromatics and oligomers can't be used as transportation fuels directly due to their high oxygen content, poor chemical stability and immiscibility with hydrocarbon fuels [2]. Consequently, for better uses of aromatics derived from lignin, process of hydrodeoxygenation (HDO) is needed to make lignin oils more suitable as substitutes for the conventional fuels.

The HDO reaction of lignin oligomer fragments is divided into the cleavage of C-C and C-O linkages and decarbonylation or decarboxylation of oxygen-containing groups. The formation of hydrocarbon products depends on the relative cleavage rate of C-C and C-O bond [3]. In most cases, the selectivity of liquid alkanes is very low due to the severe cracking reaction of C-C bond. Therefore, the cleavage C-C bond should be effectively inhibited for lignin oil conversion to C6-C9 alkanes. The distribution of the alkane products can be controlled by varying the metal active sites and adjusting the acid strength [4-5].

Industrial sulphide catalysts (such as CoMo and NiMo) have a good HDO effect on biomass derivatives. However, the deactivation of catalyst is fast due to the severe leaching of lattice sulphur and the poisoning of water. In recent years, molybdenum oxide exhibits a high selectivity for the cleavage of C-O bonds without destroying the C-C bond [6]. The activity of catalyst can be recovered by calcination or maintained in water. In general, Ru metal has significant activity for the cleavage of C-C bonds and can produce a large amount of low alkanes, especially CH_4 [5]. In order to inhibit the cracking of C-C, Ru metal catalysts are often modified by reducible metal oxides (e.g., MoO_{3-x}) [7-9].

Therefore, the activated carbon (AC) with high specific surface area was selected as the support, and the RuMo dual-functional catalyst was loaded on AC by the stepwise impregnation method. The RuMoOx/C catalyst,

MoO_x selectively break the C-O bond and maintain the integrity of carbon chain of the product in the HDO reaction. In particular, the addition of a small amount of Ru metal to the surface of MoO_x/C significantly improves HDO activity and catalyst stability. It can be concluded that the synergistic effect of Ru metal and molybdenum oxide make the C-O bond selective cleavage and deoxygen to obtain high yield of alkane. The preparation method is simple and suitable for industrial large-scale preparation.

2. MATERIAL AND METHODS

2.1 Catalyst preparation

A The RuMoOx/C catalysts were synthesized by continuous wet impregnationas our prevous work [10].

2.2 Catalyst characterzation

The Brunauer-Emmett-Teller (BET) specifc surface area, average pore diameter and pore volume of catalysts were determined with N_2 isothermal adsorption at 77 K using Micromeritics ASAP 2460 analyzer equipped with MicroActive software system. XRD patterns were recorded by an X'Pert Pro Philips diffractometer using Cu Kα radiation. The measurement conditions were in the range of 2θ = 5–80°, step counting time 10 s, and step size 0.0167° at 298 K. Transmission electron microscopy (TEM) microphotographs and element mapping were acquired on a JEM-2100F electron microscope with an accelerating voltage of 200 kV. A Thermo Scientifc Escalab 250Xi X-ray photoelectron spectrometer was used for X-ray photoelectron spectra (XPS) analysis.

3. RESULTS AND DISCUSSION

3.1 Characterization of the catalyst

The X-ray diffraction patterns of three kinds of catalysts after reducing were presented in Fig. 1. Because of the low Ru loadings of RuMo/C samples, there were no peaks attributed to metal ruthenium, indicating that the Ru metal was well dispersed over the AC surface. The two broad and not well-defned peaks of all samples, at 2θ angles of about 23.83° and 26.60° [3, 10], were characteristic of AC. Three other peaks were detected at 26.03°, 37.02° and 53.97°, which corresponded to MoO_2 (JCPDS 32-0671). Comparsion the diffraction patterns of samples, for the Ru-MoO_x/C sample, the MoO_2 diffraction peaks very strong, while weak peaks in MoO_xRu/C case and no MoO_2 diffraction peak can be detected in RuMoO_x/C. Which suggest that

the load order of metal precursors exhibited great effect on the distribution of metal. The diffraction peaks of the metal Ru and molybdenum oxide are hardly observed on the surface of the RuMoO_x/C catalyst, which is probably because the molybdenum salt pre-loaded in proes or highly dispersed on the surface of the activated carbon, or may be affected by the post-loaded $RuCl_3$. The molybdenum oxide was redispersed due to hydrogen overflow phenomenon during the ruthenium salt reduction process. During the synthesis of MoO_xRu/C, Ru^{3+} is firstly loaded and entered the pores of the activated carbon, thus the post-loaded molybdenum salt was lacked of hydrogen overflow to help to redispersed and formed small molybdenum oxide particles. The effect can not be redispersed into more uniform small particles; Ru salt and molybdenum salt were added simultaneously for Ru-MoO_x/C preparation, leading to Ru was surrounded with molybdenum oxide and cannot be effectively reduced to faciliate molybdenum oxide redispersion. It is also the reason for the strong diffraction peak of MoO_2 in Ru-MoO_x/C case.
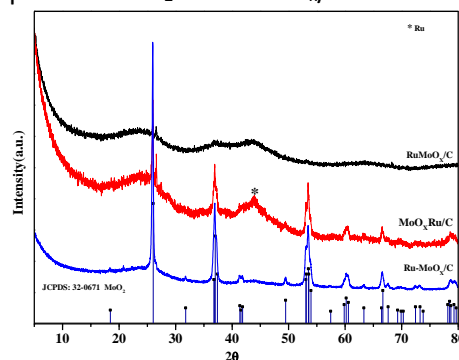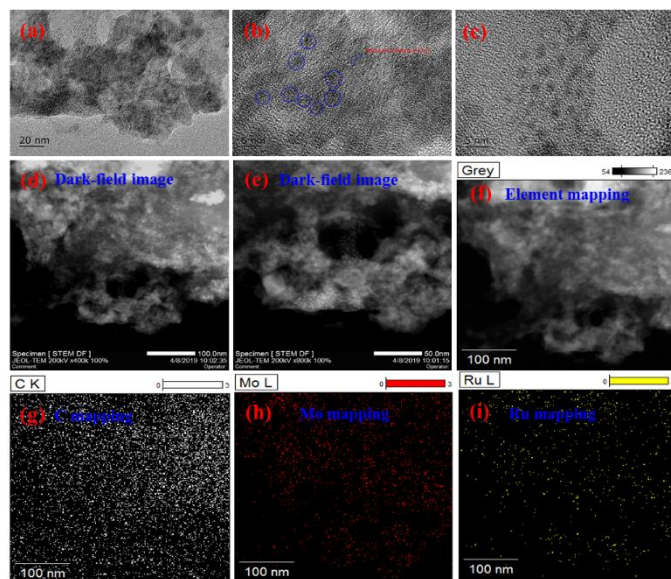

Fig.1 The XRD patterns of catalysts

Fig. 2. The TEM images and corresponding elemental mapping images of RuMoO_x/C

Fig.2 displayed the representative TEM images of RuMoO$_x$/C catalyst as well as the corresponding elemental mapping analysis of the Ru and MoO$_x$ particles. As evident from Fig.2, the two metal particles were well dispersed on the AC supports, which were also confrmed by the XRD patterns. These results suggested that the preferential impregnation of Mo onto the AC support does not lead to an obvious growth of the Ru nanoparticles.

XPS was employed to investigate the metal and oxidative states of the metal particle of RuMoO$_x$/C catalyst (Fig. 3). Due to the overlapping of the Ru 3d$_{5/2}$ peak with C 1s peak, the binding energy of Ru 3p$_{3/2}$ orbital was measured. However, no Ru 3p$_{3/2}$ peaks at 462.1 and Ru 3p$_{1/2}$ at 484.2 eV ascribed to metallic Ru was not detected [3, 10-13]. Accordingly, it indicated that the Ru species wasn't on the surface of C support but in the channel. From the XPS results of molybdenum oxide (Fig.3), the Mo3d binding energy at 232.9 eV (Mo^{6+}), 236.1 eV(Mo^{6+}), 231.2, 234.4eV(Mo^{5+}) and 229.8, 233.0eV(Mo^{4+}) indicated three kinds of molybdenum oxidation states [10-11], implying that the higher molybdenum oxidation states were obtained on the surface of support during the heat treatment under a nitrogen atmosphere. The distribution of Mo in different oxidation states was calculated according to the peak area, and the peak area ratio of Mo^{6+}/Mo^{5+}/Mo^{4+} was 10:3:7. However, no molybdenum oxide species was observed on XRD, indicating that MoO$_x$ was highly dispersed on activated carbon.
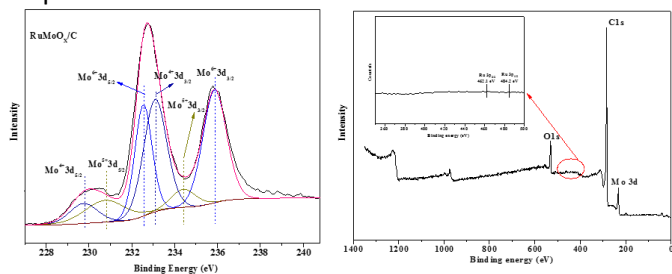
Fig.3 XPS spectra of Ru 3p and Mo 3d for RuMoO$_x$/C

3.2 Catalytic activity in model compounds HDO

Table 1 Hydrodeoxygenation of diphenyl ether over different catalysts[a]

catalyst	conversion (%)	selectivity (%)					
RuMoO$_x$/C	80.4	66.9	27.5	0	0	1.8	3.6
MoO$_x$Ru/C	74.1	59.2	26.4	2	4.3	2.6	5.5
Ru-MoO$_x$/C	68.9	46.5	23.3	9.2	7.6	5.5	7.9
RuMoO$_x$/C[b]	18.9	29.2	36.5	13.8	5.4	6.8	8.2
RuMoO$_x$/C[c]	37.6	32.5	43.7	15.6	0	1.6	6.4
RuMoO$_x$/C[d]	56.3	68.3	5.9	25.2	0.2	0.2	0.2

[a] Reaction conditions: 0.1mmol diphenyl ether,50mg catalyst, 25mL decalin,120℃,3h,30bar H$_2$

[b]100℃, [c]120℃, [d] 140℃,1h,25mL decalin, 30bar H$_2$.

The HDO properties of the catalysts prepared by three methods were investigated using diphenyl ether as model reactant. As shown in Table 1, the catalytic activity and product selectivity of the catalysts were controlled by the used catalysts. the highest catalytic activity for cyclohexane was given by RuMoO$_x$/C, followed by MoO$_x$Ru/C. which may be related to the size and dispersion of active metal particles (Fig.1-3).

Table 2 Hydrodeoxygenation of lignin-derived phenolic monomers/dimers over RuMoO$_x$/C

substrate	conversion (%)	selectivity (%)			
	98.8	97.4	2.1	0.3	
	99.9	96.5	2.5		
	96.7	93.8	0.7	2.2	2.8
	99.2	38.1	19.1	15.4	27.4
	99.3	38.2	24.7	23.5	13.6
	99.5	95.5	2.2	Ring-opening products 2.3	

Reaction conditions: 0.1mmol diphenyl ether,50mg catalyst, 25mL decalin,160℃,3h,30bar H$_2$

The effect of reaction temperature on the HDO reaction of diphenyl ether catalyzed by RuMoO$_x$/C was investigated (Table 1). The temperature plays an important role in the HDO process. Generally speaking, the conversion of diphenyl ether increased from 18.9% to 56.3% after 1 h of reaction when the temperature raised from 100 to 140 C. At the same time, the selectivity for hydrocarbons, i.e. cyclohexane and benzene, increased significantly from 29.2% / 13.8% to 68.3% / 25.2% (while the selectivity of cyclohexanol decreased from 36.5% to 5.9%). Obviously, high reaction temperature accelerated the conversion of cyclohexanol to cyclohexane. When diphenyl ether was converted over RuMoOx/C catalyst under 140 ℃, the HDO performance is superior to other catalytic results (or is comparable to that of HDO at higher temperatures) reported in literature. For example, at 200℃, the HDO performance of diphenyl ether is and RuMoOx/C catalyst is superior to that of other catalyst systems [14-17]. Ru

leaching was not detected in liquid products after the reaction, indicating that no Ru leaching or Ru leaching was below the detection limit during the reaction.

The bond of β-O-4, α-O-4 and 4-O-5 are the three most common linkages in lignin [7]. Therefore, we further studied the HDO performance of lignin-derived dimer model compouns with β-O-4, α-O-4 and 4-O-5 linkages over RuMOx/C catalyst. As shown in Table 5, diphenyl ether (4-O-5) was converted at 160℃, and the yield of cyclohexane was >93%. Compared with RuMOx/C catalyst, other catalyst systems, such as Pd/C, H-ZSM-5 [18] and Ru/H-ZSM-5 [19] should be at a higher temperature (200℃ or higher). The conversion higher than 99% were obtained when Benzyl phenyl ether (a-O-4) and phenylethylbenzene (β-O-4) were catalyzed over RuMoOx/C under160℃for 5h. After reaction at 160℃ for 5 h. The distribution of HDO products of a-O-4 and β-O-4 dimers were quite different from that of 4-O-5. Such as, cyclohexane (38.7%), methylcyclohexane (19.1%), cyclohexylmethanol (15.4%) and cyclohexanol (27.4%) were the major conversion products of a-O-4, while the main products from β-O-4 dimer were cyclohexane (38.2%), ethylcyclohexane (24.7%), ethylcyclohexanol (23.5%) and cyclohexanol (13.6%). The relatively high cyclohexylmethanol and cyclohexylethanol in the products are mainly due to their slow dehydroxylation rate (9.5 and 8.8 h^{-1}, respectively, while phenol is 1020.3 h^{-1}) [20]. The distribution of products from α-O-4 dimer are similar to that of the ZSM-5 and Ni/ZSM-5 catalysts when reacted at a higher temperature of 250℃. During the thermal cracking process, the product dicyclohexylmethane is considered to be formed by a free radical reaction. It can be seen that the cyclohexane, methylcyclohexane and cyclohexylmethanol were formed by hydrogenation and/or dehydroxylation, but only trace amounts of bicyclic products can be detected, such as dicyclohexylmethane. Pyrolysis is a more important pathway than hydrogenolysis and hydrolysis for the cleavage of C-O-C bond in a-O-4 dimer.

In addition to C-O-C, the C-C linkage is another important type of aryl-aryl bond. The HDO reaction of (5-5 linkage) was also studied (Table 5-5). The conversion of 2,2-bisphenol was 99.9% and a selectivity of 95.5% of bicyclohexane was obtained at conditions of 160 oC for 5h. At the same time, a small amount of ring-opening products (2.3%) was found. However, no C-C bond cleavage product was found, indicating that MoOx effectively inhibited the C-C bond cleavage activity from Ru.

3.3 RuMoOx/C catalytic hydrodeoxygenation of lignin depolymerization oil

A better HDO performance of the typical model compound were given over RuMoOx/C catalyst. Therefore, RuMoOx/C was further applied to the HDO reaction of lignin oil. The lignin oil derived from the hydrogenolysis of hydrolysis residue (riched lignin)over the synergistic catalysis of Ru/C and MgCl₂. First, the lignin oil's component and structure before and after HDO were analyzed. As the GC-MS results shown (Fig.4), The volatile components are complex and the aromatics are mostly oxygenated compounds (hydroxyl, carbonyl, carboxyl and other functional groups).Comparing the components of lignin oils before and after HDO, the volatile components of the depolymerization product differ greatly after the HDO reaction. After the reaction, the color of the liquid products changed from brownish black to transparent beige, which are attributed to the hydrogenation saturation of the chromogenic functional group, such as carbonyl and hydrazine. Methyl intermediates, etc. The results of 1H NMR spectrum show that the components of lignin oils were significant difference before and after HDO. For instance, the fingerprint signal intensity at 3.51 ppm is obviously weakened after HDO treatment, implying the linkage of β-O-4 was remarkably cleaved [13, 21]. The signal between 1.85 and 2.22 ppm shows little change, indicating that the ester bond structure is stable in the HDO reaction. A significant increase in the characteristic signal at 2.15-2.56, 1.22 and 1.35 ppm indicates that a large amount of C-OH bonds in the products were removed, which are consistent with GC-MS results. Therefore, from the 1H NMR spectrum of the products before and after HDO reactions, it can be known that in the HDO process, the ether bond such as β-O-4 is broken (but not completely broken), and the -OH bonds in side chain of aromatics were removed. Which may be the cause of the color change of the products, and the dehydroxylation helps to inhibit the occurrence of the polycondensation reaction.
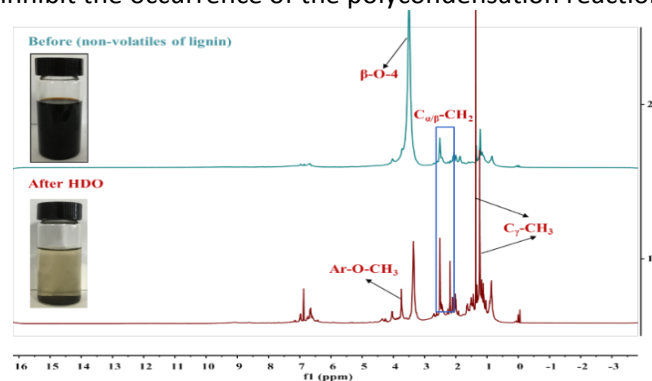

Fig.4 The ¹H NMR specturm of non-volatiles of lignin before and

The volatiles of lignin oil were analyzed by GC-MS and quantified by the acetophenone internal standard compound. The measured components and contents are shown in Table 3, Before HDO, the total aromatics content was 78.73% with mostly G and S type monomer aromatics. After HDO, main products were 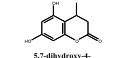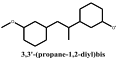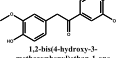hydrocarbons (56.93%) and cyclohexyl alcohol / ether (18.74%) over RuMoOx/C at the conditions of 280°C and 30bar H2. Compared with the results of the bis-benzene compound HDO, the hydrogenation of the biphenyl ring in the actual lignin oil was not detected obviously during HDO process, which is probably related to the steric hindrance and multiple substitutions limited the hydrogenation of the biphenyl ring [2].

Table 3 The components of lignin oil and their HDO products [a]

Lignin-derived phenolic		HDO products	
components	content /%	components	Yield /%
phenol	1.20	**Total of cyclic hydrocarbons**	**75.67**
4-hydroxybenzaldehyde	1.23	**Cyclic alkanes**	**50.55**
3-Phenyl-1-propanol, acetate	4.32	cyclohexane	14.85
Phenol, 2-methoxy	18.6	Methylcyclohexane	12.30
4-(2-hydroxyethyl)-2,6 -dimethoxyphenol	10.3	Propylcyclohexane	6.63
1-(3-ethyl-5-methoxyphenyl) ethan-1-one	0.82	1-methyl-4-propylcyclohexane	7.34
2,6-dimethoxyphenol	0.63	ethylcyclohexane	3.35
Methyl-guaiacol	1.97	1-ethyl-4-methylcyclohexane	3.40
Trimethylphenol	3.58	1-(1,1-Dimethylethyl)-3-methylcyclohexane	1.43
Isopropylphenol	0.47	**cyclohexanols**	**12.97**
1-(2-Ethylphenyl)-1-propanone	1.84	Trimethylphenol	1.64
1-(4-hydroxy-3-methoxyphenyl) propan-2-one	6.02	cyclohexylmethanol	1.26
4-hydroxy-3-methoxybenzaldehyde	1.76	2-methoxycyclohexan-1-ol	4.47
4-(hydroxymethyl)phenyl furan-2-carboxylate	2.32	cyclohexanol	3.94
1-(4-hydroxy-3,5-dimethoxyphenyl)ethan-1-one	3.44	4-ethyl-2-methoxycyclohexan-1-ol	1.09
2-methoxy-4-propylphenol	3.62	4-(sec-butyl)cyclohexane-1,3-diol	0.82
Eugenol	2.68	**Aryl ethers**	**5.77**
2-(1,1-Dimethylethyl)-4 -methyl-phenol	2.20	1,3-dimethoxy-5-propylcyclohexane	4.61
5,7-dihydroxy-4-methylchroman-2-one	3.45	3,3'-(propane-1,2-diyl)bis (methoxycyclohexane)	0.63
1,2-bis(4-hydroxy-3-methoxyphenyl)ethan-1-one	1.71	tetrahydrofuran	0.53
Phenanthrene and its derivatives	**5.57**	**Others (aromatics)**	**6.38**
			1.77
			2.86
Total	**78.73**		1.75

[a] Reaction condition:0.1g RuMoOx/C, 40mL decalin, T =280°C, 30bar H2, t= 5 h. Determined by GS–MS and quatified by GC using n-dodecane as internal standard. The yields of HDO products were estimated by the mass of HDO products divided by mass of the identified lignin-derived aromatic compounds.

The obtained oxygen-free compounds are mainly cyclohexane, methylcyclohexane, dimethylcyclohexane, propylcyclohexane,p-methylpropylcyclohexane,benzene, toluene, ethylbenzene, etc. (Table 3) , these anaerobic products have a higher octane number. For example, the octane number (RON-definition) of cyclohexane is 97. In addition, the vapor pressure and carbon number of these oxygen-free products are in the range of gasoline. Therefore, they will be the ideal components to replace liquid transportation fuels.

From the distribution of the products and the results of 1H-NMR, RuMoOx/C showed an excellent activity for the cleavage of C-O ether bond, hydrogenation saturation C=C bond (other hydrogenation of benzene ring) and deoxidation, confirming the high catalytic depolymerization-hydrogenation activity of the RuMoOx/C catalyst. Compared with the ether bond cleavage and hydrogenation reaction of phenolic model compounds, the overall hydrogenation effect of real lignin oil was not much different and the phenolic hydroxyl group had a strong ability to break. However, the deoxygenation abilities of hydroxyl group and methoxy group were weak. The special removal ability. It is worth noting that the deoxidation effect need to be improved.

The durability of the catalyst was discussed due to high cost of Ru. We conducted the recycle experiment of catalyst three times under the given conditions (0.4g of lignin-derived aromatics, 0.1g of catalyst, at 280°C, under 30 bar H2 pressure for 5h. After reaction, RuMoOx/C was collected and reduced for next run). As Fig.5 shown, the yield of hydrocarbons anf cyclohexyl alcohol/ether just slightly decreased in the second and third runs. In order to clarify the change of main products yield, the reused catalyst relative characterization analyzed by XRD and liquid products by ICP-AES analysis. After reaction, the X-ray diffraction patterns displayed no Ru diffraction peak was detected as fresh catalyst, implying Ru particles were not obviously aggregated . While obvious difference between fresh and used RuMoOx/C (Fig. 5) due to the diffraction peaks

of MoO_2 (PDF # 32-0671). For instance, after reaction, the evident diffraction peak of MoO_2 might be ascribed to the aggregation or the migration of MoOx species from carbon interchannel. It is worth noting that no obvious difference of the diffraction peak of MoO_2 after each run except the peak at $2\theta=18.20°$, suggesting the MoO_2 specie was relatively stable on A support after HDO reaction. Meanwhile, the Ru and Mo species leaching off from C support to hot wet solutions during reaction, the Ru metal leaching was not detected under the limit of detection (were <0.1 and <0.1 mg·L^{-1}, respectively) (Table 4). Therefore, almost no obvious Ru and Mo species was dissolved by catalytic HDO and intermediate organic compounds in the process, and the slightly decresed yield of main products were attribute to the aggregation or the migration of MoOx species. After three runs, Ru mental maintained the stable activity at the given operating conditions.
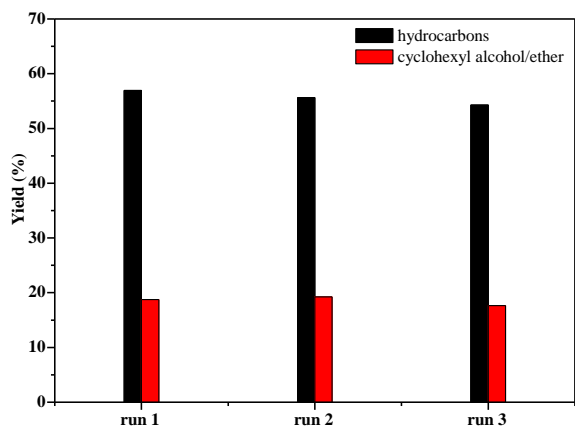

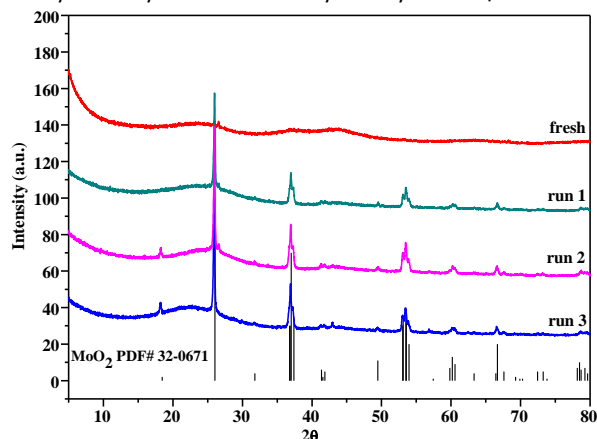Fig.5 the yield of hydrocarbons and cyclohexyl alcohol/ether each run

Fig.6 The XRD patterns of fresh and used RuMoOx/C

Table 4 The ICP-AES result of Ru leaching concentration from fresh and spent Ru/C catalysts

Entry	Ru$_{aq}$ (mg·L^{-1})	Mo$_{aq}$ (mg·L^{-1})
Ru/C-run 1	<0.10	<0.10
Ru/C-run 2	<0.10	<0.10
Ru/C-run 3	<0.10	<0.10

Reaction condition: 0.4g of lignin-derived aromatics, 0.1g of catalyst, at 280℃, 40 mL decalin, 30 bar H$_2$, 5h.

4. CONCLUSION

The RuMoOx/C catalyst was synthesized by step-by-step impregnation, the molybdenum oxide and Ru nanoparticles highly dispersed on activated carbon, for the lignin depolymerization products HDO upgrade. The lignin oil was efficiently converted into hydrocarbons with a hydrocarbon yield of 56.93% and a cyclohexanol/ether yield of 18.74% at the condintions of 280℃ and 30 bar H$_2$. The effective upgrade of the lignin oil can be attributed to the synergy of the active center of Ru and the active species of MoO$_x$. The catalytic activity of RuMoO$_x$/C is mainly hydrogenolysis, followed by hydrogenation and dehydroxylation.

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