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An efficient bifunctional Ru-NbOPO₄ catalyst for the

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Hongye Zhao^a, Xun Hu^b, Jianxiu Hao^a, Na Li^a, Keduan Zhi^a, Runxia He^a,

Yunfei Wang^c, Huacong Zhou^a*, Quansheng Liu^a*

^aCollege of Chemical Engineering, Inner Mongolia University of Technology; Inner Mongolia Key

Laboratory of High-Value Functional Utilization of Low Rank Carbon Resources, Hohhot 010051,

Inner Mongolia, China

^bSchool of Material Science and Engineering, University of Jinan, Jinan, 250022, China.

^cCollege of Chemical Engineering, Ordos Institute of Technology, Ordos 017000, China

*Corresponding author: Tel: +86 0471 6575722;

Email addresses: <u>hczhou@imut.edu.cn</u> (H. Zhou), <u>liuqs@imut.edu.cn</u> (Q. Liu).

Graphical Abstract



An efficient bifunctional Ru-NbOPO₄ catalyst was designed for the hydrodeoxygenation of aromatic ethers, phenols and real bio-oil into hydrocarbon.

Highlights

- Combining the strong acidity of NbOPO₄ and excellent hydrogenation activity of the metallic Ru, bifunctional Ru-NbOPO₄ catalysts can catalyze the hydrodeoxygenation of real bio-oil.
- Different acid varieties and strengths could be attributed to the different structures of the Nb-O species.

• The product distribution can be tuned by varying the acidic strength and reaction conditions.

Abstract

An efficient bifunctional NbOPO₄ supported Ru catalyst (Ru-NbOPO₄) was applied to the hydrodeoxygenation of aromatic ethers and phenols and the upgrading of bio-oil. Characterization results revealed that the Ru-NbOPO₄ catalyst possessed strong acidity, including Lewis and Brønsted acids. The Lewis acid sites originated from the Nb-O bonding structures, including slightly distorted octahedral NbO₆, regular tetrahedral NbO₄ and highly distorted octahedral NbO₆. In combination with the strong acidity of the Nb-O species and excellent hydrogenation activity of the metallic Ru, the bifunctional Ru-NbOPO₄ catalyst exhibited an excellent catalytic activity in the hydrodeoxygenation of aromatic ethers and phenols with different structures, and even real bio-oil to alkanes. The hydrocarbon yield after real bio-oil upgradation was up to 88.2%. Carbon deposition and enlargement of the Ru nanoparticles resulted in slight deactivation of the catalyst. The catalytic activity could be mostly recovered after being calcined and reduced.

Keywords: Hydrodeoxygenation, Niobium phosphate, Lewis acid, Anisole, Bio-oil

1 Introduction

Being the only sustainable source of organic carbon, biomass is playing an increasingly important role in our energy landscape. The conversion of renewable lignocellulosic biomass into liquid fuels is particularly attractive but extremely challenging due to its recalcitrant nature [1].

Lignocellulose, as the structured portion of woody biomass, is composed of cellulose (40-50 wt%), hemicellulose (16-33 wt%) and lignin (15-30 wt%). Lignin is a heavily cross-linked polymer containing three monomers of coumaryl, coniferyl and sinapyl alcohols [2, 3]. Methoxyl (-OCH₃) and hydroxyl (-OH) are the major functional groups of lignin and lignin-derived compounds. Three primary routes have been used to convert lignocellulosic material into liquid oil, including syngas production by gasification [4], hydrolysis of biomass to produce sugar monomer units [5, 6] and bio-oil production by flash pyrolysis or hydrothermal liquefaction [7]. Synthesic gas can be used to produce hydrocarbons, methanol and other fuels [8]. Sugar monomer units [9, 10] and associated lignin intermediates [11] have been selectively converted into targeted transportation fuels. The hydrolyzation of biomass has achieved a leap from the initial use of model compounds [12, 13] to the direct conversion of raw biomass to liquid fuels [14, 15]. Although the above studies have succeeded in converting lignocellulosic biomass into liquid fuels or other high-valued chemicals, the selective production of hydrocarbons with higher yield is still a challenge. Another strategy for obtaining hydrocarbons efficiently is to link the biomass to the hydrocarbon products through a bio-oil intermediate. The biopolymer in biomass can be broken down by flash pyrolysis and then used to generate high concentrations of phenolic molecules known as bio-oil [16]. Bio-oil has a high potential as a liquid fuel since it retains up to 70% of the initial energy of the starting biomass and contains less nitrogen and sulphur than fossil fuels [17, 18]. Three types of C-O bonds, C_{AR}-OCH₃, CAR-OH and CAR-R, are frequently found in biomass-derived bio-oil. However, bio-oil cannot be directly used as a liquid fuel owing to its high oxygen content, poor chemical stability and corrosivity to the equipment [3, 19]. Therefore, bio-oil should be upgraded to improve its energy

density and stability.

Catalytic hydrodeoxygenation is an effective bio-oil upgrading strategy, which can selectively remove oxygen from raw bio-oil under moderate temperatures and hydrogen pressures in the presence of efficient catalysts. Catalytic hydrodeoxygenation has been observed to take place via complex reaction pathways. Generally, the two main routes for hydrodeoxygenation of model compounds are direct deoxygenation (DDO) retaining the aromatic character and hydrogenation (HYD) saturating the aromatic ring [20, 21]. A number of catalysts have been investigated for hydrodeoxygenation, including metal sulfides [22, 23], noble metals [20, 24], transition metal carbides [25, 26], phosphides [27, 28] and bifunctional catalysts [29-31]. Bifunctional catalysts can conveniently provide both hydrogenation and deoxygenation sites on a single catalyst, converting the oxygen-containing compounds directly to alkanes in one pot. Among the kinds of hydrogenated metals, Ru has been regarded as a very effective species and is relatively cheaper than other noble metals [32]. Materials with acidity such as ZrO₂, TiO₂, molecular sieves and other acidic materials have been widely used in the construction of bifunctional catalysts for deoxygenation [17, 33-35], but relatively high reaction temperatures and catalyst deactivation are still major disadvantages that need to be solved.

Niobium compounds and related materials have attracted great interest in recent years in the field of catalysis, especially as solid acids [6, 12]. Several important reactions such as hydration, hydrolysis and esterification can be readily catalyzed by Nb-based materials [36-39]. In addition, Nb-based materials can also be used to construct bifunctional catalysts and obtain relatively good deoxygenation effects. For example, Nb₂O₅ was applied in the deoxygenation of fatty acids,

triglycerides and alcohol for the cleavage of the C_{AR} -O bond [40, 41]. In order to improve the deoxygenation performance of bifunctional catalysts, the acidity of the Nb-based support should be further enhanced. Different treatment methods have been attempted to change the composition and structure of niobium compounds, such as acid treatment [6] or introducing other metal ions to the Nb-based system [12]. Bifunctional catalysts based on improved niobium compounds were also used in the conversion of oxygen-containing substances, such as sorbitol and furan-based compounds, into hydrocarbon fuels [9, 42, 43].

There have also been attempts in the direct hydrodeoxygenation of lignin and raw woody biomass, and a relatively high hydrocarbon yield and selectivity were obtained [14, 15]. At present, hydrodeoxidation of bio-oil to produce hydrocarbon fuels by various bifunctional catalysts has been reported. For example, Lee et al. deoxidized a bio-oil model compound and bio-oil with Pt/HY as the catalyst, and the results showed that the heating value of the bio-oil increased from 18.9 MJ/kg to 24.4 MJ/kg [44]. Shu et al. upgraded phenolic compounds and bio-oil using highly dispersed Ru/TiO₂ [45] and a Pt/TiO₂ catalyst [46], and a series of value-added products composed of hydrocarbons and alkylphenols were achieved. The Ru catalysts were used to upgrade fast pyrolysis bio-oil to drop-in fuel [47]. Additionally, in-situ hydrogenation of model compounds and raw bio-oil over the Raney Ni catalyst [48] and Ni/CMK-3 catalyst [49] were reported. Although many studies have reported the advantages of bifunctional catalysts for the hydrogenation of model compounds and raw bio-oil, there is a paucity of reports on the Nb-based bifunctional catalyst applied in real bio-oil systems to produce hydrocarbons efficiently. In addition, the acidity of the Nb-based support is important in the activity of the noble metals for hydrodeoxygenation of bio-substrates and NbO_x

species were considered to play a key role in the cleavage of the C_{AR} -O bond in the hydrolysis of biomass [9, 14, 40-42, 50], but the structure of NbO_x species in Nb-based supports has not been further analyzed in the previous works, and the relationship between the different structures of NbO_x species and the deoxygenation effect still needs to be further studied.

In this work, a bifunctional Ru-NbOPO₄ catalyst was designed for the hydrodeoxygenation of the model compound anisole into cyclohexane (Scheme 1), and the effect of the catalyst structures and reaction parameters on the hydrodeoxygenation performance was systematically investigated. The catalytic activity of bifunctional Nb-based catalysts was synergistically affected by the deoxygenation ability of the Nb-based supports and the hydrogenation ability of the Ru species. The acidic property of the supports and the metallic property of the Ru species were revealed by various characterizations. The acid source of the Nb-based catalyst and the effect of the Nb-O structure on the acidity were studied in detail. After these, the catalytic pathway and the stability of Ru-NbOPO4 further studied. The bifunctional Ru-NbOPO₄ catalyst effective for the were was hydrodeoxygenation of various aromatic ethers and phenolic compounds with different structures. In addition to the model compound reactions, hydrodeoxygenation of real bio-oil into liquid alkanes was also carried out to evaluate the feasibility of the Ru-NbOPO₄ catalyst for practical applications.



Scheme 1 Schematic diagram of the preparation of the Ru-NbOPO₄ catalyst and its application in the deoxygenation of biomass-derived anisole into cyclohexane.

2 Experimental

2.1 Materials

Anisole (99%), phenyl ether (99%), veratrole (99%), ethoxybenzene (99%), diphenyl ether (98%), p-cresol (99%), 3-methylanisole (99%), 4-allylanisole (98%), 2,6-dimethoxyphenol (98%), 4-ethyl-2-methoxyphenol (98%), cyclohexane (99.5%), methylcyclohexane (99%), ethylcyclohexane (99%), propylcyclohexane (99%), dodecane (99%), ruthenium chloride (RuCl₃, 99.5%, Ru 47.0%), methoxycyclohexane (98.0%), niobium oxide (Nb₂O₅, 99.9%) and hexadecy ltrimethyl ammonium bromide (CTAB, 99%) were provided by J&K Scientific Ltd. Decane (98.5%), hexane (99%), tartaric acid (99%), hydrofluoric acid (HF, 40%), ammonium hydroxide (NH₃·H₂O, 99.99%), diammonium hydrogen phosphate ((NH₄)₂HPO₄, A.R) and phosphoric acid (H₃PO₄, A.R) were provided by Sinopharm Chemical Reagent Co. Ltd. H₂ (99.99%) was provided by the Hohhot Hengsheng Scientific Instrument Department. All chemicals were directly used as received without purification. The raw bio-oil used in this study was produced from the pyrolysis of cornstalk in a

grinding pyrolysis reactor at 500°C. The preparation process was according to that reported in the literature [51]. The elemental composition of the raw bio-oil is shown in Table 1.

Table 1 The elemental composition of raw bio-oil

Sample	C(%)	N(%)	H(%)	S(%)	O(%)
Raw bio-oil	57.42	0.44	8.43	0	33.24

2.2 Catalyst preparation

The preparation method of the Nb-based supports is described in SI 2.2. The Ru-NbOPO₄, Ru-Nb₂O₅(P) and Ru-Nb₂O₅ catalysts were prepared by the incipient wetness impregnation method using a calculated amount of RuCl₃·3H₂O as the Ru precursor. After impregnation, the obtained materials were dried at 105°C for 4 h. Subsequently, RuCl₃-NbOPO₄, RuCl₃-Nb₂O₅(P) and RuCl₃-Nb₂O₅ were put into a hydrogenation kettle, and the internal air was replaced by nitrogen three times in sequence. Finally, the kettle was filled with 4 MPa hydrogen and then heated to 150°C for 3 h. After the process was done, the Ru³⁺ in the sample was reduced to Ru⁰, then the Ru-NbOPO₄, Ru-Nb₂O₅(P) and Ru-Nb₂O₅ catalysts were obtained. Ru-Nb₂O₅, using commercial Nb₂O₅ as support (Ru-Nb₂O₅(com)), Co-NbOPO₄ and Ru-SiO₂ catalysts were also prepared as comparison samples by the above method. Cyclohexane, methoxycyclohexane and cyclohexanol are denoted as CHE, MCH and CHL, respectively, in the catalytic reaction section.

2.3 Catalytic activity tests

The hydrodeoxygenation of anisole was performed in a 15 mL Teflon lined stainless steel autoclave equipped with a magnetic stirrer. Decane was chosen as the solvent because of its good ether (phenols) solubility and its inertia in the hydrodeoxygenation reaction [44]. Typically, according to a molar ratio of the catalyst to anisole of 0.056, the catalyst Ru-NbOPO₄ was first added

into the reactor, and then, 1.1 g 10% (wt%) anisole solution with decane as the solvent was added. After replacing the internal air with nitrogen three times, hydrogen was charged into the reactor to the desired pressure, and the reactor was placed in a constant temperature air bath with stirring for the desired reaction time. After the reaction, the reactor was cooled in cold water to quench the reaction, and the organic phase was diluted with decane. The liquid products were analyzed quantitatively by a gas chromatograph (GC, TECHCOMP GC7890 II) equipped with a flame ionization detector using dodecane as the internal standard. Identification of the products and the reactant was done using a GC-MS (Agilent 7890 series GC with a 5977 MS detector) equipped with an HP-5MS UI capillary column as well as by comparing the retention times with respective standards in GC traces.

In the reusability experiments, the catalyst was separated by centrifugation, washed with fresh decane three times, and then reused for the next run without further reduction. Heterogeneity of catalysts was detected by removing the solid catalysts from the reaction mixture, and the supernatant was allowed to react to see if the product yield could further increase without the presence of the solid catalysts.

In the conversion of real bio-oil experiments, 0.1 g raw bio-oil was first extracted by 3 g hexane solvent and added into the autoclave as a substrate. A total of 0.1 g Ru-NbOPO₄ catalyst was added into the autoclave. After purging with hydrogen three times, the reactor was pressurized to 5 MPa at room temperature and heated to 170°C for 10 h under stirring. The components of the liquid products were analyzed by GC-MS, and the contents were calculated based on the peak areas.

3 Results and discussion

3.1 Screening and characterization of the Nb-based catalysts

The catalytic performance of the Nb-based catalysts was tested using the hydrodeoxygenation of anisole as a model reaction. As a control experiment, the effects of the support materials Nb₂O₅, Nb₂O₅(P) and NbOPO₄ on the hydrodeoxygenation were first investigated. The test results showed that there was no catalytic activity in the absence of Ru immobilization. As shown in Table 2, the catalytic activities were directly affected by the catalysts employed. Typically, the anisole conversion and cyclohexane yield of Ru-Nb₂O₅ (P) gave high conversion but low cyclohexane yield and high methoxycyclohexane content. Ru-NbOPO₄ showed the highest activity for the production of cyclohexane, and the cyclohexane yield was much higher than those for Ru-Nb₂O₅ and Ru-Nb₂O₅(P) and had no detectable oxygen-containing compounds under identical reaction conditions. It was also obvious that Co-NbOPO₄, Ru-Nb₂O₅(com) and Ru-SiO₂ exhibited poor deoxygenation activities.

Entry	Entry Catalysts Anisole					CH3OH
		X _{Anisole} (%)	Y _{CHE} (%)	S _{CHE} (%)	Y _{МСН} (%)	S _{MCH} (%)
1	Ru-Nb ₂ O ₅	68.7	50.9	74.1	8.5	12.3

Table 2 Comparison of the Nb-based catalysts for deoxygenation of anisole^{*a*}

2	Ru-Nb ₂ O ₅ (P)	91.7	46.3	50.4	19.4	21.1
3	Ru-NbOPO ₄	99.3	93.5	94.1	0	0
4	Ru-Nb ₂ O ₅ (com)	48.4	7.4	15.2	12.9	26.6
5	Co-NbOPO ₄	24.5	3.1	12.6	0.3	1.2
6	Ru-SiO ₂	42.8	14.7	34.4	8.7	27.3

Reaction conditions: anisole: 0.1 g, catalyst: 0.1 g, reaction temperature: 170° C, H₂ pressure: 1 MPa and reaction time: 2 h.

^a A small amount of cyclohexanol in the product was not quantified.

In order to determine the specific properties of the Nb-based catalysts, detailed characterizations were conducted. Optical images of the as-obtained Nb-based catalysts are shown in Fig. S1. SEM (Fig. S2) and TEM (Fig. 1) results showed that the morphologies of Nb₂O₅, Nb₂O₅(P) and NbOPO₄ obviously changed from nanoparticles to nanosheets. The TEM also displayed that the Ru nanoparticles were uniformly distributed on the nanosheet supports (Fig. 1a–c) with an average particle size decreasing from 4.5 nm on Ru-Nb₂O₅ to 3.5 nm on Ru-NbOPO₄ (Fig. 1d–f). EDS showed that the molar ratios of P/Nb in the three catalysts changed significantly with the addition of different kinds of phosphorus sources (Table S1). The molar ratio of P/Nb increased as the pH of the phosphorus precursor decreased. Nitrogen adsorption-desorption isotherms showed that the supports and corresponding catalysts were porous (Fig. S3). The porosity properties are summarized in Table S2. It can be seen that the addition of phosphorus sources in the precursor solution decreased the surface area in order from Nb₂O₅ to NbOPO₄. After loading the Ru nanoparticle, the surface area and pore volume decreased for all three catalysts.



Fig. 1 TEM images of (a) Ru-Nb₂O₅, (b) Ru-Nb₂O₅(P) and (c) Ru-NbOPO₄; The particle size distributions of (d) Ru-Nb₂O₅, (e) Ru-Nb₂O₅(P) and (f) Ru-NbOPO₄.

In order to understand the acidic properties of the Nb-based catalysts well, systematic studies of NH₃-TPD (Fig. 2) and Py-FTIR (Fig. 3) were undertaken. Three main NH₃ desorption peaks in the regions of 100–200°C (T₁), 200–500°C (T₂) and 500–800°C (T₃) are shown in Fig. 2, which can be assigned to the desorption of NH₃ from weak, medium and strong acid sites, respectively [52]. The distribution and the quantitative estimation of acidity are summarized in Table S3. It can be seen that the medium and strong acids of Ru-NbOPO₄ were much higher than those of Ru-Nb₂O₅(P) and Ru-Nb₂O₅. This result could be attributed to the function of the acidic medium H₃PO₄ in the synthesis. The Py-FTIR spectra were used to investigate the types of acidic sites. As shown in Fig. 3, both Lewis acid and Brønsted acid sites could be identified for the three catalysts after evacuation at different temperatures. The quantification of acidity at different temperatures (Table 3) showed that the Lewis acid was much stronger than the Brønsted acid on each catalyst, and the Lewis acid of Ru-NbOPO₄ was stronger than that in the other catalysts. The NH₃-TPD and Py-FTIR results indicated that the addition of different phosphorus substances in the precursor solution influenced the

acidity of the Nb-based catalysts. The differences in acidity may be directly related to the structure of the catalysts. Therefore, the structures of the catalyst were characterized in detail in the following studies.



Fig. 2 NH₃-TPD profile of the Nb-based catalysts.



Fig. 3 FTIR spectra of the Nb-based catalysts after pyridine adsorption and evacuation at different temperatures. B: Brønsted acid sites; L: Lewis acid sites.

Table 3 Strength and distribution of the Lewis and Brønsted acids on the surface of the catalysts by FTIR of pyridine adsorbed at different temperatures

	Evacuated	Py-FTIR (μmol g ⁻¹)							
Catalysts	temperature	Brønsted	Lewis	Total acid	The ratio of				
	(°C)	acid	acid	(B + L)	B/L				
	200	38.38	300.40	338.78	0.13				
Ru-NbOPO ₄	350	24.46	150.25	174.71	0.16				
	450	8.22	46.14	54.36	0.18				
	200	29.04	274.06	303.10	0.11				
Ru-Nb ₂ O ₅ (P)	350	14.68	128.63	143.31	0.11				
	450	9.02	43.68	52.70	0.21				
	200	18.73	180.54	199.26	0.10				
Ru-Nb ₂ O ₅	350	9.55	115.04	124.58	0.08				
	450	0.58	41.23	41.81	0.01				



Fig. 4 The (A) P 2p, (B) Nb 3d and (C) O 1s spectra of the Nb-based catalysts.

The structures of the catalysts were further characterized by XPS, FTIR and Raman. The chemical state of the P, Nb and O elements was investigated by XPS (Fig. 4). The P 2p of Ru-NbOPO4 and Ru-Nb₂O₅(P) was at a similar binding energy of 133.7 eV, which could be assigned to the surface metal phosphate species PO4³⁻ (Fig. 4A) [53, 54]. The addition of a phosphorus substance enhanced the strength of the Brønsted acid in the catalysts [55]. The Nb 3d5/2 of Ru-Nb₂O₅ (206.5 eV), Ru-Nb₂O₅(P) (207.0 eV) and Ru-NbOPO4 (207.4 eV) shifted towards higher binding energies sequentially, which may be due to the variation in the oxidation states of the Nb species (Fig. 4B). The fitting analysis of Nb 3d indicated that Nb⁴⁺ in Ru-Nb₂O₅ was oxidized to the highest valency state Nb⁵⁺ in Ru-NbOPO4 (Fig. S4). The high oxidation state Nb⁵⁺ was more deoxygenated than the low oxidation state Nb⁴⁺ due to its oxyphilicity [33]. The O Is spectra

revealed the different chemical environments of oxygen (Fig. 4C). The O element mainly existed in the binding form of a Nb-O interphase six-membered ring in Ru-Nb₂O₅ (Fig. S5) [56]. The niobium oxygen coordinational octahedron with a binding form of Nb=O appeared in Ru-Nb₂O₅(P), and this form existed dominantly in Ru-NbOPO₄. The different binding forms of Nb with O provided the basis for the acidity of the three catalysts.

The FTIR spectra of the Nb-based supports, the corresponding Ru catalysts, and the peak attributions are shown in Fig. 5A and Table S4. All three Nb-based samples had vibration peaks at 630/582 cm⁻¹, suggesting the Nb-O stretching vibration existed in the Nb-based samples [38, 57]. Ru-NbOPO₄ showed a strong band at 986 cm⁻¹ due to the asymmetric vibration mode of the Nb=O species [58, 59]. A weaker band appeared in Ru-Nb₂O₅(P) at 1005 cm⁻¹ but was lost in Nb₂O₅. This phenomenon was associated with the binding form of Nb and O in the catalysts. The bands around 1620 cm⁻¹ and 900 cm⁻¹ may be related to the bending vibrations of O-H groups [38, 58, 60]. Raman spectroscopy further revealed the relationship between the binding structures and their corresponding acidic properties, as shown in Fig. 5B. It can be seen that the peak shapes of the supports and corresponding catalysts were essentially the same. From the summary of the relationship between the structure and the Raman band frequency in Table S5, it can be seen that three different binding forms of Nb with O were present in Ru-Nb₂O₅(P) and Ru-NbOPO₄ at bands of 675 cm⁻¹, 820 cm⁻¹ and 956 cm⁻¹ [61-65]. An additional band was found at 450 cm⁻¹ on the Ru-NbOPO₄ catalyst, which was in agreement with the stretching modes of the P-O group in the phosphate ion, indicating the P was involved in the catalyst construction [66, 67]. Combined with the acidity measurements (NH₃-TPD and Py-FTIR) and the structural analysis (XPS, FTIR and Raman), the origin of the acidic properties

for the Nb-based catalysts was further investigated (Fig. S6). It could be inferred that the acid sites originated from their specific molecular structures. The slightly distorted octahedral NbO₆ [61, 62], regular tetrahedral NbO₄ [63, 64] and highly distorted NbO₆ octahedra [63, 65] served as coordinatively unsaturated surface acid sites resulting in Lewis acids. Brønsted acids may be attributed to the presence of Nb-OH and P-OH groups on the surface [55]. For Ru-NbOPO4, the structures of the regular tetrahedral NbO₄ and highly distorted NbO₆ octahedra were present in large quantities, resulting in strong Lewis acidity. In Ru-Nb₂O₅(P), comparatively, these two structures were much less prevalent than that of Ru-NbOPO₄, resulting in a medium Lewis acidity. As to Ru-Nb₂O₅, only the slightly distorted surface NbO₆ octahedra existed, leading to the lowest Lewis acidity among the three catalysts. A large number of phosphorus species effectively enhanced the strength of the Brønsted acid, such as in Ru-NbOPO₄. The combination of strong Lewis acids with strong Brønsted acids made the total acidity of the Ru-NbOPO₄ catalyst far exceed the other two catalysts (Table S3).



Fig. 5 (A) FTIR and (B) Raman spectra of the Nb-based supports and catalysts.

The properties of the metallic Ru species determined the hydrogenation performance of the

catalysts. As the XPS results show in Fig. 6, the Ru 3d spectra of RuCl₃ (Fig. 6a) and unreduced Ru catalysts (Fig. 6b) indicated that both unsupported Ru species and Ru species immobilized on different supports existed in similar cationic states before reduction treatment. After hydrogen reduction (Fig. 6c), the position shifted to the lower binding energy, suggesting the cationic state was successfully reduced to the metallic state. The fitting analysis of the Ru 3d spectra (Fig. S7) indicated that the Ru⁰ species was present on the surface of the three catalysts [68]. The Ru 3d5/2 peaks of Ru-Nb₂O₅(P) and Ru-NbOPO₄ shifted to higher values, implying that there were different degrees of interaction between the active Ru and the Nb-based supports [56]. The existing states of the Ru species on different supports were further investigated by means of H2-TPR (Fig. 7). Since the Nb-based supports were almost irreducible below 500°C, the reduction peaks in the temperature range of 80-500°C should come from the reduction of the cationic ruthenium species [69]. Unsupported RuCl₃ gave a hydrogen reduction peak around 157°C, and the reducibility of the Ru species on different supports was observed in the order of Ru-NbOPO₄>Ru-Nb₂O₅(P)>Ru-Nb₂O₅ (Fig. 7), correlating well with the catalytic activity. Compared with the other two catalysts, the Ru-NbOPO₄ supported Ru species was more reducible, which may be related to the smaller particle size, the uniform distribution of Ru nanoparticles on the NbOPO4 support, and the interaction between the Ru species and supports [70].



Fig. 6 The Ru 3d spectra of (a) $RuCl_3$ and the Nb-based catalysts, (b) before and (c) after H_2 reduction.



Fig. 7 H₂-TPR of RuCl₃ and the Nb-based supports and catalysts.

The Ru loading in the catalysts showed distinct impacts on the catalytic performance of anisole.

As shown in Fig. S8A, with Ru loading changed from 1 wt% to 10 wt% at 140°C, the anisole conversion and cyclohexane yield increased accordingly, while the methoxycyclohexane yield decreased. However, methoxycyclohexane could not be completely converted to cyclohexane even if the Ru loading increased to 10 wt%. Increasing the reaction temperature had an obvious effect on improving the selectivity of cyclohexane. When the reaction temperature increased to 170°C (Fig. S8B), the cyclohexane yield reached up to 95.5% and the methoxycyclohexane reduced to an undetectable level when Ru loading was 5%. The conversion performance was not further improved by increasing the Ru loading. Therefore, a Ru loading of 5% was considered to be the optimal condition and used in further studies. This may be due to the fact that synergistic catalysis can only be achieved if the surface of the catalyst provides a sufficient amount of both active metal and acid centers. When the Ru loading was less than 5%, few metal sites were provided leading to a poor catalytic performance. However, when the amount of Ru was more than 5%, the catalytic activity decreased due to the increase in the Ru nanoparticle size. Different metal loading also had significant influence on the production of hydrocarbons in other substrate systems [71]. Except for the Ru loading quantities, the particle size of the Ru nanoparticles on the NbOPO₄ support may also affect the catalytic activity. It is well known that the particle size of noble metals plays an important role in the catalytic activities and product distributions [72-74]. According to the experimental results, the size distribution of Ru nanoparticles for the three catalysts was different, and the performances of the catalysts had obvious differences. As the Ru particle size decreased from 4.5 nm on Ru-Nb₂O₅ to 3.5 nm on Ru-NbOPO4, the conversion of anisole increased gradually from 68.7% on Ru-Nb₂O₅ to 99.3% on Ru-NbOPO₄. Therefore, it could be postulated that Ru nanoparticles with smaller particle sizes

are more conducive for hydrodeoxygenation of C_{AR} -O bonds, which is consistent with the above literature [72-74]. In conclusion, the catalytic activity of bifunctional Nb-based catalysts is directly affected by the Ru loading and particle size.

The performances of the prepared Nb-based catalysts were compared with other analogous hydrodeoxygenation catalysts reported in the literature (Table S6). It can be seen that the conversion and the final cyclohexane yield were nearly at the same level for Ru-Nb₂O₅(P) and Ru-Nb₂O₅ as Ru loaded on other acidic supports (Entries 4-7, 15-18, 20, 22, 23, 29, 30), while the cyclohexane yield for Ru-NbOPO₄ was much higher than all other catalysts. Compared with other analogous catalysts, the reaction temperature of the Ru-NbOPO₄ catalyst was significantly reduced to 170°C (Entries 4-30), and the required hydrogen pressure was reduced to 1 MPa (Entries 4-7, 12-24, 28-30). The Ru-NbOPO₄ catalyst prepared in this work exhibited a higher TOF value than most other analogous catalysts (Entries 4-8, 11-20, 22, 25, 27-30) and was only lower than a few catalysts (Entries 10, 21, 23, 24, 26). These results indicate that the prepared Ru-NbOPO₄ catalyst is highly efficient for the deoxygenation of anisole under mild conditions. The relatively high catalytic activity of the Ru-NbOPO₄ catalyst could be attributed to the strong acidity produced by the Nb-O species and the excellent hydrogenation ability of the Ru nanoparticles. The synergistic promotion of these two effects provided more active sites to break CAR-O bonds and hydrogenation of hydrocarbons, and the porosity of the catalyst promoted the mass transfer and thus reduced the hydrogen pressure and shortened the reaction time.

3.2 Effect of the reaction conditions

The effect of catalyst dosage on the conversion of anisole was then studied (Fig. 8). It can be

seen that both the anisole conversion and the cyclohexane yield increased significantly as the molar ratio of the catalyst to anisole increased in the range of 0.012–0.107. However, the methoxycyclohexane yield first increased and then decreased for all three catalysts. When the molar ratio of the catalyst to anisole increased to 0.056, the cyclohexane yield of Ru-NbOPO4 was the highest, reaching 93.5%, and was much higher than Ru-Nb₂O₅(P) and Ru-Nb₂O₅. At the same molar ratio of catalyst to anisole, the anisole conversion for Ru-Nb₂O₅(P) was significantly higher than that for Ru-Nb₂O₅, and the methoxycyclohexane yield also increased obviously. These results may be due to the relatively higher acidity of Ru-Nb₂O₅(P) than Ru-Nb₂O₅, enhancing the deoxygenation activity. For Ru-NbOPO4, when the molar ratio of the catalyst to anisole was 0.056, the anisole conversion and cyclohexane yield reached a maximum, and methoxycyclohexane was no longer generated. Further increasing the ratio only slightly improved the conversion and yield, which indicated a molar ratio of catalyst to anisole of 0.056 was sufficient for the complete deoxygenation of anisole under the studied reaction conditions.



Fig. 8 Effect of the molar ratio of catalyst to anisole on the deoxygenation performance. Reaction conditions: anisole: 0.1 g, decane: 1.0 g, reaction temperature: 170° C, H₂ pressure: 1 MPa and reaction time: 2 h.

The effects of reaction temperature on the hydrodeoxygenation of anisole over Nb-based catalysts were also investigated (Fig. 9). Reaction temperature plays an essential role in the hydrodeoxygenation process. The anisole conversion and cyclohexane yield of the three catalysts were significantly improved with an increase of temperature. On Ru-NbOPO₄ at 120°C, the cyclohexane yield was 39.9% with 13.7% methoxycyclohexane also being created, which came from a coexistence of the DDO and HYD reaction routes. Increasing the temperature from 120°C to 170°C, the cyclohexane yield increased accordingly and the methoxycyclohexane yield decreased remarkably, which strongly suggested the direct cleavage of aromatic C-O bonds in favor of the DDO route at high temperature. Notably, at 170°C, the cyclohexane yield reached the maximum value of 93.5%, while methoxycyclohexane was no longer generated. Clearly, increasing temperature

accelerated the conversion of anisole and reduced the generation of methoxycyclohexane and thus improved the cyclohexane yield. This trend could also be seen on Ru-Nb₂O₅(P) and Ru-Nb₂O₅. Further increasing the tempreture to 190°C, the conversion performance on Ru-NbOPO₄ changed little while that on Ru-Nb₂O₅(P) and Ru-Nb₂O₅ continued to grow. It can be concluded that Ru-NbOPO₄ is a powerful catalyst for hydrodeoxygenation, and a reaction temperature of 170°C is capable of highly selective conversion of anisole into cyclohexane.



Fig. 9 Effect of the reaction temperature on deoxygenation of anisole. Reaction conditions: anisole: 0.1g, decane: 1.0 g, catalyst: 0.1g, H₂ pressure: 1 MPa and reaction time: 2 h.

Besides reaction temperature, H_2 pressure is another key factor for the high yield of cyclohexane, as shown in Fig. 10. The H_2 pressure affected both the anisole conversion and the product distribution. For Ru-Nb₂O₅, Ru-Nb₂O₅(P) and Ru-NbOPO₄, the cyclohexane yield reached the maximum value when the H_2 pressure was 0.5 MPa, 0.75 MPa and 1 MPa, respectively. Further

increasing the H₂ pressure promoted the generation of methoxycyclohexane, and the cyclohexane yield decreased accordingly. On Ru-NbOPO₄, when the H₂ pressure was less than 1.0 MPa, there was no methoxycyclohexane generated. Increasing the H₂ pressure to 3 MPa, a small amount of methoxycyclohexane appeared. GC-MS was used for identifying the product composition in the reactant solution catalyzed by Ru-NbOPO₄, as shown in Fig. S9. The typical GC-MS spectra showed that there was no methoxycyclohexane formation when the hydrogen pressure was 1 MPa (Fig. S9A). In contrast, a certain amount of methoxycyclohexane was detected in the product when the H₂ pressure was 3 MPa (Fig. S9B). The results of the GC-MS further confirmed that H₂ first saturated the aromatic ring, and the subsequent deoxygenation process was achieved at high H₂ pressure, which attributed to the high HYD activity of the Ru active sites [75, 76]. Nevertheless, low H₂ pressure will hinder the hydrogenation of the aromatic rings. Accompanied by the decrease of hydrogenation of the aromatic ring at low hydrogen pressure, the DDO pathway became the dominant reaction owing to the oxytropic performance of the strong acidity [3, 77]. The DDO and HYD coexisted in the Ru-Nb₂O₅(P) catalyzed system (Fig. S10), while only HYD presented in the Ru-Nb₂O₅ system (Fig. S11). Therefore, a combination of the appropriate temperature and H₂ pressure conditions can be used to tailor the reaction product distribution.



Fig. 10 Effect of the H_2 pressure on the deoxygenation of anisole. Reaction conditions: anisole: 0.1 g, decane:1.0 g, catalyst: 0.1 g, reaction temperature: 170°C and reaction time: 2 h.

The influence of the reaction time at different temperatures was also investigated (Fig. 11). It can be seen that the conversion of Ru-Nb₂O₅(P) was much higher than that of Ru-Nb₂O₅, while the difference in the yield was relatively small at the same reaction time. After a 3 h reaction, the cyclohexane yield was still lower than 60%, and the methoxycyclohexane remained on the two catalysts. As for Ru-NbOPO₄, the reaction proceeded quickly within the first 0.5 h, and no methoxycyclohexane formed. Under these experimental conditions, anisole could be completely converted with a high cyclohexane yield of 93.5% within 2 h with a high selectivity of 94.1%, indicating the high efficiency of the catalyst. The performance of Ru-NbOPO₄ under a lower temperature of 100°C was also investigated. As shown in Fig. S12, the cyclohexane yield in the initial reaction stage was relatively low but was enhanced to 90.9% when reaction time was

prolonged to 14 h, but there was still 5.0% methoxycyclohexane that could not be deoxygenated.

100 Ru-NbOPO 80 Conv. 60 CHE Yield CHE Sel. 40 MCH Yield 20 MCH Sel. 0 100 Conv., yield, and sel. (%) Ru-Nb₂O₅(P) 80 60 40 20 0 100 Ru-Nb₂O₅ 80 60 40 20 0 1.0 1.5 2.0 2.5 3.0 0.5 Reaction time (h)

These results imply that Ru-NbOPO₄ can also remove oxygen at a very low temperature.

Fig. 11 Effect of the reaction time on the deoxygenation of anisole. Reaction conditions: anisole: 0.1 g, decane: 1.0 g, catalyst: 0.1 g, H₂ pressure: 1 MPa and reaction temperature: 170°C.

3.3 Reaction pathway for the hydrodeoxygenation of anisole

The results obtained above showed that the catalytic activity and product distribution were significantly affected by the catalyst properties and reaction conditions. According to the above results, two different reaction pathways took place during the hydrodeoxygenation of anisole: DDO and HYD, as shown in Scheme 2. More specifically, in the DDO route, Lewis acid sites were abundantly distributed on the surface of Ru-NbOPO₄. The lone pair electrons of oxygen in the methoxy group of anisole would be adsorbed strongly on the Lewis acid site Nb cations [78, 79], resulting in the activation of the C_{AR} -O bond. The activated C_{AR} -O bond cleaved heterolytically, and

then the positively charged phenyl group could combine with the active hydrogen originating from the dissociation of hydrogen promoted by Ru sites, forming the intermediate benzene. Subsequently, benzene was converted into cyclohexane via hydrogenation. The product distribution on Ru-NbOPO4 (Fig. S9A) showed that only the DDO product dimethyl ether formed, but no other oxygen-containing substances appeared. The Lewis acid sites had strong oxyphilicity [15, 40, 80]. Comparatively, for Ru-Nb₂O₅, the route of HYD was the main reaction pathway. The metallic Ru accepted the delocalized aromatic ring electron, resulting in the activation of the ring, which allowed the nucleophilic addition reaction to occur through the adsorbed H attacking the aromatic rings, anisole methoxycyclohexane completing the conversion of to [78, 81]. Then, the methoxycyclohexane was converted to cyclohexanol and further to cyclohexane via dehydration over the Brønsted acid sites. It was found that no DDO product dimethyl ether was produced (Fig. S11). The generation of the HYD route may result from the insufficient acidity of the Lewis acid on the Ru-Nb₂O₅ catalyst. From the typical GC-MS spectra of Ru-Nb₂O₅(P) (Fig. S10), both dimethyl ether and methoxycyclohexane were present in the products. It can be concluded that both the DDO and HYD pathways were active during the course of anisole hydrodeoxygenation on Ru-Nb₂O₅(P). Lower H₂ pressure favored DDO, while higher H₂ pressure was conducive to HYD. Therefore, the superior performance of the Nb-based material supported Ru catalysts for hydrodeoxygenation of anisole was probably due to the oxophilic sites represented by Nb cations and the efficient hydrogenation of metallic Ru.



Scheme 2 Possible reaction pathway for the deoxygenation of anisole on the Nb-based catalysts.

3.4 Reusability and heterogeneity of the catalyst

The reusability of the Ru-NbOPO₄ catalyst in the deoxygenation of anisole was investigated and shown in Fig. 12. After each reaction cycle, the catalyst was first separated from the liquid phase by centrifugation and washed twice with decane before the next run. Fresh catalyst was not added to compensate for any loss of the catalyst in the prior run. The results showed the anisole conversion at 170°C was above 70%, and about 50% yield of cyclohexane was obtained. After five successive runs, a slight decline in the anisole conversion and cyclohexane yield was observed, and the conversion and yield decreased to 57.6% and 42.6%, respectively. However, the conversion and yield decreased obviously after the catalyst was used five times at 100°C, which decreased to 35.5% and 21.4%, respectively (Fig. S13). The decrease of the catalytic activity may be for two reasons. One is carbon deposition on the catalyst surface, which was confirmed by the weight loss of the used catalyst from the TG analysis (Fig. S14a). The weight loss of fresh catalyst and used catalyst was 6.1% and 11.2% respectively. The weight loss difference of 5.1% could be caused by carbon deposition. The carbon deposition may reduce the surface acidity and specific surface area, even obstructing the contact

between the reactants and the active sites of the catalyst. Another reason may be the aggregation of Ru nanoparticles. SEM-EDS (Fig. S15a-d), XRD (Fig. S14b) and FTIR (Fig. S14c) results demonstrated that the morphology, the composition of elements and the crystal structure of the catalyst did not change significantly after five cycles, but a slight growth or aggregation of Ru nanoparticles was observed for the used catalyst compared with the fresh one via TEM (Fig. S15e-h). The enlargement of the Ru nanoparticles might decelerate the hydrogenation rate owing to a decrease of the active sites in the hydrodeoxidation reaction, leading to a slight decrease of the cyclohexane yield. After being calcined at 500°C for 3 h in a muffle furnace under air and reduced by H₂ at 150°C for 2 h, the activity was almost restored to its initial activity with the same product distribution at different tempertures (Figs. 12 and S13). The leaching and heterogeneity of the catalyst were also studied (Fig. S14d). It was seen that the cyclohexane yield did not increase without the presence of the solid catalysts, confirming that it was a heterogeneously catalytic process and the active species did not leach into the solvent. The above evidence indicated that the Ru-NbOPO₄ presented good stability for the deoxygenation of anisole into cyclohexane in decane media.



Fig. 12 Reusability of the Ru-NbOPO₄ catalyst. Reaction conditions: anisole: 0.1 g, decane: 1.0 g, catalyst: 0.1 g, H₂

pressure: 1 MPa, reaction temperature: 170°C and reaction time: 1 h.

3.5 Conversion of different aromatic ethers and phenols

To get an insight into the possibility of cleaving C-O covalent linkages between aromatic units in lignin under hydrodeoxygenation conditions, the reactivity of other model substances such as veratrole, phenetole, p-cresol, 4-allylanisole, 2,6-dimethoxyphenol diphenyl ether, and 4-ethyl-2-dimethoxyphenol was investigated (Table 4). All of these lignin derivatives converted with high conversion and yield at 170°C within 3 h. A lower reaction temperature (100°C) was also used to investigate the substrate universality of the catalyst. The conversion and cyclohexane yield were improved gradually by prolonging the reaction time at lower temperature. The results showed that Ru-NbOPO₄ also showed excellent activity for the compounds containing hydroxyl phenols. Generally, the cyclohexane yield of anisole, diphenyl ether, veratrole and phenetole reached about 70% at 100°C within 14 h, while the reaction temperature needed to be increased to 120°C to reach the same level of conversion and cyclohexane yield of p-cresol, 4-allylanisole, 2,6-dimethoxyphenol and 4-ethyl-2-dimethoxyphenol. The latter (Entries 5-8) required a higher temperature to achieve similar conversion and cyclohexane yield compared with the former (Entries 1-4), which might be caused by the steric hindrance resulting from long aliphatic chains and the higher bond energies of the phenolic hydroxy structure [82]. These results showed that the Ru-NbOPO₄ catalyst was efficient for the conversion of different aromatic ethers and phenols with various structures.

Entry	Substrate	Product	Temp. (°C)	T (h)	X _{Anisole} (%)	У _{СНЕ} (%)	Sche (%)
1	0	\bigcirc	170	2	99.3	93.5	94.1
1			100	14	97.1	90.9	93.7
2		\bigcirc	170	2	94. 8	93.6	98.8
2			100	14	94.0	70.0	74.5
3	0	\bigcap	170	3	99.4	83.8	84.2
5		\bigvee	100	14	94.9	58.5	61.7
Δ^a	0		170	3	99.8	87.6	87.8
T		100	15	99.7	71.6	71.8	
5	5 OH OH		170	3	99.9	91.9	91.8
5			120	14	97.0	85.9	88.6
6	ОН		170	3	99.9	95.7	95.7
-		Ť	120	14	99.9	85.2	85.3
7	7 OH 7		170	3	98.5	94.1	95.6
1			120	14	99.7	58.4	58.6
8^b			170	3	99.7	94.7	95.0
		Ĵ	120	14	93.6	66.2	70.7

Table 4 Hydrodeoxygenation of aromatic ethers and phenols over the Ru-NbOPO₄ catalyst

Reaction conditions: reactant: 0.1 g, catalyst: 0.1 g, decane: 1.0 g, H_2 pressure: 1 MPa, and the internal standard was dodecane.

^{*a*} Undecane was used as the solvent.

^b Tridecane was used as the internal standard substance.

3.6 Conversion of real bio-oil

Considering the quite high catalytic activity for the hydrodeoxygenation of various phenolic compounds, the Ru-NbOPO₄ catalyst was also used for the hydrodeoxygenation of real bio-oil. The mass balance of the reaction was performed on the basis of the weight of the liquid and solid phases. The mass of the extracted raw bio-oil and the upgraded bio-oil is shown in Table 5. The results showed that the mass remained the same before and after the reaction, which means the mass was in equilibrium. The bio-oil samples were comparatively measured by GC-MS before and after upgrading (Fig. 13), and the detailed components are listed in Table S7. The composition of the raw bio-oil was still extremely complex, and the kinds of detectable compounds reached as high as hundreds of species (Fig. 13, Table S7). It was mainly composed of 5.5% hydrocarbons, 92.2% oxygenated compounds and others (Table 5). The oxygen-containing compounds mainly included ethers, phenols and small amounts of ketones, acids and esters. Catalytic hydrodeoxygenation was carried out to decrease the oxygen content and enhance the quality of the bio-oil. A high yield of hydrocarbons up to 88.2%, was obtained and the content of oxygen-containing chemicals was decreased to 6.9% based on the areas of GC-MS peaks after it was upgraded by the Ru-NbOPO4 catalyst (Table 5). The obtained hydrocarbon products contained alkanes and cycloalkanes, among which cyclohexane, methyl cyclohexane, ethyl cyclohexane and propyl cyclohexane had very high proportions. The Ru-NbOPO₄ catalyst exhibited excellent activity for the hydrodeoxygenation process, and almost all ether and phenolic compounds were converted into hydrocarbons under mild reaction conditions at 170°C. The elemental analysis of the extracted bio-oil and upgraded bio-oil (Table 5) showed that the hydrodeoxygenation over the Ru-NbOPO₄ catalyst reduced the oxygen

content from 2.52% to 0.47%, while increasing the carbon content from 82.25% to 83.65% and hydrogen content from 15.20% to 15.88%, resulting in a low ratio of oxygen to carbon. Moreover, the extracted raw bio-oil was a light brown liquid, and the hydrodeoxygenation product was colorless and clear. This difference between the extracted raw bio-oil and the upgraded bio-oil was probably due to the contribution of the saturation of color-developing groups, such as carbonyls [46]. Compared with the other hydrodeoxidation catalysts reported in the literature [45-49, 83], the catalyst in this work could realize the catalytic conversion of raw bio-oil to hydrocarbons at a lower reaction temperature. The advantage of this work lay in the high hydrocarbon yield and relatively mild reaction conditions.



Fig. 13 GC-MS profiles and real images of the extracted raw bio-oil and upgraded bio-oil. Reaction conditions: hexane extracted raw bio-oil: 3 g, Ru-NbOPO₄: 0.1 g, H₂ pressure: 5 MPa, reaction temperature: 170°C and reaction time: 10 h.

		-		-					-		
	Quantitative analysis ^a (%)				Elemental analysis (wt%)						
Samples	Hydrocarbons	Oxygenated chemicals	Others	Mass ^b (g)	С	Н	N	S	0	H/C	O/C
Extracted bio-oil	5.5	91.8	2.3	2.9874	82.25	15.20	0	0	2.52	18.48	3.06
Upgraded bio-oil	88.2	6.9	4.89	2.9780	83.65	15.88	0	0	0.47	18.98	0.56
Hexane	100	0	0	-	83.85	16.13	0	0	0	19.24	0

Table 5 Comparison of the bio-oil composition before and after upgrading

^{*a*} The contents were calculated based on the peak areas.

^b Mass refers to the mass of hexane extracted raw bio-oil before and after hydrodeoxidation.

The reusability of the Ru-NbOPO₄ catalyst in upgrading real bio-oil was also investigated. After each reaction cycle, the catalyst was first separated from the liquid phase by centrifugation and washed twice with hexane before the next run. After three runs, the hydrocarbon yield decreased slightly from 47.5% to 28.3% (Fig. 14). SEM (Fig. S15a and b), TEM (Fig. 15e and f), and XRD (Fig. 16a) results demonstrated that the morphology and the structure of the Ru-NbOPO₄ did not change significantly before and after use. The ICP-OES results (Table 6) showed that the content of Ru in the recycled catalyst was 1.85%, similar to the level of 2.00% in the fresh catalyst, which was consistent with the EDS results (Fig. 15c and d). However, TG results (Fig. 16b) showed that the used catalyst had a carbon deposit of 4.39%. In addition, the existence of carbon deposition was confirmed by FTIR (Fig. 16c). Therefore, carbon deposition may be the main reason for the decrease of catalytic activity. The hydrocarbon yield was recovered to 34.2% after regeneration.



Fig. 14 The composition of bio-oil after upgrading. The 4th use is the result after regeneration at 500°C for 3 h and being reduced at 150°C for 2 h. Reaction conditions: extracted raw bio-oil: 3 g, Ru-NbOPO₄: 0.1 g, H₂ pressure: 5 MPa, reaction temperature: 170°C and reaction time: 4 h.



Fig. 15 SEM-EDS of the fresh (a, c) and used (b, d) Ru-NbOPO₄; TEM of the fresh (e) and used (f) Ru-NbOPO₄.

Samples	Nb (wt%)	P (wt%)	Ru (wt%)
Fresh Ru-NbOPO ₄	29.53	12.13	2.00
Used Ru-NbOPO ₄	31.30	11.85	1.85

Table 6 The elemental analysis of the fresh and used Ru-NbOPO₄.



Fig. 16 XRD (a), TG (b) and FTIR (c) of the fresh and used Ru-NbOPO₄.

4 Conclusions

In this study, an efficient bifunctional Ru-NbOPO₄ catalyst was synthesized and applied to the hydrodeoxygenation of the model compound anisole to produce cyclohexane and the conversion of real bio-oil. The structure of the Nb-based catalysts was well characterized, and the reaction conditions were systematically investigated. The characterized results indicated that the Ru-NbOPO₄ catalyst possessed the strongest acidity, including the most Lewis and Brønsted acids among the three Nb-based catalysts. The Lewis acid sites originated from the Nb-O bonding structure including the slightly distorted octahedral NbO₆, regular tetrahedral NbO₄ and highly distorted octahedral NbO₆, while the Brønsted acid sites were attributed to the combined action of the P-OH and Nb-OH bonding structure. The improved deoxygenation performance of the Ru-NbOPO₄ catalyst was attributed to the oxophilic sites represented by the Lewis acid sites. The reaction temperature, H₂ pressure and the acidity of the catalysts played essential roles in the reaction pathway and product

distribution. The Ru-NbOPO₄ catalyst could be reused for at least five times, and the activity could be recovered by simple calcination and reduction. Furthermore, the obtained Ru-NbOPO₄ catalyst was efficient for the hydrodeoxygenation of aromatic ethers, phenols and real bio-oil under mild conditions. The hydrocarbon yield after real bio-oil upgrading was up to 88.2%. The high efficiency, mild reaction conditions and excellent stability of the Ru-NbOPO₄ catalyst may give it potential applications in the conversion of renewable lignocellulosic biomass into liquid fuels.

Author Contributions Section

Hongye Zhao: Obtain experimental data, Writing the initial draft, Revision

Xun Hu: Provide raw bio-oil

Jianxiu Hao: Analysis of experimental data

Na Li: Provide analysis tool

Keduan Zhi: Provide instrumentation

Runxia He: Analysis of experimental data

Yunfei Wang: Provide instrumentation

Huacong Zhou: Ideas, Formulation of overarching research goals, Management for the research activity planning and execution

Quansheng Liu: Acquisition of the financial support, Oversight and leadership responsibility for the research activity planning and execution

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