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Investigation on the cleavage of β -O-4 linkage in dimeric lignin model compound over nickel catalysts supported on ZnO-Al₂O₃ composite oxides with varying Zn/Al ratios

Chen Xu^{a,b,1}, Si-Fu Tang^{a,1}, Xianyong Sun^c, Yuanyuan Sun^a, Guangci Li^a, Jingbo Qi^{a,b}, Xiaoyu Li^{a,b}, Xuebing Li^{a,*}

^a Key Laboratory of Biofuels, Qingdao Institute of Bioenergy and Bioprocess Technology, Chinese Academy of Sciences, Qingdao, 266101, PR China

^b University of Chinese Academy of Sciences, Beijing, 100049, PR China

^c National Institute of Clean-and-Low-Carbon Energy (NICE), Beijing, 102211, PR China

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ABSTRACT

Catalytic depolymerization of lignin is still a challenge due to its low conversion and repolymerization of the reactive intermediates. Reductive depolymerization over supported nickel catalysts with probable surface acidic and basic properties is a very promising process. It is therefore very important to investigate the effect of acidity and basicity of the supports on catalytic reactivity. In this paper, we synthesized a series of nickel based catalysts supported on ZnO-Al₂O₃ composites with varying Zn/Al atom ratios (Zn/Al = 2, 3, 5, ∞) and tested their catalytic performances over a model compound 2-phenoxy-1-phenylethanone containing β -O-4 bond. All these catalysts showed 100% conversion by reacting at 250 °C for 2 h under 2 MPa of H₂. Higher selectivity towards ethylcyclohexane could be obtained over the catalyst Ni/ZnO-Al₂O₃-5. The possible cleavage pathways of selective oxidized β -O-4 ether linkage have been proposed.

1. Introduction

The increasing energy demand and fossil fuel depletion have inspired great interest in developing alternative energy sources, especially in direct transformation of biomass into hydrocarbon fuels. Lignin, the second most abundant lignocellulose resource, is rich in aromatic rings and energy density that makes it attractive as a promising renewable bio-resource to produce fuels and chemicals [1]. Although lignin constitutes 15–30% by weight [1,2] and ca. 40% of the energy [1–3] of lignocellulosic biomass, it is currently of low utilization and especially burned as a low value fuel in industrial applications [2]. Lignin is a three-dimensional, highly branched, polyphenolic substance containing plenty of hydroxy- and methoxysubstituted phenylpropane units [4] through several types of C–O–C (β -O-4, α -O-4, 4-O-5, and so on) and C–C (5-5', β -1, β -5, β - β) linkages [2]. Theoretical calculations have revealed that the ether bonds are more fragile than the C-C bonds. Therefore, it is currently feasible to break down the former ones while retaining the latter ones which can be utilized to optimize the composition of traffic fuel via subsequent deoxygenation and hydrogenation at the same time. So, selective cleavage and deoxygenation of $C{-}O{-}C$ bonds are the heart aspects of these conversions.

Some technologies (thermochemical, hydrolytic, reductive, and oxidative approaches) have been proposed to depolymerize the complex lignin into phenolic mixtures which are called bio-oil. Among these technologies, reductive depolymerization has been realized a very promising strategy for the producing of fuel additives and aromatic chemicals. Comparing with other technologies, it combines the depolymerization and hydrodeoxygenation (HDO) reactions in a single step [5]. In the presence of hydrogen, not only the complex structure of lignin can be broken apart but also the oxygen content of the product can be greatly reduced to increase the energy density which is usually denounced in the fast pyrolysis process [6]. For example, Kou and coworkers have reported that lignin can be catalytically depolymerized to yield 46 wt% monomeric phenols over noble metal catalysts (Pt, Ru, Pd, and Rh supported on activated carbon) under 4 MPa of H₂ [7]. Raw woody biomass can be hydrogenated to diols and monophenols (yield: 46.5%, based on lignin) at 235 °C under 6 MPa of H₂ over Ni-W₂C catalyst supported on carbon [8]. Abu-Omar and co-workers reported the selective cleavage and HDO of the β -O-4 ether linkages in wood lignin and model compounds over a bimetallic Pd/C and Zn^{II} catalyst

* Corresponding author.

¹ These authors contributed equally to this paper.

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E-mail address: lixb@qibebt.ac.cn (X. Li).

system under moderate reaction conditions (150–225 °C, 300–500 psi H₂) [9]. Xu and co-workers reported high yields and selectivity of 4-ethylguaiacol and 4-propylguaiacol via the catalytic conversion of lignosulfonate over heterogeneous nickel catalysts [10].

To have a better understanding of the depolymerization mechanism and simplify the analysis of the products, monomeric and dimeric substituted ethers and phenols have been selected as model compounds to mimic the depolymerization and HDO of lignin and lignin-derived bio-oils over supported metal catalysts. The commercial sulfided CoMo and NiMo catalysts, which are widely used in the hydrodesulfurization (HDS) of petroleum, can also be used for the HDO of bio-oil [11]. However this kind of sulfided catalysts can cause serious sulfur contamination and have poor stability. Noble metals (Ru, Pd, Pt, Re, and Rh), base metals (Ni and Cu), and metal phosphides and carbides supported on activated carbon, alumina or silica have also been reported in the hydrocracking/upgrading of lignin model compounds to produce aromatic compounds and alkanes [12-15]. The noble metals show superior catalytic performance than the transition metals while the limited reserves and high cost inhibit their application in a large scale. In recent years, nickel-based catalysts have attracted more and more attentions and shown excellent chemoselectivity for aromatic products or high activity for C-O bond cleavage [16,17]. The work reported by Xu et al. proved that nickel not only had high activity for C-O bond cleavage but also had a propensity towards the protection of the benzene ring [10]. Lercher and coworkers reported that quantitative yields of C5-C9 gasoline-range hydrocarbons could be obtained from hexane-extracted pyrolysis oil over Ni/HZSM-5 under mild conditions (250 °C and 5 MPa H₂) in water [18]. Supported nickel catalyst (Ni/SiO₂) could selectively and quantitatively cleave C-O bonds in aromatic ethers to generate smaller aromatic molecules, cycloalkanes, and cyclohexanol under very mild conditions in water [19].

It should be noted that the surface acidic and basic properties of a catalyst may have a remarkable impact on its catalytic reactivity because of their different adsorption and desorption behaviors towards reactants and products [20]. Metal catalyst supported on acidic supports has been considered as the most effective catalyst for the HDO of lignin and lignin-derived bio-oil. Previous studies have revealed that the hydroprocessing of lignin and lignin-derived bio-oil involves cascade of reactions including hydrogenolysis, hydrolysis, hydrogenation and dehydration [21]. The active metal phase can catalyze the cleavage of Carvi-OH, Carvi-OCH3, and Calkvi-OR bonds via hydrogenolysis whereas the acid sites can catalyze the cleavage of Carvl-OR and Calkyl-OR bonds through hydrolysis. However, this kind of bifunctional catalyst system suffers from remarkable carbon deposition and moderate hydrothermal stability. In contrast, catalysts supported on solid base have long been regarded as robust catalysts and show the resistance to carbon deposition but have moderate HDO catalytic activity [22]. It is therefore highly desirable to combine both the advantages of these two catalytic processes. Additionally, solid base substrates are mesoporous materials which are benefit to the transfer and diffusion of depolymerization monomer. The oxygen vacancy on the solid base surface is similar to that on the sulfide type catalyst surface and is advantageous to the removal of oxygen atoms. In our previous work, it was found suitable amount of basicity on the support was favorable for oleic acid deoxygenation [23]. Nickel catalyst supported on ZnO-Al₂O₃ composites exhibited excellent catalytic activity and stability without obvious coke formation.

In the present work, a series of nickel catalysts supported on ZnO-Al₂O₃ composites with varying Zn/Al atom ratios (Zn/Al = 2, 3, 5, ∞) have been prepared and tested for the hydroprocessing of lignin model compound (2-phenoxy-1-phenylethanone). 2-Phenoxy-1-phenylethanone contains a β -O-4 bond which is the most abundant one among the ether linkages of lignin. Additionally, it has been reported that the selective oxidation of the β -O-4-alcohol to β -O-4-ketone can decrease the bond dissociation energy (BDE) from 274.0 to 227.8 kJ mol⁻¹ and thus facilitates the depolymerization of lignin [24,25]. Therefore, it is quite typical to select it as model compound for the study of lignin depolymerization. The effect of the Zn/Al atom ratio in the support on the cleavage of β -O-4 linkage was investigated and the possible reaction pathways proposed.

2. Experimental

2.1. Catalysts and model compound preparation

The supports were prepared through hydrothermal synthesis process and followed by thermal treatment at high temperature [23]. Briefly, a certain molar ratio of Zn(NO₃)₂·6H₂O, Al(NO₃)₃·9H₂O and urea were dissolved in 40 mL of deionized water to form a colorless solution, where the molar ratio of $[urea]/[NO_3^-]$ was set at 3.0. Then the solution was transferred into a 100 mL Teflon-lined stainless steel autoclave and heated at 180 °C for 3 h. The obtained precipitate was collected by filtration, washed with deionized water to get neutral pH, and then dried overnight in an oven at 80 °C. Finally, the dry substance was calcined in air from room temperature to 500 °C at a heating rate of 2 °C/min and maintained at that temperature for 4 h, leading to the formation of ZnO-Al₂O₃ support. In order to discuss the effect of surface acidic and basic properties of support on the hydroprocessing of dimeric lignin model compound, a series of supports with varying Zn/Al atom ratios (2, 3, 5 and ∞) were prepared using the same procedure as above.

Nickel based catalysts supported on the above ZnO-Al₂O₃ supports were prepared by an incipient wetness impregnation method and the procedure was carried out as follows: An aqueous of solution of Ni $(NO_3)_2$ ·6H₂O (3.4 mmol) corresponding to a 10.0 wt% metal loading was added dropwise onto 1.8 g of the as-prepared ZnO-Al₂O₃ support with continuously agitation at room temperature for 2 h. Then, the obtained substance was dried overnight at 80 °C and calcined in a flow of N₂ at 400 °C for 4 h (flow rate: 100 mL min⁻¹), followed by reduction at 500 °C in a flow of H₂ for 4 h (flow rate: 100 mL min⁻¹). The heating rate for calcination and reduction was 2 °C/min. A series of nickel-based catalysts were then obtained and labeled as Ni/ZnO and Ni/ZnO-Al₂O₃-n (n = 2, 3 and 5), where n indicates the Zn/Al atom ratio.

The dimeric model compound (2-phenoxy-1-phenylethanone) was synthesized from the reaction of phenol with 2-bromoacetophenone according to literature procedure [26]. The detailed synthesis procedure and characterization data can be found in the supporting information (Fig. S1).

2.2. Characterization

The textural properties of supports were determined by nitrogen adsorption/desorption isotherms that were acquired at -196 °C on Micromeritics ASAP 2020 adsorption analyzer. Prior to adsorption-desorption experiments, each sample was degassed in vacuum at 200 °C for 200 min. The specific surface area was calculated by Brunauer-Emmett-Teller (BET) method. The pore volumes and pore size were determined by the Barrett-Joyner-Halenda (BJH) method from desorption branch of the isotherms.

The crystalline structures of supports were characterized by powder X-ray diffraction (XRD) on a Bruker AXS-D8 Advance diffractometer using Cu K α radiation ($\lambda = 1.5406$ Å) generated at 40 kV and 40 mA. The patterns were recorded at a scanning rate of 4°/min from 5° to 80° (2 θ).

The surface basic properties of the catalysts were determined using carbon dioxide temperature programmed desorption (CO₂-TPD) on a Micromeritics AutoChem II 2920 instrument. Each sample was loaded in a U-shaped quartz cell and pretreated in Ar (flow rate: 20 mL min⁻¹) at 150 °C for 2 h (ramp rate: 10 °C min⁻¹), then cooled to 100 °C followed by changing the gas flow to a mixture of 10% vol. CO₂/He

(flow rate: 20 mL min⁻¹) for 150 min. The sample was then cleaned up with He (20 mL min⁻¹) at 100 °C for 1 h to eliminate free adsorbed CO₂. Subsequently, the sample was heated up to 900 °C at a rate of 5 °C min⁻¹ and maintained for 30 min. The desorbed CO₂ was monitored with a thermal conductivity detector (TCD) during this process.

The acid sites in the supports were determined from the IR spectra of adsorbed pyridine (Py-IR) which were recorded at room temperature on a Thermo Nicolet 6700 FTIR Spectrometer with a resolution of 0.5 cm^{-1} . The sample was pressed into a thin self-supporting wafer and activated in a vacuum (p = 10^{-7} mbar) at 350 °C for 1 h (heating rate = 5 °C min⁻¹). After cooling to ambient temperature, the activated sample was exposed to 0.1 mbar of pyridine vapor for 1 h, followed by outgassing at 150 °C for 2 h.

The reduction process of Ni species of the catalysts was investigated by means of hydrogen temperature programmed reduction (H₂-TPR) measurements on a Micromeritics AutoChem II 2920 chemisorption analyzer. Each sample was charged in a U-shaped quartz cell and pretreated in Ar (flow rate: 20 mL min⁻¹) at 300 °C for 1 h (ramp rate: $10 °C min^{-1}$), then cooled to 100 °C. Afterwards, a mixture of 10 vol.%H₂/Ar was introduced into the sample tube at a flow rate of 20 mL min⁻¹. After blowing for 20 min, the sample was heated to 600 °C at a rate of $10 °C min^{-1}$ and maintained at that temperature for 20 min, during which the hydrogen consumption was measured with a TCD detector.

The morphologies of the supports were observed with a Hitachi S-4800 field emission scanning electron microscopy (FE-SEM) with an accelerating voltage of 1.5 kV. The reduced catalysts were ultrasonically dispersed in ethanol and dropped onto a carbon-coated copper grid. Then it was tested by transmission electron microscopy (TEM) analysis which was carried out on a JEM-2100HR electron microscopy with an accelerating voltage of 200 kV. At least 200 Ni particles were measured in order to determine Ni nanoparticle size distribution.

The electronic states of surface active metal of the nickel catalysts were analyzed by means of X-ray photoelectron spectroscopy (XPS) on an Escalab 250Xi Thermo Spectrometer equipped with a monochromatic X-ray source of Al K α under ultra-high vacuum (2–3 × 10⁻⁶ Pa) and a hemispherical analyzer. The XPS data related to the Ni2p core level were recorded for the samples. The obtained spectra were fitted by mixed Gaussian-Lorentzian functions. The respective binding energies (BE) were calibrated against the C1 s peak of carbon (284.8 eV), respectively.

2.3. Catalytic reactions

All the experiments were carried out in a 300 mL batch stainless autoclave equipped with a mechanical stirrer. In a typical reaction, 0.25 g of fresh catalyst, 1.0 g of lignin model compound and 50 mL of nhexane were added into the reactor. Prior to the reaction, the reactor was purged with H_2 for three times to exclude the residue air and then pressurized with H_2 to 2 MPa at ambient temperature. After that, the reaction system was heated to reaction temperature and maintained for a designated time with a stirring rate of 500 rpm. Finally, the reaction system was cooled to ambient temperature, and the liquid products were collected for subsequent analysis. The products were analyzed using GC–MS (Agilent 7890A-5975C) equipped with a flame ionization detector (FID) and a HP-5MS column.

3. Results and discussion

3.1. Characterization of the supports and catalysts

3.1.1. Characterization of the supports

The powder X-ray diffraction patterns of the supports are shown in Fig. 1. After heat treatment, all precursors were transformed to ZnO or ZnO-Al₂O₃ composite oxides. The ZnO sample exhibits sharp peaks at 20 ca. 31.8, 34.5, 36.3, 47.6, 56.6, 62.9, 66.4, 68.0, 69.1, 72.6, 76.9°,

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Fig. 1. XRD patterns of different supports: ZnO (a), ZnO-Al₂O₃-5 (b), ZnO-Al₂O₃-3 (c), ZnO-Al₂O₃-2 (d).

corresponding to the characteristic reflections of ZnO phase (JCPDS #65-3411). For the ZnO-Al₂O₃ composite oxides, their XRD patterns are similar and mainly consisted of ZnO phase and ZnAl₂O₄ phase (JCPDS #55-0669). With the decrease of Zn/Al ratio, the diffraction peaks of ZnO phase get visibly weaker (Fig. 1b–d) while the peaks of ZnAl₂O₄ phase become evident (31.2, 36.8, 44.8, 58.5, 65.4°), indicating the increasing content of spinel phase. The diffraction peaks of ZnO-Al₂O₃ composite oxides are much weaker and broader than those of ZnO, suggesting their modrate crystallinity and highly dispersion of ZnAl₂O₄ phase in ZnO phase.

The pore structure parameters of the supports, including specific surface area (S_{BET}), pore volume and average pore size are shown in Table 1. A clear decreasing trend of S_{BET} with the increase of Zn/Al atom ratio is observed. As we know that particles with smaller size may possess larger S_{BET} . On the contrary, support comprises of larger secondary particles will have a lower S_{BET} , such as ZnO in the present work. Additionally, the change of particle size affects the pore volume of the supports as well. For a certain amount of solid powder, larger particles will occupy more inner space, which leads to a decrease in pore volume.

To investigate the influence of Zn/Al atom ratio on the morphology and microstructure of the supports, all the supports were characterized by means of SEM, and the images are shown in Fig. 2. It can be found that the ZnO-Al₂O₃ composite oxides (Fig. 2d to b) mainly exhibit lamellar and particle morphology and the proportion of lamellar structure as well as their size increased gradually with the increase of Zn/Al atom ratio. At the same time, the shape of these lamellas becomes more regular and smoother (Fig. 2d to a). Combining with the results in Fig. 1, it is proposed that the crystallites of ZnAl₂O₄ phase tend to aggregate into larger irregular particles while that of ZnO phase preferentially grow into regular micro-sheets, and this difference further affects the textural properties of the supports.

To probe the acidities of the supports, IR spectra of adsorbed pyridine (Py-IR) were recorded (Fig. 3). As expected, there was nearly

 Table 1

 Textural properties of the supports with different Zn/Al ratios.

Sample	$S_{BET} (m^2/g)$	Pore volume (cm ³ /g)	Average pore size (nm)				
ZnO-Al ₂ O ₃ -2	121.5	0.21	6.91				
ZnO-Al ₂ O ₃ -3	121.3	0.20	6.60				
ZnO-Al ₂ O ₃ -5	119.2	0.18	6.04				
ZnO	21.05	0.01	1.90				

The average pore size data were calculated by this formula (4 \times Pore volume/S_{BET}).



Fig. 2. SEM images of the supports: ZnO (a), ZnO-Al₂O₃-5 (b), ZnO-Al₂O₃-3 (c), ZnO-Al₂O₃-2 (d).



Fig. 3. The infrared spectra of adsorbed pyridine of the suports: ZnO (a), ZnO-Al₂O₃-5 (b), ZnO-Al₂O₃-3 (c), ZnO-Al₂O₃-2 (d).

no acid in ZnO because of its alkaline character. For the zinc aluminum composite oxide supports, the peaks around 1450 cm⁻¹ clearly indicate the existence of Lewis acid sites, whereas the peaks around 1540 cm⁻¹ are absent, suggesting the composite oxide supports have only Lewis acid sites. The area at 1450 cm⁻¹ for Lewis acid sites increased with the increasing of Al content which suggusted the acidity increased in the support.

3.1.2. Characterization of the catalysts

Fig. 4 shows the diffraction patterns of the catalyst samples. As expected, these catalyst samples exhibit characteristic ZnO and $ZnAl_2O_4$



Fig. 4. XRD patterns of the nickel catalysts: Ni/ZnO (a), Ni/ZnO-Al₂O₃-5 (b), Ni/ZnO-Al₂O₃-3 (c), Ni/ZnO-Al₂O₃-2 (d).

diffraction peaks and these peaks are obvious narrower than those of the corresponding supports, indicating better crystallinity or larger size after calcination and reduction. Besides the ZnO and ZnAl₂O₄ peaks, the diffraction peaks of NiO phase also appear on the catalyst samples ($2\theta = 43.6$ and 62.9° , JCPDS #44-1159) which can be assigned to the (012) and (110) planes. The NiO phase could be formed during the passivation process using 10 vol.% O₂/He. Because of the low content and small particle size, no evident diffraction peak of nickel metal can be detected. But the color change from grey to black after reduction adequately indicated the Ni species on the surface have been reduced.

Table 2

Textural properties of the Ni-based catalysts with different Zn/Al ratios.

Sample	S_{BET} (m ² /g)	Pore volume (cm ³ /g)	Average pore size (nm)				
Ni/ZnO-Al ₂ O ₃ -2	71.2	0.14	7.8				
Ni/ZnO-Al ₂ O ₃ -3	64.5	0.18	11.2				
Ni/ZnO-Al ₂ O ₃ -5	53.0	0.15	11.2				
Ni/ZnO	3.425	0.003	3.5				

The average pore size data were calculated by this formula (4 \times Pore volume/S_{BET}).

The textural properties of the catalysts are shown in Table 2. It is found that the surface area values of the nickel catalysts are obvious less than those of the supports but showing the same trend which decreases with the increasing Zn/Al atom ratio. The introduction of nickel could block the pores of the supports, resulting in smaller BET surface area. The average pore sizes of the catalysts are in the range of 7.8 nm to 11.2 nm, demonstrating their mesoporous characters.

The morphology and metal dispersion of the catalysts were characterized by TEM as shown in Fig. 5. It can be seen that the Ni particles in the four catalysts all display regular shapes and are well dispersed on the composite oxide supports. These Ni particles can steadily attach to the surface of the supports even though the catalysts were prepared at 500 °C, demonstrating the good anti-sintering ability of this kind of composite oxide supports. The Ni particle size decreases from 36.2 nm to 12.1 nm with the Zn/Al atom ratio varies from ∞ to 2. One reason could be related to the specific surface area of the catalysts, because large surface area is advantageous to the dispersion of Ni particles and results in smaller particles. However, the BET surface areas of the supports are very close (see Table 1). The underlying reason could be the Ni-support interaction. Ni species preferably interact with the acidic alumina support to form Ni-O-Al bonds which can potentially inhibit the migration and aggregation of Ni species and improve the dispersion. With the increase of Zn content, the amount of acid sites is decreased and the metal-support interaction is weakened.

The spent catalysts (reaction temperature: 250 °C) were also

characterized using TEM. As shown in Fig. 6, the Ni particles in the used catalysts are still well dispersed. The average particle sizes are around 35.1, 22.3, 18.2, 13.1 nm, respectively, which are very similar to those of fresh catalysts. This indicates that these catalysts are very stable under current reaction conditions.

To gain the basicity information of the catalysts, the catalysts were tested by CO_2 -TPD as shown in Fig. 7. The strength and amount of basic sites are reflected by the desorption temperature and the peak area in the TPD plots, respectively. In this study, the catalysts supported on ZnO-Al₂O₃ composite oxides exhibit similar profiles showing three desorptioni peaks at about 150, 250 and 350 °C, corresponding to weak, moderate and strong basic sites, respectively[27,28]. For the catalysts supported on ZnO, a desorption peak is observed at about 650 °C, suggesting stronger basicity. It can be seen that the total basicity of these catalysts increases with the content of Al, which is consistent to the order of surface area, demonstating that the surface area has a significant influence on amount of basic sites. Among these catalysts, Ni/ZnO-Al₂O₃-5 possesses larger specific surface area and moderate basicity which are advantageous to the reaction.

In order to further explore the force between the support and nickel species, unreduced nickel-based catalysts were tested by H2-TPR as shown in Fig. 8. It was found that the H₂-TPR curves of the unreduced catalysts supported on composite oxides displayed one reduction peak at about 260 °C which could be attributed to the reduction of oxidized nickel nanoparticles by air in the atmospheric environment [29]. Comparing with bulk NiO (reduced at 362 °C) in nature [30], the reduction temperature of "re-oxidized" NiO phase is lower. The sample supported on ZnO displayed a reduction peak at about 400 °C, indicating stronger interaction between the support and NiO. Additionaly, the peak appearing above 500 °C, could be ascribed to the dehydration of Al-OH groups (see Fig. S2) and more difficult reducible NiO because nickel aluminum spinel can be formed from the reaction of Ni species with surface Al-OH groups of the supports. Through integration the area of the reduction peaks, the hydrogen consumptions per gram catalyst before 500 °C are calculated to be: 1.177, 0.471, 0.451,



Fig. 5. TEM of the fresh catalysts: Ni/ZnO (a), Ni/ZnO-Al₂O₃-5 (b), Ni/ZnO-Al₂O₃-3 (c), Ni/ZnO-Al₂O₃-2 (d).



Fig. 6. TEM of the spent catalysts: Ni/ZnO (a), Ni/ZnO-Al₂O₃-5 (b), Ni/ZnO-Al₂O₃-3 (c), Ni/ZnO-Al₂O₃-2 (d). Reaction condition: catalyst 0.25 g, 2-phenoxy-1-phenylethanone (1.0 g), n-hexane (50 mL), H₂ (2.0 MPa), 250 °C, 2 h.



Fig. 7. The CO₂-TPD curves of the catalysts: Ni/ZnO (a), Ni/ZnO-Al₂O₃-5 (b), Ni/ZnO-Al₂O₃-3 (c), Ni/ZnO-Al₂O₃-2 (d).

0.439 mmol g⁻¹ for the unreduced samples supported on ZnO and Zn-Al₂O₃-n (n = 5, 3 and 2), respectively. It should be noted that the theoretical hydrogen consumption is 1.7 mmol g⁻¹ if NiO is totally reduced for all the catalysts, which explains less NiO was reduced in the reduction condition.

In order to determine the electronic states of the surface nickel species, the reduced nickel catalysts were analyzed by X-ray photon-



Fig. 8. H₂-TPR curves of the unreduced catalysts: Ni/ZnO (a), Ni/ZnO-Al₂O₃-5 (b), Ni/ZnO-Al₂O₃-3 (c), Ni/ZnO-Al₂O₃-2 (d).

electron spectroscopy (XPS) as shown in Fig. 9. The two peaks appearing at 879.8 and 873.4 eV can be ascribed to Ni2p_{1/2}, whereas the peaks of Ni2p_{3/2} can be found in this range of 851.9–860 eV and can be deconvoluted into three peaks. The peak at 852.2 eV can be ascribed to the nickel metal phase, while the peaks at 854.6 eV and 856.1 eV belong to the nickel oxide and nickel aluminate phase, respectively [31–33]. The integration of the three peaks reveals the content of nickel

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Fig. 9. XPS spectra of Ni2p for the catalysts: Ni/ZnO (a), Ni/ZnO-Al₂O₃-5 (b), Ni/ZnO-Al₂O₃-3 (c), Ni/ZnO-Al₂O₃-2 (d).

aluminate is the most. It is found the percentage of surface metallic nickel decreases with the Zn/Al ratio reaching a minimum at Zn/Al = 5 and increasing again for Ni/ZnO (see Fig. S3).

XPS measurements were also performed on the used catalysts to explore the change of oxidation state of nickel after reaction (reaction temperature: 250 °C) (Fig. 10). It was found the percentages of surface metallic nickel in the used catalysts except Ni/ZnO-Al₂O₃-2 increased because the catalysts were further reduced during the reactions. It was also found that the increasing extent reduced with the increasing of Al content (see Fig. S3). The reason should be that nickel aluminum spinel phase in the catalysts increased with the decreasing of Zn/Al ratio. Additionally, with the increase of surface area of the catalysts, the nickel particles became well dispersed and smaller which were difficult to reduce due to size effect.

3.2. Role of the support

In order to investigate the role of acidic and basic properties of the support on the catalyst activity, the hydrotreating experiments of 2-phenoxy-1-phenylethanone over different nickel catalysts with varying Zn/Al atom ratios were performed, and the results are summarized in Fig. 11. From the reaction results, it was found that complete conversions of 2-phenoxy-1-phenylethanone could be achieved for all catalysts at 250 °C with ethylcyclohexane, ethylbenzene and cyclohexanol being the main products. With the increase of Zn/Al atom ratio from 2 to 5, the selectivity of ethylcyclohexane increased from 20.4% to 45.2% while the selectivity of ethylbenzene decreased from 29.9% to 4.5%. This indicates the hydrogenation and deoxygenation performance of

the catalysts could be improved by increasing the Zn/Al atom ratio of the support. On the contrary, aromatic ring can be retained and results in high selectivity towards ethylbenzene. From the above results, it may be concluded that bond cleavage (hydrogenolysis) and hydrogenation of the dimeric model compound are favored over the highly basic support. However for the catalyst supported on pure ZnO (Ni/ZnO), the selectivity of ethylcyclohexane (15.0%) was even lower than that of Ni/ ZnO-Al₂O₃-2 (20.4%). Probably, it could be ascribed to the smaller specific surface area of ZnO support which can lead to poor dispersion of the active nickel phase (see Table 2). Considering the high selectivity of ethylcyclohexane obtained on Ni/ZnO-Al₂O₃-5, it was selected as the catalyst for the subsequent studies.

3.3. Effect of reaction temperature

The effect of reaction temperature on the conversion of the dimeric model compound was investigated in the range of 120–250 °C to evaluate the catalytic performance of Ni/ZnO-Al₂O₃-5. As can be seen from Table 3, the conversion of the dimeric model compound at 120 °C was only 20% and 2-phenoxy-1-phenylethanol was the dominant product. This indicates this temperature was favor to the hydrogenation of the carbonyl group but not sufficient for the cleavage of β -O-4 bond. As the temperature was increased from 120 to 190 °C, the conversion increased remarkably from 20 to 100%, demonstrating the significant role of reaction temperature. The content of the three main products (ethylcyclohexane, ethylbenzene and cyclohexanol) also increased gradually while the content of 2-phenoxy-1-phenylethanol reduced from 93.2% to 4.6%. With the further increase of temperature, the selectivity of ethylcyclohexane can be enhanced greatly accompanied



Fig. 10. XPS spectra of Ni 2p for various catalysts after reaction: Ni/ZnO (a), Ni/ZnO-Al₂O₃-5 (b), Ni/ZnO-Al₂O₃-3 (c), Ni/ZnO-Al₂O₃-2 (d). Reaction condition: catalyst 0.25 g, 2-phenoxy-1-phenylethanone (1.0 g), n-hexane (50 mL), H₂ (2.0 MPa), 250 °C, 2 h.



Fig. 11. Product distribution over the catalysts: Ni/ZnO (a), Ni/ZnO-Al₂O₃-5 (b), Ni/ZnO-Al₂O₃-3 (c), Ni/ZnO-Al₂O₃-2 (d). Reaction condition: catalyst 0.25 g, 2-phenoxy-1-phenylethanone (1.0 g), n-hexane (50 mL), H₂ (2.0 MPa), 250 °C, 2 h.

by the reduction of ethylbenzene.

3.4. Reaction routes

Based on the above results, the possible reaction pathways of the dimeric model compound (2-phenoxy-1-phenylethan-1-one) can be proposed as shown in Scheme 1. The conversion of the dimeric model compound mainly proceeds through two parallel competitive pathways.

At relatively lower temperature, the reaction mainly proceeds through the hydrogenation of the keto group in β -O-4-ketone to produce β -O-4alcohol instead of hydrogenolysis of the β -O-4 ether bond. Therefore, the conversion at 120 °C was quite low and 2-phenoxy-1-phenylethan-1-ol was observed as the dominant product. With the increase of temperature, 2-phenoxy-1-phenylethan-1-ol can be either converted to phenethoxybenzene or cleaved into phenol and 1-phenylethan-1-ol via hydrogenolysis. These intermediates can be further converted to cyclohexanol and ethylcyclohexane via cascade reactions of hydrogenolysis-hydrogenation (see Scheme 1(a)). The controlled experiments at 190 °C also confirmed this (see Table S1). The selectivity of 2-phenoxy-1-phenylethan-1-ol diminished with the reaction time while the selectivity of phenethoxybenzene increased with reaction time reaching a maximum at 2 h and decreased again thereafter. There were 10% of phenethoxybenzene and 3.7% of 2-phenoxy-1-phenylethan-1-ol in the products even after three hours of reaction, suggesting that hydrogenolysis could happen at lower temperature but still very slow. When the reaction temperature was further increased above 200 °C, 2phenoxy-1-phenylethan-1-ol and phenethoxybenzene disappeared in the products. With the extension of reaction time, the selectivity of ethylcyclohexane increased while the selectivity of ethylbenzene diminished constantly (see Table S2). The selectivity of cyclohexanol and 1-cyclohexylethan-1-ol remains about 45% and 1.1%, respectively. It could be concluded that the conversion at higher temperature occurred in a different way as illustrated in Scheme 1(b). Because the bond dissociation energy of β -O-4-ketone (227.8 kJ mol⁻¹) is lower than that of β -O-4-alcohol (274.0 kJ mol⁻¹), the dimeric model compound can be first cleaved into acetophenone and phenol via hydrogenolysis at relatively higher temperature. The intermediate acetophenone is then

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Table 3

Product distribution of 2-phenoxy-1-phenylethanone over Ni/ZnO-Al₂O₃-5 as a function of temperature.

Reaction Temperature (°C)	Conversion (%)	Selectivity of the products (%)											
		6	5	OH	o	OH	\downarrow°	Joh	→OH	→°	others		он
120	20.0	0	0.0	FO	0	0	0	0	0	0	0	0	02.2
120	20.0	21	0.9	10.9	15	37	03	10	35	5.8	0	32	93.2 50.4
180	02.0	6.4	14.4	22.1	0.7	6.5	0.5	1.0	2.5	5.0	12	11	34.0
100	100	0.4	25.9	20.7	0.7	0.5	0	1.0	2.0	0.5	1.5	14.0	34.0
190	100	9.3	25.8	39./	0	0	0	2.1	1.0	0	4.0	14.2	4.0
200	100	13.7	26.8	48.9	U	0	0.02	4.6	0	0	4.8	1.3	U
250	100	45.2	4.5	47.0	0	0	0	1.3	0	0	2.0	0	0

Typical reaction conditions: Ni/ZnO-Al₂O₃-5 (0.25 g), 2-phenoxy-1-phenylethanone (1 g), n-hexane (50 mL), H₂ (2 MPa), 2 h, stirred at 500 rpm.

hydrogenated either at the benzene group to produce 1-cyclohexylethan-1-one or at the carbonyl group to produce 1-phenylethan-1-ol, which can be further converted to cyclohexanol and ethylcyclohexane via steps of hydrogenation-hydrogenolysis. indicates the catalyst has outstanding adhesion of the Ni metal on the support and maintained a high catalytic activity during the recycling tests, which have been confirmed by the results of XPS and TEM obtained on the spent catalysts.

3.5. Recycling tests

The recyclability of Ni/ZnO-Al₂O₃-5 was tested in *n*-hexane at 190 °C under 2 MPa H₂ for 2 h (Fig. 12 and Table S3). After each reaction, the catalyst was collected and washed with n-hexane and dried at 70 °C for the next run. From the results, it can be seen that the conversion of lignin model compound (2-phenoxy-1-phenylethanone) slightly decreased from 100% to 95% after three runs of reactions. The selectivities of the main products (ethylcyclohexane, ethylbenzene, cyclohexanol) and the two intermediates (phenethoxybenzene and 2-phenoxy-1-phenylethanol) are very similar in the three runs. This result

4. Conclusion

In summary, the catalytic hydroprocessing of 2-phenoxy-1-phenylethan-1-one, a β -O-4-ketone dimeric lignin model compound, over a series of nickel catalysts supported on ZnO-Al₂O₃ composite oxides was studied. It was found that the Zn/Al atom ratio played an important role in the selectivity of the products. Higher selectivity towards ethylcyclohexane could be obtained by increasing the Zn/Al atom ratio in the catalyst, on the contrary higher selectivity of ethylbenzene could be obtained instead. The reaction temperature had a major impact on the catalytic hydroprocessing of β -O-4-ketone dimeric lignin model com-



Scheme 1. Proposed reaction pathways of 2-phenoxy-1-phenylethanone conversion on $Ni/ZnO-Al_2O_3-5$.





pound. With the increase of temperature, both the conversion and selectivity increased greatly. It was also revealed that the conversion of the dimeric model compound mainly proceeded through two parallel competitive pathways. At relatively lower temperature, the reaction mainly proceeded through the hydrogenation of the keto group in β -O-4-ketone to produce β -O-4-alcohol instead of hydrogenolysis of the β -O-4 ether bond. At relatively higher temperature (above 200 °C), the dimeric model compound can be first cleaved into acetophenone and phenol via hydrogenolysis. The intermediates can be further converted to cyclohexanol and ethylcyclohexane via cascade reactions of hydrogenolysis-hydrogenation. Further work will be undertaken to apply this strategy to the depolymerization of real lignin.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.cattod.2017.05.048.

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