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**High-Efficiency Catalytic Hydrodeoxygenation of Lignin-Derived Vanillin
with Nickel-Supported Metal Phosphate Catalysts**

Jie Gao ^{a, b}, Yang Cao ^{a, b}, Gang Luo ^{a, b}, Jiajun Fan ^c, James H. Clark ^{a, b, c}, Shicheng
Zhang ^{a, b, *}

^a Shanghai Technical Service Platform for Pollution Control and Resource Utilization
of Organic Wastes, Shanghai Key Laboratory of Atmospheric Particle Pollution and
Prevention (LAP3), Department of Environmental Science and Engineering, Fudan
University, Shanghai 200438, China

^b Shanghai Institute of Pollution Control and Ecological Security, Shanghai 200092,
China

^c Green Chemistry Centre of Excellence, Department of Chemistry, University of
York, York, YO10 5DD, UK

* Corresponding author.

Tel/Fax numbers: +86-21-31242297

E-mail address: zhangsc@fudan.edu.cn

Abstract

Lignin is a natural and renewable aromatic raw material of aromatic chemicals and its depolymerization and downstream products conversion has drawn considerable attention. Herein, a series of Ni loaded metal phosphates (Ni/MP, M=Ti, Zr, Nb, La, or Ce) catalysts were fabricated for the hydrodeoxygenation (HDO) of lignin-derived vanillin (VAN) to produce 2-methoxy-4-methylphenol (MMP). It has been demonstrated that 97.25% VAN conversion could be obtained with a yield of 88.39% of MMP under the mild condition of 220 °C and 0.5 MPa H₂ for 30 min with 15wt% Ni/ZrP. The highest activity of Ni/ZrP was attributed to its small Ni particle size, large specific surface area, strong metal-support interaction, and optimal acidity. It has been proven that Ni, Lewis acid sites (LAS) and Brønsted acid sites (BAS) have a synergistic effect in VAN conversion: Nano-sized Ni catalyze the dissociation of H₂ to form active hydrogen species (H^{*}). LAS promote the adsorption and activation of VAN and isopropanol. BAS play a vital role in the dehydration reaction. Additionally, H₂ was the primary hydrogen donor in the system, while isopropanol was the reaction medium as well as the secondary hydrogen donor, helping to reduce the external H₂ supply requirement. By optimizing the reaction conditions and studying the promotion mechanism, we hope to provide an experimental basis for lignin catalytic hydrogenolysis.

Keywords: Vanillin; Nickel; Metal Phosphate; Hydrodeoxygenation; Aromatic Compounds;

1. Introduction

In the past few decades, the fossil energy crisis has drawn wide attention to produce high-quality fuels and value-added chemicals from renewable and sustainable biomass sources [1, 2]. As one of the three major biomass components, lignin is the largest renewable aromatic compound resource in nature, and can be broken down to phenolic compounds (called bio-oil) by various approaches [3, 4]. However, due to the high oxygen content in lignin molecules, bio-oil always has low energy density, high viscosity, and is unstable to combustion, and cannot be utilized directly [5, 6]. Hydrodeoxygenation (HDO) is an effective lignin or bio-oil upgrading strategy for its advantages of mild reaction conditions, high heating value product, and low formation of coke [7, 8].

Vanillin (VAN) is a model biomass phenolic compound derived from lignin. It is also a common component of pyrolysis oil derived from the lignin fraction [9]. Containing three different types of oxygenated functional groups (aldehyde, ether, and hydroxyl), VAN can be selectively hydrogenated into 2-methoxy-4-methylphenol (MMP), which is a potential future biofuel, and has been widely used in fragrances or as the intermediate for the manufacture of drugs [10, 11]. Tremendous efforts have been devoted to develop supported noble metal catalysts for their distinguished catalytic performance in VAN HDO process, such as Pd [12, 13], Ru [14] and Au [15]. However, the loss of active metals and the limited reserve of costly noble metals are bottlenecks of such catalytic processes. Moreover, their excessive hydrogenation capacity will inevitably lead to the overhydrogenation of the aromatic ring [16]. Therefore, it is

imperative to develop high-activity, economical and stable non-noble metal catalysts. What is more, their moderate hydrogenation capacity can effectively prevent the aromatic ring from being hydrogenated, thereby improving the selectivity of the targeted aromatic product [17]. As a more cost-effective metal, nickel was widely adopted in the VAN HDO process due to its low cost, high abundance, and marvelous hydrogenation activity [18, 19]. Li et al. developed Ni/CCNTs-X (the Ni nanoparticles supported on carboxylic carbon nanotubes with varied tube diameters) and Ni₂P@YSS catalysts (YSS represents “yolk-shell structure”, and Ni₂P@YSS means Ni₂P particles were like yolk, which were coated with a silica shell), obtaining MMP yields of 78.9% and 65.2%, respectively (above 180 °C, 5 h) [20, 21]. Nie et al. reported that HDO of VAN to MMP in the liquid phase can be achieved with a yield of 48.1% over Ni/NCB-900 (a highly dispersed Ni/N-doped carbon black catalyst) [22]. Fan and co-workers synthesized HD-Ni/N-CMS (highly dispersed Ni at the atomic level anchored on a N-doped carbon molecular sieve) for VAN HDO, achieving 60.0% MMP yield within 1 h at 150 °C [23]. Nevertheless, the activity of reported Ni-based catalysts still lower than that of noble metal catalysts, such as more severe reaction conditions and higher energy consumption, or poorer selectivity. Thus, it is necessary to explore highly efficient Ni-based catalysts for the HDO of VAN under mild reaction conditions.

Catalyst supports also have a significant impact on catalyst activity. Some novel supports, including porous organic polymer [24] and metal-organic framework [23], have been demonstrated due to their excellent catalytic performance in the VAN HDO reaction (Table S3). In recent years, the emergence of metal phosphides (MP) has

aroused a lot of attention because of their environmental friendliness, low cost, facile synthetic routes, and their textural properties, which can be easily modified for the desired chemical transformations [25]. The BAS in MP arises from the presence of geminal P-OH groups, whereas LAS originates from the electron deficient M^{x+} sites (x represents the valence state of the metal) [26]. The research group of Wang extensively studied the activity of niobium phosphate loaded with various noble metals on the conversion of lignin-derived components and lignin to liquid alkanes [4, 27, 28]. They claimed that the BAS could be tuned by regulating phosphorus acid content, and it was efficient for the formation of active hydrogen and the cleavage of the lignin molecule.

Several works have been carried out to prove the good catalytic dehydration activity of solid metal phosphate catalysts, such as titanium phosphates (TiP) [29, 30], zirconium phosphates (ZrP) [29-33], lanthanum phosphate (LaP) [32, 34], and cerium phosphate (CeP) [32, 34]. Loading Ni on metal phosphates to synthesize bi-functional catalysts is a promising approach for the hydrodeoxygenation of lignin-derived compounds. For example, Ma has focused on the selective depolymerization of lignin by ZrP supported Ni catalysts, proving that 87.3% of lignin could be converted to para ethyl phenol with a yield of 6.1 wt% and less than 5.2% char at 260 °C for 4 h [35]. Different metal phosphates possess different amount of LAS that can be explored to optimize the surface acidity of catalysts. The crucial role of metal phosphate in optimizing catalytic performance and the reaction mechanism should be further studied.

Low-carbon alcohols have been widely employed in the VAN HDO reaction as *in situ* hydrogen donors [36]. Isopropanol with a hydrogen capacity of up to 3.3 wt% is a

suitable and noncorrosive hydrogen source. It can be continuously obtained from renewable biomass, and its dehydrogenation products (aldehydes or ketones) can be easily separated from reaction systems [37]. Rinaldi et al. reported that isopropanol is an important hydrogen source in Ni-based catalytic system: the interaction of isopropanol with the Ni(111) surface can cleave both the O-H and the α -C-H bonds [38]. As a result, acetone can be generated and released into the gas phase, and the hydrogen atoms are adsorbed on the Ni surface for hydrogenation reactions. Therefore, the usage of isopropanol as a hydrogen-donor solvent could reduce the requirement of external H₂ supply or high-pressure hydrogen. Consequently, the Ni-catalyzed system, especially its combination with isopropanol as a green reaction solvent, has a great potential for further industrial application in upgrading of lignin-derived platform chemicals in the future.

Therefore, we synthesized a series of Ni loaded metal phosphate catalysts (Ni/MP, M = Ti, Zr, Nb, La, or Ce) with the optimized acid sites and nano-sized Ni particles. The surface modification of phosphorus acid can tune BAS sites and the different metal species (Ti, Zr, Nb, La, or Ce) is responsible for LAS sites. The strong interaction between Ni and MP support could contribute to the formation of Nano-sized Ni particle and accelerate HDO of VAN. A comparative study of the catalytic behavior of different catalysts was carried out in the system using isopropanol as the hydrogen-donating solvent and the Ni/ZrP catalyst showed the highest activity in the HDO of VAN reaction due to the optimal BAS/LAS ratio and high dispersion of Ni species. Moreover, the respective roles of Ni, BAS, and LAS in the H₂ dissociation, adsorption, and

dehydrogenation of VAN were carefully evaluated to prove the crucial factors that may govern the HDO of VAN, and the possible reaction mechanism over Ni/ZrP catalyst was clarified. Reusability tests were also conducted and the Ni/ZrP catalyst showed no obvious activity loss after several cycle runs.

2. Experimental section

2.1. Synthesis of MP

The precursor of various metal phosphates (metal=Ti, Zr, Nb, La, or Ce) were prepared by the mixtures of 50 mL metal chlorides (1.0 mol/L) and 140 mL $\text{NH}_4\text{H}_2\text{PO}_4$ (0.5 mol/L). Then, the obtained white precipitate was washed with deionized water (250 mL \times 8) and dried at 60 °C for 24 h. After drying, the white solid powder was passed through a 100-mesh sieve. Then, it was annealed at 400 °C in the air for 4 h to give the final MP supports.

2.2. Synthesis of Ni/MP

1.0 g MP was impregnated with a $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ solution containing a Ni loading of 15 wt% with continuous stirring at room temperature for 24 h. Then, the solution was dried at 100 °C for 1 h, and then dried overnight in an electric blast drying oven. Finally, after trituration to 100-120 mesh, the solid powder was annealed at 550 °C for 4 h in the air, and reduced at 550 °C for another 4 h in a flow of reducing gas (5 vol. % H_2/N_2). After reduction, it was inactivated in 1% O_2 flow for 4 h to give the final Ni/MP catalyst.

2.3. Characterization of the catalysts

The detailed information on various characterization methods including

transmission electron microscopy (TEM), low-temperature N₂ adsorption-desorption, inductively coupled plasma optical emission spectroscopy (ICP-OES), powder X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), hydrogen temperature-programmed reduction (H₂-TPR), NH₃-temperature-programmed desorption (NH₃-TPD), infrared spectra of pyridine adsorbed catalysts (Py IR) can be found in Supporting Information.

2.4. Typical process for HDO of vanillin

The reactions were carried out in a 50 mL stainless steel batch reactor (MC50, Senlong). In a typical experiment, vanillin (300 mg, 2 mmol), catalyst (30 mg), and isopropanol (20 mL) were added into the reactor before sealing. After purging the reactor with hydrogen for 6 times, a certain pressure of hydrogen was pressurized into it. After cooling to the room temperature, the H₂ pressure was released, and 2 wt% DL-Menthol was introduced as an internal standard. Then, the catalyst was removed from the reaction mixture, and the remained solvent was analyzed by gas chromatography mass spectrometry (GC-MS) (Details were presented in the Supporting Information).

The conversion of vanillin and the selectivity and yield of products were calculated by the following equations:

$$\text{Conversion(\%)} = (1 - W_{\text{feedstock after reaction}} / W_{\text{feedstock}}) \times 100\% \quad (1)$$

$$\text{Yield(\%)} = W_{\text{single product}} / W_{\text{feedstock}} \times 100\% \quad (2)$$

$$\text{Selectivity(\%)} = W_{\text{single product}} / \sum W_{\text{single product}} \times 100\% \quad (3)$$

The poisoning tests were performed by adding 1 mL pyridine to the reaction system. To investigate the stability of the catalyst, the used catalyst was annealed at 550

°C for 4 h in the air to eliminate the deposit carbon, and reduced at 550 °C for another 4 h in a flow of reducing gas (5 vol. % H₂/N₂) before reuse. All the experiments were conducted in triplicate.

3. Results and discussion

3.1. Morphology analysis of catalysts

The morphology and structure of Ni/MP catalysts were studied through TEM, HRTEM, and EDS (Figure 1). Different distributions of Ni particle size were shown in Figure S1 and Table S1. The average size of Ni particles supported on TiP was huge, which was caused by the aggregation of small particles of Ni, which made it difficult to distinguish. The average Ni particle size of Ni/ZrP catalyst was 20.74 nm, which was smaller than that of other catalysts. It is widely recognized that high specific surface area of supports favors the dispersion of metal particles [39]. In addition, strong metal-support interactions also contributed to the generation of small-sized metal particles [40]. Among TiP, ZrP, and NbP, TiP had the lowest specific surface area (237.54 m²/g, Table S2) and the weakest metal-support interaction (Section 3.2), which result in the large Ni particle size of Ni/TiP. The Ni particle size in Ni/ZrP was the smallest due to the large S_{BET} of ZrP (254.45 m²/g, Table S2) and the strong metal-support interaction between Ni and ZrP (Section 3.2). Another possible reason was that Zr could stabilize the active Ni species and prevent its sintering and agglomeration [41]. For Ni/CeP and Ni/LaP, the well-dispersed Ni could be due to that the promotion effects of rare earth elements. Ce and La could regulate the electron property of the metallic active sites due to their unique d-orbit electron structures, thereby increasing the d-orbit electron

density of Ni and improving the dispersion of Ni [42]. The smaller the Ni particles, the more active sites it could provide, which was one of the reasons for its highest catalytic activity (Section 3.3). The lattice spacings of Ni phase in all catalysts were around 0.203 nm, corresponding to the interplanar spacing values of Ni (111). All supports of the prepared catalysts displays an irregular morphology. The elemental mapping images displayed that Ni, Zr, and P were well dispersed on the catalysts, and the high dispersion of Ni species in Ni/ZrP, Ni/CeP, and Ni/LaP catalysts were observed.

Nitrogen adsorption-desorption isotherms are used to evaluate the textural structure of different catalysts, and the corresponding data are shown in Table 1 and Table S2. The bare supports exhibited considerably higher S_{BET} , V_t , and microporosity than their corresponding Ni-loaded catalysts, probably due to the pores were partially blocked by Ni particles. Moreover, Ni/ZrP catalyst possessed the largest specific surface area (132.56 m^2/g) among those five catalysts, which was anticipated to accommodate more catalytic sites. The Ni loadings measured by ICP-OES proved that all Ni/MP catalysts prepared by the impregnation method had about 15 wt% Ni, which is close to the theoretical loading (Table 1).

XRD was adopted to analyze the phase structure of the samples. The powder XRD patterns of TiP, ZrP, and NbP in Figure 2 exhibited two broad peaks in $2\theta=20-40^\circ$ and $40-70^\circ$, indicating their amorphous structures. They are attributable to layered metal pyrophosphate, and are very likely semi-crystalline anhydrous metal hydrogen phosphate [43]. Even calcined at 550°C , there were no individual crystalline peaks in TiP, ZrP, and NbP, confirming their high thermal stability. The results were

consistent with Weingarten [31, 44]. In contrast, the characteristic diffraction peaks at 19.96°, 28.32°, 31.0°, 37.08°, and 41.56° were attributed to (101), (200), (102), (112), and (003) plane of LaP with monoclinic monazite structure (JCPDS file no. 32-0493), respectively [45]. And $2\theta=20.6^\circ, 28.56^\circ, 31.04^\circ, 36.84^\circ, 41.92^\circ, 48.28^\circ,$ and 52.16° were the diffraction peaks of (101), (200), (102), (210), (211), (212), and (220) plane of hexagonal CePO₄ phase (JCPDS file no. 34-1380), respectively [46]. Besides, the peaks at 44.36°, 51.76°, and 76.32° indicated Ni (111), Ni (200), and Ni (220) (JCPDS file no. 04-0850), indicating that all catalysts were loaded with Ni and reduced successfully [47]. However, Ni/TiP, Ni/ZrP, and Ni/NbP showed the reflection of Ni₂P (JCPDS file no. 03-0953) [48, 49], and the high intensity diffraction peak of Ni₂P may affect its catalytic activity due to the loss of active Ni sites and BAS (P-OH groups). We speculated that the formation of Ni₂P was related to the metal-support interaction. Specifically, the strong interaction between Ni and NbP, ZrP, and TiP led to the easy combination of Ni and P, so the diffraction peaks of Ni₂P were obvious in the XRD patterns of Ni/NbP, Ni/ZrP, and Ni/TiP. There were no diffraction peaks of Ni₂P on LaP and CeP, which were also due to the weak interaction between Ni and rare earth phosphates.

3.2. Surface properties of catalysts

XPS was evaluated in order to analyze the chemical composition, interfacial interaction, and chemical composition of the catalysts surface (Figure 3). The peaks of Ni 2p_{3/2} and Ni 2p_{1/2} in Ni/LaP and Ni/CeP were covered by the signal of La and Ce, respectively, so Figure 3 only showed the peaks of Ni 2p_{1/2} in Ni/LaP and Ni 2p_{3/2} in

Ni/CeP. The spectra of Ni 2p exhibited two sets of peaks with binding energy (BE) of 851-854 eV and 866-868 eV, which were assigned to Ni⁰ species. The peaks at 854-857.8 eV and 872-883 eV were attributed to Ni²⁺ species [50]. The presence of Ni⁰ in the catalysts reflected the successful loading and reduction of Ni. The lowest BE of Ni⁰ 2p_{3/2} in Ni/NbP may be due to the lack of phosphorus and surface hydroxyl groups, which was corresponding to the results of Py IR [51].

H₂-TPR was used to investigate the reduction behavior of Ni²⁺ species (Figure 4). Different reduction temperatures were observed due to the strong/weak metal-support interactions existed in the prepared catalysts. The peaks centered at 622 °C and 660 °C in the TPR profiles of Ni/ZrP and Ni/NbP can be assigned to the reduction of NiO species, indicating the strong interaction between Ni species and NbP or ZrP supports [52]. The following experiments also verified that the enhanced metal-support interaction of the Ni/ZrP catalyst can improve the catalytic activity. However, the reduction temperature of NiO loaded LaP or CeP supports was lower (500 °C). It can be due to the fast electron transfer ability of rare earth elements (e.g., La and Ce) that promote the reduction of NiO to Ni [53, 54]. The reduction peaks of Ni/TiP, Ni/ZrP, and Ni/NbP at 800 °C, 795 °C and 775 °C can be corresponded to the reduction of Ni-O-Ti, Ni-O-Zr, and Ni-O-Nb, respectively [55, 56]. It can be due to that Ti, Zr, and Nb with the similar ionic radii (0.60 Å, 0.72 Å, 0.64 Å, and 0.69 Å respectively) can be easily introduced into NiO lattice. The high reduction temperature at 880 °C and 860 °C in Ni/TiP and Ni/ZrP can be assigned as the reduction of Ni₂P [57].

Different acidity would undoubtedly influence the catalytic activity, especially the

strength and types of acidities. Therefore, this study used NH₃-TPD and Py IR to characterize the acidic strength and types in several materials. To shed light on the surface acidic centers, we have undertaken NH₃-TPD studied various compounds. In this study, the gases that desorbed at relatively low temperatures (< 250 °C) come from weak acidic sites, while the gases that desorbed at high temperatures (250 - 500 °C) come from strong acidic sites [58]. As shown in Figure S2, the amount of strong acid site of Ni/ZrP is larger than that of other catalysts, reaching 1.72 mmol/g, but the amount of weak acid sites was low (1.58 mmol/g). On the contrary, Ni/LaP catalyst had the largest amount of weak and total acid sites, up to 3.79 and 4.48 mmol/g, respectively. The amount of strong acid sites of Ni/TiP and Ni/LaP were similar, both about 0.6 mmol/g. In addition, Ni/TiP, Ni/ZrP, and Ni/CeP had similar total acidity, both in the range of 3.07 to 3.44 mmol/g. However, Ni/NbP had the least strong acid sites and total acidity, approximately 0.26 and 2.43 mmol/g, which may be detrimental to the HDO reaction.

The types of acidity present in the sample were determined using pyridine adsorbed FT-IR measurement. Figure 5 showed the concentration and the ratio between BAS and LAS according to the normalization of the peak area of the spectrum. It is widely recognized that M centers in serious Ni/MP catalysts are the LAS and -OH groups on P centers are BAS [59]. As shown in Figure 5, the catalysts had mainly LAS, especially Ni/CeP, which was 168.81 mmol/g, while that in Ni/NbP was the least, only 91.52 mmol/g. In addition, different supports contained different concentration of LAS, while the concentration of BAS was similar. This was because that different M led to a

larger difference in LAS content, but the mole of P used during the catalyst synthesis process was the same. The order of BAS and LAS concentration were all Ni/CeP> Ni/TiP> Ni/LaP> Ni/ZrP> Ni/NbP. Besides, the ratio between BAS and LAS followed the order of Ni/TiP> Ni/ZrP> Ni/LaP> Ni/CeP> Ni/NbP. Specifically, the ratio between BAS and LAS of Ni/NbP and Ni/CeP were too small (0.158 and 0.163), while that of Ni/TiP was the largest, reaching 0.193. Previous studies suggested the hydrodeoxygenation process of VAN required the synergistic effect of BAS and LAS [60, 61]. The value of BAS/LAS ratio that was either too large or too small both might have a negative effect on catalytic activity, as will be discussed in later sections. Therefore, the surface acidity and ratio of BAS/LAS of the catalyst could be optimized and controlled through the selection metal phosphate support.

3.3. Catalytic activity

VAN as a lignin model compound was selected to examine the catalytic HDO activity of various catalysts. The main products from the hydrodeoxygenation of VAN were 4-hydroxymethyl-2-methoxyphenol (HMP), 4-hydroxy-3-methoxybenzylalcohol, isopropyl ether (HMA), MMP, guaiacol (GUA). Only 10.08% of VAN was converted with a low yield of VAN-derived products when no catalyst was used in the system (Figure 6a). The results obtained with the bare supports showed that NbP and ZrP had the higher catalytic activity (VAN conversion were above 30.00%, and HMA yield were above 16.00%), while lower conversion and HMA yield were obtained when using TiP, NbP, and LaP.

The series of Ni/MP catalysts exhibit higher yield of MMP than their

corresponding bare supports, suggesting that Ni phases significantly promotes the catalytic conversion of VAN (Figure 6b). Specifically, Ni/ZrP afforded the highest conversion of VAN (97.25%) and MMP yield (88.39%). When using Ni/LaP and Ni/CeP as catalysts, the conversion of VAN could reach up to 90.00%, and the yield of MMP was slightly lower than that of Ni/ZrP. However, the yields of MMP obtained with Ni/NbP and Ni/TiP were the lowest, only 55.79% and 54.52% respectively. Considering the yields of MMP followed by Ni/ZrP (88.39%) > Ni/CeP (82.64%) > Ni/LaP (78.61%) > Ni/NbP (55.79%) > Ni/TiP (54.52%), Ni/ZrP catalyst was selected for further optimization of catalytic conditions, including catalyst dosage, reaction temperature, reaction time and initial H₂ pressure.

The results depicted in Figure 7a showed that the yield of MMP increased remarkably from 0.79% to 88.39% when the dose of catalyst increased from 0.00 to 0.03 g. The high dosage of the catalyst was wasted since there was no further improvement in VAN conversion and MMP yield when using 0.04 g of Ni/ZrP catalyst. Therefore, 0.03 g was an optimal dosage for this reaction system. The influence of reaction temperature on the conversion of VAN and MMP yield was shown in Figure 7b. The conversion of VAN was low (below 50.00% at 100 °C and 140 °C), and the conversion of VAN were all above 97.00% when the reaction temperature was higher than 180 °C, indicating that VAN could be easily converted at a high temperature. Besides, the yield of HMP increased sharply when the temperature increased from 100 to 140 °C and then decreased rapidly. The HMA yield firstly increased to 57.17% when the temperature was raised from 140 to 220 °C, and then quickly dropped to 2.87%. A

similar trend of the MMP yield in the entire temperature range was also observed. Its yield increased rapidly from 0.29% at 100 °C to 88.39% at 220 °C, and then decreased slightly to 85.15% at 260 °C (Figure S3). It is worth noting that the yield of MMP showed a decline of 4.24% from 220 °C to 260 °C probably due to the formation of coke at a high temperature, which is consistent with the observations by Oregui-Bengoechea et al.⁵³ In addition, high temperature promoted the production of GUA and its yield increased from 0.00% at 100 °C to 1.72% at 260 °C. Therefore, we deduced the conversion path of VAN based on the order in which the products appeared with the increasing temperature: VAN → HMP → HMA → MMP → GUA. At 140 °C, 46.96% of VAN was converted to HMP (selectivity reached 70.42%), which indicated that VAN can be easily hydrogenated to HMP. So, we inferred that the hydrogenation reaction mainly occurred at a relatively low temperature (140 °C). When the reaction temperature reached 180 °C, HMA showed a high selectivity (45.80%) and the selectivity to MMP was 46.19%. VAN could be fully converted into HMA, but HMA were not fully converted into MMP. It was because at this temperature, the cleavage activity of ether bonds in HMA molecules was not high. According to the molecular structure of HMA, we deduced that the generation of HMA was the result of the dehydration of HMP and isopropanol through hydrogen transfer reaction to form ether bonds. Therefore, hydrogen transfer could occur at 180 °C. The effect of reaction time on the HDO of VAN was evaluated as shown in Figure 7c. The HMA yield decreased rapidly from 40.53% to 2.87% and MMP yield increased sharply from 56.88% to 88.39% when increasing the reaction time from 0 to 30 min at 220 °C, while the conversion of

VAN and the yields of main products were not changed when the reaction time was over 30 min. Hence, 30 min was selected as for further condition optimization.

Solvents can act as both a reaction medium and a hydrogen donor during VAN HDO reaction, so the performance by using five types of solvents (e.g., water, methanol, ethanol, n-propanol, and isopropanol) were investigated and shown in Figure 7d. The low conversion of VAN (44.00%) and 30.23% MMP yield were obtained in water, which could be due to the competitive adsorption of water and VAN on the active sites of Ni/ZrP [62]. In contrast, better conversion of VAN to MMP were obtained in low-carbon alcohols. The intermediate products HMA-ME (4-Hydroxy-3-methoxybenzyl alcohol, methyl ether), HMA-DE (4-Hydroxy-3-methoxybenzyl alcohol, diethyl ether), and HMA-NE (4-Hydroxy-3-methoxybenzyl alcohol, n-propyl ether) were obtained when using methanol, ethanol, and n-propanol as solvents, respectively. Previous studies showed that alcohols absorbed extensively on the Ni center surface [63, 64] and competed with substrate molecules. This absorption ability of alcohol decreased as the carbon chain length elongates [64]. For example, the amount of absorbed methanol was approximately twice that of the absorbed ethanol [65]. Obviously, this reduced alcohol absorption released more Ni centers, therefore, a promoted yield of MMP was demonstrated when methanol was replaced by high-carbon alcohols. Besides, the reduction potential of the alcohol increased with the lengthening of the carbon chain [66], which indicated that primary alcohols had higher reduction potentials than secondary alcohols. Namely, secondary alcohols had stronger hydrogen donating capability than primary alcohols, which helped to explain why the VAN HDO reaction

had the best conversion in isopropanol compared to other low-carbon alcohols. In addition, there was almost no conversion of VAN at 100 °C under N₂ atmosphere (1.47% VAN conversion). However, under the same atmosphere at 220 °C, 32.60% conversion of VAN and 13.19% yield of MMP were obtained. The above results demonstrated that isopropanol can act as a hydrogen source to participate in the HDO process, probably through the surface acidic site-promoted Meerwein-Ponndorf-Verley (MPV) path [66]. However, there is a quite high energy barrier for VAN conversion in the case of using isopropanol as the only hydrogen source.

The reaction atmosphere also had a great influence on the conversion of VAN (Figure 7e). When the reaction atmosphere was N₂, the VAN conversion and MMP yield were only 32.60% and 13.19%, respectively. When using H₂ even at different pressures, the conversions of VAN were all above 95.00%, and the MMP yields were approximately 85.00%. The results suggested that as a hydrogen donor, isopropanol could only provide limited active hydrogen for the conversion of VAN to MMP, and the main hydrogen donor of the system was H₂. Therefore, isopropanol used in the system could dissolve VAN and promote the contact between VAN and Ni/ZrP. Moreover, it as a hydrogen donor could provide part of H^{*} used in the hydrogenation reaction [38]. Although H₂ was the main hydrogen donor, the use of isopropanol could help in lowering the external H₂ supply requirement, which meant high-pressure hydrogen was not necessary. In addition, the sufficient hydrogen was a crucial factor to optimize the catalytic activity, and hydrogen pressure had only a mild effect on this reaction. In summary, considering catalytic efficiency, economy and energy consumption, the

optimal reaction system was to convert 2 mmol of VAN in 20 ml isopropanol at 220 °C and 0.5 MPa H₂ for 30 min with 0.03 g Ni/ZrP catalyst.

Different activities of Ni/MP catalysts can be explained as follows: **The poor catalytic activity of Ni/TiP may be due to its large size of Ni particles [67-70]. It is widely acknowledged that when the loading of Ni was the same, the smaller the size, the more active sites, and the higher its hydrogenation activity. In addition, the small metal size reflected the strong metal-support interaction, which was also beneficial for catalytic reactions.** The negative catalytic activity of Ni/NbP was affected by its lack of BAS and LAS. Notably, due to the lack of LAS, the carbonyl groups in VAN could not be fully adsorbed and activated, so the conversion of VAN was slightly lower (93.22%). Low total acidity of Ni/NbP was not conducive to dehydration reaction. The BAS in Ni/NbP was also insufficient to adsorb HMP, and the solvent transfer hydrogenation of HMP with isopropanol was affected and limited, so 3.37% yield of HMP appeared in the final product. In contrast, the good dispersion of Ni particles and suitable acidity of the Ni/ZrP, Ni/LaP, and Ni/CeP catalysts ensured the high VAN conversion and MMP yield. In particular, the best catalytic activity of Ni/ZrP catalyst could be associated with its most strong acid sites (1.72 mmol NH₃/g cat.), nano-sized Ni particles (~20.74 nm), largest specific surface area (132.56 m²/g), strong metal-support interaction, and its suitable acidity (sufficient BAS concentration and moderate BAS/LAS ratios).

In order to gain more insights toward the role of Ni, BAS, and LAS in the HDO of VAN, ZrP, Ni/ZrO₂, and Ni/ZrP catalysts were explored under the same reaction condition. Furthermore, the poisoning tests were performed by adding pyridine to the

reaction system due to BAS and LAS could be poisoned with pyridine [71]. Significant reduce in VAN conversion and MMP yield with Ni/ZrP catalyst were observed in the presence of pyridine (Figure 7f). The VAN conversion and MMP yield dropped from 97.25% to 38.60% and from 88.39% to 9.31%, respectively, which indicated the important role of acid sites for this reaction. On the other hand, VAN conversion and MMP yield dropped to 52.37% and 9.62% with the Ni/ZrO₂ catalyst that was lack of P-OH groups as BAS [72]. Figure S4 demonstrated its small amount of weak, strong, and total acid sites, indicating BAS could contribute to the catalytic activity. As compared with the catalytic performance of ZrP support (31.32% conversion of VAN and 5.21% yield of MMP), it can be concluded that the nano-sized Ni particles and abundant acid sites over the Ni/ZrP catalyst had a synergistic effect for the HDO of VAN to MMP.

3.4. Study on the mechanism of Ni/ZrP for the HDO of VAN to MMP

Based on the above structural characterization and catalytic experimental results, a possible mechanism for the HDO of VAN was tentatively proposed in Scheme 1. The reaction pathways of VAN HDO may be performed via the following: 1) Firstly, VAN was hydrogenated to HMP and this reaction could occur at a relatively low temperature (below 140 °C); 2) Then, HMP transformed into HMA when increasing reaction temperature; 3) After that, MMP formed through the deoxidation of HMA; 4) Finally, small part of MMP could be converted to GUA at above 220 °C.

For this reaction, LAS of the catalyst could activate the carbonyl group of VAN. Meanwhile, the adjacent LAS adsorbed isopropanol through -O of the hydroxyl group. Ni exposed on ZrP can firstly catalyze the dissociation of molecular hydrogen to form

active hydrogen species (H^*). In the first step, H^* attacks the weakened $C=O$ bond in VAN molecule and breaks it, obtaining HMP. A part of it desorbed to form the product, whereas the rest continues to be adsorbed on the BAS of Ni/ZrP. Then, solvent transfer hydrogenation and BAS play vital roles in the dehydration reaction between HMP and the isopropanol to give HMA as products. HMP was difficult to convert to MMP when there was no BAS in the catalyst (Figure S5). The formation of HMP as the intermediate were observed. Finally, large amounts of MMP are generated from the breakage of ether bonds.

The progress of the reaction was significantly affected by temperature. With reference to noble metals that could efficiently catalyze the HDO of VAN to MMP at room temperature [73], the low yield of MMP at a low temperature with Ni/ZrP catalyst was due to the insufficient H^* produced by Ni species. Therefore, when the temperature was lower than 140 °C, the product was mainly HMP. When the temperature increased up to 180 °C, solvent transfer hydrogenation reaction mainly occurred, which was manifested as the generation of HMA. At the same time, part of the ether bond in HMA was broken to produce MMP by the attack of the remaining H^* . When the temperature was higher than 220 °C, Ni could accelerate the formation of H^* . Therefore, HMA could be entirely converted into MMP through the hydrogenation reaction. Both the higher and lower BAS/LAS ratio might have negative effects on catalytic activity. HMA could be entirely converted into MMP through the hydrogenation reaction. On the one hand, the BAS/LAS ratio had a crucial effect on the reaction. Specifically, the high BAS/LAS ratio meant that there was more LAS than the required ones, which could adsorb

excessive VAN and isopropanol, leading to the covering their adjacent BAS, which in turn resulted in fewer BAS to participate in the reaction [74]. On the other hand, the low BAS/LAS ratio meant that the amount of LAS was less than the required value, which directly affected the first step of VAN HDO and the process of entire reaction.

3.5. Catalyst reusability

Ni/ZrP showed the best catalytic performance in the HDO of VAN, and thus, we reused it for three times in order to check its reusability (Figure 8a). It can be noticed that there was no significant change in the conversion of VAN after the third cycle, and the high yield of MMP were observed (82.89%), which proves its stable catalytic performance in cycle runs. After the reaction, the spent catalysts were collected and characterized by XRD, TEM and ICP-OES. The broad peaks between 20-40° and 40-70° showed no significant changes of the fresh and spent catalysts, revealing its stable structure (Figure 8b). Meanwhile, the characteristic peaks at $2\theta=19.8^\circ$, 24.8° , and 33.8° remained, which indicated that Ni was still loaded on ZrP, further mirroring the strong interaction between Ni and ZrP. ICP-OES analysis revealed that almost no leaching of Ni species from solid catalysts to liquid phase after each cycle, and the Ni loading of the spent Ni/ZrP was maintained (around 12 wt%), implying the high stability of Ni/ZrP. It is worth noting that if the catalyst was reused in the next reaction run directly without annealing and reduction steps, the conversion of VAN and the yield of MMP dropped to 62.04% and 29.64% respectively in the third cycle (Figure S6). Additionally, we found that the size of Ni particles became larger (72.59 nm), which may due to the sintering of Ni particles on the surface of the catalyst (Figure S7a). Additionally, the

deposited cook was observed on the surface of the catalyst (Figure S7b-d) and it could cover the active sites, which is the reason for the loss of activity. Carbon deposits can be removed by annealing steps. However, the annealing of catalyst in the air inevitably lead to the oxidation of Ni. So, it is necessary to reduce it in a flow of H₂. Therefore, the regeneration of spent catalysts by further annealing and re-reduction is also a crucial factor for achieving high catalytic activity in the HDO reaction.

4. Conclusion

In this work, a series of Ni/MP (M=Ti, Zr, Nb, La, or Ce) catalysts were synthesized. Ni/ZrP had best catalytic activity and high stability, giving 97.25% VAN conversion with a yield of 88.39% of MMP under the mild condition. Through morphological structure characterization and physicochemical properties analysis, the high catalytic activity of Ni/ZrP is due to the small Ni metal particle size, large specific surface area, strong metal-support interaction, and the optimal acidity. Additionally, the possible reaction mechanism was proposed and highlighted the crucial role of BAS/LAS ratio in the HDO reaction as well as the important role of nano-sized Ni particles in the dissociation of H₂ (the primary hydrogen donor). Furthermore, isopropanol was the reaction medium as well as the secondary hydrogen donor, helping to reduce the external H₂ supply requirement. Through this study, we hope to develop Ni/MP catalyst and provide a better understanding of its structure-catalytic performance for the HDO of lignin/lignin-derived feedstocks.

Notes

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