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 $\begin{array}{l} \textbf{PAPER} \\ \text{Na Ji $et al.} \\ \text{Highly selective demethylation of anisole to phenol over} \\ \text{H}_{4}\text{Nb}_{2}\text{O}_{7} \text{ modified MoS}_{2} \text{ catalyst} \end{array}$ 

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## PAPER

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## 1. Introduction

Phenol, as an important chemical raw material, could be employed for the synthesis of rubber, pesticides, and medicines, the annual demands of which in the global market could reach 8 million tonnes.<sup>1</sup> Now, phenol is prepared by treating benzene and propylene in most chemical industries while the energy crisis has accelerated the search for cleaner phenol production. Lignin hydrogenolysis, which has attracted many researchers' attention in recent years contributing to energy conservation and environmental protection,<sup>2-5</sup> is a relatively green process where the target product phenol could be obtained by breaking the chemical bond in lignin over a suitable catalyst in the presence of hydrogen.<sup>6-9</sup> Breaking the C-O bond of methoxyl in the anisole (CArO-CH3) to obtain phenol efficiently is more realistic and there are reports focused on this reaction, where the catalyst plays the vital role in the product yield. Noble metal,<sup>10-14</sup> non-noble metal,<sup>15,16</sup> sulfides,<sup>17</sup> phosphides,<sup>18-20</sup> and oxides<sup>21,22</sup> have been studied and Mo-based catalysts,

## Highly selective demethylation of anisole to phenol over $H_4Nb_2O_7$ modified $MoS_2$ catalyst<sup>+</sup>

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Hydrogenolysis of lignin to obtain value-added phenolic chemicals is an important approach for its comprehensive utilization. Herein,  $H_4Nb_2O_7$  modified MoS<sub>2</sub> catalyst with short slabs and narrow stacking degree was successfully synthesized by the one step hydrothermal method and used in the selective demethylation of anisole to phenol. The MoS<sub>2</sub>-H<sub>4</sub>Nb<sub>2</sub>O<sub>7</sub>-160 catalyst exhibited the best activity with 97.7% conversion of anisole and 98.0% selectivity of phenol under 3 MPa H<sub>2</sub> pressure at 270 °C for 4 h, which has been rarely reported on anisole transformation over heterogeneous catalysts so far. The characterizations results demonstrated that the H<sub>4</sub>Nb<sub>2</sub>O<sub>7</sub> modification reduced the slab length and stacking degree of MoS<sub>2</sub> during the hydrothermal process and enhanced the acidity property therefore improved the cleavage ability of C<sub>Ar</sub>O-CH<sub>3</sub> bond. This study provides a new scheme for the activity enhancement of MoS<sub>2</sub> in lignin demethylation, laying a foundation on the improvement of lignin utilization and the development of renewable energy strategy.

especially Mo-based sulfides, exhibited good performance in the selective production of phenol from anisole compared with other catalysts.<sup>17,19,23-27</sup> Great efforts have been made to improve the selectivity of phenol from anisole conversion. However, it can also be seen from the summary in Table S1<sup>†</sup> that the reaction temperature needed to be above 350 °C when the phenol yield was greater than 90%. It's meaningful to reduce the reaction temperature for practical applications. Wang et al.<sup>28</sup> have reported a simple method to prepare low crystalline MoS<sub>2</sub> with more active sites exposed and different ways have been studied to improve the catalytic performance of unsupported MoS<sub>2</sub> by changing the slab length and the stacking degree of MoS<sub>2</sub>.<sup>29-33</sup> However, the phenol yield was still influenced by the weak catalyst activity under mild conditions and the generation of benzene at certain temperature.

It is well known that surface acidity also plays an important role in catalytic performance,<sup>34,35</sup> indicating that the product selectivity could be improved availably by changing the amount and strength of surface acidity. Niobium-based acid has been applied to lignin conversion and it demonstrated its ideal properties depending on its abundant surface acidity. Wang *et al.*<sup>36–38</sup> have reported a battery of catalysts containing niobium-based acid for the transformation of lignin and the niobyl acids group owning a high acid amount with a better capacity of C–O bond adsorption as well as the strong synergistic effect of active metals and NbO<sub>x</sub> accelerated the cleavage of C–O bond,

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leading to a higher hydrodeoxygenation activity. A similar phenomenon that the modification of strong solid acid could further improve the cleavage of C-O bond was also observed by Liang,<sup>39</sup> Wang,<sup>40</sup> and Fábio B. Noronha.<sup>14</sup> The introduction of niobium-based acid on the supported MoS<sub>2</sub> was also studied, and it indicated that the addition of niobic acid possessing Lewis acid and Brønsted acid sites could enhance the hydrodesulfurization activity efficaciously, which was ascribed to an increase in the acidic environment, with the crystal length and stacking degree of the MoS<sub>2</sub> particles changed.41-44 Inspired by previous research, we attempted to synthesize the MoS<sub>2</sub> catalyst with more activity sites exposed and simultaneously created the modification of H<sub>4</sub>Nb<sub>2</sub>O<sub>7</sub> on MoS<sub>2</sub>, presuming that the decoration of H<sub>4</sub>Nb<sub>2</sub>O<sub>7</sub> could ameliorate the surface acidity of the catalyst, simultaneously the slab length and stacking degree of MoS<sub>2</sub> could be reduced, resulting in a better cleavage ability of CArO-CH<sub>3</sub> bond. To our knowledge, it was rarely reported about the surface acidity engineering for the enhancement of unsupported MoS<sub>2</sub> in lignin conversion.

Herein, the  $H_4Nb_2O_7$  modified  $MoS_2$  catalysts were synthesized by a one-step hydrothermal method and used for the demethylation of anisole to produce phenol. The optimal synthesis conditions were investigated, and different characterizations were introduced to measure the effect of  $H_4Nb_2O_7$  modification in detail. The influences of resultant conditions were explored, and the suitable reaction conditions was found to maintain higher phenol yield. The reaction pathway was proposed. Finally, the stability of the catalyst was tested and characterized in detail.

#### 2. Experimental section

#### 2.1 Catalyst preparation

The MoS<sub>2</sub>-H<sub>4</sub>Nb<sub>2</sub>O<sub>7</sub> catalyst was prepared by a facile hydrothermal method while MoS2 and H4Nb2O7 were synthesized synchronously. Typically, the steps of MoS2-H<sub>4</sub>Nb<sub>2</sub>O<sub>7</sub>-160 synthesis were as follows: 0.2 g Sn<sub>2</sub>Nb<sub>2</sub>O<sub>7</sub>, 0.92 g ammonium molybdate, and 1.2 g thiourea were dispersed into 48 mL deionized water, and then the mixture was transferred into a 100 mL Teflon-lined stainless autoclave. The pH value was adjusted to 0.9 by adding 12 mL hydrochloric acid into the mixed solution under stirring. The autoclave was sealed and heated in an oven at 160 °C for 12 h. When the reaction finished, the products were separated and washed with deionized water and dried in an oven. The catalyst synthesized under different hydrothermal temperature for 12 h with the Mo/Nb ratio fixed at 7 was denoted as  $MoS_2-H_4Nb_2O_7-X$  (X) is hydrothermal temperature). The catalyst synthesized at 160 °C with the Mo/ Nb ratio fixed at 7 for different hydrothermal time was denoted as  $MoS_2-H_4Nb_2O_7-Yh$  (Y is hydrothermal time). Different ratio catalyst was named MoS2-H4Nb2O7-Z. For comparison, MoS<sub>2</sub>-H<sub>4</sub>Nb<sub>2</sub>O<sub>7</sub>-mix was prepared by fixing MoS<sub>2</sub> and H<sub>4</sub>Nb<sub>2</sub>O<sub>7</sub> physically and the Mo/Nb ratio was 7, same as the optimal synthesis condition. H<sub>4</sub>Nb<sub>2</sub>O<sub>7</sub> and pure MoS<sub>2</sub>

were prepared through the same hydrothermal process at 160  $^{\circ}$ C for 12 h. Sn<sub>2</sub>Nb<sub>2</sub>O<sub>7</sub> was synthesized according to the literature.<sup>45</sup> More details of the preparation were provided in ESI.<sup>†</sup>

#### 2.2 Characterization

The samples were characterized by powder X-ray diffraction on the D8-Focus powder diffractometer operated at 40 kV and 200 mA with Ni-filtered Cu K $\alpha$  irradiation ( $\lambda = 1.5406$  Å). The 2 theta was ranged from 5° to 80° at a speed of 10° min<sup>-1</sup>. Scanning electron microscopy (SEM) was used to test the morphology of the samples. SEM images were obtained on a JSM-7800F thermal field emission instrument. The nitrogen adsorption and desorption isotherms were measured with an ASAP2020M apparatus and the surface area was calculated using the BET method. Catalysts were dehydrated at 300 °C for 12 h before determination. Transmission electron microscopy (TEM) was measured on a JEM-2100F transmission electron microscope to observe the morphology and structure of catalysts. The average length (L)and stack number  $(\bar{N})$  of the slabs were calculated by the eqn (1) and (2), where  $n_i$  was the number of slabs in the unit and  $L_i$  and  $N_i$  were the length of the slab and the stacking number of the unit. n' was the number of Mo atoms along one side of a  $MoS_2$  slab,  $f_e$  was the fraction of Mo atoms at the edge sites, and  $f_{\rm c}$  was the fraction of Mo atoms at the corner sites.

$$ar{L} = \sum_{i=1}^n n_i L_i / \sum_{i=1}^n n_i$$
 (1)

$$\bar{N} = \sum_{i=1}^{n} n_i N_i / \sum_{i=1}^{n} n_i$$
 (2)

$$n_i' = \left(10 \times \frac{\bar{L}}{3.2} + 1\right)/2 \tag{3}$$

$$f_{\rm e} = (6n_i' - 12) / (3n_i'^2 - 3n_i' + 1)$$
(4)

$$f_{\rm c} = 6/(3n_i'^2 - 3n_i' + 1) \tag{5}$$

The chemical valence of each element on the catalyst surface was measured by X-ray photoelectron spectroscopy (XPS) with a ThermoFisher ESCALABTM 250Xi spectrometer. The acidity of the investigated catalysts was tested by NH<sub>3</sub> temperature-programmed desorption (NH<sub>3</sub>-TPD) on a Micromeritics AutoChem II 2920 automatic analyzer. The samples were pretreated at 150 °C for 0.5 h in the N<sub>2</sub> flow. After that, NH<sub>3</sub> was introduced at 50 °C until the samples were saturated. Subsequently, the physically adsorbed NH<sub>3</sub> was swept by inert gas at 100 °C. Afterwards, the catalysts were heated to 700 °C at 10 °C min<sup>-1</sup> and the desorbed NH<sub>3</sub> was detected by continuous effluent gas monitoring equipped with a thermal conductivity detector (TCD). Inductively coupled plasma optical emission spectrometer (ICP-OES) was conducted on a Thermo 7000 series analyzer to test the loss of S and Nb elements in the used catalysts. 0.05 g catalyst was added in 10 mL chloroazotic acid ( $V_{\rm HCl}/V_{\rm HNO_3} = 3/1$ ), then the solution was digested by microwave at 120 °C for at least 20 minutes until completely dissolved. It was transferred to a 1000 mL volumetric flask and diluted for testing.

#### 2.3 Activity evaluation

The catalytic activity measurements were carried out in a 50 mL autoclave. The prepared catalyst (0.135 g) without any pretreatment and anisole solution (20 mL, 0.125 mol L<sup>-1</sup>, *n*-dodecane as the internal standard, *n*-hexane as the solvent) were placed into the autoclave. Hydrogen was used to purge the reactor and kept at an initial pressure. The reaction was carried out at a certain temperature within a specified time. When the reaction finished, the liquid products were separated and analyzed by GC (SP-7890) using a flame ionization detector (FID) with a 30 m × 0.25 mm × 0.25 µm WondaCap WAX capillary column. Conversion and products yield were calculated using the following formula where *c* represented the mole concentration:

Conversion = 
$$\left(1 - \frac{c(\text{residual anisole})}{c(\text{initial anisole})}\right) \times 100\%$$
 (6)

Product yield = 
$$\frac{c(\text{product})}{c(\text{initial anisole})} \times 100\%$$
 (7)

#### 3. Results and discussion

#### 3.1 Catalysts characterization results

To identity the crystal phase structure of the catalysts, XRD measurements were carried out. As shown in Fig. 1, high crystallinity  $H_4Nb_2O_7$  and  $MoS_2$  were synthesized by the hydrothermal method. Peaks located at 14.5°, 27.9°, and 29.2° were matched well with the (111), (311), and (222)



Fig. 1 XRD spectra of  $H_4Nb_2O_7,\ MoS_2,\ MoS_2-H_4Nb_2O_7-mix,\ and MoS_2-H_4Nb_2O_7-160.$ 

lattice planes of  $H_4Nb_2O_7$ .<sup>46</sup> Obviously, the peak at  $2\theta = 14.5^{\circ}$  was much higher than any other peaks, which meant that  $H_4Nb_2O_7$  prepared in this work was dominated by (111) crystal plane. MoS<sub>2</sub> (JCPDS No. 37-1492) represented with broader and gentle peak was related to the poor crystallinity.<sup>47</sup> After the addition of  $H_4Nb_2O_7$ , the position of feature peaks of MoS<sub>2</sub> and  $H_4Nb_2O_7$  were not shifted after the hydrothermal process in comparison with pure MoS<sub>2</sub> and  $H_4Nb_2O_7$  while the intensity of peaks was similar at the same molar ratio of Mo/Nb.

The crystallinity and purity of  $MoS_2-H_4Nb_2O_7$  catalysts prepared under different temperatures were tested by XRD. As shown in Fig. S1,† samples prepared under different hydrothermal temperature presented a similar crystal structure.

And as the hydrothermal temperature increased, the intensity of H<sub>4</sub>Nb<sub>2</sub>O<sub>7</sub> first increased and then decreased, while the sample MoS2-H4Nb2O7-140 showed the best H<sub>4</sub>Nb<sub>2</sub>O<sub>7</sub> purity and crystallinity. It can be seen the XRD spectra of the MoS<sub>2</sub>-H<sub>4</sub>Nb<sub>2</sub>O<sub>7</sub>-180 and MoS<sub>2</sub>-H<sub>4</sub>Nb<sub>2</sub>O<sub>7</sub>-200 catalysts contained few peaks of H<sub>4</sub>Nb<sub>2</sub>O<sub>7</sub> and there were some Nb<sub>2</sub>O<sub>5</sub> formed during the hydrothermal reaction because of the higher temperature. The peaks of MoS<sub>2</sub> represented the same phenomenon which can be seen from the mountain slope around  $2\theta = 14.4^{\circ}$ , the characteristic plane (002) of MoS<sub>2</sub>, which signified the formation of layered structure.48,49 With the increase of temperature, the peak intensity of (002) increased firstly and then decreased. At lower temperatures, less S2- was not sufficient to form the layered structure so the characteristic peaks of (002) of MoS<sub>2</sub> were not obvious and the Mo2S3 component formed unexcepted. MoS<sub>2</sub>-H<sub>4</sub>Nb<sub>2</sub>O<sub>7</sub>-160 represented broader (002) peak with high intensity indicated that a good structure of MoS<sub>2</sub> obtained.<sup>47</sup> While the XRD spectra of the samples prepared under different hydrothermal time, as shown in Fig. S2,† represented that the hydrothermal time had a little influence on the crystal formation. A weak fluctuation of the (002) plane peak intensity could be attributed to the loss of S at the edge of MoS<sub>2</sub> due to the corrosion at low pH value.<sup>47</sup> As the XRD spectra of different Mo/Nb ratio samples shown in Fig. S3,† there were no obvious differences among the peaks of MoS<sub>2</sub>, while the intensity of H<sub>4</sub>Nb<sub>2</sub>O<sub>7</sub> peaks increased with the augment of its content.

The morphological characteristics of the samples were investigated using scanning electron microscopy and the results were shown in Fig. 2. As shown in Fig. 2(a and b), pure  $MoS_2$  consisted of stacked sheets with a smooth surface, and  $H_4Nb_2O_7$  presented as microspheres as shown in Fig. 2(c and d). Microspheres provided more foothold for the growth of  $MoS_2$  particles and the addition of  $H_4Nb_2O_7$  resulted in a decrease in the size of the  $MoS_2$  particles distinctly. Moreover, the agglomeration between  $MoS_2$  particles was effectively inhibited, and the similar phenomena have been obtained by Klimova.<sup>43</sup> Generally, on the one hand, reducing the size and enhancing the particle dispersion of the catalyst could increase the number of active



Fig. 2 SEM images of (a and b)  $MoS_2$  and (c and d)  $MoS_2\text{--}H_4Nb_2O_7\text{--}160.$ 

sites exposed on the margin, which has been proved to be the main factor for the catalytic activity of MoS<sub>2</sub> catalysts.<sup>50</sup> On the other hand, size reduction and dispersion promotion were beneficial to the increase of specific surface area. As expected, after the modification of H<sub>4</sub>Nb<sub>2</sub>O<sub>7</sub>, surface area of the catalyst increased from 6.4 m<sup>2</sup> g<sup>-1</sup> to 15.9 m<sup>2</sup> g<sup>-1</sup>. In a word, the incorporation of an appropriate amount of H<sub>4</sub>Nb<sub>2</sub>O<sub>7</sub> reduced the size and agglomeration of MoS<sub>2</sub> particles and improved the specific surface area of the catalyst, which may provide more exposed active sites for the reaction.

For more direct evidences, the change of the morphology of sulfide active phases was characterized by TEM measurements, and the images were shown in Fig. 3. The typical layered structure was observed and 0.65 nm interplanar distance was attributed to the (002) plane of  $MoS_2$ . The stacking number and the slab length of  $MoS_2$ slabs were statistically analyzed more than 80 stacks from different parts of each sample, and the results were listed in Table 1.  $MoS_2$  showed a lower stacking number and small slab length, which was consistent with XRD results. The increase in MoS<sub>2</sub> dispersion with the embellishment of H<sub>4</sub>Nb<sub>2</sub>O<sub>7</sub> was also agreed with the SEM results. The average length of the MoS<sub>2</sub> phase in the catalysts was reduced from 3.1 nm to 2.4 nm and the stacking degree of the MoS<sub>2</sub> particles was decreased, which were attributed the addition of H<sub>4</sub>Nb<sub>2</sub>O<sub>7</sub> to unsupported MoS<sub>2</sub>. More morphology parameters of MoS<sub>2</sub> in different catalyst were listed in Table S2.<sup>†</sup> The structural model of MoS<sub>2</sub> was described as stacks of several slabs and the active sites were the sulfur vacancy at the edge sites and the corner sites. According to the literature, smaller slab length, which was conductive to more accessible active phase, was beneficial to expose more corner sites where the formation of sulfur vacancy was easier.34,51,52 As shown in Table S2,† the smaller slab length of MoS<sub>2</sub> resulted from the H<sub>4</sub>Nb<sub>2</sub>O<sub>7</sub> modification led to a higher corner-to-edge ratio, which was consistent with the conclusion of the literature. In addition, studies have shown that the shorter slab length was in favor of better hydrodesulfurization capability.43,44 Based on the similarity of the two catalytic reactions and the decrease in the average length of MoS<sub>2</sub> slabs resulted from the modification of H<sub>4</sub>Nb<sub>2</sub>O<sub>7</sub>, a stronger catalytic capability of the MoS<sub>2</sub>-H<sub>4</sub>Nb<sub>2</sub>O<sub>7</sub>-160 sample was expected.

To identify the surface chemical state of the samples, the XPS measurements of the samples were performed, as shown in Fig. 4. As for pure MoS<sub>2</sub>, the XPS spectra of the Mo 3d region showed signals of Mo<sup>4+</sup>, Mo<sup>5+</sup>, Mo<sup>6+</sup>, and S 2s. The presence of Mo<sup>5+</sup> and Mo<sup>6+</sup> on the surface may be related to the formation of oxysulfide species and MoO<sub>3</sub>-like compounds.<sup>41</sup> For the spectra of MoS<sub>2</sub>–H<sub>4</sub>Nb<sub>2</sub>O<sub>7</sub>-160, there were some noticeable differences. The intensity of Mo<sup>4+</sup> and S 2s peaks increased significantly but the intensity of peaks corresponding to Mo<sup>5+</sup> and Mo<sup>6+</sup> were reduced to varying degrees in the spectra of MoS<sub>2</sub>–H<sub>4</sub>Nb<sub>2</sub>O<sub>7</sub>-160, which meant that the concentration of Mo oxide species was reduced. It indicated that there may be an interaction between Mo species and H<sub>4</sub>Nb<sub>2</sub>O<sub>7</sub> so that the incorporation of H<sub>4</sub>Nb<sub>2</sub>O<sub>7</sub>



Fig. 3 TEM images and length distributions of (a-c) MoS<sub>2</sub> and (d-f) MoS<sub>2</sub>-H<sub>4</sub>Nb<sub>2</sub>O<sub>7</sub>-160.

Table 1 Structure properties of the prepared catalysts

Sample	$S_{\rm BET} \left({ m m}^2 ~{ m g}^{-1}  ight)$	Stacking number <sup>a</sup>	Length <sup>a</sup> (nm)
MoS <sub>2</sub>	6.4	5.6	3.1
$MoS_2\text{-}H_4Nb_2O_7\text{-}160$	15.9	4.6	2.4

<sup>a</sup> As determined from TEM micrographs (average value).



could accelerate the reduction process of Mo oxide species. It was clear that the intensity of the S 2s signal on MoS2-H<sub>4</sub>Nb<sub>2</sub>O<sub>7</sub>-160 was higher than that on MoS<sub>2</sub>, corresponding to the S<sup>2-</sup> in MoS<sub>2</sub>, which was positively related to the concentration of activity component on the catalyst surface. This was consistent with the previous SEM and TEM conclusions that niobic acid modification could effectively increase the number of active sites on MoS<sub>2</sub>. The signals located at 161.7 and 162.8 eV were assigned to the S<sup>2-</sup> state and  $S_2^{2^-}$ -like chemical states, respectively. The  $SO_4^{2^-}$  peak located at 168.5 eV on the MoS<sub>2</sub> catalyst was absent on the MoS<sub>2</sub>-H<sub>4</sub>Nb<sub>2</sub>O<sub>7</sub>-160 catalyst, which was consistent with the conclusion that the proper addition of H<sub>4</sub>Nb<sub>2</sub>O<sub>7</sub> could enhance the reduction process to a certain extent so that the sulfidation was promoted. Therefore, the area of S<sup>2-</sup> peak increased after the modifying process, representing the improvement in the content of  $MoS_2$ . As for  $H_4Nb_2O_7$ , the binding energy of Nb had no shift after the combination according to the spectra of Nb 3d shown in Fig. S4.†

The acidity of the catalyst surface plays an important role in its catalytic performance. Fig. 5 represented the NH<sub>3</sub>-TPD profiles of the MoS<sub>2</sub>, MoS<sub>2</sub>-H<sub>4</sub>Nb<sub>2</sub>O<sub>7</sub>-mix, and MoS<sub>2</sub>-H<sub>4</sub>Nb<sub>2</sub>O<sub>7</sub>-160 catalysts. It was well known that the area of the NH<sub>3</sub> desorption peak was related to the total acidity on the catalyst and the strength of acid sites was in connection with the NH<sub>3</sub> desorption temperature.<sup>39</sup> As shown in Fig. 5, peak around 304 °C was identified as the weak acid sites, and peaks centered at 396.3 °C and 434.8 °C were corresponded to the strong acid sites. The total acidity of MoS<sub>2</sub>, MoS<sub>2</sub>-H<sub>4</sub>Nb<sub>2</sub>O<sub>7</sub>-mix, and MoS<sub>2</sub>-H<sub>4</sub>Nb<sub>2</sub>O<sub>7</sub>-160 was 6.3 mmol g<sup>-1</sup>, 16.4 mmol g<sup>-1</sup>, and 16.7 mmol g<sup>-1</sup>, respectively. Results revealed that the modification of  $H_4Nb_2O_7$  increased the desorption peak area and shifted it to a higher temperature, which meant that the concentration and strength of acid sites on the catalysts both increased significantly after the addition of  $H_4Nb_2O_7$ , whether through physical mixing or hydrothermal synthesis. Although both  $MoS_2$ - $H_4Nb_2O_7$ -mix and  $MoS_2$ - $H_4Nb_2O_7$ -160 catalysts had a similar amount of acid sites, the  $MoS_2$ - $H_4Nb_2O_7$ -160 catalyst synthesized by the hydrothermal method exhibited more stronger acid sites than that of the  $MoS_2$ - $H_4Nb_2O_7$ -mix catalyst. The formation of stronger acid sites confirmed that there was a strong interaction between  $MoS_2$  and  $H_4Nb_2O_7$  coming into being



Fig. 5 NH<sub>3</sub>-TPD profiles of H<sub>4</sub>Nb<sub>2</sub>O<sub>7</sub> modified MoS<sub>2</sub> catalysts.

during the hydrothermal synthesis process. Generally, the stronger acid sites, affecting the electron-deficient character of the active metal and enhancing the adsorption of C–O bond, were more favorable for the cleavage of the C–O bond of the methoxy group, which was more conducive to the demethylation of anisole.<sup>14</sup>

Based on the above results, the effects of H<sub>4</sub>Nb<sub>2</sub>O<sub>7</sub> modification and the presence of interaction between MoS<sub>2</sub> and H<sub>4</sub>Nb<sub>2</sub>O<sub>7</sub> can be concluded easily. For one thing, the addition of H<sub>4</sub>Nb<sub>2</sub>O<sub>7</sub> promoted the dispersion of Mo species, then the reduction and sulfidation process were accelerated resulting in the increasing of MoS<sub>2</sub> concentration, as depicted in SEM and XPS results. At the same time, the growth of MoS<sub>2</sub> slabs was slightly influenced due to the modification of H<sub>4</sub>Nb<sub>2</sub>O<sub>7</sub> with shorter slab length and narrow stacking degree obtained. For another, stronger acid sites formed during the hydrothermal process, which were essential for the cleavage of CArO-CH3 bond. In a word, the effects of H<sub>4</sub>Nb<sub>2</sub>O<sub>7</sub> decoration were manifested in the concentration and microstructure change of MoS<sub>2</sub> and the strong interaction between MoS2 and H4Nb2O7 reflected by the more strong acid sites.

#### 3.2 Catalytic activity

To show the advantage of the samples modified with H<sub>4</sub>Nb<sub>2</sub>O<sub>7</sub> prepared by our method, a series of controlled experiments were carried out. As listed in Table 2, the products consisted of phenol, benzene, and cyclohexane, where phenol was the main product. In the absence of a catalyst, little conversion of anisole was obtained. And for the pure H<sub>4</sub>Nb<sub>2</sub>O<sub>7</sub> and MoS<sub>2</sub> catalysts, the yield of phenol was 12.8% and 67.8%, respectively, indicating that H<sub>4</sub>Nb<sub>2</sub>O<sub>7</sub> had almost no activity and the activity of the prepared catalyst mainly came from MoS<sub>2</sub>. For comparison, MoS<sub>2</sub>-H<sub>4</sub>Nb<sub>2</sub>O<sub>7</sub>mix was also tested the catalytic activity and the conversion of anisole was 84.7% and the phenol yield was 74.1%. Higher activity over the MoS<sub>2</sub>-H<sub>4</sub>Nb<sub>2</sub>O<sub>7</sub>-mix catalyst mainly resulted from the difference of acidity amount between the MoS<sub>2</sub> and MoS<sub>2</sub>-H<sub>4</sub>Nb<sub>2</sub>O<sub>7</sub>-mix catalyst, which was consistent with the previous statement that the increase in acidity amount could indeed improve the demethylation ability of the catalyst. Different combination method, different roles H<sub>4</sub>Nb<sub>2</sub>O<sub>7</sub>

Table 2 Catalytic performance in the transformation of anisole to phenol

	Conv.	Yield (%)		
Catalyst	(%)	Phenol	Benzene	Cyclohexane
None	6.2	5.7	0.2	0.3
H <sub>4</sub> Nb <sub>2</sub> O <sub>7</sub>	15.3	12.8	0.5	2.0
$Nb_2O_5$	13.8	12.2	0.0	1.5
MoS <sub>2</sub>	68.9	67.8	0.7	0.4
MoS <sub>2</sub> -H <sub>4</sub> Nb <sub>2</sub> O <sub>7</sub> -mix	84.7	74.1	2.7	2.7
MoS <sub>2</sub> -H <sub>4</sub> Nb <sub>2</sub> O <sub>7</sub> -160	97.7	95.7	0.8	0.6

Reaction conditions: 270 °C, 3 MPa, 4 h.

played. With an appropriate amount of H<sub>4</sub>Nb<sub>2</sub>O<sub>7</sub> added into the catalyst by the hydrothermal method, the yield of phenol improved significantly which reached 95.7% with 97.7% conversion of anisole obtained. The 98% selectivity of phenol was achieved over the MoS2-H4Nb2O7-160 catalyst, which was much higher than the result of MoS<sub>2</sub>-H<sub>4</sub>Nb<sub>2</sub>O<sub>7</sub>-mix, indicating that the hydrothermal method was more conducive to the niobic acid modification process and the activity enhancement. It was worth mentioning that the increase of acid amount of MoS2-H4Nb2O7-mix and MoS2-H<sub>4</sub>Nb<sub>2</sub>O<sub>7</sub>-160 was about the same, while the morphology change and more stronger acid sites formed by the interaction between MoS2 and H4Nb2O7 during the hydrothermal process were more effective in the improvement of cleaving ability of CArO-CH3 bond so the MoS<sub>2</sub>-H<sub>4</sub>Nb<sub>2</sub>O<sub>7</sub>-160 catalyst exhibited better catalytic activity. Compared with the results reported before, the catalyst as prepared in this work could catalyze anisole to obtain high vield phenol under relatively mild conditions, as listed in Table S1.† Furthermore, the formation of benzene was also effectively inhibited at higher temperature, as shown in Table S3.†

According to the characteristic results, the modified catalyst MoS<sub>2</sub>-H<sub>4</sub>Nb<sub>2</sub>O<sub>7</sub>-160, prepared under optimal conditions, showed more stronger acid sites with the microstructure and content change of MoS<sub>2</sub> obtained. On the one hand, lower agglomeration and shorter slab length were beneficial for the exposing of activity sites and the concentration of MoS<sub>2</sub> in the catalyst was increased. More importantly, the stronger acid sites resulted from the interaction between MoS2 and H4Nb2O7 as determined by NH<sub>3</sub>-TPD led to better adsorption and cleavage ability of CAr-O-CH<sub>3</sub> bond in the methoxy group. On the other hand, lower stacking degree of MoS<sub>2</sub> slabs preferred to weaker cleavage capability of C<sub>Ar</sub>–O bond.<sup>29</sup> As a result, the good performance of MoS2-H4Nb2O2-160 in anisole conversion and phenol production under mild conditions was originated from the synergistic effect between MoS<sub>2</sub>, H<sub>4</sub>Nb<sub>2</sub>O<sub>7</sub> and stronger acidic sites, confirming that the addition of H<sub>4</sub>Nb<sub>2</sub>O<sub>7</sub> to MoS<sub>2</sub> was essential for the highly catalytic activity and phenol yield.

The catalytic performance of the catalysts prepared under different conditions was evaluated at 270 °C, 3 MPa for 4 h, and the results were listed. As shown in Table S4,† it was easy to see that the activities of the samples were strongly related to the synthesis temperature. Firstly, the formation of MoS<sub>2</sub> was proved by the XPS results, as shown in Fig. S5.† Besides, the H<sub>4</sub>Nb<sub>2</sub>O<sub>7</sub> modification played diverse degrees of effect on the activity of catalyst at different synthesis temperatures, by comparing the results in Tables S4 and S5.† When the resultant temperature was 120 °C, the anisole conversion and phenol yield over MoS2-H4Nb2O7-120 were just 58.5% and 55.9%, while there was little activity increase. Then with the temperature increased, the yield of phenol over H<sub>4</sub>Nb<sub>2</sub>O<sub>7</sub> modified catalysts showed a parabolic trend and reached the highest point 95.7% when the resultant temperature was 160 °C. However, when the temperature was 200 °C, the

formation of  $Nb_2O_5$  lowered the catalyst reactivity simultaneously (entry 3, Table 2). Only 80.9% conversion of anisole and 76.8% yield of phenol were obtained. Therefore, 160 °C was selected as the optional synthesizing temperature.

The samples obtained at 160 °C with different hydrothermal time and Mo/Nb molar ratios were also tested the breaking ability of CArO-CH3 bond and the results were shown in Tables S6 and S7.† When the hydrothermal time was 6 h, the conversion of anisole was 87.0% and the yield of phenol was 67.3%. Extend the hydrothermal time to 12 h, the conversion of anisole was 97.7% and the yield of phenol reached 95.7%. About 5% yield reduction with further extending hydrothermal reaction time may be related to the loss of S at the edge of MoS<sub>2</sub>, as shown in Fig. S2.† Different Mo/Nb molar ratio determined the content of MoS<sub>2</sub> in the unit catalyst. As shown in Table S7,† the influence of niobic acid addition determined by the different Mo/Nb molar ratios on the catalyst activity became significant with the proportion increasing and it was the greatest when the ratio was 7. Excessive niobic acid may cover the active site of  $MoS_2$ or formed agglomeration so the phenol yield decreased to 72.5% and 60.2% when the ratio was 5 and 4, respectively. Through the control variable experiment, the MoS<sub>2</sub>-H<sub>4</sub>Nb<sub>2</sub>O<sub>7</sub>-160 catalyst prepared under the optimal synthesis condition (the hydrothermal temperature was 160 °C, the hydrothermal time was 12 hours, and the Mo/Nb ratio was 7) exhibited the best catalytic activity and the yield of phenol was the highest 95.7%.

#### 3.3 Studies on different reaction conditions

The temperature has a great influence on the product distributions in lignin hydrogenolysis. The effects of temperature on the anisole conversion reaction were investigated and the results were shown in Fig. S6.† When the temperature increased from 260 °C to 270 °C, the yield of phenol increased from 82.1% to 95.7%, which was attributed to the relatively complete cleavage of the CArO-CH<sub>3</sub> bond. Then as the reaction temperature continued to rise to 300 °C, although an increase in anisole conversion was achieved, suggesting the cleavage of CArO-CH3 bond in anisole could be promoted at the higher temperature, the yield of phenol barely increased due to the formation of side-product benzene. However, compared with the product distributions over MoS<sub>2</sub> (entry 1, Table S3<sup>†</sup>) at 300 °C, less benzene was received under longer reaction time. It also confirmed that the addition of H<sub>4</sub>Nb<sub>2</sub>O<sub>7</sub> limited the cleavage of C<sub>Ar</sub>-O bond. As for the yield of cyclohexane, no significant changes were observed as the reaction temperature increased. Therefore, 270 °C was selected as a critical temperature for the demethylation of anisole in this catalytic system.

The results of anisole demethylation at different initial hydrogen pressures over the  $MoS_2-H_4Nb_2O_7$ -160 catalyst were shown in Fig. S7.† When the initial H<sub>2</sub> pressure was changed from 2 MPa to 3 MPa, the yield of phenol significantly improved from 86.4% to 95.7% while the anisole conversion

increased from 88.5% to 97.7%. Then the yield of phenol increased inconspicuously as the initial hydrogen pressure further increased, which was related to the formation of further hydrogenation products. From the results, it could be concluded that the initial  $H_2$  pressure had a great effect on the conversion of anisole when the pressure was lower, while it had a little influence on the yield of hydrogenation products when the pressure was higher. To retain the phenol yield and save energy as much as possible, the pressure of 3 MPa of  $H_2$  was finally considered as suitable initial  $H_2$ pressure for further study of anisole demethylation.

To explore the reaction pathways, the yield of products at different reaction time under the optimized reaction conditions were carefully analyzed and shown in Fig. S8.<sup>†</sup> When the reaction time was extended to 3 h, the conversion rate of anisole increased from 75.6% to 84.2% and the yield of phenol increased from 74.6% to 83.2%, respectively. A greater increase occurred when the reaction time was extended to 4 h, where the anisole conversion rate increased to 97.7% at the same time the yield of phenol reached 95.7%. However, when the reaction time was further extended, the phenol yield changed little, mainly resulted from phenol deoxidization to produce benzene which was reached from 0.8% to 2.4%. In the process of extending reaction time, the yield of cyclohexane was increased by only 0.5%.

Anisole is a typical lignin monomer, and its hydrodeoxygenation reaction process is studied to describe according to the product distributions shown in Fig. S8.† In the general catalytic reaction, the C-O bond breaking occurs in two ways in the process of hydrodeoxygenation of anisole. Namely, anisole could convert to phenol and benzene by demethylation and demethoxylation, respectively. Direct cleavage of C-O bond via demethoxylation is very difficult due to the strong CAr-O bond energy.<sup>53</sup> It could be seen that production of phenol is the first step of the hydrodeoxygenation of anisole and benzene could be gained by further deoxygenation of phenol. And the side reaction that methyl transferred from the methoxyl to the phenolic rings to form cresols could also occur during the process. Considering that almost no cresol or cresol hydrogenation products existed in our results, we think this step hardly occurred in this catalytic system. Cyclohexane could be obtained by two pathways. One is that phenol undergoes aromatic ring hydrogenation to form cyclohexanone and cyclohexanol which are dehydrated to cyclohexene, then cyclohexane is generated by the complete hydrogenation of cyclohexene. The other way is the benzene hydrogenation. According to the product distributions in this study,



 $\label{eq:scheme1} \begin{array}{l} \mbox{Reaction pathway of anisole over the $MoS_2$-$H_4$Nb_2$O_7$-160 catalyst.} \end{array}$ 

Table 3 Catalytic performance in the transformation of methylanisole to cresol

Substrate	Time (h)	Conversion (%)	Product	Selectivity (%)
	4	81.0		80.5
	6	85.7		92.6
	8	98.1		91.3
	6	96.9		76.8
	6	98.2	Он	77.9
Reaction conditions:	270 °C, 3 MPa.			

cyclohexane was yielded by the hydrogenation of benzene. The reaction of phenol over this catalyst was also tested, and the product consisted of benzene and cyclohexane. Based on the above analysis, the reaction pathway could be summarized as the following steps shown in Scheme 1. The first and foremost step was anisole demethylation to phenol. The further cleavage of the  $C_{Ar}$ -O bond happened to produce benzene. Then, the saturation of benzene yielded cyclohexane. The first step was the main process in this reaction while the next two steps rarely occurred to maintain a high yield of phenol.

#### 3.4 Transformation of other substituted anisole

Besides anisole, the transformation of other substituted anisole to phenols was tested to evaluate the activity of the  $MoS_2-H_4Nb_2O_7-160$  catalyst in lignin conversion. As shown in Table 3, the catalyst represented high activity for the conversion of other ethers to obtain phenols. When 4-methylanisole as the substrate, 92.6% selectivity of *p*-cresol was received by extending the reaction time to 6 h. When the reaction time was further extended to 8 h, 4-methylanisole was almost converted but the selectivity of *p*-cresol was 91.3% with little toluene generated. When the methyl substituted at *ortho* or *meta* position, the substrates were almost converted with 77.9% and 76.8% selectivity of cresol, respectively. Therefore, the  $MoS_2$ - $H_4Nb_2O_7$ -160 catalyst showed ideal activity to cleave the C–O bond of methoxy group to obtain phenols according

Table 4 Recyclability test of  $MoS_2$ -H<sub>4</sub>Nb<sub>2</sub>O<sub>7</sub>-160 in the transformation of anisole to phenol

	Conversion	Yield (%)	Yield (%)			
Run	(%)	Phenol	Benzene	Cyclohexane		
1st	97.7	95.7	0.8	0.6		
2nd	96.0	92.9	2.5	0.6		
3rd	81.4	78.2	1.6	0.6		

Reaction conditions: 270 °C, 3 MPa, 4 h.

to the above results, especially when the methyl was substituted in the *para* position, which may due to the steric and electronic effects resulting in different energy change.<sup>54,55</sup>

#### 3.5 Recyclability of the catalyst

The recyclability of the  $MoS_2-H_4Nb_2O_7-160$  catalyst was investigated over three reaction runs for the transformation of anisole under the optimal reaction conditions. The catalyst recovered from each run was washed with *n*-hexane for several times and then dried at ambient before next use. It was worth mentioning that neither the conversion of anisole nor the yield of phenol had decreased much in the second run, indicating that the catalyst still retained a relatively high activity. As shown in Table 4, it represented a certain deactivation at the third run. The conversion of anisole was decreased from 97.7% to 81.4%, accompanied by the yield of phenol decreased from 95.7% to 78.2%. In



Fig. 6 XRD spectra of fresh  $MoS_2\text{-}H_4Nb_2O_7\text{-}160$  catalyst and used catalyst.



Fig. 7 TEM images of (a) fresh  $MoS_2$ - $H_4Nb_2O_7$ -160 and (b) the sample after the 2nd run.

Table 5  $\,$  ICP analysis of S and Nb content in MoS2–H4Nb2O7-160 before and after used

Sample	S content (wt%)	Nb content (wt%)
Fresh	35.0	7.7
After the 2nd run	23.8	8.5



Fig. 8 SEM images of (a) fresh  $MoS_2$ - $H_4Nb_2O_7$ -160 and (b) the sample after the 2nd run.

order to investigate the reason for the decrease in catalyst activity, several characterization tests were conducted to compare the properties of fresh and the used catalysts. As shown in Fig. 6, it was clear to see that the intensity of diffraction peak of the sample after being used two times had almost content, 32% sulfur loss occurred. Some defects in black layers shown in Fig. 7 were observed, providing a direct evidence of the S loss on active sites.<sup>56</sup> Meanwhile, results showed no Nb element loss took place. As reaction proceeded, as shown in reduced in comparison with the peaks of the fresh sample. The intensity decrease of characteristic crystal plane (002) of  $MoS_2$  might be attributed to the various degrees loss of S, which was supported by the ICP results. As shown in Table 5, the S content decreased from 35.0 wt% to 23.8 wt% after the second run. According to the ratio of actual S content to theoretical S Fig. 8, some particles aggregated and activity sites might be covered so that the conversion and the phenol yield of the third run were lower. As a result, the loss of sulfur and the aggregation may be the main reasons for the decrease in catalyst activity. CS2, which could be used as the sulfiding agent, was added 0.2 mL in each experimental reaction to keep the catalyst activity. As shown in Table S8,† the addition of CS2 was effective to slow down the deactivation of the catalyst.

## 4. Conclusion

The H<sub>4</sub>Nb<sub>2</sub>O<sub>7</sub> modified MoS<sub>2</sub> catalyst with short slabs and narrow stacking degree was successfully synthesized by the one step hydrothermal method and used in the selective demethylation of anisole to phenol. Under 3 MPa H<sub>2</sub> initial pressure and 270 °C for 4 h, MoS2-H4Nb2O7-160 exhibited the best performance with 97.7% conversion of anisole and 98.0% selectivity of phenol which was an ideal phenol yield compared with other heterogeneous catalysts in the previous studies. The stronger CArO-CH3 bond cleavage ability of the MoS<sub>2</sub>-H<sub>4</sub>Nb<sub>2</sub>O<sub>7</sub>-160 catalyst was related to the decrease of the slab length and stacking degree of MoS<sub>2</sub> and the enhancement of the surface acidic sites. Furthermore, the stability of the MoS2-H4Nb2O7-160 catalyst was studied and the recyclability of the catalyst was affected mainly by the loss of S and the aggregation of MoS<sub>2</sub> particles. This research provides a novel way to improve the catalytic performance of MoS<sub>2</sub> catalyst in lignin demethylation to phenols and promote the process of lignin utilization. Further study has been focused on the improvement of the catalyst stability and the selective production of other valueadded chemicals.

## Conflicts of interest

The authors declare no competing financial interest.

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