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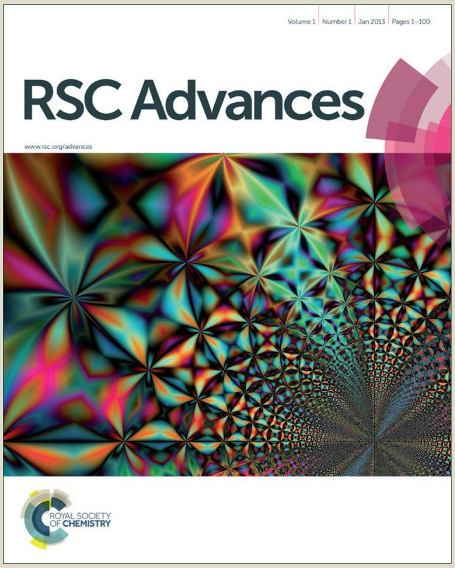

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ARTICLE TYPE

High dispersed molybdenum carbide nanoparticles supported on activated carbon as an efficient catalyst for the hydrodeoxygenation of vanillin

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Characterized by XRD, TEM, high dispersed molybdenum carbide (Mo_2C) nanoparticles with diameter of 1-4 nm are effectively synthesized on the activated carbon at 700 °C. The Mo_2C-based catalyst exhibits high activity and stability for hydrodeoxygenation (HDO) of vanillin under mild conditions (100 °C, 1.0 MPa of H_2, 3 h) in aqueous solution. According to the distribution of products with time, a HDO mechanism involved vanillyl alcohol as intermediate product was proposed. Moreover, after being recycled for several times, the loss of catalytic activity is negligible, which uncovers that the catalyst has the property of resistance for deactivation.

1.Introduction

Nowadays, the continuous requirement for energy which is mainly got from fossil fuel source has caused the exhausting of petroleum reserves and the arising world-wide environmental concerns, it is urgent to search for renewable feedstocks as a replacement for traditional fossil fuels to meet the huge need in the future. Attributed to their amity for environment, world-wide abundance and renewability within a relatively short cycle,[1, 2] bio-oils, as a prospective resource for replacing fossil fuels have attracted more and more attention. However, bio-oils must be up-graded to meet the requirement of current infrastructure due to its high oxygen content[3], in which carboxylic acid, hydroxyketones, hydroxyaldehydes, phenolic compounds and dehydrosugars constitute the main oxygenated compounds in bio-oil. Accordingly, to achieve desired target an active catalyst must be applied here. Previous works had already made great efforts for searching for an appropriate catalyst for up-grading bio-oils. Noble metal catalysts, such as Pd,[4, 5] Ru,[6, 7] Rh,[6] Pt[8, 9] heterogeneous and homogeneous catalysts deposited on various supports had been employed for up-grading bio-oils, while the limitations of expensive cost, coke deposition and low selectivity toward carbon-oxygen bonds made them an unsatisfactory choice. As alternatives to the noble metal catalysts, sulfide NiMo and CoMo catalysts[10, 11] with various surfaces chemistry had also been widely researched, however, their application for industrialization was restricted by the less resistance to deactivate and low energy efficiency caused by severe conditions of reaction. Other catalysts included: zeolites,[12, 13] transition metal catalysts[14] and so on. Among these catalysts, Mo_2C-based catalysts had been extensively studied for its inexpensive cost and platinum-like characterization.[15, 16, 17] Additionally, coke resistance, high selectivity, water-stability and chemical stability[18, 19] as its attractive properties also make them the excellent candidates for many reactions, such as hydrogenation,[15] hydrodesulfurization,[20] hydrocarbon isomerization,[21] methane reforming[22] and so on.

Our previous research concerning the high catalytic activity of Mo_2C supported on AC (Mo_2C/AC) in the HDO of vegetable oils demonstrated that the permeated carbon in the lattice of Mo metal caused the elongation of the Mo–Mo distance and the increase of d-band electron density at the Fermi level of molybdenum, which was proved to be effective to hydrogenise.[23, 24]

In this paper, we used carbothermal hydrogen reduction (CHR) method based on TPR to prepare Mo_2C/AC catalyst at 700 °C, and explored the effects of different reaction conditions on HDO of vanillin, which was one typical aldehydes compound of pyrolysis oil derived from the lignin fraction. Conducted at mild conditions in aqueous solution, the results of catalytic tests stated that the Mo_2C-based catalyst showed high selectivity toward C=O bonds, and possessed the ability of water-stability and coke resistance.

2. Experimental section

2.1 Materials

All reagents were commercially available and used as supplied without further purification. HNO_3, $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (AHM), vanillin, raw activated carbon, ethanol, anisole, glucose, deionized water was used throughout the experiment.

2.2 Methods

2.2.1 Preparation of catalysts

Catalysts preparation: supported on AC, the different loadings molybdenum carbide catalysts were accomplished by the CHR method. Prior to the impregnation, the carbon was treated with HNO_3 to remove amorphous carbon and to increase the number of surface oxygen-containing functional groups which were useful for the metal deposition and dispersion.[25] The pretreatment of raw activated carbon was carried out by mixing raw activated carbon (4.00 g) and 6 M HNO_3 (100.0 mL) at 80 °C for 3 hours. After the mixture being cooled to room temperature, the sample was washed with plenty of water and dried at 120 °C for one night. Incorporation of Mo onto carbon support to prepare catalysts with different loadings of Mo was completed through mixing activated carbon (2.00g), the corresponding amount AHM and 15 mL deionized water in a 100 mL round-bottom flask, followed by sonicating at 120 W for 1.5 hours and removing the water at 60 °C with a rotatory evaporator, then the sample was dried at 120 °C for 12 hours. All of these catalysts were carbonized at 700 °C to obtain desired molybdenum phase. The carbonization process was performed in a H_2 flow by heating to 450 °C from room temperature at the ramping rate 5 °C min^{-1} and 1 °C min^{-1} from 450 °C to 700 °C, and holding 2 hours at final temperature. Before exposure to air, the catalyst was passivated in a flow of 1.0 % O_2/N_2 for 12 hours at room temperature. Here as-synthesized catalyst was denoted as Mo_2C/AC, and the theoretical percentage of Mo_2C to carbon in the prepared catalysts were 10.0, 20.0, 30.0, 50.0 and 80.0 %, respectively. The CHN analysis result revealed that the content of C, H and N in 20.0 % Mo_2C/AC were 68.8, 0.75 and 0.64 %, respectively. The theoretical content of C in 20.0 % Mo_2C/AC was 84.0 %, so the percentage of carbon loss during the preparation was 47.1 %. According to the previous reports,[26] in the process of preparing Mo_2C through temperature-programmed reaction, CH_4, CO and H_2O would be released in the gaseous products, which accounted for the carbon loss. According to the CHN analysis, the actual content of Mo_2C in 20.0 % Mo_2C/AC was 31.7 %, but in this article we still denoted the catalyst as 20.0 % Mo_2C/AC.

Preparation of bulk Mo_2C catalyst: glucose was employed as carbon resource in the preparation of bulk Mo_2C catalyst. The CHR method was used with some modification to guarantee the glucose pyrolyzed to carbon, specifically, the sample was heated to 400 °C at the rate of 5 °C min^{-1}, then 1 °C min^{-1} to 700 °C and held for 2 hours.

2.2.2 Experimental procedure

HDO reactions: All reactions were carried out in a 100 mL stainless steel autoclave equipped with a mechanical stirrer. For a typical run, the catalyst (0.050 g for loaded catalyst, and 0.100g for bulk catalyst) was introduced into the reactor together with reagent (0.100 mmol of vanillin) and water (20.0 mL). Subsequently, the samples were heated to a temperature range of 80–180 °C after being pressurized with hydrogen to relevant pressure (0.6 MPa, 1.0 MPa, 2.0 MPa), and then reacted for a certain time.

Regeneration of the catalyst: the catalyst filtered from the mixture after reaction was refluxed in ethanol at 85 °C for 4 hours; a separated catalyst was treated at 290 °C in the flow of air for 2 hours to remove the adsorbate; then the reduction of catalyst was taken at 700 °C for 2 hours in the flow of H_2 by CHR method, and the reductive catalyst was passivated in a flow of 1.0 % O_2/N_2 for 12 hours at room temperature.

2.2.3 Analytical methods

After each reaction, the gas products were collected and qualitatively analyzed on GC (sp−6800A) equipped with packed column (TDX−01), while the qualitative analysis of liquid products was analyzed by GC-MS (HP 6890GC and 5973MSD) with HP-5 column. Whereafter, with anisole as internal standard, the quantitative analysis was operated on a High Performance Liquid Chromatography (HPLC) equipped with Hypersil BDS (C_{18} chromatographic column with the diameter of 5 μm, 150 mm × 4.6 mm) at ultraviolet ray wavelength of 270 nm. The mass balance was defined as the moles ratio of products after reaction to total vanillin in feed (Mass balance=$(P+M)/M_0$, P, M and M_0 were for the molar mass of the products, the vanillin after reaction and the vanillin in feed, respectively).

2.2.4 Catalysts characterization

Raman spectra were operated on a LabRam HR800 with an excitation wavelength of 514.5 nm. X-ray diffraction (XRD) patterns were recorded on a RIGAKUD/MAX2550/PC diffractometer using Cu Kα radiation(λ= 0.15406 nm) at a scan rate of 5°/min over the range of 10 ° to 80 °. Transmission electron microscopy (TEM) equipped with a FEI Tecnai F30 microscope was performed at an accelerating voltage of 300 kV. The acidity of catalysts was evaluated by NH_3-temperature-programmed desorption (NH_3-TPD) with BEL CAT-B instrument. Before adsorption, the samples were activated in Helium at 500 °C (10 °C/min ramp) for 1 h, then cooled down to 100 °C, saturated with NH_3 for 30 min. Subsequently, the samples were purged with 50 mL/min He for 15 min to remove NH_3 in gas phase and in physical adsorption state, and then the temperature was heated to 550 °C with an increment of 10 °C/min.

3 Results and discussion

3.1 Characterization of Mo_2C/AC catalysts

The XRD patterns of catalysts with different loading were demonstrated in figure 1. Corresponding to the standard XRD patterns of hexagonal closed-packed β-Mo_2C, the diffraction peaks locating at 34.4 °, 38.0 °, 39.4 °, 61.5 °, 69.6 °, illustrating β-Mo_2C successfully formed at 700 °C. Additionally, from Scherrer's formula, the average size of the 20.0 % Mo_2C/AC crystallites at (101) was 2.6 nm, which was in good agreement with the average value 2.6 nm predicted by TEM, while the value was 15.0 nm for 50.0 % Mo_2C/AC, suggesting the increase of particles size with loading.

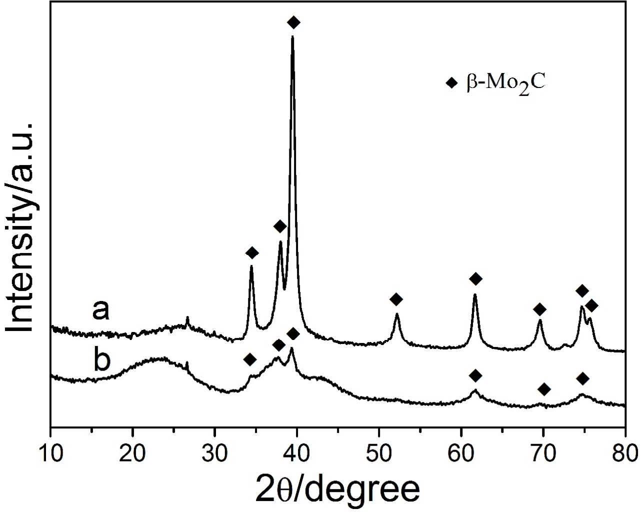

Fig. 1 XRD patterns of (a-b): 50.0 % Mo_2C/AC and 20.0 % Mo_2C/AC.

The TEM images of 20.0 % Mo_2C/AC shown in figure 2, together with XRD results, revealed that the Mo_2C particles with an average diameter of 2.6 nm well dispersed on the support. Figure 2b showed the TEM micrographs of Mo_2C with the d-spacing values of 0.221 nm for the (101) crystallographic planes. The TEM images of catalysts with different loading were shown in figure 3, from which it easily got the conclusion that the particles were well-distributed on the surface with low loading, while with loading increasing the stacking of the particles resulted in agglomeration.

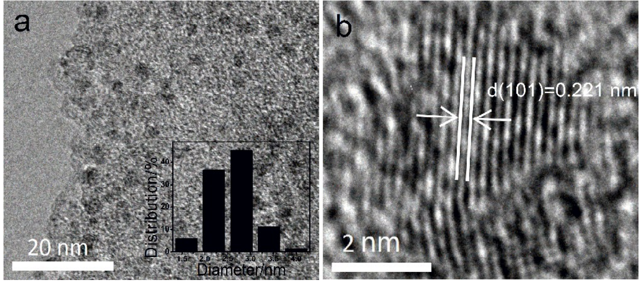

Fig. 2 TEM images and diameter distribution of 20.0 % Mo_2C/AC catalyst.

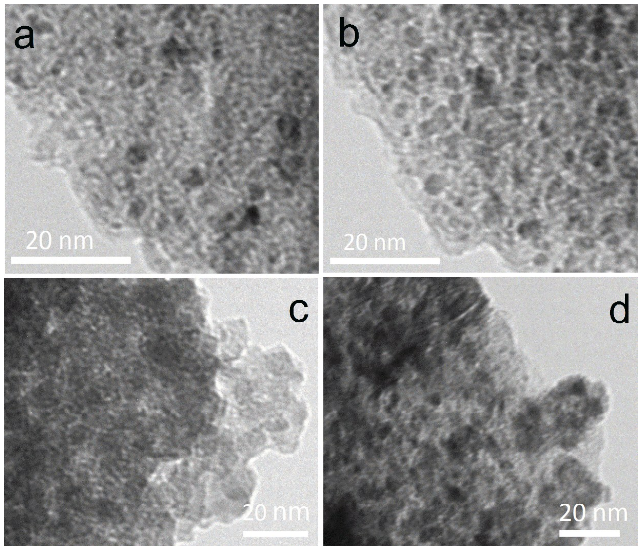

Fig. 3 TEM images (a－d) of Mo_2C/AC catalysts with loading of 10.0, 30.0, 50.0, 80.0 %, respectively.

In the Raman spectra of 20.0 % Mo_2C/AC and untreated AC shown in Figure 4, after being loaded, the increase of the intensity of D band at ~1350 cm^{-1}, a defect-induced Raman feature representing the nonperfect crystalline structure of the material, was related to the oxygen-containing functional groups induced by the treatment of HNO_3 and the passivation of 1.0 % O_2/N_2.

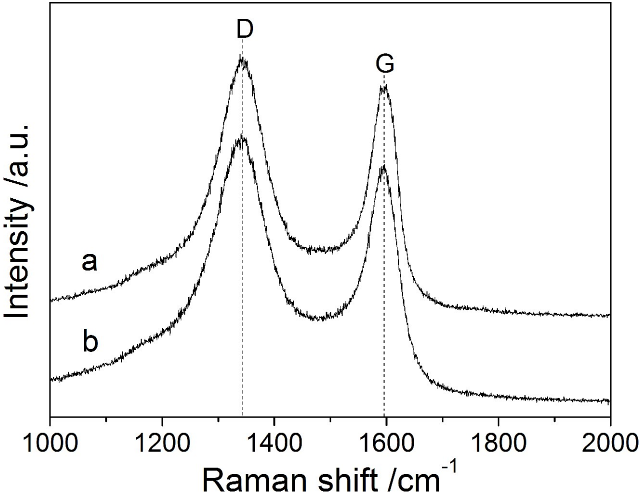

Fig. 4 Raman spectra of (a-b): 20.0 % Mo_2C/AC and untreated AC.

Compared with AC, the NH_3-TPD results displayed in figure 5 revealed that 20.0 % Mo_2C/AC catalyst had NH_3 desorption peak located at the temperature around 179 °C, indicating the load of active components imported weak acid sites, which could be explained by the Mo-OH on the catalyst surface. Furthermore, according to previous reports, the weak acidity of catalyst not only contributed to the adsorption of reactant and the procedure of hydrogenation, but also accounted for less mass balance.[27]

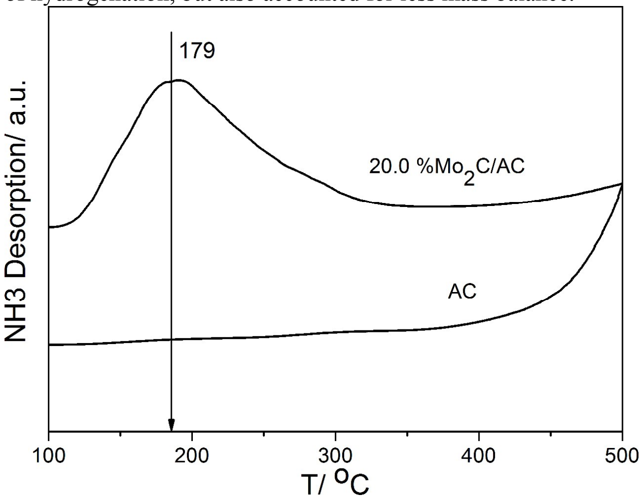

Fig. 5 NH_3-TPD profiles of catalysts with 20.0 % Mo_2C/AC and AC.

Exhibited in table 1, the Brunauer-Emmett-Teller (BET) results of AC and Mo_2C/AC catalysts with different loading showed that being loaded of Mo_2C caused the reduced of S_{BET}, which was induced by the slightly destroy of AC surface for preparing Mo_2C in the procedure of carbonization. After being loaded, the pore volume increased within a certain range of loading due to the insertion of Mo_2C particles, while with high loading the overlapping particles would block the pore and result in decreased pore volume.

Table 1 Textural parameters for AC and Mo_2C/AC catalysts with different loading

Sample	S_{BET} (m^2/g)	Pore volume (cm^3/g)
AC	967	0.16
10.0 % Mo_2C/AC	945	0.26
20.0 % Mo_2C/AC	794	0.22
30.0 % Mo_2C/AC	683	0.14
50.0 % Mo_2C/AC	494	0.10
80.0 % Mo_2C/AC	418	0.07

The N_2 adsorption-desorption isotherms of Mo_2C/AC catalyst was shown in figure 6, the isotherm was of type II according to IUPAC classification. The adsorption and desorption branches of the isotherm coincide, that was, there was no adsorption-desorption hysteresis. Depending on the surface properties of the catalyst, it can be pronounced the stage of monolayer formation.

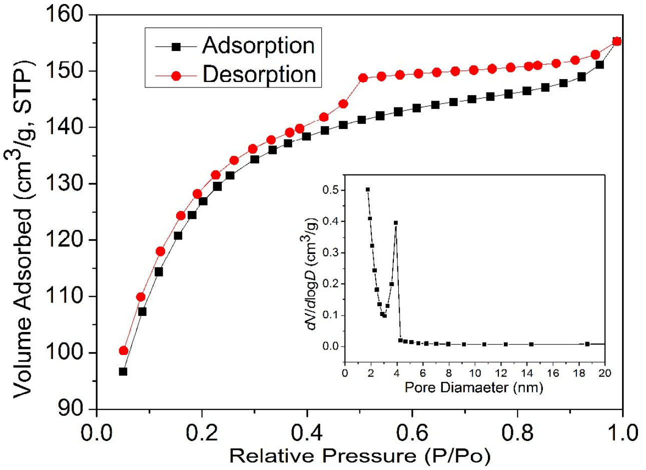

Fig. 6 Nitrogen adsorption-desorption isotherms of 20.0 % Mo_2C/AC catalyst.

3.2 HDO of vanillin

3.2.1 The blank reaction

Table 2 the results of blank reaction[a]

catalyst	Mass /g	T/°C	t/h	Conv ./%	Yield/%		Mass balance /%
					p-creosol	Vanillin alcohol	
no	--	100	3	0	0	0	100
AC	0.05	100	3	3.0	0	3.0	100
Mo_2C	0.10	150	6	33.8	12.9	17.1	99.9

[a]Reaction conditions: vanillin (0.1 mmol), water (20 mL), $p(H_2)$=1.0 MPa.

The blank experiment with no catalyst or AC was ran at 100 °C, 1.0 MPa of H_2 for 3 hours to verify the active part for this reaction, the results shown in table 2 clearly indicated that the HDO reaction could not proceed without catalyst and the effect of AC was negligible.

3.2.2 The distribution of products with time

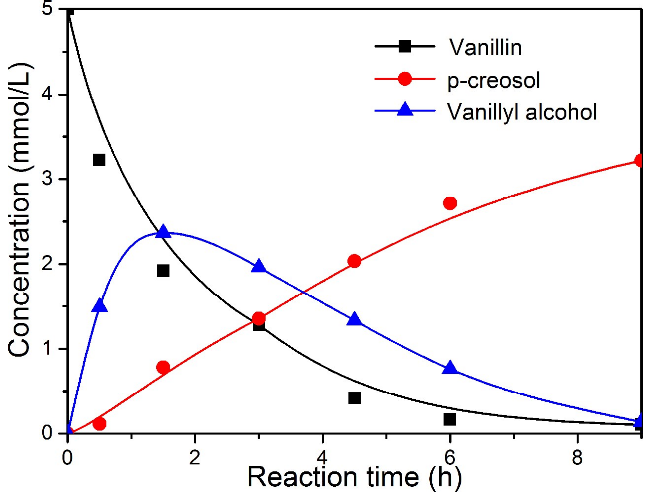

Fig. 7 the changes of products and reactant concentration with time over 50.0 % Mo_2C/AC at 100 °C, 0.6 MPa of H_2.

From the figure 7, in the first 1.5 hours, the reaction was accompanied by a rapid increase in the conversion and yield of vanillyl alcohol, while a slowly increase in yield of p-creosol, suggesting vanillin was mainly hydrogenated to vanillyl alcohol in the first step. With time increasing, the main initial product, vanillyl alcohol, gradually converted to p-creosol via hydrogenolysis, meanwhile, the conversion increased with time until approximated 100 %. According to the experimental results, we speculated that the reaction was a consecutive reaction consisting of two first-order reaction, in the first step the adsorbed vanillin by acid sites was hydrogenated to vanillyl alcohol, the second step was completed by hydrogenation and dehydration of vanillin alcohol to p-creosol. Correspondingly, the HDO mechanism was proposed and shown in figure 8 (a), in which p-cresol was produced by side reaction. Additionally, based on the slight CO detected in gas products, the mechanism of reacting to guaiacol was shown in figure 8 (b).

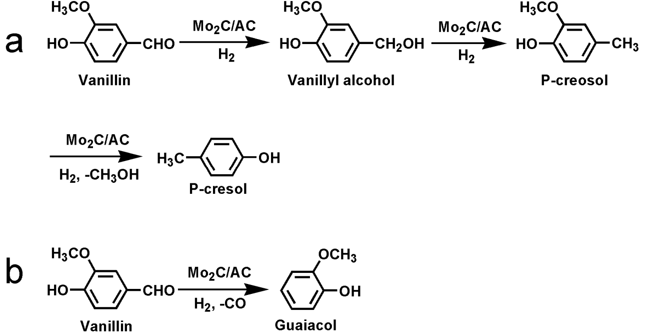

Fig. 8 the mechanisms of vanillin HDO (a) and decarbonylation (b).

3.2.3 The effect of different reaction conditions

The experimental results catalyzed by Mo_2C/AC catalysts with different loadings were exhibited in figure 9. With a 93.2 % conversion of vanillin and 50.1 % yield of p-creosol under mild conditions (1.0 MPa, 100 °C, 3 h), the highest efficiency of vanillin HDO was achieved over 20.0 % Mo_2C/AC. Associated with the increase of conversion and yield of p-creosol, the augment of loading induced an increase in catalytic activity within a certain scope, but no more increase when the loading was higher than 50.0 %. Together with the XRD and TEM results, the stacking of active particles accounted for the agglomerate and low catalytic activity. Compared with the result catalyzed by bulk Mo_2C, the high activity of Mo_2C/AC implied that AC played a part in dispersing active sites and changing the characteristics of catalysts.

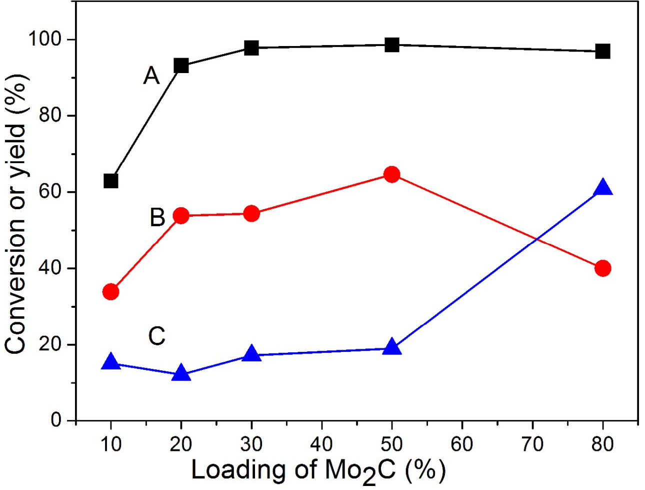

Fig. 9 The reaction results catalyzed by catalysts with different loading, reaction conditions: 50.0 % Mo_2C/AC, $p(H_2)$=1.0 MPa, 100 ° C for 3 hours. In which A is for the conversion of vanillin, B and C are for the yield of p-creosol and vanillyl alcohol, respectively.

Results displayed in figure 10 demonstrated that reaction temperature had a significant influence on conversion and yield of products. When the temperature rose from 80 °C to 100 °C, the conversion of vanillin improved remarkably from 51.4% to 98.6 %, stating that in this range of temperature, the reaction was thermodynamic control. When conducted at temperature higher than 100 °C, the increase of conversion was negligible, suggesting the reaction was under kinetic control at this conditions. The reaction temperature also had influence on the distribution of products. Hydrogenation of vanillin to vanillyl alcohol was the main reaction at low temperature (80 °C), while owing to the promoted rate of dehydration by elevating reaction temperature, p-creosol with the yield of 63.7 % had become the dominating product at 100 °C. Further enhancing temperature offered an augment in the yield of p-creosol, as well as the yield of guaiacol, high yield of 82.0 % was achieved at 180 °C. According to the previous reports, as the temperature rising, the accelerated speed of dehydrogenation would cause the increase of polycondensation,[28] which was believed to be responsible for the loss in mass balance. Considering energy efficiency and distribution of products, the optimal temperature was at 100 °C.

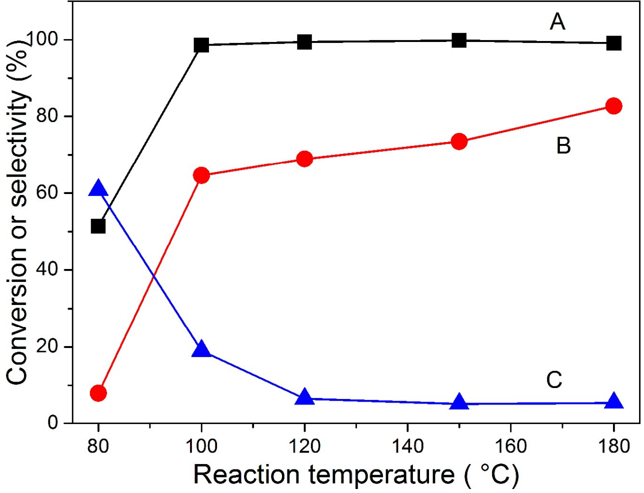

Fig. 10 Reaction results proceeded at different reaction temperature, reaction conditions: 50.0 % Mo_2C/AC, $p(H_2)$=1.0 MPa, for 3 h. In which A is for the conversion of vanillin, B and C are for the selectivity of p-creosol and vanillyl alcohol, respectively.

To inspect the relationship of hydrogen pressure to the rate of hydrogenation, the tests with the initial pressure from 0.6 MPa to 2.0 MPa were conducted at 100 °C for 3 hours. As shown in figure 11, the results indicated that increasing hydrogen pressure could accelerate the step of dehydration to p-creosol significantly. However, the gradual increase of vanillin and yield of p-creosol with the pressure increase from 1.0 MPa to 2.0 MPa was attributed to the adsorbing capacity of hydrogen. In view of the equipment and the capacity of adsorption, the optimal hydrogen pressure was at 1.0 MPa.

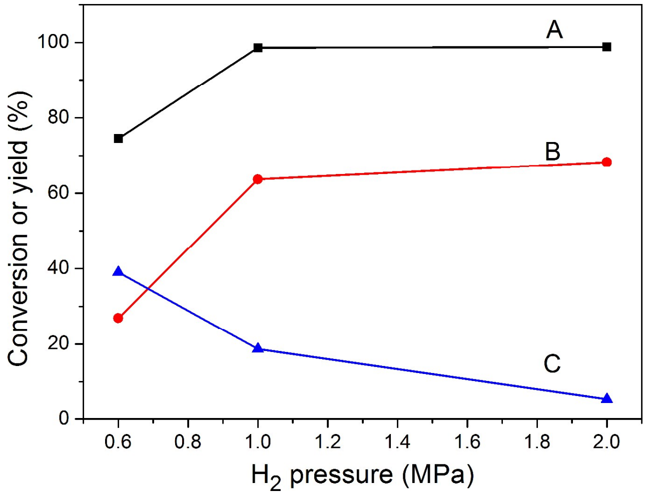

Fig. 11 The effect of H_2 pressure to HDO, the reaction conditions: 50.0 % Mo_2C/AC, 100 °C for 3 h. In which A is for the conversion of vanillin, B and C are for the selectivity of p-creosol and vanillyl alcohol, respectively.

3.2.4 The reutilization of catalyst

The recycling of 20.0 % Mo_2C/AC was operated at 100 °C, 2.0 MPa of H_2 for 3 hours, the results were exhibited in table 3. After being reused for several times, the activity loss of Mo_2C/AC catalyst was negligible, indicating that the catalyst was stable, coke resistance and had a promising prospect of industrial application.[29, 30]

Table 3 the recycling results of 20.0 % Mo_2C/AC catalyst[a]

Recycle times	Conv./ %	Yield/%				Mass balance/ %
		p-creosol	Vanillin alcohol	Guaiacol	p-cresol	
1	99.6	57.4	2.40	0.30	3.60	67.1
2	99.5	53.7	3.20	0.9	6.90	65.1
3	99.3	52.9	6.90	1.70	6.90	68.9
4	99.1	49.9	11.8	2.40	5.30	70.4
5	99.4	52.3	6.63	1.01	6.90	67.4

[a]Reaction condition: vanillin (0.2 mmol), catalyst (0.10 g), water (40 mL), $p(H_2)$=2.0 MPa, 100 °C, 3 h.

In this reaction, it was difficult to achieve 100 % of mass balance due to the instability of vanillin. Our research indicated that the loss in mass balance was mainly cause by the following reasons. Firstly, vanillin was easy to polymerize to oligomer which was difficult to be quantified. Part of the oligomer deposited on the catalyst, whereas the others was in the separate phase. When high concentration of vanillin participated in this reaction at the same conditions, the transparent, colorless polymer was obtained. The adsorption of products by catalyst also contributed to the mass balance.

4. Conclusions

The Mo_2C catalysts with good crystalline structure directly synthesized by carbothermal hydrogen reduction method at relative low temperature highly dispersed on the support. Taking experimental results and energy efficiency into account, the optimal conditions of HDO reaction catalyzed by Mo_2C/AC catalyst were at 100 °C, 1.0 MPa of H_2 for 3 hours, and 20.0 %

for catalyst loading. The Mo_2C/AC catalysts was tested to have the character of water-stability, and high selectivity to the C=O bond at mild conditions. Moreover, attributing to be recycled for several times with slight loss of activity, the Mo_2C/AC catalyst was coke resistant and possessed a promising prospect in being used for up-grading bio-oil in the future.

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Notes and references

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