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Conversion of palmitic acid to jet fuel components over Mo/H-ZSM-22 bifunctional catalysts with high carbon reservation



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ARTICLE INFO	A B S T R A C T
Keywords:	The optimal preparation conditions of Mo/H-ZSM-22 bi-functional catalysts were obtained via the sublimation
Mo/H-ZSM-22	phenomenon of MoO ₃ at high calcination temperatures, which was beneficial for the well-dispersion of MoO_{γ}
Palmitic acid	species with $5-10$ nm particles. High reduction temperature enhanced the reduction from Mo ⁶⁺ to Mo ⁴⁺ and
Hydrodeoxygenation	even from Mo ⁴⁺ to Mo°, which would be beneficial for <i>iso-alkanes</i> formation with higher carbon reservation.
Isomerization	Importantly, 89.3 % selectivity of C ₁₆ alkanes of which 61.7 % were iso-C ₁₆ alkanes were obtained with complete
	deoxygenation of palmitic acid, which was the highest selectivity of C ₁₆ alkanes over Mo/H-ZSM-22 bi-func-
	tional catalyst prepared at a calcination temperature of 550 °C and at a reduction temperature of 600 °C. The
	results would offer a novel candidate of bi-functional catalysts for upgrading of microalgae-based bio-oil to high-

value jet fuel components with high selectivity of iso-alkanes and carbon reservation.

1. Introduction

The depleting petroleum and the increasing CO₂ emission have been generally considered as two big challenges of the development for air transport industry, which motivated researchers to seek for other renewable energy sources. Currently, many publications have reported that bio-oil obtained from hydrothermal liquefaction of microalgae (so called "microalgae-based bio-oil"), was recognized as one of the most promising alternatives to produce jet fuel alkanes [1,2]. Moreover, it could alleviate energy shortages and reduce greenhouse gas CO2 emissions beyond 55 % [3]. Microalgae-based bio-oil containing a large amount of C14-C22 long-chain fatty acids, has similar carbon numbers with jet fuel components; while such high oxygen content (10-40 wt)%) causes many unsatisfactory properties such as poor ignition, inferior heating value, thermal instability and so on [4-7]. Therefore, deoxygenation of microalgae-based bio-oil is necessary for its upgrading, and palmitic acid (C15-COOH) or stearic acid (C17-COOH) are usually selected as model compounds to study their deoxygenation performance [8–14]. According to published literatures [13–19], three deoxygenation routes of fatty acids have been summarized as follows: decarboxylation (DCX: R-COOH \rightarrow R-H + CO₂), hydrodecarbonylation (HDC: R-COOH + $H_2 \rightarrow$ R-H + CO + H_2O) and hydrodeoxygenation (HDO: R-COOH + $3H_2 \rightarrow$ R-CH₃ + $2H_2O$). From the perspective of atomic economy, hydrodeoxygenation (HDO) without carbon loss exhibits the unique advantage with eliminate oxygen in the form of $\rm H_2O$, compared to decarboxylation and hydrodecarbonylation.

Conventional metal catalysts, including sulfided NiMo and CoMo, noble metal and transition metal (Ni/Co/Mo) with no acidity of supports, have been reported. However, these catalysts can only convert microalgae-based bio-oil or its model compounds into n-alkanes [20-23]. As well known, the freezing point is a crucial standard to evaluate the quality of jet fuel [24]. In comparison with *n*-alkanes as shown in Table 1 [25], iso-alkanes are considered as one of the ideal components for jet fuel with the low freezing point. Thus, deoxygenated products of *n*-alkanes need to be isomerized to meet the requirement for the low freezing point of jet fuel ranges components [24-26]. Based upon above analysis during upgrading of microalgae-based bio-oil or its model compounds (palmitic acid or stearic acid) to iso-alkanes in jet fuel, the catalysts must possess two functions with the hydrogenationdeoxygenation of oxygenated compounds and further isomerization of deoxygenated products (n-alkanes). Recently, metal/zeolite bi-functional catalysts, such as Mo/ZSM-22, Ni/Beta, Ni/ZSM-5 and so on [16,27-30], have been developed for upgrading microalgae-based biooil to hydrocarbons. In our previous work [16], Mo/H-ZSM-22 bifunctional catalyst, prepared via the wetness impregnation method, has been developed for upgrading palmitic acid (C15-COOH) to high selectivity of iso-alkanes (59.7 %) and C16 alkanes (75.5 %) with beyond 99.9 % conversion of palmitic acid, which indicated that H-ZSM-22

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Table 1Freezing points of paraffin [23].

thylparaffin 5-Methyparaffin
-31
-20
-7

possessed excellent isomerization of *n*-alkanes. The sublimation of MoO_3 occurred under certain conditions [16,31–33], would be more effective for gas to diffuse into zeolitic channels than solids in theory. According to the results of SEM, TEM, XRF and TEM-EDS characterizations in our previous work [16], no obvious observation of MoO_3 over these calcinated Mo/ZSM-22 catalysts but MoO_2 particles were observed clearly, which was ascribed to the sublimation of MoO_3 existed at high energy spotting in TEM/TEM-EDS analysis and at beyond 550 °C calcination [16,31–33]. The dispersion and state of MoO_x further influence the catalytic performance and final products distribution.

Therefore, we tried to optimize the preparation conditions of Mo/H-ZSM-22 catalysts for upgrading of long-chain fatty acids to high-value added jet fuel with more *iso*-alkanes just via the phenomenon of MOO_3 sublimation at high temperature (> 500 °C). In this paper, we intentionally designed MOO_x /H-ZSM-22 bi-functional catalysts via tailoring the calcination temperatures (450 °C, 550 °C and 650 °C for 5 h) and reduction temperatures (500 °C, 600 °C and 700 °C for 4 h), to study the optimal preparation conditions for Mo/H-ZSM-22 bi-functional catalysts and to upgrade palmitic acid (model compounds of microalgae-based bio-oil) for more *iso*-alkanes in jet fuel ranges as possible as decreasing carbon loss.

2. Experimental

2.1. Catalysts preparation

Firstly, commercial H-ZSM-22 zeolite was offered by Sinopec Research Institute of Petroleum Processing (Beijing, China) as parent support, which was synthesized via the conventional hydrothermal method [39]. Secondly, (NH₄)₆Mo₇O₂₄·4H₂O (Sinopharm Chemical Reagent Co. Ltd, Shanghai, China) was purchased, which were further dissolved in distilled water with the mass ratio of 1 ((NH₄)₆Mo₇O₂₄·4H₂O) to 10 (H₂O) for Mo source. Thirdly, we intentionally prepared a series of Mo/H-ZSM-22 precursors with 20 wt% Mo loading by a wetness impregnation method according to our previous work [16]. And then, different calcination (450 °C, 550 °C or 650 °C for 5 h) and reduction (500 °C, 600 °C or 700 °C for 4 h in hydrogen) temperatures were carried out for optimizing the preparation conditions of Mo/H-ZSM-22 bi-functional catalysts to achieve the higher selectivity of iso-alkanes with complete deoxygenation of palmitic acid. A series of Mo/H-ZSM-22-n bi-functional catalysts were named as Mo/HZ-22-450C-500R, Mo/HZ-22-650C-500R, Mo/HZ-22-550C-600R and Mo/HZ-22-550C-700R based upon calcination and reduction temperatures, respectively. It's worth noting that Mo/HZ-22-550C-500R bi-functional catalyst was calcined at 550 °C for 5 h and reduced at 500 °C for 4 h, as the same sample as in previous work [16].

2.2. Characterization

XRD patterns of Mo/H-ZSM-22 bi-functional catalysts in the 2θ range of 5° to 80° were characterized by D/MAX-III X-ray diffractometer (Rigaku Corporation, Japan) equipped with a Cu K α radiation source working at 35 kV and 35 mA. The morphology of these catalysts was obtained using on a FEI Quanta scanning electron microscope (SEM) and transmission electron microscopy (TEM). The surface areas and pore volumes of these catalysts were obtained according to nitrogen

adsorption-desorption isotherms recorded by a Micromeritics ASAP 2010 instrument with outgassing at 90 °C for 1 h and at 350 °C for 15 h under vacuum. X-ray fluorescence (XRF) spectrometer (MagiX, Philips) determined the elemental analyses of the solid sample and X-ray photoelectron spectroscopy (XPS) detected states and concentration of Mo species. NH₃-TPD was performed to characterize the acidity of catalysts on Autochem II 2920. Temperature programmed reduction by hydrogen (H₂-TPR) was used to determine the interaction between metal and support and reducibility of these bi-functional catalysts.

2.3. Catalytic performance

Palmitic acid (0.5 g), *n*-decane (50 mL), and catalyst (0.1 g) were put to the stainless-steel autoclave with 100 mL. Pure hydrogen under ambient temperature was introduced into the autoclave for three times in order to replace the air inside the autoclave, and then sealed reactor was pressurized to 4 MPa with hydrogen. Finally, the system was heated to 260 °C and conducted for 4 h at a stirring speed of 300 rpm. The final liquid phase products were analyzed by GC–MS (Agilent 7890-597-5, FSFS J &W 122-5532- $30 \text{ m} \times 250 \text{ µm} \times 0.25 \text{ µm}$) equipped with a flame ionization and mass spectrometry detection using the area normalization method [40,41]. The conversion of palmitic acid and selectivity of products were calculated as follows:

Conversion of palmitic acid=
$$(\frac{\text{moles of converted palmitic acid}}{\text{moles of the starting palmitic acid}}) \times 100\%$$

Selectivity of products= $(\frac{\text{moles of each product}}{\text{moles of total products}}) \times 100\%$

3. Results and discussion

3.1. Physicochemical properties

According to XRD patterns of all materials in Fig. 1, there were similar diffraction peaks between these Mo/HZ-22 catalysts and HZ-22 parent zeolite without any other compete crystalline phase, except for the diffraction peaks of MoO_x species, which obviously indicated that all Mo/HZ-22 catalysts possessed parent zeolite HZ-22 structure even at high calcination and reduction temperatures. Compared to HZ-22, some decrease of diffraction intensities for Mo/HZ-22 catalysts was observed. The diffraction intensities of Mo/HZ-22-650C-500R, Mo/HZ-22-550C-600R and Mo/HZ-22-550-700R were decreased significantly, which may illustrate the obvious destruction of parent zeolite caused by too



Fig. 1. XRD patterns of parent zeolite H-ZSM-22 (a) and Mo/H-ZSM-22 (b: Mo/ HZ-22-450C-500R; c: Mo/HZ-22-550C-500R; d: Mo/HZ-22-650C-500R; e: Mo/ HZ-22-550C-600R; f: Mo/HZ-22-550C-700R) bi-functional catalysts.

Table 2

Textural properties of Mo/H-ZSM-22 bi-functional catalysts.

Samples	SiO ₂ / Al ₂ O ₃	Mo (wt %)	$S_{BET} (m^2/g)$	$S_{micro} (m^2/g)$	S_{ext} (m ² /g)	V _{micro} (cm ³ /g)	V _{total} (cm ³ /g)	The ratios of Weak/Medium strong sites
HZ-22	75	-	204	161	43	0.080	0.31	0.27
Mo/HZ-22-450C-500R	75	19.8	44	12	33	0.005	0.12	3.17
Mo/HZ-22-550C-500R	75	20.3	54	21	33	0.009	0.24	0.82
Mo/HZ-22-650C-500R	75	22.4	25	5	20	0.002	0.06	2.57
Mo/HZ-22-550C-600R	75	21.2	50	8	42	0.003	0.13	0.77
Mo/HZ-22-550C-700R	75	21.6	52	8	44	0.003	0.17	0.96

high calcination and reduction temperature. Characteristic diffraction peaks of MoO_2 phase were observed at $2\theta = 36.8^{\circ}$ and 53.3° over Mo/ HZ-22-450C-500R, Mo/HZ-22-550C-500R and Mo/HZ-22-650C-500R [16], indicating that reduction procedure at 500 °C allowed to obtain the desired Mo^{4+} species. Additionally, Mo° species of $2\theta = 40.6^{\circ}$ were obviously observed over Mo/HZ-22-550C-600R and Mo/HZ-22-550C-700R catalysts, which disclosed that Mo^{4+} was further reduced to Mo° at reduction temperature of 600 °C and 700 °C for 4 h. The intensity of Mo° diffraction peak increased with the rising of reduction temperature, while the diffraction peak intensities of HZ-22 zeolite of Mo/HZ-22 catalysts were opposite. That is, high reduction temperature could improve more Mo° formation; on the contrary, too high reduction temperature destructed the structure of parent zeolite support resulting in low relative crystallinity.

The main textural properties of HZ-22 and Mo/HZ-22 bi-functional catalysts are summarized in Table 2 based upon BET and XRF analysis. There were identical ratios of SiO₂/Al₂O₃ (75) and similar Mo loading (19.8 wt% for Mo/HZ-22-450C-500R, 20.3 wt% for Mo/HZ-22-550C-500R, 22.4 wt% for Mo/HZ-22-650C-500R, 21.2 wt% for Mo/HZ-22-550C-600R, and 21.6 wt% for Mo/HZ-22-550C-700R). The surface area and volume of all Mo/HZ-22 bi-functional catalysts presented much decrease than parent zeolite HZ-22 in Table 2, due to the obvious pores blockage by MoOx species. While it is worth noting that the surface area and volume of Mo/HZ-22-650C-500R was much less than other Mo/HZ-22 bi-functional catalysts, which was in accordance with XRD analysis (Fig. 1d) based upon the serious destruction of parent zeolite. Too high calcination (650 °C) temperature may cause the obvious destruction of parent zeolites during preparation of Mo/HZ-22 bi-functional catalysts. Compared to calcination temperatures, reduction temperatures even at 600 °C and 700 °C showed less influence on the structure of Mo/HZ-22 catalysts owing to the protection of structure in hydrogen atmosphere to some extent (Table 2).

3.2. Morphology of Mo/HZ-22 bi-functional catalysts

The influence of calcination temperature (450 °C, 550 °C and 650 °C) on the morphology of Mo/HZ-22-n-500R (n = 450C/550C/650C) was performed over SEM and TEM analysis in Fig. 2 and Fig. 3. It could be seen that Mo/HZ-22-450C-500R and Mo/HZ-22-550C-500R had similar noodle-like shape with HZ-22, which disclosed that 450 °C and 550 °C calcination did not change the shape of parent zeolites. There were many reduced MoO_x species over the external surface of HZ-22, which was not like parent zeolite HZ-22 with smooth shape. The noodle-like shape of Mo/HZ-22-450C-500R and Mo/HZ-22-550C-500R seemed shorter than parent zeolite HZ-22. However, much shorter and broader noodle-like shapes were observed over Mo/HZ-22-650C-500Rd and (Fig. 2d and Fig. 3d) than those over Mo/HZ-22-450C-500R and Mo/ HZ-22-550C-500R, which may be due to the obvious destruction of parent zeolite at too high calcination temperature (650 °C). SEM and TEM images were in accordance with XRD (Fig. 1) and BET results (Table 2), which suggested that calcination temperature at 550 °C would be one of appropriate candidates for Mo/HZ-22 bi-functional catalysts.

SEM, TEM and TEM-EDS analysis of Mo/HZ-22 calcinated at 450 °C/550 °C/ 650 °C for 5 h were carried out as shown in Fig. 4.

Clearly, there was no any significant particles over calcinated Mo/HZ-22 catalysts (a: Mo/HZ-22-450C, b: Mo/HZ-22-550C; c: Mo/HZ-22-650C) according to SEM images, which looked like the smooth noddleshape as well as parent zeolite HZ-22 (a and Fig. 2a and Fig. 3a). Especially, Mo/HZ-22-650C seemed to be out of parent zeolite HZ-22 shape to some extent caused by the destruction of structure at too high calcination temperature (650 °C). Based upon TEM analysis in Fig. 4d, no obvious particles of MoO3 species were observed over Mo/HZ-22-550C bi-functional catalyst before reduction, which was in accordance with our previous work [16]. Based upon the TEM-EDS analysis, it has been proven directly the presence of Mo contents over Mo/HZ-22-550C in Fig. 4e, which seemed to be much lower (area 1: 11.3 wt%; area 2: 8.1 wt%; area 3: 10.6 wt%) than XRF analysis (20.3 wt% Mo). This phenomenon may be caused by the sublimation of MoO₃ owing to high energy spotting in TEM-EDS conditions and/or at high calcination temperature [16,31-33], while it could be seen clearly the particles of reduced MoO_x species over HZ-22 supports for Mo/HZ-22 bi-functional catalysts (Fig. 2 and Fig. 3).

Additionally, the reduction temperature (500 °C, 600 °C and 700 °C) effects on Mo/HZ-22 preparation were investigated as shown in Fig. 2 and Fig. 3. Compared to Mo/HZ-22-550C-500R (c and Fig. 2c and Fig. 3c), more reduced MoO_x species were significantly observed over Mo/HZ-22-550C-600R (e and Fig. 2e and Fig.3e) and Mo/HZ-22-550C-700R (f and Fig. 2f and Fig. 3f). The higher reduction temperature resulted in the more MoO₂ and Mo species obtained over HZ-22 parent zeolite. While too high reduction temperatures (700 °C) probably led to the obvious destruction of HZ-22 parent zeolite, like the case of Mo/HZ-22-650C-500R at high calcination temperature. Mo/HZ-22-550C-700R also exhibited shorter and broader noodle-like shapes, compared to parent zeolite HZ-22 (a and Fig. 2a and 3a). Importantly, reduced MoO_x species particles over HZ-22 supports were regular shape and uniform distribution based upon SEM and TEM analysis, and the particle size distributions was summarized in Fig.3, suggesting that reduced $\ensuremath{\text{MoO}_x}$ species size of all catalysts centered at about 5-10 nm. For Mo/HZ-22-650C-500R, reduced MoO_x species particles were slightly larger than other catalysts, which may be due to higher calcination temperature leading to serious destruction of parent zeolite. The diameters of these MoO_x species were more than 20 times as comparison of parent zeolite HZ-22 channels. Thus, some of reduced MoO_x species were exposed on the external surface of HZ-22, as well as some lied in channels, resulting in blocking the pores, as shown in Table 2 by BET analysis. Such uniform dispersion of reduced MoOx species over HZ-22 supports also illustrated the sublimation of MoO₃ via the gas-phase diffusion during the process of catalysts preparation, compared to liquid-phase via the wet impregnation method. According to the above analysis, too high calcination and reduction temperatures usually led to the obvious destruction of zeolite supports with out of noodle-like shapes. Therefore, it could predict that Mo/HZ-22-550C-600R bi-functional catalyst would be one of the best candidates for upgrading palmitic acid to produce more iso-alkanes without loss of carbon numbers, and the catalytic performance would be discussed in detailed in next section.

3.3. Active centers analysis

The acidic properties of HZ-22 and Mo/HZ-22 bi-functional



Fig. 2. SEM images of parent zeolite H-ZSM-22 (HZ-22) and Mo/H-ZSM-22 (a: Mo/HZ-22-450C-500R; b: Mo/HZ-22-550C-500R; c: Mo/HZ-22-650C-500R; d: Mo/HZ-22-550C-600R; e: Mo/HZ-22-550C-700R) bi-functional catalysts.

catalysts were detected by NH₃-TPD, as shown in Fig. 5 and Table 2. Firstly, HZ-22 exhibited a large number of medium strong acid sites around 380 °C and a small number of weak acid sites around 200 °C. Compared with parent zeolite HZ-22, the weak acidic sites increased significantly over all Mo/HZ-22 bi-functional catalysts, and the weak acid strength became stronger around at 230 °C. This result may be the contribution of MoO_x species in the global acidity, like the cases of reported literatures [34–36]. Secondly, medium strong acid sites of Mo/ HZ-22 bi-functional catalysts seem to be determined by the various calcination and reduction temperatures. As for Mo/HZ-22-450C-500R, medium acid sites were covered by MoO_x species due to blockage effects of pore windows at 450 °C (low calcination temperature) to some extent. Mo/HZ-22-550C-500R, Mo/HZ-22-550C-600R and Mo/HZ-22550C-700R catalysts showed similar acidity, in whose acid sites were slightly more than HZ-22, as well as even medium strong acid sites. High reduction temperature of Mo⁶⁺ into Mo⁴⁺ and Mo° was beneficial for the acidity presentation. However, Mo/HZ-22-650C-500R gave much poorer medium strong acid sites than other Mo/HZ-22 bi-functional catalysts, which was related to the obvious destruction of parent zeolite after high calcination temperature (650 °C: Fig. 1d, Fig. 2d and Fig. 3d). Additionally, the ratios of medium strong acid to weak acid were as followed: 0.32 for Mo/HZ-22-450C-500R, 1.22 for Mo/HZ-22-550C-500R, 1.03 for Mo/HZ-22-550C-500R, 1.29 for Mo/HZ-22-550C-600R, 1.03 for Mo/HZ-22-550C-700R, in comparison with 3.67 for HZ-22. It could be clearly seen that Mo/HZ-22-550C-500R, Mo/HZ-22-550C-600R and Mo/HZ-22-550C-700R retained more medium strong



Fig. 3. TEM images of parent zeolite H-ZSM-22 (HZ-22) and Mo/H-ZSM-22 (a: Mo/HZ-22-450C-500R; b: Mo/HZ-22-550C-500R; c: Mo/HZ-22-650C-500R; d: Mo/HZ-22-550C-600R; e: Mo/HZ-22-550C-700R) bi-functional catalysts.

acid sites than Mo/HZ-22-450C-500R and Mo/HZ-22-650C-500R, indicating that 550 °C was may be appropriate calcination temperature for preparing Mo/HZ-22 bi-functional catalysts to be beneficial for acidcatalysis (dehydration and isomerization).

After high reduction temperatures at 600 °C and 700 °C, acid sites over Mo/HZ-550C-600R and Mo/HZ-550C-700R bi-functional catalysts could recover and even increase obviously. One is that high temperatures (600 °C and 700 °C) in H₂ atmosphere improved the reduction of Mo^{6+} to Mo^{4+} and Mo° , which may be beneficial for the recovery of acid sites; the other is the contribution of MoO_x species in total acidity based upon literatures [34–36]. The morphology, porosity and acidity of Mo/HZ-22-550C-600R were similar with Mo/HZ-22-550C-500R, while diffraction intensities of these two catalysts decreased obviously. Therefore, Mo/HZ-22 bi-functional catalysts were prepared by appropriate calcination (550 °C) and reduction temperatures (500 °C and 600 °C) according to above characterization results. Reduction temperature at 700 °C was too high to destruct the structure of HZ-22 support.

Based on H₂-TPR results in Fig. 6, the broad peak was observed around at 573 °C for Mo/HZ-22-450C precursor, 620 °C for Mo/HZ-22-550C precursor and 660 °C for Mo/HZ-22-650C precursor, respectively, which was assigned to the reduction of Mo⁶⁺ to Mo⁴⁺. Clearly, the higher calcination temperature of Mo/HZ-22 bi-functional catalysts usually led to more MoO_x into HZ-22 pores/channels, and then resulted in the higher reduction temperature of Mo⁶⁺ to Mo⁴⁺. The high calcination temperature of preparation catalysts facilitated the



Fig. 4. SEM (a: Mo/HZ-22-450C; b: Mo/HZ-22-550C; c: Mo/HZ-22-650C), TEM (d: Mo/HZ-22-550C) and TEM-EDS (e: Mo/HZ-22-550C) analysis of Mo/H-ZSM-22 after calcination.

sublimation of MoO_3 to allow more MoO_3 gas-phase into HZ-22 pores/ channels, which also increased the difficulty reduction of MoO_3 reduction. As for Mo/HZ-22-650C precursor, hydrogen adsorption peak at 720 °C was ascribed to the reduction of $Mo^{4+} \rightarrow Mo^{\circ}$ [18]. Additionally, there was a small peak at 160 °C for Mo/HZ-22-450C precursor, which was probably contributed to the adsorbed hydrogen of partial MoO_x exposed over HZ-22 external surface at low calcination temperature (450 °C).



Fig. 5. NH_3 -TPD curves of parent zeolite H-ZSM-22 (HZ-22) and Mo/H-ZSM-22 (Mo/HZ-22-450C-500R; Mo/HZ-22-550C-500R; Mo/HZ-22-650C-500R; Mo/HZ-22-550C-600R; Mo/HZ-22-550C-700R) bi-functional catalysts.



Fig. 6. H₂-TPR curves of Mo/H-ZSM-22 precursors.

The Mo 3d XPS spectra of Mo/HZ-22-n bi-functional catalysts was depicted in Fig. 7, and it could be seen that the reduction temperature significantly affected the chemical state of Mo species. The concentration of MoOx species was also different at different calcination and reduction temperatures (the XPS analysis of Mo/HZ-22-650C-500R did not performed due to the obvious destruction of parent zeolite structure at calcination temperature of 650 °C). According to XPS spectra of Mo/ HZ-22 bi-functional catalysts, Mo°/Mo⁴⁺, Mo°/Mo⁶⁺ and Mo⁴⁺/Mo⁶⁺ ratios for Mo/HZ-22-450C-500R, Mo/HZ-22-550C-500R, Mo/HZ-22-550C-600R and Mo/HZ-22-550C-700R were calculated and listed in Table 3. The peaks at binding energy (BE) value of 229.0 and 232.6 eV were assigned to Mo^{4+} , the peaks emerged at 231.7 and 234.9 eV were attributed to Mo⁶⁺, and the peaks centered at 227.5 eV and 231.0 eV were assigned to metallic Mo. Firstly, increasing calcination temperature would be helpful the dispersion of MoO₃ due to its sublimation, which might also be further beneficial for the reduction of Mo⁶⁺ to Mo^{4+} at identical reduction temperature (500 °C), as comparison of Mo/HZ-22-450C-500R (Mo⁴⁺/Mo⁶⁺ = 0.30) with Mo/HZ-22-550C-500R ($Mo^{4+}/Mo^{6+} = 0.58$). Secondly, Mo° species (227.5 eV and 231.0 eV) was detected for Mo/HZ-22-550C-600R and Mo/HZ-22-550C-700R bi-functional catalysts [16,37,38], which was in accordance with XRD and H₂-TPR analysis (Fig. 1). High reduction temperature enhances more Mo^{4+} and even Mo° formation: $Mo^{\circ}/Mo^{4+} = 2.34$, $Mo^{\circ}/Mo^{6+} = 0.56$ and $Mo^{4+}/Mo^{6+} = 0.27$ for Mo/HZ-22-550C-600R; $Mo^{\circ}/Mo^{4+} = 1.45$, $Mo^{\circ}/Mo^{6+} = 0.63$ and $Mo^{4+}/Mo^{6+} = 0.49$ for Mo/HZ-22-550C-700R. Too high reduction temperature led to the destruction of HZ-22 support with out of noodle-like shape as shown in Fig. 1, Fig. 2 and Fig. 3. Therefore, $600 \,^{\circ}C$ was considered as the most appropriate reduction temperature for Mo/H2-22-550C compared to $500 \,^{\circ}C$ and $700 \,^{\circ}C$. It is well known that Mo^{4+}/Mo^{6+} ratio of Mo/HZ-22-550C-500R directly influenced HDO/HDC selectivity, and Mo^{4+} (or MoO_2) was proven to improve HDO without any carbon atom loss [16]. It is anticipated for the better catalytic performance over Mo° and M^{4+} active centers of Mo/HZ-22-550C-600R catalyst without carbon loss during the process of palmitic acid conversion.

3.4. Catalytic performance over Mo/HZ-22 bi-functional catalysts

In our previous work [16], it concluded that the stronger acid sites were, the more iso-alkanes formed was and the less C16 produced was over Mo/HZ-22-550-500R via HDC route. The acidity of bi-functional catalysts generally influences the distribution of final products through dehydration and isomerization of intermediates during palmitic acid conversion. On the other hand, Mo⁴⁺/Mo⁶⁺ ratio significantly determined HDO/HDC selectivity over Mo/HZ-22-550-500R bi-functional catalyst. Mo⁶⁺ supported HDC route with one carbon atom loss, while Mo4+ facilitated HDO route without carbon atom loss. At 260 °C in presence of 4 MPa H₂ for 4 h, palmitic acid could be completely converted to hydrocarbons over Mo/HZ-22-550C-500R [16]. Thus, Mo/HZ-22 with different calcination and reduction temperatures catalyzed palmitic acid to hydrocarbons at identical conditions as shown in Table 4 and Fig. 8, which could seek for the optimal conditions for preparation of Mo/HZ-22 bi-functional catalyst to achieve the higher iso-alkanes without loss of carbon numbers. It is worth noting that the parallel tests of palmitic acid conversion over Mo/HZ-22 bi-functional catalysts were performed, and the repeatability of data were excellently stable as shown in Fig. 8. It could be seen that the error bar of mono.iso-C₁₆ alkanes, *multi.iso*-C₁₆ alkanes and *n*-C₁₆ alkanes were all below 5 %.

As for Mo/HZ-22-550C-500R in our previous work, its catalytic performance (iso-alkanes/n-alkanes = 1.5 and $C_{16}/C_{16-x} = 3.1$) were shown in Table 4 (line 2) and Fig. 8b [16]. Compared to Mo/HZ-22-550C-500R, Mo/HZ-22-450C-500R with lower calcination temperature could also completely convert palmitic acid to hydrocarbons with 100 % selectivity. While there was less iso-alkanes and C_{16} alkanes formation with *iso*-alkanes/*n*-alkanes = 1.0 and C_{16}/C_{16-x} = 2.8, which was ascribed to the less acid sites especially for strong acid sites (Fig. 5 and Table 2). It is worth noting that calcination temperature at 650 °C was considered as too high to destruct seriously structure of parent zeolite HZ-22, thus Mo/HZ-22-650C-500R catalyst was not considered as one of the candidates to upgrade palmitic acid. Combining the characterization and catalytic performance, 550 °C is considered as the appropriate calcination temperature for Mo/HZ-22 bi-functional catalysts. Additionally, Mo/HZ-22-550C-600R and Mo/HZ-22-550C-700R also converted completely palmitic acid to achieve 100 % selectivity of alkanes at identical conditions (Table 4 and Fig. 8). With similar iso-alkanes selectivity (Fig. 8c and 8d), much more C16 alkanes were formed over Mo/HZ-22-550C-600R ($C_{16}/C_{16-x} = 8.4$) and Mo/HZ-22-550C-700R ($C_{16}/C_{16-x} = 6.8$), which directly disclosed that Mo° (Fig. 1 and Table 3) emerged at higher reduction temperature was apt to enhance HDO reaction without carbon atom loss. Meanwhile, more MoO₃ species were reduced over HZ-22, which led to the recovery of more acid sites (Fig. 5) and further the production of more iso-alkanes.

The similar level of conversion (85.6 % over Mo/HZ-22-550C-500R for 150 min, 83.7 % over Mo/HZ-22-550C-600R for 120 min, 84.6 % over Mo/HZ-22-550C-700R for 120 min) lower than 100 % was obtained as shown in Fig. 9 at 260 °C in presence of 4.0 MPa H_2 for different reaction time, which indicated that Mo/HZ-22-550C-600R and



Fig. 7. XPS curves of Mo/H-ZSM-22 (Mo/HZ-22-450C-500R; Mo/HZ-22-550C-500R; Mo/HZ-22-550C-600R; Mo/HZ-22-550C-700R) bi-functional catalysts.

Table 3

APS analysis of MO/H-ZSM-22 DI-functional catalysis.						
Catalysts	Mo ⁰ /Mo ⁴⁺	Mo ⁰ /Mo ⁶⁺	Mo ⁴⁺ /Mo ⁶			
Mo/HZ-22-450C-500R	-	-	0.30			
Mo/HZ-22-550C-500R	-	-	0.58			
Mo/HZ-22-550C-600R	2.34	0.56	0.27			
Mo/HZ-22-550C-700R	1.45	0.63	0.49			

CM. (II 70M 00 h: Constitued actions

Mo/HZ-22-550C-700R exhibited higher hydrogenation activity than Mo/HZ-22-550C-500R based upon shorter reaction time. C_{15} – CHO and C_{15} – CH₂ – OH selectivity were 29.1 % and 11.3 % over Mo/HZ-550C-500R, 15.2 % and 3.7 % over Mo/HZ-22-550C-600R, 12.2 % and 2.1 % over Mo/HZ-22-550C-700R, also disclosing the hydrogenation activity increased in order: Mo/HZ-22-550C-500R < Mo/HZ-22-550C-600R < Mo/HZ-22-550C-600R. That is, Mo° and Mo⁴⁺ especially for Mo° possessed high hydrogenation activity. Compared to Mo/HZ-22-

550C-500R with 59.6 % alkanes and 26.0 % *iso*-alkanes selectivity (10.2 % n-C₁₅, 5.3 % *multi-iso*-C₁₆, 20.7 % *mono-iso*-C₁₆ and 23.4 % n-C₁₆), more alkanes and *iso*-products were obtained over Mo/HZ-22-550C-600R (81.1 % and 44.4 %) and Mo/HZ-22-550C-700R (85.7 % and 40.8 %), which was ascribed to more amounts of acid sites over Mo/HZ-22 after higher reduction temperature. According to *iso*-alkanes especially for *multi-iso*-C₁₆ selectivity, it could be seen that Mo/HZ-22-550C-600R presented the best isomerization activity among these three Mo/HZ-22 bi-functional catalysts. In all, Mo/HZ-22-550C-600R catalyst exhibited the best catalytic performance during palmitic acid conversion among Mo/HZ-22 bi-functional catalysts.

Based upon above results, the possible reaction pathway was proposed as shown in Scheme 1: (i) hydrodeoxygenation and then isomerization for n-C₁₆ and iso-C₁₆ alkanes, (ii) hydrodecarbonylation and then isomerization for n-C₁₅ and iso-C₁₅ alkanes, (iii) direct cracking deoxygenation for n-C₁₄ alkane. It could be seen that enhancement in dehydration and isomerization reactions would decrease the concentration of n-alkanes in these consecutive reactions over acid sites,

Table 4

Upgrading of palmitic acid over Mo/H-ZSM-22 bi-functional catalysts reacted for 4 h in presence of 4 MPa H₂ at 260 °C.

Catalysts	Conv. (%)	Selectivity (mol/mol%) of each product after reaction					iso-alkanes/n-alkanes (mol/mol)	C ₁₆ /C _{16-x} (mol/mol)	
_		alkanes	<i>n</i> -C ₁₄	<i>n</i> -C ₁₅	multi. <i>iso</i> -C ₁₆	mono. <i>iso-</i> C ₁₆	<i>n</i> -C ₁₆		
Mo/HZ-22-450C-500R	> 99.9	100	1.5	24.8	9.4	41.7	22.6	1.0	2.8
Mo/HZ-22-550C-500R	> 99.9	100	0.9	23.6	15.6	44.1	15.8	1.5	3.1
Mo/HZ-22-550C-600R	> 99.9	100	3.2	7.5	30.3	31.4	27.6	1.7	8.4
Mo/HZ-22-550C-700R	> 99.9	100	4.4	8.5	32.9	28.5	25.7	1.6	6.8



Fig. 8. Selectivity of C₁₆ alkanes over different Mo/H-ZSM-22 (a: Mo/HZ-22-450C-500R; b: Mo/HZ-22-550C-500R; c: Mo/HZ-22-550C-600R; d: Mo/HZ-22-550C-700R) bi-functional catalysts (General conditions: 50 mL *n*-decane, 0.5 g palmitic acid, 0.1 g Mo/HZ-22-n catalysts, 4 MPa H_2 , stirring at 300 rpm).



Fig. 9. Conversion and selectivity of products over Mo/HZ-22-550C, Mo/HZ-22-550C-600R and Mo/HZ-22-550C-700R bi-functional catalysts (General conditions: 50 mL *n*-decane, 0.5 g palmitic acid, 0.1 g Mo/HZ-22-n catalysts, 4 MPa H₂, stirring at 300 rpm).

which could motivate hydrogenation forward. Moreover, enhancement in hydrogenation lead to increasing the concentration of $C_{15}-CH_2-OH$ over Mo⁴⁺ and/or Mo° active centers, which would drive the dehydration and isomerization reactions moving to produce the more *iso*-alkanes. That is, the interaction between metal active centers and acid sites and their influence on the overall reaction over Mo/H-ZSM-22 bi-functional catalysts during upgrading of palmitic acid. It is a pity that too high reduction temperature (700 °C) resulted in some destruction and out of noodle-like shape for Mo/HZ-22-550C-700R (Fig. 2f and 3ff and f). Mo/HZ-22-550C-600R bi-functional catalyst presented the outstandingly catalytic performance, which obtained about 61.7 % *iso*-alkanes selectivity and 89.3 % selectivity of C₁₆ alkanes during complete deoxygenation of palmitic acid.

4. Conclusions

Different calcination and reduction temperatures were selected to optimize the conditions for preparing Mo/H-ZSM-22 bi-functional catalysts, which would apply in upgrading palmitic acid to iso-alkanes with minimizing loss of carbon numbers. Parent zeolite support was seriously destructed after too high calcination and/or reduction temperatures. Reduced MoO_x species with well dispersion of 5-10 nm over H-ZSM-22, were successfully prepared at 550 °C calcination and 600 °C reduction. After reduction at 500 °C, only Mo⁴⁺ centers were observed; while Mo° was detected over Mo/H-ZSM-22 with high reduction temperatures (600 $^\circ \rm C$ and 700 $^\circ \rm C$). Importantly, more $n\text{-}C_{16}$ alkanes were obtained over Mo/H-ZSM-22 bi-functional catalysts via 550 °C calcination and 600 °C reduction, which may be caused by Mo° species exhibited higher hydrodeoxygenation (HDO) activity than Mo⁴⁺ centers. Furthermore, the selectivity of iso-alkanes was reached up to 61.7 %. Mo/H-ZSM-22 bi-functional catalysts could achieve simultaneously deoxygenation and isomerization during upgrading of palmitic acid to jet fuel ranges iso-/n- alkanes with less carbon loss, which may be afford new strategy to design bi-functional catalysts for conversion of microalgae-based bio-oil to jet fuel in future.

CRediT authorship contribution statement

Jimei Zhang: Investigation, Software, Writing - original draft. Yanchun Shi: Writing - review & editing, Visualization. Hongbin Cao: Resources. Yulong Wu: Validation, Methodology, Conceptualization, Supervision. Mingde Yang: Formal analysis.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to



Scheme 1. Possible reaction pathway over Mo/H-ZSM-22 bi-functional catalysts during palmitic acid conversion.

influence the work reported in this paper.

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