

View Article Online View Journal

RSC Advances

This article can be cited before page numbers have been issued, to do this please use: M. Lu, L. Zheng, R. Li, Q. Guan and W. Li, *RSC Adv.*, 2016, DOI: 10.1039/C6RA09862B.



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. This Accepted Manuscript will be replaced by the edited, formatted and paginated article as soon as this is available.

You can find more information about *Accepted Manuscripts* in the **Information for Authors**.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard <u>Terms & Conditions</u> and the <u>Ethical guidelines</u> still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.



www.rsc.org/advances

DOI: 10.1039/C6RA09862B

ROYAL SOCIETY

RSC Advances

ARTICLE

Received 00th January 20xx, Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Efficient hydrogenation performance improvement of MoP and Ni₂P catalysts by adjusting the electron distribution around Mo and Ni atoms

Mingyue Lu, ^a Lirong Zheng, ^c Rongguan Li, ^a Qingxin Guan^a and Wei Li^{a, b*}

MoP and Ni₂P catalysts were modified by elements with different electronegativities. Based on this method, two series of catalysts were designed and synthesized: Mo based phosphide catalysts (MoP, Mo₈WP₉, Mo₈CuP₉) and Ni based phosphide catalysts (Ni₂P, Ni₃₈W₂P₂₀). The consistency between synthetized and designed materials was mainly verified by XRD, SEM-EDS, TEM, EXAFS. Then, relative catalyst parameters were further characterized using BET, and CO chemisorption. The hydrogenation properties of verified synthetized catalysts are evaluated by hydrodeoxygenation of methyl palmitate. The activity of the catalysts followed the order: Mo₈WP₉ > MoP > Mo₈CuP₉, Ni₃₈W₂P₂₀ > Ni₂P. In particular, the W modified catalysts (Mo₈WP₉ and Ni₃₈W₂P₂₀) exhibited hydrogenation activities 2.83 and 3.68 times that of MoP and Ni₂P, respectively. Further, the products selectivities of different catalysts were analysed detailedly. The C16/C15 molar ratio was increased as the incorporation of W, which represented the selectivity of HDO parthway increased. While the C16/C15 molar ratio was decreased as the introduction of Cu, and this suggested that the selectivity of decarbonylation increased. These results indicate that the adjustment of the electron distribution around Mo and Ni atoms could successfully control the hydrogenation property of catalysts.

1. Introduction

Numerous studies have been devoted to the studies of the hydrogenation catalysts due to their wide applications in many fields, such as synthesis of organic chemicals, crude oil processing and production of bio-fuel¹⁻⁶. Among these catalysts, transition metal phosphides, which exhibit unexpected catalytic activity and excellent stability, have attracted considerable attention as new catalysts for hydrotreating process⁷⁻⁹. Particularly, metal phosphides have definitely emerged as research focus because of their better hydrodenitrogenation, catalytic activity in hydrodesulfurization, and hydrodeoxygenation (HDO)¹⁰⁻¹², and they have potential to be next-generation catalysts in hydrogenation. Of all the phosphides, previous works have shown that MoP and Ni_2P are more active and stable than others in HDO reactions¹³⁻¹⁶.

The promising performance of MoP and Ni_2P has prompted many studies on their synthetic modification to enhance the activity of the active phases. The promotion methods can be divided into surface modification and crystal modification. In surface modification, the modifier is attached to the catalyst surface. The normal modified catalysts were reported as Ni–P–S^{17, 18} and Ni–P–O¹⁹, which were recognized as the real active phases in the process of HDS and HDO, respectively. In crystal modification, the modifier is inserted into the crystal of catalyst. Representative modified catalysts were bi/trimetal phosphides^{20–24}. These modified catalysts exhibit higher hydrogenation activities than the original metal phosphides.

In our previous work¹⁹, we had inferred and provided an electronegativity modification method, which could enhance effectively the hydrogenation performance of the catalysts. The protocol is 'modifying elements with relatively high electronegativity will favour an increase in the hydrogenation activity, provided crystal metallic properties are retained'. Based on this method, the crystal-modified Ni-W alloy was designed. However, this modification changed the original hexagonal crystal of Ni₂P. This was unfavourable for determining whether the enhancement of catalyst activity was caused by lattice change or by electronegativity change. In addition, the metal phosphides represented by Ni₂P were reported to have superior activities to traditional metal catalysts in some hydrotreating processes. It was important to improve the activity of metal phosphides, while retaining their original crystal structure and properties.

In this paper, the electronegativity modification method was further expanded and extended. We attempted to maintain the original crystal structure of MoP, choosing the higher electronegativity atom W to enter the crystal lattice to

^{a.} College of Chemistry, Key Laboratory of Advanced Energy Materials Chemistry (Ministry of Education).Address here.

^{b.} Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Nankai University, Tianjin, 300071, China. E-mail: weili@nankai.edu.cn, Fax: +86-22-23508662; Tel: +86-22-23508662.

^c Institute of High Energy Physics, the Chinese Academy of Sciences, Beijing 100049, China.

[†] Footnotes relating to the title and/or authors should appear here.

Electronic Supplementary Information (ESI) available: extra figures and tables. See DOI: 10.1039/x0xx00000x

RSC Advances

replace Mo atom, in accordance with the above electronegativity modification method. To prove further the reliability of the theory, another common phosphide (Ni₂P) was also modified by W atom. In addition, we chose the lower electronegativity atom Cu to modify the MoP catalyst to test briefly this method from the opposite perspective. Preliminary, we propose two assumptions about the Cu dopant in virtue of the electronegativity of Cu being lower than those of Mo and P: (1) Cu could partly enter the crystal lattice randomly, applying the electronegativity modification to decrease the catalyst activity, and (2) little Cu could enter the crystal lattice, also causing the activity declined. In order to investigate purely the effect of the incorporation of modified elements on the catalysts, the catalysts were prepared in bulk form to eliminate the influence of the support on the catalytic activity. In detail, two series of catalysts were synthesized in this research: Mobased phosphide catalysts (MoP, Mo₈WP₉, Mo₈CuP₉) and Nibased phosphide catalysts (Ni₂P, Ni₃₈W₂P₂₀).

Nowadays, HDO reactions, as an effective way to upgrade bio-oil, were commonly used to test the hydrogenation performance of catalysts. Therefore, the activity of modified catalysts was investigated in the methyl palmitate HDO evaluation reaction. Methyl palmitate is a derivative of palm oil and widely distributed in nature. It has a lower melting point (30 °C) compared with palmitic acid, and is more suitable for use in laboratory studies²⁵. The activity results showed that the hydrotreating performance of the catalysts was controlled by the electronegativity of the modifier. The electronegativity modification method was consummated further.

2. Experimental

2.1 Material synthesis

MoP, as a reference, was prepared in two steps: precursor preparation, precursor reduction. In the preparation of precursor, the Mo/P mole ratio = 1. $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ and $(NH_4)_2HPO_4$ were dissolved in an appropriate amount of water, followed by stirring for 1 h. The mixture solution was marked with solution A. Then, the solution A was dried adequately at 120 °C for 12 h, calcined at 550 °C for 2 h. After that, the catalyst precursor was obtained. In the precursor reduction, the precursor was directly reduced at 700 °C for 1 h in flowing H₂. After cooled down to room temperature under H₂ atmosphere, MoP catalysts were prepared.

W or Cu were introduced into the bulk MoP catalyst by the mixture $(NH_4)_6W_7O_{24}\cdot 6H_2O$ or $Cu(NO_3)_2\cdot 3H_2O$ with the solution A according to the corresponding ratio. The Mo/W/P molar ratio = 8/1/9, and the Mo/Cu/P molar ratio = 8/1/9. The above solution was dealt with following the same processes as the preparation of MoP.

The syntheses of Ni₂P and Ni₃₈W₂P₂₀ were in the similar procedures with Mo based phosphide catalysts. The Ni/P molar ratio = 2, and the Ni/W/P molar ratio = 38/2/20. Whereas, Ni(NO₃)₂·6H₂O was used as the source of Ni. The resulting catalysts were prepared from the precursors by reducing at 600 °C for 2 h in flowing H₂.

2.2 Material Characterization

The catalysts were studied by a series of characterizations as follows:

X-ray diffraction (XRD) was studied with a Bruker D8 FOCUS instrument using Cu-K α radiation. The measurement was made in the 20 range of 10–80 ° at 40 kV and 40 mA.

The specific surface area of materials was analysed with the BET method using nitrogen adsorption-desorption isotherms measured at 77 K on a BELSORP Mini instrument.

CO uptake was obtained on Micromeritics Chemisorb 2750 instrument using 100 μL loop ring. CO chemisorption was taken at 30 °C in the flowing He (100 mL/min). The samples were pre-reduced in flowing H_2 at corresponding temperature for 1 h.

H₂-TPD was carried out using the Micromeritics Chemisorb 2750 instrument. 0.15 g of sample was reduced at 600 °C for 1 h by a stream of gas containing 10% H₂ and 90% Ar (50 mL/min). After reduction, the sample was cooled down to room temperature, and the sample was swept with a N₂ flow (50 mL/min) for 1 h. The H₂-TPD was conducted by sample heating at a rate of 10 °C/min from room temperature to 850 °C under a N₂ flow (20 mL/min).

The surface morphologies of the alloys were observed using scanning electron microscopy (SEM, VEGA III SBH) linked with energy-dispersive X-ray spectrometer (EDS). The samples were plated with gold before measurement to avoid the electric charge accumulation.

High-resolution transmission electron microscopy (HRTEM) images were obtained on a Tecnai F20 electron microscope operated at an accelerating voltage of 200 kV equipped with a field emission source.

X-ray photoelectron spectroscopy (XPS) was performed using a Kratos Axis Ultra DLD spectrometer employing a monochromatic Al K α X-ray source (hv = 1486.6 eV), hybrid (magnetic-electrostatic) optics, and a multichannel plate and delay line detector. All XPS spectra were recorded using an aperture slot of 300 × 700 μ m, survey spectra were recorded with a pass energy of 160 eV, and high resolution spectra with a pass energy of 40 eV.

Extended x-ray absorption fine structure (EXAFS) of the catalysts were measured at the 1W1B beamline of Beijing Synchrotron Radiation Facility (BSRF) using a Si (111) doublecrystal as monochromator. The storage ring was operated at 2.5GeV, with an average ring current of 200 mA. The Mo Kedge spectra of Mo-based phosphides, the Ni K-edge spectra of Ni-based phosphides, the W L₃-edge spectra of W modified catalysts, and the Cu K-edge spectra of Cu modified catalysts were collected in transmission mode. During measurements, Mo, Ni, W, and Cu foils were used to calibrate the energy, respectively. The obtained spectra were back-subtracted and converted to k space. Then the Fourier transforming was performed on the k³-weighted EXAFS data using a Hanning window function to get the radial structure functions (RSFs). The XAFS data were analysed using the IFEFFIT²⁶ software package. Final fits of all the samples were made in Artemis.

RSC Advances

2.3 Hydrogenation performance test

Methyl palmitate was chosen as the model compound to investigate the catalysts hydrogenation performance. The HDO reaction was carried out in a continuous flow fixed-bed reactor equipped with a high-pressure pump.

Take the Mo based phosphide catalysts for example, the reaction procedure was stated in detail here. The catalysts were pelleted, crushed, and a particle size fraction of 20-40 mesh was used for the test. And the catalysts were diluted with quartzs sand before loaded into the reaction tube. Before reaction, the catalysts were reduced at the same temperature as preparation for 1 h in flowing H₂. After prereduction, the system was adjusted to the desired reaction temperature (300 °C) and pressure (3.0 MPa). The feedstock containing methyl palmitate in decalin (30 wt %) was continuously pumped into the reactor at the rate of 0.1mL/min. The weight hourly space velocity (WHSV) was equal to 6 h^{-1} , and the H₂/oil ratio was kept at 1000 (V/V).

The hydrogenation reactions for Ni based phosphide catalysts were conducted in the same procedure. Nevertheless, the reaction temperature was desired as 370 °C. The weight hourly space velocity (WHSV) was 3 h^{-1} .

Liquid products were collected every hour in all assays. The reactant and products were analysed using a gas chromatograph (Agilent 7890A), equipped with an HP-5 capillary column and a flame ionization detector (FID). The products compositions were identified by GC-MS (Shimadzu QP2010 SE). The hydrogenation performance of catalysts was determined by the methyl palmitate conversion and turnover frequency (TOF). The conversion, selectivity and TOF value were calculated following Eq. (1) Eq. (2) and Eq. (3).

$Conversion = \left(1 - \frac{n}{n_0}\right) \times 100\%$	(1)
Product selectivity = $\frac{n_i}{\sum n_i}$	(2)
$TOF = \frac{F_{A0}}{W} \frac{X_A}{CO_{uptakes}}$	(3)

Where n and n_0 denote the moles of methyl palmitate in the product and feed, respectively, and n_i is the moles of product i. F_{A0} is the molar rate of reactant pumped into the reactor (µmol s⁻¹), W is the catalyst weight (g), $CO_{uptakes}$ is the uptake of chemisorbed CO (µmol g⁻¹), and X_A is the reactant conversion (%).

3. Results and discussion

3.1 Catalyst Characterization

3.1.1 X-ray Diffraction

Figure 1 shows the XRD patterns of both series of catalysts. As seen from Figure 1a, all the Mo-based phosphide samples exhibited peaks due to the phases of MoP. This suggested the new phase preferred to remain more like the



Figure 1. XRD patterns of different catalysts.

MoP phase. No peak shifting was observed in the curve of Mo₈WP₉ compared with MoP, because of the atom size of W (atomic radius, 137 pm), which is similar to Mo (atomic radius, 137 pm). Although the atom size of Cu (atomic radius, 128 pm) is smaller than that of Mo, no peak shifting was found in the plot of Mo₈CuP₉. This could probably be explained as the retention the original MoP lattice structure, It could be ascribed that part of Cu atom might enter MoP lattices by a random replacement of Mo without causing the original lattice structure collapsed. For the Ni-based phosphide catalysts (Figure 1b), a series of Ni-W-P materials with different Ni/W ratios was prepared (Figure S1, ESI⁺). When the Ni/W ratio = 19/1, there was no Ni_5P_4 detected in the pattern, and the tungsten could be well dispersed. The diffraction peak positions of Ni₃₈W₂P₂₀ slightly shift to a lower angle compared with Ni_2P . This shows that the lattice parameters of $Ni_{38}W_2P_{20}$ are larger than those of Ni₂P calculated using the Bragg equation ($2d\sin\theta = n\lambda$), as has been reported for the NiMoP system²⁷. This lattice expansion was formed by the substitution of smaller Ni atoms (atomic radius, 125 pm) by bigger W atoms (atomic radius, 137 pm).

DOI: 10.1039/C6RA09862B RSC Advances



Figure 2. SEM (a, b, c, d, e) and HRTEM (f, g, h, I, j) micrographs of MoP (a, f); Mo₈WP₉ (b, g), Mo₈CuP₉ (c, h), Ni₂P (d, i) and Ni₃₈W₂P₂₀ (e, j). Insets of figure (f); (g), (h), (i) and (j) show the corresponding FFT diffraction pattern.

3.1.2 SEM and TEM

Published on 04 July 2016. Downloaded by University of Sussex on 10/07/2016 05:57:57.

The morphologies and microstructures of catalysts were observed by SEM and HRTEM images (Figure 2). Mo based phosphide catalysts (Figures 2a-c) showed similar appearances, and there were no significant differences in particle sizes among MoP, Mo₈WP₉ and Mo₈CuP₉ samples. Comparing SEM images of Ni₂P (Figure 2d) with Ni₃₈W₂P₂₀ (Figure 2e), it can be seen that the particle sizes of $Ni_{38}W_2P_{20}$ are much smaller than those of Ni₂P. The results correspond to the XRD patterns (Figure 1b), in which $Ni_{38}W_2P_{20}$ showed weaker and broader peaks than Ni₂P. This was attributed essentially to the substitution of the larger W atom for smaller Ni atom, leading to lattice expansion. This expansion, which could be seen from XRD spectra (Figure 1b), partially broke the original crystal, and destroyed the long-range ordered structure to make the crystal become smaller. Moreover, in the SEM–EDS results (Table S1, ESI⁺), Mo₈WP₉ contained 19.86 wt% W and $Ni_{38}W_2P_{20}$ contained 13.93 wt% W, while there were no W diffraction peaks detected in the XRD patterns. The results demonstrated that the W atom might enter MoP and Ni₂P lattices. In Figures 2f-j, the crystal lattice fringe was clearly observed in the TEM images. In the fast Fourier transform diffraction patterns of MoP, Mo₈WP₉, Mo₈CuP₉, Ni₂P and Ni₃₈W₂P₂₀ (inserts of Figure 2f-j, respectively), one set of distinguishing points was regularly distributed. This possibly elucidates that W- and Cu-modified catalysts maintained their original crystal forms.

3.1.3 EXAFS

The main objective of EXAFS characterization was to investigate the structure of the catalysts. Figure 3a shows the magnitude of the k^3 -weighted Fourier transforms (FTs) of the EXAFS spectra of the Mo K-edge on the Mo-based phosphide catalysts. From this figure, it can be seen that the FT of the EXAFS spectrum of the Mo₈WP₉ is very similar to that from

MoP. The samples give rise to two peaks at distances of 2.02 Å and 2.85 Å roughly, which correspond to Mo–P and Mo–Mo bond distances²⁸. This indicates that Mo in Mo_8WP_9 maintained the



Figure 3. (a) Comparison of Fourier transforms of the Mo K-edge EXAFS spectra for MoP and Mo8WP9 catalysts. (b) Comparison of Fourier transforms of the Mo K-edge and W L3-edge EXAFS spectra for Mo8WP9 catalysts. (c) Comparison of Fourier transforms of the Ni K-edge EXAFS spectra for Ni based phosphide catalysts. (d) Comparison of Fourier transforms of the Ni K-edge and W L3-edge EXAFS spectra for Ni38W2P20 catalysts. (e) Comparison of Fourier transforms of the Mo K-edge EXAFS spectra for MoP and Mo8CuP9 catalysts. (f) Comparison of Fourier transforms of the Cu K-edge and W L3-edge EXAFS spectra for Mo8CuP9 catalysts.

RSC Advances

Figure 4. XPS spectra of Mo 3d and Ni 2p in phosphide catalysts.

original structure and co-ordination of MoP after doping with W. Nevertheless, the peak intensity of further shells (Mo-Mo) in Mo₈WP₉ is lower, demonstrating that the disorder of the sample increased with W into the crystal lattice. Figure 3b compares the FTs for the k^3 -weighted Mo K-edge and W L₃edge EXAFS spectra obtained from Mo₈WP₉ catalyst. The W L₃edge EXAFS radial structure plot of Mo₈WP₉ gives one peak at around 2.12 Å due to W-P²⁹. Moreover, another two distinctive peaks are located at similar positions (2.91 Å, 4.23 Å) with Mo K-edge spectra of the Mo₈WP₉ sample. This indicates that the W in the Mo₈WP₉ samples took a structure with lattice parameters close to MoP. Similar trends are evident from the values presented in the fitting parameters (Table S2, ESI[†]). The W–M (M = W or Mo) fitted bond distance is 3.21 Å, which is considerably longer than the W-W bond distance in WP crystal (2.86 Å)²⁹, demonstrating that W hardly existed in the form of WP. Above all, it could be concluded that W occupied the site of Mo in the Mo₈WP₉ catalyst.

Considering the Mo_8CuP_9 (Figure 3e and 3f), from the spectra of K-edge FT of EXAFS, it could be observed that the Cu-modified

MoP catalyst retained its original structure. The Cu K-edge FT of the EXAFS spectrum shows a broad peak at around 2.1 Å, approximating to the first peak for the Mo K-edge of Mo_8CuP_9 derived from Mo–P. Therefore, it is speculated that this peak corresponds to the Cu–P bond. However, in the Cu K-edge spectra, a small broad peak was found between the position of the Cu–Cu bond (2.24 Å) on the Cu K-edge spectrum of Cu foil and the position of the Mo–Mo (2.85 Å) bond on the Mo Kedge spectrum. This indicates that there were probably a few Cu-Mo bonds in Mo_8CuP_9 crystallite. It is assumed that Cu may be partly enter the MoP crystallite. We also need further experiments to research the local structure of Cu in Mo_8CuP_9 catalyst.

The Ni K-edge FTs of EXAFS collected in Ni-based phosphide catalysts are given in Figure 3c. Both samples give two dominant peaks located at 1.77 and 2.27 Å characteristic for Ni-P and Ni-Ni, respectively^{30, 31}. Analogously, Ni₃₈W₂P₂₀ maintained the original structure and co-ordination of Ni₂P after doping with W. Figure 3d shows the FTs of the Ni K-edge and W L_3 -edge EXAFS spectra for $Ni_{38}W_2P_{20}$ catalysts. The W L_3 edge EXAFS spectrum shows a broad radial distribution between about 1.15 Å and 2.80 Å, which comprises both W-P and W-M (M = W or Ni) contributions. The W L₃-edge EXAFS spectra for $Ni_{38}W_2P_{20}$ catalyst was fitted with Ni_2P as a model. From the fitting parameters (Table 1), the bond lengths of W-P (2.46 Å) and W-M (M = W or Ni) (2.72 Å) were longer than those of Ni-P (2.24 Å) and Ni-Ni (2.62 Å). These could be attributed to the atom size of W (atomic radius, 137 pm) being longer than that of Ni (atomic radius, 125 pm). These results demonstrated that W entered the Ni₂P crystal lattice to replace Ni.

3.1.3 XPS

Figure 4 shows the XPS spectra in the Mo 3d and Ni $2p_{3/2}$ regions for the phosphide catalysts. For MoP, the Mo $3d_{5/2}$ peaks at 227.8, 229.5 and 232.0 eV are attributed to the Mo^{δ^+}

Figure 5. H2-TPD profiles of the phosphide catalysts.

ARTICLE

species in MoP, Mo⁴⁺ and Mo⁶⁺, respectively¹⁴. The peak due to Mo^{δ +} in Mo₈WP₉ was located at about 228.2 eV, which was higher than that in MoP. Analogously, In the Ni 2p_{3/2} spectra of Ni₂P, two peaks were visible at 852.9 and 855.9 eV, which were assigned to Ni^{δ +} species in Ni₂P and Ni²⁺ ions, respectively¹⁴. The peak attributed to Ni^{δ +} in Ni₃₈W₂P₂₀ was at about 852.8 eV, higher than that in Ni₂P. These results indicated that the positive charge of Mo^{δ +}/Ni^{δ +} in W modified phosphides was more than that in original catalysts. These could be ascribed to the electron transfer from Mo/Ni to W, which was consistent with that the electronegativity (2.16) of Mo/Ni is lower than that (2.36) of W.

Conversely, the Mo 3d spectra of Mo_8CuP_9 exhibited one peak at about 227.7 eV corresponding to Mo^{δ^+} species, which was slightly lower than that of MoP. This meant that the positive charge of Mo^{δ^+} in Mo_8CuP_9 was less than that of MoP, partly due to the addition of Cu leading to an increase in the electron density around the Mo.

3.1.3 H₂-TPD

H₂-TPD was performed to investigate the effects of modifier (W and Cu) on the interaction between metal and hydrogenation. The H₂-TPD profiles recorded on different samples are shown in Figure 5. Usually, the hydrogen species desorbed below 400 °C are related with those adsorbed on the metal sites, while those desorbed above 400 °C are attributed to the spilt-over hydrogen species²⁷. It was worth noting that the desorption peak below 400 °C of the W modified sample slightly shifted to lower temperature, and the amount of desorbed H₂ of the W modified sample decreased compared with the unmodified catalyst (MoP). This shift is attributed to the decreased binding energy between the adsorbed hydrogen and active sites, which due to the W modifier effects, leading to the decrease of electron density around metal sites. On the contrary, in the case of Cu modified phosphide, the area of the peak below 400 °C was much smaller than that of MoP though the peak shifted toward a low temperature. This could suggest that the interaction between the adsorbed hydrogen and active sites enhanced with the Cu modification, resulting in the increase of electron density around metal sites.

Table 1. The physical properties and catalytic activities of different samples.				
Samples	BET Area [m²/g]	CO uptake [µmol/g]	Conversion (%)	TOF [s ⁻¹]
MoP	8.70	8.05	26.71 ^ª	0.21
Mo_8WP_9	9.67	11.65	75.67ª	0.40
Mo ₈ CuP ₉	3.29	2.24	3.50 ^ª	0.09
Ni ₂ P	0.42	0.04	6.92 ^b	11.86
$Ni_{38}W_2P_{20}$	1.92	0.11	25.48 ^b	14.29

^areaction conditions: 3 MPa, 300 °C, WHSV = 6 h^{-1} , H₂/oil = 1000 ^breaction conditions: 3 MPa, 370 °C, WHSV = 3 h^{-1} , H₂/oil = 1000

3.2 Hydrogenation activity

3.2.1. Hydrogenation Performance

To evaluate the hydrogenation performance of these catalysts, they were tested on the HDO reaction of the model compound, methyl palmitate. As the activity of the Ni-based phosphides was lower than Mo-based phosphides, the hydrogenation performance of the Mo-based phosphides were performed at 300 °C, while the activity test of the Ni-based phosphides catalysts was employed at an elevated temperature (370 °C). The variations of the conversion and products selectivity with the reaction time were observed to tend to stable (Figure S2-S6, ESI⁺). The catalytic activities of catalysts are

presented as conversions at in Table 1. It is clearly observed that both of the W-modified catalysts (Mo_8WP_9 and $Ni_{38}W_2P_{20}$) showed higher activities, whereas Cu-modified catalysts exhibited lower activities than those of the reference catalysts, as anticipated. In practical terms, the conversions of methyl palmitate on Mo_8WP_9 were approximately 2.83 times those on MoP, while the conversion on Mo_8CuP_9 was more than two times lower than those on MoP. In terms of Ni-based phosphide catalysts, the conversion of $Ni_{38}W_2P_{20}$ increased from 6.92% on Ni_2P to 25.48%.

3.2.2. Catalyst TOF

In order to get rid of the influence of different exposed active sites on different catalysts, we chose TOF as a significant the activity of per active site in unit time. The Brusnaeur-Emmett-Teller (BET) surface area, CO uptake and Turn over frequency (TOF) value of different catalysts are given in Table 1.The distinctions reflected among these BET values of catalysts were in accordance with the SEM images. The number of active sites was determined by the CO uptake value. Mo₈WP₉ and $Ni_{38}W_2P_{20}$ chemisorbed more CO than MoP and $Ni_2P,$ respectively, indicating that the amount of active sites increased through W modification. Crucially, TOF displays a same variation tendency as the conversion. The TOF value of Mo₈WP₉ was 1.9 times that of MoP, and Ni₃₈W₂P₂₀ maintained a TOF value 1.2 times that of Ni₂P, while Mo₈CuP₉ maintained a TOF value less than half that of MoP. Indeed, the active site of Mo₈WP₉ was intrinsically more active than that of MoP for the conversion of methyl palmitate, the same for $Ni_{38}W_2P_{20}$ and Ni₂P. These phenomena can possibly be explained by the higher electronegative W entering the original crystal and giving rise to electron transfer from Mo (or Ni) to W, leading to the electron density around Mo (or Ni) decreased and causing the interaction between Mo (or Ni) and

RSC Advances

atomic hydrogen weakened. It could be investigated in the H₂-TPR results. The interaction between active sites and atomic hydrogen has been proved to be the lynchpin to determine the activation of atomic hydrogen, which revealed the improvement of hydrogenation properties¹⁹. Conversely, the activity of active sites decreased after the MoP catalyst modified by Cu. On the one side, this is might due to the electron transfer from Cu to Mo, caused by the interaction between Mo and Cu entered the crystal. On the other, it is supposed that the introduction of lower electronegativity Cu likely favoured more electrons around Cu to transfer to P, which could be shown by the existence of the Cu-P bond obtained from the EXAFS results. Instead, the electrons transferred from Mo to P might be reduced. The two approaches of electron transfer make the electron density around Mo increased, which resulted in the enhancement of the interaction between Mo and hydrogen. This is not conducive to the activation of hydrogen. In summary, these results testified that the addition of elements W and Cu with different electronegativities

Figure 6. The methyl palmitate conversions and products selectivity of two different series catalysts at different reaction conditions. The reaction conditions of Mo-based phosphides were: 3 MPa, 300 °C, WHSV = 6 h^{-1} , H₂/oil = 1000; and the reaction conditions of Ni-based phosphides were: 3 MPa, 370 °C, WHSV = 3 h^{-1} , H₂/oil = 1000

Figure 7. The C16/C15 molar ratios of two different series catalysts. The reaction conditions of Mo-based phosphides were: 3 MPa, 300 °C, WHSV = 6 h^{-1} , H₂/oil = 1000;

the reaction conditions of Ni-based phosphides were: 3 MPa, 370 °C, WHSV = 3 $h^{-1},$ H_2/oil = 1000

successfully controlled the hydrogenation performance of catalysts.

3.2.3. Product selectivity

Figure 6 compares the products distribution of different catalysts resulted at steady state. Analysis of the products showed that in the presence of all these catalysts, the major products were pentadecane (C15) and hexadecane (C16), which were generated from the decarbonylation (DCO) and HDO pathways, respectively^{32, 33}. The detected oxygenated intermediates were hexadecanol, hexadecanoic acid (trace) and palmityl palmitate (trace). Hexadecanol was an important intermediate in the process of HDO reaction. The selectivity of different products showed remarkable dependency on composition of catalysts. Figure 7 shows the C16/C15 molar ratios on different catalysts, which represents the selectivity between the HDO and the DCO pathways. For Mo based phosphides (MoP and Mo₈WP₉), the C16/C15 ratio was larger than 1. While the C16/C15 ratio obtained from the Ni based phosphides (Ni₂P and Ni₃₈W₂P₂₀) was less than 1. It could turn out that MoP and Ni₂P preferentially catalysed HDO and DCO reaction, respectively¹⁴. This could also be partly due to the higher reaction temperature employed in the case of Ni-based phosphides than that of Mo-based phosphides catalysts. Because it has been reported that the increase of the temperature in HDO reactions would favor the DCO parthway³⁴.

As to the MoP catalyst, the selectivity of C15 was 21% and the selectivity of C16 was 27%, while the selectivity of the intermediate hexadecanol was 53%. For comparison, the selectivity of C16 was markedly increased to 67% over Mo₈WP₉ after the incorporation of W into MoP, while the selectivity of hexadecanol showed an apparent decline. Simultaneously, the C16/C15 molar ratio increased significantly. This indicated that the addition of W promoted the formation of C16 proceeded via the dehydration and hydrogenation of hexadecanol. Analogously, in case of Ni based catalysts, the selectivity of C16 increased and the selectivity of C15 decreased as the dopant of W, resulting in the enhancement of C16/C15 molar ratio. In summary, the HDO reaction on Mo (or Ni) sites was promoted and the DCO pathway was inhibited to a certain degree. It can partially be explained by the electronic interaction between Mo (or Ni) and W (i.e., electron transfer from Mo or Ni to W), which lead to the decrease of electron density around metal sites (Mo and Ni). The Mo and Ni sites with higher electrophilicity were more easily combined with electronegative oxygen in methyl palmitate or oxygencontaining intermediates (hexadecanol) and were favourable to the activation of C = O and C-O group, predominately giving rise to the HDO product (C16)^{14, 35}.

DOI: 10.1039/C6RA09862B

RSC Advances

ARTICLE

In regard to Cu with lower electronegativity modified MoP catalyst, the selectivity of C15 increased and the selectivity of hexadecanol decreased (i.e., C16/C15 molar ratio declined). The introduction of Cu to MoP catalysts facilitated the decarbonylation and inhibited the HDO pathway. This may partially because of the interaction between Mo and Cu entered the crystal, the electron transferred from lower electronegative Cu to higher higher electronegative Mo. Meanwhile, the interaction between P and Cu not entered the crystal made more electrons transfer from Cu to P, and lead to the electrons transferred from Mo to P reduced. In both cases, the electrophlicity of Mo was decreased to give rise to the promotion the DCO pathway on Mo site³⁶.

4. Conclusions

The electronegativity modification method for enhancing hydrogenation activity of catalysts was further studied in this paper. The XRD and EXAFS results revealed that the W occupied the position of Mo and Ni on the premise of maintaining the original crystal structures. The interaction between W and Mo (or Ni) made the electrons around the Mo (or Ni) atom transfer to the W atom, which was accounted by the greater electronegativity of W. The activity evaluations gave the results that the TOF value of W-modified catalyst (Mo_8WP_9) was higher than that of the original catalyst (MoP). Meanwhile, the C16/C15 ratio on W-modified catalyst (Mo_8WP_9) was increased, which represented the enhancement of the selectivity of HDO route. A similar TOF and C16/C15 ratio changing trends were observed between Ni₃₈W₂P₂₀ catalyst and Ni₂P catalyst. However, both the TOF value and C16/C15 ratio of the Cu-modified catalyst (Mo₈CuP₉) were lower than those of MoP. It turned out that the hydroprocessing performance of the catalyst could be controlled by the addition of modifiers with higher or lower electronegativities. This finding may give valuable information for designing more effective hydrogenation catalysts.

Acknowledgements

This work was financially supported by the NSFC (21376123, U1403293), MOE (IRT-13R30 and 113016A), and the Research Fund for 111 Project (B12015).

Notes and references

- 1 R. Kuwano, R. Ikeda and K. Hirasada, Chem. Commun., 2015, **51**. 7558-7561.
- S. Liu, Q. Zhu, Q. Guan, L. He and W. Li, Bioresour. Technol., 2 2015, **183**, 93-100.
- P. A. Nikulshin, P. P. Minaev, A. V. Mozhaev, K. I. Maslakov, 3 M. S. Kulikova and A. A. Pimerzin, Appl. Catal. B- Environ., 2015, **176-177**, 374-384.
- X. Hu, S. Kadarwati, Y. Song and C. Li, RSC Adv., 2016, 6, 4647-4656.
- A. K. Rathi, M. B. Gawande, V. Ranc, J. Pechousek, M. Petr, K. Cepe, R. S. Varma and R. Zboril, Catal. Sci. Technol., 2016, 6, 152-160.

- 6 C. Tu, M. Li, H. Li, Y. Chu, F. Liu, H. Nie and D. Li, RSC Adv., 2016. 6. 33177-33183.
- F. Han, Q. Guan, and W. Li, RSC Adv., 2015, 5, 107533-107539.
- 8 N. Koike, S. Hosokai, A. Takagaki, S. Nishimura, R. Kikuchi, K. Ebitani, Y. Suzuki and S. T. Oyama, J. Catal., 2016, 333, 115-126
- 9 Y. Chen, C. Li, J. Zhou, S. Zhang, D. Rao, S. He, M. Wei, D. G. Evans and X. Duan, ACS Catal., 2015, 5, 5756-5765.
- 10 C. A. Badari, F. Lónyi, E. Drotár, A. Kaszonyi and J. Valyon, Appl. Catal. B- Environ, 2015, 164, 48-60.
- 11 L. Yang, X. Li, A. Wang, R. Prins, Y. Chen and X. Duan, J. Catal., 2015, **330**, 330-343.
- 12 H. Song, J. Gong, H. Song and F. Li, Appl. Catal. A- Gen., 2015, 505, 267-275.
- 13 S. T. Oyama, J. Catal., 2003, 216, 343-352.
- 14 J. Chen, H. Shi, L. Li and K. Li, Appl. Catal. B- Environ, 2014, 144.870-884.
- 15 S. J. Sawhill, D. C. Phillips and M. E. Bussell, J. Catal., 2003, 215. 208-219.
- 16 P. Bui, J. A. Cecilia, S. T. Oyama, A. Takagaki, A. Infantes-Molina, H. Zhao, D. Li, E. Rodríguez-Castellón and A. Jiménez López, J. Catal., 2012, 294, 184-198.
- 17 J. Bai, X. Li, A. Wang, R. Prins and Y. Wang, J. Catal., 2012, 287, 161-169.
- 18 T. Wada, K. K. Bando, T. Miyamoto, S. Takakusagi, S. T. Oyama and K. Asakura, J. Synchrotron Radiat., 2012, 19, 205-209.
- 19 R. Li, Q. Guan, R. Wei, S. Yang, Z. Shu, Y. Dong, J. Chen and W. Li, J. Phys. Chem. C, 2015, 119, 2557-2565.
- 20 S. Ted Oyama, H. Zhao, H. J. Freund, K. Asakura, R. Włodarczyk and M. Sierka, J. Catal., 2012, 285, 1-5.
- 21 V. Teixeira da Silvaa, L. A. Sousaa, R. M. Amorimb, L. Andrinic, S.J.A. Figueroad, F. G. Requejoc, F. C. Vicentinifa, J. Catal., 2011, 279, 88-102.
- 22 I. I. Abu and K. J. Smith, J. Catal., 2006, 241, 356-366.
- 23 A. W. Burns, A. F. Gaudette and M. E. Bussell, J. Catal., 2008, 260. 262-269.
- 24 V. Zuzaniuk, R. Prins, J. Catal., 2003, 219, 85-89.
- 25 Q. Guan, F. Wan, F. Han, Z. Liu and W. Li, Catal. Today, 2016, 259.467-473.
- 26 M. Newville, J. Synchrotron Rad., 2001, 8, 322-324.
- 27 K. Li, R. Wang and J. Chen, Energy & Fuels, 2011, 25, 854-863.
- 28 S. T. Oyama, P. Clark, V. L. S. T. da Silva, E. J. Lede and F. G. Requejo, J. Phys. Chem. B, 2001, 105, 4961-4966.
- 29 S. T. Oyama, P. Clark, X. Wang, T. Shido, Y. Iwasawa, S. Hayashi, J. M. Ramallo-López and F. G. Requejo, J. Phys. Chem. B, 2002, 106, 1913-1920.
- 30 Y.-K. Lee and S. T. Oyama, J. Catal., 2006, 239, 376-389.
- 31 G. N. Yun and Y. K. Lee, Appl. Catal. B- Environ, 2014, 150-151, 647-655.
- 32 N. Chen, Y. Ren and E. W. Qian, J. Catal., 2016, 334, 79-88.
- 33 R. G. Kukushkin, O. A. Bulavchenko, V. V. Kaichev and V. A. Yakovlev, Appl. Catal. B- Environ, 2015, 163, 531-538.
- 34 F. Han, Q. Guan and W. Li, RSC Adv., 2015, 5, 107533-107539.
- 35 V. M. L. Whiffen and K. J. Smith, Energy & Fuels, 2010, 24, 4728-4737.
- 36 J. Chen, Y. Yang, H. Shi, M. Li, Y. Chu, Z. Pan and X. Yu, Fuel, 2014. 129. 1-10.

The catalyst (MoP) was modified by higher electronegativity element W and lower electronegativity element Cu, realizing the control of hydrogenation performance of the catalysts.

