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A novel surface modification approach for synthesizing supported nickel

phosphide catalysts with high activity for hydrodeoxygenation of

benzofuran

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Highlights ►

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Highlights ► >A novel modification approach for preparing a highly active Ni₂P is proposed. ► >The catalyst was modified with oxygen, no pre-treatment of the catalyst is needed. ► >The Ni₂P preparation step is simplified and therefore energy-efficient.
► >The O-free products yield of Ni₂P-O/MCM41 improved by 60% compared to Ni₂P-N/MCM41.

Abstract

A novel and simple surface modification approach for preparing a highly active nickel phosphide hydrodeoxygenation (HDO) catalyst is proposed, in which the original nickel phosphide catalyst is modified with oxygen at 373 K under a flow of air for 1 h instead of being passivated with an O_2/N_2 mixture. In this way, no pre-treatment of the catalyst prior to reaction is needed. The effect of surface modification with oxygen on catalytic performance in HDO of benzofuran was investigated. This surface modification apparently promotes the formation of smaller Ni₂P particles in catalyst, favoring more dissociation of molecular hydrogen. The Ni₂P preparation step is simplified and therefore energy-efficient, and the obtained catalyst exhibits a much higher O-free products yield (88%) than that with the unmodified catalyst (38%).

Key words: Nickel phosphide; Surface modification; Oxygen; Hydrodeoxygenation;

Benzofuran

1. Introduction

The increasing demand for energy, environmental issues, and depletion of oil reserves have highlighted the need to develop alternatives to fossil fuels. As a kind of renewable energy resource, biomass has been attracting much attention for the production of liquid fuels [1]. One method of biomass conversion is pyrolysis, but unfortunately the liquid products obtained by pyrolysis contain a high fraction of oxygen (35–50 wt.%) [2]. The high oxygen content of pyrolysis oil leads to higher viscosity, acidity, and lower heating values [3]. To upgrade the physical and chemical stability of these liquid products, the oxygen must be removed as water or carbon oxides by a hydrodeoxygenation (HDO) process [4]. Oxygen removal can be carried out by conventional hydrodeoxygenation processes, which are generally operated under a high pressure (3–10 MPa) of hydrogen at moderate temperatures (573–773 K) [5]. The majority of organooxygen compounds that are found in synthetic feed-stocks have either a phenolic or furanic structure [6,7]. Benzofuran (BF) is a commonly used

probe molecule to evaluate catalyst performance in HDO reactions [6,8-14]. It has a structure similar to those of the most commonly studied organosulfur and organonitrogen compounds for hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) reactions, respectively, and thus provides an analogue that facilitates comparisons of HDO with these processes.

HDO catalysts composed mainly of conventional sulfide catalysts, noble metal catalysts, and transition metal phosphides [3,15-20]. However, sulfide catalysts suffer from a progressive deactivation during the HDO reaction due to oxidation of the active phase [21]. Noble metal catalysts exhibit higher HDO activity than sulfide catalysts, but their high cost prevents their wide practical application. In recent years, transition metal phosphides have attracted great attention as new hydroprocessing catalysts. Ni₂P has recently been reported as a novel catalyst with unique physical and chemical properties in the HDO of furan, benzofuran, phenol, guaiacol, and anisole [4, 20, 22-23].

Metal phosphides and metal catalysts synthesized by reduction of precursors in H_2 are usually passivated prior to their removal from the synthesis apparatus. Passivation of a freshly prepared catalyst most frequently involves passing a dilute oxygen flow (0.5 vol.% O_2/N_2) over it in order to form a protective layer. In such cases, re-reduction to the metal phosphide is necessary, and this operation consumes energy. Duan et al. [23] examined H_2S as a passivation agent for Ni₂P catalysts. They found that a small degree of surface reconstruction took place during HDS reaction at the surface of the H_2S -passivated catalyst, and that more extensive reconstruction occurred at the surface

of the in-situ reduced catalyst. Therefore, surface modification of the metal phosphide is required.

In this work, a novel and simple surface modification approach for preparing a highly active supported nickel phosphide hydrodeoxygenation (HDO) catalyst is proposed. The supported nickel phosphide catalyst was synthesized according to a previously described method [24] from ammonium hypophosphite and nickel chloride at a lower reduction temperature of 673 K. Then as-obtained nickel phosphide catalyst was modified with oxygen at 373 K under a flow of air for 1 h instead of the passivation with an O_2/N_2 mixture. In this way, pre-treatment of the catalyst prior to reaction was not needed, thereby saving energy. Finally, a possible mechanism was proposed to interpret the improved catalytic behavior of the modified catalyst.

2. Experimental

2.1. Preparation of supports and catalysts

Siliceous MCM-41 was synthesized using tetraethyl orthosilicate (TEOS) as the silica source and cetyltrimethylammonium bromide (CTAB) as the template, following the procedure as described in the literature [25]. The supports obtained were named MCM-41.

The supported Ni₂P catalyst precursor was prepared by impregnating an ammonium hypophosphite (NH₄H₂PO₂) and nickel chloride (NiCl₂·6H₂O) solution with the mesoporous MCM-41. The precursor, was prepared with Ni loading of 8.8 wt.% and an initial Ni/P molar ratio of 1/2. In a typical experiment, 1.8 g (20.62 mmol)

NH₄H₂PO₂ and 2.5 g NiCl₂·6H₂O (10.31 mmol) were dissolved in 20 mL of deionized water at room temperature to form a uniform solution. A quantity of 6.0 g MCM-41 was wet-impregnated with the above solution for 8 h. The volume of the solution of precursors during the impregnation was 26 mL. The mixture was heated to evaporate the water, the obtained solid was dried at 363 K overnight. The precursor was then pelleted, crushed, and sieved to 16/20 mesh. For the reduction, precursor was placed in a fixed-bed reactor by heating to 673 K, at a rate of 2 K/min in a flow of H₂ (200 mL/min), held for 2 h, then naturally cooled to room temperature in a continuous H₂ flow. The prepared catalyst was passivated in O_2/N_2 mixture (0.5 vol.% of O_2) at a rate of 20 mL/min for 1 h. The catalyst obtained was named as Ni₂P-N/MCM41. A highly active supported nickel phosphide catalyst (Ni₂P-O/MCM41) for HDO was synthesized in flowing H₂ at 673 K(200 mL/min), at a rate of 2 K/min, held for 2 h, then cooled to 373 K under flowing air (20 mL/min) for 1 h instead of passivation with O_2/N_2 mixture.

2.2 Characterization methods

The X-ray diffraction (XRD) analysis were carried out on a D/max-2200PC-X-ray diffractometer using CuK α radiation under the setting conditions of 40 kV, 30 mA, scan range from 10 to 80° at a rate of 4°/min.

The typical physico-chemical properties of supports and catalysts were analyzed by BET method using Micromeritics adsorption equipment of NOVA2000e. All the

samples were outgassed at 473 K until the vacuum pressure was 6 mm Hg. The adsorption isotherms for nitrogen were measured at 77 K.

Transmission electron microscope (TEM) examinations were performed using the JEM-1010 instrument supplied by JEOL. The samples were dispersed in ethanol and placed on a carbon grid before TEM examinations.

The X-ray photoelectron spectroscopy (XPS) spectra were acquired using ESCALAB MKII spectrometer under vacuum. XPS measurements have been performed for Mg radiation (E = 1253.6 eV) and equipped with a hemi-spherical analyzer operating at fixed pass energy of 40 eV. The recorded photoelectron binding energies were referenced against the C 1s contamination line at 284.8 eV.

Irreversible CO uptake measurements were used to titrate the surface nickel atoms and to provide an estimate of the active sites on the catalysts [26,27]. The CO adsorption capacity of Ni₂P-N/MCM41 catalyst was measured after passivation without re-reduction, while Ni₂P-O/MCM41 catalyst was measured after surface modification with oxygen without re-reduction using a Builder PCA-1200 analyzer. CO uptake was obtained by pulsing calibrated volumes of CO into a He carrier. CO uptake was calculated by measuring the decrease in the peak areas caused by adsorption in comparison with the area of a calibrated volume.

2.3 Catalytic activities

The HDO of BF over prepared catalysts were performed in a flowing high-pressure fixed-bed stainless steel catalytic reactor (8 mm in diameter, and 400 mm in length),

using a feed consisting of a decalin solution of BF (2 wt.%). Prior to reaction, 0.7 g of the Ni₂P-N/MCM41 catalyst was pretreated at 673 K for 2 h in a H₂ flow (30 mL·min⁻¹). For the Ni₂P-O/MCM41 catalyst this step was saved. For comparison, we also tried treatment Ni₂P-N/MCM41 catalyst without H₂ reduction prior to HDO in the same reactor. The catalyst obtained was named as Ni₂P-N/MCM41-nr. Catalytic activities were measured at different temperatures (493-573 K) 3.0 MPa, WHSV=4 h⁻¹, and hydrogen/oil ratio of 500 (V/V). Sampling of liquid products was started 6 h after the steady reaction conditions had been achieved. Temperature was varied as follows: $573 \text{ K} \rightarrow 533 \text{ K} \rightarrow 493 \text{ K} \rightarrow 513 \text{ K} \rightarrow 553 \text{ K} \rightarrow 573 \text{ K}$, with the reaction held at each temperature for 3 h. The feed and reaction product was analyzed by FID gas chromatography with a GC-14C-60 column.

The total conversion was calculated from the ratio of converted benzofuran/initial benzofuran. The selectivity to the different reaction products was calculated based on the moles of each chemical as follows: ethylbenzene (EB), ethylcyclohexane (ECH), methylbenzene (MB), benzene (B), methylcyclohexane (MCH),

2,3-dihydrobenzofuran (2,3-DHBF), 2-ethylphenol (2-EtPh), and phenol (Ph).

Turnover frequency (TOF) values of the samples containing supported nickel phosphide were calculated using Eq. (1) : [28]

$$TOF = \frac{F}{W} \frac{y}{M}$$
(1)

Where *F* is the molar rate of BF fed into the reactor (μ mol·s⁻¹), *W* is the weight of catalyst (g), *y* is the conversion of BF (%), and *M* is the mole of sites loaded determined by the CO uptake.

3. Results and discussion

3.1. XRD

XRD patterns were used to identify the crystalline phases formed after reduction (Fig. 1). In order to study the effect of surface modification on the crystal structure of supported nickel phosphide catalysts, the structures of MCM-41 support, Ni₂P-O/MCM41 and Ni₂P-N/MCM41 were determined. For MCM-41, a broad diffraction line located at $2\theta = 23^{\circ}$ is due to the amorphous nature of mesoporous structure [29]. For all catalysts, the peaks at $2\theta = 40.6^{\circ}$, 44.5°, 47.1°, 54.1°, and 54.8° (PDF: 03–0953) can be ascribed to Ni₂P. No other additional phase related to Ni and P was observed, indicating that the active phase formed was mainly Ni₂P for both samples. After modification by the oxidation process, Ni₂P-O/MCM41 retained the crystal structure of Ni₂P, suggesting that such surface modification of the catalyst did not disrupt its crystal structure. The average size of the Ni₂P crystallites (column 5 of Table 1) estimated by the Scherrer equation was 20 nm for Ni₂P-O/MCM41, smaller than that for Ni₂P-N/MCM41 (24 nm). This indicates that surface modification with oxygen can promote the formation of smaller, highly dispersed Ni₂P particles on the catalyst.

3.2 N₂ adsorption

Fig. 2 shows the N₂ adsorption–desorption isotherms and BJH pore size distributions for the MCM-41 support, Ni₂P-O/MCM41 and Ni₂P-N/MCM41 catalysts. Table 1 summarizes the BET surface areas and pore volume results. The surface area

and pore volume of the MCM-41 support used were 1051 m²·g⁻¹ and 0.84 cm³·g⁻¹, respectively. It can be seen that both catalysts led to decreases in surface area and pore volume due to blocking of their pores by Ni₂P. The catalyst Ni₂P-N/MCM41 showed a surface area of 502 m²·g⁻¹, whereas that of Ni₂P-O/MCM41 was slightly higher at 509 m²·g⁻¹. This can be attributed to the decrease in the enrichment of phosphorus on the surface of Ni₂P-O/MCM41 compared with Ni₂P-N/MCM41 (see Table 2). This is discussed in Section 3.5 below.

As can be seen from Fig. 2a, all the samples displayed a type IV isotherm and a standard H4 type hysteresis loop according to the IUPAC classification, showing the presence of some mesopores. The pore size distributions obtained by Barrett–Joyner–Halenda (BJH) analysis of these curves show no marked differences among the samples. The average pore diameters of these samples lie in the range of 2.5–3.5 nm (see Fig. 2b).

3.3. CO uptake

The CO uptakes at room temperature of the samples are listed in column 6 of Table 1. It may be assumed that CO molecules are mainly adsorbed at Ni sites and so the amount of CO molecules adsorbed on P sites may be very small [30]. As shown in Table 1, the CO uptake of Ni₂P-O/MCM41 was 53 μ mol·g⁻¹, much higher than that of Ni₂P-N/MCM41 (31 μ mol·g⁻¹). This is possibly because the enrichment of phosphorus on the surface of Ni₂P-O/MCM41 is suppressed by surface modification with oxidization, which leads to the increase in the amount of exposed nickel atoms on the

surface (See Table 2, the superficial atomic ratio of Ni/P/O obtained from XPS analysis). This will discussed further in section 3.5. Similar results were reported by Li et. al [31]. The high CO uptake of Ni₂P-O/MCM41 is also attributed to the highly dispersed smaller Ni₂P particles. (See the provided TEM spectra).

3.4. TEM

The morphologies and microstructures of Ni₂P-O/MCM41 and Ni₂P-N/MCM41 catalysts were observed by TEM (Figure 3). It can be seen from Fig. 3(a), the Ni₂P particle sizes in the Ni₂P-N/MCM41 catalyst ranged from approximately 6 to 18 nm. Unlike the typical stacked morphologies of Mo and W sulfides, Ni₂P are not layered and form spherical particles that can be well dispersed on supports [24]. Fig. 3(b) shows that the Ni₂P particle sizes in the Ni₂P-O/MCM41 catalyst ranged from approximately 2 to 6 nm. The TEM data, combined with the crystallite size estimates from XRD indicate that the Ni₂P-O/MCM41 catalyst has smaller and more uniform Ni₂P particles that nNi₂P-N/MCM41, and surface modification with oxygen is beneficial to the formation of small Ni₂P particles.

3.5. X-ray photoelectron spectroscopy

In order to gain further insight into the surface composition of surface oxidation layer and the valence states of active components, the X-ray photoelectron spectroscopy (XPS) spectrum of fresh and spent catalysts were performed. Table 2 shows the binding energy values and the Ni/P/O atomic ratios. Table 3 shows the proportion of each species for the Ni2*p* and P2*p* spectra obtained by XPS analysis. As shown in Fig. 4(a), all spectra were decomposed, taking into account the spin-orbital

splitting of the Ni $2p_{3/2}$ and Ni $2p_{1/2}$ lines (about 17 eV) and the presence of satellite peaks at about 6 eV higher than the binding energy of the parent signal. This observation is consistent with that of Korányi et al. [32]. For the fresh and spent catalysts, Ni $2p_{3/2}$ core-level spectrum consists of three components, the first of which centered at 851.6–853.5 eV can be assigned to Ni^{δ +} in the Ni₂P phase, and the second at 856.3–857.6 eV corresponds to the possible interaction of Ni²⁺ ions with phosphate ions, as a consequence of superficial passivation, along with the broad satellite at approximately 6.0 eV higher than that of the Ni²⁺ species, and this shake-up peak is ascribed to divalent species [33]. Other broad peaks on the high binding energy side can be assigned to the Ni $2p_{1/2}$ components [34]. The P 2p binding energy spectrum features a peak at 129.5 eV due to P^{δ} of the metal phosphides and a peak at 134.5eV due to surface metal phosphate species arising from the superficial oxidation of the nickel phosphide particles [35].

As shown in Fig. 4(a), the XPS pattern of the as-prepared Ni₂P-N/MCM41 exhibited Ni 2*p* peaks at 852.3 and 856.3 eV, which can be attributed to the Ni^{δ^+} bands of Ni₂P (40.6%, See Table 3) and Ni²⁺ species (59.4%), respectively. Compared with fresh Ni₂P-N/MCM41, the binding energy for Ni species on the fresh Ni₂P-O/MCM41 catalyst was almost the same. However, the intensity of the peak at around 852.4 eV (5.7%) was clearly lower for the fresh Ni₂P-O/MCM41 catalyst, indicating that some of the reduced Ni^{δ^+} on the surface had been oxidized during the surface modification. Compared with the fresh Ni₂P-O/MCM41 catalyst, the intensity of the Ni^{$\delta^+} signal (24.7%)$ for spent Ni₂P-O/MCM41 was stronger, indicating that more Ni₂P particles were exposed on its surface. This may result from the fact</sup>

that Ni²⁺ species in the oxidized layer formed during surface modification with oxygen were reduced back to Ni^{δ^+} species by the hydrogen flow during the HDO reaction. In contrast, the intensity of the Ni^{δ^+} signal (31.3%) from the spent Ni₂P-N/MCM41 catalyst decreased rather than increased after the HDO reaction. Interestingly, compared with the fresh Ni₂P-O/MCM41 catalyst, the binding energy for Ni^{δ^+} shifts to a slightly lower value, while on the opposite, a shift to higher binding energies is observed for Ni²⁺ on the spent Ni₂P-O/MCM41. This indicates that during HDO reaction, the modifier oxygen changed the electron density of nickel species.

As shown in Fig. 4(b), for fresh Ni₂P-N/MCM41, peaks centered at 133.7 eV for $H_2PO_3^-$ (41.8%, See Table 3) and 134.6 eV for PO_4^{3-} (28.1%) were observed, together with a low intensity peak at 129.3 eV that can be assigned to the P^{δ} band (0.9%) of Ni₂P. It is noteworthy that a new band at 132.8 eV was also observed. This binding energy is higher than the value reported for elemental phosphorus (130.2 eV) and lower than the 133.5 eV reported for $H_2PO_3^-$. The band at 132.8 eV may possibly be due to $H_2PO_2^-$ (29.2%) [35]. However, the fresh Ni₂P-O/MCM41 shows only the two bands at 133.8 (49.7%) and 134.9 eV (49.4%), with the band at 132.8 eV diminished. This implies that the phosphorus on the surface of the catalyst was further oxidized during the modification with oxygen. Compared with fresh Ni₂P-N/MCM41, the total intensity of the P 2p features of fresh Ni₂P-O/MCM41 decreased, with a broadening towards the high binding energy side, indicating a strong interaction between oxygen and phosphorus to generate an oxy-phosphide. This is in accordance with the results obtained by Liu et al. [36]. In addition, an increase in the content of surface oxygen was observed for fresh Ni₂P-O/MCM41, which also confirms this point. This result discussed in the Ni/P/O atomic ratios below. For spent Ni₂P-N/MCM41, the contribution from $P^{\delta-}(0.9\%)$ species remained essentially unchanged, and the peak

due to the $H_2PO_2^-$ species at 132.8 eV disappeared compared to the fresh sample. The disappearance of the $H_2PO_2^-$ peak confirmed that the $H_2PO_2^-$ was transformed into $H_2PO_3^-$ (21.6%), PO_4^{3-} (77.5%), and $P^{\delta-}$ species (0.9%), and mainly existed in the forms of $H_2PO_3^-$ and PO_4^{3-} during the HDO reaction.

As shown in Fig. 4(c), the fresh Ni₂P-N/MCM41and Ni₂P-O/MCM41 catalysts showed a peak at around 532.5 eV, which could be attributed to OH⁻ [36]. Interestingly, for the fresh Ni₂P-O/MCM41 catalyst, the binding energy of OH⁻ shifts to a slightly higher value. This indicates that oxygen was strongly adsorbed on the surface of Ni₂P-O/MCM41. Compared with fresh Ni₂P-O/MCM41, a new peak at 533.2 eV was observed for spent Ni₂P-O/MCM41, while the band at 532.6 eV was diminished. The band at 533.2 eV could be assigned to adsorbed water [37]. This is discussed in Section 3.6 below.

XPS analyses were used to calculate the surface Ni/P/O atomic ratios. The theoretical Ni/P ratio corresponding to the precursor materials was 1/2. However, all as prepared samples exhibited lower

Ni/P values than 1/2, which may be due to the enrichment of phosphorous on the surface of the catalysts. However, an increase in the Ni/P ratio was observed for all spent samples compared to their corresponding as prepared samples. This may be due to a partial loss of phosphorous due to the formation of volatile P species, such as PH₃, during the HDO process, leading to a decrease in the amount of P on the surface. Both the fresh and spent Ni₂P-O/MCM41 samples have comparatively higher Ni/P atomic ratio compared to the Ni₂P-N/MCM41 catalysts. This implies that the enrichment of phosphorus on the surface of Ni₂P-O/MCM41 can be suppressed by surface modification with oxidization, which leads to

the increase in the amount of exposed nickel atoms on the surface of the sample. The enrichment of nickel atoms on the surface of catalysts modified with oxidization is possibly due to the formation of an oxide layer. This is in accordance to the CO uptake results. The oxygen contents of the fresh Ni₂P-O/MCM41 catalyst was slightly higher than that of the fresh Ni₂P-N/MCM41 catalyst, which indicates a much higher proportion of Ni and P atoms are at higher oxidation state on the surface of the Ni₂P-O/MCM41 catalyst. Moreover, after HDO reaction, the oxygen contents increased slightly for all spent samples compared to their corresponding fresh samples. We conclude that the high oxygen contents in the superficial for all spent samples may be due to adsorbed oxygen species.

3.6. Catalytic results and reaction pathways

The prepared catalysts have been tested using the HDO of BF for 48h. The Ni₂P-O/MCM41 catalyst did not suffer deactivation for 48 h, displaying high stability. Fig. 5 depicts the HDO conversion as a function of the reaction temperature. As expected, BF conversion increased with increasing reaction temperature over all the catalysts. It is clear that surface modified Ni₂P-O/MCM41 catalyst showed a higher BF conversion than the Ni₂P-N/MCM41 catalyst prepared with O₂/N₂ mixture passivation–H₂ reduction (673 K for 2 h), and Ni₂P-N/MCM41-nr catalyst prepared with O₂/N₂ mixture passivation without H₂ reduction over the entire temperature range tested. Compared with Ni₂P-N/MCM41 (31%), Ni₂P-O/MCM41 showed much higher BF HDO conversion (57%) at relatively low temperature (493 K). On increasing the reaction temperature, the conversion over the Ni₂P-O/MCM41 catalyst increased and reached 95% at 573 K.

The BF conversion and CO uptake for samples were used to calculate the HDO TOF and listed in Table 1, column 8. As can be seen from Table 1, the HDO TOF of the Ni₂P-N/MCM41 is 0.0016 s^{-1} . The Ni₂P-O/MCM41 possesses a TOF value of 0.0018 s^{-1} , indicating the intrinsic activity of sites is increased slightly (12.5%) by the surface modification with oxidization.

With regards to the selectivity and reaction pathways of BF HDO over the as-prepared catalysts, the products and intermediates formed were analyzed. The main oxygen-free compounds products detected were: ethylbenzene (EB), ethylcyclohexane (ECH), methylbenzene (MB), benzene (B), and methylcyclohexane (MCH). The oxygen-containing intermediates observed were 2,3-dihydrobenzofuran (2,3-DHBF), 2-ethylphenol (2-EtPh), and phenol (Ph).

Fig. 6 shows the effect of reaction temperature on the selectivity to different reaction products. It can be seen that at a lower temperature (Fig. 6a, 6b), the main products over the Ni₂P-N/MCM41 and Ni₂P-O/MCM41 catalysts were O-containing intermediates, mainly 2,3-DHBF and 2-EtPh. With increasing reaction temperature, the yield of 2-EtPh initially increased and then decreased, and that of the 2,3-DHBF decreased. With these two catalysts, the first step involved in the transformation of BF was hydrogenation of the C=C bond leading to 2,3-DHBF as reported previously [11]. 2-EtPh was formed as a secondary product by C–O bond cleavage in 2,3-DHBF.

For the Ni₂P-N/MCM41 catalyst, 2,3-DHBF was the main product at 493–513 K, whereas 2-EtPh was the main product at 533–573 K. 2-EtPh was probably transformed

by two pathways: a primary pathway leading to EB by direct deoxygenation (DDO) pathway and a secondary way leading to phenol by dealkylation. At 493 K, the oxygen-free products over the Ni₂P-N/MCM41 catalyst were ECH (3%), EB (4%) and MCH (2%). At 573 K, the main oxygen-free products were ECH (17%), EB (9%), and MCH (7%), B (4%) and MB (2%). EB was converted ECH by hydrogenation and to MB and B by dealkylation. B was also formed by DDO of Ph. ECH converted to MCH by dealkylation. According to the detected product distribution and reaction pathways previously discussed in the literature [38], possible reaction routes that may occur during HDO of BF over the Ni₂P-N/MCM41 catalyst are shown in Scheme 1. A similar reaction mechanism was established by Bunch et al. [8], who suggested that C–O bond cleavage occurs through Hofmann-type elimination reaction (E₂) and nucleophilic substitution reaction (SN₂).

From Fig. 6b it can be seen that the selectivity for the deoxygenated product ECH was much higher than those for all of the other products over the Ni₂P-O/MCM41 catalyst. In addition, with increasing reaction temperature, selectivity for ECH over the Ni₂P-O/MCM41 catalyst increased significantly. ECH (selectivity of 68.0% at 573 K) became the major product at temperatures higher than 553 K. However, the selectivity in favor of EB and MCH increased much more slowly than that for ECH with increasing temperature. The selectivity for MCH, which was formed by the dealkylation of ECH, was about 11%, and the selectivity for EB was about 9% at 573 K. This suggests that the transformation of EB to ECH was fast, whereas that of ECH to

MCH was slow at higher temperature. Compared with the products formed over the Ni₂P-N/MCM41 catalyst, phenol was hardly detected in the products over the Ni₂P-O/MCM41 catalyst, indicating that 2-EtPh was probably transformed by one pathway, which is leading to EB by DDO. B was not detected and the selectivity for MB was less than 0.6%, indicating that EB was mainly converted to ECH. On the basis of the above description, possible reaction routes that may occur during HDO of BF under the experimental conditions over the Ni₂P-O/MCM41 catalyst are shown in Scheme 2. Moreover, the selectivity of the non-reduced catalyst (Ni₂P-N/MCM41-nr) is shown in Figure S1.

Fig. 7 shows the effect of reaction temperature on yields of O-free products over all the catalysts. Over the entire temperature range tested, the Ni₂P-O/MCM41 catalyst gave higher yields of O-free products than the Ni₂P-N/MCM41 and Ni₂P-N/MCM41-nr catalysts, the difference becoming more marked with increasing temperature. The Ni₂P-N/MCM41 showed higher yields of O-free products compare to Ni₂P-N/MCM41-nr, indicating that the re-reduction at 673 K before HDO reaction by hydrogen improved the HDO performance of the Ni₂P-N/MCM41 catalyst. However, the yields of O-free products of Ni₂P-N/MCM41 was significantly lower that of the Ni₂P-O/MCM41 catalyst. These results suggest that H₂ re-reduction at 673 K before HDO reaction is essential to restoring the desired catalytic properties of the Ni₂P-N/MCM41 catalyst and this operation consumes energy. For Ni₂P-O/MCM41 catalyst, the re-reduction before HDO reaction is omitted, therefore, the proposed

surface modification approach is simplified and therefore energy-efficient.

 Ni_2P -O/MCM41 catalyst was highly effective for promoting O-removal reactions in the range 553–573 K. At a reaction temperature of 573 K, the yield of O-free products over the Ni_2P -O/MCM41 catalyst reached 88%, improved by 50% compared with that over the Ni_2P -N/MCM41 catalyst (38%).

It is worth noting that the selectivity for ECH was significantly increased at > 553K over Ni₂P-O/MCM41. This suggests that surface modification with oxygen promoted the conversion of 2-EtPh, and that the transformation of EB to ECH over Ni₂P-O/MCM41 was very fast since the selectivity for ECH over the Ni₂P-O/MCM41 catalyst was much higher than that for EB. Edelman [12] proposed that after ring-opening in 2, 3-DHBF, the subsequent HDO of the 2-EtPh intermediate will govern the overall HDO of BF. HDO is generally conducted over traditional hydrotreating catalysts, which consist of metal sulfides such as Ni-MoS/Al₂O₃ or CoMoS/Al₂O₃ [8-9,38]. The active sites of these catalysts are coordinatively unsaturated sites at the edges of MoS₂ slabs. In addition, the surface configuration of the catalyst is known to strongly affect the reaction activity [11]. Recently, Romero [11] proposed that over sulfided NiMoP/Al₂O₃ catalysts the C–O bond cleavage of 2-EtPh could occur by an elimination process involving a basic site (presumably a sulfur anion) and a coordinatively unsaturated site. In a similar manner, the active site configuration of the Ni₂P catalyst upon the production of H₂O during the HDO can be understood. Ji-Sue Moon et al. [40] reported HDO of guaiacol over Ni₂P/SiO₂ catalysts,

and suggested that the active sites of these catalysts involved H or OH groups on Ni or P sites on the surface of the Ni₂P, and that the DDO pathway was favored by the surface OH groups. The mechanism involved in the transformation of 2-EtPh into EB over supported nickel phosphide catalysts is shown in Scheme 3. As mentioned above, there are OH groups on the fresh Ni₂P-O/MCM41 catalyst and water on the spent Ni₂P-O/MCM41 catalyst (Fig. 4(c)). The adsorbed OH groups on the surface of Ni₂P-O/MCM41 were effectively activated at a certain temperature. They could then bond with hydrogen from 2-EtPh to form water, which was subsequently removed from the surface of the Ni₂P-O/MCM41. The OH absorption sites were thereby regenerated. These regenerated absorption sites could further accommodate the OH groups of 2-EtPh, allowing the reaction to proceed. These absorbed OH groups may behave somewhat like a reaction initiator in the initial reaction. In this way, the DDO pathway can be significantly promoted. As a result, the transformation of 2-EtPh to EB is remarkably enhanced, and then EB is rapidly converted to ECH by hydrogenation. In the case of Ni₂P-N/MCM41, the adsorbed OH groups were not as active as those on Ni₂P-O/MCM41 catalyst since no water was detected on the spent Ni₂P-N/MCM41. This indicated the transformation of 2-EtPh to EB over the Ni₂P-N/MCM41catalyst proceeded by a different route.

Surface modification of the supported nickel phosphide catalysts with oxygen greatly improved their HDO performance. It has been reported that the HDS performance was improved when an Ni₂P catalyst was partially covered with sulfur

[23,40]. Analogously, modification of Ni₂P with oxygen may exert a similar effect on HDO. On the basis of the above discussion, a possible mechanism may be proposed to explain the effect of surface modification of the supported nickel phosphide catalysts with oxygen on their HDO performance (Fig. 8). In the HDO process, molecular hydrogen is cleaved into active atomic hydrogen over the catalyst. The surface modification with oxygen changes the electronic environment of the Ni₂P active phase, which may induce more dissociation of molecular hydrogen (Ni₂P behaves somewhat like hydrogenase) and improve the properties of the active atomic hydrogen. This is understandable, since the surface modification of Ni₂P/MCM41 with oxygen, which mainly leads to an interaction between oxygen and the phosphorus, generates a new active phase for HDO. The shift of the P2p binding energy of Ni₂P-O/MCM41 catalyst confirms interaction between oxygen and phosphorus (Fig. 4b). Finally, the surface modification results in an increase in catalytic performance (mainly through the DDO route shown in scheme 3). This is much like the modification by adsorbed sulfur leading to an improvement in the HDS performance of Ni₂P catalysts [40, 41]. As with sulfur, the modification with oxygen introduces highly electronegative atoms, which attract electrons and thus decrease the electron density around the H atoms bonded to Ni. Li et al. [31] have reported that the oxygen modifier improves the ionic property of the catalyst surface, which in turn improves the generation of active atomic hydrogen. On the other hand, the surface modification is beneficial for the formation of smaller Ni₂P particles (see the TEM results in Fig. 3) and enhances the performance of HDO of

BF. This is in good agreement with the results of a previous study reported by Liu et. al [36]. They concluded that the cooperation between oxygen and metal centers with moderate activity was responsible for the high performances of catalysts in the water-gas-shift reaction.

4. Conclusions

A novel surface modification approach for preparing a highly active hydrodeoxygenation (HDO) catalyst (Ni₂P-O/MCM41) was proposed. A supported nickel phosphide catalyst was synthesized from ammonium hypophosphite and nickel chloride at a relatively low reduction temperature of 673 K. Then as-obtained catalyst was then modified with oxygen at 373 K under a flow of air for 1 h instead of the usual passivation with an O_2/N_2 mixture. Prior to its use in catalytic reactions, no pre-treatment of the modified Ni₂P-O/MCM41catalyst was needed. The effect of the surface modification of the Ni₂P catalyst with oxygen on its performance of HDO of BF was investigated. The results showed that this surface modification did not disrupt the crystal structure of Ni₂P. The oxygen on the modified Ni₂P catalyst interacts mainly with the phosphorus to generate a new active phase for HDO, which may induce more dissociation of molecular hydrogen on the surface. The Ni₂P-O/MCM41 catalyst showed very high catalytic activity, with BF conversion close to 95% at 573 K, and a much higher O-free products yield (88%) than that with the Ni₂P-N/MCM41 catalyst (38%), indicating that the surface modification of the support nickel phosphide catalyst was highly effective for promoting O-removal reactions. In conclusion, the proposed

surface modification approach of the Ni₂P catalyst is simplified and energy-efficient because of no pre-treatment of the catalyst prior to reaction is needed, and the prepared catalyst exhibits much higher HDO activity and selectivity for O-free products. Finally, a possible mechanism was proposed to interpret the improved catalytic behavior of the highly active Ni₂P-O/MCM41 catalyst.

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1s core level spectra

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catalysts (Reaction temperature=493–573 K, pressure=3.0 MPa, WHSV=4.0 h⁻¹, and

hydrogen/oil ratio=500 (V/V))

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Sch. 2 Reaction pathways for HDO of BF over Ni₂P-O/MCM41catalyst

Sch. 3 Proposed reaction schematic of 2-EtPh HDO over Ni₂P catalysts

Tab. 1 Properties of catalyst samples

Sample	$S_{\rm BET}$	$V_{ m BJH}$	D^{a}	$d_{ m XRD}{}^{ m b}$	CO uptake	Conversion (%)	TOF	
Sumpro	$(m^2 \cdot g^{-1})$	$(cm^{3} \cdot g^{-1})$	(nm)	(nm)	$(\mu mol \cdot g^{-1})$	493 K	(s ⁻¹)	
MCM-41	1051	0.84	3.2	_			_	
Ni ₂ P-N/MCM41	502	0.37	2.9	24	31	31	0.0016	
Ni ₂ P-O/MCM41	509	0.37	2.9	20	53	57	0.0018	

 D^{a} : pore diameter, $D \approx 4V_{BJH}/S_{BET}$.

 $d_{\text{XRD}}^{\text{b}}$: Calculated from the $Dc = K\lambda/\beta \cos(\theta)$ (Scherrer equation) based on the Ni₂P {1 1}.

		Superficial						
Sample	Ni 2p _{3/2}		P 2 <i>p</i>			0	1 <i>s</i>	atomic ratio
	Ni ²⁺	Ni ₂ P	PO ₄ ³⁻	$H_2PO_3^-$	Ni ₂ P	OH	H_2O	Ni/P/O
Ni ₂ P-N/MCM41-fresh	856.3	852.3	134.6	133.7	129.2	532.4		1/3.16/3.40
Ni ₂ P-O/MCM41-fresh	856.3	852.4	134.8	133.8	129.2	532.7	_	1/2.54/4.99
Ni ₂ P-N/MCM41-spent	856.7	852.5	134.8	133.7	129.3	532.7	_	1/3.11/4.48
Ni ₂ P-O/MCM41-spent	857.4	851.7	134.5	_	129.3		533.2	1/2.15/5.27

Tab. 2 Spectral parameters obtained by XPS analysis

Tab.3 proportion of each species for the Ni2p and P2p spectra obtained by XPS analysis

Comple	Ni (%)			P (%)		
Sample	Ni ²⁺	Ni ₂ P	PO4 ³⁻	$H_2PO_3^-$	$H_2PO_2^-$	Ni ₂ P
Ni ₂ P-N/MCM41-fresh	59.4	40.6	28.1	41.8	29.2	0.9

Ni ₂ P-O/MCM41-fresh	94.3	5.7	49.4	49.7	0	0.9
Ni ₂ P-N/MCM41-spent	68.7	31.3	77.5	21.6	0	0.9
Ni ₂ P-O/MCM41-spent	75.3	24.7	61.7	31.6	0	6.7

Tab. 1 Properties of catalyst samples

Sample	S_{BET} $(\text{m}^2 \cdot \text{g}^{-1})$	$V_{\rm BJH}$ (cm ³ ·g ⁻¹)	D ^a (nm)	$d_{\rm XRD}^{\ b}$ (nm)	CO uptake (µmol·g ^{−1})	Conversion (%) 493 K	TOF (s ⁻¹)
MCM-41	1051	0.84	3.2	_		_	_
Ni ₂ P-N/MCM41	502	0.37	2.9	24	31	31	0.0016
Ni ₂ P-O/MCM41	509	0.37	2.9	20	53	57	0.0018

 D^{a} : pore diameter, $D \approx 4V_{BJH}/S_{BET}$.

 $d_{\text{XRD}}^{\text{b}}$: Calculated from the $Dc = K\lambda/\beta \cos(\theta)$ (Scherrer equation) based on the Ni₂P {1 1 }.

Tab. 2 Spectral parameters obtained by XPS analysis

		Superficial						
Sample	Ni 2p _{3/2}		P 2 <i>p</i>			0	1 <i>s</i>	atomic ratio
	Ni ²⁺	Ni ₂ P	PO4 ³⁻	H ₂ PO ₃ ⁻	Ni ₂ P	OH-	H_2O	Ni/P/O
Ni ₂ P-N/MCM41-fresh	856.3	852.3	134.6	133.7	129.2	532.4		1/3.16/3.40
Ni ₂ P-O/MCM41-fresh	856.3	852.4	134.8	133.8	129.2	532.7	_	1/2.54/4.99
Ni ₂ P-N/MCM41-spent	856.7	852.5	134.8	133.7	129.3	532.7	_	1/3.11/4.48
Ni ₂ P-O/MCM41-spent	857.4	851.7	134.5		129.3	_	533.2	1/2.15/5.27

Tab.3 proportion of each species for the Ni2p and P2p spectra obtained by XPS analysis

Consula	Ni	(%)		P (%		
Sample	Ni ²⁺	Ni ₂ P	PO ₄ ³⁻	$H_2PO_3^-$	$H_2PO_2^-$	Ni ₂ P
Ni ₂ P-N/MCM41-fresh	59.4	40.6	28.1	41.8	29.2	0.9
Ni ₂ P-O/MCM41-fresh	94.3	5.7	49.4	49.7	0	0.9
Ni ₂ P-N/MCM41-spent	68.7	31.3	77.5	21.6	0	0.9
Ni ₂ P-O/MCM41-spent	75.3	24.7	61.7	31.6	0	6.7