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Citation for published version (APA):
Lan, X., Pestman, R., Hensen, E. J. M., & Weber, T. (2021). Furfural hydrodeoxygenation (HDO) over silica-supported metal phosphides – the influence of metal - phosphorus stoichiometry on catalytic properties. Journal of Catalysis, 403, 181-193. https://doi.org/10.1016/j.jcat.2021.01.031

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DOI:
10.1016/j.jcat.2021.01.031

Document status and date:
Published: 01/11/2021

Document Version:
Publisher’s PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

• A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
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Furfural hydrodeoxygenation (HDO) over silica-supported metal phosphides – The influence of metal–phosphorus stoichiometry on catalytic properties

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A R T I C L E   I N F O

Article history:
Received 14 September 2020
Revised 28 January 2021
Accepted 30 January 2021
Available online 5 February 2021

Keywords:
Metal phosphide
Ni2P
Co2P
Hydrodeoxygenation
Furfural
Biomass
Mechanism
Infrared spectroscopy

A B S T R A C T

The gas-phase hydrodeoxygenation (HDO) of furfural, a model compound for bio-based conversion, was investigated over transition metal phosphide catalysts. The HDO activity decreases in the order Ni2P ≈ MoP > Co2P > Fe2P. Nickel phosphide phases (e.g., Ni2P, Ni3P5, Ni5P) are the most promising catalysts in the furfural HDO. Their selectivity to the gasoline additives 2-methylfuran and tetrahydro-2-methylfuran can be adjusted by varying the P/Ni ratio. The effect of P on catalyst properties as well as on the reaction mechanism of furfural HDO were investigated in depth for the first time. An increase of the P stoichiometry weakens the furan-ring/catalyst interaction, which contributes to a lower ring-opening and ring-hydrogenation activity. On the other hand, an increasing P content does lead to a stronger carbonyl/catalyst interaction, i.e., to a stronger η2(C, O) adsorption configuration, which weakens the C1—O1 bond (Scheme 1) in the carbonyl group and enhances the carbonyl conversion. Phosphorus species can also act as Brønsted acid sites promoting C1-O1 bond hydrogenolysis of furfuryl alcohol, hence contributing to higher production of 2-methylfuran.

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1. Introduction

Second generation biomass is a renewable feedstock with a lower carbon footprint than fossil crudes and is thus a promising alternative raw material to produce fuels and chemicals [1–3]. One of the interesting biomass-derived platform molecules is furfural (Scheme 1), which can be produced on an industrial scale by dehydration of hemicellulose from agricultural waste and forest residue [4–7] and has been identified as one of the numerous oxygenated compounds in pyrolysis bio-oils [8–14].

Currently, the most relevant use of furfural as a chemical feedstock is in the production of furfuryl alcohol (FOL) and tetrahydrofurfuryl alcohol (THFOL) from selective hydrogenation, which have significant applications in furan resins industry as solvents or chemical intermediates [5,15–21]. Besides, it is also feasible to obtain furan and tetrahydrofuran (THF) via decarboxylation and hydrogenation as an environmental benign industrial solvent in the synthesis of plastics, pharmaceuticals and agrochemicals [5,22,23]. Furthermore, the production of biofuels from furfural has received extensive attention during the last decades. Aldol-condensation of furfural with acetone, self-condensation of furfural, or condensation of intermediate products (e.g. furan, 2-methylfuran) with other substrates are promising approaches to produce higher alkanes (C8-C15) for diesel fuel applications. Cu-based catalysts have been found being active in the MF production [29–32]. However, Cu-Cr catalysts [29] used in the industrial MF production are highly toxic, while Cu supported on SiO2, Al2O3 or ZnO [30] suffers from sintering during long reaction periods. Group 9–10 metal catalysts (Ni [5,33], Co [33], Pt [13,34] and Pd [4,5,35]) are also active in the MF production. However, the strong interaction between the furan ring and the transition metal surface leads to undesired ring-hydrogenation or ring-opening reactions; the unstable η2(C, O) adsorbate configuration tends to turn into an η1(C)
configuration at high temperature enabling undesired decarbonylation reactions [5].

To optimize MF production over pure transition metals (e.g. Ni, Pt), more oxophilic metals (e.g. Fe, Zn) have been added to design alloy catalysts (e.g. PtZn [7] and NiFe [6,27]) for furfural HDO. The addition of more oxophilic elements provides more stable $\eta^2$(C, O) configurations to the catalyst surface, in which the furan ring is tilted away from the catalyst surface and the carbonyl group is bonded stronger to the catalyst surface by the additional interaction of the carbonyl O to the oxophilic metal [6,7]. Such $\eta^2$(C, O) configurations suppress furan-ring hydrogenation or ring-opening, and enhance the conversion of the carbonyl group by weakening the C1–O1 bond (Scheme 1) [6,7]. By adjusting the Fe loading from 0 to 5 wt% in FeNi/SiO2 catalysts at a constant Ni loading of 5wt%, the MF yield was improved from 20% for Ni/SiO2 to 80% for 5/5 wt% FeNi/SiO2 [6]. Besides alloying metals, ceramic materials like Mo2C [36–39] have also been explored for the furfural to MF conversion. Mo2C shows a high MF selectivity of 70% [36–38], but suffers from rapid deactivation with the furfural conversion decreasing from 90% to 18% over a period of 3 h [38]. Metal borides like NiB, CoB and NiP/P [14,19,40,41] have also been considered as catalysts in the furfural conversion. The electron-deficient B can attract the O atom of the carbonyl group, which weakens the C=O bond and thus promotes its hydrogenation to the alcohol [14,19]. Nevertheless, only FOL, instead of MF, has been obtained as main products on these metal boride catalysts.

Metal phosphides have extensively been investigated in hydrodesulfurization (HDS) [42–44] and hydrodenitrogenation (HDN) [44–48] reactions in recent years. Due to their promising catalytic performance, they are also increasingly applied in hydrodeoxygenation (HDO) reactions [49–52]. So far, there was a focus on investigating HDO model compounds[53], such as phenol [50,54–56], anisole [2,56], or guaiacol [1,57–62], furfural [63–65], and some aliphatic model compounds [50,54–56], which were empirically found to be precursors. The unreduced precursors are referred to as NiO-P/SiO2, MoO3-P/SiO2, WO3-P/SiO2, Fe2O3-P/SiO2, Co3O4-P/SiO2, and Cu2O-P/SiO2. A H3PO3/P/SiO2 sample with a phosphorus loading of 3 mmol/g was prepared as reference sample. Ni0.6Mo0.4P/SiO2 catalysts with atomic Ni/Mo ratios of 1:1 and 2:1 were prepared similarly by co-impregnation with a solution containing both Ni and Mo. The loading of Ni/Mo/P on the Ni0.6 Mo0.4P/SiO2 samples was 1.5, 1.5/3 or 1.5/0.75/3 mmol (for the elements Ni/Mo/P, respectively) per gram of SiO2.

Nip(x)/SiO2 and CoP(x)/SiO2 were prepared by incipient wetness impregnation as in our previous work [42]. Catalysts were prepared by a one-step impregnation of metal nitrates and H3PO3 followed by direct reduction of as-prepared precursors. The molar P/Ni ratio was varied from 0 to 2 (0, 0.33, 0.5, 1.0, 2.0) in the precursors. Catalyst with different P/Ni ratio were labeled as Ni0.6Mo0.4P/SiO2, NiP(0.33)/SiO2, NiP(0.5)/SiO2, NiP(1)/SiO2, and NiP(2)/SiO2, respectively. Molar ratios of P/Co were varied from 0 to 2 (0, 0.5, 1.0, 1.5, 2.0) in the catalyst precursors. Catalysts are denoted as CoP(0.5)/SiO2, CoP(1.0)/SiO2, CoP(1.5)/SiO2, and CoP(2.0)/SiO2, respectively.

2.3. Characterization

The metal loading was determined by inductively coupled plasma atomic emission spectrometry (ICP-AES) analysis performed on a Spectro Blue apparatus. Prior to analysis, samples were dissolved in an HF/HNO3/H2O solution with a volumetric ratio of 1:1:1. HF (VWR, 40%) and HNO3 (VWR, 65%) were used to prepare the acidic solvent for ICP measurements.

X-ray diffraction (XRD) patterns were acquired on a Bruker D2 Phaser powder diffraction system using Cu Kα radiation (1.5406 Å). Scans were taken at a rate of 1°/min in the range of 10° ≤ 2θ ≤ 80°.

BET surface area measurements were performed on a Micromeritics ASAP3020 Tristar system and a nitrogen stream was applied for N2 physisorption at ~196 °C. The specific surface area was determined by the Brunauer-Emmett-Teller (BET) equation using the adsorption data.

X-ray photoelectron spectroscopy (XPS) measurements were performed on a Thermo Scientific K-Alpha XPS apparatus equipped with a monochromatic Al Kα X-ray source. Samples were reduced and sealed in a turbular quartz reactor, transferred into a glovebox without exposure to air, then loaded in an airtight transfer vessel and introduced into the XPS analysis chamber for analysis. The background pressure prior to analysis was 2 × 10−9 mbar. Survey
scans were collected at constant pass energy of 200 eV, and region scans at 50 eV. The spectra were calibrated to the Si 2p line at 103.3 eV and fitted with the CasaXPS program. Temperature programmed reduction measurements in H₂ (H₂-TPR) were carried out between 50 °C and 700 °C. Typically, 15 mg catalyst precursor was heated in a 20 ml/min H₂ flow from 50 °C to 700 °C at a heating rate of 5 °C/min. The effluent gas composition was analyzed by an online mass spectrometer. The mass signals of 2 (H₂), 18 (H₂O), 34 (PH₃), and 30 (NO) were monitored.

Temperature programmed desorption of NH₃ (NH₃-TPD) was conducted between 25 °C and 400 °C. Typically, 15 mg catalyst precursor was reduced at 550 °C for 1 h and cooled down to 25 °C in a 20 ml/min flow of H₂. Afterwards, the reduced samples were first flushed with He for 30 min to remove physisorbed species, then with NH₃/He (10 v/v%) for 30 min to adsorb NH₃, followed by He for 30 min to remove weakly absorbed NH₃. Subsequently, the pretreated samples were heated from 25 °C to 400 °C in a 20 ml/min He flow with a heating rate of 5 °C/min. The effluent gas flow was monitored by a TCD detector.

Infrared (IR) spectroscopy of CO adsorbed samples were carried out with a Bruker Vertex 70v Fourier Transform IR spectrometer equipped with a DTGS detector. The catalysts were pressed into a self-supporting wafer with a diameter of 13 mm and then mounted in an in-situ cell equipped with CaF₂ windows. Prior to CO adsorption, the samples were reduced at 500 °C for 2 h, applying a heating rate of 10 °C/min, followed by evacuating the cell to a pressure below 2 × 10⁻⁶ mbar for 0.5 h at 500 °C. Afterwards, the reduced sample was cooled down to 25 °C under vacuum. CO was introduced into the cell with a metering valve until the CO pressure reached 5 mbar. The catalyst was exposed to CO for 5 min, subsequently evacuated for 5 min to 2 × 10⁻⁶ mbar, followed by heating to 425 °C at a rate of 10 °C/min under vacuum. The IR spectrum was recorded by accumulating 64 scans at a resolution of 2 cm⁻¹. Spectra of the freshly reduced as well as CO saturated catalysts were recorded during the heating process.

In case of furfural-IR, catalyst pretreatment and experimental parameters were the same as those of the CO-IR experiments. Liquid furfural was expanded into the evacuated cell at a pressure of 2 × 10⁻³ mbar for 5 min at 25 °C and then evaporated until a pressure of 2 × 10⁻⁶ mbar was reached. Afterwards, the catalyst was heated to 300 °C at a rate of 10 °C/min at 2 × 10⁻⁶ mbar. Spectra of the furfural-saturated catalysts were recorded during the heating process. Spectra of freshly reduced catalysts were taken to use as background correction reference.

The particle size of active Ni-phosphide phase was investigated with a FEI Tecnai 20 transmission electron microscopy (TEM).

2.4. Catalytic activity measurements

The catalytic performance of synthesized materials was evaluated in a plug flow fixed-bed reactor with 4 mm internal diameter. Furfural was fed by a syringe pump (Hewlett Packard 1050) and gasified at 170 °C using H₂ as carrier gas.

Prior to reaction, catalysts were reduced in-situ at the desired temperature in a hydrogen flow for 2 h. After reduction, the reactor was cooled to reaction temperature, then fed with a furfural/H₂ flow (H₂/furfural molar ratio = 74). The products were analyzed by an in-line gas chromatograph using a flame ionization detector (GC-FID) and a DB-1 (30 m, 0.32 mm, 1.00 μm) column.

The reaction was carried out at atmospheric pressure between 120 °C and 200 °C. In a typical run, the H₂ flow, the feeding rate of furfural, H₂ and the loading amount of catalysts were 20 ml/min, 0.001 ml/min in liquid phase, and 60 mg, respectively. This corresponds to a weight hourly space velocity (WHSV) of ca. 3 h⁻¹. All activity measurements were carried out in duplicate to verify reproducibility. The product gas stream was analyzed after 2 h on stream.

Conversion and selectivity were calculated as follows:

\[
\text{Conversion} (\%) = \frac{\text{mol of the products}}{\text{mol of furfural fed}} \times 100
\]

\[
\text{Selectivity} (\%) = \frac{\text{mol of one product}}{\text{mol of all products}} \times 100
\]

3. Results and discussions

3.1. Basic properties

The metal and phosphorus content of unreduced precursors as determined with ICP and the textural properties are listed in Table S1. Each precursor shows a P/metal molar ratio close to the target value. BET surface areas are between 150 m²/g and 250 m²/g, which are all lower than the surface area of bare SiO₂ (305 m²/g) and decrease with increasing P content due to pore blocking [72].

3.2. TPR

Temperature programmed reduction (TPR) was used (Figure S1) to determine the right reduction temperature for each catalyst. As revealed by Figure S1, the NiO-P/SiO₂, WO₃-P/SiO₂ and MoO₃-P/SiO₂ samples are reduced at 500 °C, 600 °C and 550 °C, respectively. A higher reduction temperature (650 °C) is required to reduce CoO₂P-P/SiO₂ and CuO-P/SiO₂, while Fe₂O₃-P/SiO₂ reduces at 680 °C.

In case of the NiP(x)/SiO₂ catalysts (Figure S1b), the reduction temperature is determined as 450 °C for Ni₃SiO₂ and 550 °C for NiP(x) (x = 0.33, 0.5, 1, 2). Although the TPR profiles of NiP(1) and NiP(2) show the most significant signals at 650 °C as a result of PO₃⁻ reduction, we have chosen 550 °C as reduction temperature since P species formed by reduction of excessive H₃PO₄ suffice for nickel phosphate formation.

In the case of the CoP(x)/SiO₂ catalysts (Figure S1c), Co/SiO₂ is reduced at 400 °C, while a high temperature of 650 °C is required for CoF(x) reduction.

3.3. XRD & TEM

X-ray diffraction (XRD) reveals that each catalyst formed crystalline phases after reduction (Fig. 1). All catalysts show a broad diffraction peak in the 20 range of 15–35°, typical of amorphous silica [60,74,75]. In Fig. 1a, all reduced samples contain pure phases of the corresponding metal phosphides (i.e. Ni₃P, MoP, Co₆P, Fe₆P, and Cu₆P) except WP/SiO₂, which displays reflections of both WP and unphosphided WO₃ phases. The sharp diffraction peaks of WP/SiO₂, Fe₂P/SiO₂, Co₅P/SiO₂ and Cu₅P/SiO₂ indicate that the metal phosphides consist of relatively large particles due to the rather high reduction temperature. For MoP/SiO₂ and Ni₃P/SiO₂, milder phosphidation conditions were applied and consistently the XRD patterns show broad diffraction peaks, suggesting smaller particles.

Fig. 1b shows XRD patterns of reduced NiP(x)/SiO₂ (x = 0, 0.33, 0.5, 1.0, and 2.0). Pure metallic NiP is formed in Ni₃SiO₂. Ni₃P is obtained on NiP(0.33), Ni₁₂P₅ on NiP(0.5), and Ni₂P on NiP(1) and NiP(2). FWHM indicates comparable particle sizes.

Fig. 1c shows that reduced CoP(x)/SiO₂ (x = 0, 0.5, 1.0, 1.5, and 2.0) contains a pure CoP phase on reduced Co/SiO₂. As the P/Co ratio increases, the active phase shifts from Co₃P to CoP with
Co₃P present in CoP(0.5), CoP, CoP(1.5), and CoP(2.0), and both phases in CoP(1).

Different from NiₓPy (Ni₂P, Ni₃P, Ni₁₂P₃) and CoₓPy (Co₂P, CoP), only one single phosphide phase has been obtained for Mo, Fe, Cu, and W. Hence we explored the effect of metal/P ratio on the catalytic performance only for nickel and cobalt phosphides.

Reduced Ni, NiP(0.5), NiP(1) and NiP(2) samples were also characterized by TEM to determine the particle size distributions (Fig. 2). Besides some large particles observed in the Ni catalyst, all catalyst show small nanoparticles of a comparable size of ~ 5 nm, consistent with the XRD data for the NiP(x) catalysts.

![XRD patterns of different metal phosphides.](image)

Fig. 1. XRD patterns of different metal phosphides.

![TEM images of NiP(x) (x = 0, 0.5, 1, 2) catalysts.](image)

Fig. 2. TEM images of NiP(x) (x = 0, 0.5, 1, 2) catalysts.
3.4. XPS

The XPS results reveal the type and amount of chemical species on the surface of reduced catalysts, which confirm the formation of metal phosphides.

Fig. 3 and Table S2 show the results of the reduced NiP(x) (x = 0, 0.33, 0.5, 1, and 2) catalysts. The contribution at 852.2 eV in Ni 2p spectra is assigned to Ni0 in metallic nickel, the contribution at 852.7 eV is assigned to Ni0+ (0 < d < 1) in nickel phosphide phases (Ni2P, Ni5P2 and Ni9P), and the signal at 856.4 eV to Ni2+ species [42]. Concerning the P 2p spectra, the three peaks at 134.4 eV, 133.5 eV and 129.1 eV are due to PO43−, PO32− and Pd− (0 < d < 1) species in nickel phosphides [42], respectively. PO43− originates from un-reduced H3PO4, while PO32− forms from the disproportionation or reduction of H3PO3 [42]. The presence of Ni0+ (0 < d < 1) and P− (0 < d < 1) in nickel phosphide phases points to an interphase Ni → P transfer of electron density as a consequence of the electron withdrawing nature of P [76]. The electron density on Ni0+ is expected to decline at higher P content due to the electron withdrawing nature of P atoms. Note that the presence of Ni0 species in NiP(2), NiP(1), NiP(0.5) and NiP(0.33) catalysts cannot be excluded, since the P/Ni ratios of these samples (Table S2) are all lower than the theoretical P/Ni ratios of Ni2P, Ni5P2 and Ni9P phases (0.5, 0.4, and 0.33, respectively).

Figure S2 displays the Co 2p and P 2p core-level spectra of reduced CoP(x) catalysts. Peaks at 777.4–777.9 eV are assigned to the Co0 or Co0+ (0 < d < 1) sites in catalysts, while peaks at 129.0 eV are the fingerprint of Pd− (0 < d < 1) in cobalt phosphides. Similar to NiP(x) catalysts, the presence of Co0+ (0 < d < 1) and Pd− (0 < d < 1) in Co2P and CoP phases points to an interphase Co → P transfer of electron density as a consequence of the electron withdrawing nature of P [76]. The binding energy of Co0+ is slightly higher than that of Co0 due to the slight positive charge it bears. Different from NiP(x) catalysts, the P/Co molar ratios of the reduced phases are higher than the elemental analysis in the respective phases (i.e. 0.5 in Co2P and 1 in CoP), indicating a P rich surface of Co2P and CoP phases.

3.5. NH3-TPD

NH3-TPD is used to characterize acid properties of the catalysts. Fig. 4 shows the NH3-TPD profiles of reduced Ni/SiO2 and NiP(x)/SiO2 (x = 0.33, 0.5, 1, 2). The TPD profiles consist of two peaks: one at low temperature in the range between 100 °C and 300 °C and another at high temperature between 500 °C and 650 °C. The low temperature peak in the profile of H3PO4/SiO2 corresponds to the POA−H groups with weak Brønsted acidity, while the high temperature peak in the profile of Ni/SiO2 might be attributed to Lewis acid sites stemming from Ni0+ species bearing a small positive charge or un-reduced Ni2+ species [2]. Both Brønsted acid and Lewis acid sites are present on NiP(x)/SiO2 samples due to the POA−H groups and Ni0+/Ni2+ species, respectively. The amount of Brønsted acid sites evidently increases as the P content increases.

3.6. CO-IR and furfural-IR

To get insight into how P influences the nature of active sites on the catalyst surface, further characterization of the reduced NiP(x) catalysts by CO-IR (Fig. 5) and furfural-IR (Fig. 6) was performed. The strength of the CO adsorption is directly related to the transfer of electrons from the metal to the p* orbital of the CO molecule. More back-donation of electrons to the p* orbital results in a stronger metal-CO bond and a weaker C=O bond. The latter is reflected

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**Fig. 3.** Ni 2p core-level (a) and P 2p core-level (b) spectra of reduced NiP(x)/SiO2 (x = 0, 0.33, 0.5, 1, and 2).
in a lower frequency of the CO stretching vibration. CO-IR can thus be used to probe the C–O bond strength after adsorption as well as the electron density of the adsorption site.

Fig. 5 shows the effect of varying P content on the chemical nature of catalysts by CO-IR. The bands at 3745 and 3670 cm$^{-1}$ are due to the $\nu$(O–H) stretching vibrations of Si–OH and P–OH surface groups [58]. The intensity of the $\nu$(PO–H) vibration (3670 cm$^{-1}$) increases with the P content, indicating a higher amount of Brønsted acid sites on catalyst surface. This is in alignment with the NH$_3$-TPD results shown above.

For the Ni/SiO$_2$ catalyst, the band at 2045 cm$^{-1}$ is assigned to CO molecules bonded to a single Ni atom [77,78]; the band at 1962 cm$^{-1}$ is attributed to CO molecules bonded to two Ni atoms (bridge-CO species) [77,78]. The band at 2086 cm$^{-1}$ is assigned to coordination of multiple CO molecules to a single coordinatively unsaturated Ni$^0$ site.

The infrared spectra of NiP(x)/SiO$_2$ catalysts show the strong bands between 2096 and 2086 cm$^{-1}$ (linear-CO bonded on Ni sites [57,78–80]). NiP(0.33) and NiP(0.5) exhibit a weak band at 1905 cm$^{-1}$ (bridge-CO species [77,81]), and NiP(1) and NiP(2) a very weak band at 2202 cm$^{-1}$ (P=O surface species) [77,80]. The peak broadening at 2096 cm$^{-1}$ is observed on NiP(0.33) and NiP(0.5) samples likely due to the dipole-dipole interaction of absorbed CO since the XPS results (Table S2) reveal that more...
neighboring Ni sites (i.e. lower P/Ni ratios) are available on NiP(0.33) and NiP(0.5) surfaces than on NiP(1) and NiP(2) surfaces [82,83].

The absorption band at 2086 cm\(^{-1}\) can tentatively be assigned to CO adsorbed on a single Ni in a phosphide matrix. As nickel in NiP(x) is positively charged according to XPS results (see Fig. 3), less back donation of electrons will occur creating a blue shift for the vibrational frequency of linearly adsorbed CO from 2045 cm\(^{-1}\) to 2086 cm\(^{-1}\). If the P content is reduced, more adjacent Ni will be available, increasing the dipole interaction and thus shifting and broadening the peak towards 2096 cm\(^{-1}\). Since both adsorption on positively charged nickel as adsorption of multiple CO on unsaturated nickel atoms lead to less back donation, it is not unexpected that the adsorption band of CO adsorbed on Ni in NiP(x) has a frequency (Fig. 5b colored lines) similar to that of multiple CO adsorbed on unsaturated sites of pure nickel (Fig. 5b, black line). The frequency of bridging-CO bands in NiP(x)/SiO\(_2\) (1905 cm\(^{-1}\)) is lower than those in the Ni catalyst (1962 cm\(^{-1}\)), indicating the presence of stronger bonded bridge-CO species in NiP(x)/SiO\(_2\). This allows us to conclude that the addition of P alters the properties of the adsorption site, apparently leading to a stronger bridge-CO adsorption. The intensity of the bridge-CO bands (1962 and 1905 cm\(^{-1}\)) decreases significantly with increasing P content, indicating that P lowers the amount of bridge-CO species (Fig. 5b). This is expected since P could block the availability of adjacent Ni atoms, which would act as adsorption sites for bridge-CO [77,78]. Since adjacent Ni sites are required for a planar adsorption of furan, the planar adsorption of the furan ring is also expected to decrease with increasing P content and so do the furan-ring hydrogenation or the ring-opening reaction in the furfural HDO.

The strength of CO adsorption on the catalyst surface is also explored by IR spectra obtained during temperature programmed desorption (Figure S3). As temperature increases, the intensity of the linear-CO band declines due to CO desorption. Increasing P content facilitates the desorption of linear-CO (Figure S3f), indicating a weaker CO adsorption on Ni sites at higher P content. This confirms the conclusions drawn from Fig. 5b that the adsorption band of linearly absorbed CO shifts to higher frequencies at higher P content as the adsorption is weaker due to the lower electron density on Ni\(^{+}\). Based on this understanding, the increasing P content is also expected to weaken the furan adsorption on the catalyst surface from an electronic point of view, because it contributes to a lower electron density on Ni\(^{+}\) sites providing a lower back donation of electrons from to the d-band of Ni to the \(\pi^*\) bond of the furan ring.

The adsorption bands (Fig. 5b) as well as the CO desorption behaviors (Figure S3f) are similar for NiP(0.33) and NiP(0.5) catalysts, as well as for NiP(1) and NiP(2), which is consistent with the XPS results (Table S2) showing that NiP(0.33) and NiP(0.5) have a similar Ni reduction degree of 0.67 and 0.68, respectively, and NiP(1) and NiP(2) of 0.74 and 0.75, respectively. This suggests that NiP(0.33) and NiP(0.5), as well as NiP(1) and NiP(2), possess active sites with similar geometrical and electronic properties.

In summary, P addition decreases the amount of adjacent Ni sites and the electron density on Ni sites, which is expected to suppress the planar adsorption of furan ring from both geometrical and electronic view.

IR spectra of adsorbed furfural on silica supported Ni/SiO\(_2\) and NiP(x)/SiO\(_2\) are shown in Fig. 6. The bands at 1675 and 1695 cm\(^{-1}\) are assigned to the \(\nu(C=O)\) stretching vibration of the carbonyl group; bands at 1570, 1465, and 1475 cm\(^{-1}\) are due to \(\nu(C=C)\) stretching vibration of the furan-ring [84–88]. The broad bands between 1400 and 1300 cm\(^{-1}\) are a result of the background correction.

As the P/Ni molar ratio increases, the \(\nu(C=O)\) bands gradually shift to lower frequency from 1675 cm\(^{-1}\) of Ni/SiO\(_2\) to 1655 cm\(^{-1}\) for NiP(2)/SiO\(_2\), which suggests that the interaction between the carbonyl group and catalyst surface is notably enhanced by P addition. Furthermore, new bands at 1625 cm\(^{-1}\) and 1622 cm\(^{-1}\) are observed on NiP(0.33) and NiP(0.5), indicating the formation of a second adsorption mode of the carbonyl group. In case of NiP(1) and NiP(2), the shoulder at 1635 cm\(^{-1}\) may also result from this new adsorption configuration of carbonyl groups.

Based on geometric and electronic considerations, the tendency of planar furan ring adsorption is expected to decrease with increasing P content. Nevertheless, no frequency shift of the \(\nu(C=C)\) band (at 1465 and 1475 cm\(^{-1}\)) is observed (Fig. 6). Likely because the interaction between the furan-ring and the catalyst surface is strong and the weakening effect of P on the furan-catalyst interaction insufficient to cause a frequency shift of IR bands. The intensity of the \(\nu(C=C)\) IR bands, however, clearly decrease with increasing P content. We therefore calculated the intensity ratios of \(\nu(C=O)/\nu(C=C)\) during a temperature programmed heating process to further investigate the adsorption situation of carbonyl groups and furan-rings on the catalyst surface. As temperature increases above 150 \(^\circ\)C, a significant decrease is observed in the \(\nu(C=O)/\nu(C=C)\) ratios on Ni/SiO\(_2\) and NiP(0.5)/SiO\(_2\), while only a slight decrease is detected on NiP(1)/SiO\(_2\) and NiP(2)/SiO\(_2\). This does again confirm that NiP(1)/SiO\(_2\) and NiP(2)/SiO\(_2\) with higher P content exhibit a stronger carbonyl adsorption than Ni/SiO\(_2\) and NiP(0.5)/SiO\(_2\).

The CO-IR investigation of CoP(x) was also conducted (Figure S4). As in the case of P in the NiP(x) samples, the P addition does suppress the presence of adjacent Co sites, i.e. bridging-CO adsorption sites. As argued above, P atoms do likely “dilute” Co atoms at the surface hence suppressing the bridge-CO adsorption [77].

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The intensity of the 2066 cm\(^{-1}\) band assigned to multiple CO adsorbed on unsaturated sites, declines with increasing P content, suggesting saturation of coordinated unsaturated Co sites by P. Furthermore, a decrease in electron density of Co\(^{+}\) is expected at higher P content due to the electron withdrawing nature of P, in line with the declining adsorption strength of linear-CO at higher P content (Figure S5f). Since adjacent Co sites are necessary for the planar adsorption of the furan ring and a lowered electron density of Co\(^{+}\) contributes to weaker adsorption of furan ring, the P addition exerts a suppressing effect on the planar adsorption of furan rings on CoP(x) surface for reasons of geometric constrains and electronic structure, which is very similar to the situation in NiP(x).

4. Catalytic activity measurements

4.1. Catalyst screening

The activity of different metal phosphides was tested in furfural HDO at a WHSV of 3 h\(^{-1}\), a pressure of 1 bar and a temperature of 200 °C (Fig. 7a). MoP, NiP, CoP, and WP show promising furfural conversions in the order Ni\(_2\)P \(\approx\) MoP > CoP \(\approx\) WP with values around 90%, 91%, 53%, and 50%, respectively. Cu\(_2\)P and Fe\(_2\)P show almost no activity and are excluded from our study. Subsequently, Ni\(_2\)P, MoP, CoP, and WP were further tested at different contact times to explore the reaction mechanism of furfural HDO over these catalysts (Fig. 7b,c,d,e).

According to previous research employed pure metal catalysts [5,6,21,35], mainly two reaction pathways are proposed for furfural HDO (Scheme 2). One is a hydrogenation pathway (pathway 1), in which the carbonyl group is first hydrogenated to an aliphatic hydroxyl group, which is then removed by hydrogenolysis,
Fig. 7. (a) HDO conversion of furfural over different metal phosphides at varying WHSV; Conversions (white squares in the bars) and selectivity of furfural HDO over (b) Ni$_2$P, (c) MoP, (d) Co$_2$P and (e) WP at different WHSV. Catalyst loading = 60 mg, T = 200 °C, H$_2$/furfural molar ratio = 74. Data collected after 2 h time on stream. MF: 2-methylfuran; THFOL: tetrahydrofurfuryl alcohol; FOL: furfuryl alcohol; THMF: tetrahydro-2-methylfuran.

Scheme 2. Reaction pathways in the HDO of furfural according to literature [5,6,21,35]. FOL: furfuryl alcohol, MF: 2-methylfuran, THF: tetrahydrofuran, THMF: tetrahydro-2-methylfuran, THFOL: tetrahydrofurfuryl alcohol.
generating furfuryl alcohol (FOL) and subsequently 2-methylfuran (MF) as products. The other one is decarbonylation (pathway 2) yielding furan as a product. If applied catalysts (e.g., Ni, Co, Pd [5,33]) have a high hydrogenation capacity, furfuryl alcohol (FOL), 2-methylfuran (MF) and furan can be further hydrogenated to tetrahydrofurfuryl alcohol (THFOL), tetrahydro-2-methylfuran (THMF) and tetrahydrofuran (THF), respectively. If catalysts possess high hydrogenolysis capability, the formation of ring-opening products (e.g., butanol, butane, pentanol, pentane, etc.) would be obtained.

In our cases, metal phosphides show a promising performance in the furfural HDO with activity orders of Ni₂P ≈ MoP > Co₂P ≈ WP and a desirable product selectivity towards 2-methylfuran. Product distributions differ across the series of metal phosphides significantly. WP and MoP show highest selectivity towards MF (>90%), whereas Co₂P mainly produces the less-desired furan product (>40%). This shows that each metal phosphide sample favors the hydrogenation and decarbonylation routes in a different way.

At decreasing furfural conversions (attained by increasing WHSV), all catalysts showed increasing furfural alcohol selectivity at the expense of 2-methylfuran production, revealing the hydrogenation mechanism (pathway 1) of metal phosphide catalysts. The constant furan selectivity revealed a decarbonylation pathway (pathway 2), which is independent from the hydrogenation pathway. Small amounts of THFOL and THMF, and no trace of ring-opening products were detected, indicating that furan-ring hydrogenation and ring-opening reactions are successfully suppressed over these catalysts. Accordingly, these catalysts can contribute to lower hydrogen consumption and lower light-product formation in comparison to traditional transition metal catalysts (i.e. Ni [5,6] or Pd [5]).

For MF production, indirect and direct reaction pathways have been reported over metal and metal alloy surfaces (e.g., PtZn, NiFe, and Mo₃C [6,7,20,37]). The indirect reaction pathway consists of hydrogenation of κ₁(C, O) surface adsorbed species to FOL, followed by conversion into MF via FOL hydrogenolysis [6,20]. The direct reaction pathway involves the conversion of the κ₁(C, O) species into C₄H₄O-CH₂ or C₄H₄O-CH intermediates, which are anticipated to directly produce MF in a H₂-rich environment [7,20,37]. The presence of FOL at high WHSV over Ni₂P, MoP, Co₂P, and WP catalysts (Fig. 7) confirms the indirect MF formation mechanism. Yet, the direct MF formation pathways cannot be excluded, especially for MoP and WP, where high MF production can be still obtained at low conversion (Fig. 7).

4.2. NiP(x)/SiO₂

As shown above, NiP₄/SiO₂ is practically the most active catalyst among our metal phosphides with a promising product distribution. We therefore decided to study this catalyst in more detail: Nickel phosphide samples were prepared by varying the P/Ni molar ratios NiP(x) (with x = 0.33, 0.5, 1, 2) and were tested in the furfural HDO (Fig. 8). Since the focus of our work is to optimize selectivity and to develop a mechanistic explanation of the furfural HDO reaction, instead of optimizing reaction rates, TOF investigations at low conversion are not included here. Nevertheless, upper bound estimates of TOFs based on the given data are provided in Table S3.

Significant yields of FOL and THFOL are produced over metallic Ni, demonstrating the high hydrogenation ability, i.e. strong interaction between furfural and the Ni metal surface. Higher amounts of MF and THMF are produced at the expense of FOL and THFOL over NiP(0.33) and NiP(0.5), implying an enhanced C–O1 (Scheme 1) hydrogenolysis ability of these catalysts, i.e. a stronger interaction between the carbonyl group and the Ni-P catalyst surface. The decreasing production of THMF over NiP(0.33) and NiP(0.5), as well as the absence of THMF over NiP(1) and NiP(2), reveals a suppressing effect of P on the furan-ring hydrogenation, i.e. a weaker interaction between furan-ring and catalyst surface. High reaction temperatures contribute to high production of undesired decarbonylation and ring-opening reactions, consistent with the effect of reaction temperature on furfural HDO over pure metal catalysts [5,6,33]. The NiP(1) and NiP(2) catalysts show similar catalytic performance, which can be attributed to the fact that these catalysts contain the same active (Ni₂P) phase (XRD). In line with this, their surface characteristics as probed for XPS, CO-IR and furfural-IR spectroscopy are also similar. The behaviors of the NiP(0.33) and NiP(0.5) catalysts are clearly different from those of NiP(1) and NiP(2), most likely due to the different active phases of Ni₃P and NiP₄. Reasons of different catalytic behavior of the Ni₃P, Ni₁₂P₅ and NiP₄ active phases are discussed below.

4.2.1. Furan-ring/Ni(P) interaction

The interaction between the furan-ring and the catalyst surface (labeled below as the furan-ring/Ni interaction) is essentially the interaction between the d-band of Ni and the π* bonding of the furan-ring. As the Ni/SiO₂ catalyst accommodates the highest electron density on Ni sites and the largest concentration of bridge-CO sites among all of our catalysts, the furan-ring/Ni interaction is expected to be the strongest here, contributing to ring-hydrogenation and ring-opening reactions in the furfural conversion. Therefore, it is plausible that substantial amounts of THFOL are obtained on a Ni catalyst.

As the P content increases, the number of adjacent Ni sites, required to form bridge-CO species, is substantially suppressed (Fig. 5) and the electron density on Ni sites is gradually reduced due to the electron withdrawing nature of phosphorus. From a geometric viewpoint, the furan-ring/Ni interaction is expected to decrease due to the decreasing amount of adjacent Ni sites. From an electronic structural point of view, the interaction between the Ni d-band and the furan π-system is expected to decline at higher P content due to the lower electron density on Ni³⁺ sites. Therefore, the furan-ring/Ni interaction as well as the ring-hydrogenation capability of the catalysts are expected to decline as the P content increases, which is consistent with our activity results that the product distribution shifts from THFOL for Ni/SiO₂ to THMF for NiP(0.33), then to MF for NiP(0.5), NiP(1), and NiP(2).

4.2.2. Carbonyl/Ni(P) interaction

The interaction between the carbonyl group and the catalyst surface, which can be characterized by furfural-IR, is another key factor influencing furfural HDO performance.

According to literature, the carbonyl group adopts an κ₁(C, O) configuration on the Ni surface, which is unstable and tends to rearrange into an κ¹(C) configuration at higher temperature (Scheme 4c) [5]. As the κ¹(C) configuration is most likely the precursor for decarbonylation, an increasing furan production is observed as reaction temperature increases [5]. Our results are consistent with those published in literature [5]: the ν(C=O)/ν(C=O)/ν(C=O) ratio of the adsorbed species decreases at higher temperature (Fig. 6f) confirming the κ¹(C, O) → κ¹(C) conversion at higher temperature. In accordance with the formation of the κ¹(C) configuration, more furan is produced at higher temperature (Fig. 8).

After P addition, the ν(C=O) stretching vibration of adsorbed furfural shifts to lower frequency and the downward shift tends to be more prominent when the P content increases (Fig. 6), indicating a stronger carbonyl/catalyst interaction at higher P content. It is likely that electron-deficient Ni³⁺ binds to the lone pairs of the carbonyl O, while electron-rich P³⁺ donates electrons to the antibonding orbitals of the C=O moiety, contributing to a stronger carbonyl/catalyst interaction (i.e., a more stable κ¹(C, O)).
configuration, Scheme 4). Such stronger carbonyl/catalyst interaction weakens the C1\(^{-}\)O1 bond (Scheme 1) in the carbonyl group. Consequently, the carbonyl hydrogenation and subsequent C1\(^{-}\)O1 hydrogenolysis of FOL could be enhanced, which is consistent with the product distribution shift from FOL and THFOL of Ni catalyst to MF and THMF of NiP(0.33) catalyst. Besides, the MF yields are relatively stable for NiP(1) and NiP(2) at low or high furfural conversions. Likely that the Ni\(_2\)P surface exposes sites with the appropriate geometry and electronic properties that enable a direct MF formation from furfural deoxygenation via C\(_4\)H\(_3\)O\(_\@\)CH\(^@\) or C\(_4\)H\(_3\)O\(_\@\)CH\(_2\)O\(^@\) intermediates (Scheme 3).

Another explanation for the changing catalytic performance by P addition is based on the role of Brønsted acid sites: In the hydrodeoxygenation of phenolic compounds, a Brunsted acid site adjacent to a metal site is considered to facilitate C\(^{-}\)O hydrogenolysis by protonating the oxygen in \(\text{C}^{-}\text{OH}\) or \(\text{C}^{-}\text{OCH}_3\) groups \(^{[87,88]}\). Since the P species in NiP(x) catalysts could also act as Brønsted acid which would facilitate the C1\(^{-}\)O1 (Scheme 1) bond breaking. The MF production is enhanced at the expense of the FOL production by increasing the P content as a result of Brønsted acid sites facilitating the C1\(^{-}\)O1 (Scheme 1) bond breaking. Besides, phosphorus could act as a Brønsted acid which would facilitate the C1\(^{-}\)O1 (Scheme 1) bond breaking.

4.3. CoP(x) catalysts

Since Co\(_2\)P is the third active catalyst in furfural HDO (Fig. 6) and the active phases of cobalt phosphide are adjustable by varying the molar P/Co ratio, we investigated the effect of the P stoichiometry in CoP(x) phases on the furfural HDO as well (Figure S6). The conversion decreases with increasing P content, indicating the decreasing activity in the order Co\(_2\)P < CoP < Co. Similar to NiP(x), the ring-opening products are suppressed with increasing P content. This is understandable, since as in the case of the nickel phosphides, P suppresses the formation of adjacent Co sites required for the planar adsorption of the furan ring, and lowers the electron density of Co\(_d\)\(^{+}\) sites leading to a weaker interaction between furan ring and catalyst surface. In addition, the MF production is enhanced at the expense of the FOL production by increasing the P content as a result of Brunsted acid sites facilitating the C1\(^{-}\)O1 (Scheme 1) bond breaking. A higher furan production is found on CoP(x) than on NiP(x); a possible explanation for this observation is as follows. The \(\eta^2\)(C, O) configurations on the catalyst surface are stabilized by the carbonyl O donating electrons to electron-deficient Co\(^{3+}\) or Ni\(^{3+}\) sites.

![Fig. 8. Activity results of (a) NiP(2)/SiO\(_2\), (b) NiP(1)/SiO\(_2\), (c) NiP(0.5)/SiO\(_2\), (d) NiP(0.33)/SiO\(_2\), (e) Ni/SiO\(_2\) for furfural HDO at different reaction temperature. Catalyst = 60 mg, H\(_2\) = 20 ml/min, furfural = 0.001 ml/min in liquid. Data after 2 h on stream. MF: 2-methyl furan, FOL: furfuryl alcohol, THFOL: tetrahydrofurfuryl alcohol, THF: tetrahydrofurfuryl alcohol, THMF: tetrahydro-2-methylfuran. The diamond in the bars indicates furfural conversion.](image-url)
and the antibonding orbitals of C=O accepting electron density from electron-rich P\(^{5-}\). Since the density of Co\(^{2+}\) sites on CoP(x) surfaces is lower than that of Ni\(^{2+}\) on NiP(x) (P/Co > P/Ni, Table S2), the binding of carbonyl O to the catalyst surface will be lower on CoP(x) surfaces, which contributes to an easier \(\eta^2(C, O)\) transformation and, consequently to a higher furan formation rate on CoP(x) catalysts.

Overall, we summarize that increasing the P/Co stoichiometry in CoP(x) samples suppresses the ring-opening reactions but does not suppress the undesired decarbonylation. In comparison with
NiP(x), CoP(x) catalysts are not desirable in furfural conversion due to the higher furan production and the lower MF yield (furan has a lower C yield than MF in furfural conversion). Our characterization and activity results of CoP(x) and NiP(x) demonstrate that the type of metal phosphide and the phosphorus/metal ratio plays a crucial role in determining the furfural adsorption on the catalyst surface, as well as the catalytic performance in furfural HDO.

5. Conclusions

A series of transition metal phosphides was evaluated in the furfural HDO reaction, showing the following activity trend: Ni₃P ≈ MoP > Co₂P ≈ WP > Cu₄P > Fe₃P. In comparison to traditional transition metal catalysts (i.e. Ni or Pd), metal phosphides like Ni₃P, MoP, Co₄P, and WP are promising catalysts for furfural HDO as they produce 2-methylfuran and furan as major products and contribute to lower hydrogen consumption and lower light-product formation.

By varying the P/ Ni molar ratios in NiP(x) precursors, the effect of P stoichiometry on catalytic properties and performance are investigated in depth. A higher P content weakens the furan-ring/catalyst interaction contributing to lower furan ring-hydrogenation and ring-opening reaction. On the other hand, it provides a stronger carbonyl/catalyst interaction by providing a more stable η¹(C, O) configuration with the electron-deficient Ni⁺⁺ binding to the lone pairs of carbonyl O and the electron-rich P⁺⁺ donating electrons to the antibonding orbitals of C=O. Such enhanced carbonyl/catalyst interaction weakens the C–O bond in the carbonyl group promoting its hydrogenation and further conversion. Moreover, P species could also act as Brønsted acid sites that facilitate hydrogenolysis of POF and THFOL, contributing to a higher production of MF and THMF. A comparable role of P was observed in CoP(x) samples, except that the undesired decarbonylation is suppressed to a lesser extent. This is likely because the density of available Co⁺⁺ sites on CoP(x) surfaces is lower than that of Ni⁺⁺ on NiP(x). This reduces the binding of the carbonyl O to the catalyst surface, thereby contributing to an easier η¹(C, O) → η¹(C) transformation and consequently a higher furan formation rate on CoP catalysts.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper. We consulted the author’s guide when submitting the manuscript. Manuscripts are prepared in accordance with publishing ethics policies described in the Author’s Guide.

Acknowledgements

The China Scholarship Council (CSC) is acknowledged for financial support. We thank Tiny Vrheooven for performing XPS measurements and Adelheid Elemans for the ICP measurements.

Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jcat.2021.01.031.

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