ARTICLE IN PRESS

Catalysis Today xxx (xxxx) xxx-xxx



Contents lists available at ScienceDirect

Catalysis Today



journal homepage: www.elsevier.com/locate/cattod

Hydrodeoxygenation of phenol using nickel phosphide catalysts. Study of the effect of the support

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ARTICLE INFO

Keywords: Hydrodeoxygenation Nickel phosphide: effect of support Phenol

ABSTRACT

This work studied the performance of nickel phosphide phases supported on various supports (SiO₂, Al₂O₃, TiO₂, CeO₂ and CeZrO₂) for the hydrodeoxygenation of phenol in gas phase at 300 °C and 1 atm. The nature of the phosphide phase obtained by the temperature programmed reduction at 700 °C depended on the type of support. Only Ni₂P was formed on SiO₂, TiO₂, and CeZrO₂, whereas the Ni₁₂P₅ was the preferred phase on Al₂O₃. A mixture of both Ni₂P and Ni₁₂P₅ phases was obtained on CeO₂. Unsupported Ni₂P exhibited high selectivity to benzene (95%), indicating that the Ni₂P phase is responsible for the direct deoxygenation of phenol. Ni₁₂P₅ phase promoted the formation of cyclohexanone, cyclohexane and cyclohexene. However, the supported catalysts showed lower selectivity to benzene, even when the Ni₂P was the only phase present. The supports favored the formation of hydrogenation products via the tautomerization route. All catalysts only slightly deactivated with time on stream, which is likely due to the high activity of the phosphide phase.

1. Introduction

The depletion of fossil fuels reserves and the increase in CO_2 emissions have stimulated the search for cleaner and renewable solutions. In this context, the use and valorization of lignocellulosic biomass for the production of fuels and chemicals has great potential due to its wide availability and carbon neutral emissions [1]. Among the biomass conversion routes, fast pyrolysis is one of the most economically viable, producing a liquid (so-called bio-oil) that can be used as fuel for transportation and for industry [1–3]. However, pyrolytic bio-oil presents low calorific value, high corrosivity, high viscosity and thermal and chemical instability due to the high concentration of oxygen compounds in its composition [4]. The hydrodeoxygenation process (HDO) can be used to upgrade bio-oil by decreasing its oxygen content and making possible its utilization as a transportation fuel.

The HDO process involves the deoxygenation of bio-oil molecules using hydrogen and a catalyst. The studies about HDO of bio-oil model compounds used different catalysts containing various active phases such as sulfide [5,6], oxide [7,8] and metallic [9–11] phases. Currently, phosphide catalysts have been extensively studied because they are more economical than noble metal catalysts and less susceptible to secondary reactions (e.g., hydrogenolysis of the C–C bond) than non-noble metal catalysts [4,12,13]. Furthermore, it has been reported that the phosphide phase exhibits higher activity to deoxygenation than noble metals.

Regarding the comparison between metallic Ni and Ni phosphide, Yang et al. [14] performed the HDO of methyl oleate under different experimental conditions (pressure and temperature). According to the authors, Ni₂P/SBA-15 catalyst favored deoxygenation and decarboxylation reactions instead of decarboxylation and cracking over Ni/SBA-

https://doi.org/10.1016/j.cattod.2019.08.028

Received 17 February 2019; Received in revised form 4 August 2019; Accepted 27 August 2019 0920-5861/ © 2019 Elsevier B.V. All rights reserved.

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15. Gonçalves et al. [15] studied the HDO of m-cresol under 4 MPa of total pressure and 340 °C over nickel and nickel phosphide catalysts supported on silica and zirconia. The authors observed that Ni phosphide phase was much more active than the metallic Ni phase, regardless of the support. Moreover, the deoxygenation activity also depended on the type of support. The following order of deoxygenation activity was observed: Ni₂P/ZrO₂ > Ni₂P/SiO₂ > Ni/ZrO₂ > Ni/SiO₂. The selectivity to toluene was higher for Ni₂P/ZrO₂ and Ni₂P/SiO₂ catalysts than for metallic Ni supported on silica or zirconia.

Even though it is known that the nature of the support influences product distribution and the extent of the HDO reaction [16,17], only few studies have investigated the effect of the type of support on the performance of nickel phosphide based catalysts, especially compared to other active phases [15,18–21]. Gonçalves et al. [15] attributed the higher activity to deoxygenated products for the HDO of m-cresol of Ni₂P/ZrO₂ in comparison to Ni₂P/SiO₂ to the oxophilic sites of the support represented by the Zr^{3+}/Zr^{4+} cations. The same effect was observed for Pd catalysts in the phenol HDO reaction (300 °C, 1 atm), in which the ones supported by oxophilic materials (ZrO₂, Nb₂O₅, TiO₂) showed higher benzene selectivity [22,23].

The type of support affects the nature of phosphide phase formed since the oxide may react with the phosphorous precursor salt leading to the formation of phosphate species with the support during calcination [24]. For example, Al₂O₃ tends to interact strongly with P forming AlPO₄ that inhibits Ni₂P synthesis and yields various Ni phases, such as Ni₁₂P₅ [18]. Gonçalves et al. [25] prepared nickel phosphide catalysts with different P/Ni ratios (0.8, 2 and 3) and observed that the activity of the catalysts was dependent on the active phase formed on the solid. The authors demonstrated that the highest P/Ni ratio presented higher activity because only a pure Ni₂P phase was obtained with P/Ni = 3, whereas the other samples containing either a mixture of Ni₂P and Ni₁₂P₅ (NiP-2/ZrO₂) or Ni₁₂P₅ (NiP-0.8/ZrO₂) alone were less active. The higher P/Ni ratio required to obtain the Ni₂P active phase is clear evidence of the influence of the support during preparation of nickel phosphides. During the phosphide synthesis, phosphorous tends to simultaneously be released from the surface as PH₃ by temperature programmed reduction and/or to stay on the surface forming POH groups, which imparts some acidity to the catalysts, as observed in NH₃-TPD and IR-pyridine experiments [26,27].

Deoxygenation activity and product distribution are also significantly influenced by the nature of the nickel phosphide phase as well as by the type of support. For example, Chen et al. [28] prepared different nickel phosphide catalysts using SiO₂, Al₂O₃, CeO₂, TiO₂, SAPO-11 and HY as supports. The authors observed that the Ni₂P phase was obtained using SiO₂, CeO₂, TiO₂ and SAPO-11 supports. The Ni₃P and Ni₁₂P₅ phases were formed using Al₂O₃ while Ni₁₂P₅ and Ni₂P were obtained on HY. From these results it is clear that the support displays different interactions with the atoms of nickel and phosphorus giving rise to the formation of different phases. The authors also showed that the activity for HDO methyl laurate followed the order: Ni₂P/SiO₂ > Ni₃P-Ni₁₂P₅/Al₂O₃ > Ni₂P/TiO₂ > Ni₂P/SAPO-11 > Ni₂P-Ni₁₂P₅/HY > Ni₂P/CeO₂.

The aim of this work was to investigate the effect of the type of support (SiO₂, Al₂O₃, TiO₂, CeO₂ and CeZrO₂) on the structure of the nickel phosphide phases and on their catalytic properties for the HDO of phenol reaction.

2. Experimental

2.1. Catalyst preparation

The unsupported and supported nickel phosphides catalysts were prepared by temperature programmed reduction (TPR) method. In general, this methodology is based on two steps: (i) phosphate formation and; (ii) reduction of phosphate to phosphide.

The unsupported NiP catalyst with a P/Ni molar ratio of 0.8 was

synthesized using the nickel nitrate hexahydrate (Ni(NO₃)₂.6H₂O, Merck) and ammonium hydrogen phosphate (NH₄)₂HPO₄, Vetec) salts. First, both salts were solubilized separately and then, the solution of (NH₄)₂HPO₄ was slowly dripped to the Ni(NO₃)₂.6H₂O solution under constant stirring. Then, nitric acid was added to the mixture until complete solubilization of the precipitate. The obtained solution was placed in a silicone bath held at 105 °C under moderate agitation. After 4 h, a gel was formed, which was dried at 150 °C. The solid was calcined at 500 °C for 6 h (10 °C min⁻¹). Before catalytic tests, this material was reduced ex situ using two heating steps with different rates: 30-350 °C $(10^{\circ}\text{C min}^{-1})$, 350–650 °C $(1^{\circ}\text{C min}^{-1})$. H₂ was fed into the reactor with a flow rate of 1 mL min⁻¹ for each mg of phosphate. Then, the reactor was cooled down to room temperature and fed with a 30 mL min^{-1} of 0.5% O₂/N₂ mixture during 16 h. For the catalytic experiments, in situ catalyst reactivation was done with a 30 mL min⁻¹ flow of pure H₂ at 300 °C for 1 h (10 °C min⁻¹).

For supported nickel phosphide catalysts, the following materials were used as supports: SiO₂ (Hi-Sil 915), Al₂O₃ (Puralox), TiO₂ (Aeroxide TiO₂ P25), CeO₂ and CeZrO₂. Silica (Hi-Sil 915, Aldrich), alumina (Puralox, Sasol) and titania (Aeroxide TiO₂ P25, Evonik Industries) were commercial materials. Silica and alumina were previously calcined under air flow (50 mL min⁻¹ at 5 °C min⁻¹) at different temperatures (800 °C: SiO₂, 1000 °C: Al₂O₃) for 5 h, while titania was not pre-treated. Cerium oxide and mixed cerium-zirconium oxide were synthesized by the precipitation method using cerium ammonium nitrate, zirconium nitrate and aqueous ammonia [29]. For cerium oxide, a 4.0 mol/L solution of cerium ammonium nitrate ((NH₄)₂Ce $(NO_3)_6$ (Sigma-Aldrich) was slowly dripped with stirring in an aqueous ammonia solution (7.85 mol/L). After the mixture was stirred for 30 min, the precipitate was filtered, washed with distilled water to neutral pH, dried in a oven for 24 h and finally calcined at 500 °C (5 °C/ min) for 6 h. For the preparation of ceria-zirconia mixed oxide (Ce/Zr molar ratio = 0.5), the precursor salts of zirconia nitrate $(ZrO(NO_3)_2)$ and $((NH_4)_2Ce(NO_3)_6$ were used. The salts were solubilized separately in a suitable concentration and the precipitate was filtered and washed with distilled water to neutral pH. The solid was then dried in an oven for 24 h and finally calcined at 500 °C at a heating rate of 5 °C/min in synthetic air stream (50 mL/min) for 6 h.

The nickel phosphide phases were synthesized by the temperature programmed reduction (TPR) method. This procedure can be divided into three steps: preparation of the solution of the nickel phosphide precursor, and impregnation of the precursor onto the support followed by calcination and reduction. In the first step, appropriate amounts of nickel nitrate (Ni(NO₃)₂.6H₂O) and dibasic ammonium phosphate ((NH₄)₂HPO₄) were solubilized in water and both solutions were mixed and kept under constant stirring. The catalysts were prepared to obtain 10 wt.% of Ni using an excess of phosphorus (molar ratio P/Ni = 3). Subsequently, a small amount of nitric acid (HNO₃) was added into the resulting solution. At this stage, the precipitate formed from the mixture of the two solutions was dissolved and the resulting solution was used for the impregnation of the supports by the incipient wetness impregnation method. After impregnation, the samples were dried in a oven at 120 °C for 24 h and calcined under air flow (60 mL/min) at 500 °C (10 °C/min) for 6 h. The samples were ground and sieved in the range of 250–315 µm. Finally, the reduction step was carried out in situ before the catalytic tests at 700 °C (5 °C/min) for 1 h. The reduction temperature before the catalytic tests was chosen based on the results of in situ XRD and temperature programmed experiments. All reduced catalysts were identified as NiP/support.

2.2. Catalyst characterization

The chemical composition was determined by inductively coupled plasma optical emission spectrometry (ICP-OES) using an SPECTRO ARCOS ICP-OES instrument. The specific area of the support and the precursor of phosphide catalysts were measured by nitrogen adsorption at -196 °C on a Micromeritics ASAP 2000 analyzer.

In situ XRD was carried out for unsupported nickel phosphide catalyst in XRD1 light line of the Brazilian Synchrotron Light Laboratory (LNLS). The sample to be analyzed was placed in a quartz capillary of 1 mm internal diameter between two pieces of wool of quartz. The capillary was added to a reaction cell connected to diffractometer of 3 circles of Newport (model N3050-P1). The temperature of analysis was controlled with a robotic arm (Yaskawa) used to maintain a blower (FMB Oxford (modelo GSB1300) of hot air above the capillary. A Si double crystal monochromator (111) positioned more than 10 m before the experimental station selected the wavelength equal to 1.0332 Å. The instrument was calibrated using Si (SRM 640d) and Al₂O₃ (SRM 640a), which are NIST standards (National Institute of Standards and Technology). The measurements were performed with a flow rate of 10 mL min^{-1} of pure H₂ in the capillary and with two heating ramps. Initially, the samples were warmed from room temperature to 400 °C at 10 °C min⁻¹. Then, the samples were heated at 3 °C min⁻¹ from 400 °C up to the final synthesis temperature, 650 °C. The XRD patterns were obtained in the interval from 30° to 60°. The X-ray powder diffraction (XRD) patterns of supported nickel phosphides were obtained using a Rigaku model DMax 2200 powder diffractometer with a copper tube (λ =1.54056 Å) with diffracted beam graphite monochromator and a single channel scintillator detector. The diffraction data were obtained in 0.02° steps in the range $15 < 2\theta < 70^\circ$. An Anton Paar reaction chamber (model XRK 900) was installed on the sample stage. In such configuration, the gases flow through the catalyst bed. The sample was reduced under pure H₂ flow (60 mL/min) from 25 to 750 °C at a heating rate of 5 °C/min, holding at each temperature for 0.5 h. NiP/TiO₂ was reduced ex situ at 700 $^{\circ}$ C (5 $^{\circ}$ C min⁻¹) and passivated under 0.5% O₂/ N₂ mixture for overnight before the XRD measurements.

Temperature programmed reduction (TPR) was performed in a multipurpose unit coupled to a Pfeiffer Vacuum mass spectrometer (MS) model QME 200. Prior to reduction, the sample (0.1 g) was pretreated under He (20 mL/min) at 200 °C (10 °C/min) for 30 min and then cooled to 30 °C. The samples were reduced under pure H₂ (100 mL/min H₂) at a heating rate of 5 °C/min up to 1000 °C. For the unsupported NiP catalyst, pretreatment was performed by He (50 mL min⁻¹) at 450 °C (10 °C min⁻¹) for 30 min. After that, the catalyst was cooled down to 30 °C. Finally, He was replaced by H₂, which had its flow rate adjusted to 100 mL min⁻¹, and H₂O signal (m/Z = 18) started to be measured at the spectrometer. During reduction measurements, temperature was increased linearly from 30 °C to 1000 °C at 1 °C min⁻¹.

The nature of acid sites was determined by DRIFTS of adsorbed pyridine using a Perkin Elmer model Spectrum 100 instrument with a DTGS-TEC detector and a Thermo Spectra-Tech reaction chamber with ZnSe windows. The samples were reduced at 300 °C for a period of 1 h, and the temperature was decreased to 150 °C while He was flowed to record a spectrum for use as a background. Pyridine adsorption involved bubbling He (30 mL/min) through a saturator for 30 min, followed by a He purge. The scan resolution was 4 cm⁻¹, and 512 scans were taken.

DRIFTS of adsorbed cyclohexanone was carried out using a Nicolet S10 instrument with a DTGS-TEC detector and a Harrick Scientific praying mantis reaction chamber with ZnSe windows. The samples underwent the same H_2 reduction treatment previously described. Then, the catalyst was cooled to 50 °C while He was flowed through a bubbler containing cyclohexanone at 60 mL/ min, and spectra were recorded at 100, 150, 300, and 200 °C. Peak fitting was performed on the band corresponding to adsorbed cyclohexanone by using Gaussian peaks and the nonlinear generalized reduced gradient (GRG) algorithm for the spectra obtained at 50 °C.

Raman was used to characterize the nature of carbon formed on the catalysts after 24 h of time on stream (TOS). The Raman spectra were collected with a Horiba Jobin-Yvon LabRAM HR system equipped with He – Ne laser ($\lambda = 632$ nm), a CCD detector and an Olympus BX-41 microscope.

2.3. Catalytic experiments

The hydrodeoxygenation of phenol was carried out in a gas phase fixed bed quartz reactor, operating at atmospheric pressure of H₂ and 300 °C. First, the samples were diluted with inert material (mSiC/mcatalyst = 3.0), except for bulk NiP. Prior to the reaction, the sample was reduced in situ under pure hydrogen (60 mL/min) at 700 °C (5 °C/min) for 1 h. In case of unsupported NiP, the catalyst was reduced ex situ as mentioned previously in section 2.1. Its in situ reactivation occurred under pure hydrogen (30 mL min⁻¹) at 300 °C (10 °C min⁻¹). The reaction mixture was obtained by flowing H₂ (at the same flow rate used in reduction/reactivation) through a saturator containing phenol, which was kept at the specific temperature required to obtain the desired H₂/phenol molar ratio (about 60). To avoid condensation, all lines were heated to 250 °C. The reaction products were analyzed by a gas chromatograph (Shimadzu – GC-2014 model), using Innowax capillary column and a flame-ionization detector (FID).

The product phenol conversion and selectivity for each product were calculated as follows:

$$Conversion (\%) = \frac{(mol_{phenol}^{fed} - mol_{phenol})}{mol_{phenol}^{fed}} \times 100$$
(1)

$$Selectivity(\%) = \frac{molofproductproduced}{molofphenolconsumed} \times 100$$
(2)

3. Results and discussion

3.1. Catalyst characterization

Table 1 summarizes the chemical composition and the surface area of oxide precursors of the phosphide catalysts. Considering the Ni and P content measured by ICP, the calcined samples showed a P/Ni molar ratio close to the expected value (3.0). The specific surface areas of precursors of nickel phosphides catalysts were lower than those of the respective supports. This result can be attributed to the excess of phosphorus used during the synthesis of the catalysts, which can cause the blocking of the pores of the support. It was used an excess of phosphorus in the synthesis (P/Ni = 3) of supported catalysts to ensure the Ni₂P phase formation and to prevent the presence of other phases such as Ni₁₂P₅ and Ni₃P [30,31].

In order to investigate the phase transitions of unsupported and supported nickel phosphide catalysts during phosphate reduction, in situ XRD was carried out. The diffractograms of unsupported NiP obtained during reduction are shown in Fig. 1.

No lines were detected on the diffractogram of the calcined sample, indicating that nickel phosphate is amorphous. The diffractograms

Table 1

Chemical composition and surface area of oxide precursors of the phosphide catalysts.

Samples	Ni wt.	P wt.%	P/Ni molar ratio	Specific surface area $(m^2 g^{-1})$		XRD Ni phases	d _{xrd}
	70		Tatio	Support	Catalyst		(nm)
NiP	-	-	-	-	-	Ni ₂ P, Ni ₅ P4	108 ^a
NiP/SiO ₂	6.2	9.3	2.8	208	53	Ni ₂ P	27 ^b
NiP/TiO ₂	7.8	10.7	2.6	48	19	Ni ₂ P	35 ^b
NiP/Al ₂ O ₃	7.5	10.7	2.7	207	78	Ni ₁₂ P ₅	19 ^c
NiP/CeO ₂	8.0	11.0	2.6	49	5	Ni ₂ P, Ni ₁₂ P ₅	31 ^b
NiP/CeZrO ₂	7.5	9.9	2.5	112	-	Ni ₂ P	39 ^b

^a Crystallite size of Ni₂P (111) analyze carried out at LNLS.

^b Crystallite size of Ni₂P (111).

^c Crystallite size of Ni₁₂P₅ (312).



Fig. 1. X-ray diffractograms of the bulk Ni₂P during its activation at specific temperatures. •Ni₂P, \blacklozenge Ni₅P₄, \blacklozenge Ni₁₂P₅.

remain unchanged up to 473 °C. After heating at 510 °C, it is observed the appearance of the diffraction lines characteristic of Ni₁₂P₅ (JCPDS 22–1190) and Ni₂P (JCPDS 03-0953) phases. Further increases in temperature to 533 °C decreased the intensities of the lines corresponding to Ni₁₂P₅ phase. Meanwhile, the diffraction lines of the Ni₂P phase continued to grow, indicating the transformation of the Ni₁₂P₅ were no longer detected at 548 °C. New diffraction lines typical of the Ni₅P₄ phase appeared at 593 °C and their intensities increased up to 631 °C. Increasing the temperature to 650 °C significantly decreased the intensities of these lines and the diffractograms exhibited mainly the Ni₂P phase.

The XRD patterns of the supported Ni phosphate samples are shown in Fig. 1S (Supplementary information). Comparing the intensities of the lines of the support and supported Ni phosphate samples, it is observed a decrease in the crystallinity since the calcined samples showed lower line intensities than those of the supports. NiP/SiO₂ exhibited a broad peak at 22.7° corresponding to an amorphous phase, whereas NiP/TiO₂ revealed the lines characteristic of both anatase (JCPDS 21–1272) and rutile (JCPDS 21–1276) titania phases. NiP/CeO₂ and NiP/CeZrO₂ showed the diffraction pattern of the cubic fluorite structure (JCPDS 34-0394) typical of ceria. For NiP/Al₂O₃, in addition to the diffraction lines of the support (cubic Al₂O₃, JCPDS 10-0425), a line at 21.8° corresponding to the formation of AlPO₄ by migration of phosphorus to the support structure was also observed. The absence of the lines characteristic of nickel phosphate for all catalysts indicates that this phase is amorphous, as also noted for unsupported NiP catalyst.

Fig. 2 shows the diffractograms of the supported nickel phosphide catalysts. All the samples were reduced in situ at different temperatures, with the exception of NiP/TiO₂, which was previously reduced at 700 °C and passivated before the XRD analysis. For NiP/SiO₂ catalyst (Fig. 2A), a diffraction line around $2\theta = 30.2^{\circ}$ was observed when the sample was reduced from 450 °C to 650 °C. This diffraction line could be attributed to the monoclinic Ni₂P₂O₇ phase (JCPDS 33-0950) or to the monoclinic Ni(PO₃)₂ phase (JCPDS 28-0708), produced by the

transformation of initial amorphous nickel phosphate. In addition to Ni₂P₂O₇ or Ni(PO₃)₂ phases, new lines corresponding to Ni₂P phase (JCPDS 03-0953) appeared at 600 °C. After heating to 700 °C, only the Ni₂P phase was detected. The diffractogram of reduced and passivated NiP/TiO₂ sample (Fig. 2B) displayed the lines characteristics of titania support (anatase and rutile) and Ni_2P phase, indicating that the treatment at 700 °C produced the desired nickel phosphide phase, maintaining the crystallinity of the support. For NiP/Al₂O₃ catalyst, the presence of the $Ni_{12}P_5$ phase (lines at $2\theta = 38.3$, 46.9 and 48.9°, JCPDS 22-1190) was observed at around 600 °C. Increasing the reduction temperature to 750 °C increased the intensity of the lines corresponding to Ni12P5 phase but no other nickel phosphide phase was detected. For NiP/CeO₂ sample, the reduction changed the crystal structure of the supports. The lines characteristics of monoclinic CePO₄ (JCPDS 32-0199) phase start to appear at 550 °C and their intensities continuously increased up to 750 °C. At this temperature, the diffraction lines characteristic of Ce₆O₁₁ (JCPD S 32-0196) phase were also observed, indicating the partial reduction of ceria. Concerning the nickel phosphide phase, Ni₂P (JCPDS 03-0953) and Ni₁₂P₅ (JCPDS 22-1190) were observed on the diffractogram of NiP/CeO2 at 650 °C. These diffractions lines became more evident at 700 °C. For NiP/CeZrO₂ sample, the reduction step also changed the crystal structure of the support. At 700 °C, the diffraction lines of CePO₄ (JCPDS 32-0199), Ce75Zr25O₂ (JCPDS 28-0271) and ZrO2 (JCPDS 37-0031) were identified, suggesting that the reduction led to a phase segregation. Furthermore, NiP/CeZrO₂ also exhibited the line typical of Ni₂P phase, but the presence of Ni₁₂P₅ cannot be ruled out because of the overlapping of its main line with the support.

Rodrigues et al. [32] used synchrotron-based time-resolved X-ray diffraction to study in situ the crystalline phases present during the preparation of bulk and silica-supported Ni₂P by reduction of oxidic precursors (NH₄NiPO₄,nH₂O) under a gas mixture of 5% H₂/95% He. The diffractograms of bulk NiP exhibit only the lines characteristic of Ni phosphate during heating from 25 to 400 °C. After 400 °C, the sample becomes amorphous and all of the diffraction lines disappear. The diffraction lines corresponding to Ni₂P phase appears in the temperature range of 650 to 800 °C. For the silica supported NiP sample, initially is observed the reduction of NiO to NiO around 400 °C and then, Ni₁₂P₅ is formed. Ni₂P begins to form above 600 °C, which agrees very well with our in situ diffractograms of NiP/SiO₂ catalyst.

Berhault et al. [33] investigated the reduction of the ammonium nickel phosphate NiNH₄PO₄ \cdot H₂O precursor into nickel phosphide (Ni₂P) by using a combination of magnetic susceptibility and in situ X-ray diffraction and X-ray absorption spectroscopy (XAS) techniques. The in situ XRD experiments revealed the presence of three different zones: (1) from room temperature to 250 °C, NiNH₄PO₄ \cdot H₂O was still detected; (2) from 300 to 500 °C, only amorphous phases were observed; (3) above 500 °C, a crystallization process occurred, leading to Ni₂P. in situ XAS study and magnetic susceptibility measurements showed that the amorphous region corresponds to the nickel pyrophosphate phase (Ni₂P₂O₇). In our study, the formation of Ni₂P₂O₇ and Ni₂P phases was observed in the same temperature range of the Berhault et al. [33] work.

The high phosphorous loading used in the synthesis of the catalysts favors the formation of the Ni₂P phase with high crystallinity. Depending on the support, the migration of phosphorus to the support can give rise to a deficit in phosphorus, insufficient to produce Ni₂P phase and then, leading to the Ni₁₂P₅ formation [24,34–36]. Table 1 reports the nickel phosphide phases detected by XRD and the crystallite size of phosphide phases for all catalysts. Similar and large crystallite sizes were observed for Ni₂P phase for all catalysts (NiP/SiO₂ (27 nm), NiP/TiO₂ (35 nm), NiP/CeO₂ (31 nm) and NiP/CeZrO₂ (39 nm).

Fig. 3 shows the water formation profiles of the calcined unsupported and supported phosphate precursors. This analysis was performed in order to determine the intermediate and final temperature of synthesis of the phosphides during the reduction step. The TPR of

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Fig. 2. X-ray diffractograms of the supported Ni₂P catalysts: (A) NiP/SiO₂, (B) NiP/TiO₂, (C) NiP/Al₂O₃, (D) NiP/CeO₂, (E)NiP/CeZrO₂. ∇ Ni₂P₂O₇ or Ni(PO₃)₂, •Ni₂P, ♦ Ni₁₂P₅, ♦ CePO₄, ♦ Ce₆O₁₁.



Fig. 3. Water formation profiles during TPR of unsupported and supported nickel phosphide precursors: (A) NiP, (B) NiP/SiO₂, (C) NiP/TiO₂, (D) NiP/Al₂O₃, (E) NiP/CeO₂, (F)NiP/CeZrO₂.

unsupported NiP catalyst showed three peaks of formation of water at 468, 515 and 578 °C. The first peak corresponds to reduction of the surface nickel phosphates due to the slow diffusion of hydrogen [37]. The second and the third peaks of the TPR profile correspond to the formation of Ni12P5 and Ni2P species. This is in accordance with in situ XRD analysis, which confirmed the presence of a mixture of Ni12P5 and Ni₂P phases between 495 and 540 °C, and the disappearance of the Ni₁₂P₅ phase and the predominance of the Ni₂P phase at 548 °C. Liu et al. [38] demonstrated by Raman spectroscopy that the calcined Ni₂P precursors containing P/Ni molar ratio = 0.8 or 1.0 displayed the $[P_2O_7]^{4-}$ and $[PO_4]^{3-}$ groups and the absence of Ni-O-Ni bonds typical of nickel oxide by visible/ UV spectroscopy technical. Therefore, it can be assumed that the calcined precursor is composed of a Ni₂P₂O₇ and $Ni_3(PO_4)_2$ mixture (amorphous species). The beginning of the reduction at 420 °C corresponds to the reduction of these phosphate species through a mechanism known as shrinking-core. After the reduction of surface species, the phosphate bulk is reduced forming Ni₁₂P₅ and Ni₂P, respectively. Although no other water formation peak was observed, the transition from the Ni_2P phase to a Ni_5P_4 phase was detected at 593 °C (in situ XRD).

Stinner et al. [39] showed that by varying the reduction parameters such as gas flow rate and heating rate, the type of nickel phosphide phase can change. Other factors like loading of P and type of supports can also influence the synthesis temperature of phosphide catalysts. In general, higher P/Ni molar ratio shift the initial and final reduction temperatures to higher values. Acidic supports interact strongly with phosphorus and inhibits the formation of the Ni₂P phase.

In the present work, the temperature programmed reduction profile for supported nickel phosphate precursors give rise to different reduction profiles depending on the type of support. However, the maximum reduction temperature appeared within a similar temperature range (578–586 °C) and a shoulder was observed in the low temperature region in the water formation profile as observed for unsupported phosphide catalyst, indicating that the transformation of nickel phosphate to Ni₂P also occurs in two steps. Furthermore, the peaks between 460 and 700 °C confirm the presence of nickel oxy-phosphates since free NiO species tend to reduce at lower temperatures. The reduction of NiP/Al₂O₃, NiP/CeO₂ and NiP/CeZrO₂ precursors catalysts start at lower temperature than those for NiP/SiO₂ and NiP/TiO₂, which suggests that the nickel species are more easily reduced on NiP/Al₂O₃, NiP/CeO₂ catalysts or that the reducibility characteristics of CeO₂ and CeZrO₂ promote the reduction of phosphate.

The DRIFTS of adsorbed pyridine was carried out to get information about the nature of acid sites on the catalysts. The spectra of adsorbed pyridine at 150 °C are shown in Fig. S2. Only bands at around 1449 and 1489 cm⁻¹ corresponding to pyridine adsorbed on Lewis acid site were observed on the spectra except for bulk NiP and NiP/SiO₂, which did not exbibited any detectable band.

DRIFTS experiments of adsorbed cyclohexanone followed by desorption at diff ;erent temperatures was performed in order to to probe the strength of the interaction of the carbonyl oxygen with the active sites. The spectra obtained at 50 °C are presented because the S/N ratio was unacceptable at higher temperatures. Spectra in the region between 1600 and 1750 cm⁻¹ are shown in Fig. S3. The spectra of cyclohexanone is quite complex and it can be decomposed in three regions: high (> 1695 cm⁻¹), medium (1660–1695 cm⁻¹) and low (< 1660 cm⁻¹) wavenumbers. NiP/TiO₂ and NiP/CeZrO₂ catalysts showed a higher fraction of this band located in the medium/low wavenumber region whereas the other catalysts exhibited mainly a band positioned at high wavenumber region. The shift of the cyclohexanone band to lower wavenumbers was attributed to the stronger interaction between the oxygen from the carbonyl group and metal cations of the support [23].

3.2. HDO of phenol

The HDO of phenol was carried out over the bulk NiP catalyst to shed light on the catalytic properties of this phosphide phase without the interference of the support. The choice of Ni_2P among other nickel phosphide phases (i.e. $Ni_{12}P_5$, Ni_3P and Ni_5P_4) is justified by the the fact that it is known that this phase exhibits the highest intrinsic activity for HDO reactions [30,40].

The phenol conversion and product distribution as a function of W/ F for HDO of phenol at 300 °C over all supported catalysts are shown in Fig. S4. Benzene and cyclohexane were the main products formed with minor formation of cyclohexene for NiP/SiO₂, NiP/TiO₂, NiP/Al₂O₃, and NiP/CeZrO₂ catalysts. Significant production of cyclohexene and cyclohexanol were also observed for NiP/CeO₂ catalyst.

Table 2 reports the reaction rate and product distribution for HDO of phenol at 300 °C and low phenol conversion over unsupported and supported nickel phosphide catalysts. The unsupported Ni₂P phase exhibited the activity for deoxygenation aproximately 5 to 22-fold lower than the supported materials, which is likely due to the very low surface area (lower than 5 m² g⁻¹). The HDO reaction rate was approximately the same as the direct deoxygenation rate because this catalyst produced mainly benzene (95%). The other minor products were cyclohexanoe, cyclohexane, and cyclohexene.

It is well established that bulk Ni₂P catalyst is comprised of an orthorhombic crystalline structure that can present two types of terminations with different kinds of active sites. The Ni₃P₂ presents the socalled Ni(1) site and Ni₃P has Ni(2) sites, the latter featuring a lower coordination number. Several studies about hydrotreatment have explained the product distribution obtained by the different interaction that can occur with these active sites. For hydrodesulfurization (HDS) of 4,6-dimethyldibenzothiophene, Oyama et al. [41,42] proposed that Ni(1) was involved in the DDS route leading to dimethylbiphenyl, whereas Ni(2) is likely involved in the hydrogenation route toward methylcyclohexyltoluenes. Gonçalves et al. [25] suggested that Ni(1) sites present on the Ni₃P₂ termination interact with the oxygen atom of

Table 2

Product distribution from the HDO of phenol at 300 °C over unsupported and supported phosphide nickel catalysts.

Catalyst	W/F (h)	X _{PHE} (%)	HYD rate ^a (mmol g_{cat}^{-1} min ⁻¹)	HDO rate ^b (mmol g_{cat}^{-1} min ⁻¹)	Selectivity (mol%)					
					\bigcirc	°	ОН	\bigcirc	\bigcirc	Others
NiP	0.84	4.5	0.00	0.01 (0.01) ^c	94.6	2.8	-	1.2	1.4	0
NiP/SiO ₂	0.03	5.4	0.14	0.22 (0.18)	50.8	30.5	7.5	3.2	8.1	0.0
NiP/TiO ₂	0.11	5.5	0.02	0.08 (0.05)	48.3	16.2	0.0	16.3	17.9	1.3
NiP/Al ₂ O ₃	0.13	3.8	0.01	0.05 (0.02)	35.8	9.7	1.1	32.2	20.4	0.0
NiP/CeO ₂	0.03	5.2	0.10	0.19 (0.14)	41.3	32.7	9.3	8.2	8.1	0.5
NiP/CeZrO ₂	0.03	2.2	0.02	0.11 (0.08)	58.6	17.2	1.7	13.6	7.9	1.0

^a Reaction rate for hydrogenation (cyclohexanone, cyclohexanol).

^b Reaction rate for hydrodeoxygenation (benzene, cyclohexane, cyclohexene).

^c Value in parentheses corresponds to the reaction rate for direct deoxygenation to benzene.

cresol molecules in the same way that it interacts with C–SH, facilitating hydrogenolysis reactions and producing toluene. Furthermore, it was proposed that Ni(2) sites would promote hydrogenation reactions, promoting flat adsorption of ring-containing compound such as phenolic groups [15,27,30].

In our work, it seems that bulk Ni₂P contains mainly Ni(1) sites. Indeed, Density Functional Theory (DFT) calculations have demonstrated that Ni₃P₂ termination is more stable than Ni₃P [43,44]. However, Hernandez et al. [45] performed dynamical LEED analysis for Ni₂P (0 0 0 1) and observed that Ni₃P termination (Ni(2) sites) accounts for about 80% of the total surface. The authors pointed out that the P adsorbs on the three-fold sites present in Ni₃P₂ structure, which further stabilize the Ni₃P₂ structure by filling the dangling bonds and do not expose such termination. These findings are somehow conflicting and the determination of Ni₃P₂ and Ni₃P proportions is not an easy task, especially regarding supported phases.

3.3. HDO of phenol of supported NiP catalysts

The influence of the support on the performance of nickel phosphide phases was evaluated for the HDO of phenol at 300 °C under atmospheric pressure. The hydrogenation rate was quite low for all the supported phosphide catalysts, except for NiP/SiO₂ and NiP/CeO₂. The reaction rate for HDO followed the order: NiP/CeO₂ \approx NiP/SiO₂ > NiP/CeZrO₂ > NiP/TiO₂ > NiP/Al₂O₃. The order for the reaction rate for direct deoxygenation is the same: NiP/CeO₂ \approx NiP/SiO₂ > NiP/CeZrO₂ > NiP/TiO₂ > NiP/Al₂O₃. NiP/Al₂O₃ exhibited very low reaction rates, which could be attributed to the presence of Ni₁₂P₅ phase that is less active than Ni₂P. For the hydrogenation rate, the following order was observed: NiP/CeO₂ \approx NiP/SiO₂ > NiP/TiO₂ \approx NiP/CeZrO₂ \approx NiP/Al₂O₃.

In comparison to the previous results obtained by our group using Pd supported on SiO₂, Al₂O₃, TiO₂, ZrO₂, CeO₂ and CeZrO₂, the variation of the HDO rate for supported NiP catalysts was approximately the same as that observed for supported Pd catalysts [29]. For Pd supported materials, the support acts as a center for phenol adsorption, whereas Pd activates hydrogen. In that case, the HDO activity followed the order of support oxophilicity, with Pd/TiO₂ (0.72 mmol $g_{cat}^{-1} min^{-1}$) and Pd/ZrO₂ (0.59 mmol $g_{cat}^{-1} min^{-1}$) displaying the highest values. It is noteworthy to mention that the lowest HDO activity was found for Pd/SiO₂ (0.09 mmol $g_{cat}^{-1} min^{-1}$), which was 8-fold lower than that for Pd/TiO₂. From Table 2, regarding NiP supported catalysts, the HDO activity varied from 0.05 mmol $g_{cat}^{-1} min^{-1}$ (NiP/Al₂O₃) to 0.22 mmol $g_{cat}^{-1} min^{-1}$ (NiP/Al₂O₃ suggests that the intrinsic activity of Ni₂P phase is higher than that of Ni₁₂P₅.

The addition of phosphorus changed the structure of some supports

such as ceria, ceria-zirconia and alumina. For NiP/CeO₂ and NiP/Al₂O₃, new phases were created such as CePO₄ and AlPO₄, respectively. In the case of NiP/CeZrO₂, in addition to CePO₄, it was also observed a phase segregation, producing Ce₇₅Zr₂₅O₂ and ZrO₂ phases.

Regarding product distribution, benzene was the main product formed over NiP/SiO₂, NiP/TiO₂ and NiP/CeZrO₂, whereas cyclohexanone was mainly obtained over NiP/CeO₂ and NiP/SiO₂. Significant formation of cyclohexane and cyclohexene was observed for all supported catalysts in comparison to bulk Ni₂P. NiP/Al₂O₃ exhibited the highest selectivities to cyclohexane and cyclohexene. These results suggest that the support significantly affects the product distribution regardless of the nature of phosphide phase. For instance, NiP/SiO₂, NiP/TiO₂ and NiP/CeZrO₂ catalysts contains only the Ni₂P phase but the selectivity to benzene for the bulk NiP catalyst was almost double that of the supported catalysts. The higher selectivity to cyclohexane and cyclohexene observed for the supported phosphide catalysts in comparison to bulk phosphide catalyst is likely due to the presence of Lewis acid sites on the supports, as shown by the DRIFTS of adsorbed pyridine experiments.

Recently, we studied the effect of support on the reaction mechanism for HDO of phenol over supported metal catalysts. This mechanism is based on the tautomerization of phenol to a keto intermediate that can be hydrogenated to cyclohexanone and then cyclohexanol, which may be dehydrated to cyclohexene over supports with enough acidity, followed by hydrogenation to cyclohexane. The second reaction route involves the hydrogenation of the carbonyl group of the keto tautomer, leading to the production of benzene after dehydration [23]. According to this reaction pathway, oxophilic supports such as TiO₂, Nb₂O₅, and ZrO₂ promote C=O hydrogenation leading to deoxygenated products. In our work, the higher selectivity to cyclohexanone and cyclohexanol over NiP/SiO2 and NiP/CeO2 suggestes that the hydrogenation of the ring pathway is favored over these supports. This result agrees very well with the DRIFTS of adsorbed cyclohexanone experiments that revealed a weaker interaction between the oxygen of the carbonyl group and the cation of the support.

Furthermore, it has been suggested that more oxophilic metals such as Ru as well as supports like TiO_2 strongly interact with the oxygen atom, reducing the energy barrier for the direct cleavage of the C–O bond of the aromatic ring (Direct deoxygenation – DDO), leading to the formation of benzene as well as hydrogenolysis products. A similar reaction pathway has been proposed for phosphide catalysts. The stronger adsorption of m-cresol over Ni₂P phase favored the direct cleavage of C–O bond and the production of toluene in comparison to metallic Ni particles [15]. In our work, NiP/SiO₂, NiP/TiO₂ and NiP/ CeZrO₂ catalysts contained only the Ni₂P phase and resulted in the highest selectivity to benzene, suggesting that this phosphide phase promotes the direct deoxygenation pathway. The lowest formation of

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Fig. 4. Conversion of phenol and selectivity to products as a function of TOS for: (A) NiP/SiO₂, (B) NiP/TiO₂, (C) NiP/Al₂O₃, (D) NiP/CeO₂, (E)NiP/CeZrO₂.

benzene on NiP/Al₂O₃ catalyst is likely due to the presence of Ni₁₂P₅ phase. Therefore, the nature of the phosphide phase affected the product distribution. In addition, the use of zirconia as a support enhanced the deoxygenation activity comparing to NiP/SiO₂ [15]. This result was attributed to the oxophilic sites of the support (Zr^{3+} and Zr^{4+}) that strongly adsorbed phenol and favored the cleavage of C=O bond. The same result was observed in our work for TiO₂ and CeZrO₂ supported catalysts. In the present work, the diffractograms detected the presence of a ZrO₂ segregated phase. The DRIFTS of adsorbed cyclohexanone experiments showed a stronger interaction between the oxygen of the carbonyl group and the Ti⁴⁺ and Zr⁴⁺ cations of the support.

Then, the results of this work demonstrated that the Ni_2P phase is responsible for the direct deoxygenation of phenol. Furthermore, the support affected the nature of the phosphide phase and product distribution. For alumina and ceria supported catalysts, the $Ni_{12}P_5$ phase was also observed and promoted the hydrogenation reaction pathway.

3.4. Stability of supported NiP catalysts for HDO of phenol

The stability of all catalysts was compared at similar initial phenol conversion (between 30–40%), as shown in Fig. 4. All catalysts only slightly deactivated during time on stream (TOS). For instance, the phenol conversion decreased from 42 to 32% after 20 h of TOS over NiP/SiO₂. NiP/CeZrO₂ exhibited the highest deactivation rate at the beginning of reaction and then remained quite stable as a function of time. Concerning the product distribution, the selectivity to benzene decreased while the formation of cyclohexanone, cyclohexane and cyclohexene increased depending on the catalyst. This result indicates that the selectivity to deoxygenated products decreases as the selectivity to hydrogenation products increases.

Catalyst deactivation is one of the main challenges for the HDO of model molecules and it has been attributed to carbon deposition, metal sintering or strong adsorption of the model molecules. Carbon deposition on supported phosphide catalysts during HDO of phenol was investigated by Raman spectroscopy of the used catalysts. The spectra of the used catalysts did not detect the presence of bands at around 1350 and 1580 cm⁻¹ characteristic of carbonaceous materials, indicating that deposition of carbon does not occur to a significant degree over these supported NiP catalysts under the conditions used in this work.

de Souza et al. [29] investigated the stability of Pd-based catalysts for HDO of phenol. Pd/SiO₂, Pd/Al₂O₃, Pd/TiO₂ and Pd/ZrO₂ catalysts strongly deactivated. For Pd/Al₂O₃ and Pd/ZrO₂ catalysts, the phenol conversion after 20 h of reaction decreased from 58% to 10% and 65% to 18%, respectively. They proposed that the main cause for catalyst deactivation was Pd sintering, which resulted in an accumulation of intermediate species, blocking the active sites. Furthermore, a stronger interaction between the oxygen of the tautomer intermediate and the oxophilic site could also contribute to catalyst deactivation by retaining more strongly adsorbed intermediates formed. Temperature programmed oxidation (TPO) was used to investigate the presence of carbonaceous species on the used catalysts after 22 h of TOS. The TPO profile of the of NiP/TiO₂ spent catalyst after HDO of phenol (Fig. S5) exhibited one broad peak between 250 and 500 °C. This is attributed to the oxidation of phenol adsorbed on the catalyst surface.

In our work, the phenol is strongly adsorbed on the phosphide sites, which promotes the direct deoxygenation. However, the strong adsorption should cause the deactivation of supported phosphide catalysts. This could also explain the changes in selectivity observed during the reaction. The deactivation of the sites responsible for deoxygenation would favor the hydrogenation route. The same result was reported Moon et al. [46], who studied the HDO of guaiacol at different temperatures and pressures. They proposed that the hydrogenation pathway was less susceptible to coke deposition and catalyst deactivation than the direct deoxygenation pathway. Cecilia et al. [47] investigated the stability of NiP/SiO₂ catalysts with different P/Ni molar ratio (1-3) for the HDO of dibenzofuran. Catalyst stability depended on

the P/Ni molar ratio. The catalyst containing the higher P/Ni ratio remained quite stable during the reaction, whereas the one with P/Ni = 1 underwent gradual deactivation. According to the authors, the excess of phosphorus for the P-rich catalysts protected the Ni₂P phase against oxidation with the water formed in the reaction.

Comparing the deactivation of supported Pd catalysts [29] with that observed for the phosphide catalysts supported on the same oxides, it is clear that the deactivation rate is much lower on the phosphide catalysts. This is likely due to the high activity of phosphide catalysts that efficiently turnover the adsorbed phenol molecule, preventing the retention of intermediate species; therefore, the catalyst only slightly deactivated. Furthermore, phosphorus atoms located on the surface of the nickel phosphide phase could inhibit carbon formation by the dilution effect on Ni atoms.

4. Conclusion

This work investigated the effect of the type of support on the performance of supported nickel phosphide catalysts for HDO of phenol.

Unsupported NiP catalyst exhibited high selectivity to benzene (95%), which demonstrate that the direct deoxygenation of phenol is promoted by the Ni_2P phase. The strong adsorption of the phenol on the nickel phosphide reduces the energy barrier for the cleavage of the C–O bond, leading to the formation of benzene.

The type of the support affected the nature of the phosphide phase and, consequently the product distribution. For NiP/SiO₂, NiP/TiO₂, and NiP/CeZrO₂catalysts, Ni₂P was the only phosphide phase formed. These catalysts exhibited the highest selectivity to benzene among the supported catalysts (around 57%). Ni₁₂P₅ was the main phase on Al₂O₃, whereas a mixture of both Ni₂P and Ni₁₂P₅ phases was obtained on CeO₂. For these catalysts, hydrogenation products (cyclohexanone, cyclohexane and cyclohexene) were mainly formed. However, all supported catalysts showed lower selectivity to benzene, despite the presence of only the Ni₂P phase. The supports favored the formation of hydrogenation products via the tautomerization route.

All catalysts only slightly deactivated with time on stream. The supported phosphide catalysts exhibited a lower deactivation rate than supported metallic catalysts. This is likely due to the high activity of the phosphide phase that turns over the adsorbed phenol molecule in an efficient manner, preventing the retention and buildup of intermediate species that result in catalyst deactivation.

Therefore, nickel phosphide catalysts are promising HDO catalysts to selectively produce aromatics from phenol with a high degree of deoxygenation and without significant deactivation.

Acknowledgments

This contribution is dedicated to the memory of Victor Teixeira da Silva. Priscilla M. de Souza and Carlos V. M. Inocêncio thanks Coordenação de Aperfeicoamento de Pessoal de Nível Superior (CAPES) and Fundação de Amparo à Pesquisa do Estado do Rio de Janeiro (FAPERJ) for the scholarships. Vinicius Ottonio O. Goncalves and Fabio B. Noronha also acknowledge the financial support of the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq -446066/ 2014-1), Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES - CAPES - COFECUB program -88881.142911/2017-01), Fundação de Amparo à Pesquisa do Estado do Rio de Janeiro (FAPERJ) and Fundação de Amparo à Pesquisa do Estado de Minas Gerais (FAPEMIG -2444946/2018). Vinicius Ottonio O. Gonçalves and Frédéric Richard acknowledge financial support from the European Union (ERDF) and "Region Nouvelle Aquitaine". Research conducted at UTSA was supported by a UTSA College of Engineering scholarship, the State of Texas, and the STARs program.

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.cattod.2019.08.028.

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