Development Of New Multifunctional Catalysts for The Hydrodeoxygenation Of Biomass-Derived Oxygenated Molecules

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Abstract

New bifunctional catalysts comprising heteropoly acids have been developed for the hydrodeoxygenation (HDO) of guaiacol, a biomass model compound. Three catalysts groups were studied by using three different supports: $Pt-Al_2O_3$, $Ni28-Al_2O_3$ and $NiO25-Al_2O_3$ (industrial catalyst). The heteropoly acid was introduced in two distinct ways: the first, by incipient wetness impregnation of 12-tungstophosphoric acid ($H_3PW_{12}O_{40}$, HPW) and the second, by a physical mixture of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ ($Cs_{2.5}$ salt), a cesium heteropoly salt. Each support by itself, impregnated with HPW and physically mixed with $Cs_{2.5}$ salt forms a group and at the end, nine catalysts were tested. The $Cs_{2.5}$ salt was synthetized by the dropwise addition of a cesium precursor to an aqueous HPW solution. The content of the heteropoly acid or the salt was kept constant (20 wt. %) for all the catalysts and the reaction was carried out at 300 ºC, atmospheric pressure and with a H_2 to guaiacol molar ratio of 50. The characterization of the catalysts was performed by powder X-Ray diffraction, UV-Vis DRS, IR Spectroscopy, H_2-TPR and TGA analysis. The presence of HPW could not be confirmed by all techniques although $Cs_{2.5}$ salt presence was proved. The catalytic results showed that the conversion values follow the group order $NiO25-Al_2O_3$ > $Ni28-Al_2O_3$ >> $Pt-Al_2O_3$ and that the impregnated HPW on Ni catalysts showed the best selectivity to deoxygenated products. These catalysts, however, showed a significant conversion decrease with reaction time on stream, probably due to the deposit of carbonaceous species, in particular guaiacol, that adsorbs strongly onto the alumina support. Nonetheless, $HPW/Ni-Al_2O_3$ showed to be the most promising catalysts studied in the HDO of guaiacol.

Keywords: biomass valorization, hydrodeoxygenation, heteropoly acid, heteropoly acid salt, bifunctional catalysts, guaiacol

1. Introduction

Many environmental issues have been raised over the years because of the intensive use of fossil fuels. These account for around 80 % of the primary energy use [1] and about 90 % of the CO_2 emissions which have their source on the burning of fossil fuels.[2] Although there is a need to reduce the CO_2 emissions, due to their negative environmental impact, it is unlikely that it will be done through a reduction in energy production, mainly because the energy demand is growing.[2] In this point of view, the energy sector must approach its production in an effective way, so that the prejudicial greenhouse gas emissions can be controlled.

To address this issue carbon neutral energy sources are becoming more and more popular, with biomass being one example. It is carbon neutral (the biomass consumes the CO_2 that is released when its burned, creating a cycle), renewable and available.[3] To achieve a workable starting material, biomass must go through pyrolysis to produce bio-oil.[4] However this bio-oil's composition is far from the desired for fuel, mainly due to the presence of oxygenated molecules, which make the acidity and viscosity higher than the desirable and the heating value (heat that is released during combustion) lower, amongst others problems.[5,6] Thus, an upgrade is needed and it is usually done by hydrodeoxygenation (HDO). This process conventionally accompanies hydrodesulfurization (HDS) in hydrotreating (HDT) processes. HDO is however more important than HDS for bio-oil feedstocks once the sulfur content is much lower than the oxygen content.[1] The conventional HDT process uses harsh conditions, particularly very high pressures and the catalysts are only active in their sulfided form. This constitutes a problem in bio-oil upgrading because, as stated before, the sulfur content of bio-oil is very low so an externa sulfur source must be added to maintain the catalyst active, however, this will contaminate the bio-oil stream.[1]

Thus, to make the HDO process more feasible, new catalysts that are active at lower pressures and without the presence of sulfur are the focus of the HDO research. HDO catalysts are usually bifunctional catalysts, with a metallic component, for the dissociation of H_2 and an acidic function, for the activation of the C-O bond. Examples of catalysts are metals with hydrogenation capacity, such as Pt or Ni added to acidic supports, such

as γ-Al_2O_3 or HZSM-5.[7,8] Alternatively, the acid function can be provided by heteropoly acids and their salts, whether as a support or impregnated onto other supports. These are very versatile materials that possess Brønsted acids sites and whose properties can drastically change depending on their composition.[9,10]

In this work, two forms of 12-tungstophosphoric acid, an heteropoly acid were used: i) the acid itself, $H_3PW_{12}O_{40}$ (HPW) and ii) the cesium salt of this acid, $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ ($Cs_{2.5}$ salt). The main goal here was to study the effect of the addition of the heteropoly acids in catalysts that are already applied for HDO. The supports chosen were Pt-Al_2O_3 and two forms of Ni-Al_2O_3, one totally synthetized in our lab, Ni28-Al_2O_3 and the other is an industrial catalyst that will be called NiO25-Al_2O_3. Having said that, nine catalysts were obtained: the three supports by themselves, three HPW impregnated on the supports chosen and physically mixed $Cs_{2.5}$ with the support. In all catalysts, the heteropoly acid or salt content was 20 wt. % After synthetized, the catalysts were characterized then tested for the HDO of guaiacol, an oxygenated molecule with two $C_{aromatic}$-O groups, at 300 ºC and atmospheric pressure.

2. Experimental

2.1 Catalysts Preparation

The tungsten heteropoly acid, $H_3PW_{12}O_{40} \cdot x\ H_2O$ (HPW) was purchased from ThermoFischer (Kandel) GmbH, Cesium Acetate (95%) from Fluka, Platinum on Alumina (1 wt.% of Pt) from Sigma-Aldrich, PURAL SB (Al_2O_3, 70.3 %) from Condea, Nickel (II) nitrate hexahydrate (99 %) from Merck and NiO25-Al_2O_3 (industrial catalyst).

For the supports, platinum on alumina (1 wt.% Pt) was purchased, the industrial NiO on alumina was not synthesized, however it needed to be reduced to obtain Ni in its metallic form. The third support, Ni28-Al_2O_3 was the only one prepared in our laboratory, with, with the preparation details in the following paragraph.

Firstly, the PURAL SB, a pseudo-boehmite, was calcined in air in a muffle (Nabertherm). The heating rate was 5 ºC·min^{-1} until 600 ºC, followed by a plateau of 5 h. A solution of $Ni(NO_3)_2 \cdot 6H_2O$ (6 M), was prepared and then impregnated onto the support, by incipient wetness impregnation (IWI). With the volume of solution impregnated, the amount of Ni added to the support was calculated to be 28 %. The resulting slurry was left to dry overnight at 120 ºC. The powder obtained was treated, in a reductive atmosphere, to reduce Ni and to decompose the nitrate. The same thermal treatment was applied to both Ni28-Al_2O_3 and to the NiO25-Al_2O_3. The heating rate was 5 ºC·min^{-1} with a flow of 60 mL·min^{-1} of N_2 until it reached the final temperature of 450 ºC, followed by a plateau of 30 min at this temperature. Then, a H_2 flow (20 mL·min^{-1}) was added to complete a total flow rate of 80 mL·min^{-1} (N_2 and H_2), during 4 additional hours.

For the HPW impregnated catalysts, an aqueous solution of 0.01 M of HPW was prepared and then used for impregnation onto the supports, by IWI. Because the solution of HPW was diluted and the volumes impregnated were small, the density of solution was assumed to be 1 g·mL^{-1} (the same as the solvent, water). The obtained materials were left to dry overnight at 120 ºC. The final powders were treated in an inert atmosphere with a heating rate of 5 ºC·min^{-1} with a flow of 60 mL·min^{-1} of N_2 until it reached the final temperature of 350 ºC. When this temperature was reached, there was a 2 h plateau. The final HPW content was 18 wt. % for Pt-Al_2O_2, 16 wt. % for NiO25-Al_2O_3 and 18 wt. % for Ni28-Al_2O_3.

The $Cs_{2.5}$ salt was prepared according to Okuhara et al.[11], by adding the appropriate amount of cesium precursor solution (0.04 M) dropwise to an aqueous solution of HPW (0.01 M) with continuous and vigorous stirring, at room temperature. The Cs salt starts to precipitate, forming a milky looking solution. This solution was left aging overnight and then washed several times by centrifugation (Centurion Scientific – C2 Series, 4 washings 6000 rpm, with times ranging from 15 to 20 min each). The yield of this process was 69 %. The powder obtained was calcined in air in a muffle (Nabertherm) at 350 ºC for 2 h, with a heating rate of 5 ºC·min^{-1}, for an even distribution of the cations. After thermal treatment of the supports and of the Cs salt, physical mixtures between each support and $Cs_{2.5}$ were made, comprising 20 wt. % of the salt. The powders were ground until an homogeneous mixture was obtained. . The final $Cs_{2.5}$ salt content was 20.5 wt. % for Pt-Al_2O_2 and 20 wt. % for NiO25-Al_2O_3 and Ni28-Al_2O_3. All catalysts were ground to 63-125 μm aggregate particle size.

2.2 Catalyst Characterization

The diffractograms were recorded for all catalysts (fresh and spent) on a Bruker D8 Advanced X-Ray Diffractometer, with Cu Kα radiation (1.5406 Å) and equipped with a 1D LYNXEYE XE detector. The measurement conditions were the following: 40 kV–40 mA, a step size of 0.05 º (2 Theta), a step time of 1s; a Ni filter was also used to remove Cu Kβ contribution.

The IR Spectra for all catalysts (fresh and spent) were obtained using a Nicolet 6700 FTIR from ThermoScientific, with wavenumbers between 4000 and 400 cm^{-1} and a 4cm^{-1} resolution (64 scans). The technique used was KBr in transmission mode, which was then converted in absorbance. Samples were diluted (1 wt.%) in KBr and then pressed at 8 tons to get a final pellet for transmission measurements.

UV-Vis DRS spectra were obtained for Pt-Al_2O_3 and Ni28-Al_2O_3 catalysts on a Varian Cary 5000 with wavelengths ranging from 200 to 800 nm, with a Praying Mantis (integration sphere) accessory for DRS measurements. The reflectance spectra were converted into F(R) through the Kubelka-Munk function: $F(R)=K/S=(1-R)^2/(2R)$, with K, S and R being

respectively, the absorption, scattering and diffuse reflectance.[12]

H₂-TPR profiles for Ni catalysts were recorded on a micrometrics AutoChem II by using a heating rate of 10 °C·min⁻¹ until 900 °C.

N₂ sorption measurements for the Pt-Al₂O₃ support were carried out on a Micromeritics ASAP 2010 analyzer. Prior to N₂ sorption, samples were outgassed under vacuum at 90 °C for 1h and then at 300 °C for at least 4h.

Thermogravimetric analysis on the spent cataysts was carried out on a Setaram SETSYS Evolution 16. The mass of the samples was 15 mg and temperatures ranged from 25 to 800 °C. Two cycles of temperature were applied to the sample, with the first being the cycle of the analysis itself while the second cycle was used to remove the Archimede effect on the apparent mass loss and the effect of the heat flow.

2.3 Catalytic Tests

The reactants used for the catalytic tests were guaiacol (≥ 98.0 %) from Sigma-Aldrich, n-heptane (≥ 99.5 %) from Merck and ethylbenzene from Sigma-Aldrich (> 99 %).

The reaction was carried out on a pyrex fixed bed tubular reactor (internal diameter of 1 cm). The feed consisted of a liquid solution of 5 % of guaiacol (% v/v) with n-heptane as a solvent, with a total flow rate of 3 mL·h⁻¹, corresponding to 0.15 mL·h⁻¹ of guaiacol. The liquid solution was fed to the reactor through a pump (776 Dosimat, Methrom). Both the H₂ and the liquid feed entered the reactor from the top. The H₂ to guaiacol molar ratio was 50, with a H₂ flow rate of 2 L·h⁻¹, controlled by a mass flow controller (Model 400, Hastings Instruments). At the bottom, a glass collector vase was assembled to collect the reactor effluent at 10, 20, 40, 60, 80, 100 and 120 min of time on stream. At 120 min (2 h), the reaction was stopped. At the beginning of the reaction, ice was added to the collector vase in order to condensate the majority of the gaseous effluent (although the feed was in liquid phase, at the temperature of the reaction it would turn to gaseous phase). However, probably some products that did not condensate were flushed away and lost. For all the catalytic tests, the temperature was set at 300 °C on a ThermoLab oven and controlled with a thermocouple at atmospheric pressure. The reactor was packed with 100 mg of catalyst with a particle size of 63-125 μm. Prior to the beginning of the reaction, the catalyst was pre-treated with H₂ at the reaction temperature, for 1 h.

Product Analysis was done by Gas Chromatography (GC) of the condensed reactor effluent on a Perkin Elmer AutoSystem Gas Chromatograph, with N₂ as the carrier, with a Flame Ionization Detector (FID) with an air and H₂ flame and a DB-5MS column from Agilent (30 m length × 0.250 mm internal diameter × 0.25 μm film thickness). The initial temperature was set at 50 °C for 5 min, with a 10 °C/min ramp until 200 °C, at which it was held for 10

min. The temperature of the detector was 275 °C. The peak areas were measured with the software CSW 32 (Datapex). Ethylbenzene was used as an Internal Standard (IS) by adding 3 wt.% to the liquid samples collected from the reaction. Prior to the reaction, the IS method was applied to calculate the response factors (RF) of both reagent (guaiacol) and main expected products. The conversion of guaiacol was calculated as $x_{GUA}=1-(A_{GUA}/\sum A_{peak,i})$, the yield of product P as $Y_P=(A_P/\sum A_{peak,i})$ and Selectivity of product P as $S_P=Y_P/x_{GUA}$.

3. Results and discussion

3.1 Catalysts Characterization

3.1.1 Heteropoly acids

Considering the XRD diffractogram for the HPW, it does not agree neither with literature nor with the TGA results, in what concerns the quantity of crystallization water. The Cs₂.₅ salt is arranged in a cubic Keggin structure and this was confirmed by XRD analysis, Figure 1, when compared to an heteroply salt with the same structure (not shown).
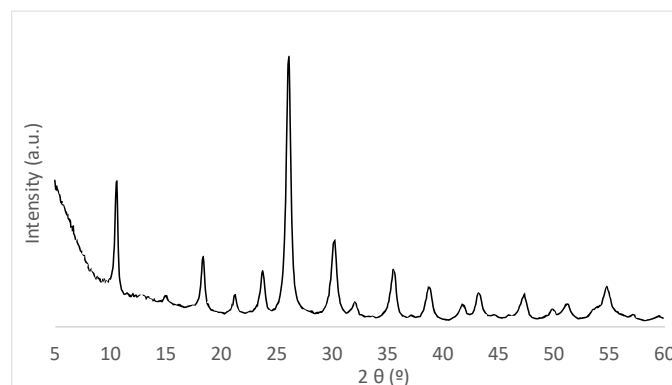

Figure 1: XRD pattern for Cs₂.₅ salt.

Regarding the IR bands, characteristic bands of the tungsten heteropoly acids appear at 1080, 982, 893 and 812 cm⁻¹ and correspond respectively to the vibrational frequencies of P-O, W=O and W-O-W (for 893 and 812 cm⁻¹[9]) and they can be seen in the experimental results in Figure 2. HPW IR spectrum results match the spectra found in literature for the tungsten heteropoly acid and confirm the Keggin anion, $PW_{12}O_{40}^{3-}$, presence in the cesium salt. [9] Furthermore, with this technique, it was possible to confirm the presence of HPW on PURAL SB calcined at 600 °C (not shown) but with some signs of HPW degradation.

Although not show, UV-Vis DRS results for both HPW and Cs₂.₅ salt are similar and in agreement with literature, showing the characteristic Keggin anion peak at 260 nm.
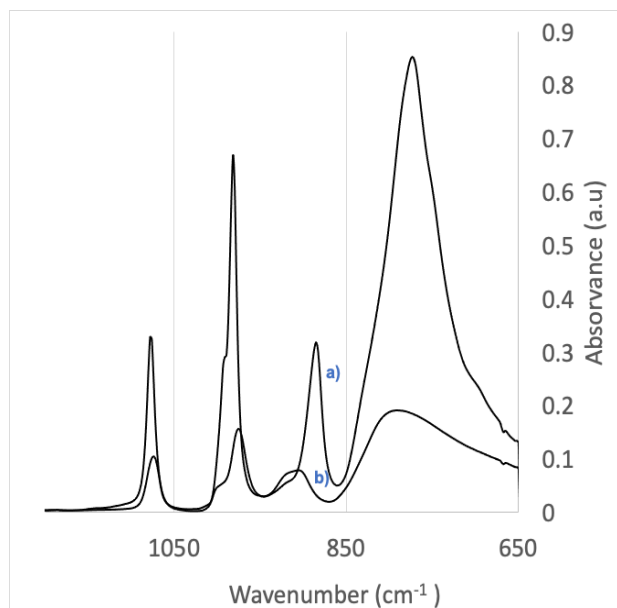
Figure 2: IR spectra of a) HPW and b) Cs2.5.

Figure 4: IR spectra of Pt-Al₂O₃ based catalysts.

3.1.2 Catalysts with Pt-Al$_2$O$_3$ as support

Concerning the Pt-Al$_2$O$_3$ supports, Pt cannot be identified in the X-Ray diffractograms (Figure 3) because it is well dispersed (35 % metal dispersion from H$_2$/O$_2$ titration) and also because of the small particles size it presents (3.2 nm calculated from metal dispersion). The presence of Keggin anionic species cannot be identified in HPW/Pt-Al$_2$O$_3$ sample, neither by XRD nor IR spectroscopy (Figure 4), however, UV-Vis DRS (not shown) confirms its presence in the support. On the contrary, for Pt-Al$_2$O$_3$/Cs$_{2.5}$ sample, the presence of Cs$_{2.5}$ phase can be detected by all techniques, where contributions of both the support and the Cs$_{2.5}$ salt are easily observed, in Figure 3 and Figure 4 (characteristic Keggin bands).
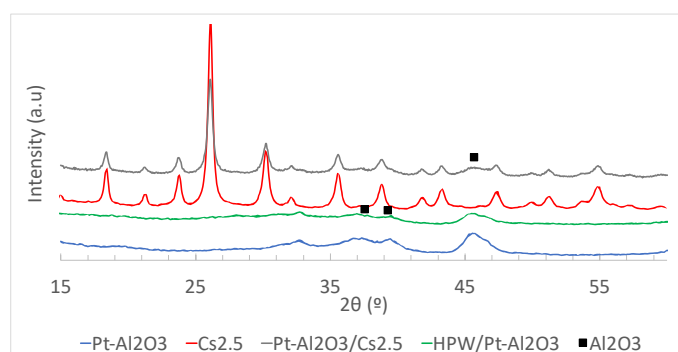
3.1.3 Catalysts with Ni28-Al$_2$O$_3$ as support

For Ni28-Al$_2$O$_3$, in the X-Ray diffractograms, a change from pseudo-boehmite can be seen upon thermal treatment (Figure 5). In these catalysts it is possible to identify by XRD a Ni phase but not a NiO phase.
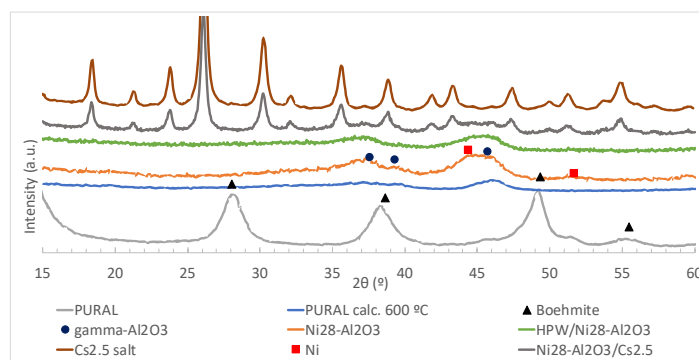
Figure 5: X-Ray Diffractograms of PURAL SB, PURAL SB calcined at 600 ºC, Ni28-Al2O3 catalyst, Ni28-Al₂O₃ /Cs2.5 and Cs2.5 salt, HPW/Ni28-Al₂O₃ catalyst. Comparison with boehmite (COD 9012247), gamma-Al2O3 (COD 1101168) and Ni (COD 2100640) from COD database.

This NiO species, however, is present, which was confirmed by H$_2$-TPR. It was also possible to see, through H$_2$-TPR and UV-Vis DRS (not shown) that a portion of the nickel interacts with the alumina support. The presence of impregnated HPW on Ni28-Al$_2$O$_3$ was not possible to be confirmed, neither from XRD, UV-Vis DRS nor IR spectroscopy (Figure 6). The presence of Cs$_{2.5}$ however, was confirmed by both XRD and IR spectroscopy.

Figure 3: X-Ray Diffractogram of Pt- Al₂O₃, Cs2.5 salt, Pt-Al₂O₃/Cs2.5, HPW/ Pt- Al₂O₃, and comparison with gamma-Al₂O₃ (COD 1101168).

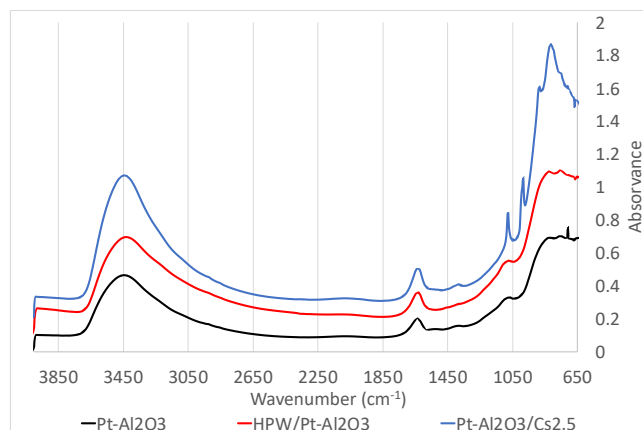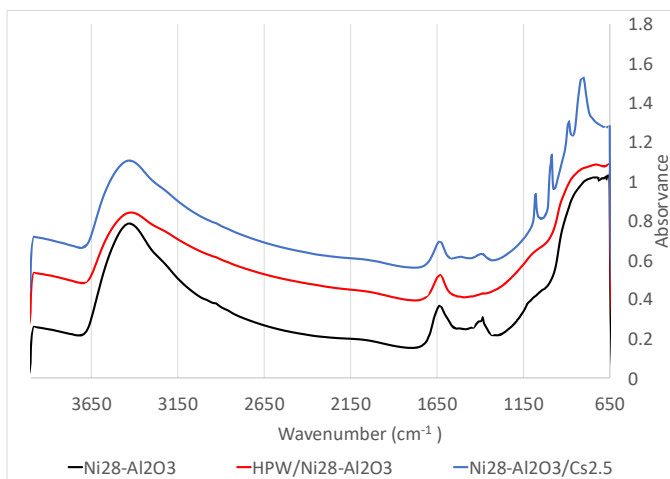*Figure 1: IR Spectra for Ni28-Al$_2$O$_3$ catalysts.*

3.1.1 Catalysts with NiO25-Al$_2$O$_3$ as support

In the case of NiO25-Al$_2$O$_3$ catalyst, the support presents more crystalline phases in its constitution when compared with the other two supports, which can be verified by the large number of identified species in the X-Ray diffractogram of these catalysts. Once again, the presence of HPW on the supports was unable to be confirmed by XRD but the presence of Cs$_{2.5}$ was. Like the other two groups of catalysts studied, the pattern of Ni28-Al$_2$O$_3$/Cs$_{2.5}$ is the sum of the contributions of the support and of the Cs$_{2.5}$ salt. It can be seen (Figure 7) a Ni phase and a NiO phase, which could not be seen in Ni28-Al$_2$O$_3$. This might mean that the NiO particles in the NiO25-Al$_2$O$_3$ catalysts are probably bigger in size or/and worse dispersed when compared with the Ni28-Al$_2$O$_3$ catalysts.
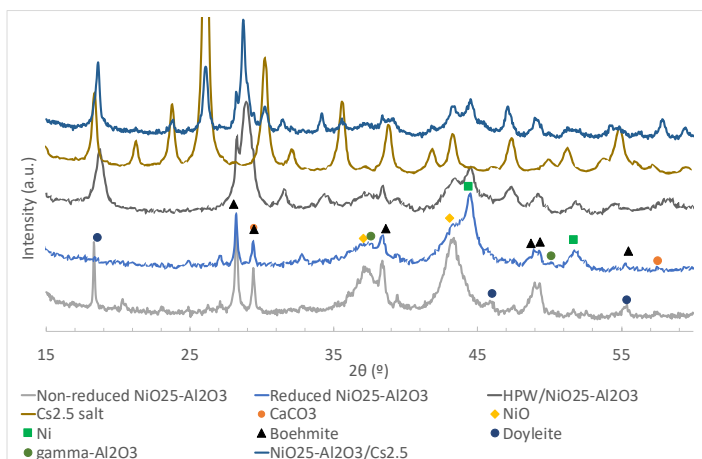

Figure 7: X-Ray diffractograms for NiO25-Al$_2$O$_3$ non-reduced and reduced, HPW/ NiO25-Al$_2$O$_3$, Cs$_{2.5}$ salt and NiO25-Al$_2$O$_3$/ Cs$_{2.5}$. CaCO$_3$ (COD 1010928), NiO (COD 4320505), Ni (COD 2100640), boehmite (COD 9012247), doyleite (COD 9011512) and gamma-Al2O3 (COD 1101168)

The presence of NiO was confirmed by H$_2$-TPR (not shown) and with this technique it was also possible to verify that this catalyst has also a nickel aluminate phase. Because of its black color, UV-Vis DRS was not performed but IR spectroscopy was. For the first time, it is possible to see evidence of HPW presence in the support, with one of the characteristic Keggin bands present in both HPW/NiO25-Al$_2$O$_3$ and NiO25-Al$_2$O$_3$/Cs$_{2.5}$ samples, Figure 8.
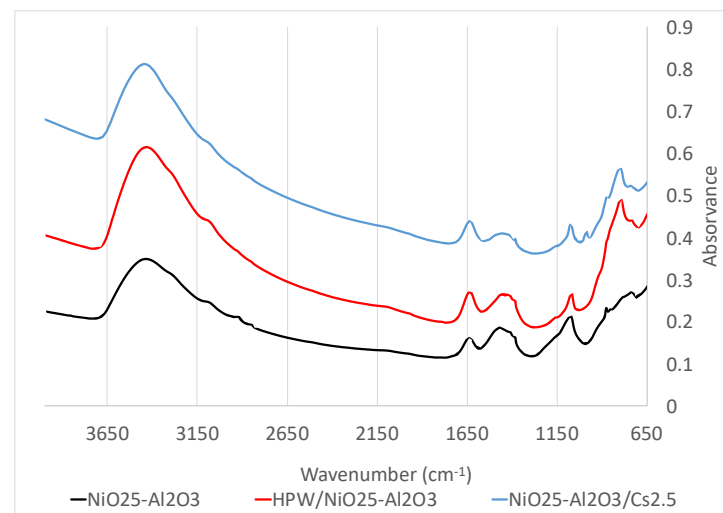

Figure 8: IR Spectra for NiO25-Al$_2$O$_3$ catalysts.

3.2 Catalytic Tests

The summary of catalytic results summary the Pt-Al$_2$O$_3$ catalysts can be seen in Figure 9 at the beginning (10 min TOS) and end of the reaction (120 min TOS).
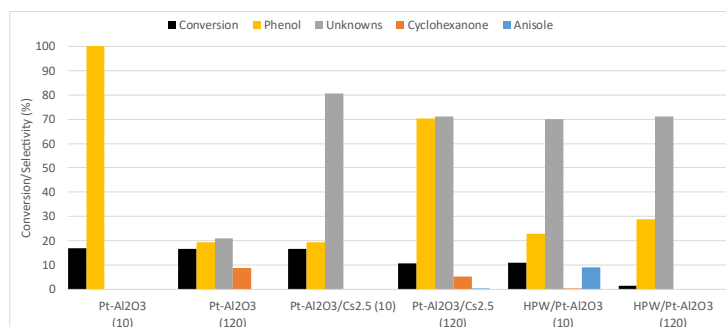

Figure 9: Summary of the results of the HDO of guaiacol for Pt-Al$_2$O$_3$. In parenthesis is shown TOS, in minutes.

For this group of catalysts, phenol was the major product. The conversion of Pt-Al$_2$O$_3$ support itself and Pt-Al$_2$O$_3$/Cs$_{2.5}$ remained roughly constant. The HPW/Pt-Al$_2$O$_3$ however showed a great conversion loss over the time, probably due to deactivation phenomena. Concerning phenol selectivity, it decreases with time for Pt-Al$_2$O$_3$, being undoubtably one of the major reaction

products. The presence of cyclohexanone suggests the occurrence of phenol hydrogenation and the presence of anisole shows that the catalysts were able to cleave the much energetic $C_{aromatic}$-OH bond before the $C_{aromatic}$-OCH_3 one, nonetheless with a lower overall selectivity when compared with phenol. Besides the main reaction products that were possible to identify, some amount of other reaction products, designated as "unknowns" or U were also detected. Because their selectivity trend was the opposite of the observed for phenol, it might indicate that phenol is suffering secondary reactions.

For the Ni28-Al$_2$O$_3$ and NiO25-Al$_2$O$_3$ reactions, the summary is present in Figure 10 and Figure 11. They will be discussed together once they are both Ni-Al$_2$O$_3$ based catalysts.
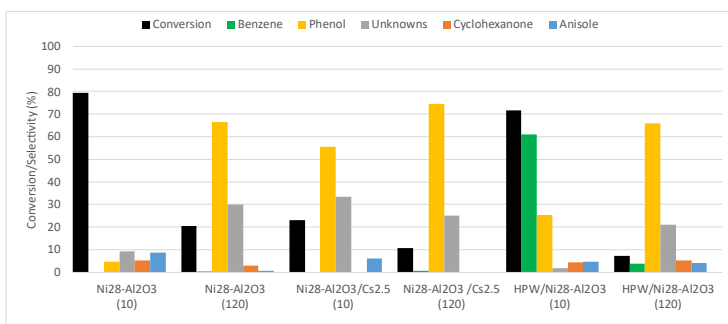

Figure 10: Summary of the results of the HDO of guaiacol for Ni28-Al$_2$O$_3$. In parenthesis TOS values, in minutes.
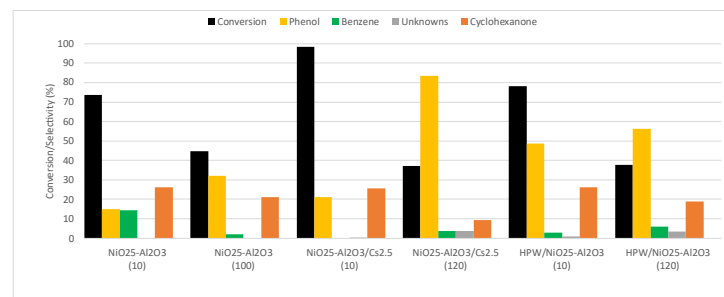

Figure11: Summary of the results of the HDO of guaiacol for NiO25-Al$_2$O$_3$. In parenthesis TOS values, in minutes.

The conversion values of Ni28-Al$_2$O$_3$ and NiO25-Al$_2$O$_3$ catalysts, when compared with Pt-Al$_2$O$_3$ ones, are significantly higher. This might be due to the fact that Pt loading in Pt catalysts is 1 wt. % and in Ni catalysts it is always higher than 10 wt. %. The major reaction products, however, was also phenol and its selectivity increases with time. The biggest difference between the Ni based catalysts and the Pt based ones is the presence of benzene, which is one of the target products because: a) it is totally deoxygenated, b) it is not hydrogenated, meaning that there is no H$_2$ "wasted" in hydrogenating the

aromatic ring. However, the evaluation of the selectivity of benzene in NiO25-Al$_2$O$_3$ products is difficult because of the overlap of the GC peaks of benzene and *n*-heptane transformation products, mainly for the physically mixed catalyst, although it seems that there is a decreasing trend overtime. The benzene is remarkably present for HPW/Ni28-Al$_2$O$_3$ catalyst. Cyclohexanone is manly present in the NiO25-Al$_2$O$_3$ catalysts, suggesting that these have a larger hydrogenation capacity when compared to Ni28-Al$_2$O$_3$. However, none of these Ni based catalysts showed significant values of anisole selectivity. Both these groups yielded unknown products, with selectivity values much lower when compared to Pt-Al$_2$O$_3$.

The spent catalysts were characterized to try to understand the reason for fast deactivation of the catalysts, specially HPW supported ones. For that purpose, the techniques used were powder XRD, to analyze structural changes, TGA, to quantify the weight loss of each catalyst and IR Spectroscopy, to evaluate the presence of organic species (e.g., coke) in the catalysts.

The XRD for fresh and spent catalysts are very similar, with no remarkable differences visible. From their analysis, it can be concluded that structural changes were not the cause of the catalysts deactivation.

When analyzing all the spectra for all the spent catalysts (although it will only be showed the results for Ni28-Al$_2$O$_3$, Figure 12), it becomes evident the appearance of two new bands: the former at around 1480 cm^{-1} and the latter at around 1250 cm^{-1}. The first band can be associated with the aromatic ring vibrations with an -OH contribution and the second band is also attributed to also aromatic ring vibrations with a C-O contribution.[13] Both these bands are characteristic of guaiacol and, in this case, confirm its presence on the catalysts.
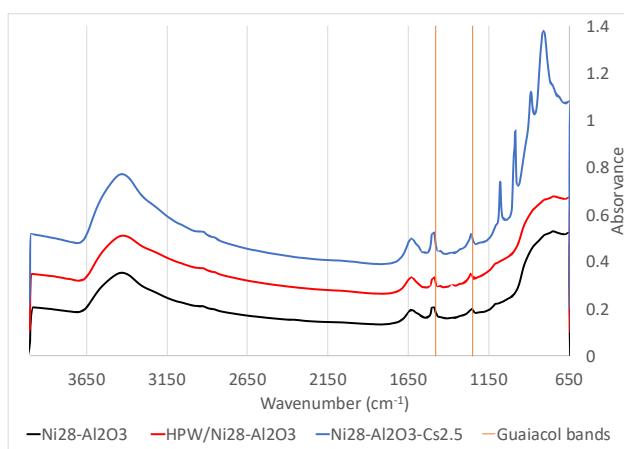

Figure12: IR spectra of spent catalyst and guaiacol band identification (orange) for Ni28-Al$_2$O$_3$ catalysts.

Table 1: TGA results summary for Ni28-Al$_2$O$_3$ catalysts

Samples	Weight loss (%)	Weight loss (%)	TOTAL WEIGHT LOSS (%)
ΔT (ºC)	25-200	200 - 640	
Ni28- Al$_2$O$_3$	2.0	**7.0**	9.0
HPW/ Ni28- Al$_2$O$_3$	4.0	**6.1**	10.1
Ni28- Al$_2$O$_3$/Cs2.5	2.4	**7.4**	9.8

The TGA results can be seen in Table 1. The first loss, which is endothermic for all catalysts and situated around 100 ºC, can be easily attributed to water desorption. The second weight loss observed is exothermic and ranges from 160 to 550 ºC for Ni catalysts. The catalyst that deactivates faster is HPW/Ni28-Al$_2$O$_3$, however it is not the one with the higher weight loss, which in this case is Ni28-Al$_2$O$_3$/Cs$_{2.5}$. A portion of the deactivation of the catalysts might come from carbonaceous deposits. It is known that not only guaiacol (that binds with both oxygens), but also phenolic compounds, such as phenol and anisole (reaction products), interact strongly with the alumina support and can act as "coke" precursors.[13] Because there is only one exothermic weight loss at considerably low temperatures for all catalysts, the deposits are probably guaiacol.

This is thought not to be the case for HPW catalysts, once these catalysts suffer the most important deactivation over time, although they do not present the highest weight losses. Because the HPW structure could not be seen in the diffractograms of fresh catalysts, a more thorough analysis should be done to investigate if the structure of the HPW impregnated on the supports is still unaltered or if it has decomposed.

The same conclusion can be drawn for the two other catalysts groups.

4. Conclusions

The objective of this work was to study heteropoly acids combined with metal-based alumina supports in the HDO of oxygenated molecules. Guaiacol, in this case, was chosen as a model compound once it has not one, but two C$_{aromatic}$-O functional groups. For that purpose, several catalysts were prepared based on three supports, 1 wt. % Pt-Al$_2$O$_3$, Ni28-Al$_2$O$_3$ and an industrial NiO25-Al$_2$O$_3$. The heteropoly acid was added to the support in two different ways, IWI of HPW and The first one was incipient wetness impregnation of an mechanical mixture of Cs$_{2.5}$ salt with the support. In both cases, the heteropoly acid or salt content was kept constant (20 wt. %). In this way, nine catalysts were prepared and tested.

Using different characterization techniques, it was possible to confirm the presence of the Cs$_{2.5}$ salts in all the "mixture" catalysts. However, for the HPW impregnated catalysts, the only catalyst where presence of the heteropoly acid on the support was confirmed was HPW/Pt-Al$_2$O$_3$ (UV-Vis DRS results). It is worth mentioning, however, that it was possible to confirm the presence of the HPW impregnated on only alumina by UV-Vis DRS.

The guaiacol conversion results follow the group order NiO25-Al$_2$O$_3$ > Ni28-Al$_2$O$_3$ >> Pt-Al$_2$O$_3$. The main product for all catalysts was phenol. For Pt catalysts, anisole and cyclohexanone were also identified. For the Ni catalysts, all these products were identified. However, benzene, a fully deoxygenated products, was also identified for these catalysts. From the catalytic tests results, it can be seen that NiO25-Al$_2$O$_3$/Cs$_{2.5}$ catalyst has a lot of potential, being the catalyst with the highest initial conversion, however its results could not be properly analyzed due to the occurrence of solvent transformations, that made the distinction between guaiacol transformation products and *n*-heptane transformation products an impossible task. The HPW impregnated on Ni catalysts led high initial conversions with also high selectivity to benzene. There was also a large amount of products that could not be identified. Based on the main reaction product, phenol, it was possible to conclude that the main reaction pathway was the direct deoxygenation of guaiacol, instead of the hydrogenation-deoxygenation pathway.

Although a decrease of conversion as a function of time on stream was observed for all catalysts, it was much more pronounced on the HPW impregnated catalysts. To understand the cause for this behavior, the spent catalysts were characterized by XRD, TGA and IR Spectroscopy. The XRD results showed no structural changes in all the catalysts after reaction. Thus, the cause of deactivation of the catalysts is thought to be caused by the strong adsorption of guaiacol on the catalysts surface. TGA and IR Spectroscopy results were in agreement. The weight losses for all catalysts are comprised between 9 and 12.7 % and occur at rather low temperatures, not commonly seen in coke oxidation. Hence it is thought to be the oxidation of lighter carbonaceous deposits. The IR Spectroscopy results show the appearance of mainly two new bands, which are characteristic bands of guaiacol, in confirmation of the deposition of this species on the

catalysts. This result, however, does not explain the reason for the faster deactivation of the HPW catalysts. Thus, this deactivation might be caused by a decomposition of the heteropoly acid on the support, which cannot be seen because, even in the fresh catalysts, the HPW presence could not be confirmed.

5. References

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