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BioEnergy IV: Innovations in Biomass Conversion for Heat, Power, Fuels and Chemicals

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Hydrodeoxygenation of biofuel-precursors on Ni-promoted catalysts

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Hydrodeoxygenation of Biofuel-precursors on Ni-promoted catalysts

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2. Scope

3. Experimental
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   4.2. HDO of model compounds mixture
   4.3 Used catalysts characterization

5. Conclusions

1.1. Introduction. New alternatives

Sustainable development :

→ Environmentally friendly clean fuels

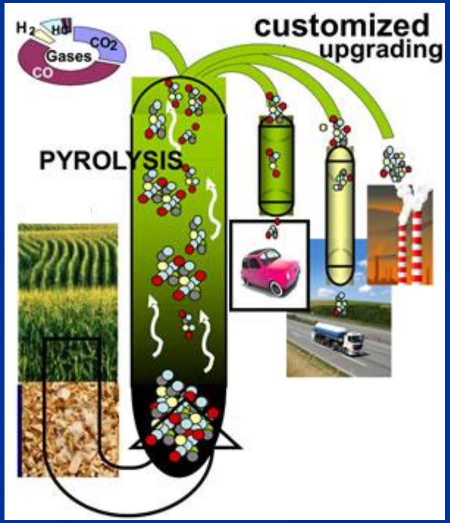
Biomass:

→ Renewable

→ Almost CO_2 neutral

→ Interesting economic potential

Biofuels: Fuels obtained from biomass
pyrolisis route η= 60-70%



Problem:

→T ype of raw material
→ Process
High content of oxygenated compounds:
Inmiscibility
High viscosity
Corrosion
Thermal inestability

1.2. Introduction. HDO

Table 1. Analysis of Biomass Samples Used for Pyrolysis

	switchgrass[a]	alfalfa-early bud	alfalfa-full flower
proximate (wt %, db)			
volatile matter	83.41	73.39	75.29
ash	2.61	8.74	5.83
fixed carbon	13.98	17.87	18.88
ultimate (wt %, db)			
C	47.53	44.30	45.97
H	6.81	5.43	5.52
N	0.51	2.52	1.60
S	0.00	0.22	0.088
Cl	—[b]	0.59	0.41
O	42.54	38.20	40.58

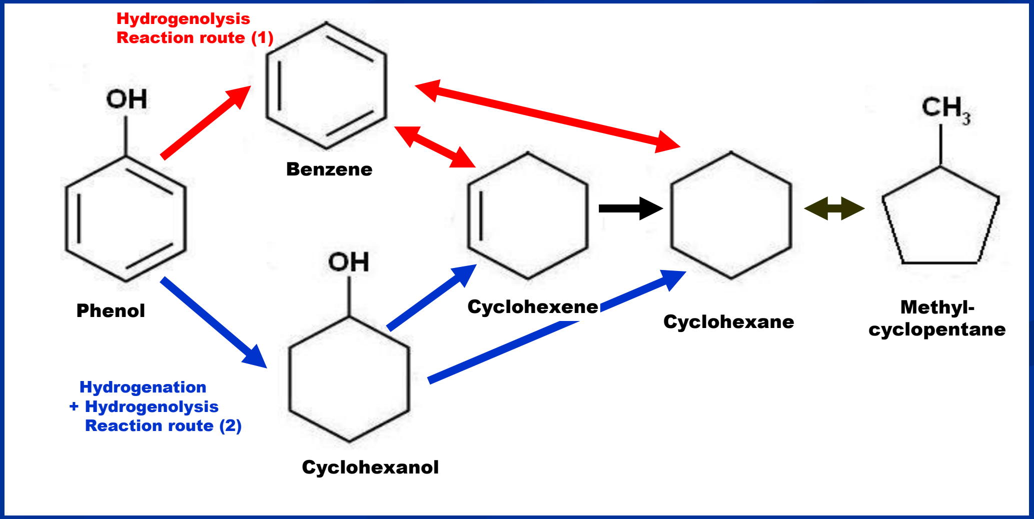
[a] Taken from Boateng et al.[4] [b] Cl content not determined for switchgrass.

Most frecuently studied catalysts: $NiMo/Al_2O_3$ and $CoMo/Al_2O_3$

Active carbon

+ W

+ Ni



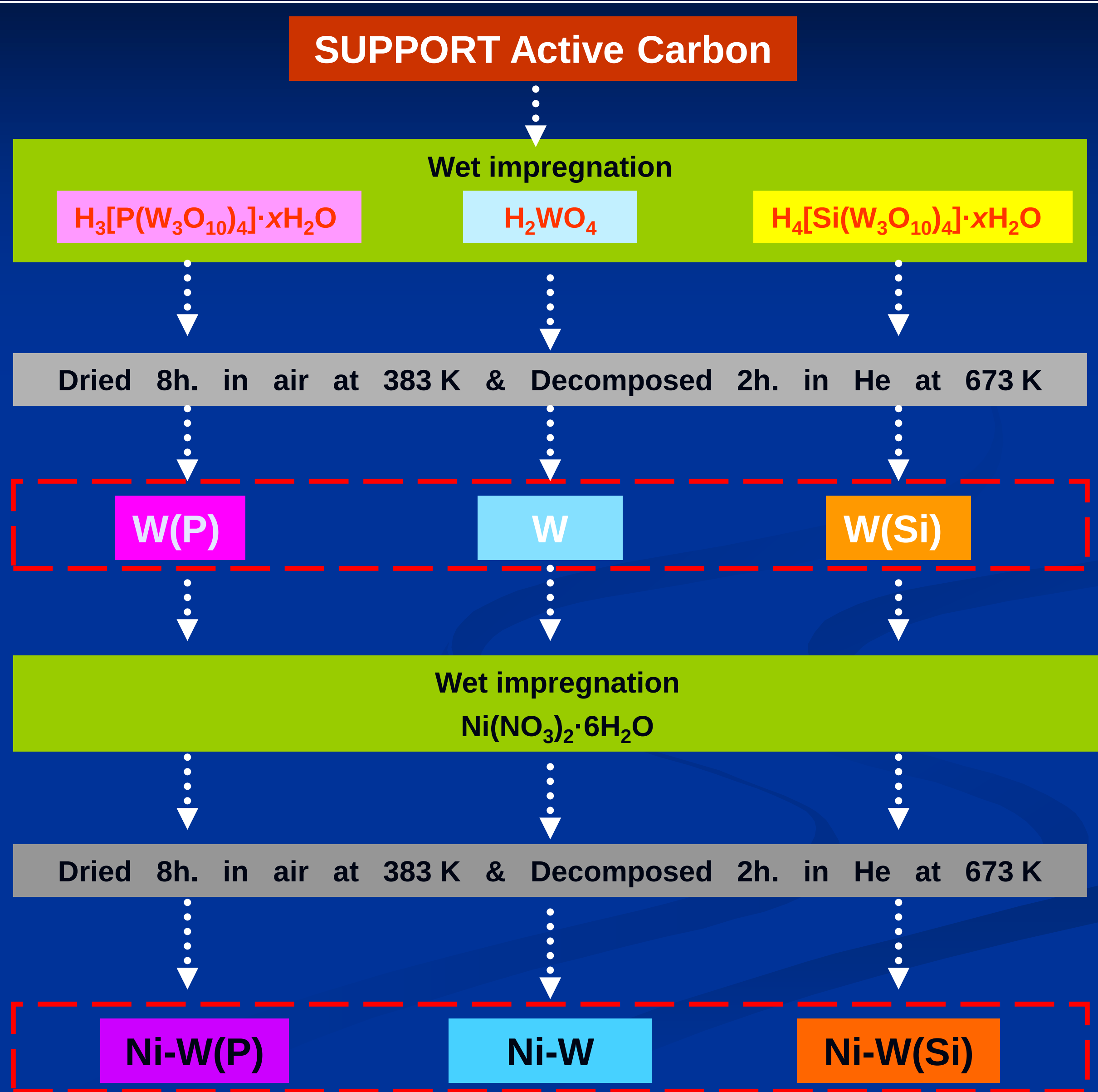
Model compound mixtures

2. Scope

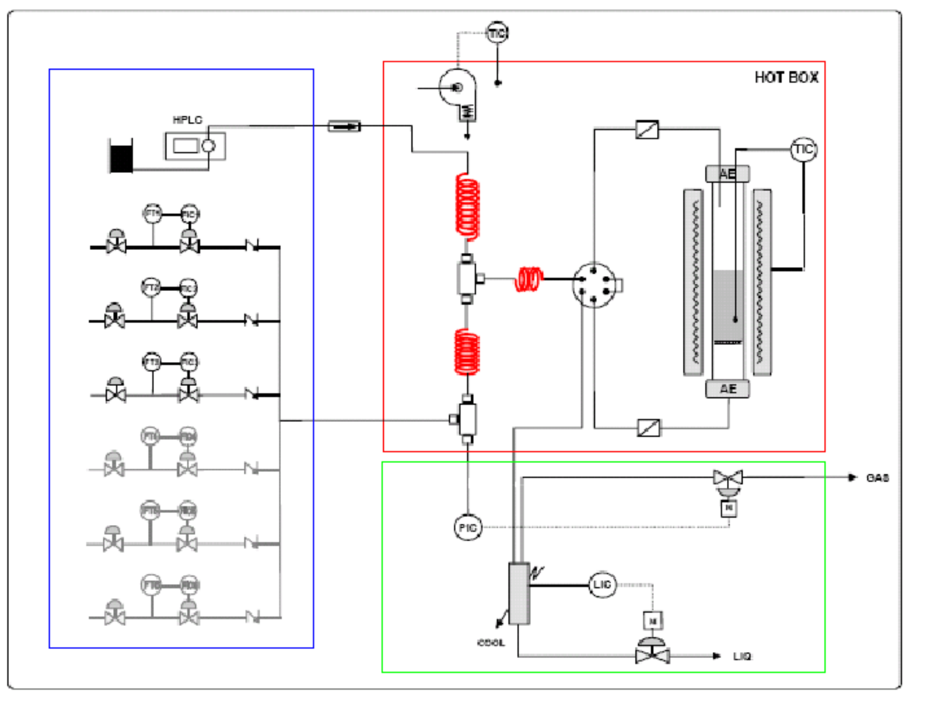
The ***objectives*** ***of this work are:***

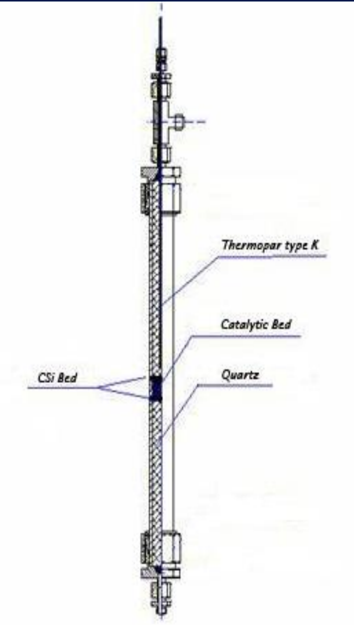
- **To detect any synergistic effect between Ni and W oxide species supported on activated carbon (AC) when used as hydrodeoxygenation (HDO) catalysts.**
- **To study the effect of different W precursors -silicotungstic (HSiW) and phosphotungstic (HPW) acids- on the activity of Ni-W/AC catalysts.**
- **To study the HDO of phenol and of model compound mixtures representative of bio-oil: ethanol, acetone, tetrahydrofuran, phenol and guaiacol .**

3.1. Catalysts preparation



3.2. Activity tests





Product Analysis:

- **GC-FID**
- **GC-MSD**

Catalyst mass: **0.2 g**

Catalysts pre-treatment :

***in situ* in a 1:3 H_2:N_2 mixture with a H_2 flow of 2,5 $L \cdot h^{-1}$ (NTP) at 593 K**
0,1 MPa of total pressure

Experimental conditions :

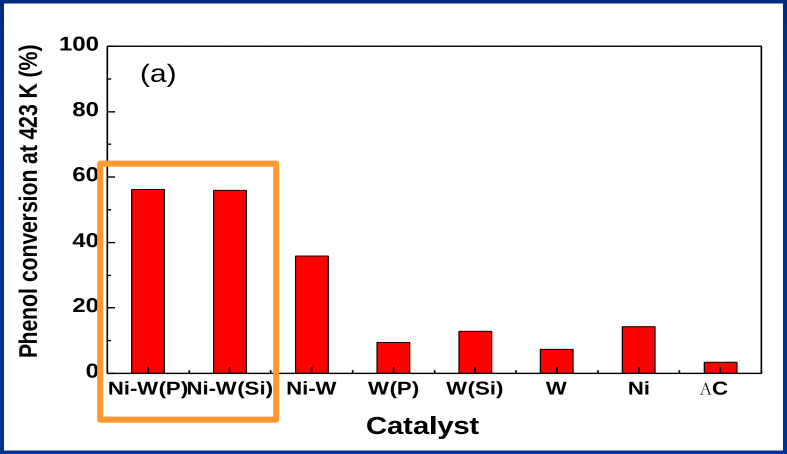
- Temperature in the range 423 – 523 K and total pressure 1,5 MPa
- Feed: * Phenol 1 wt.%
*** Model feed consisting of: ethanol, acetone, tetrahydrofuran, phenol and guaiacol (1 wt.% each) in *n*-dodecane as solvent**
- H_2:oxygenate compound molar ratio of 100:1

3.3. Catalysts characterization

- Fresh samples:
  - ICP-AES
  - BET
  - TPR
  - TPD-NH_3

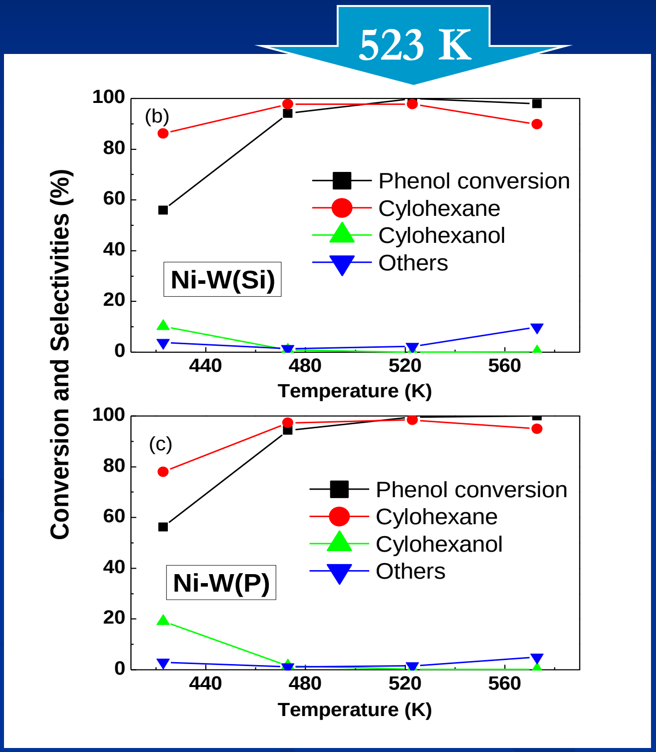
- Used samples:
  - XRD
  - XPS
  - HRTEM
  - TGA/DGT

4.1. Phenol HDO



(a) Comparison of the steady-state phenol conversions of different catalysts in HDO of phenol at *T* = 423 K, *P* = 1,5 MPa and *WHSV* = 0,5 h^{-1}.

Ni-W(P) ≈ Ni-W(Si) >> Ni-W >> Ni > W(Si) > W(P) >> W > AC support



Influence of temperature on the phenol conversion and selectivities in the HDO of phenol (*WHSV* = 0,5 h^{-1}) over:

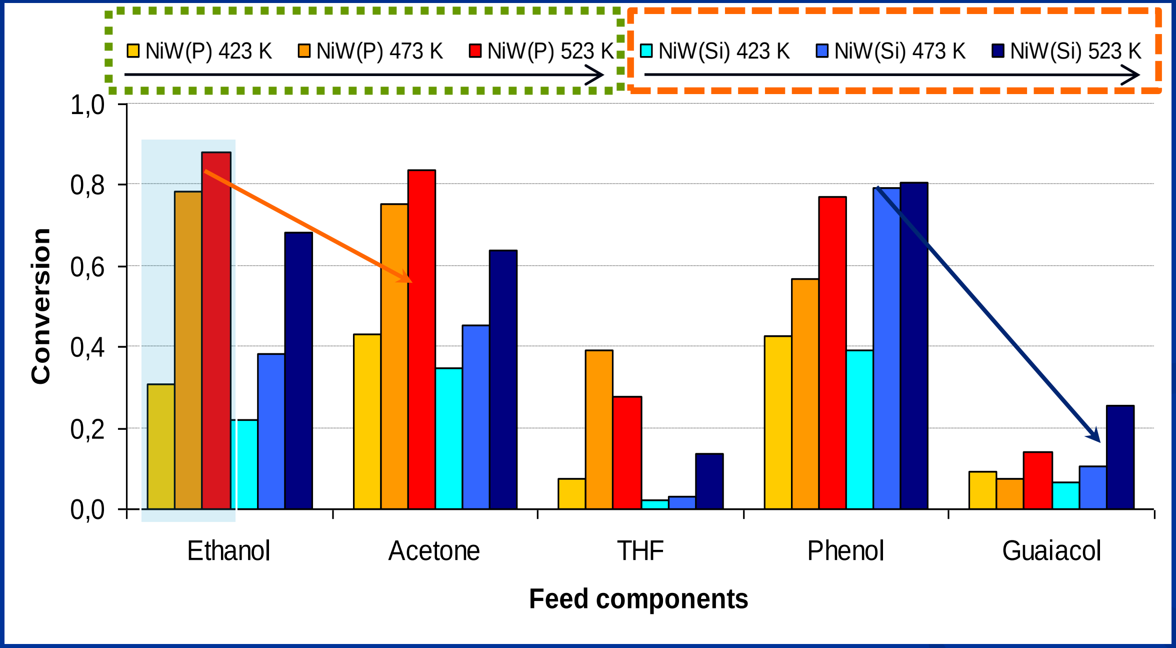
(b) Ni-W(Si) catalyst

(c) Ni-W(P) catalyst

4.2. HDO of model compounds mixture

Comparison of the conversion of AC-supported catalysts in HDO at different temperatures

(*T* = 423-523 K, *P* = 1,5 MPa)



4.2. HDO of model compounds mixture

1. Introduction
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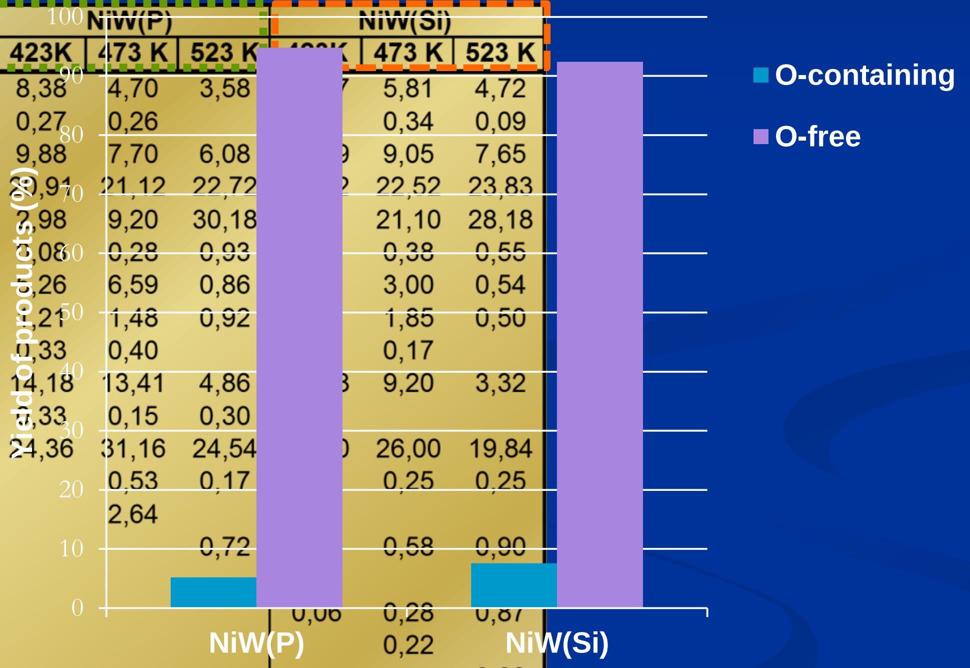
Comparison of the product distribution of AC-supported catalysts in HDO at different temperatures

(*T* = 423-523 K, *P* = 1.5 MPa)

*Relative abundance	NiW(P)			NiW(Si)		
	423K	473 K	523 K	[illegible]	473 K	523 K
Ethanol	8,38	4,70	3,58	[illegible]	5,81	4,72
2-Ethoxy propane	0,27	0,26		[illegible]	0,34	0,09
Acetone	9,88	7,70	6,08	[illegible]	9,05	7,65
THF	20,91	21,12	22,72	[illegible]	22,52	23,83
Cyclohexane	2,98	9,20	30,18	[illegible]	21,10	28,18
Cyclohexene	[illegible],08	0,28	0,93	[illegible]	0,38	0,55
Cyclohexanol	[illegible],26	6,59	0,86	[illegible]	3,00	0,54
Cyclohexanone	[illegible],21	1,48	0,92	[illegible]	1,85	0,50
Ethoxy cyclohexane	0,33	0,40		[illegible]	0,17	
Phenol	14,18	13,41	4,86	[illegible]	9,20	3,32
Decane	[illegible],33	0,15	0,30	[illegible]		
Guaiacol	24,36	31,16	24,54	[illegible]	26,00	19,84
Eicosane		0,53	0,17	[illegible]	0,25	0,25
Diethyl Phthalate		2,64		[illegible]		
Propane			0,72	[illegible]	0,58	0,90
Methoxy ethane				[illegible]		
Ethyl ether				0,06	0,28	0,87
Propoxy benzene					0,22	
Butane						0,08
Ethyl cyclohexane						0,19
Ethoxy benzene						0,39
Undecane	1,64			1,42		
Tridecane	5,57			4,79		



18

12

$$\frac{O-free}{O-containing} \geq 10$$

4.3. Used catalysts characterization

Binding energy (eV) of core electrons and surface atomic ratios of spent catalysts tested in HDO as determined by XPS.

Catalyst	W	Ni 2p	Si 2p, P 2p	Ni/AC at	W/AC at	(Ni+W)/AC at
Ni	-	853.0 (47) 856.5 (53)	-	0.0038	-	-
W	35.6	-	-	-	0.0047	-
W(Si)	35.7	-	103.1	-	0.0052	-
W(P)	35.7	-	134.2	-	0.0048	-
Ni-W	35.6	853.0 (30) 856.7 (70)	-	0.0092	0.0065	0.0157
Ni-W(Si)	35.7	852.9 (20) 856.7 (80)	103.2	0.0183	0.0146	0.0329
Ni-W(P)	35.6	852.9 (28) 856.7 (72)	134.1	0.0127	0.0082	0.0209

4.3. Used catalysts characterization

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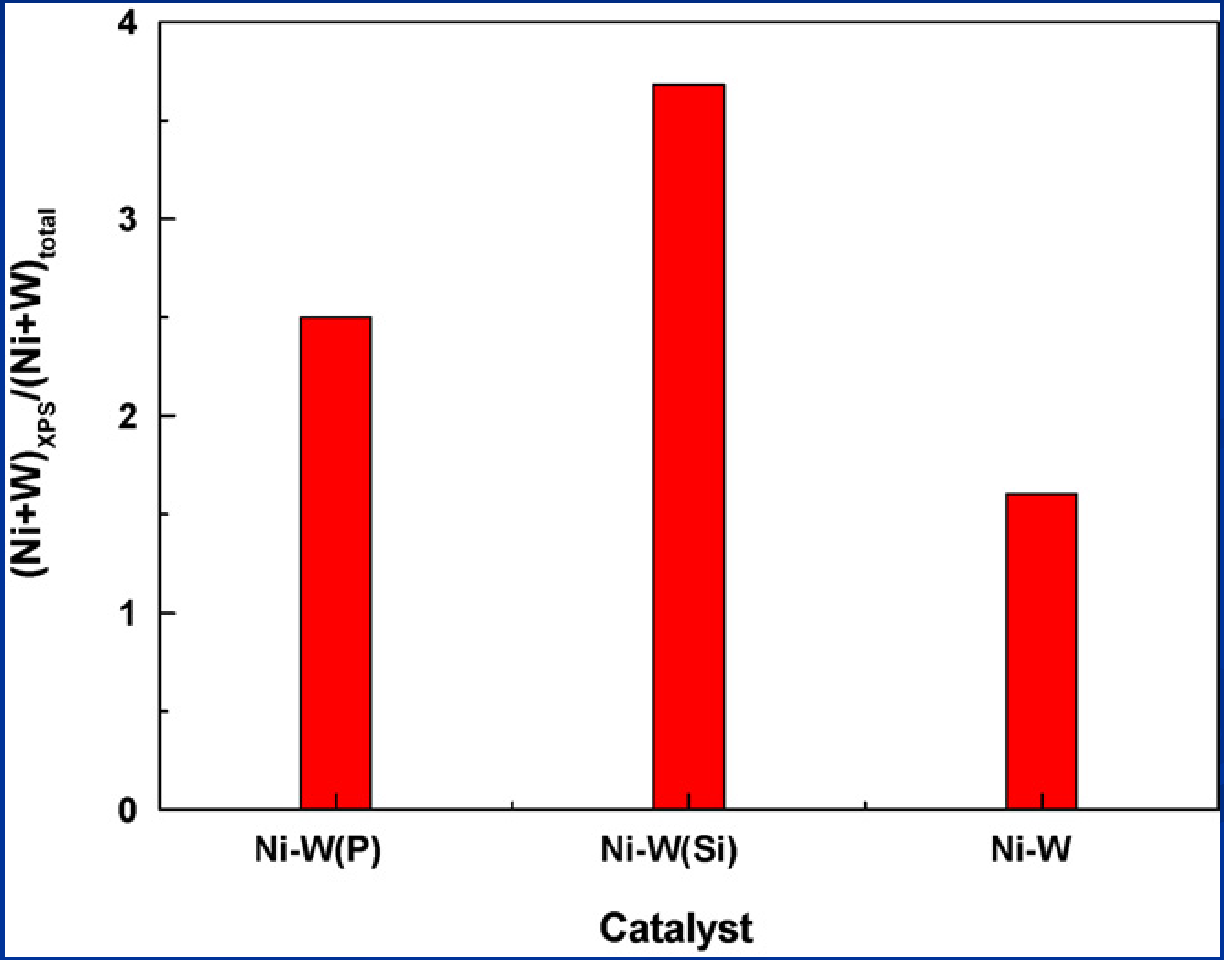
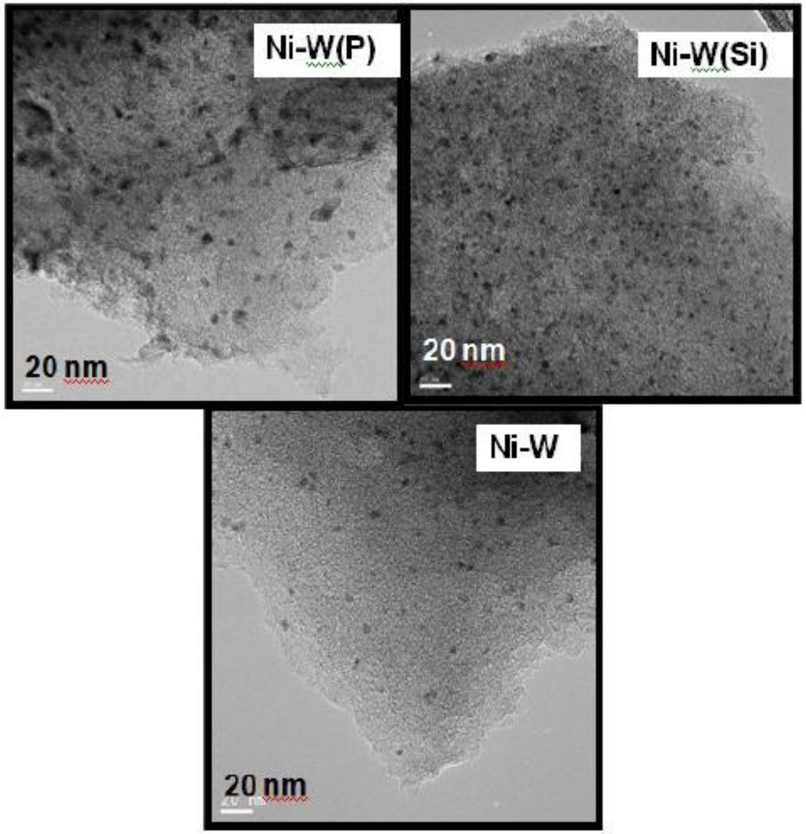
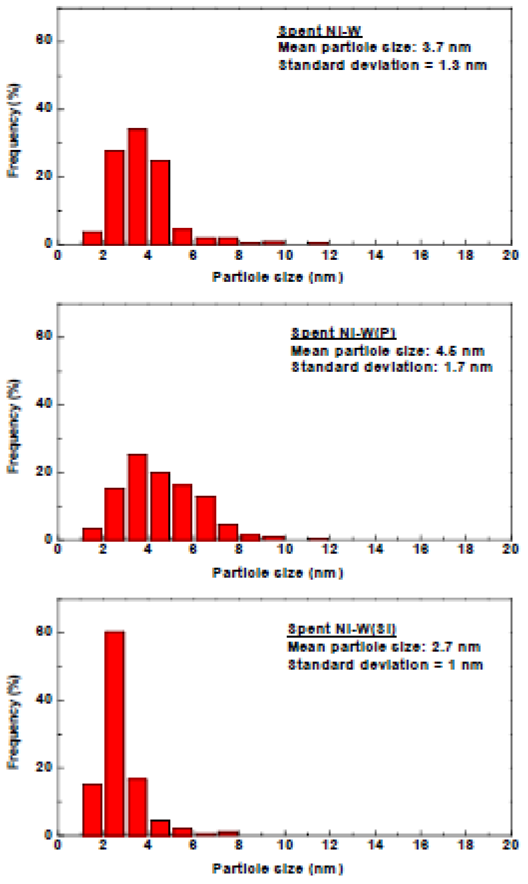
Variation of surface atomic ratio (XPS) of spent binary catalysts, (Ni +W)/C, against total (ICP) atomic ratio of the oxide precursors, (Ni +W)/C.



4.3. Used catalysts characterization

HRTEM





5. Conclusions

Hydrodeoxygenation was carried out on oxide Ni-W catalysts supported on activated carbon. The main conclusions derived from this work are the following:

The use of non-conventional W precursors (heteropolyacids) allowed the preparation of more active bimetallic hydrotreating catalysts.

Ni-W/AC catalysts are not only good HDS catalysts but also promising candidates for HDO processes. The promoting effect of Ni on W/AC catalysts was measured in the HDO of phenol and of model compounds mixtures.

Analyses of the products indicate that HDO reaction on these catalysts occurs via two separate pathways: one leading to aromatics and the other to cyclohexane, in good agreement with literature.

Using phosphotungstic (HPW) heteropolyacid -as W precursor- more active and stable catalysts are obtained as compared to the silicotungstic (HSiW) heteropolyacid.

Thank you very much for your attention

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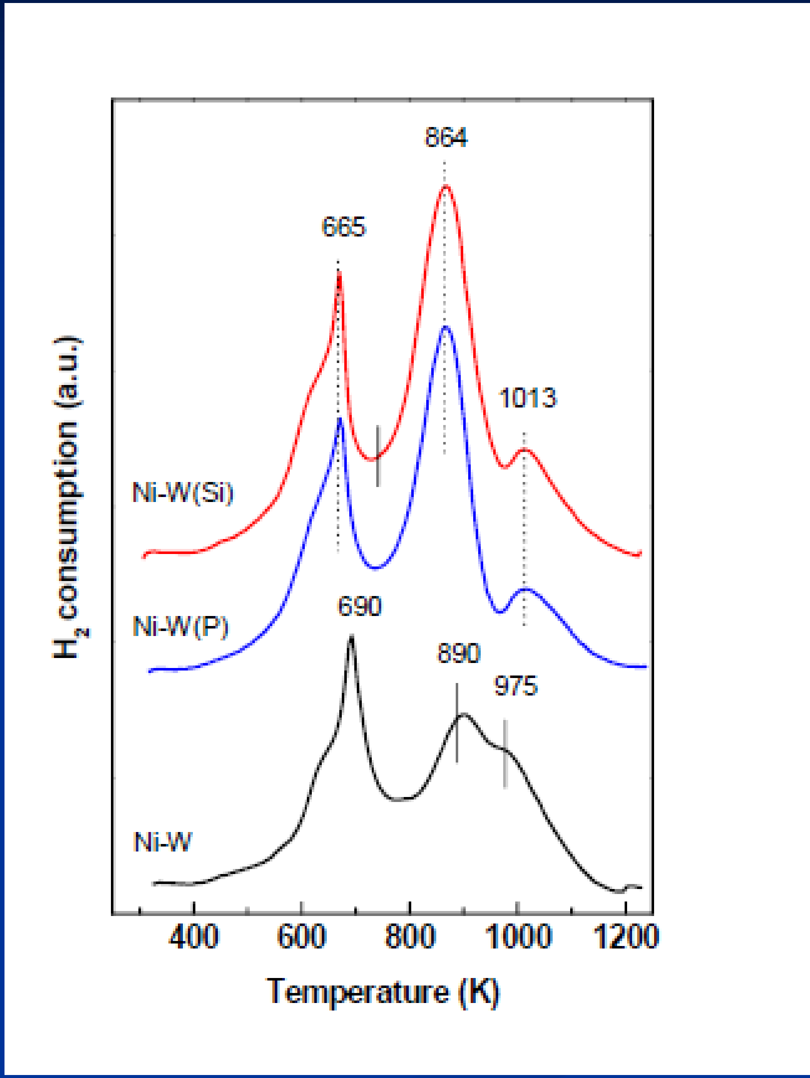
Catalizador	Ni-W(P)	Ni-W(Si)	Ni-W	W(P)	W(Si)	W	Ni
Catalizador oxidado							
Ni (wt%)	2,3	2,4	2,6	-	-	-	2.7
W (wt%)	4,7	5,2	5,8	5,6	5,5	6,0	-
P or Si (wt%)	0,4	0,7	-	0,4	1,0	-	-
S_{BET} ($m^2 \cdot g^{-1}$)	1099	1071	941	1142	1126	991	1182
$S_{\mu pore.}$ ($m^2 \cdot g^{-1}$)	708	736	604	733	766	610	770
NS_{BET}^{c}	0,91	0.89	0.78	0,92	0,91	0,80	0,93
d (nm)	2,8	2,8	1,6	2,8	2,8	1,6	2,8
Catalizador usado							
C (%)	81,7	79,4	81,5	86,9	83,7	86,4	87,5
H (%)	3,3	2,4	3,2	2,6	1,8	2,9	2,9
N (%)	0,3	0,3	0,4	0,3	0,3	0,3	0,4
S (%)	0,2	0,2	0,2	0,2	0,3	0,2	0,3



864
665
1013
690
890
975
Ni-W(Si)
Ni-W(P)
Ni-W
H_2 consumption (a.u.)
400
600
800
1000
1200
Temperature (K)