ELSEVIER
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BIMETALLIC RU:NI/MCM-48 CATALYSTS FOR THE EFFECTIVE HYDROGENATION OF D-GLUCOSE INTO SORBITOL

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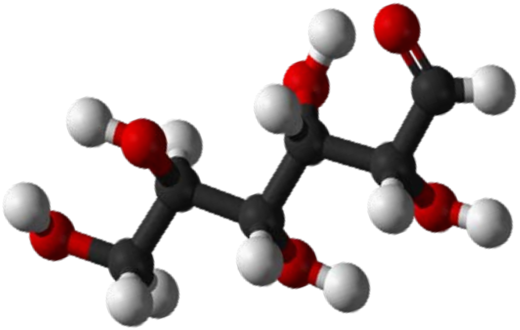
ALBERTO ROMERO CAMACHO

Berlin – May, 16th 2017



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Cathycel

Depletion of fossil fuels

+

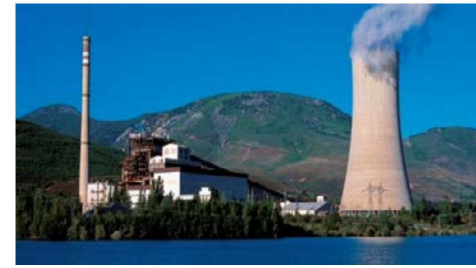
Global warming

BIOMASS →

Energy

Fuels

Chemicals



Food industry

Drugs

Cosmetics

Toothpaste

L-Ascorbic Acid

Lower polyols

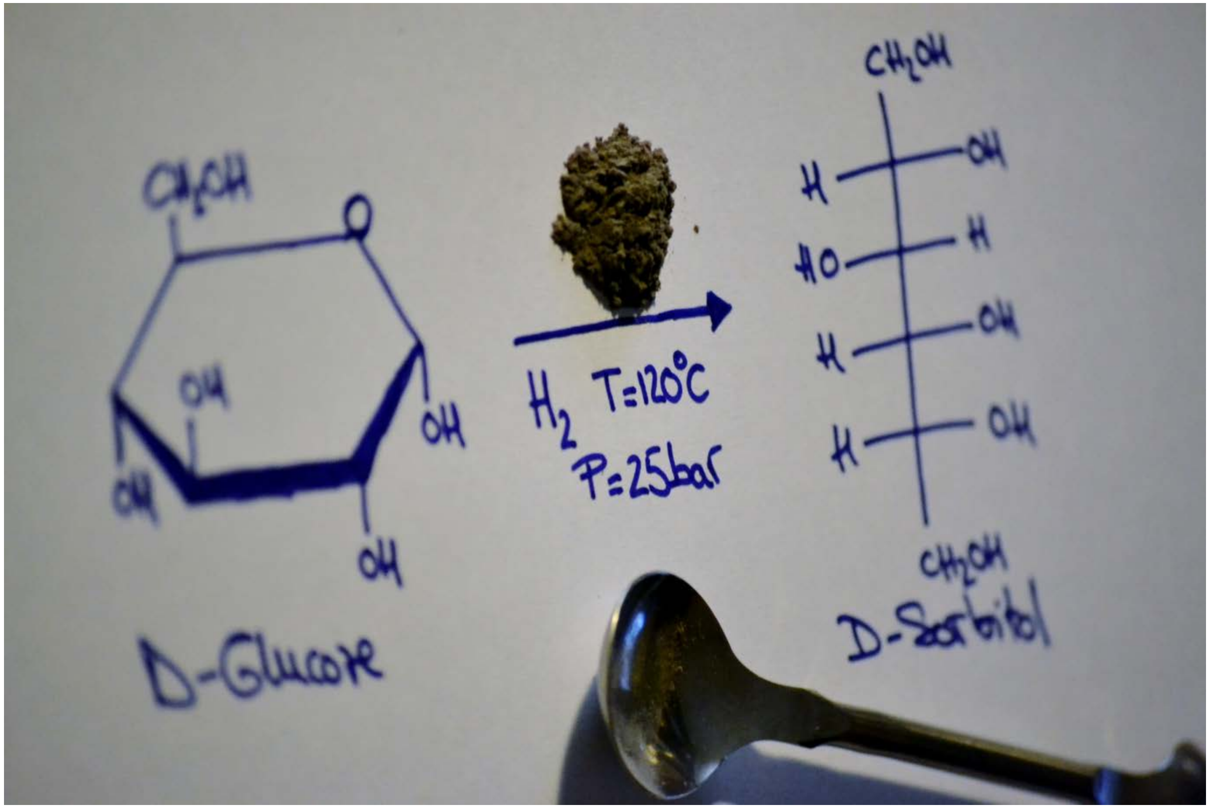
CELLULOSE →

Most abundant resource of biomass

Attractive reaction routes →

HEXITOLS (Sorbitol and Mannitol)

Catalytic hydrogenation of D-Glucose



Ni-based catalysts

✔	✘
· Low cost · Moderate to good activity	· Deactivation · Sintering · Leaching

Ru-based catalysts

✔	✘
· 20-50 times ↑ activity · No leaching	· High price

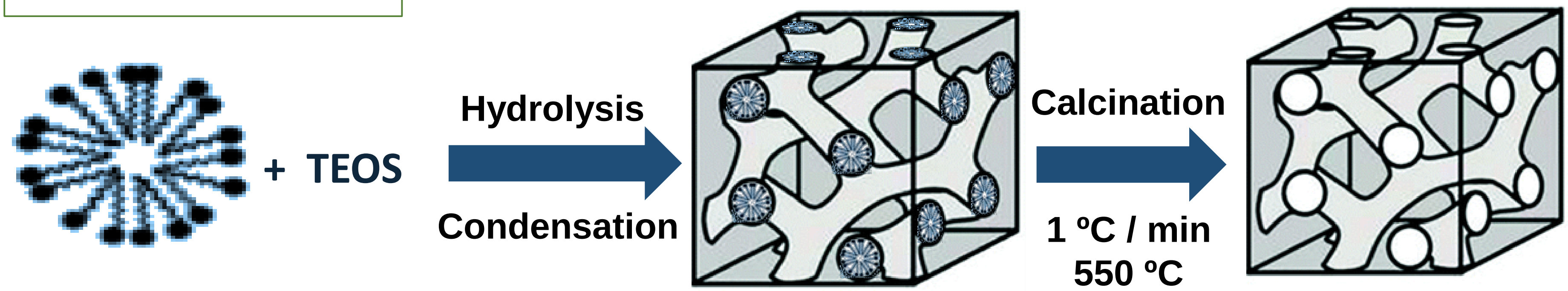
Design of bimetallic Ru:Ni/MCM-48 catalysts as alternative to monometallic Ni/MCM-48 for the catalytic hydrogenation of D-Glucose into sorbitol

Synthesis and characterization of the catalysts

Study the influence of different amounts of Ru over Ni/MCM-48 in order to improved the catalytic behavior of the monometallic catalyst in D-Glucose hydrogenation

Recycling of Ru:Ni/MCM-48

MCM-48 PREPARATION



Ni/MCM-48 AND Ru:Ni/MCM-48 PREPARATION (Wet impregnation)

Suspension MCM48

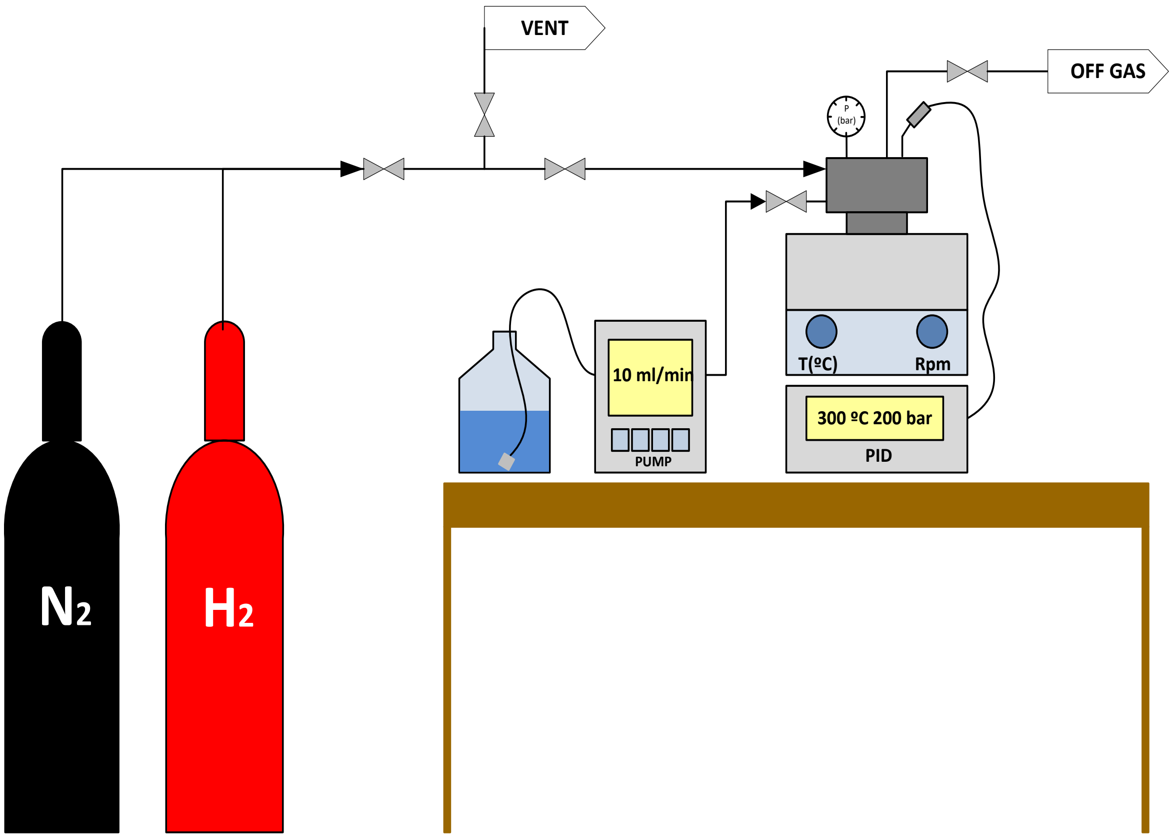
Ultrasounds
10 min

Suspensión MCM48
+
Solution Metal precurssors

H_2O

Drying 105 ºC
Milling
Reduction (TPR)

HYDROGENATION TESTS



Reactor BR-25

Stainless steel
V = 25 mL
P_{max} = 20 MPa
T_{max} = 300 ºC

Experimental conditions

T= 120–140 ºC
P = 2.5 MPa
[C/Ru] = 142
(mol·mol^{-1})

ANALYSIS AND CHARACTERIZATION TECHNIQUES

Composition
- AA

Textural properties
- A_{BET} and V_p
- XRD and SAXS

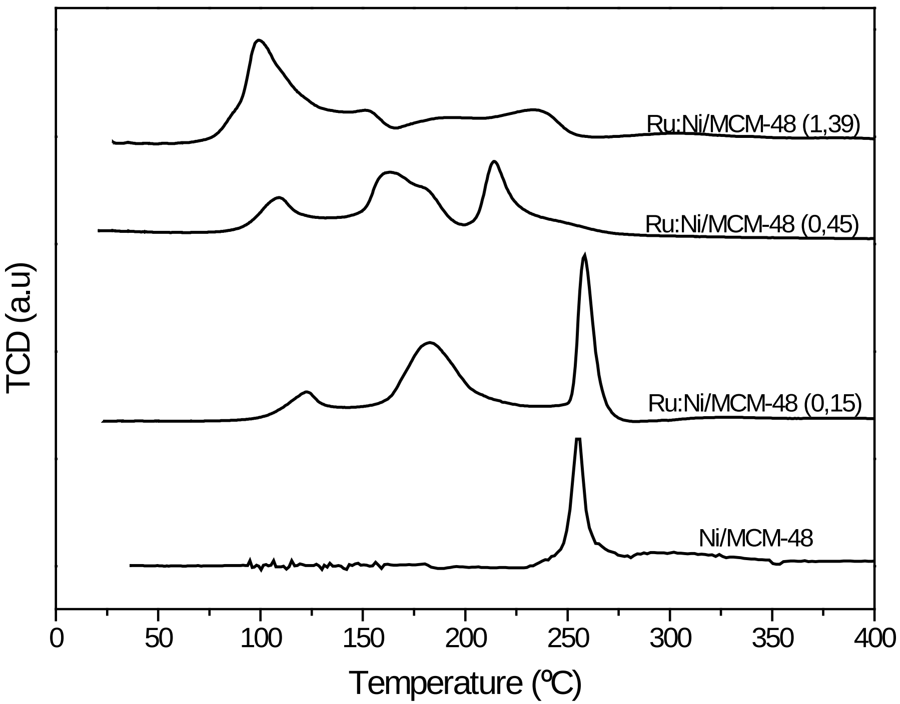
Morphology
- TEM – MAPPING

Species identification
- $TPR-H_2$

Surface acidity
- $TPD-NH_3$

Analysis of reaction products
- HPLC

TPR-H_2



Ni/MCM-48

- 255 ºC - Reduction of $(Ni(NO_3)_2{\cdot}4H_2O{\cdot}2(SiOH)$

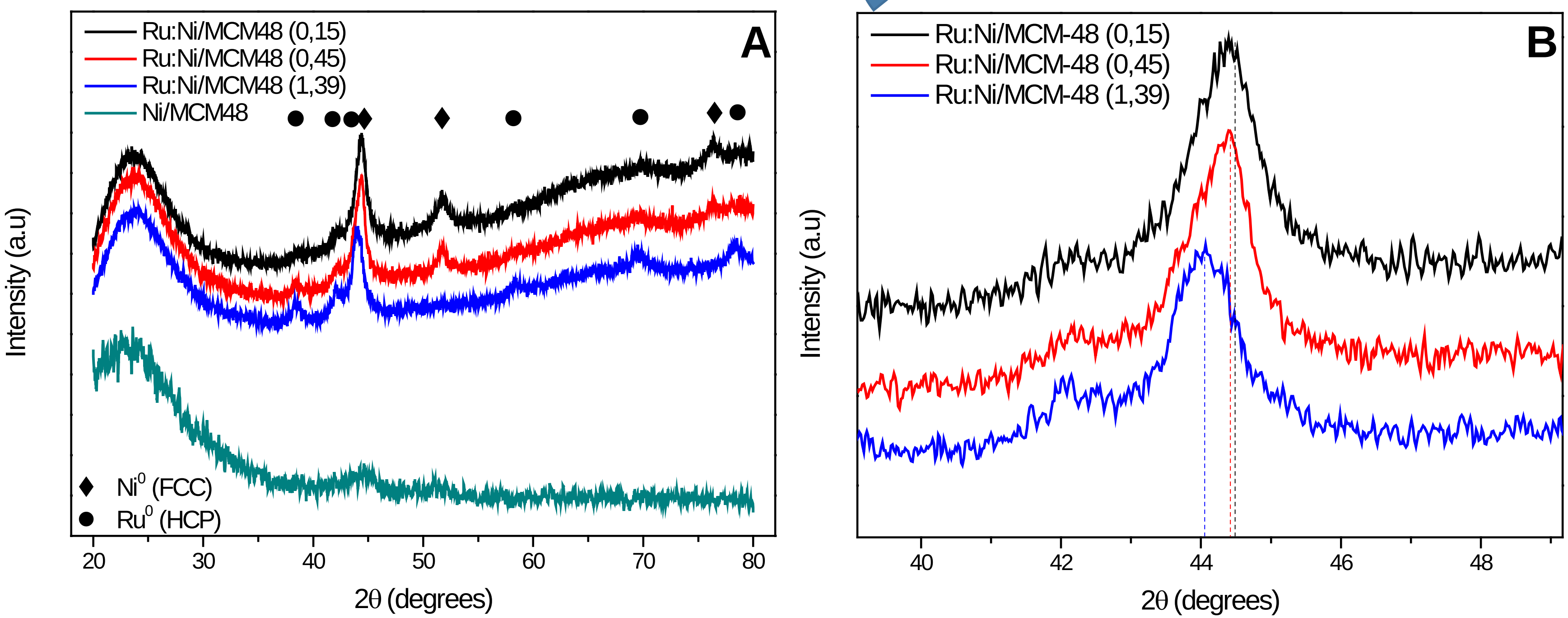
Ru:Ni/MCM-48

- 100 ºC – Reduction of $RuCl_3$
- 175 ºC – Reduction of Ru/Ni alloys
- 255 ºC – Reduction of $(Ni(NO_3)_2{\cdot}4H_2O{\cdot}2(SiOH)$

Catalyst	Ru (%)	Ni (%)	Ru:Ni
Ni/MCM-48	-	2.95	-
Ru:Ni/MCM-48 (0.15)	0.38	2.48	0.15
Ru:Ni/MCM-48 (0.45)	0.76	1.67	0.45
Ru:Ni/MCM-48 (1.39)	1.63	1.17	1.39

XRD

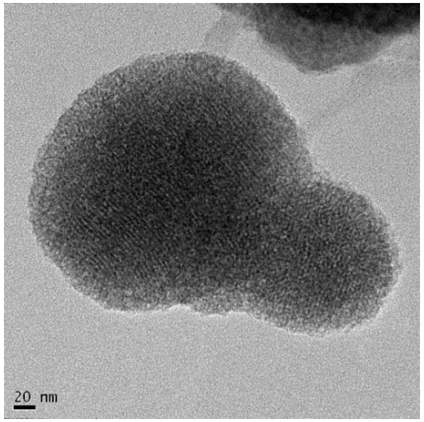
Main peaks of Ni^0 and Ru^0 overlapped

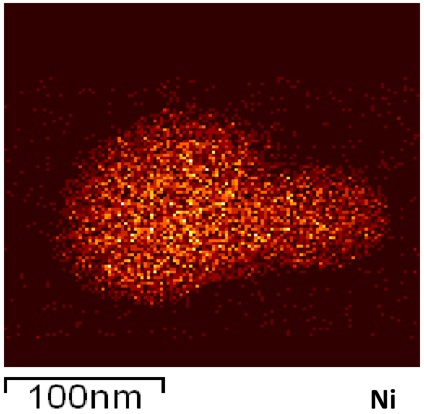


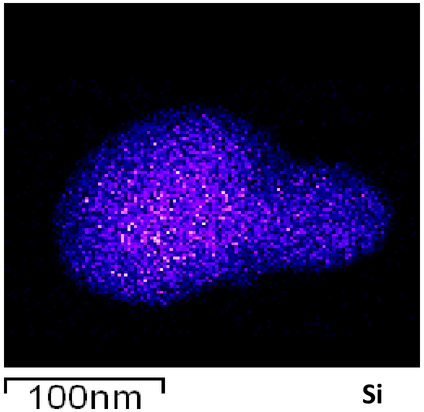
Ni^0 (FCC) 2θ = *44.5º*, *51.7º* and *76.1º* (JCPDS card No. 4-850)

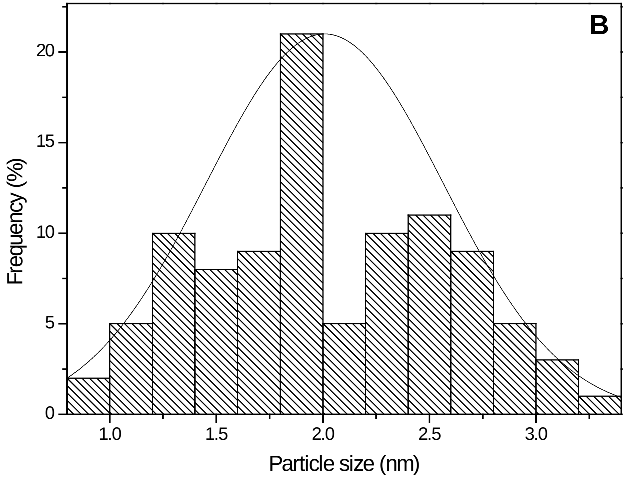
Ru^0 (HCP) 2θ = *38.8º*, *42.2º*, *43.8º*, *58.2º*, *69.6º* and *78.4º* (JCPDS card No. 06–0663)

TEM Ni/MCM-48







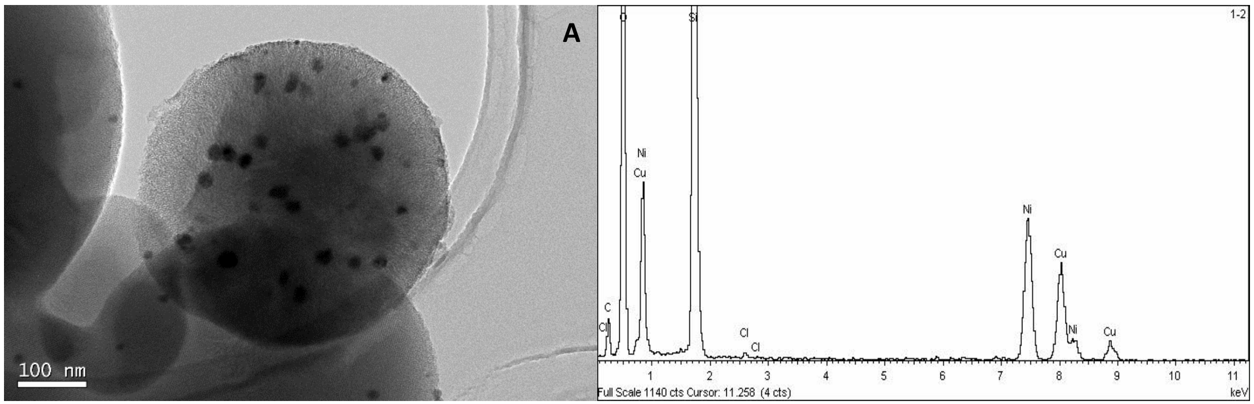


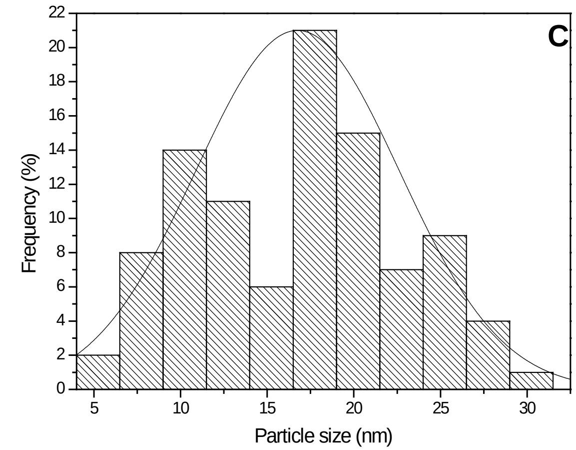
Catalyst	Ni (%)	S_{BET} ($m^2 \cdot g^{-1}$)	V_{pore} ($cm^3 \cdot g^{-1}$)	Ø $_{pore}$ (nm)
MCM-48	-	1289	0.87	2.2
Ni/MCM-48	2.95	572	0.44	4.4

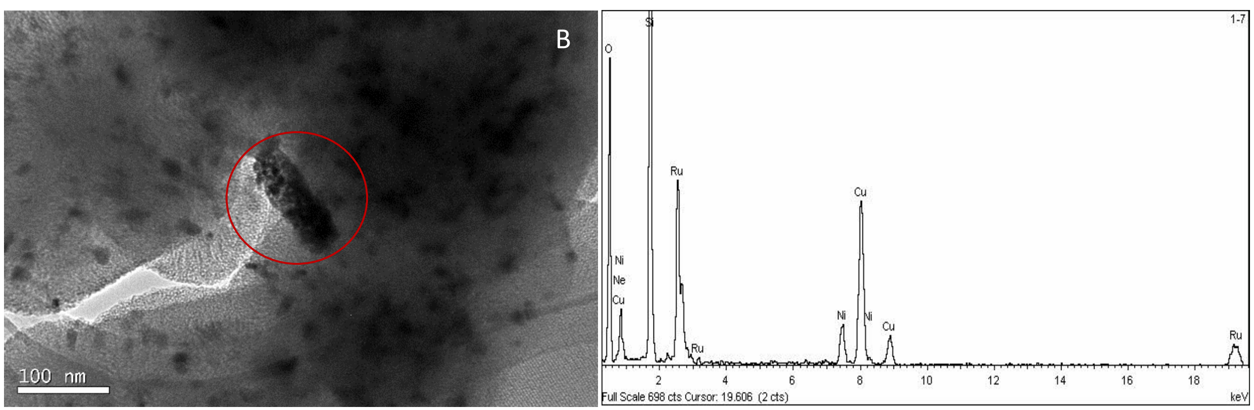
$\bar{d}_{p\,Ni}$=2.4 nm (2.7 nm XRD-Scherrer)

TEM Ru:Ni/MCM-48 (0.15)

$\overline{d}_{p\ Ni}$ =20.6 nm

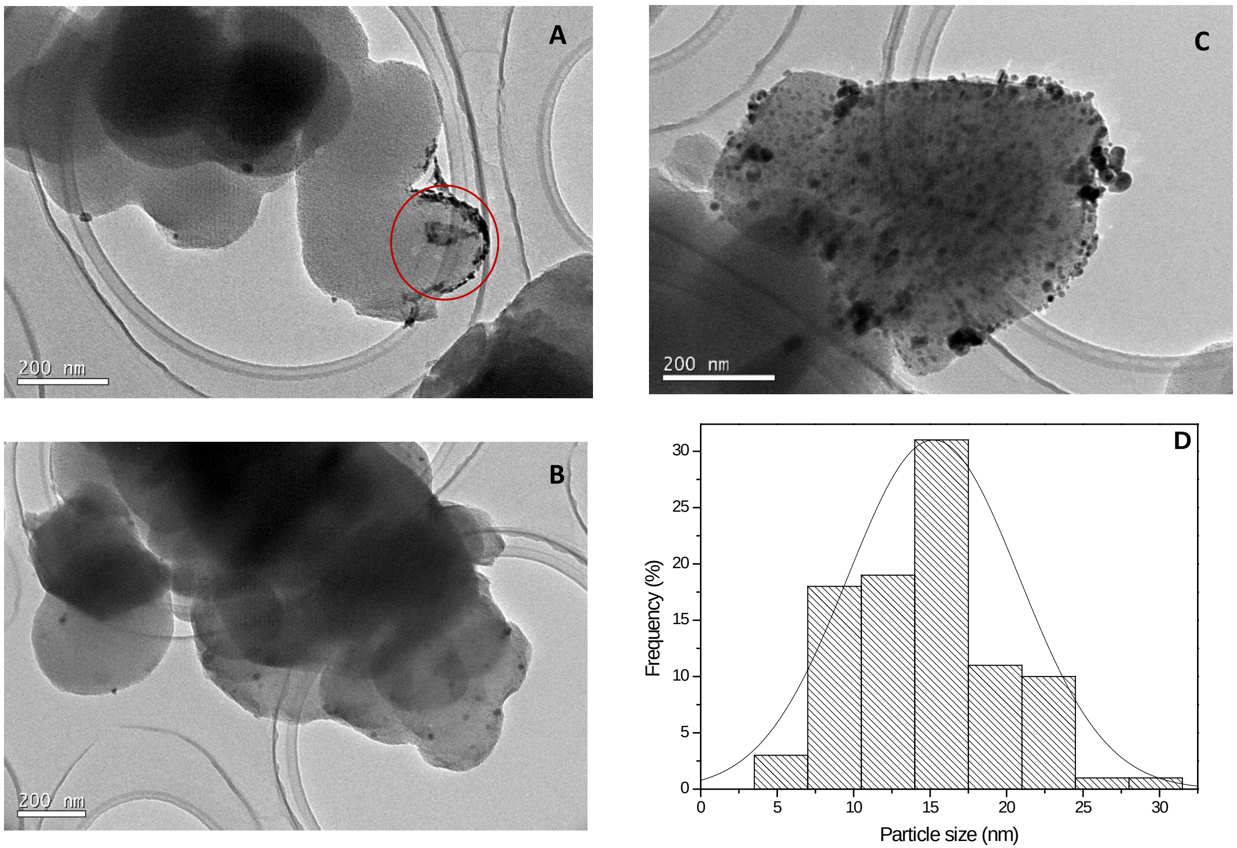






Irregular geometry of ruthenium areas

TEM Ru:Ni/MCM-48 (0.45)

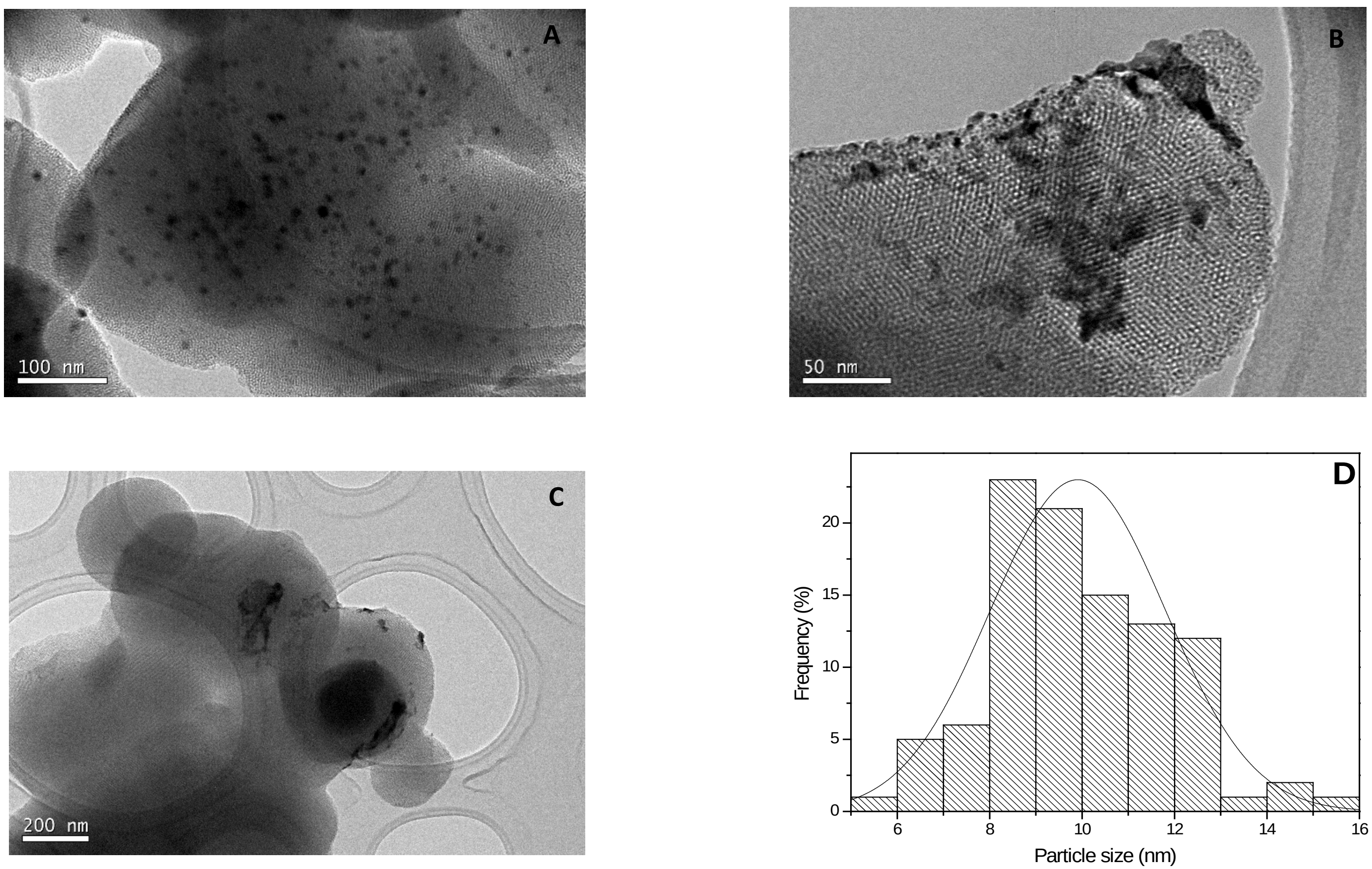


↑ Ru:Ni up to 0.45

More heterogeneous distribution of the metallic nanoparticles

$\overline{d}_{p\ Ni}$ =19.2 nm

TEM Ru:Ni/MCM-48 (1.39)



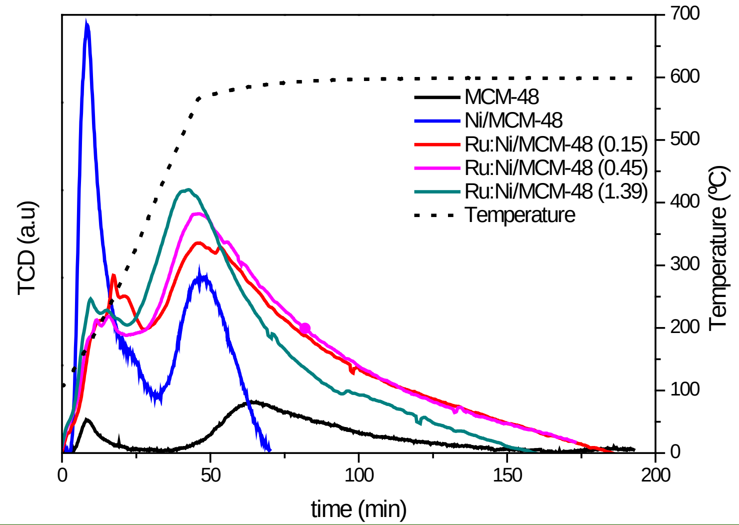
$\overline{d}_{p\ Ni}$ =10.9 nm

Textural properties bimetallic catalysts

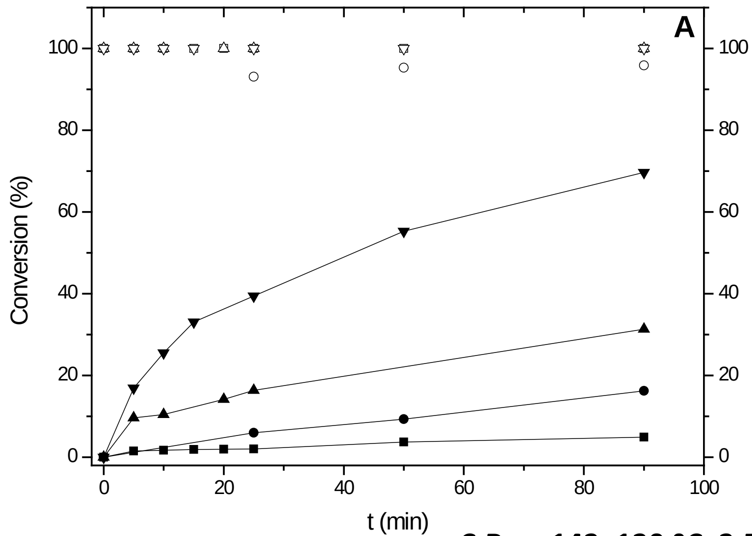
Catalyst	Ru (%)	Ni (%)	Ru:Ni	S_{BET} ($m^2 \cdot g^{-1}$)	V_{pore} ($cm^3 \cdot g^{-1}$)	$Ø_{pore}$ (nm)
MCM-48	-	-	-	1289	0.87	2.2
Ru:Ni/MCM-48 (0.15)	0.38	2.48	0.15	931	0.59	2.2
Ru:Ni/MCM-48 (0.45)	0.76	1.67	0.45	1112	0.69	2.2
Ru:Ni/MCM-48 (1.39)	1.63	1.17	1.39	1184	0.74	2.2

Acidity features

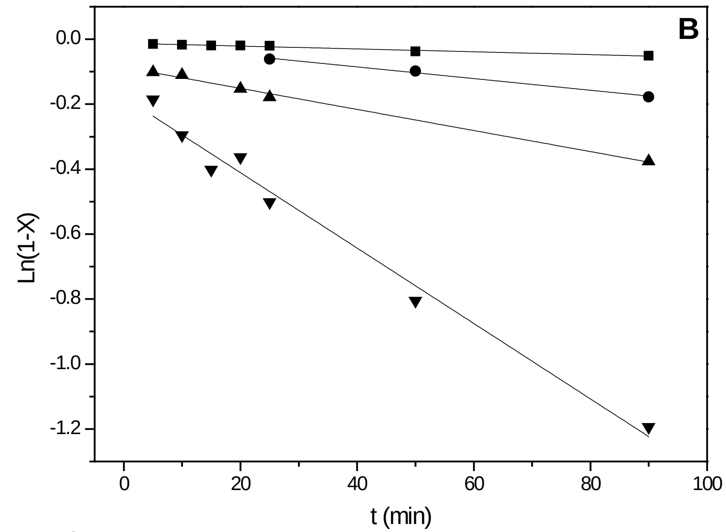
	Acidity ($mmol \cdot g^{-1}$)		
	I (170 -250 ºC)	II (520-590 ºC)	Total
MCM-48	0.157	0.343	0.500
Ni/MCM-48	0.546	0.462	1.007
Ru:Ni/MCM-48 (0.15)	0.396	0.756	1.152
Ru:Ni/MCM-48 (0.45)	0.320	0.882	1.202
Ru:Ni/MCM-48 (1.39)	0.334	0.918	1.253



Evolution of the conversion of D-Glucose



Pseudo-first order fitting

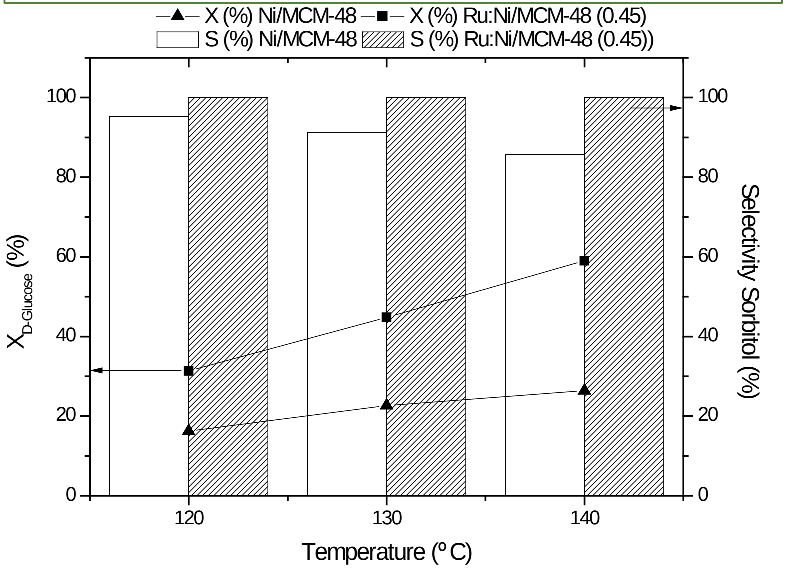


C:Ru = 142, 120 ºC, 2.5 MPa H_2 and 1400 rpm

● Ni/MCM-48, ■ Ru:Ni/MCM-48 (0.15), ▲ Ru:Ni/MCM-48 (0.45) and ▼ Ru:Ni/MCM-48 (1.39).

Catalyst	Specific reaction rate $\cdot 10^{13}$	$k \cdot 10^3$	R^2
	($mol_{sorbitol} \cdot cm^{-2}_{Ni} \cdot s^{-1}$)	($dm^3 \cdot g^{-1} \cdot min^{-1}$)	
Ni/MCM-48	2.24	9.7	0.998
Ru:Ni/MCM-48 (0,15)	3.35	2.3	0.976
Ru:Ni/MCM-48 (0,45)	19.8	18.3	0.996
Ru:Ni/MCM-48 (1,39)	24.9	66.3	0.985

Effect of reaction temperature



C:Ru = 142, 2.5 MPa H_2, 90 min and 1400 rpm

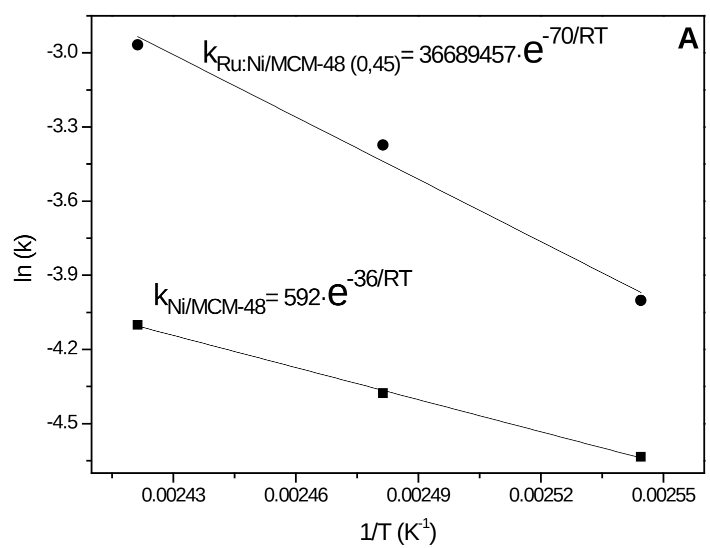
Ni/MCM-48

- Clear decrease of selectivity to sorbitol (95 – 86 %)

Ru:Ni/MCM-48 (0.45)

- Conversion of D-Glucose increased from 31 % to 59 % between 120 and 140 ºC
- Selectivity to sorbitol remained constant (100 %)

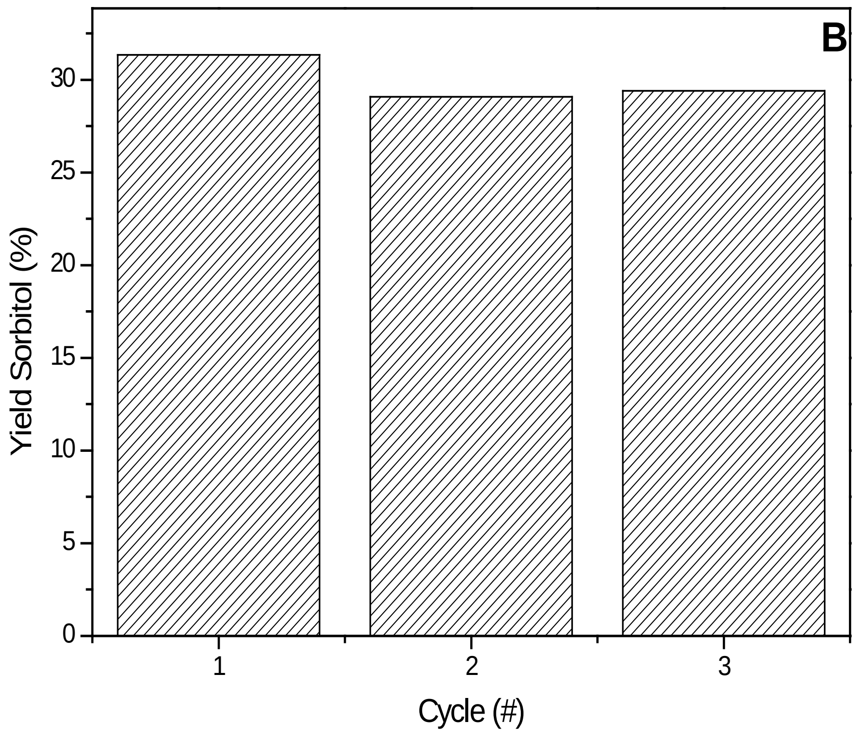
Arrhenius plot D-Glucose hydrogenation



E_a >> 12 -21 KJ/mol

Reaction was controlled by the kinetics on the metal surface

Recycling of Ru:Ni/MCM-48 (0.45)



Sligth decrease of yield to sorbitol from 31 to 29 % after three reaction cycles

Selectivity to sorbitol remained constant (100 %)

C:Ru = 142, 120 ºC, 2.5 MPa H_2 and 1400 rpm

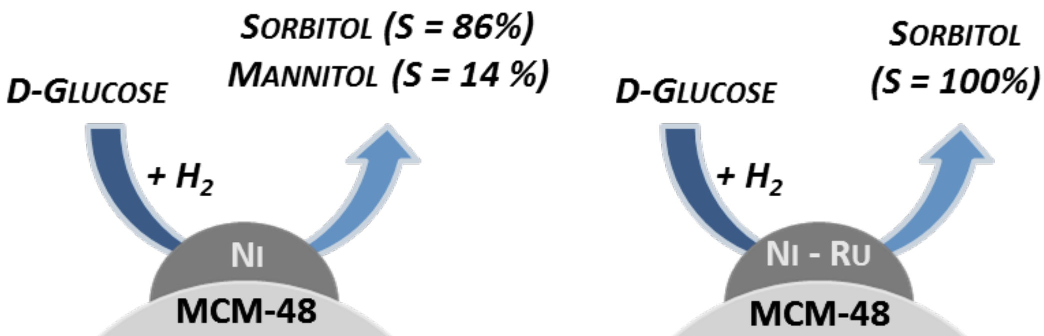
Improvement of reducibility of Ni and Ru

↑Ru:Ni than 0.45 improved catalytic behaviour of the Ni/MCM-48 (reaction rate and selectivity)

Ru:Ni/MCM-48 (0.45) improved reaction rate remaining the selectivity constant from 120 to 140 ºC

Good stability of the bimetallic catalyst

Ru:Ni/MCM-48 stands as a good material for the hydrogenation of carbohydrate sugars into sugar alcohols



T = 140 ºC, P = 2.5 MPa H_2 and t = 90 min

90 2 8

Thank you for your attention

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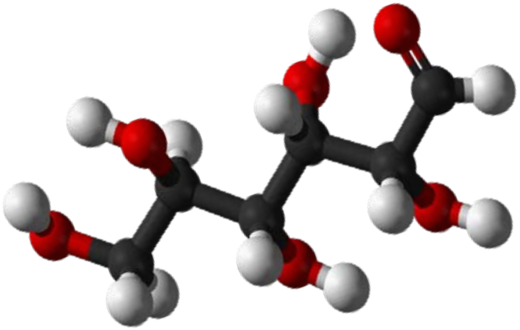

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