Hydrogen production from bio-oil aqueous phase steam reforming over agglomerated Co-Cr/SBA-15 catalysts

Workshop BIO3, Objetive 4

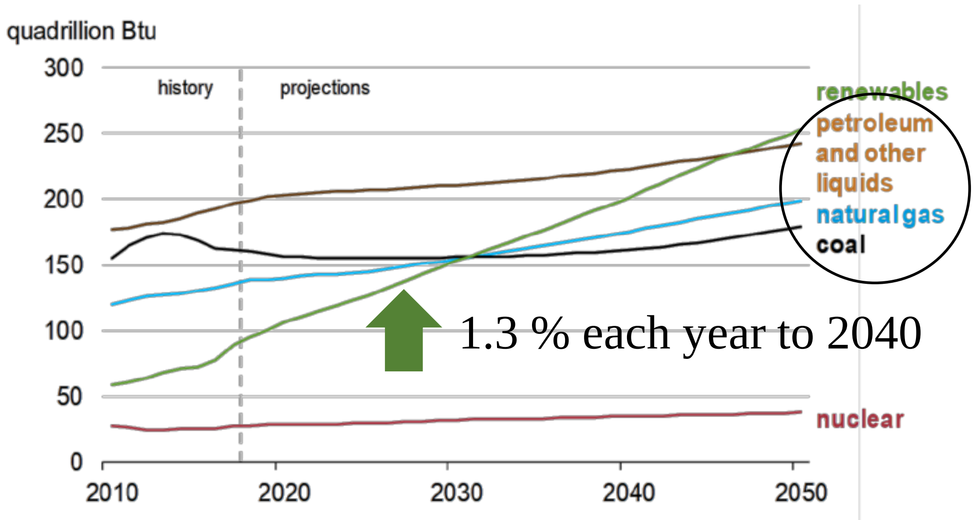
Pedro J. Megía, A. Carrero, J.A. Calles, A.J. Vizcaíno

18 de Diciembre 2020

URJC

BIO3

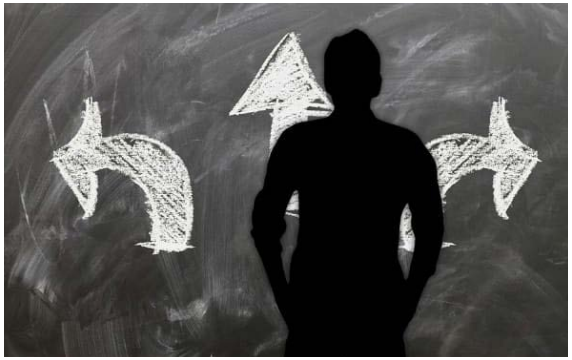
Current energy situation



fossil fuels

Emission of greenhouse gases

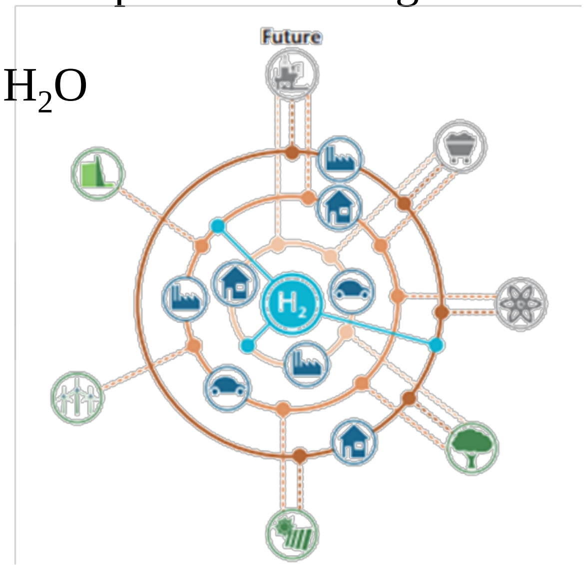
Alternatives?



URJC BIO3

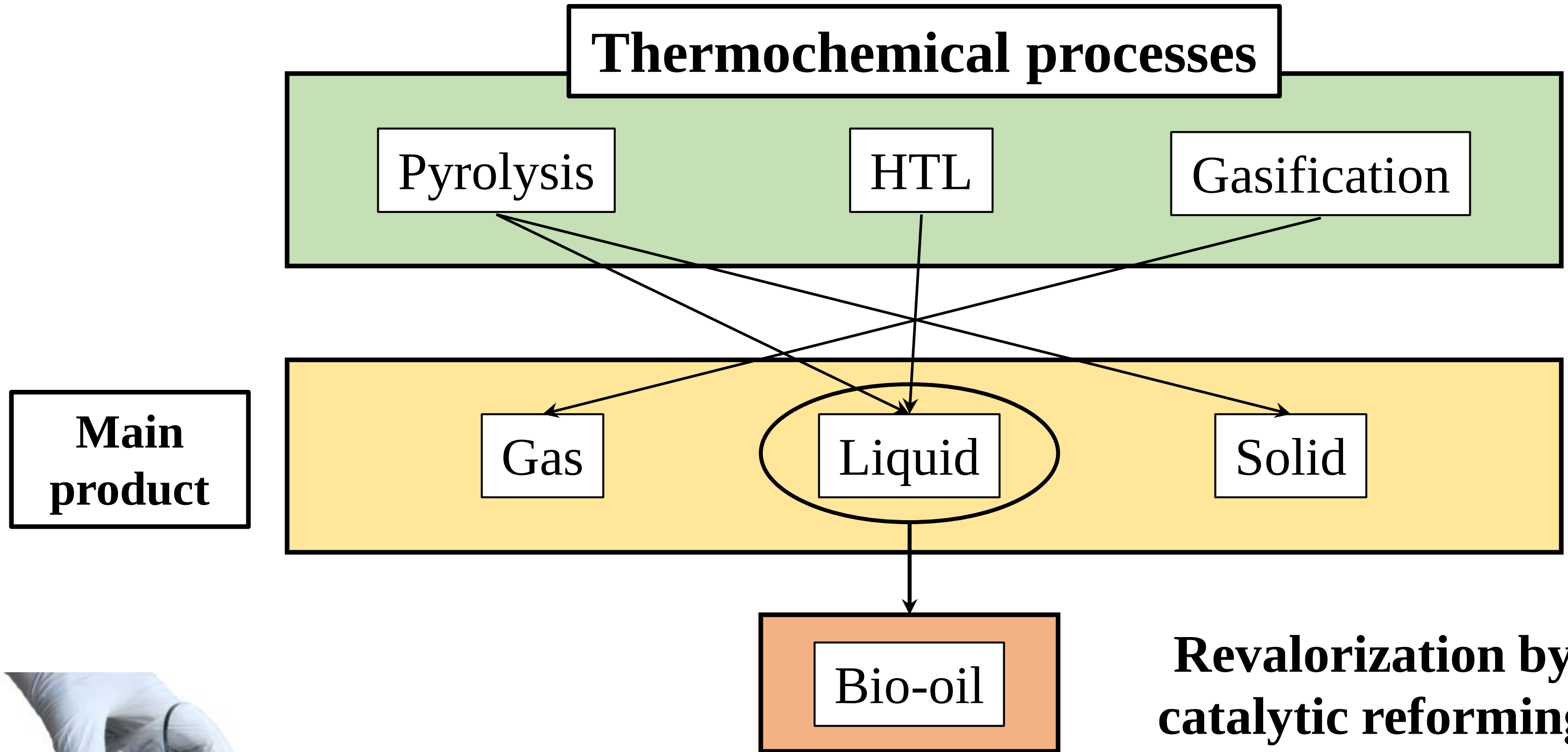
- Most abundant gas in universe ⟶ Not available in free form
- Fuel with the maximum energy content per unit of weight
- Clean fuel ⟶ $H_2 + ½ O_2 \rightarrow H_2O$

Hydrogen production from renewable sources can lead to a sustainable energy system in the near future



Currently, there are different technologies for hydrogen production from this feedstocks:

- Fossil fuels
- Water
- Biomass/waste



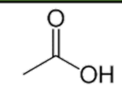
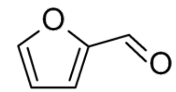
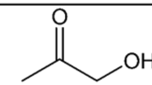
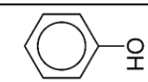
Revalorization by catalytic reforming

- Larger energy density than biomass
- Low heating power
- Corrosivity
- Instability

→ **Low-quality fuel**

- Aqueous fraction
- Organic fraction

BIOMASS → Different and complex compositions →

Aqueous phase composition	Typical compound	Typical concentration (wt. %)
Carboxylic acids		19.1-22.9
Aldehydes		0.5-5.5
Furans		
Ketones		13.9-17.5
Phenols		2.0-13.4

Alvarez J., et al. Fuel 128 (2014) 162-9

Remón J., et al. Int. J. of Hydrogen Ener., 40 (2015) 5593-608

starting POINT

Acetic acid as bio-oil **model compound**

Catalytic steam reforming of acetic acid as model compound

$$C_2H_4O_2 + 2\ H_2O \rightarrow 2\ CO_2 + 4\ H_2$$

Secondary reactions

- Methanation $3H_2 + CO \rightarrow CH_4 + H_2O$
- Coke formation $2CO \leftrightarrow CO_2 + C$
- Water-gas shift $CO + H_2O \leftrightarrow CO_2 + H_2$

→ Design of suitable catalysts

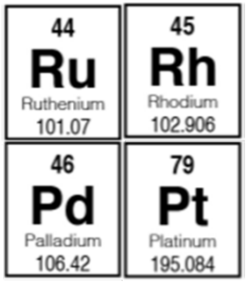
CHALLENGE

URJC BIO3

Reforming catalysts

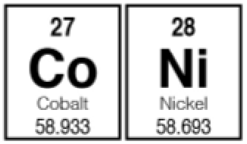
- Responsibility for cracking not only C-C and C-H bonds but also O-H bonds
- High activity
- High selectivity towards H_2
- Low deactivation (high resistance to coking and sintering)

Active phase



High activity

but high cost



Reasonable activity and

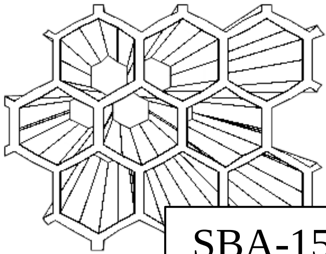
lower cost than noble metal

Noble metals

Transition metals

URJC BIO3

Support



SBA-15

- Good results in oxygenated hydrocarbons steam reforming

  Vizcaíno, A.J., et al. Catalysis Today 146(1-2) (2009) 63-70

- Improve metal dispersion and decrease sintering

  Yang, X., et al. Catalysts 5 (2015) 1721–1736

Inconvenience?

These reforming catalysts are usually prepared as **fine powders** being **not appropiate** for use **at industrial scale**

High pressure drop

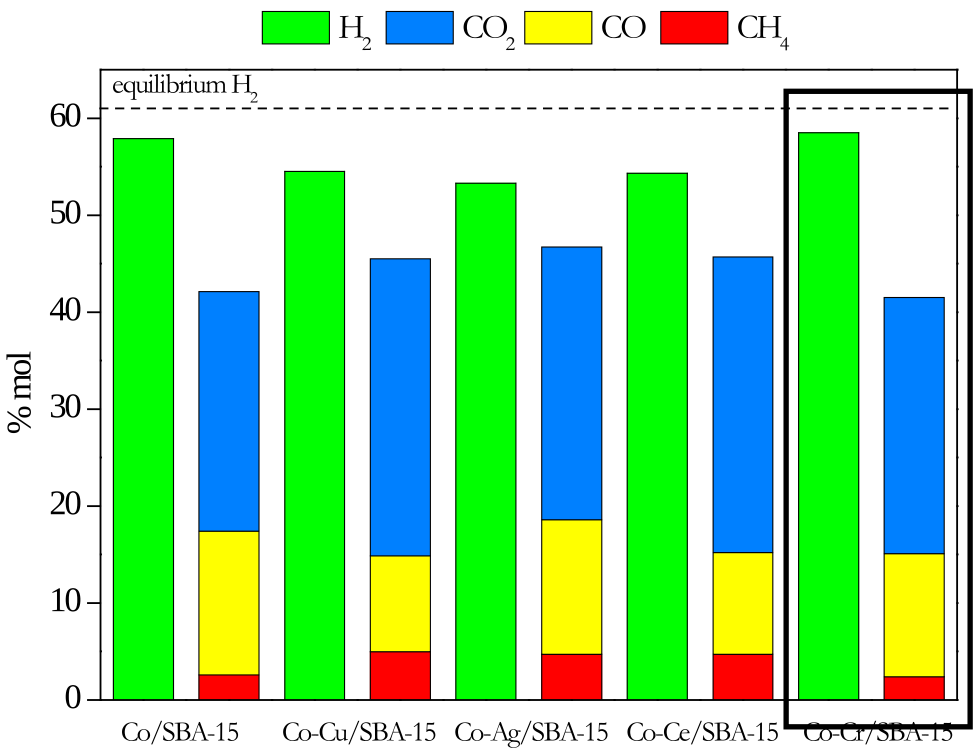
Solution

Catalysts agglomeration using binders

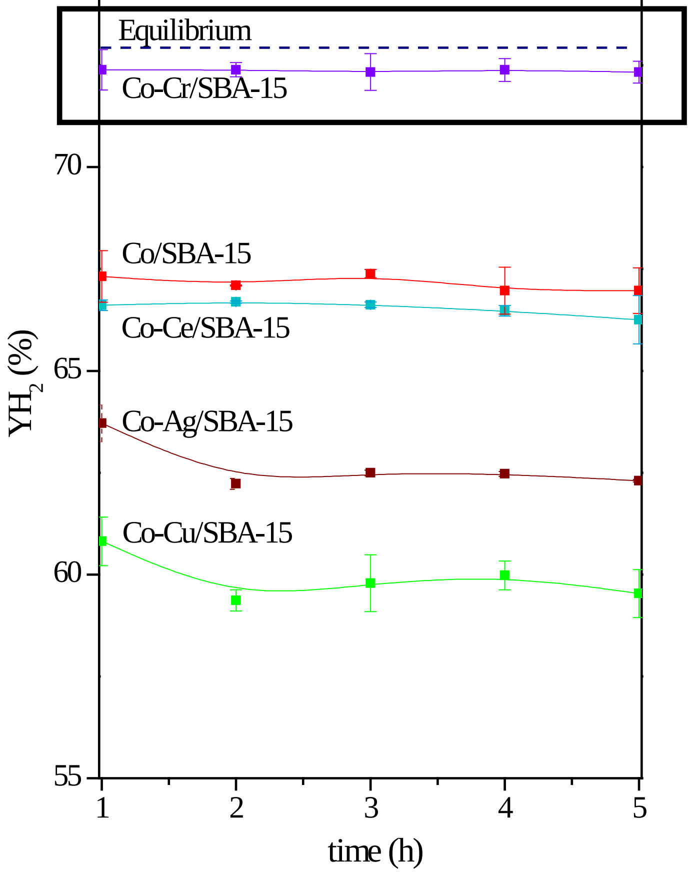
URJC BIO3

Cr addition enhances the catalytic performance towards hydrogen

Previous works



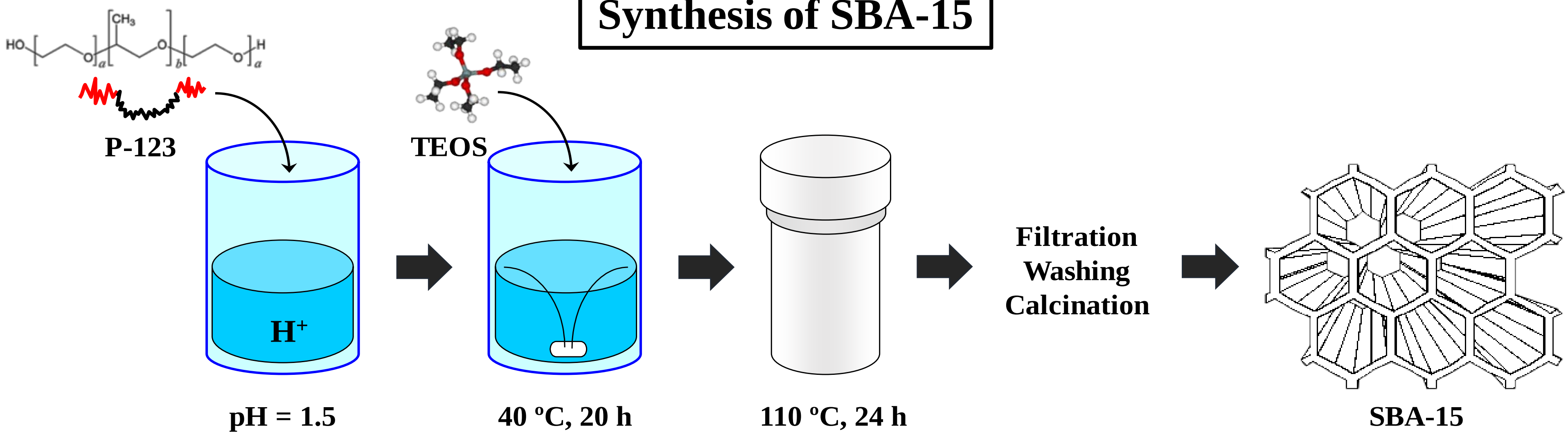
Megía P.J., Carrero A., Calles J.A., Vizcaíno A.J. Catalysts, 9 (12), 1013;



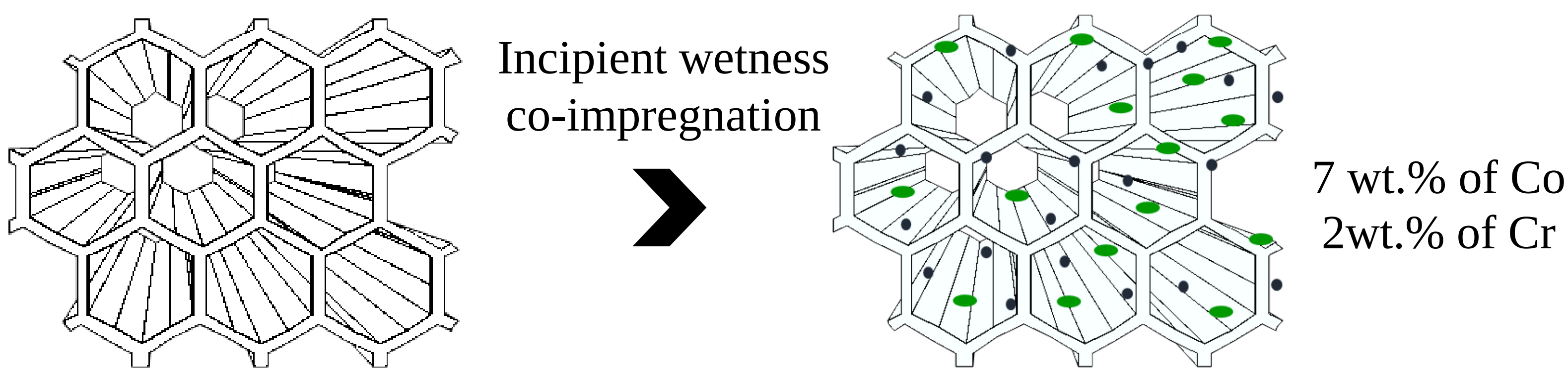
Preparation of **agglomerated Co-Cr/SBA-15** using bentonite and methylcellulose as binder through acetic acid steam reforming

URJC BIO3

Synthesis of SBA-15

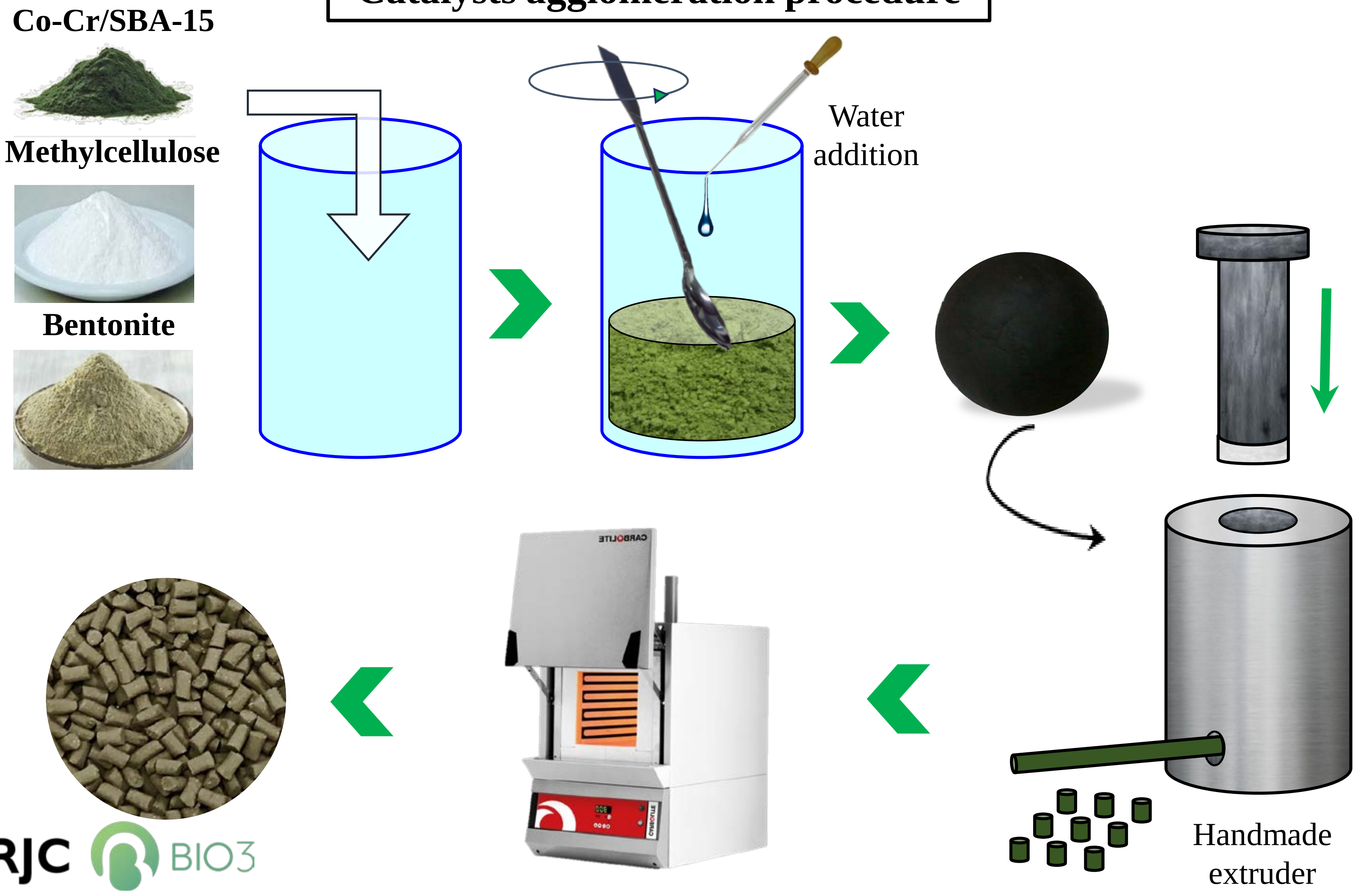


Catalysts preparation

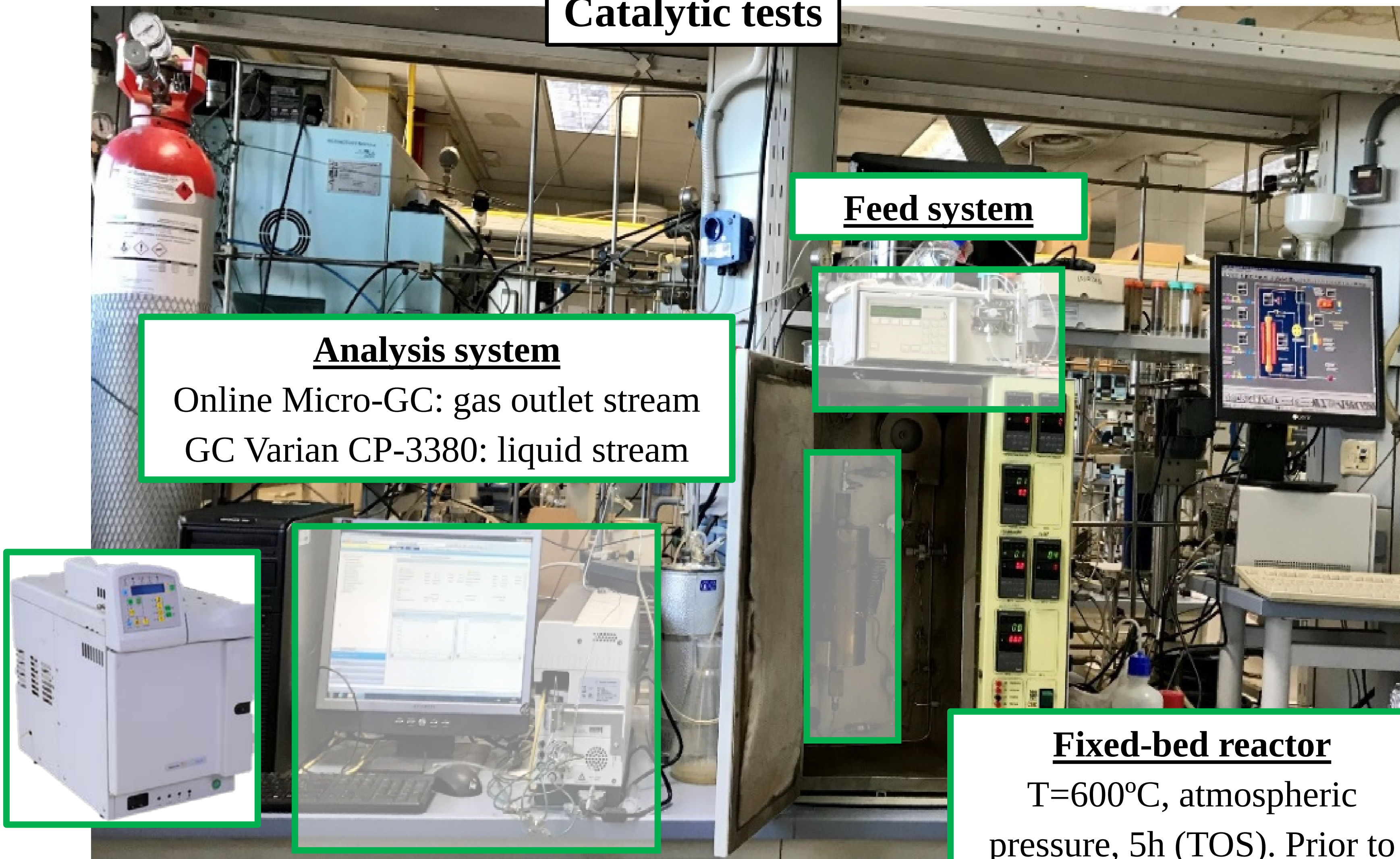


URJC BIO3

Catalysts agglomeration procedure



Catalytic tests



Feed system

Analysis system

Online Micro-GC: gas outlet stream

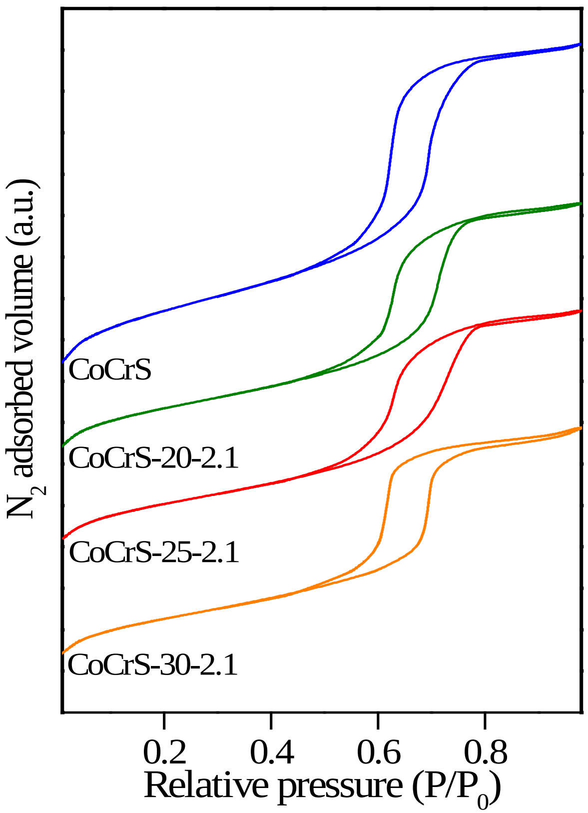
GC Varian CP-3380: liquid stream

Fixed-bed reactor

T=600ºC, atmospheric pressure, 5h (TOS). Prior to reaction: reduction under H_2

URJC BIO3

Catalysts characterization



Type IV isotherm
H1-type hysteresis loop

Preservation of the initial mesoporous structure

CoCrS-X-Y

X = wt. % of bentonite

Y = effective diameter (mm)

Physicochemical properties

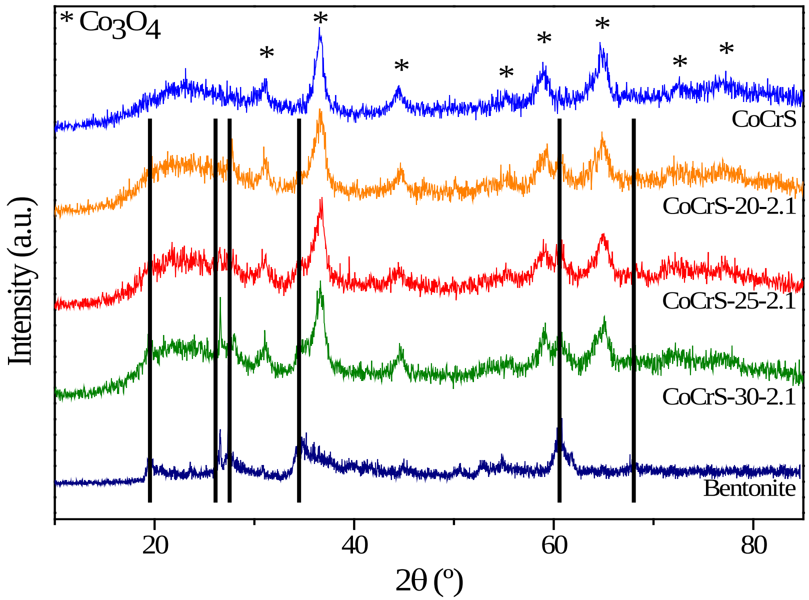
Sample	Co (wt.%)[a]	Cr (wt.%)[a]	S_{BET} (m^2/g)	V_p[b] (cm^3/g)	D_p[c] (nm)	$D_{Co_3O_4}$[c] (nm)
CoCrS	6.4	1.7	490	0.7	5.5	7.1
CoCrS-20-2.1	5.3	1.4				8.1
CoCrS-25-2.1	4.9	1.3				8.0
CoCrS-30-2.1	4.5	1.2	322	0.5	5.5	8.1

Higher calcination temperatures (>100 ºC)

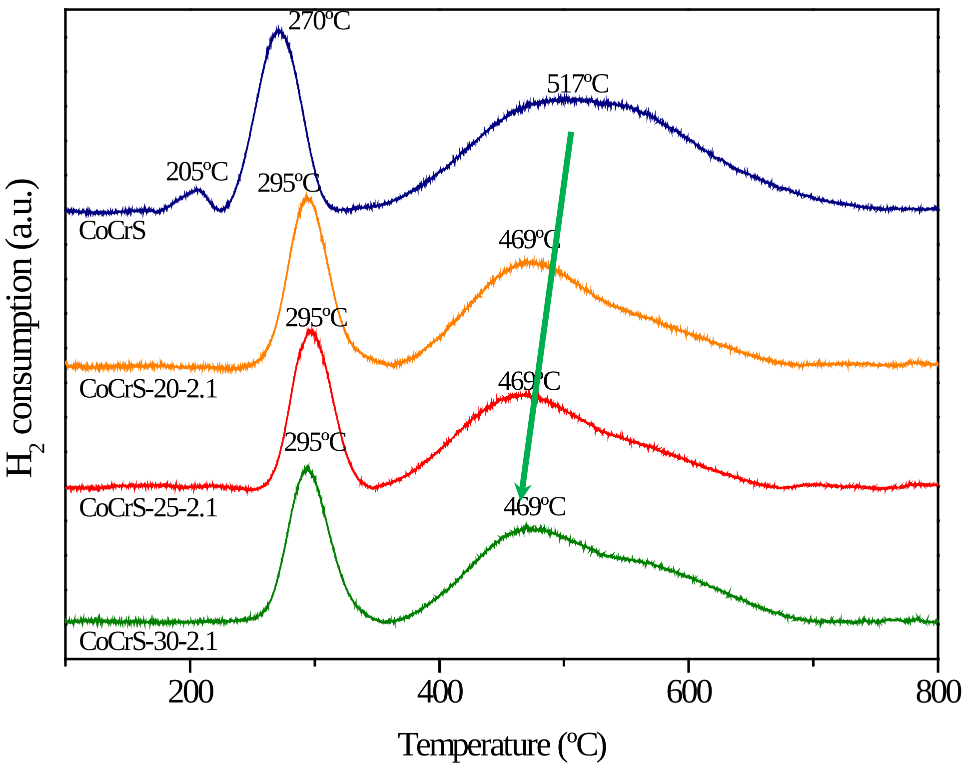
[a] Determined by ICP-AES in calcined samples
[b] Pore Volume measured at P/P_0 = 0.97
[c] BJH desorption average pore diameter
[d] Determined from XRD of calcined catalysts by Scherrer equation from the (... O4

Similar to powder sample

Catalysts characterization



Montmorillonite (Bentonite)

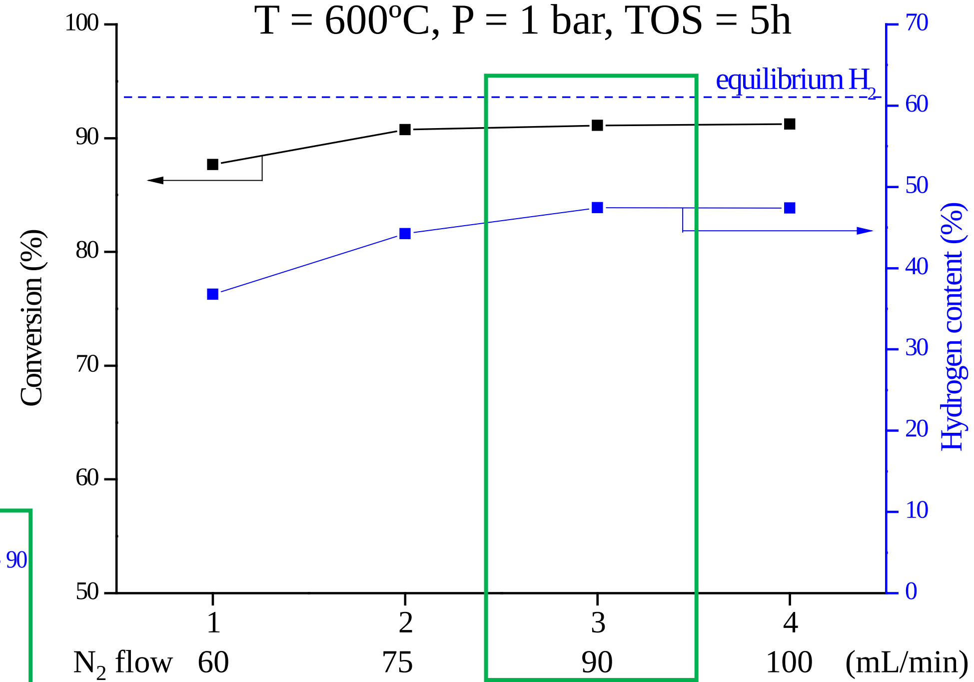


Decrease in the reduction temperature in extruded catalysts

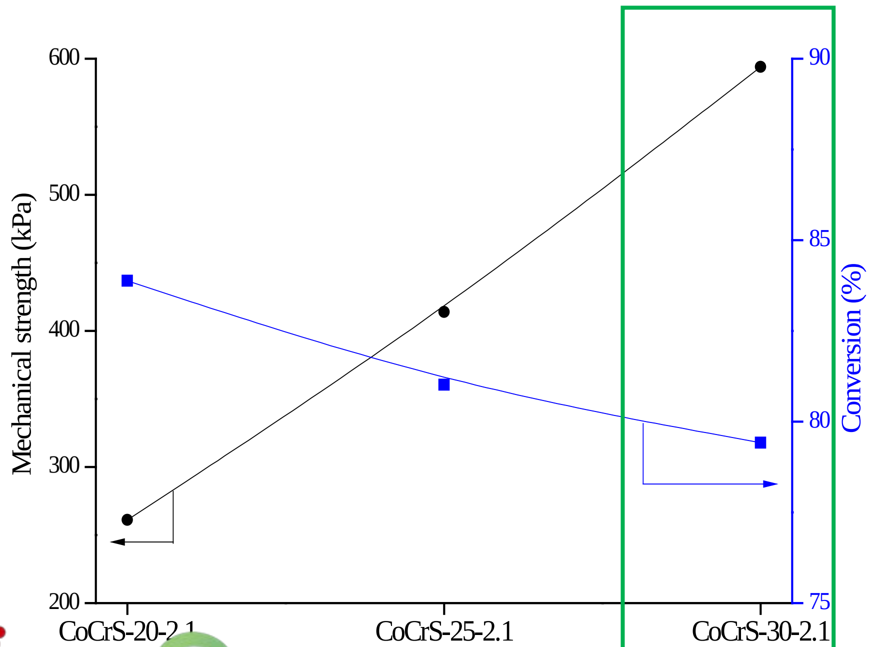
External diffusion effects

Constant WHSV = 32.1 h^{-1}

Conditions	$m_{catalyst}$ (g)	Q_{feed} (mL/min)	N_2 flow (mL/min)
1	0.300	0.0750	60
2	0.375	0.0935	75
3	0.450	0.1125	90
4	0.500	0.1250	100



CoCrS-20-2.1



CoCrS-30-2.1 highest mechanical strength

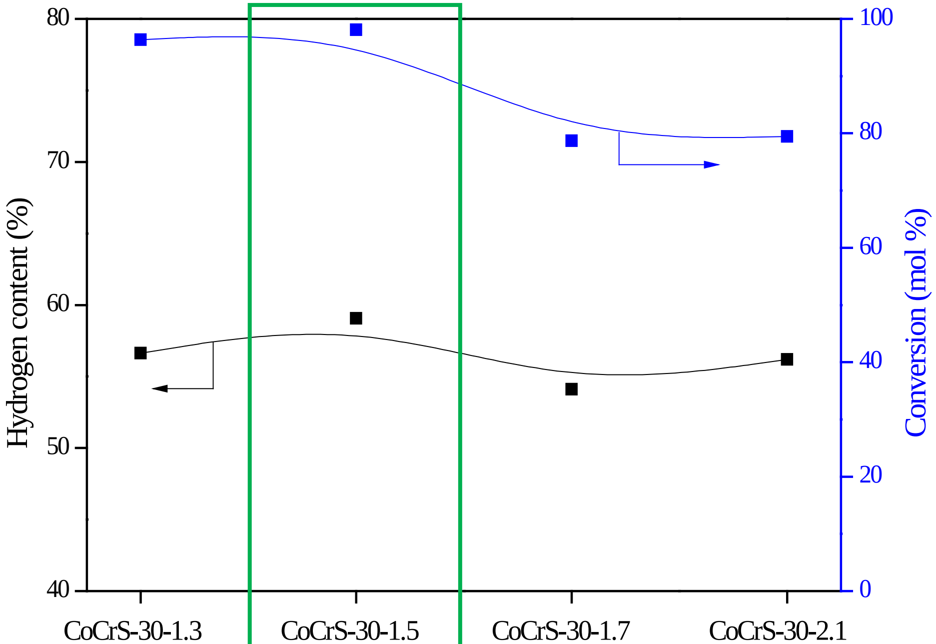
Lowest fine formation after 5h TOS

Lower conversion than the other samples

Fines observed after each test

Internal diffusion effects

T = 600ºC, TOS = 5h, 0.45 g_{cat} & 90 mL/min N_2



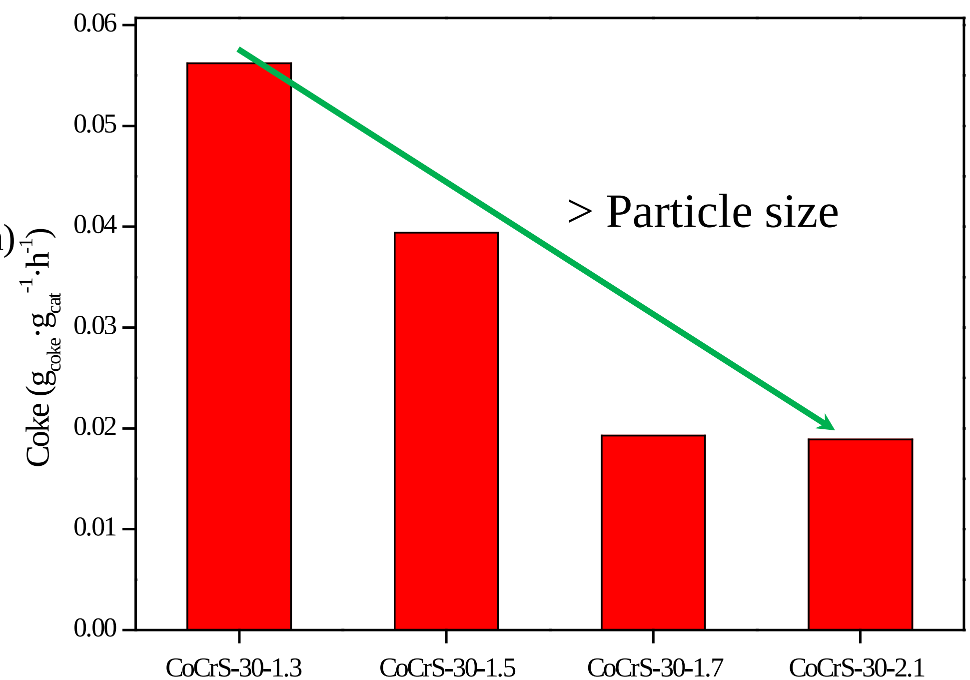
deff 1.3 1.5 1.7 2.1 (mm)

↓ Particle size → ↑ Coke formation

Different effective diameters 1.3-2.1 mm

Similar hydrogen content

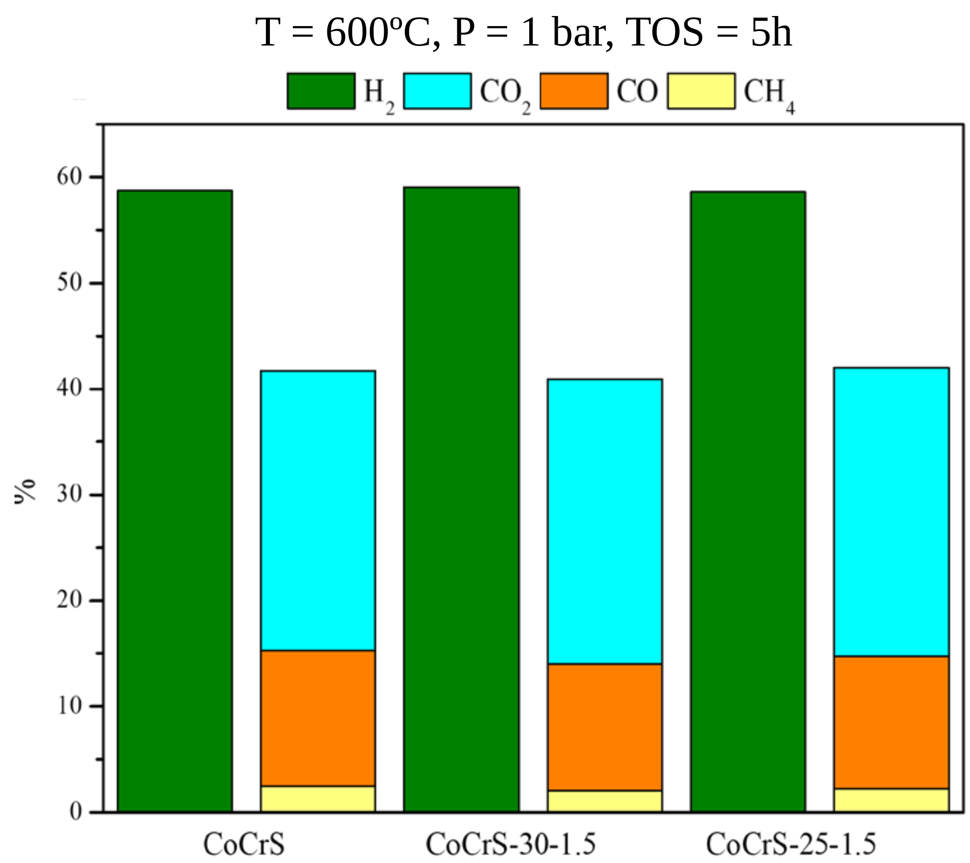
↓ Particle size → ↑ Conversion



- Higher conversion
- Non-uniform coke distribution (preferably in external surface)

Forzatti P., Lietti L. Catal. Today 52 (1999) 165-81.

Comparison with the powder sample



Conversion (5h)	99	98.1	97.3	(mol %)

Similar conversion & gas product distribution

Successful agglomeration process → **CoCrS-30-1.5** (higher mechanical strength)

URJC BIO3

D_{eff}
0.15 cm

0.45 g_{cat}
0.1125 mL/min

30 wt.% of bentonite

Similar results to powdered sample

30 wt.% bentonite hardly decreased the acetic acid conversion compared to 20 wt.% while the **mechanical strength** almost was **tripled**.

CoCrS-30-1.5 showed a good performance for hydrogen production and similar conversion compared to powder sample

Suitable agglomeration process

URJC BIO3

URJC

BIO3


THANK
YOU
GRACIAS
ARIGATO
SHUKURIA
DANKSCHEEN
TASHAKKUR ATU
YAQHANYELAY
SUKSAMA
EKHMET
TINGKI
SHUKRIA
GRAZIE
MEHRBANI
PALDIES
MERCI
GOZAIMASHITA
EFCHARISTO
JUSPAXAR
KOMAPSUMNIDA
MAAKE