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TNT 2011 Trends in NanoTechnology
November 21-25, 2011
Tenerife - Canary Islands
(Spain)

CATALYTIC OXIDATION OF CRUDE GLYCEROL USING Au CATALYST BASED ON CARBONACEOUS SUPPORTS

Sonia Gil, Miriam Marchena, Carmen María Fernández, Amaya Romero and José Luis Valverde

Tenerife, 21-25 November 2011

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The possibility of controlling porosity and surface chemistry

Easy recovery of the metals by burning off the support

Resistance to acid/basic media

Carbonaceous Materials

Discovery of nanostructured carbon (CNT, CNS, CNF…)

Absence of studies on the use/comparison of the CNS in oxidation reactions

Liquid phase selective oxidation of commercial glycerol and crude glycerol to glyceric acid

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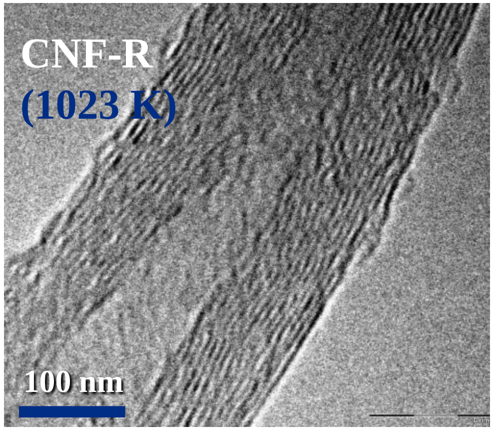
GRAPHITE (G)

• Very high stuctural order

(d_{002}= 0,338 nm, T_{TGA} = 1077 K)

• Limited porosity

(Área superficial BET ~ 10 (m^2 g^{-1}))



CARBON NANOSPHERES (CNS)

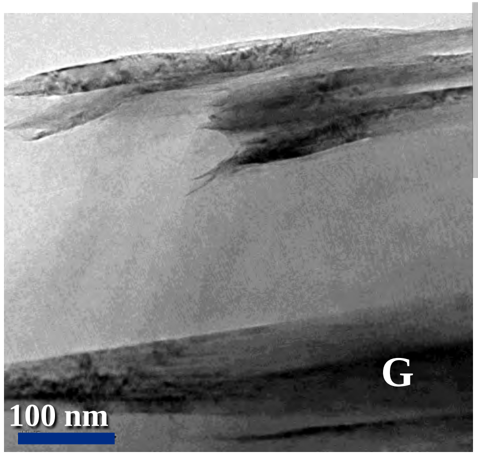
• Conglomeration of spherical bodies

•Medium structural order

(d_{002}= 0,346 nm, T_{TGA} = 952 K)

• Low surface areas

(Área superficial BET ~ 3.4 (m^2 g^{-1}))



RIBBON CARBON NANOFIBERS (CNF-R)

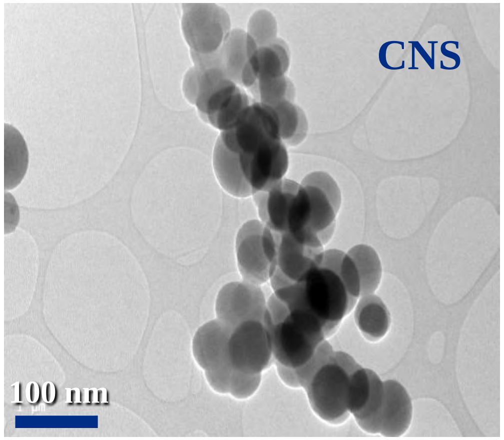
• Medium structural order

(d_{002}= 0,342 nm, T_{TGA} = 800 K)

• Mesoporous materials

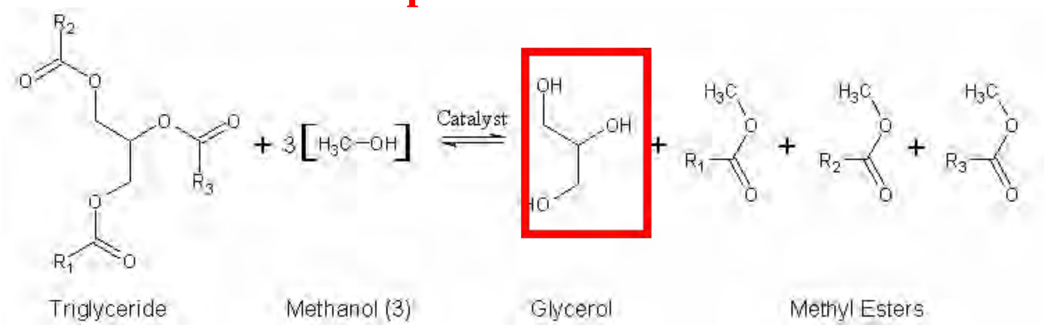
(Área superficial BET ~ 109 (m^2 g^{-1}))

• Discontinuity of the planes of graphite



IMPORTANCE OF GLYCEROL

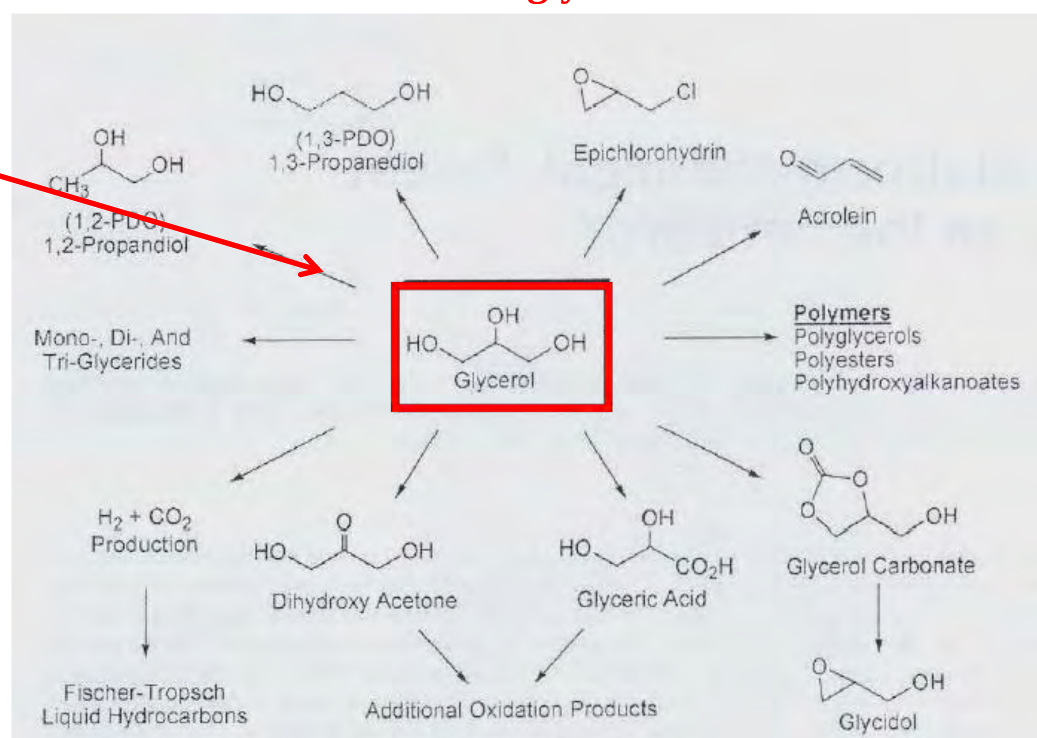
Biodiesel production :



100 kg of GLYCEROL, as a by-product, is produced per 1 tonne of biodiesel (10 wt% of the total product)

Main reactions of glycerol:

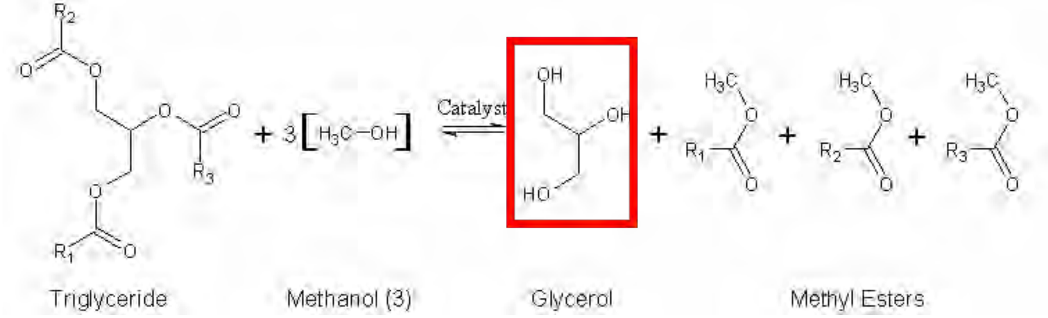
Glycerol is a highly FUNCTIONALIZED compound.



These products produced through non-environmentally stoichiometric oxidation processes, poor selectivity or low productivity fermentation processes

IMPORTANCE OF GLYCEROL

Biodiesel production :



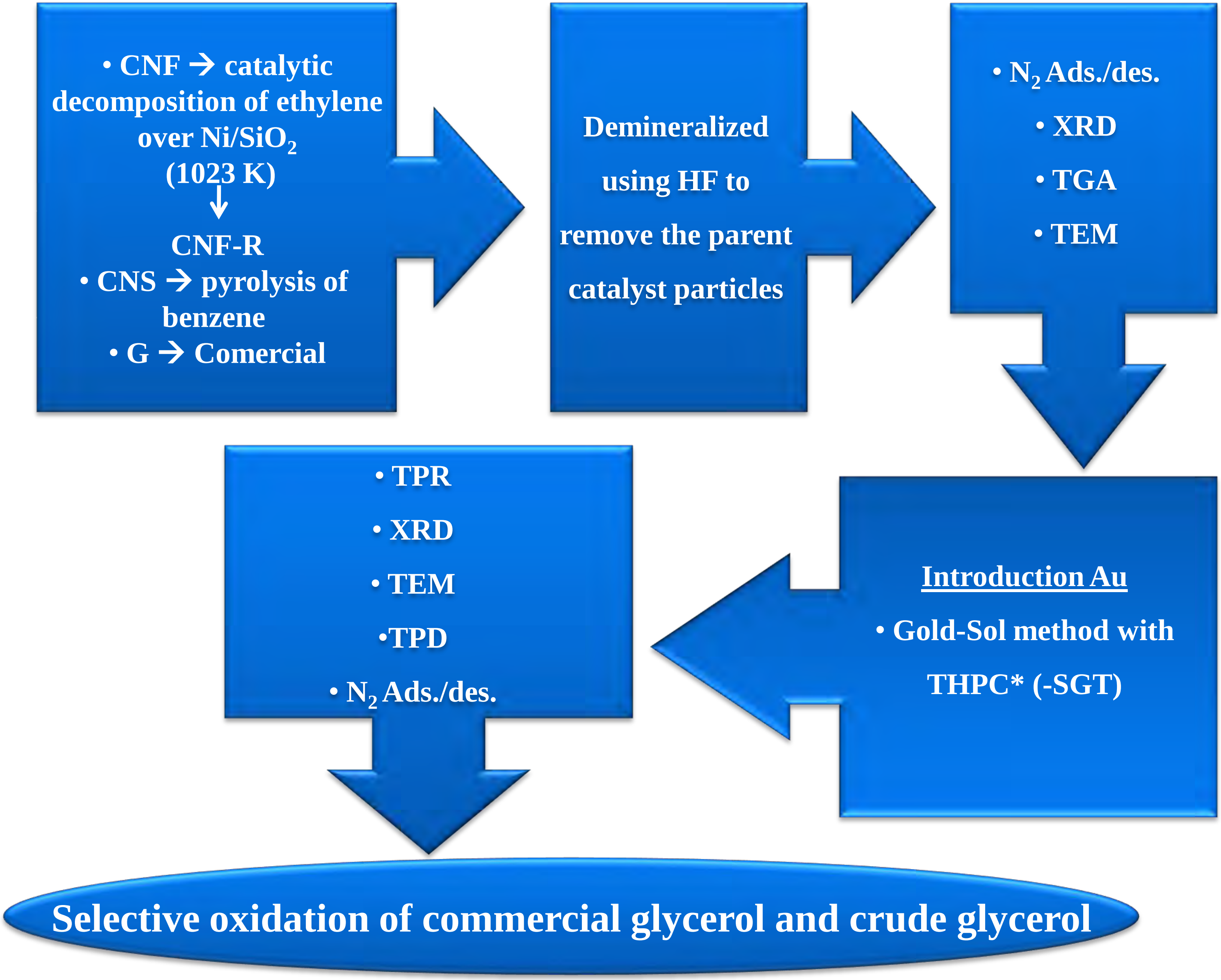
Transesterification process

IMPURITIES GLYCEROL:

- **Mixture of methanol,**
- **Water,**
- **Inorganic salts (catalyst residue),**
- **Free fatty acids,**
- **Unreacted mono-, di- and triglycerides,**
- **Methyl esters,**
- **A variety of other organic materials**

Crude glycerol, with an estimated 50% purity

REVALORIZATION of crude glycerol to obtain products of high value.



***THPC (Tetrakis-(hydroxymethyl)-phosphonium chloride)**

Results and discussion. SUPPORT CHARACTERIZATION

Table 1. Physicochemical properties of the supports.

Support	BET surface area (m^2 g^{-1})	Total pore volume (cm^3 g^{-1})	Mean pore diameter (nm)	TGA temperature range (K)
G	10	0.04	3.3	832-1078 (1077)
CNF-R	109	0.25	24.7	750-827 (800)
CNS	3.4	0.014	3.7	826-983 (952)

Low surface area and Limited porosity

Results and discussion. SUPPORT CHARACTERIZATION

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Mesoporous materials

Results and discussion. SUPPORT CHARACTERIZATION

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Low surface areas and Negligible porosity

Results and discussion. SUPPORT CHARACTERIZATION

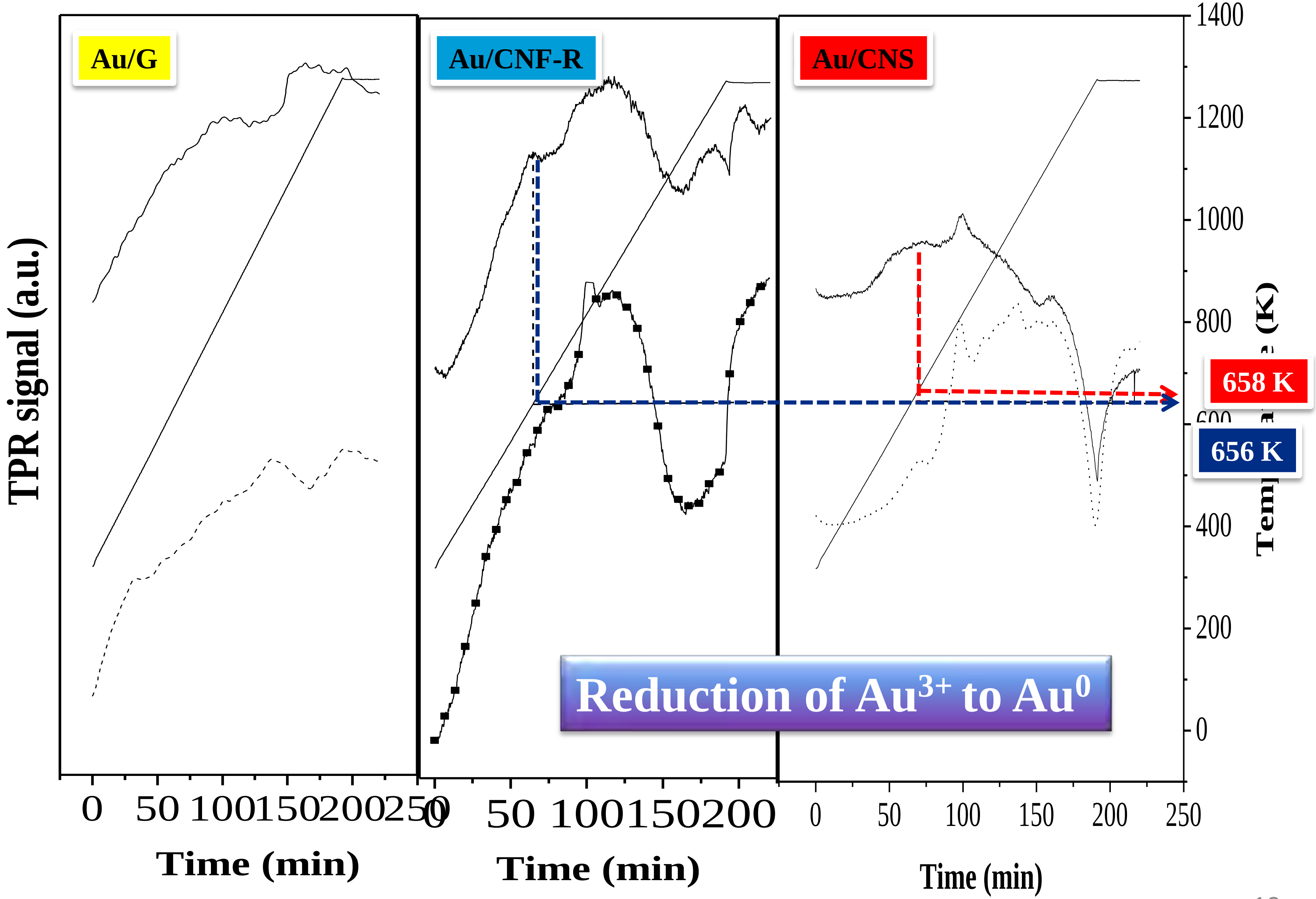
Table 1. Physicochemical properties of the supports.

Support	BET surface area ($m^2\ g^{-1}$)	Total pore volume ($cm^3\ g^{-1}$)	Mean pore diameter (nm)	TGA temperature range (K)
G	10	0.04	3.3	832-1078 (1077)
CNF-R	109	0.25	24.7	750-827 (800)
CNS	3.4	0.014	0.18	826-983 (952)

↑$T_{Gasification}$ + structured a carbon material

G > CNS > CNF-R

Results and discussion. CATALYST CHARACTERIZATION



Results and discussion. CATALYST CHARACTERIZATION

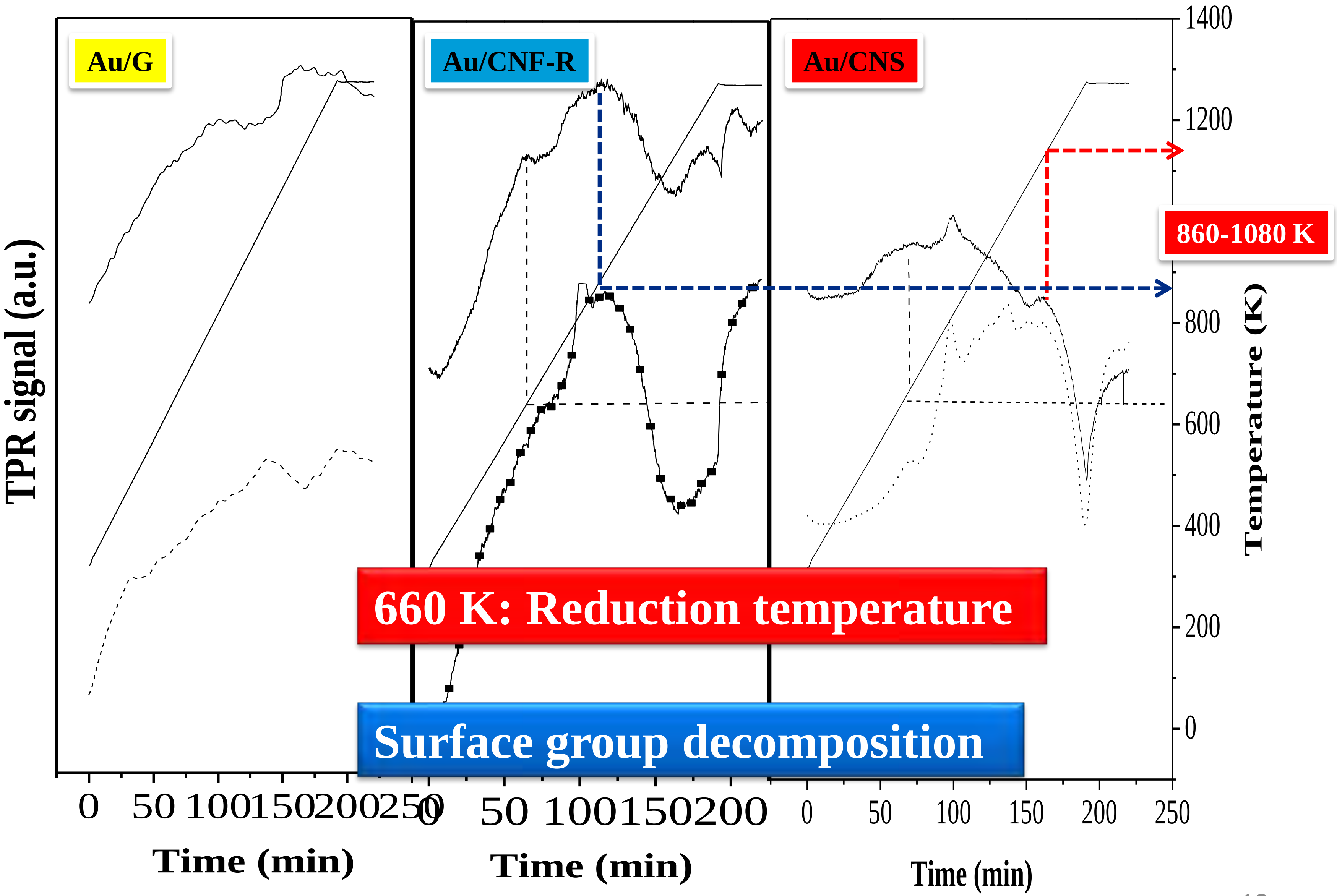


Table 2. Physicochemical properties of the Au catalysts.

	Au/G-SGT	Au/CNF-R-SGT	Au/CNS-SGT
Au loading (% w/w)	0.6	0.6	0.4
TPR $T_{máx}$ (K)	-	656	658
$\bar{d}_s$ **(nm)**	7.7	13.2	4.2
BET surface area (m^2g^{-1})	9.83	104	2.54
Total pore volume (cm^3g^{-1})	0.019	0.029	0.011
Micropore Volume (cm^3g^{-1})	0	0	0
Micropore area (m^2/g)	0	0.51	0
Mesopore area (m^2/g)	9.83	103.5	2.54
Mean pore diameter (nm)	2.8	23.9	8.4

Partial blockage of the porous structure of materials upon deposition of the metal phase.

CATALYTIC TEST. SELECTIVE OXIDATION OF GLYCEROL

TWO STUDIED PARAMETERS

↓

Played an important role in the catalytic activity of Au particles

↙ ↘

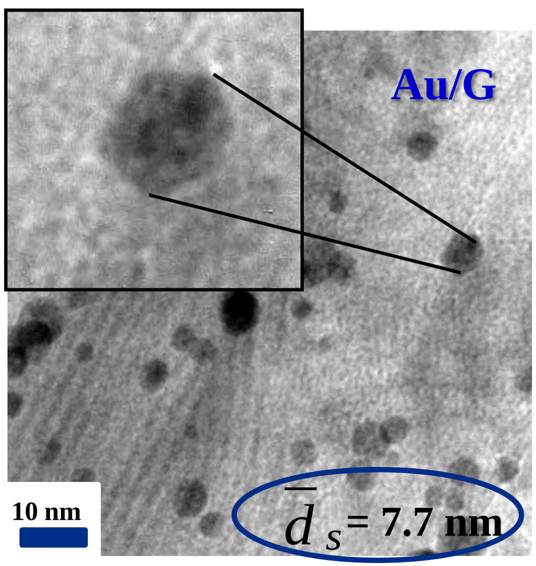
NATURE OF THE SUPPORT

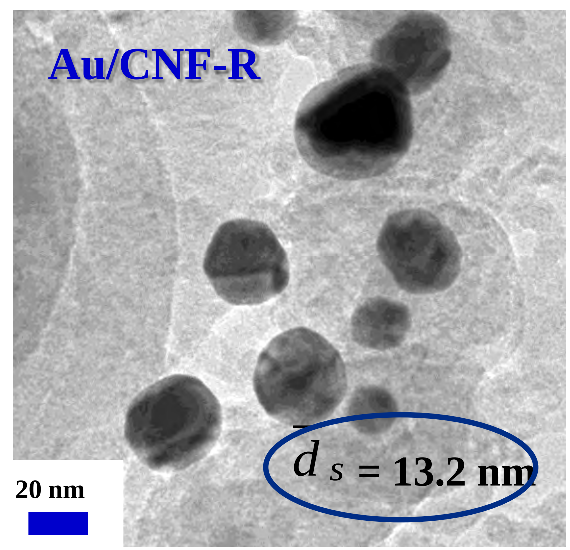
Au PARTICLE SIZE

INFLUENCE OF THE NATURE OF THE SUPPORT

Au/G	
d_{002} (Å)	T_{TGA} (K)
3.378	1077

Au/CNF-R	
d_{002} (Å)	T_{TGA} (K)
3.423	800





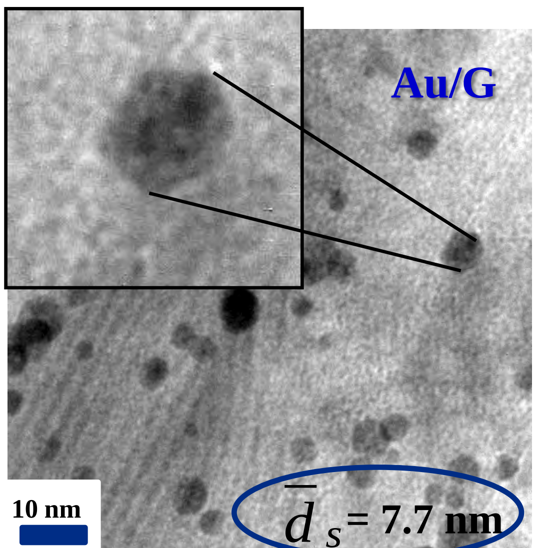
Small, thin, faceted and well dispersed Au particles

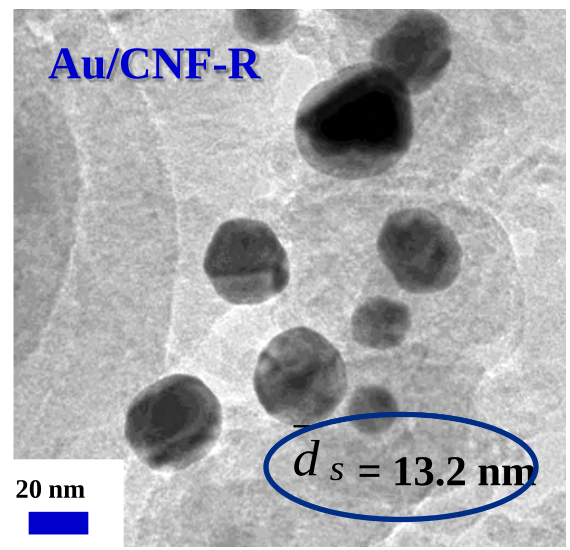
INFLUENCE OF THE NATURE OF THE SUPPORT

HIGHER CRYSTALLINITY (lower presence of structural defects) → **Greater number of graphite edges exposed in an orderly manner**

↓

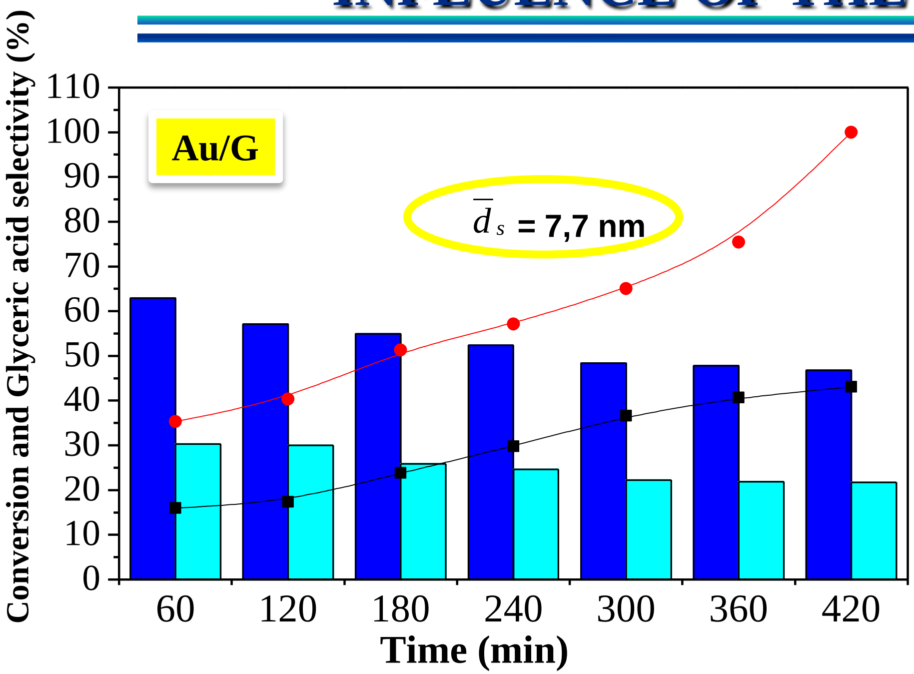
Resulting in a STRONG anchoring of small metal particles (STRONG INTERATION METAL-SUPPORT)





Small, thin, faceted and well dispersed Au particles

INFLUENCE OF THE NATURE OF THE SUPPORT



The nature of support played an important role in the Au deposition and, as consequence, in its catalytic activity.

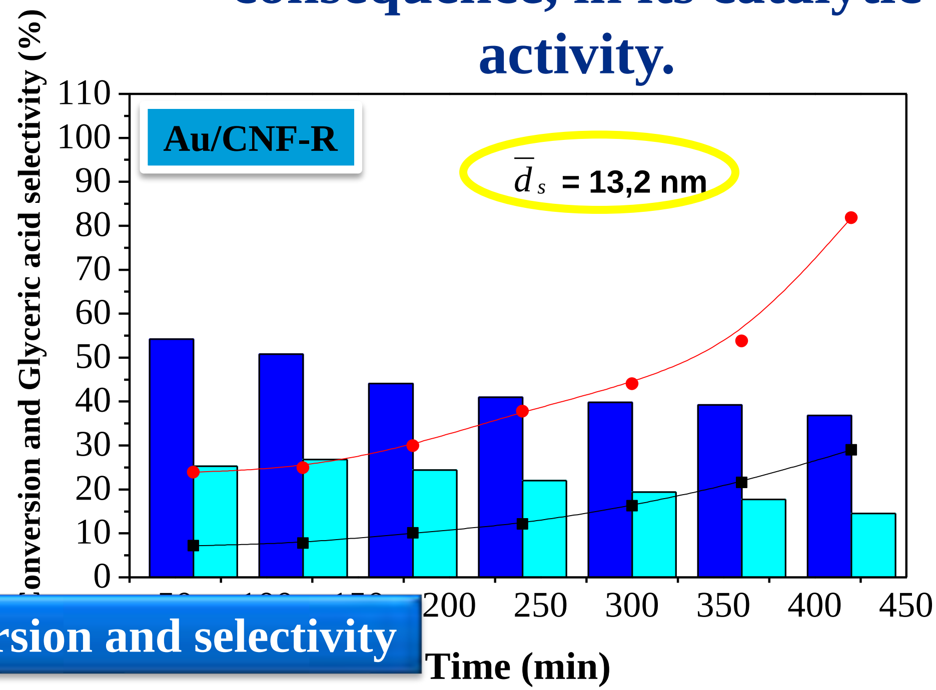
Higher graphitic character

↓

Strong interation metal-support

↓

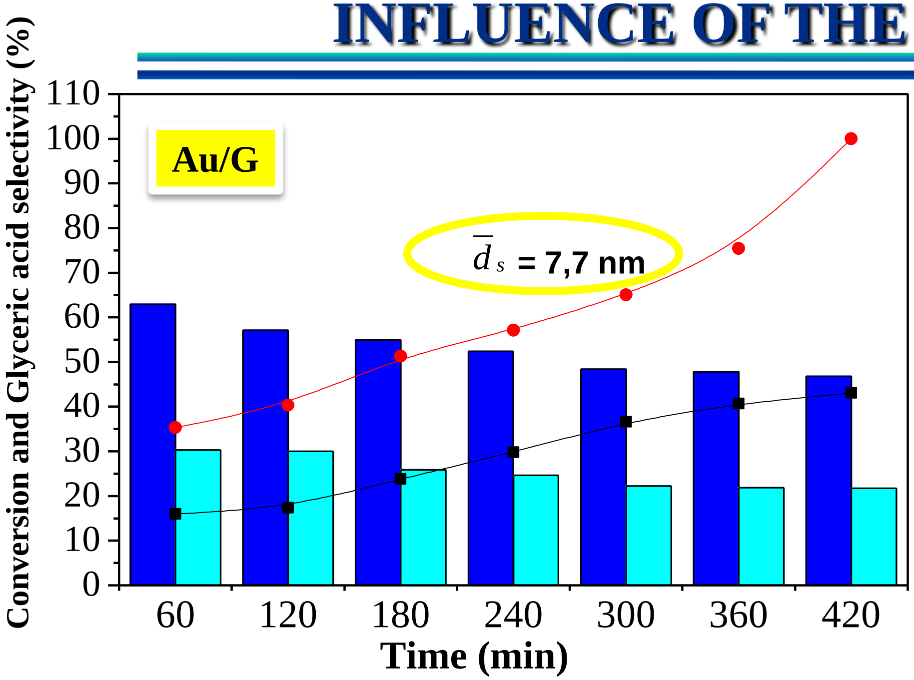
Facilitated the pronton abstraction from glycerol → ↑ Conversion and selectivity



$S_{CRUDE\ COMERCIAL}$
$S_{COMMERCIAL\ GLYCEROL}$
$X_{CRUDE\ GLYCEROL}$
$X_{COMERCIAL\ GLYCEROL}$

Reaction conditions: 0.3 M glycerol solution, glycerol/Au=3500 mol/mol, P_{O2}=5 bar, 333 K, 1000 rpm and NaOH/glycerol = 2 mol/mol.

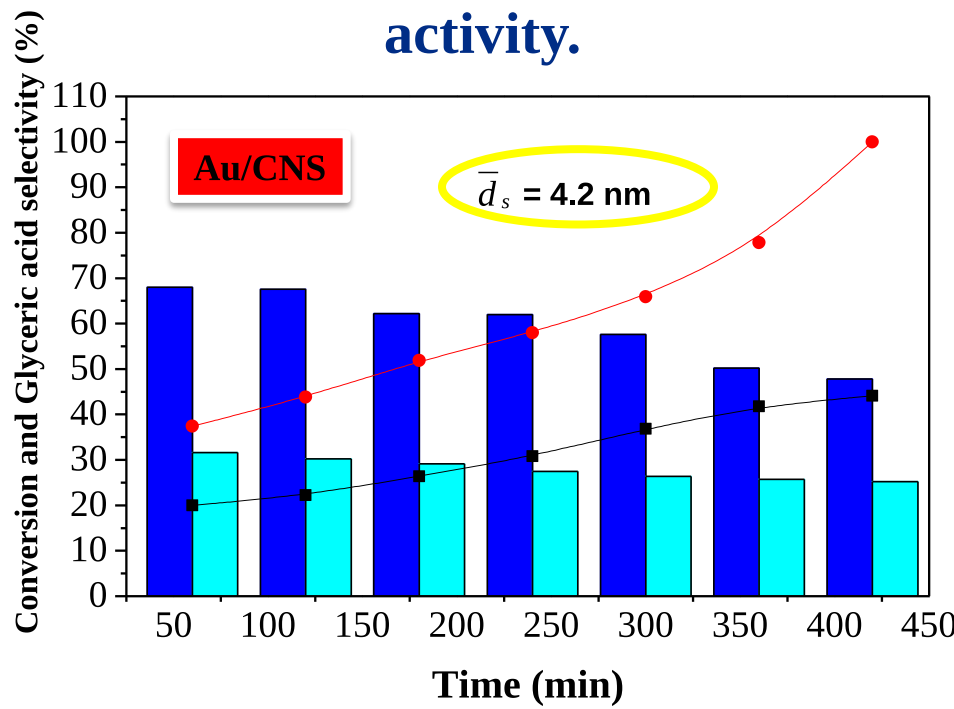
INFLUENCE OF THE NATURE OF THE SUPPORT



Au/G	
d_{002} (Å)	T_{TGA} (K)
3.378	1077

Au/CNS	
d_{002} (Å)	T_{TGA} (K)
3.462	952

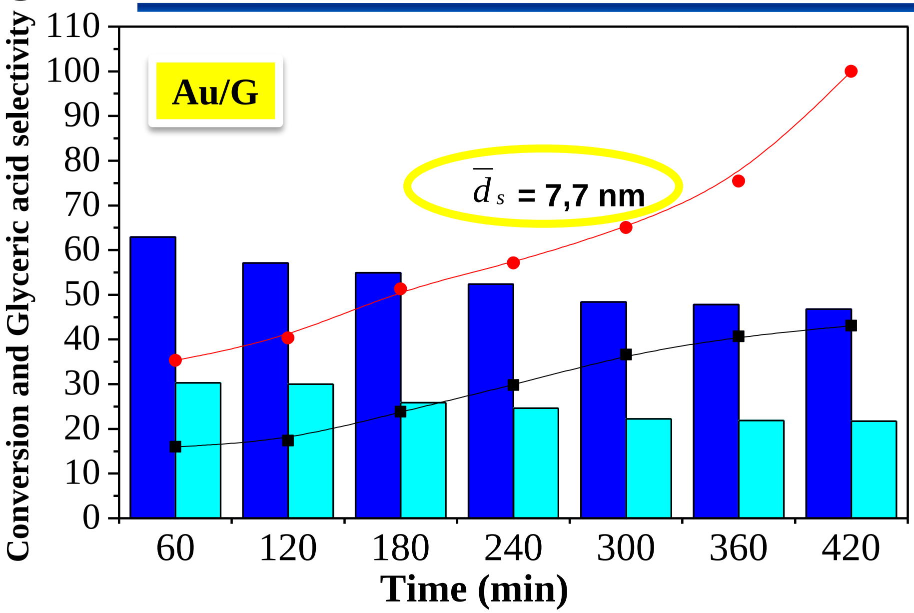
However, the Au/CNS, although it is less crystalline than Au/G, resulted in a slight increased of the catalytic activity.



Reaction conditions: 0.3 M glycerol solution, glycerol/Au=3500 mol/mol, P_{O2}=5 bar, 333 K, 1000 rpm and NaOH/glycerol = 2 mol/mol.

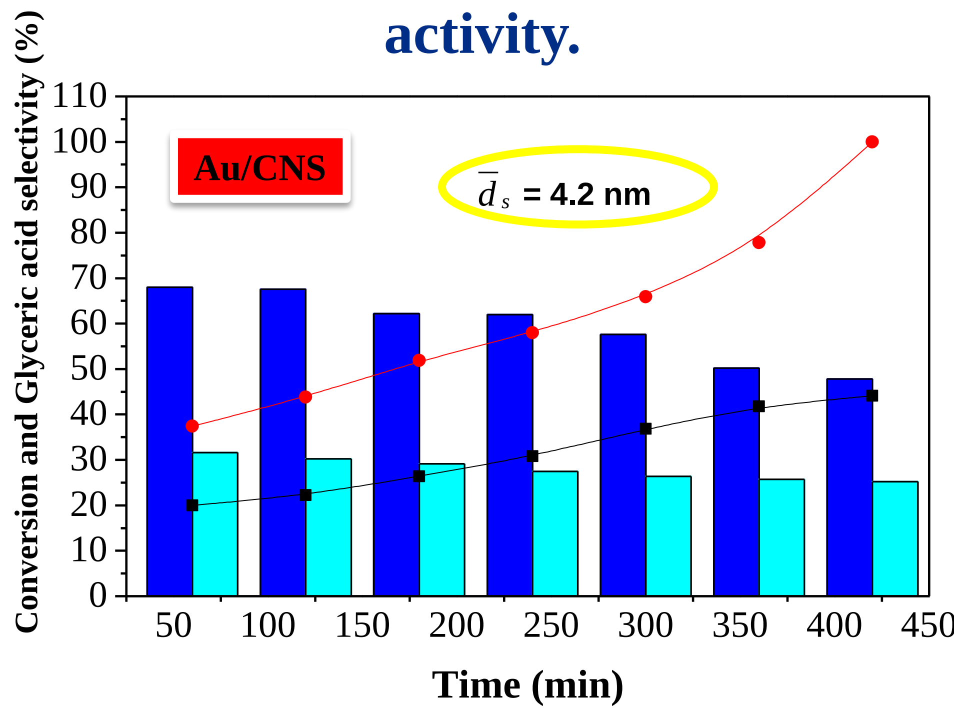
$S_{CRUDE\ COMERCIAL}$
$S_{COMMERCIAL\ GLYCEROL}$
$X_{CRUDE\ GLYCEROL}$
$X_{COMERCIAL\ GLYCEROL}$

INFLUENCE OF THE NATURE OF THE SUPPORT



However, the Au/CNS, although it is less crystalline than Au/G, resulted in a slight increased of the catalytic activity.

$$X_{Au/CNS} > X_{Au/G}$$



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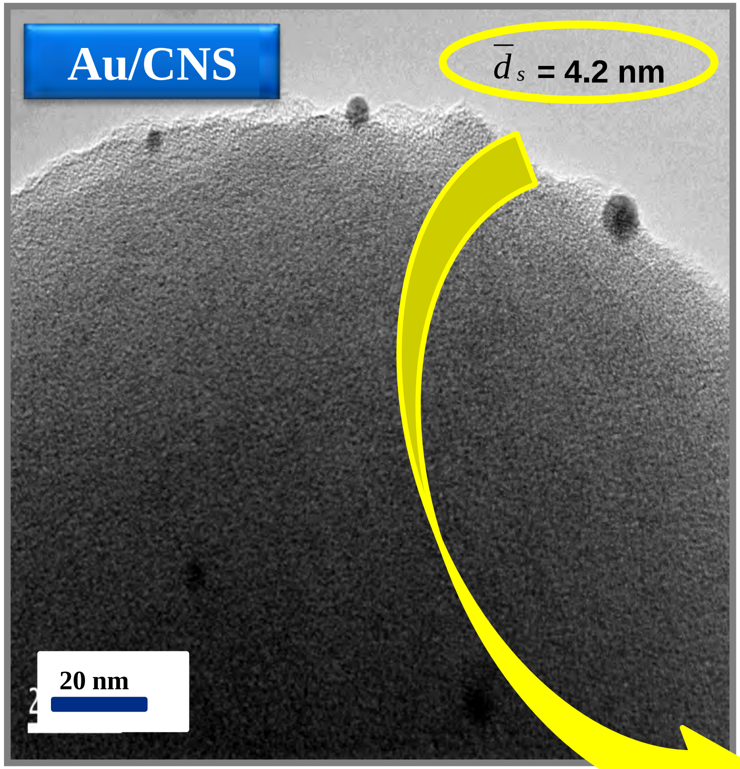
$S_{CRUDE\ COMERCIAL}$

$S_{COMMERCIAL\ GLYCEROL}$

$X_{CRUDE\ GLYCEROL}$

$X_{COMERCIAL\ GLYCEROL}$

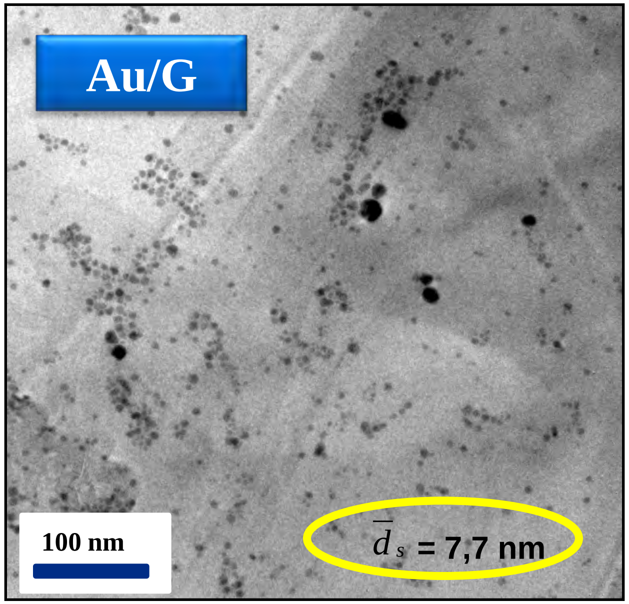
INFLUENCE OF THE NATURE OF THE SUPPORT

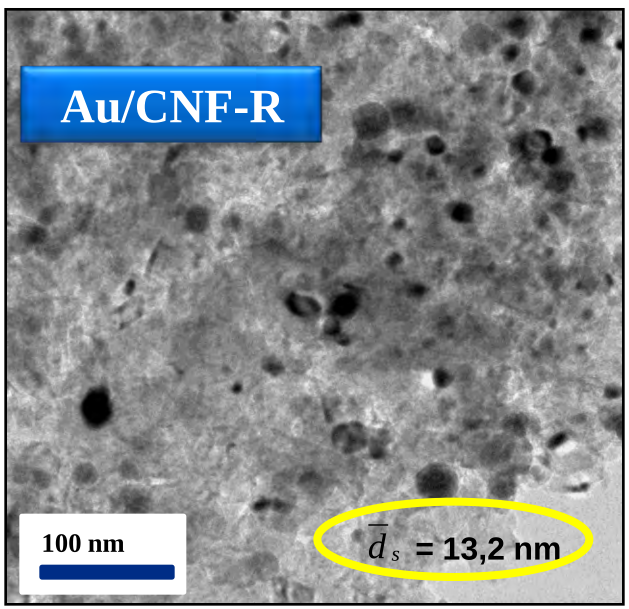


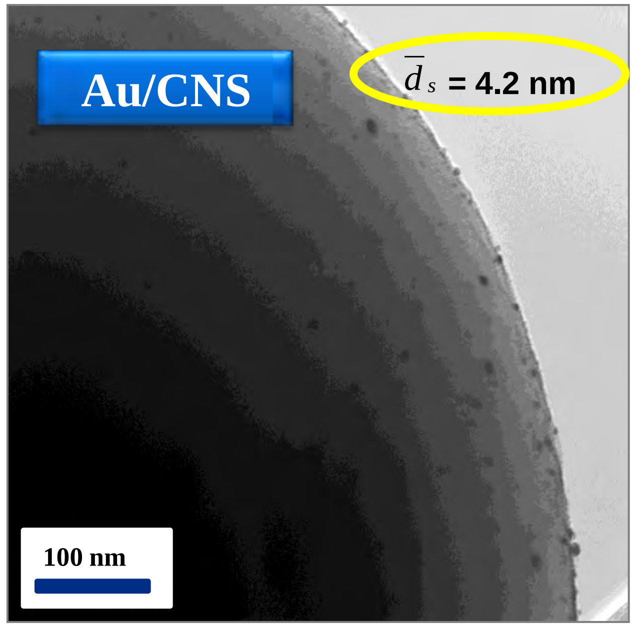
The graphite sheets are not closed shells but rather waving flakes that follow the curvature of the sphere, creating many open edges at the surface that give the structure a high chemical reactivity.

It wich causes the Au particles to disperse better than in graphite.

INFLUENCE OF THE Au PARTICLES SIZES







→ **LOWER GOLD PARTICLES SIZES (HIGHER DISPERSION)**

$\downarrow \overline{d}_s$

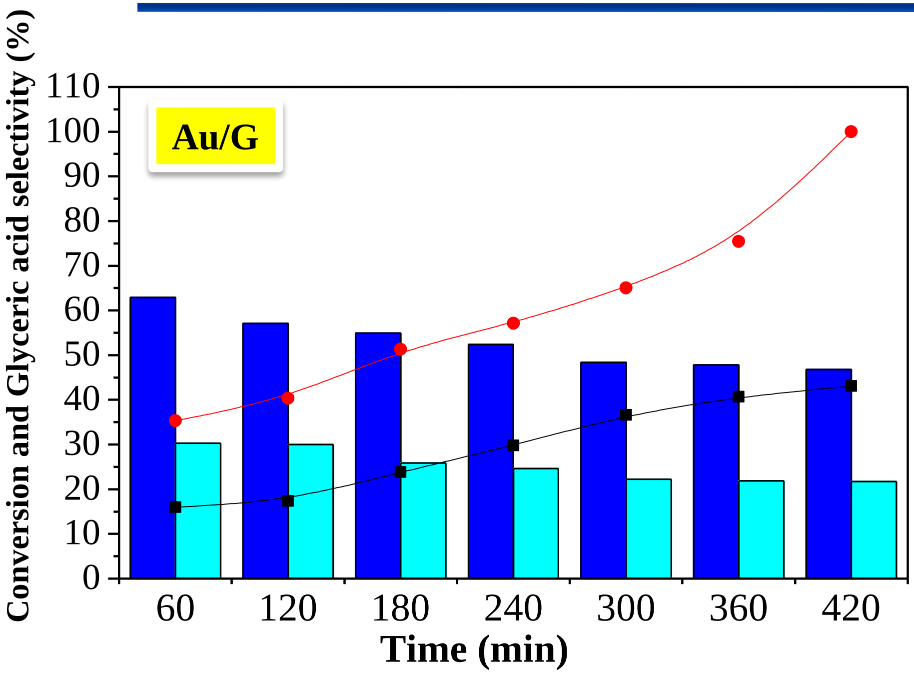
CONVERSION AND SELECTIVITY

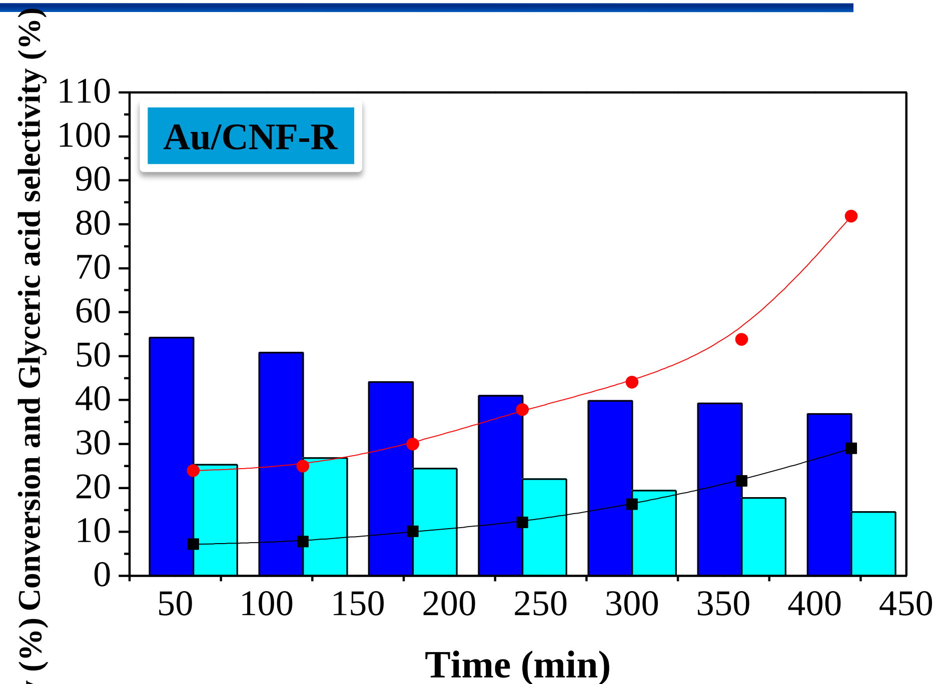
+

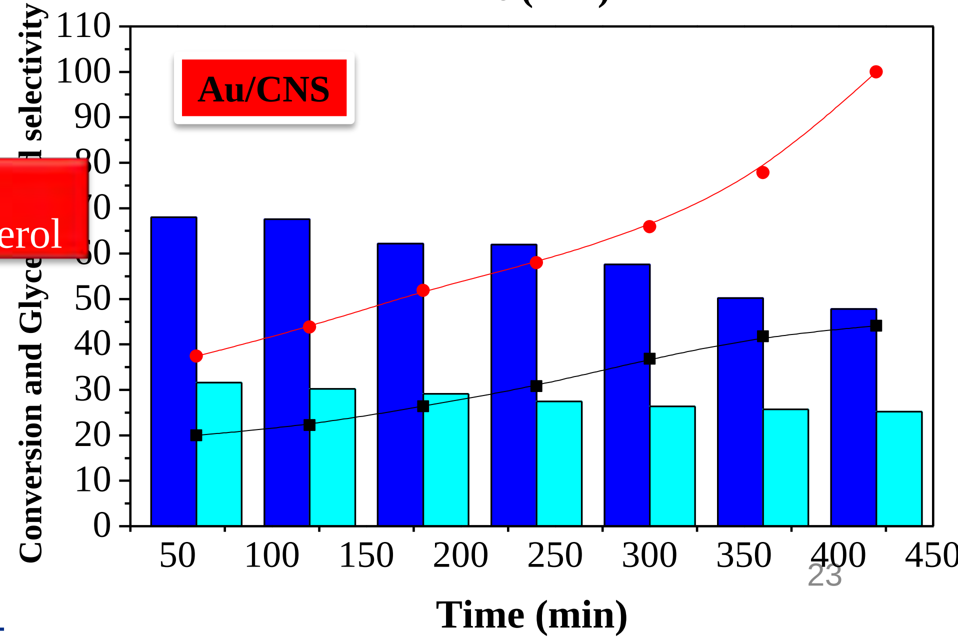
CATALYLIC ACTIVITY

Au/CNS > Au/G > Au/CNF-R

COMMERCIAL GLYCEROL AND/OR CRUDE GLYCEROL







$X_{Au/C.Commercial\ glycerol} > X_{Au/C.Crude\ glycerol}$

Reaction conditions: 0.3 M glycerol solution, glycerol/Au=3500 mol/mol, P_{O2}=5 bar, 333 K, 1000 rpm and NaOH/glycerol = 2 mol/mol.

$S_{CRUDE\ COMERCIAL}$

$S_{COMMERCIAL\ GLYCEROL}$

$X_{CRUDE\ GLYCEROL}$

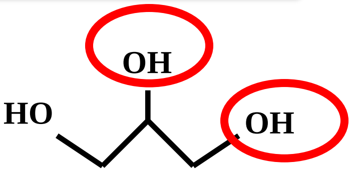
$X_{COMERCIAL\ GLYCEROL}$

COMMERCIAL GLYCEROL AND/OR CRUDE GLYCEROL

DESTABILIZATION OF THE CATALYST BY IMPURITIES IN THE CRUDE GLYCEROL

Table 3. Impurities present in the crude glycerol from the transesterification process of rapeseed oil.

IMPURITIES	CRUDE GLYCEROL (% wt.)
Catalyst (CH_3ONa)	0.05
Methanol (CH_3OH)	0.131
Phospholipids	0
Methyl esters	0.029
K	0.00021
Na	3.23
Cl	1.1
Fatty acids or triglycerides	0.0001
Water	0.001
Minimum purity	95.5



Glycerol

BRÖNSTED ACID

Its proton exchange

LONSIG CATALYSTIC ACTIVITY

INFLUENCE OF THE PURIFICATION TREATMENT OF GLYCEROL CRUDE

1. Purification by decantation and evaporation using vacuum flash process.

REMOVE:

Free fatty acids
and
Methyl esters.

REMOVE:

Methanol.

1. Purification by decantation and evaporation using vacuum flash process.

Table 4. Impurities present in the crude glycerol and evaporation glycerol.

IMPURITIES	CRUDE GLYCEROL (% wt.)	EVAPORATION GLYCEROL (% wt.)
Catalyst (CH_3ONa)	0.056	0.056
Methanol (CH_3OH)	0.131	0
Phospholipids	0	0
Methyl esters	0.029	0.029
K	0.00021	0.00018
Na	3.23	2.4
Cl	1.1	1.1
Fatty acids or triglycerides	0.0001	0
Water	0.001	0
Minimum purity	95.5	96.4

2. Purification by neutralization with hydrochloric acid.

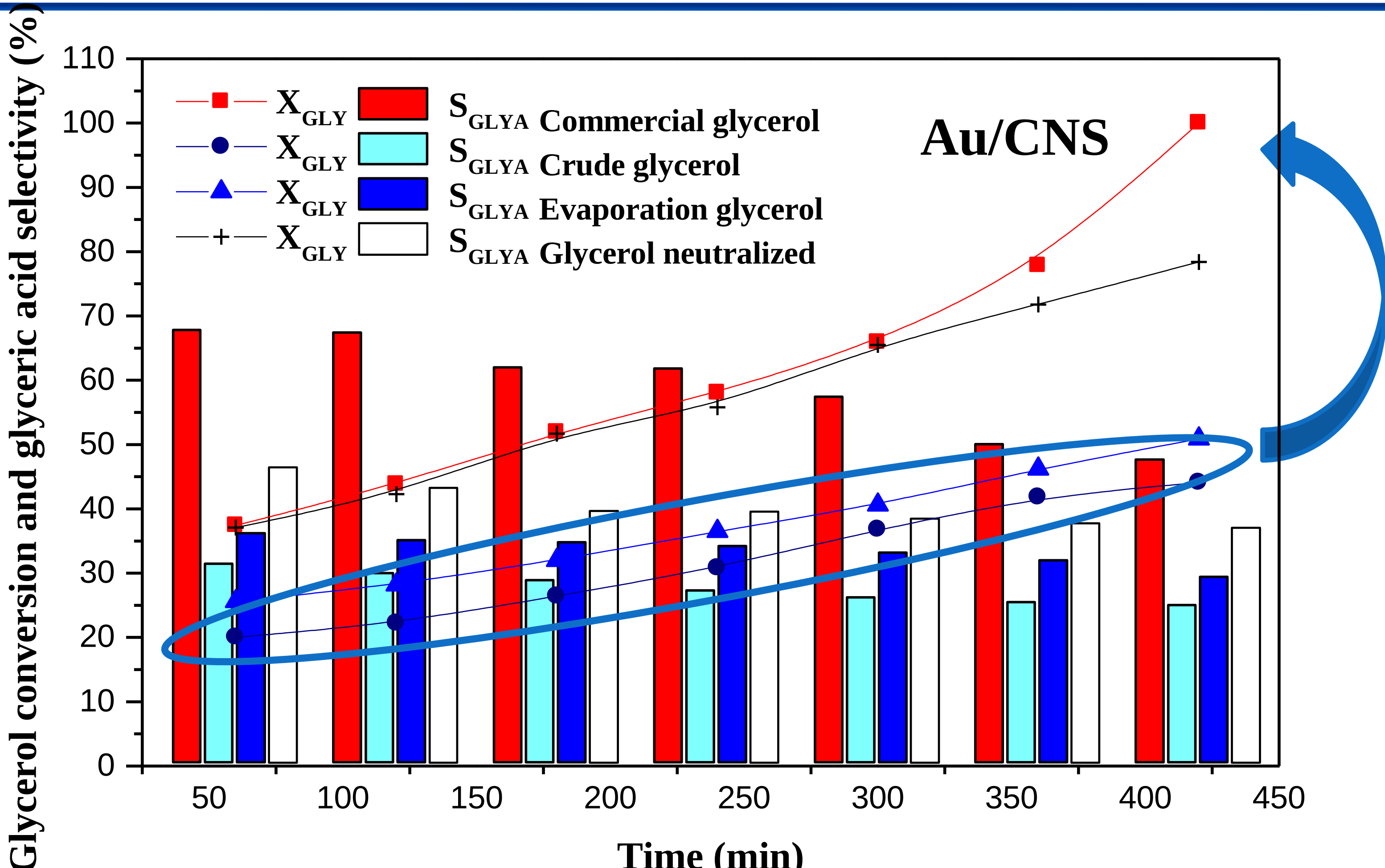
REMOVE:

Catalyst and soap.

Table 5. Impurities present in the crude glycerol and glycerol neutralized.

IMPURITIES	CRUDE GLYCEROL (% w/w)	GLYCEROL NEUTRALIZED (% w/w)
Catalyst (CH_3ONa)	0.056	0
Methanol (CH_3OH)	0.131	0
Phospholipids	0	0
Methyl esters	0.029	0.029
K	0.00021	0
Na	3.23	0.7
Cl	1.1	2.2
Fatty acids or triglycerides	0.0001	0
Minimum purity	95.5	97.1

INFLUENCE OF THE PURIFICATION TREATMENT OF GLYCEROL CRUDE

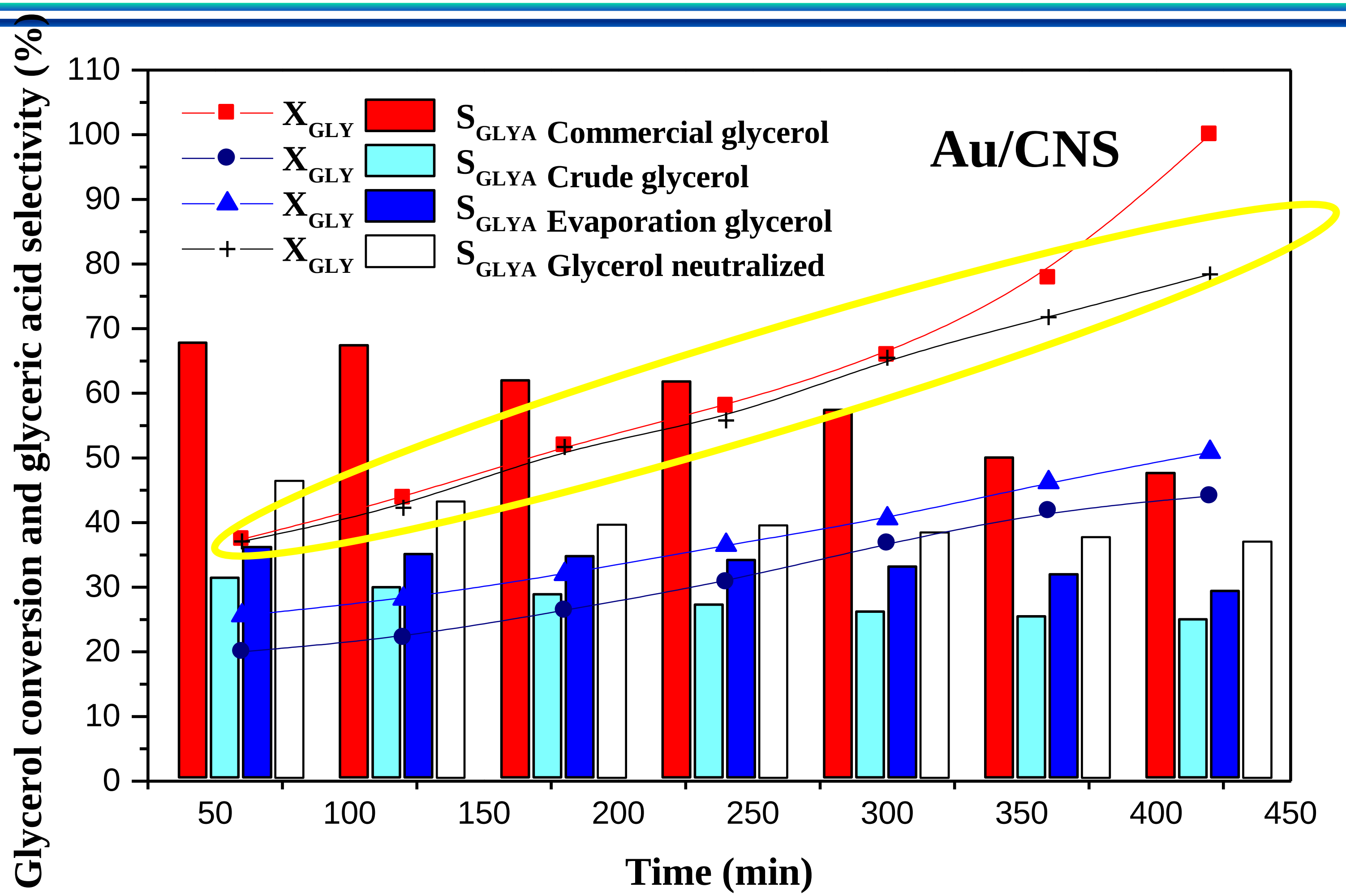


After decantation and evaporation

$X_{Au/C.Crude\ glycerol}$ are improved, however , the differences are very significant with respect to commercial glycerol.

Reaction conditions: 0.3 M glycerol solution, glycerol/Au=3500 mol/mol, P_{O2}=5 bar, 333 K, 1000 rpm and NaOH/glycerol = 2 mol/mol.

INFLUENCE OF THE PURIFICATION TREATMENT OF GLYCEROL CRUDE

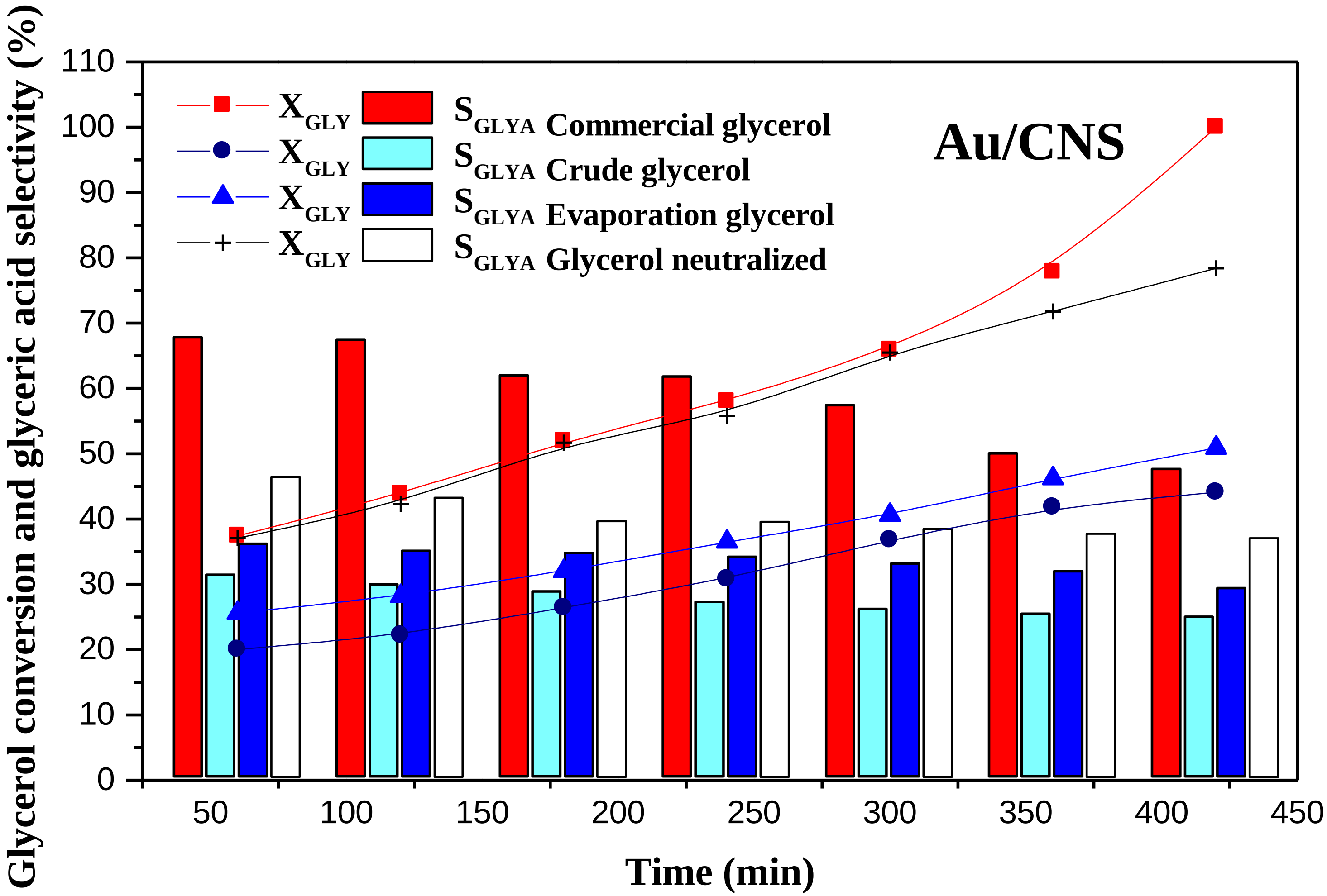


After neutralization

$X_{Au/C.Commercial\ glycerol} \approx X_{Au/C.Crude\ glycerol}$

Reaction conditions: 0.3 M glycerol solution, glycerol/Au=3500 mol/mol, P_{O2}=5 bar, 333 K, 1000 rpm and NaOH/glycerol = 2 mol/mol.

INFLUENCE OF THE PURIFICATION TREATMENT OF GLYCEROL CRUDE



This could be an interesting low cost alternative to revalorization of crude glycerol to obtain product of high added value.

Reaction conditions: 0.3 M glycerol solution, glycerol/Au=3500 mol/mol, P_{O2}=5 bar, 333 K, 1000 rpm and NaOH/glycerol = 2 mol/mol.

CONCLUSIONS

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• The results of this study show that the product distribution for the liquid phase oxidation of glycerol is clearly dependent on the nature support and Au particles size.

• Thus, the highest catalyst activity was achieved when high crystalline supports (low amount of structural defects) and lower Au particle size (high dispersion).

• Therefore, the catalyst of Au/G resulted in a higher catalytic activity than the catalyst supported on CNF-R.

• However, the catalyst supported on CNS, although it is less crystalline than graphite, resulted in a slight increased of the catalytic activity. This can be attributed to the greater dispersion of Au particles because the graphene sheets are curved and fail to close, leaving many open edges that give the structure a high chemical reactivity.

•On the other hand, it was observed that, in all cases, catalytic activity using commercial glycerol was superior respect to the crude glycerol, which may be due to destabilization of the catalyst by impurities in the crude glycerol.

• Nevertheless, after purification of the crude glycerol by neutralization, the catalytic activity was similar to that obtained using the commercial one, suggesting that this could be an interesting low cost alternative to revalorization of crude glycerol to obtain products of high added value.

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