
ECCS 2020
1st International Electronic Conference on Catalysis Sciences
10–30 NOVEMBER 2020 | ONLINE
Chaired by **PROF. DR. KEITH HOHN**
catalysts
MDPI

Cux/ZnO-y catalysts. Effect of support modification by high energy milling on the metal-support interaction

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Introduction

Selectivity towards one or more reaction products

depends

structural characteristics

physical-chemical surface of the catalyst

In the glycerol hydrogenolysis reaction

supports

- have a strong intervention in the
- selectivity determined reaction product

metal-support interaction

- plays a key role
- it has been less investigated

Cu-ZnO catalytic system

used successfully

hydrogenolysis reaction of glycerol

associated

dispersion of Cu

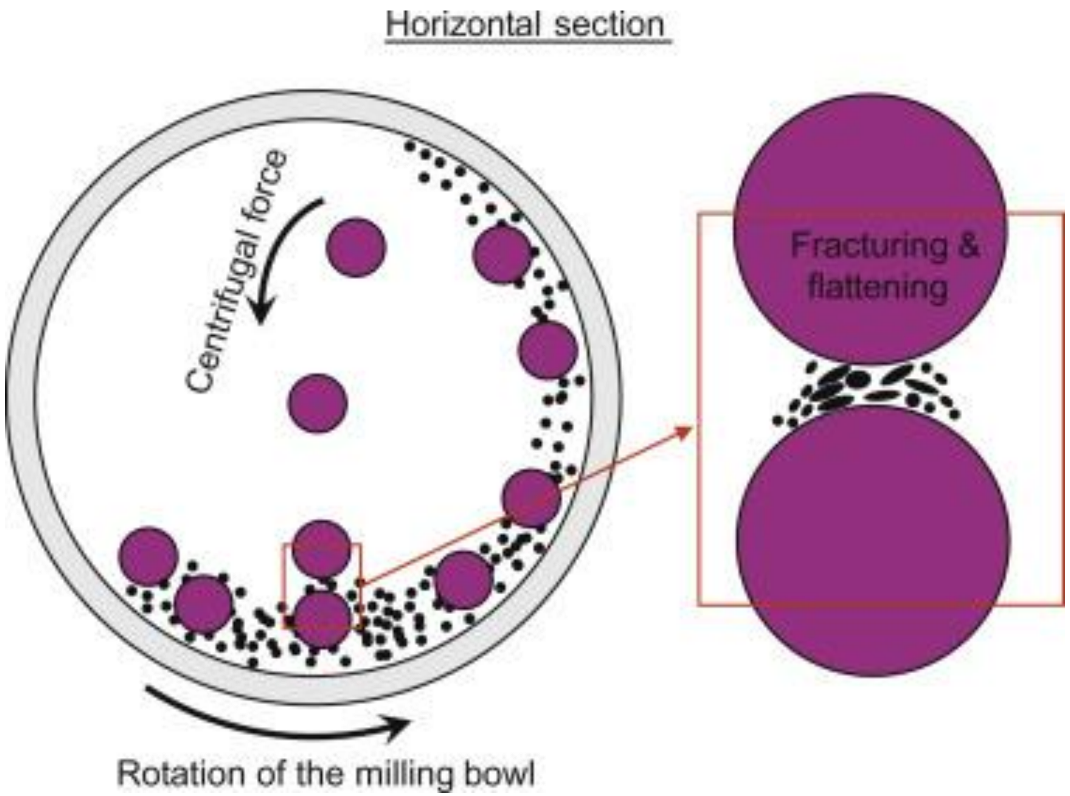
small particle sizes

Unfortunately

role of the interface between Cu and ZnO in the hydrogenolysis of glycerol has rarely been reported

Objective

Subjecting ZnO to high energy milling in order to modify its structural and surface characteristics, to be used as a catalytic support. It is intended to study the Cu-ZnO interaction achieved when the support is ground and compare it with the same system with the support without grinding.



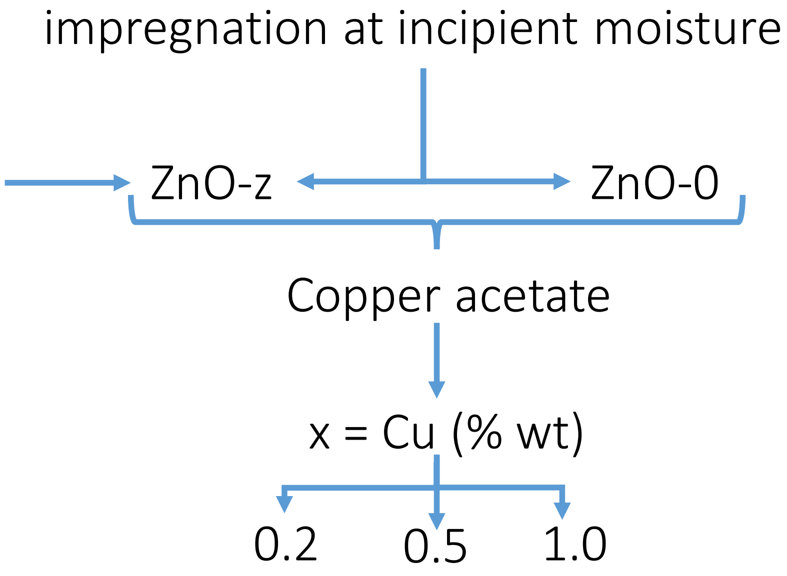
Materials and Methods

➢ Support and catalysts preparation

Commercial ZnO


Fritsch Pulverisette 6

vial and balls	WC	ZrO_2
BPR	35:1	148:1
v rotation (rpm)	300	
t milling (min)	0, 5, 30, 60, 240, 480 y 960	6


impregnation at incipient moisture

ZnO-z

ZnO-0

Copper acetate

x = Cu (% wt)

0.2

0.5

1.0

➢ Characterization

- X-ray Diffraction (XRD)
- Brunauer-Emmett-Teller (BET) method
- Raman spectroscopy
- Atomic Absorption Spectroscopy (AAS)
- X-ray Photoelectron Spectroscopy (XPS)
- Temperature Programmed Reduction (TPR)

Results and Discussion

ZnO → ↓ surface area → high energy milling

vial and balls	WC
BPR	35:1
v rotation (rpm)	300
t milling (min)	0, 5, 30, 60, 240, 480 y 960

← determine the effect →

← same →

vial and balls	ZrO_2
BPR	148:1
v rotation (rpm)	300
t milling (min)	?

6 min

- greater S_{BET} ↔ Eacum = 6.03 (m^2g^{-1}) → same Eacum — was calculated

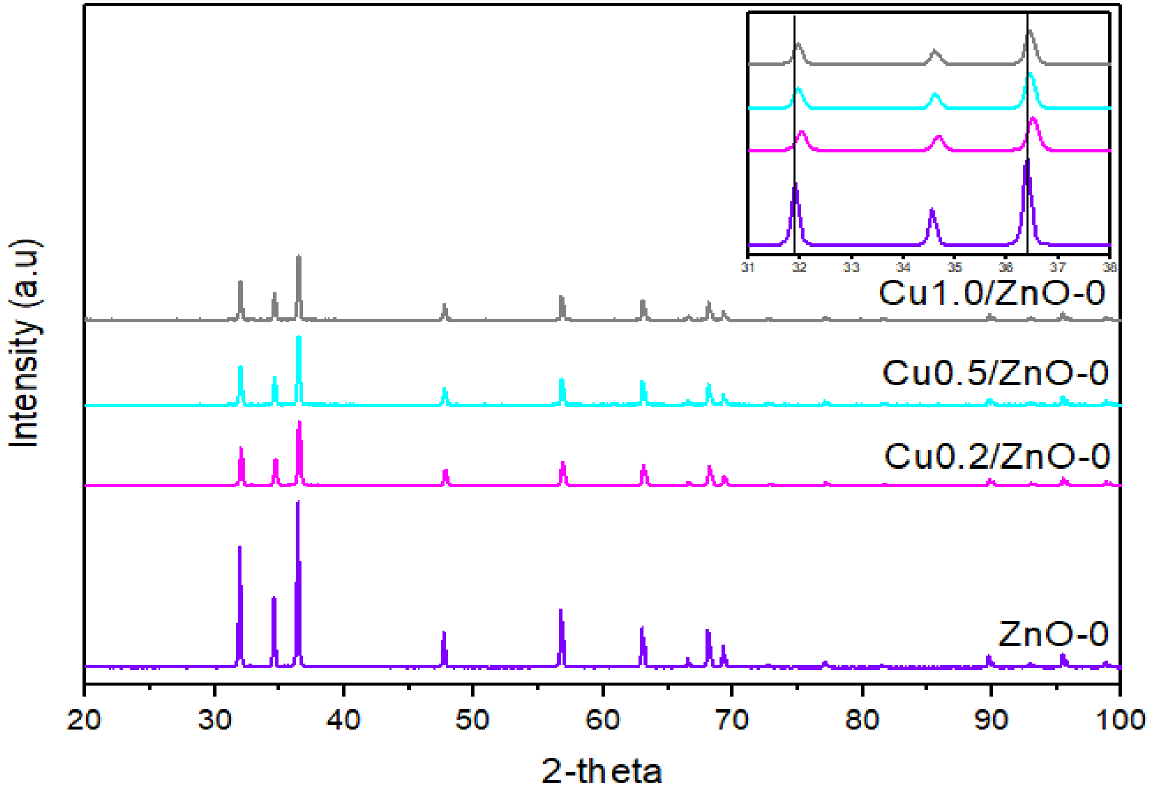
agglomeration of the particles

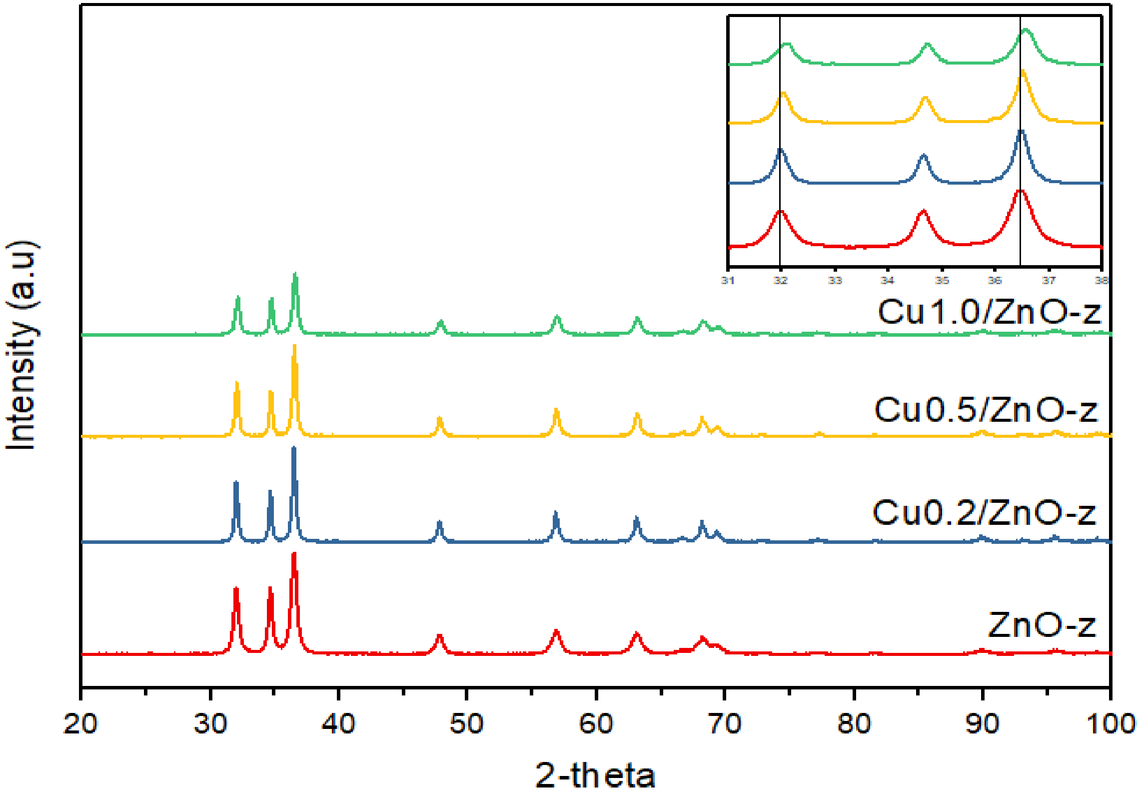
- ↑ Eacum with ↑ t milling

Support	t milling (min)	Eacum*10^2 (J g^{-1})	S_{BET} (m^2g^{-1})
ZnO-60	60	6.03	7.90
ZnO-Z	6		14.54

✓ Cux / ZnO-z ↔ selected as a support
✓ Cux / ZnO-0 ↔ selected as a reference

➢DRX



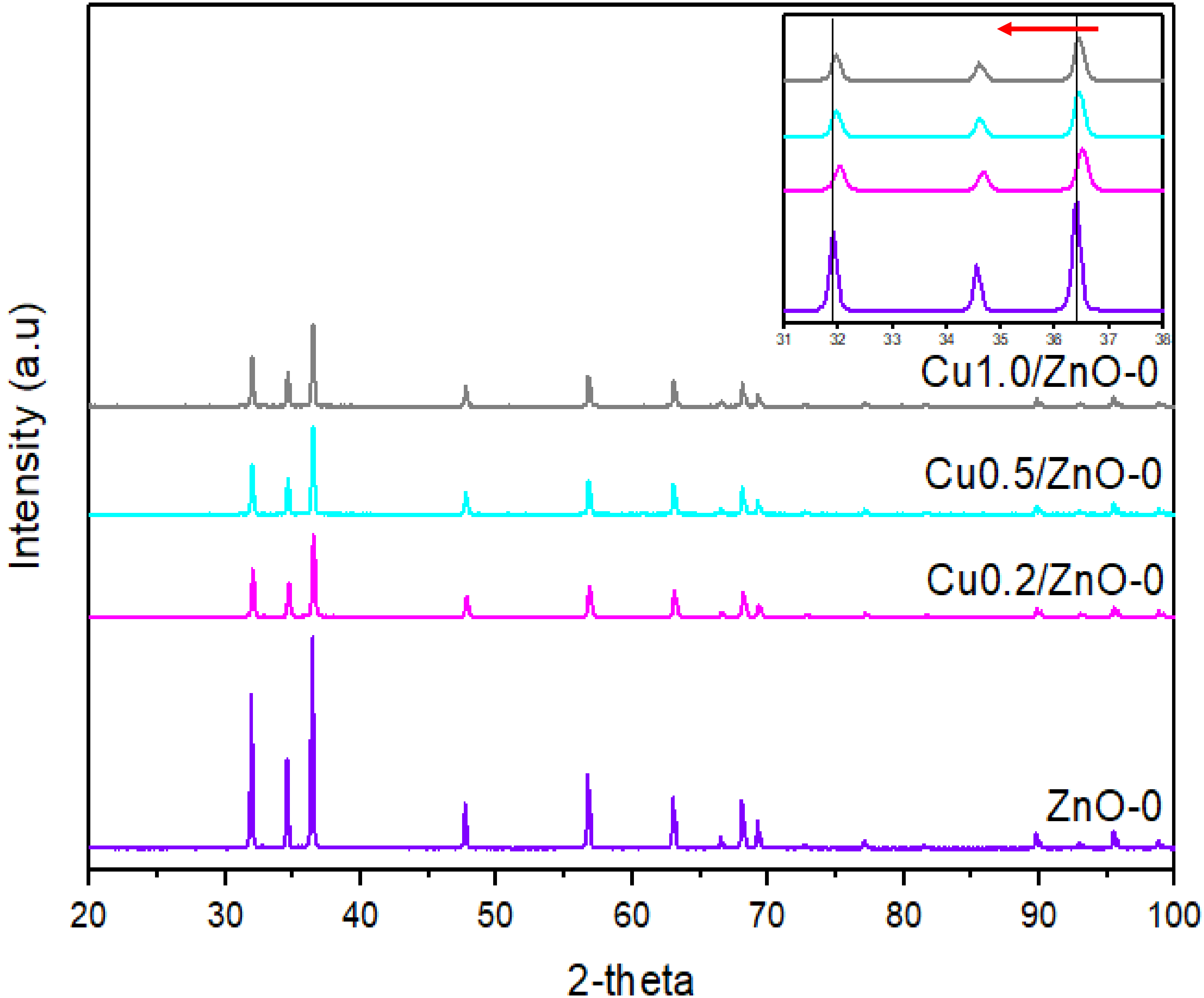


Diffraction lines → hexagonal system of wurtzite (PDF 96-90-4181)

No diffraction lines → phases containing Cu → incorporation Cu in the ZnO structure

↑ dispersion ← → ↓Cu concentration

➢DRX



diffraction lines

- ↑ Cu content ↓ displacement

- Cu0.2 / ZnO-0 ⟶ highest displacement

constant network contraction

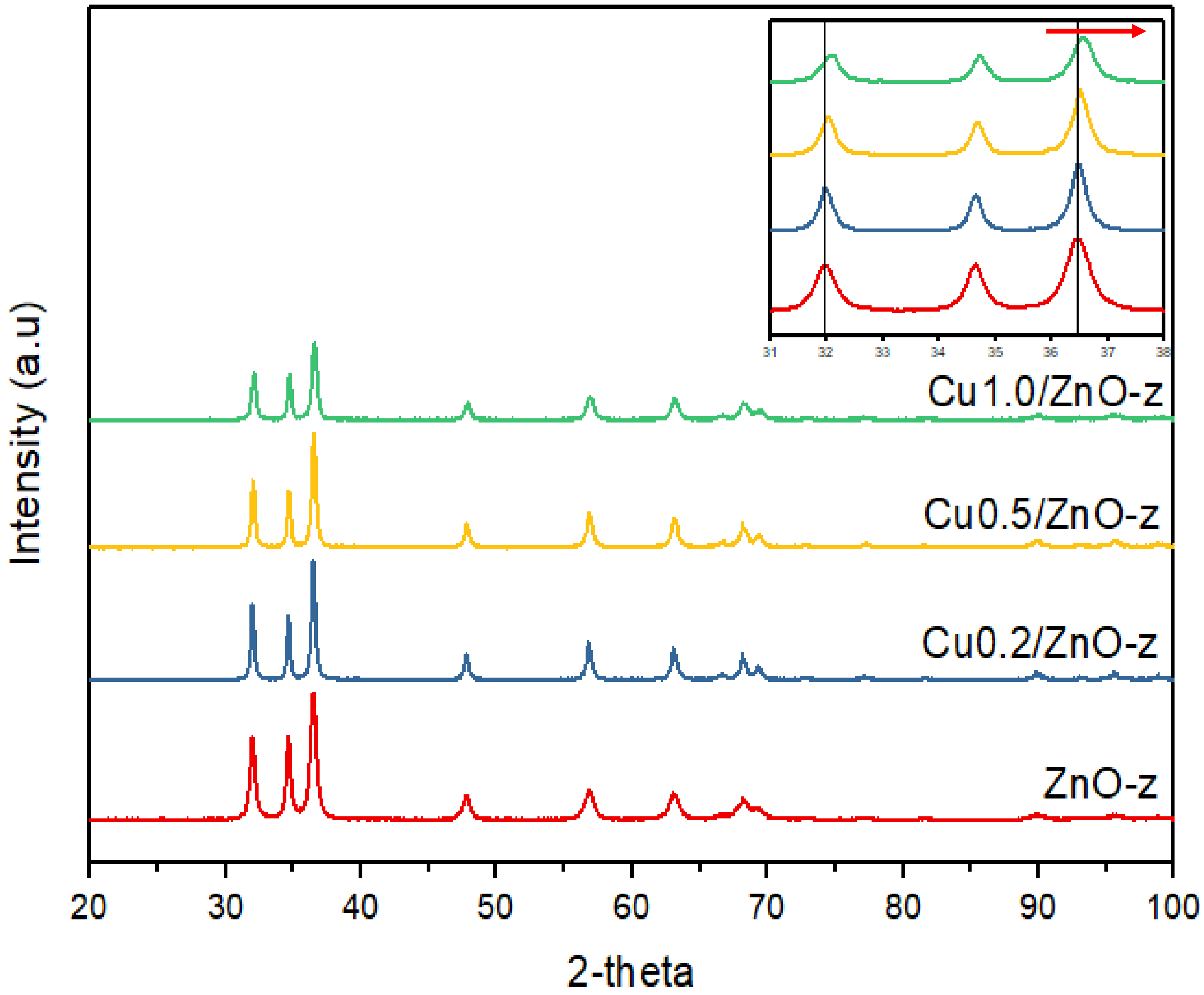
incorporation of Cu^{2+} (0.073 nm) at the sites of larger Zn (0.074 nm)

- 0.5% and 1.0% ↓ displacements

↓ incorporation of Cu^{2+} in the ZnO

favoring of the nucleation process

➢DRX



<u>diffraction lines</u>

- ↑ Cu content ↑ displacement

↓

continuous migration of the Cu^{2+} in the ZnO matrix

↓

occupying positions in its <u>planar defects</u>

↓

↑ in ZnO-z ↔milling

Scherrer and Rietveld

Catalyst	D (nm)	c/a
ZnO-0	71.2	1.6026
Cu0.2/ZnO-0	44.0	1.6020
Cu0.5/ZnO-0	50.7	1.6020
Cu1.0/ZnO-0	55.8	1.6020

- D ZnO-0 > ZnO-z ↔ milling

Catalyst	D (nm)	c/a
ZnO-z	16.8	1.6017
Cu0.2/ZnO-z	31.7	1.6020
Cu0.5/ZnO-z	28.6	1.6021
Cu1.0/ZnO-z	21.1	1.6023

- ↓ D – c/a when Cu is added

alteration in the host network ⟶ insertion of Cu

- ↑ D ↑ Cu content

- = c/a ↑ Cu content

limited insertion of Cu^{2+} in the ZnO network
(in line with XRD)

- ↑ D-c/a when Cu is added

constant incorporation of Cu in ZnO

- ↓ D ↑ Cu content

- ↑ c/a ↑ Cu content

more Cu^{2+} are incorporated
(in line with XRD)

Catalyst	ξ x 10^{-4}	δ x 10^{14} line m^{-2}
ZnO-0	15.60	1.97
Cu0.2/ZnO-0	25.09	5.16
Cu0.5/ZnO-0	22.00	3.89
Cu1.0/ZnO-0	19.98	3.21

- ZnO-0 < ZnO-z ↔ milling

stresses and defects introduced

Catalyst	ξ x 10^{-4}	δ x 10^{14} line m^{-2}
ZnO-z	66.06	35.43
Cu0.2/ZnO-z	35.02	9.95
Cu0.5/ZnO-z	38.78	12.22
Cu1.0/ZnO-z	52.52	22.46

- ↑ ξ - δ when Cu is added

change in the microstructure
size and shape of the particles

insertion of Cu

- ↓ ξ - δ ↑ Cu content

nucleation process > incorporation into the structure
(in line with XRD, D, c/a)

- **↓ ξ - δ when Cu is added**

Cu occupy positions in the network → stabilize releasing the stress generated →milling

- ↑ ξ - δ ↑ Cu content

more Cu^{2+} are incorporated
(in line with XRD, D, c/a)

➢S_{BET}, AAS, and Raman

Catalyst	S_{BET} (m^2g^{-1})	Cu (%wt)	I_{E1}/I_{2A1}
ZnO-0	3.8	-	0.18
Cu0.2/ZnO-0	3.7	0.2	0.64
Cu0.5/ZnO-0	3.5	0.56	0.31
Cu1.0/ZnO-0	4.5	0.96	0.17

S_{BET} ZnO-0 < ZnO-z ↔ milling

Cu (%wt)⟶ AAS

↓

excellent impregnation

Catalyst	S_{BET} (m^2g^{-1})	Cu (%wt)	I_{E1}/I_{2A1}
ZnO-z	14.54	-	1.78
Cu0.2/ZnO-z	6.54	0.25	1.53
Cu0.5/ZnO-z	5.97	0.68	1.37
Cu1.0/ZnO-z	7.5	1.19	1.04

- ≈ S_{BET} when Cu is added

- ≈ S_{BET} ↑ Cu content

- ↑ I_{E1}/I_{2A1} ↑ when Cu is added

- ↓ I_{E1}/I_{2A1} ↑ Cu content

(in line with ξ – δ)

- **↓ S_{BET} when Cu is added**

Impregnation ⟶ small agglomerated ZnO particles

- **↑ S_{BET} ↑ Cu content**

Impregnation ⟶ erode the surface (pH = 5.5 - 6.0)

- **↓ I_{E1}/I_{2A1} when Cu is added**

- **↓ I_{E1}/I_{2A1} ↑ Cu content**

(in line with ξ – δ)

➢XPS

Catalyst	Zn $2p_{3/2}$ (eV)	Cu $2p_{3/2}$ (eV)
ZnO-0	1021.38	-
Cu0.2/ZnO-0	1021.77	932.43
Cu0.5/ZnO-0	1021.73	932.73
Cu1.0/ZnO-0	1021.58	932.31

- ↑ (BE $_{Zn\ 2p3/2}$) when Cu is added

- (BE $_{Cu\ 2p3/2}$) < (BE $_{Cu\ 2p3/2}$) CuO

strong Cu-ZnO interaction

Catalyst	Zn $2p_{3/2}$ (eV)	Cu $2p_{3/2}$ (eV)
ZnO-z	1021.28	-
Cu0.2/ZnO-z	1021.29	932.52
Cu0.5/ZnO-z	1021.45	932.44
Cu1.0/ZnO-z	1021.59	932.39

- ↓ (BE $_{Zn\ 2p3/2}$) ↑ Cu content

↓ Cu-ZnO interaction

- ↑ (BE $_{Zn\ 2p3/2}$) ↑ Cu content

↑ Cu-ZnO interaction

- ↑ (BE $_{Zn\ 2p3/2}$) and ↓(BE $_{Cu\ 2p3/2}$)

↓

e^- transfer from the support to the metal

↓

reduction of CuO to Cu_2O → interface: metal domain-support

➢XPS

Catalyst	O 1s (eV)		$O_{ads}/(O_{ads}+O_{red})$
	O red	O ads	
ZnO-0	530.15	531.67	35.60
Cu0.2/ZnO-0	530.43	532.07	24.65
Cu0.5/ZnO-0	530.40	532.30	21.53
Cu1.0/ZnO-0	530.38	532.34	17.44

- ↑ (BE $_{\text{Ored}}$) when Cu is added

- ≈ (BE $_{\text{Ored}}$) ↑ Cu content

limited insertion of Cu in the ZnO network
(in line with XRD, D, c/a)

- ↑ (BE $_{\text{Oads}}$) when Cu is added and ↑ Cu

- ↓ total O_{ads} when Cu is added and ↑ Cu

↓ Cu is incorporated into the network
↑ Cu is adsorbed on the O vacancies

Catalyst	O 1s (eV)		$O_{ads}/(O_{ads}+O_{red})$
	O red	O ads	
ZnO-z	530.07	531.65	24.30
Cu0.2/ZnO-z	530.19	531.85	24.67
Cu0.5/ZnO-z	530.22	531.89	22.03
Cu1.0/ZnO-z	530.38	532.19	17.07

- ↑ (BE $_{\text{Ored}}$) when Cu is added **and ↑ Cu**

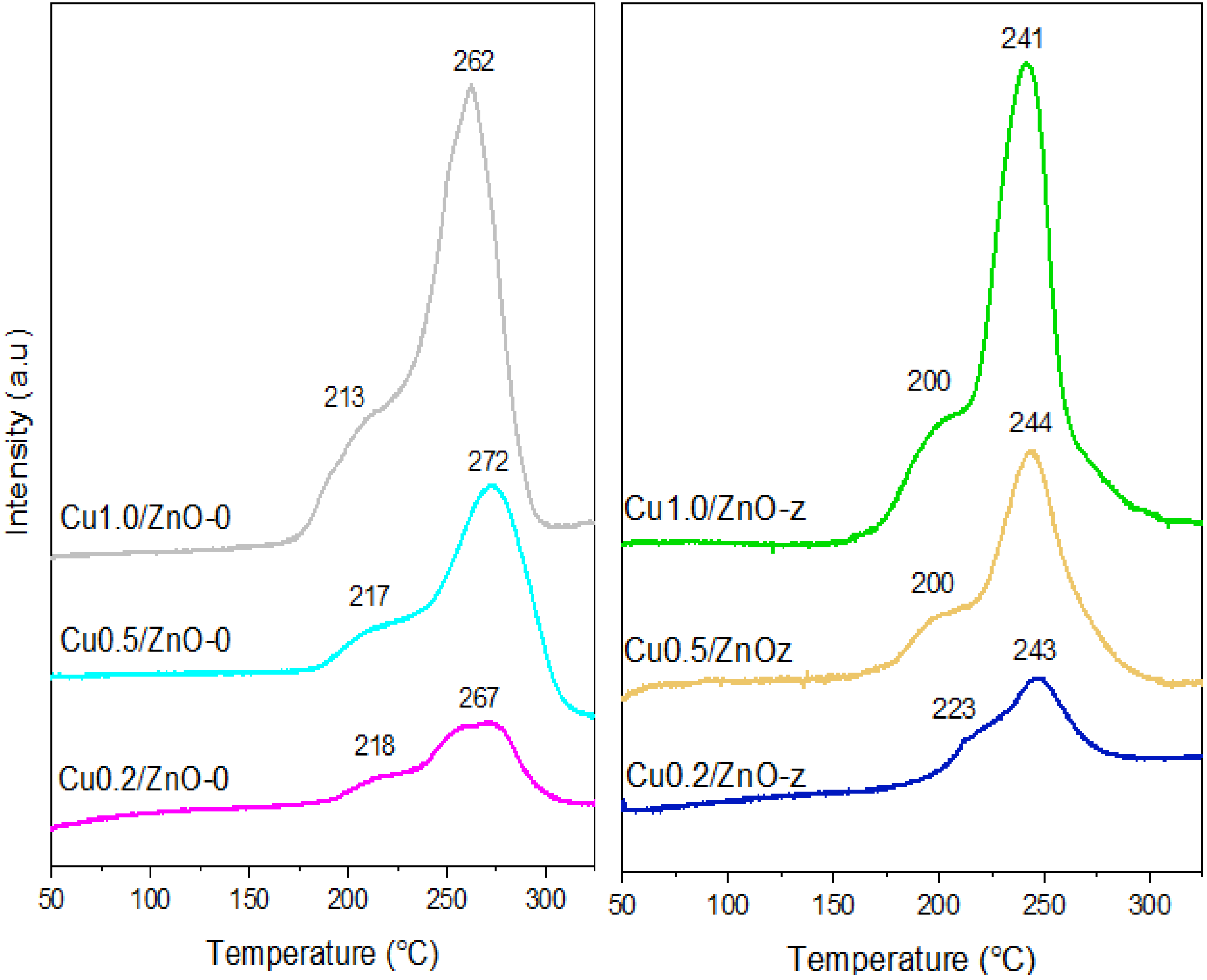
constant incorporation of Cu in ZnO
(in line with XRD, D, c/a)

- ↑ (BE $_{\text{Oads}}$) when Cu is added **and ↑ Cu**

- ↓ total O_{ads} when Cu is added and ↑ Cu

↑ Cu is incorporated into the network
↓ Cu is adsorbed on the O vacancies

➢RTP



- Present 2 superimposed signals

↓

↓ T ↑ Cu content

- Supports do not present reduction signals in the temperature range studied

- T(all catalysts) < Tu (CuO bulk)

↓

strong Cu-support

- Cux / ZnO-z Cu reducibility > Cux / ZnO-0

➢RTP

Catalyst	H_2 consuption		
	Exp.	CuO	Cu_2O
Cu0.2/ZnO-0	26.6	31.4	17.5
Cu0.5/ZnO-0	67.8	87.5	45.5
Cu1.0/ZnO-0	109.5	149.6	83.2

Catalyst	H_2 consuption		
	Exp.	CuO	Cu_2O
Cu0.2/ZnO-z	21.5	25.1	14.0
Cu0.5/ZnO-z	42.9	70.3	39.2
Cu1.0/ZnO-z	88.1	120.7	66.2

H_2 consumptions ≈ theoretical for reduction of CuO

↑ Cu content
experimental consumptions < theoretical

↓

presence of a low amount of Cu_2O

H_2 consumptions ≈ theoretical for reduction of Cu_2O

↑ Cu content
experimental consumptions > theoretical

↓

presence of a low amount of CuO

Coexistence → Cu with both valences

↓

e^- mobility that occurs from the support to the metal

(in line with XPS)

Conclusions

- High energy milling generates an increase in the specific surface area of the support, and introduces defects and micro-stresses in the crystalline lattice, making it more reactive than the original crystalline structure.

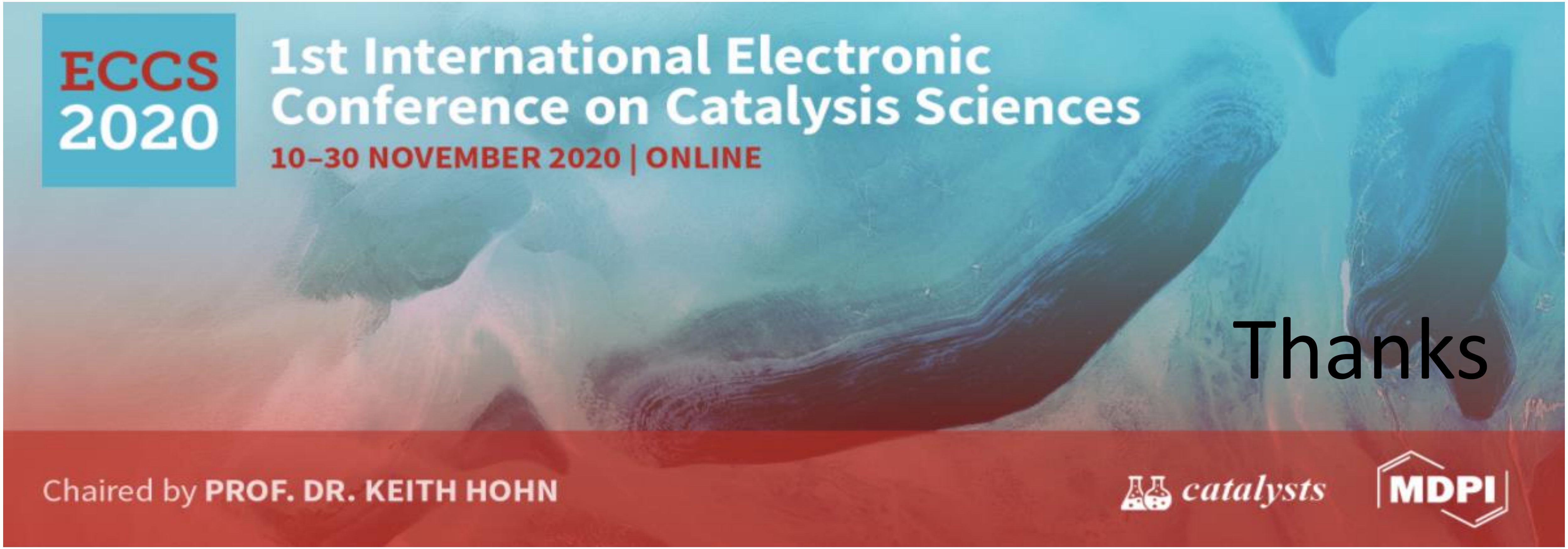
- The vial and mill balls material has a great influence on the milling time, generating different changes in the solid for the same accumulated kinetic energy.

- The defects introduced in the support by the high energy milling increase the metal-support interaction, and the reducibility of the metal; and Cu insertion could be potentially stabilizing the ZnO lattice, as inferred from the techniques discussed in this work.

- As a consequence, it is possible a decrease in the sizes of metallic domains and an increase in their dispersion, which will soon be determined by chemisorption of N_2O.

- For Cux/ZnO-z, the CuO/Cu_2O-ZnO-z generated interface could lead to an improvement in the activity, selectivity and stability of this system in the glycerol hydrogenolysis reaction.

- We can conclude that high energy milling is an environmentally friendly technique, and very powerful. It allows modifying the metal-support interactions, which could be reflected in the improvement of the performance of catalytic systems in liquid phase reactions.



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Thanks

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