H2 GREENZO Project. An alternative process for the sustainable production of hydrogen using renewable feedstocks and catalysts.

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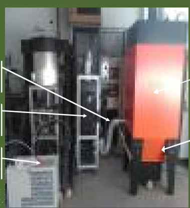
Introduction

The future scarcity of fossil fuels, the rising of their price, the pollution associated with their use and the potential environmental disasters due to their collection, make necessary to develop renewable and cleaned energy alternatives independent of fossil fuels. Hydrogen based fuels offer an attractive alternative to the current hydrocarbon fuels. But to realize the full benefits of a hydrogen economy-sustainability, increased energy security, diverse energy supply and reduced air pollution, hydrogen must be produced from available renewable resources. Reforming of renewable biomass feedstocks [1], such as bioethanol, can be used for hydrogen production [2,3]. High activity, selectivity and stability are the main behaviors for a good bioethanol reforming catalyst. Support plays an important role in the preparation of highly active and selective bioethanol steam reforming catalyst. ZnO seems to excellent support to prepare efficient bioethanol steam reforming catalysts and cobalt as active site due to its high catalytic activity in the steam reforming and water gas shift reaction [4]. Commercial ZnO is obtained from the air oxidation of Zn in a process that involves several stages during which different pollutants are emitted. 70 % of the Zn is obtained from mines and only 30 % come from recycled waste, mainly from brass and plating process. Analyzing this fact, we thought it would be interesting to use renewable ZnO for the steam reforming of bioethanol, since the "green" nature of the catalysts used to produce hydrogen from steam reforming of bioethanol has not been still considered. Thus, we have explored the activity, selectivity, and stability of Co supported over a commercial ZnO and "green" ZnO in the steam reforming of bioethanol to view the possibility to use recyclable catalyst in order to develop a global green process to produce hydrogen. A complete characterization of Co-ZnO catalysts has been carried out (XRD, BET area, TPR and TEM), which has allowed to establish interesting relationships between its catalytic performance and physicochemical properties.

Experimental, Results, and Discussion

Support Preparation

These pictures show the process to obtain the ZnO from the Zamak waste. The residue was placed in a furnace, through an arc, by a specific welding equipment are attained reach temperatures suitable for the sublimation of metal zinc for further oxidation reaction and obtaining zinc oxide. Then, the generated zinc oxide is sucked by a vacuum pump and the particles are retained by a bag filter, which allow to remove the "green" ZnO powder generated.



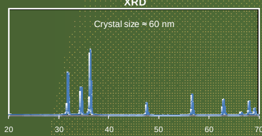
Support Characterization

Recycled ZnO

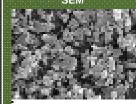
The characterization of the commercial and recycled ZnO, shows first that the purity of the recycled ZnO is lower than the commercial (96 %). As it can be seen several impurities are present such as alumina, silica, iron oxide or calcium oxide. Referent to the BET surface area it can be seen that this recycled ZnO presents a higher area. From X-ray diffraction pattern it can be seen that crystal sizes determined by the Scherrer equation, is larger for commercial zinc. This result matches quiet well with its lower BET surface area. SEM micrographs are also presented and apparently a large amount of small ZnO particles can be seen in the recycled sample.

Analysis result	
ZnO	96,2
SiO_2	0,1
Al_2O_3	1,1
Fe_2O_3	0,17
K_2O	0,01
CaO	0,1
MgO	0,03
TiO_2	0,02
CuO	0,2
NiO	0,05
S	0,01
Cl	0,2
Calcination loss at 900 ° C	1,8

XRD



SEM



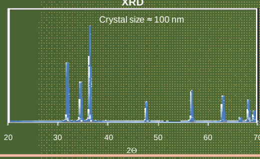
BET Area (m^2/g)

9.0

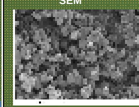
Commercial ZnO

Analysis result	
ZnO	≥ 99,0 %
Ca	≤ 0,005 %
Cd	≤ 0,005 %
Co	≤ 0,005 %
Cu	≤ 0,005 %
Fe	≤ 0,005 %
K	≤ 0,01 %
Na	≤ 0,01 %
Ni	≤ 0,005 %
Pb	≤ 0,005 %

XRD



SEM



BET Area (m^2/g)

6.6

Co Incorporation

ZnO-R, ZnO-C → 20 % Cobalt (Incipient wetness impregnation) → Drying overnight at room temperature → Cal. at 873 K 3 hours → 20Co/ZnO-R, 20Co/ZnO-C

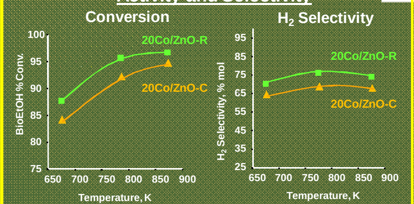
Reaction System and Conditions

Continuous Fixed Bed Reactor

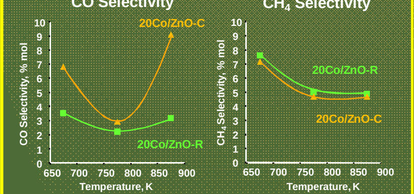
Reaction Conditions

- H_2O/BioEtOH: 13
- GHSV: 4700 h^{-1}
- Reaction T (K): 673-873
- Atmospheric Pressure

Activity and Selectivity



Higher activity and H_2 selectivity for recycled ZnO-based Catalyst



Lower CO selectivity for recycled ZnO-based Catalyst

Catalysts Characterization

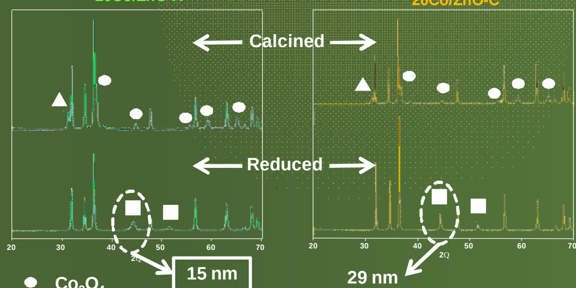
BET Surface Area (m^2/g)

Supports		Cobalt incorporation	Catalysts	
ZnO-R	9.0	2 →	14.7	20Co/ZnO-R
ZnO-C	6.6	1 →	5.8	20Co/ZnO-C

1- For commercial ZnO: Reduction of Surface Area with Co incorporation due to dilution effect (Co oxides do not contribute to the surface area) [3,6].

2- Higher area for recycled ZnO-based catalyst.

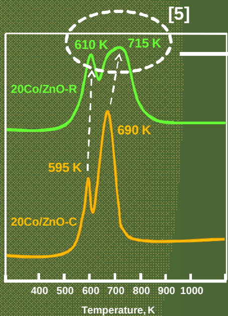
XRD



● Co_3O_4
▲ Co_2O_3
■ Co

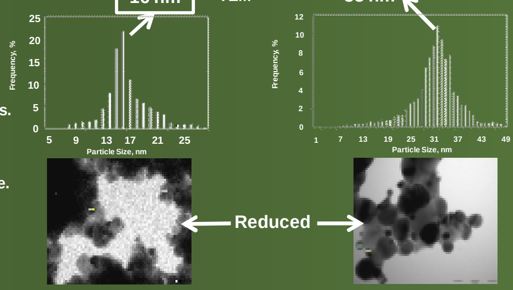
20Co/ZnO-R: Lower Co metallic particle size.

[5]



20Co/ZnO-R Higher Reduction T.
↓
Higher Co-support interactions.
↓
Lower Co metallic particle size.
↓
Smaller is better for ethanol steam reforming [7].

TEM



Conclusions

It has been designed a new production process to recycle ZnO from wastes such as Zamak slag, sludge and sludge vibrated physicochemical treatments of electroplating lines. The use of this recycled ZnO as Co catalyst support has allow to prepare a excellent bioethanol steam reforming catalyst with high activity and selectivity in the production of hydrogen. This is the first time it is described a steam reforming process where both, the raw material (bioethanol) and the catalyst support (ZnO), are of renewable nature. Now, the recyclable nature of the steam reforming catalyst together to the renewable nature of the hydrogen precursor (bioethanol) would be contributing to make more sustainable the overall process of hydrogen production.

References

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Acknowledgments

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