Recycled Catalytic Material for the Sustainable Production of Hydrogen by Steam Reforming of Bioethanol

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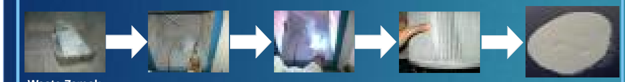
Introduction

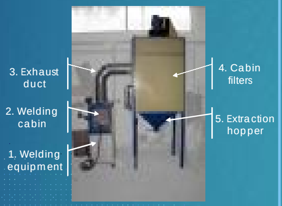
The future scarcity of fossil fuels, the rising of their price, the pollution associated with their use and the potential environmental disasters due to their collection, make necessary to develop renewable and cleaned energy alternatives independent of fossil fuels. Hydrogen based fuels offer an attractive 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 catalysts. 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 comercial ZnO and "green" ZnO in the steam reforming of bioetanol 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 physico-chemical properties.

Experimental, Results, and Discussion

Support Preparation



These pictures show the process to obtain the ZnO from the waste Zamak. The residue was placed in a furnace, through an arc, by a specific welding equipment are attained reach temperatures suitable for the sublimation of zinc metal 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.



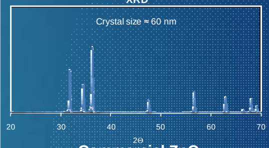
Support Characterization

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 alummina, 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 matchs 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.

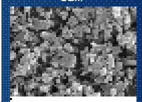
Recycled ZnO

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



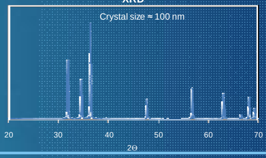
BET Area (m^2/g)

9.0

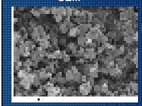
Commercial ZnO

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



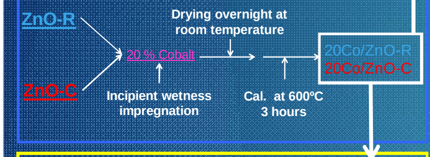
SEM



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 600ºC 3 hours
20Co/ZnO-R
20Co/ZnO-C

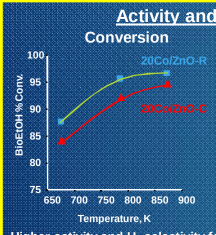
Reaction System and Conditions

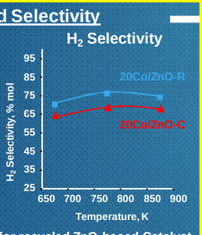
Continuous Fixed Bed Reactor

Reaction Conditions

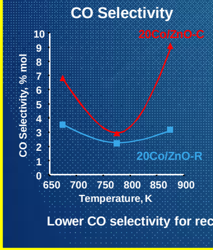
H_2O/BioEtOH: 13
GHSV: 4700 h^{-1}
Reaction T (K): 673-873
Atmospheric Pressure

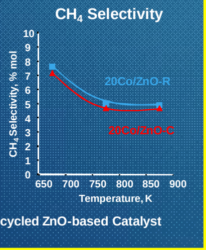
Activity and Selectivity





Higher activity and H_2 selectivity for recycled ZnO-based Catalyst

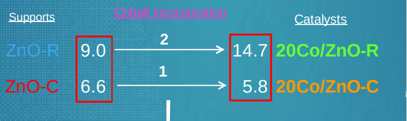




Lower CO selectivity for recycled ZnO-based Catalyst

Catalysts Characterization

BET Surface Area (m^2/g)

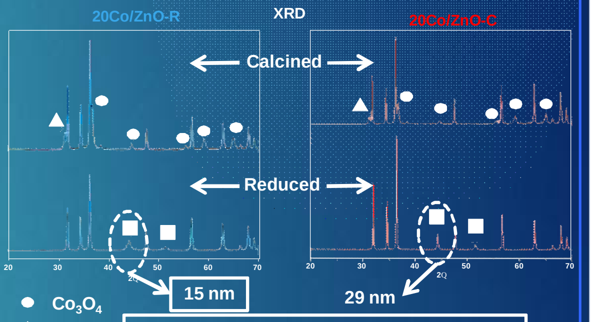


Supports		Cobalt incorporation		Catalysts
ZnO-R	9.0	2 →	14.7	20Co/ZnO-R
ZnO-C	6.6	1 →	5.8	20Co/ZnO-C

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

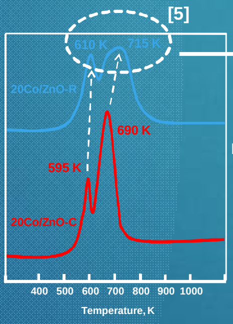
2- Higher area for recycled ZnO-based catalyst.

XRD



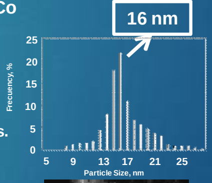
20Co/ZnO-R: Lower Co metallic particle size.

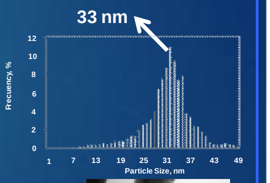
[5]

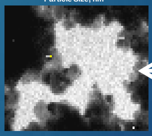


20Co/ZnO-R
Higher Reduction Tª.
↓
Higher Co-support interactions.
↓
Lower Co metallic particle size.
↓
Smaller is better for ethanol steam reforming [7].

TEM







Reduced

20Co/ZnO-R
20Co/ZnO-C

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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