Supporting Information

Tuning products selectivity in the catalytic oxidation of glycerol employing Metal-ZSM-11 materials

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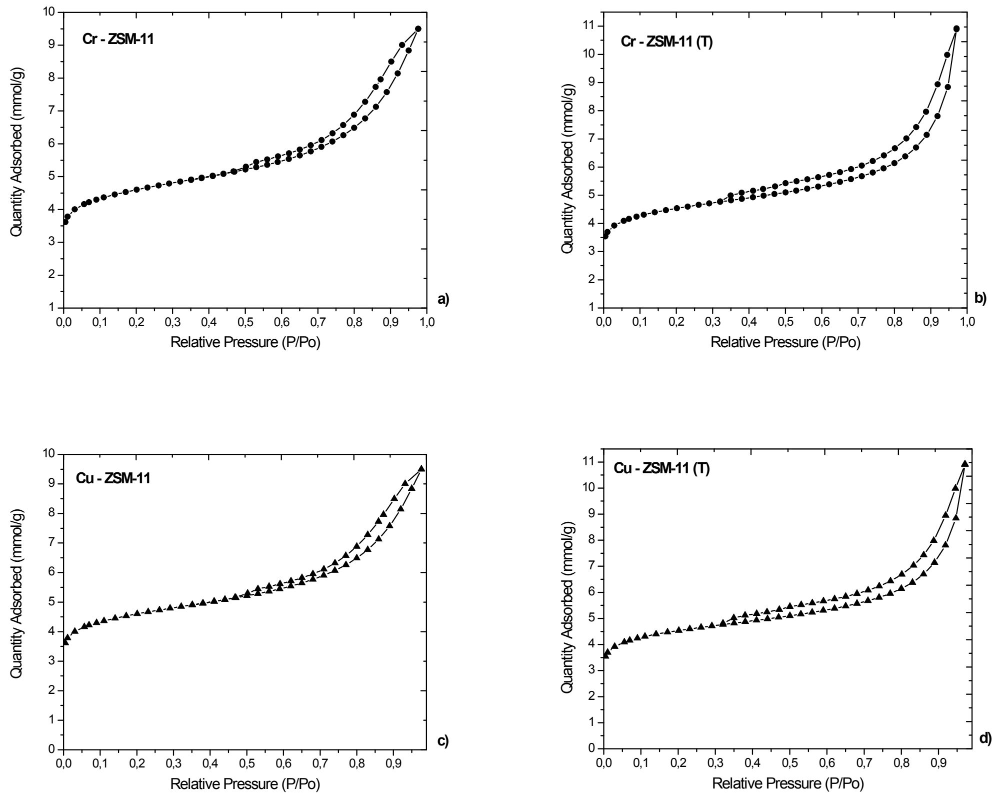
S1. N_2 sorption isotherms of synthesized zeolites.

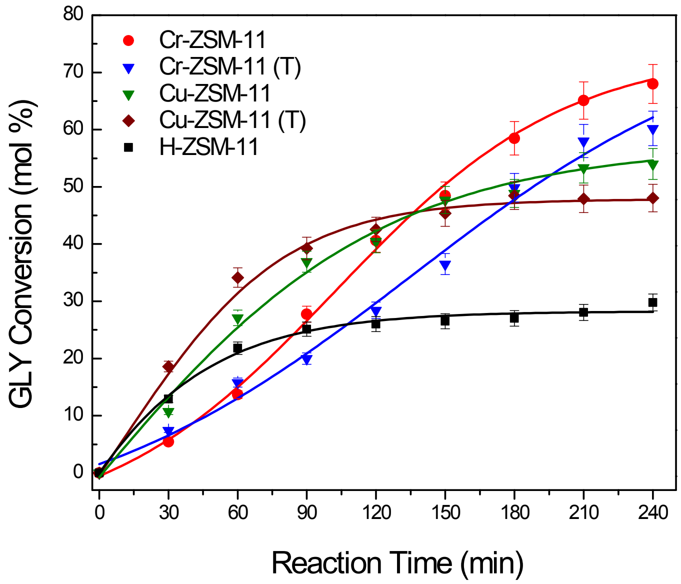


S2. Main textural properties of the catalysts.

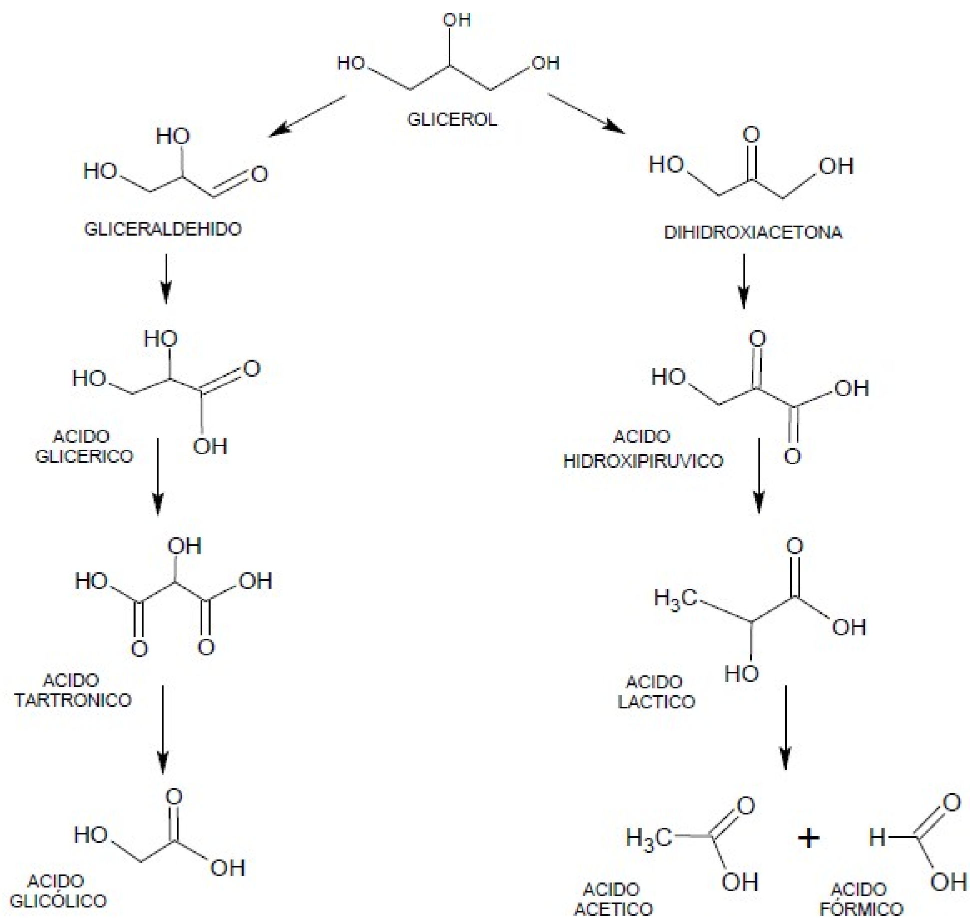
Catalysts	Micropore Volume (cm^3/g)	Mesoporous Volume (cm^3/g)	Total pore Volume (cm^3/g)	Pore Diameter (nm)
	t - Plot	$V_{Total} - V_{micro}$	**	**BJH**
ZSM-11	0,126	0.091	0.217	2.07
ZSM-11 (T)	0.061	0.314	0.376	4.22
Cu-ZSM-11	0,116	0,085	0,202	1,99
Cu-ZSM-11 (T)	0,105	0,246	0,351	5,00
Cr-ZSM-11	0,104	0,125	0,229	2,01
Cr-ZSM-11 (T)	0,104	0,257	0,361	5,20

* Results obtained using ASAP 2001 equipment

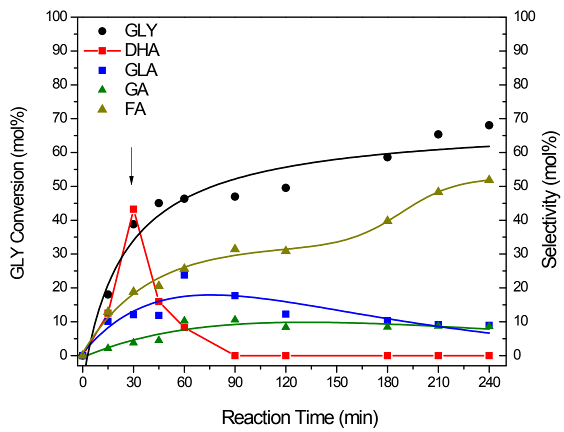
S3. Effect of type of catalyst on glycerol conversion.



S4. Reaction network



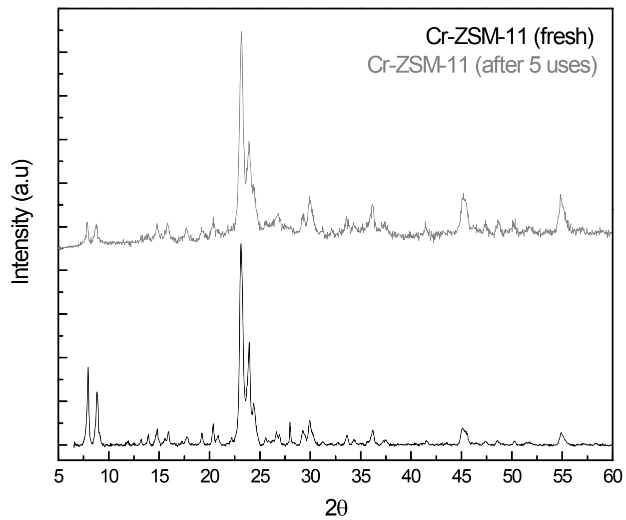
S5. Slowly addition of H_2O_2 in the reaction system and its effect on GLY conversion and DHA selectivity employing Cr-ZSM-11.



S6. Acid sites of Cr-ZSM-11 fresh and used

μmol of site/ g catalyst	B/L
Cr-ZSM-11 (Fresh)	2,9614
Cr-ZSM-11 (1st cycle)	2,7313
Cr-ZSM-11 (5th cycle)	2,7215

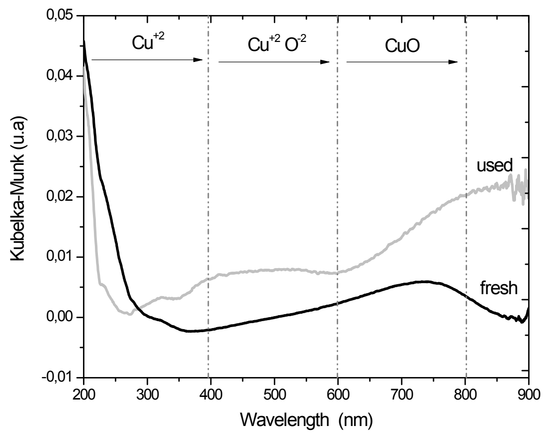
S7. XRD patterns of Cr-ZSM-11 fresh (black) and Cr-ZSM-11 after five cycles (grey).



S8. Acid sites of Cu-ZSM-11 fresh and used

μmol of site/g catalyst	L/B
Cu-ZSM-11 (fresh)	1,550
Cu-ZSM-11 (after 1h)	1,000
Cu-ZSM-11 (after 4 h)	0,783

S9. Diffuse reflectance spectra in the UV–visible region of fresh and used Cu-ZSM-11 for three cycles.



The figure above shows the UV–vis-DRS spectra of the fresh and used (after three catalytic cycles) Cu-ZSM-11 catalyst. The spectra exhibit three bands centred at about 200 and 400 nm, another from 400 to 600, and a last broad band between 600 and 800 nm. The first band is assigned to the isolated mononuclear Cu^{+} cations possibly in coordination with lattice oxygen, which suggests that some Cu ions are incorporated into the framework. The second band is assigned to [Cuı+· · ·Oı−· · ·Cuı+] clusters possibly inserted into the channels of the zeolite. The band between 600 and 800 nm can be attributed to d–d transitions of Cu^{2+} ions, which is assigned to copper species in the extra framework position (i.e. CuO). Some variations in these bands are exhibited for the fresh and used catalysts, and some significant changes in the intensity were observed. These data could indicate that the catalyst suffers modifications after the oxidation reaction, this suggesting a loss of active Cu^{+2} species probably due to the higher deposition of carbonaceous compounds on the solid catalyst (1).

References

1. Cánepa AL, Chanquía CM, Eimer GA, Casuscelli SG. Applied Catalysis A : General Oxidation of olefins employing mesoporous molecular sieves modified with copper. “Applied Catalysis A, General” [Internet]. 2013;462–463:8–14. Available from: http://dx.doi.org/10.1016/j.apcata.2013.04.031