HETEROGENEOUS CATALYTIC ACTIVITY ON Mn, Fe AND Co-BASED METALLOPORPHYRINIC SOLID COORDINATION FRAMEWORKS (SCFs)

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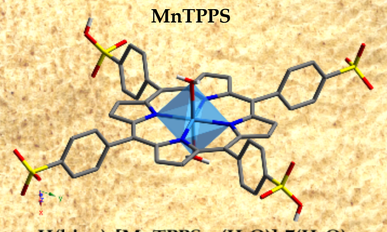
INTRODUCTION

Solid Coordination Frameworks (SCFs) have been widely explored on different catalytic reactions,[1] and during the past years metalloporphyrins have been investigating in order to mimick their natural activity in the solid state.[2]

Herein we present the catalytic activity results towards the oxidation reactions of different alcohols for MnTPPS, FeTCPP and CoTPPS based metalloporphyrinc SCFs (TPPS= *meso*-tetrasulfonatophenylporphyrin, TCPP= *meso*-tetracarboxyphenylporphyrin).[3] Additionally, Knoevenagel condensations and a "one-pot" reaction involving the FeTCPP based SCF catalyst have been carried out.

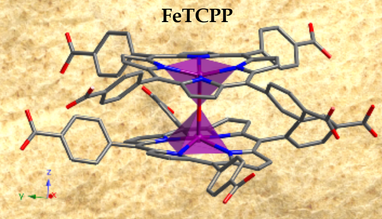
STUDIED COMPOUNDS

Monomers
MnTPPS



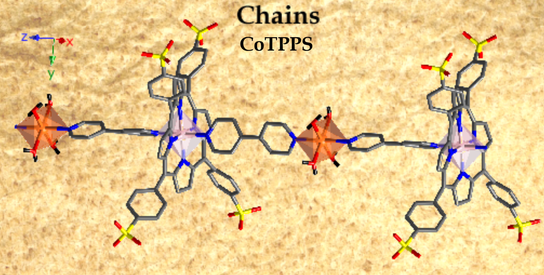
$H(bipy)_2[MnTPPS_{0.5}(H_2O)]\cdot 7(H_2O)$

Dimers
FeTCPP



μ-O-$[FeTCPP]_2\cdot 16DMF$ [3a]

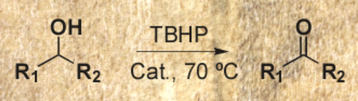
Chains
CoTPPS



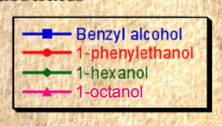
$[CoTPPS_{0.5}(bipy)(H_2O)_2]\cdot 6H_2O$ [3b]

CATALYTYC ACTIVITY TESTS

Alcohol oxidation



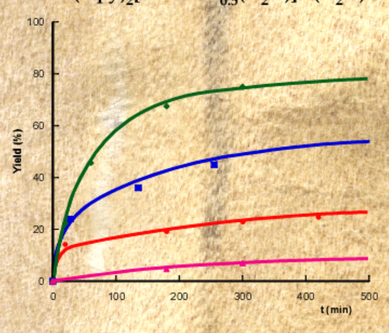
Substrates



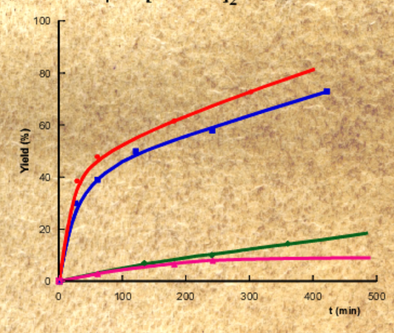
Substrate	Oxidant	MnTPPS C_T	MnTPPS TOF (h^{-1})	FeTCPP C_T	FeTCPP TOF (h^{-1})	CoTPPS C_T	CoTPPS TOF (h^{-1})
Benzyl alcohol	TBHP	70	72	73	72	77	143
1-phenylethanol	TBHP	44	46	73	91	44	8
1-hexanol	TBHP	92	66	15	3	71	22
1-octanol	TBHP	12	6	9	3	25	6

TBHP: *tert*-butyl hydroperoxyde, TOF: turnover frequency, C_T: total conversion

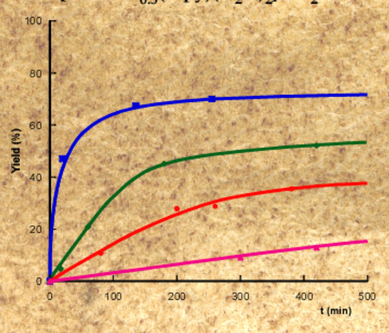
$H(bipy)_2[MnTPPS_{0.5}(H_2O)]\cdot 7(H_2O)$



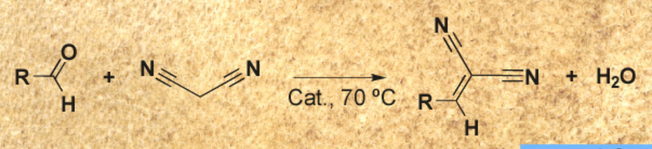
μ-O-$[FeTCPP]_2\cdot 16DMF$ [3a]



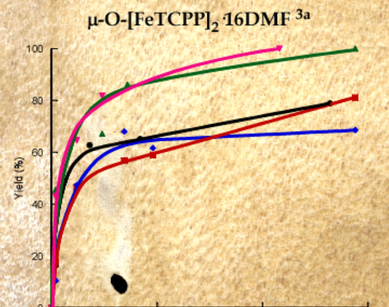
$[CoTPPS_{0.5}(bipy)(H_2O)_2]\cdot 6H_2O$ [3b]



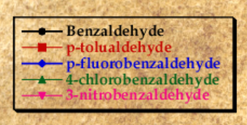
Knoevenagel condensation



μ-O-$[FeTCPP]_2\cdot 16DMF$ [3a]

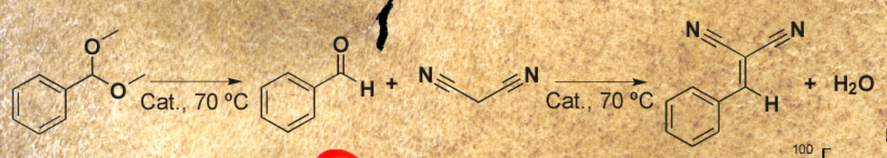


Substrates

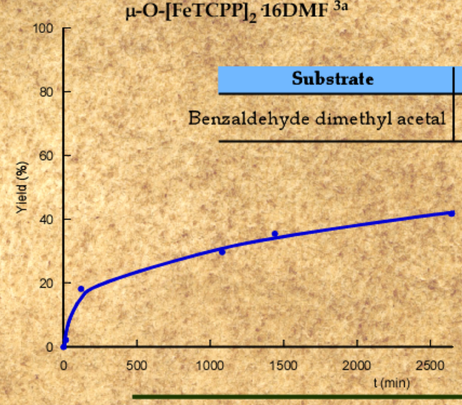


Substrate	C_T	TOF (h^{-1})
Benzaldehyde	79	49
p-tolualdehyde	81	53
p-fluorobenzaldehyde	69	32
4-chlorobenzaldehyede	100	137
3-nitrobenzaldehyde	100	129

"One-pot" reaction: hydrolysis of acetal + Knoevenagel condensation



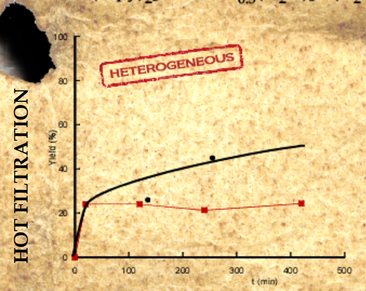
μ-O-$[FeTCPP]_2\cdot 16DMF$ [3a]



Substrate	C_T	TOF (h^{-1})
Benzaldehyde dimethyl acetal	42	10

HETEROGENEITY AND RECYCLABILITY TESTS

$H(bipy)_2[MnTPPS_{0.5}(H_2O)]\cdot 7(H_2O)$

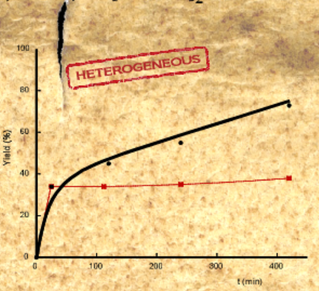


HOT FILTRATION

RECYCLING

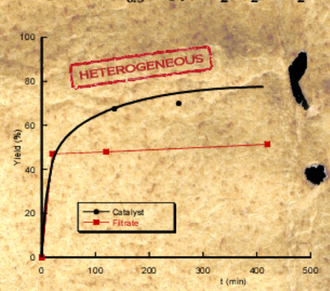
Cycles	C_T (4h)
1	40%
2	31.3%
3	30.69%
4	26.8%
5	26.4%

μ-O-$[FeTCPP]_2\cdot 16DMF$ [3a]



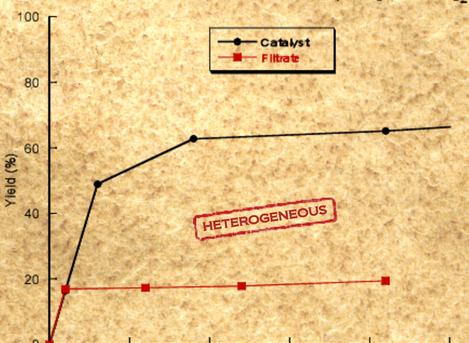
Cycles	C_T (4h)
1	58%
2	77%
3	98%

$[CoTPPS_{0.5}(bipy)(H_2O)_2]\cdot 6H_2O$ [3b]



Cycles	C_T (4h)
1	27.31%
2	31.42%
3	32%
4	26.8%
5	26%

μ-O-$[FeTCPP]_2\cdot 16DMF$ [3a]



Cycles	C_T (4h)
1	34.46%
2	33.07%
3	33.95%
4	25.6%
5	21.03%

CONCLUSIONS

-MnTPPS, FeTCPP and CoTPPS based metalloporphyrinc SCFs are promising heterogeneous catalysts.

-The most important feature of the compounds herein studied is not their dimensionality but the accesibility to the active centers of the network.

REFERENCES

[1] Liu, J.; Chen, L.; Cui, H.; Zhang, J.; Zhang, L.; Su, C-Y., *Chem. Soc. Rev.*, **2014**, *43*, 6011-6061.

[2] Zhang, Z.; Zhang, L.; Wojtas, L.; Eddaoudi, M,; Zaworotko, M.J.; *J. Am. Chem. Soc.*, **2012**, *134*, 928-933.

[3] (a) Fidalgo-Marijuan, A.; Barandika, G.; Bazán, B.; Urtiaga, M.K.; Larrea, E.S.; Iglesias, M.; Lezama, L.; Arriortua,M.I., *Dalton Trans.*, **2015**, *44*, 213-222. (b) Fidalgo-Marijuan, A.; Barandika, G.; Bazán, B.; Urtiaga, M.K.; Arriortua, M.I., *CrystEngComm*, **2013**, *15*, 4181-4188.

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