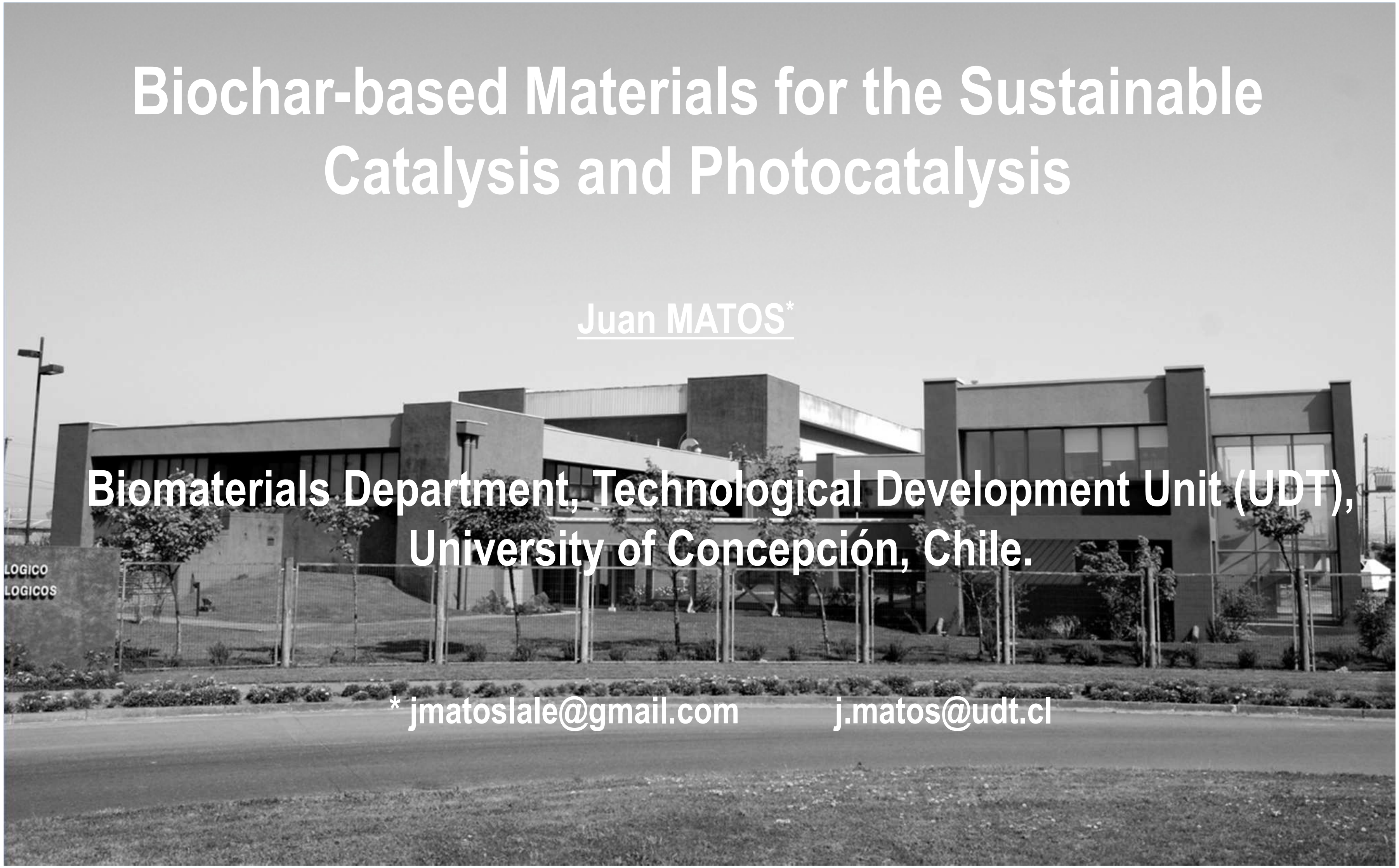

Biochar-based Materials for the Sustainable Catalysis and Photocatalysis

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1. Biochars and Photocatalysis

7300 MM People

800 MM: No Potable Water

2500 MM: Water with Insufficient Treatment

80% Common Sickness

Polluted Water:

The important problem

> 1 MM Children dead/year*

*Waterfront Inform 2014, World Health Organization (www.who.com)

TiO_2 is the best Photocatalysts for the Treatment of Polluted Water and Air

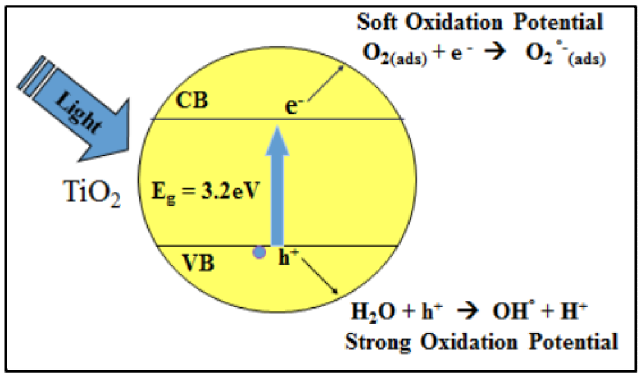
However, it has important scale-up limitations

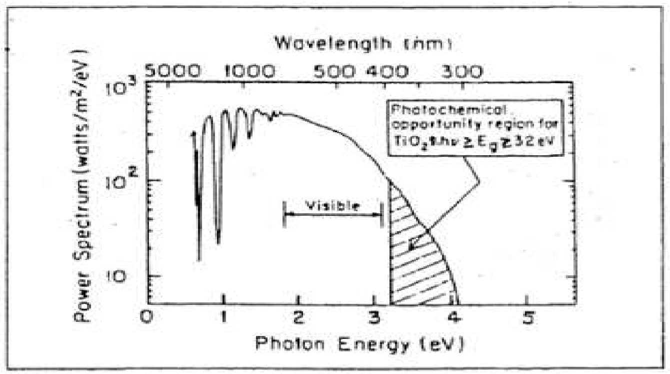
Advantages

1. Highest photoefficiency.
2. Photostable under UV.
3. Resist strong acid/bases
4. Bio-inert.
5. Relatively Cheap

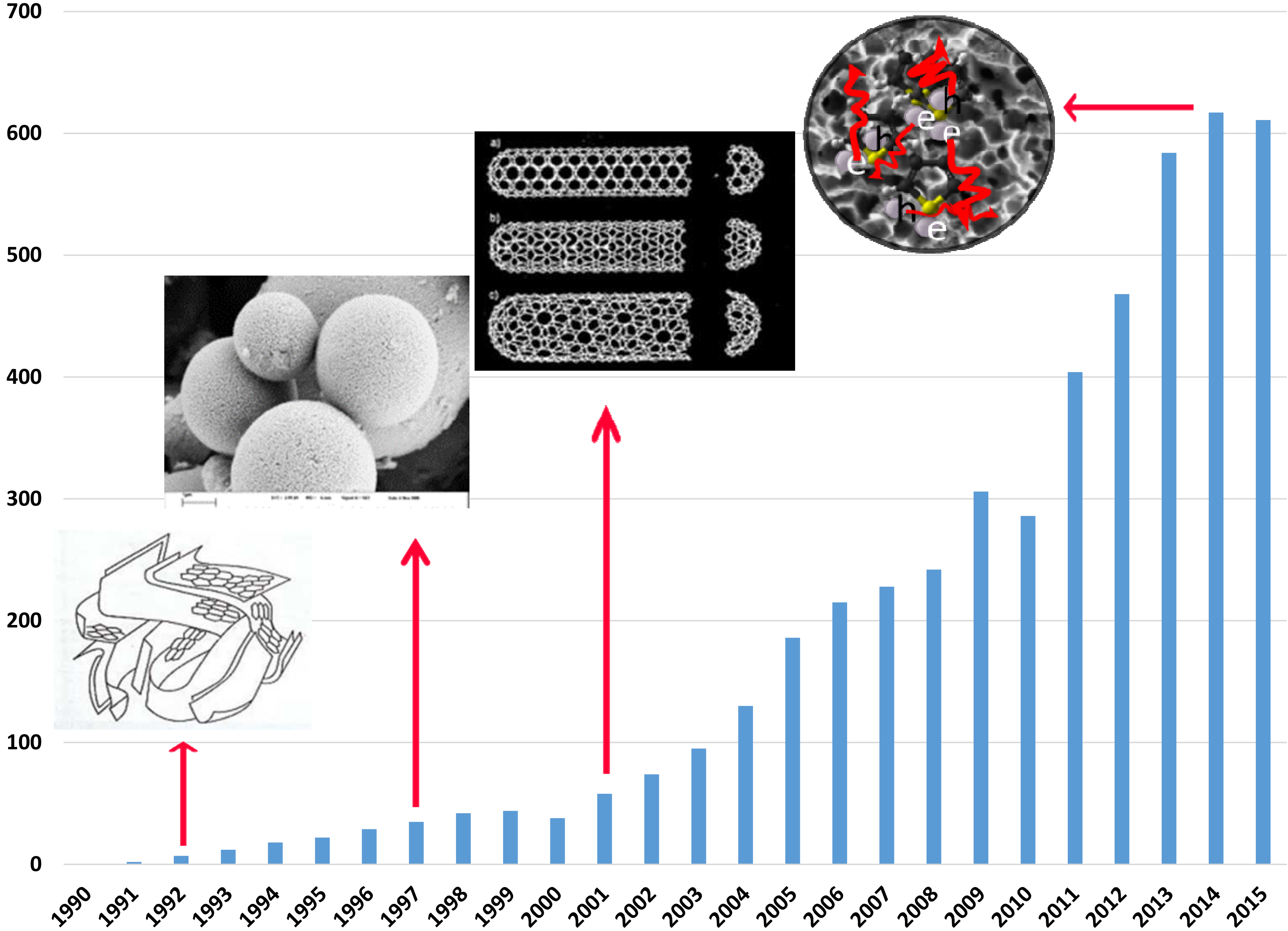
Limitations

1. High recombination rate (e^-, h^+)
2. Only absorbs 6% Solar Spectra ➔ Non-operative scaling-up.
3. Commonly low surface area ➔ Diluted systems.
4. Very sensitive to pH of solution ➔ Recombination

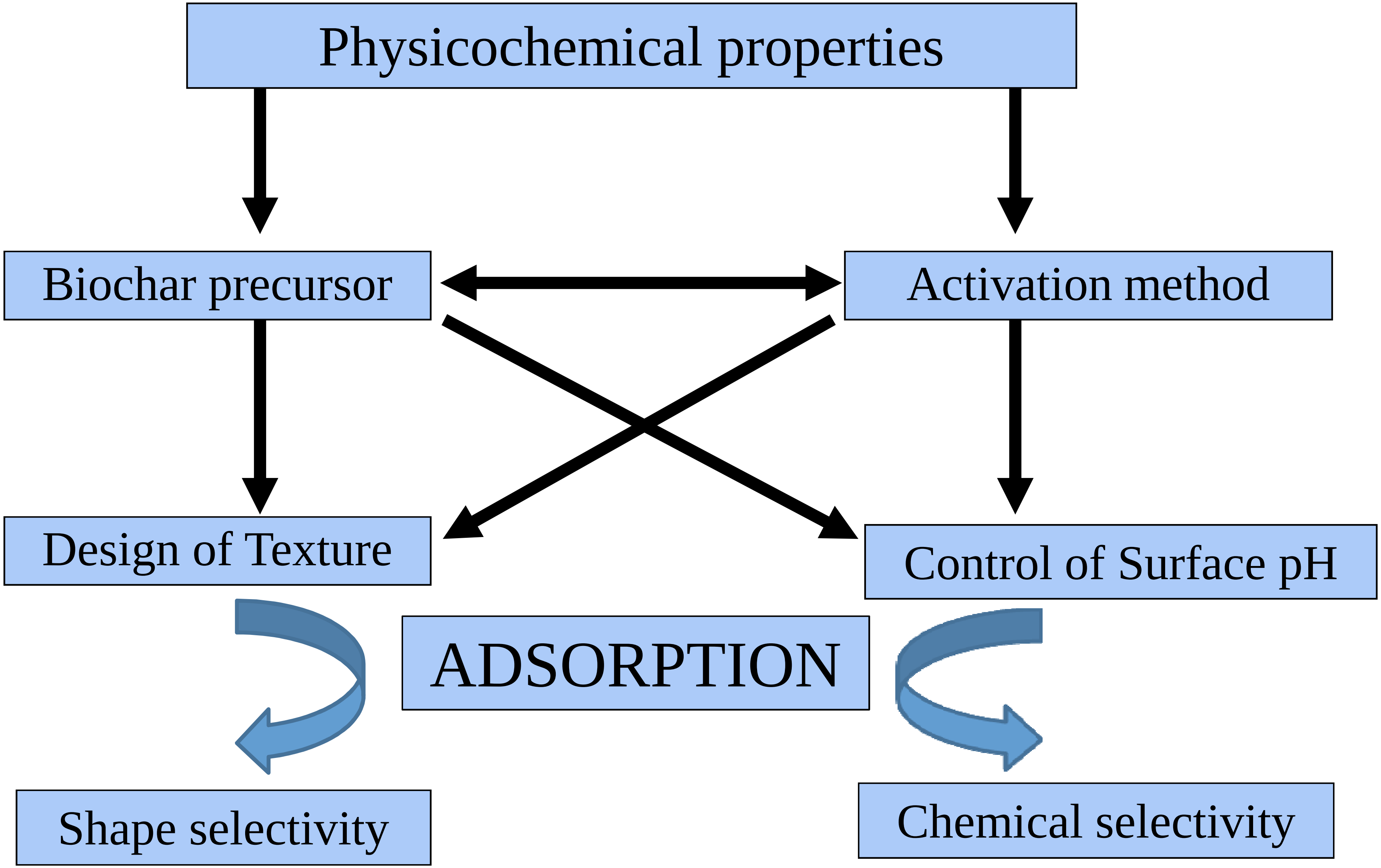




Carbon & Photocatalysis: 4753 papers (Scopus, Oct. 19, 2015)



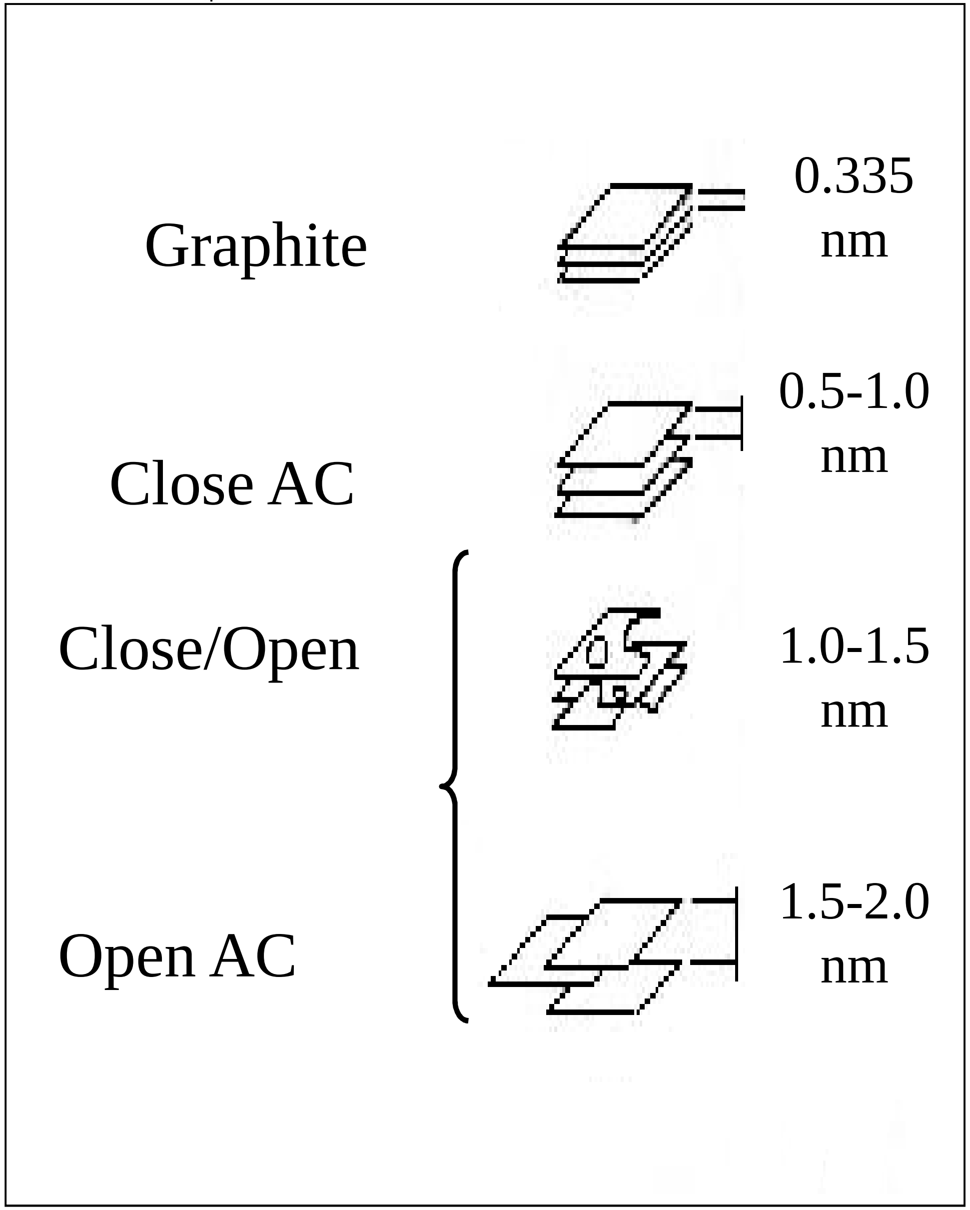
Biochars Functionality

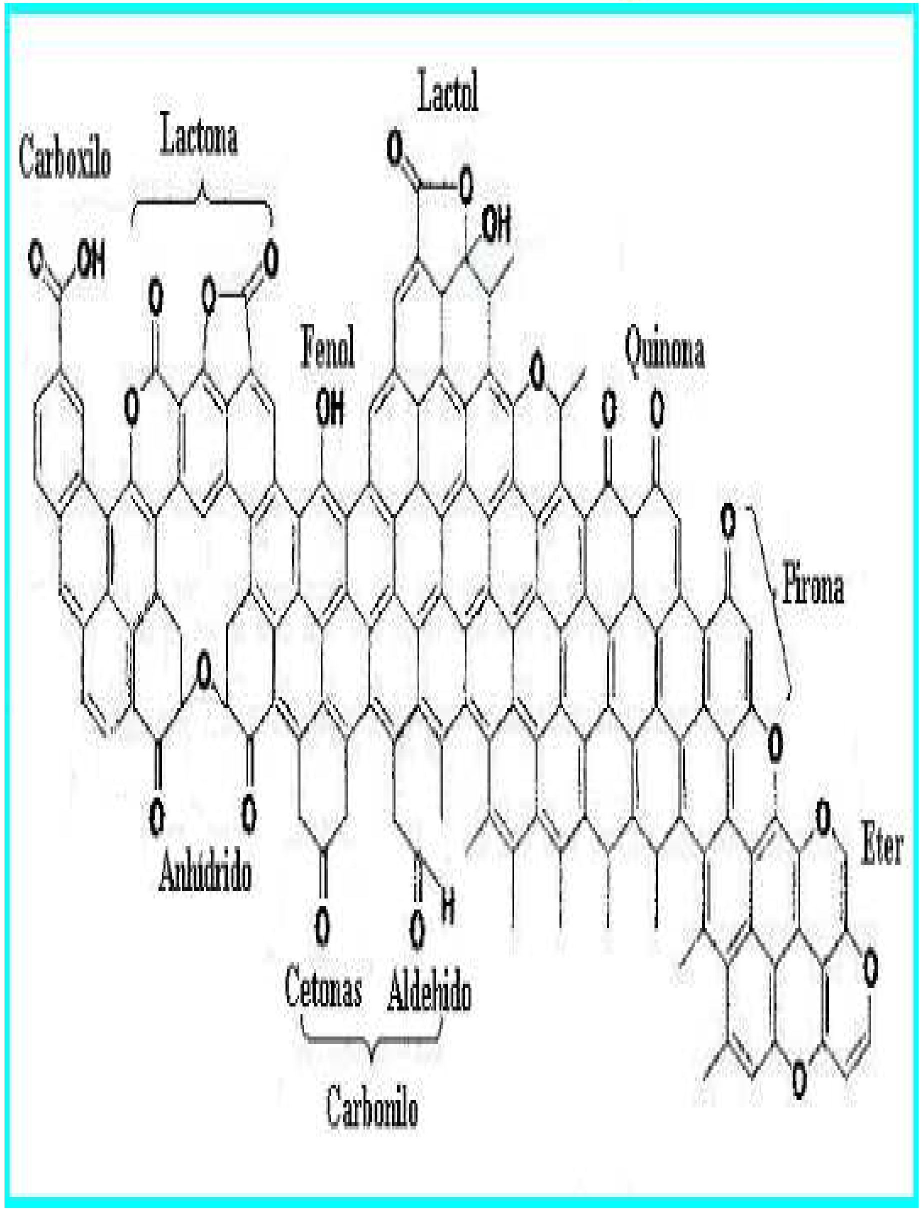


J. Mater. Sci., 39 (2004) 3705

J. Molec. Catal. A., 228 (2005) 189

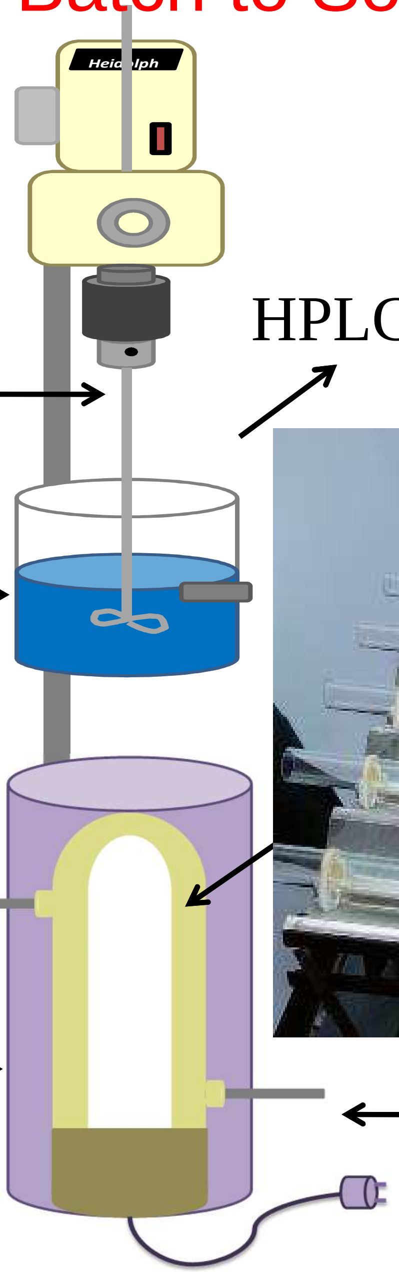
Topology/Surface Chemistry of AC





J. Matos et al., J. Mater. Sci., 39 (2004) 3705

Experimental: From Batch to Solar Photoreactors



HPLC (UV detector at 280nm)

Mechanical Stirring

TiO_2 + AC + Pollutant

Water Outlet

Water-circulating cell:

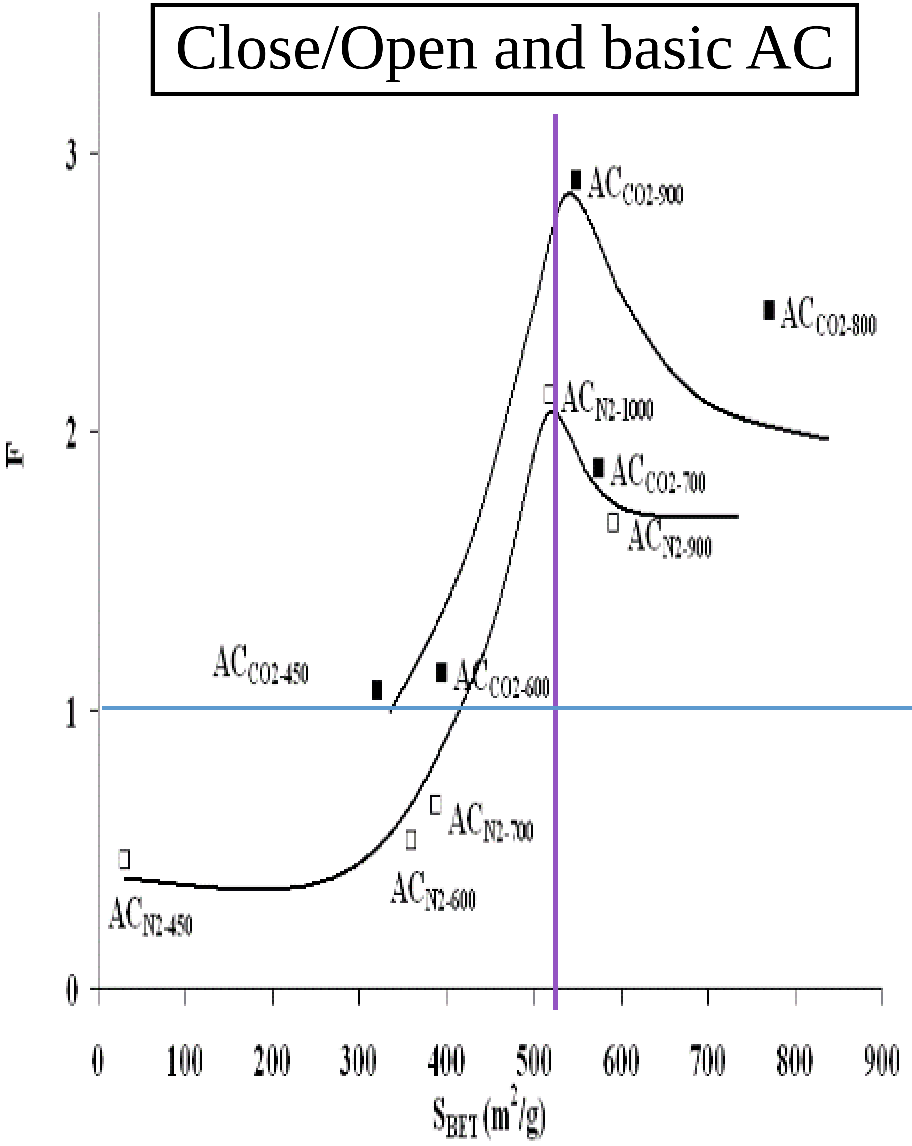
Pyrex, $\lambda < 340$nm

Water Inlet

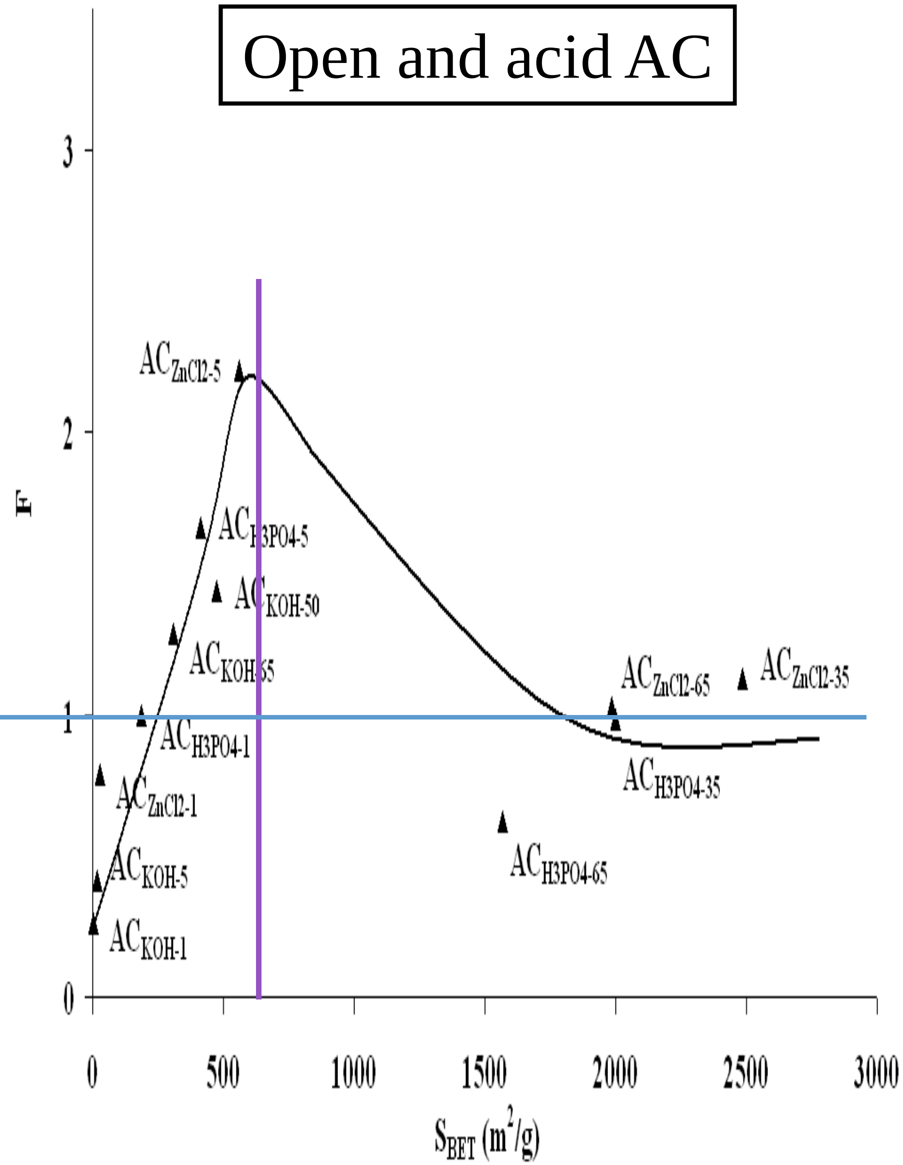
Power Supply

J. Matos et al., J. Mater. Sci., 45 (2010) 4934

4CP photodegradation as a function of S_{BET}

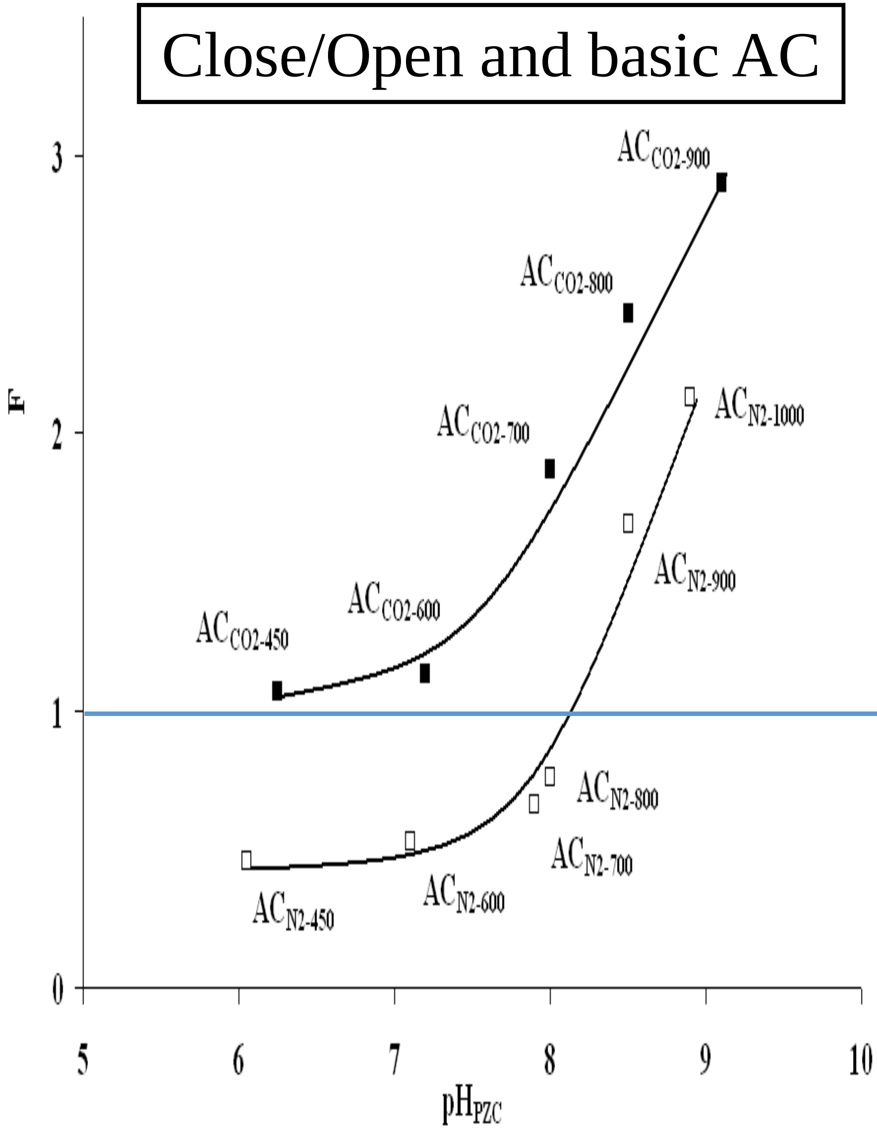


J. Matos et al., TOEEJ, 2 (2009) 21-29

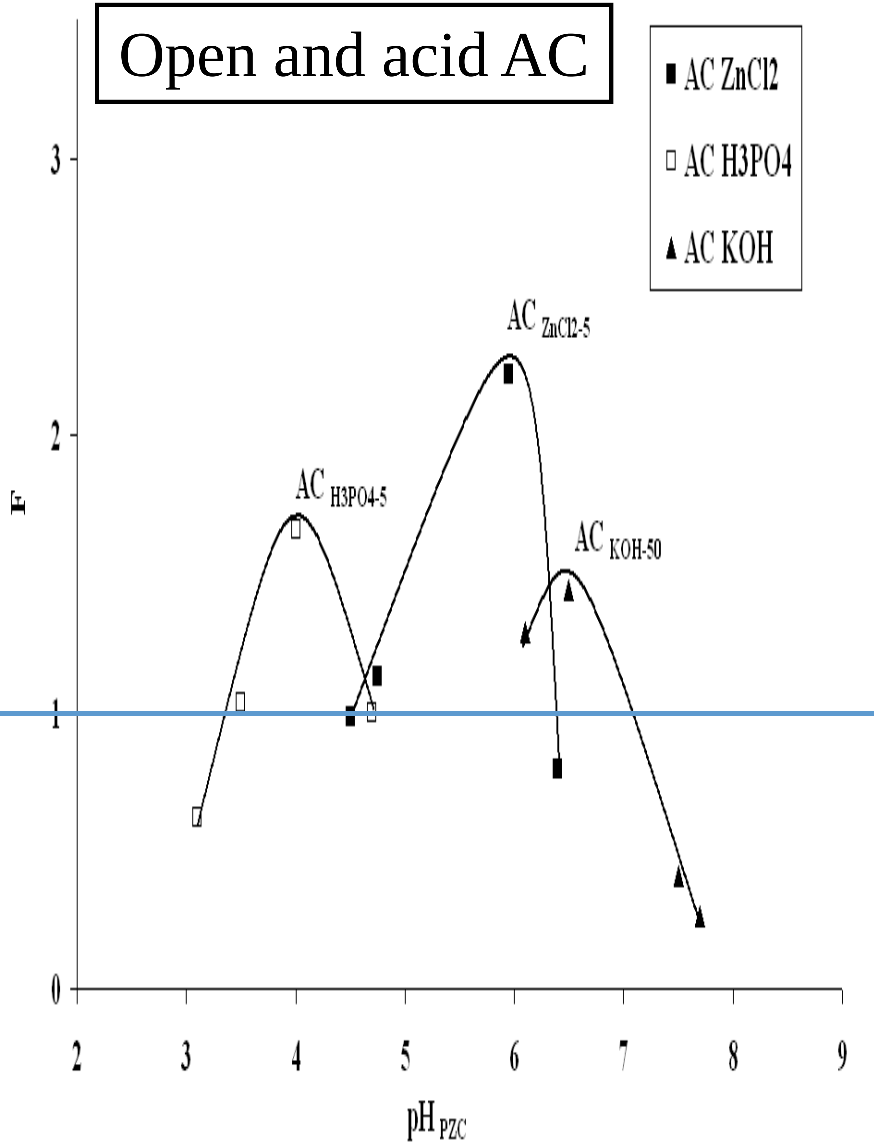


J. Matos et al., J. Mater. Sci., 45 (2010) 4934

4CP Photodegradation as a function of pH_{PZC}



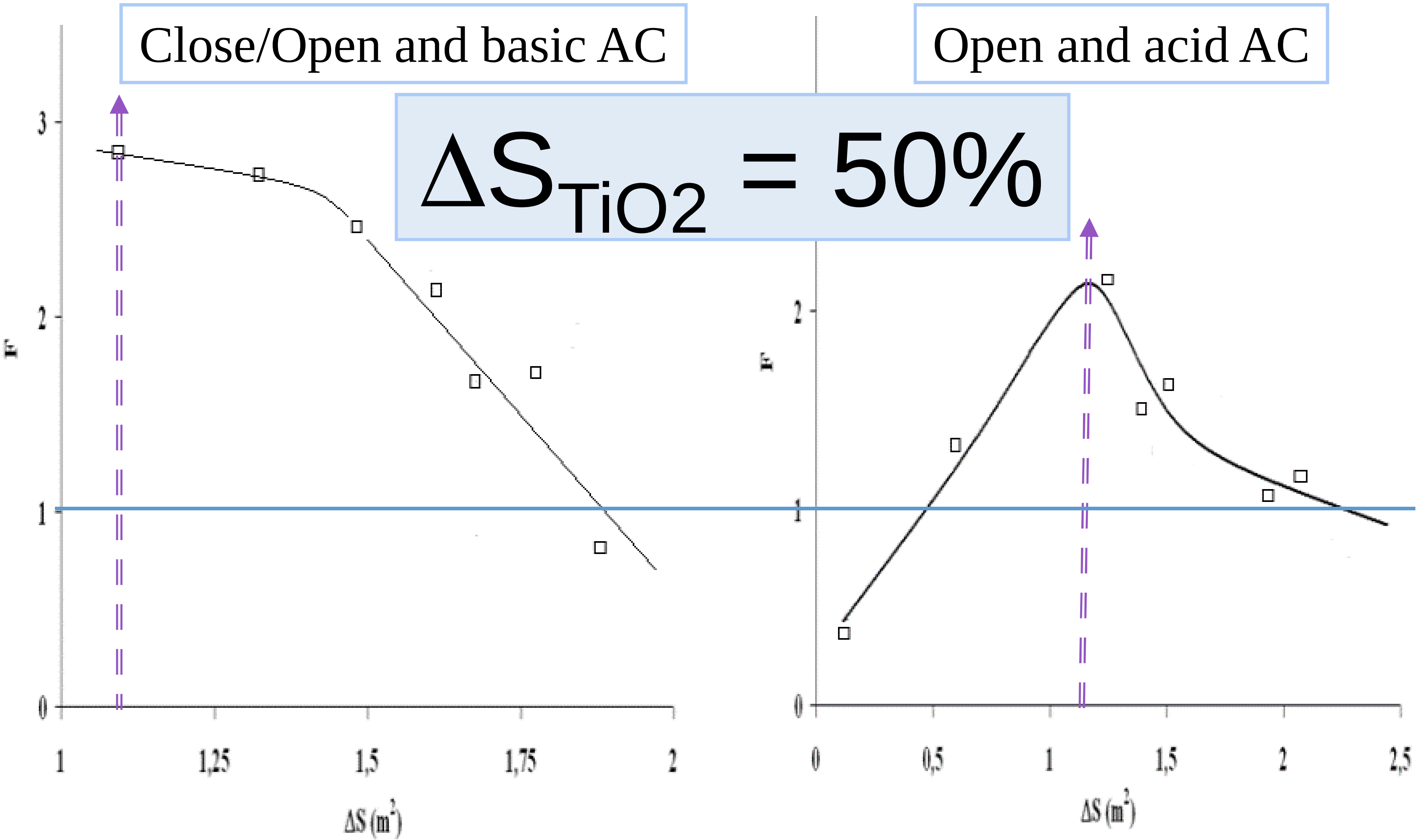
J. Matos et al., TOEEJ, 2 (2009) 21-29



J. Matos et al., J. Mater. Sci., 45 (2010) 4934

4CP Photodegradation as a function of ΔS: TiO_2-AC

$\Delta S = [\Delta n_T/d_{TiO2} + d_{AC}]$ $d_i = (n_T/S_{BET}.m)$



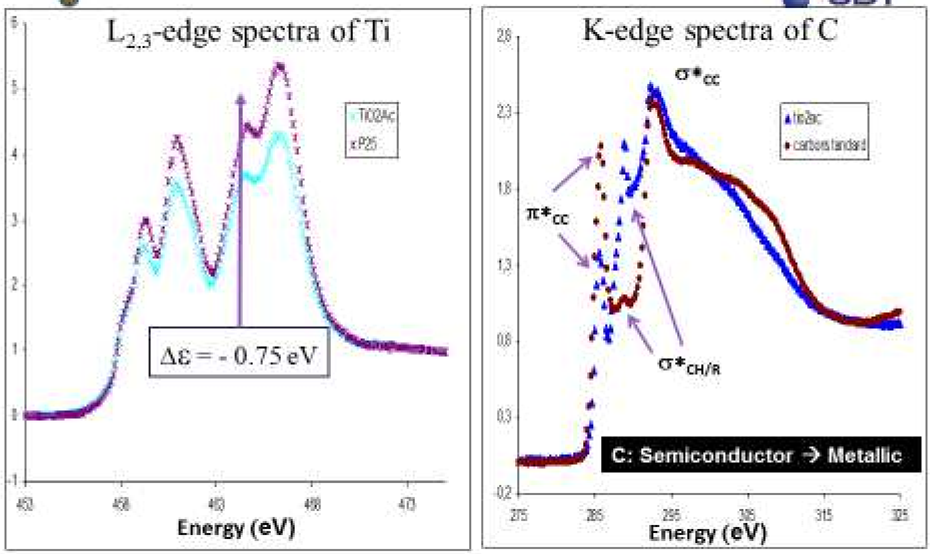
Appl. Catal. B., 18 (1998) 281 Appl. Catal. B. 99 (2010) 170 J. Mater. Sci., 45 (2010) 4934

orto- vs. para-hydroxylation

Photocatalyst	HQ+BQ (μmol)	4CT (μmol)	R(o/p)	F(o/o)
TiO_2	0.476	0.037	0.08	1.00
TiO_2-$AC_{N2-1000}$	0.487	0.059	0.12	1.60
TiO_2-AC_{N2-900}	0.300	0.068	0.23	1.84
TiO_2-AC_{N2-800}	0.210	0.700	3.33	18.9
TiO_2-AC_{N2-700}	0.139	0.817	5.88	22.1
TiO_2-AC_{N2-600}	0.135	0.805	5.96	21.8
TiO_2-AC_{N2-450}	0.106	0.790	7.45	21.4
TiO_2-$AC_{H3PO4-1\%}$	0.363	0.108	0.30	2.92
TiO_2-$AC_{H3PO4-5\%}$	0.381	0.493	1.29	13.3
TiO_2-$AC_{H3PO4-35\%}$	0.442	0.540	1.22	14.6
TiO_2-$AC_{H3PO4-65\%}$	0.690	0.642	0.93	17.4

Catal. Letters, 130 (2009) 568

NEXAFS



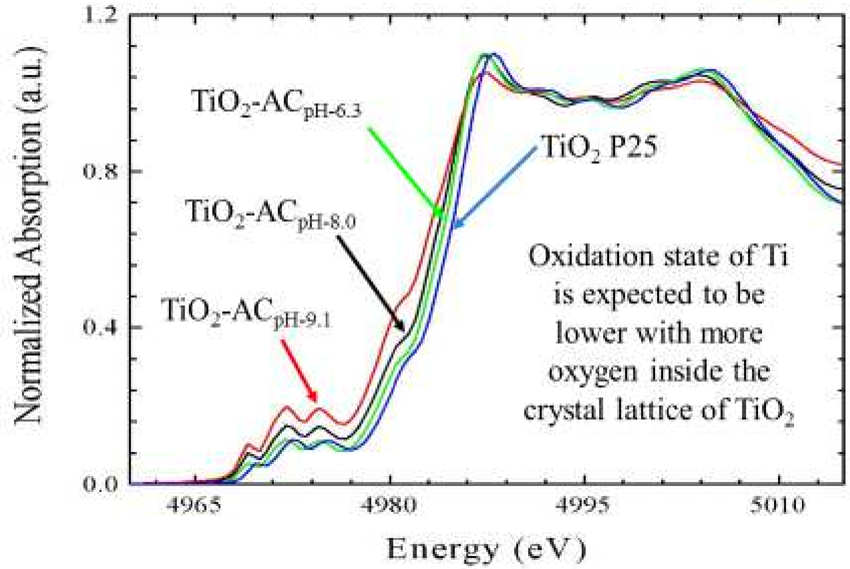
Taken at U7a of NSLS (Brookahven National Laboratory, Upton, NY)

Partial Electron Yields with HV (CEM) 1500 eV; Grid Bias ~150 V

All data normalized to make pre-edge=0 and post-edge=1.

Ex situ Ti K-edge XANES Studies

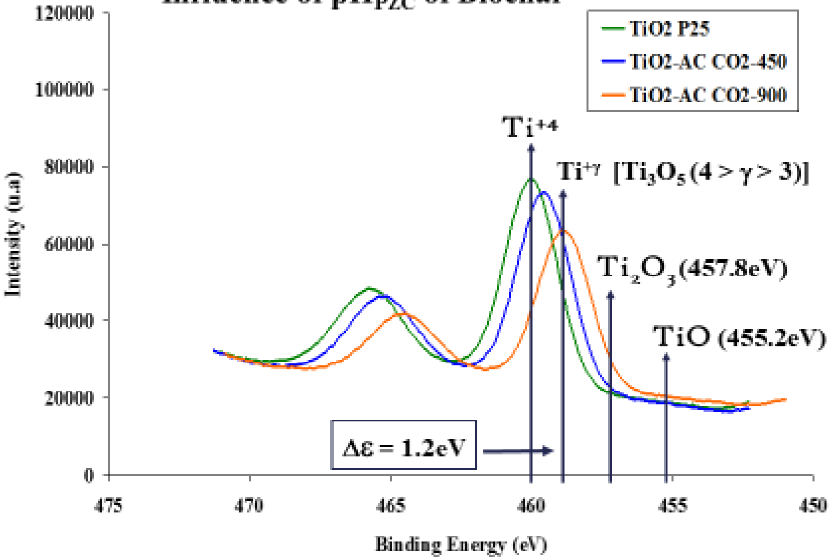
Report for Beam Run at X19A, BNL



J. Matos et al., J. Mater. Sci., 45 (2010) 4934

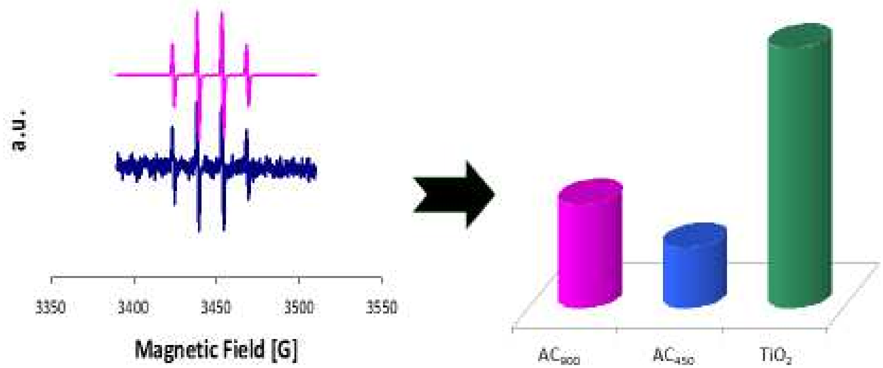
XPS in 2p Ti region

Influence of pH_{PZC} of Biochar



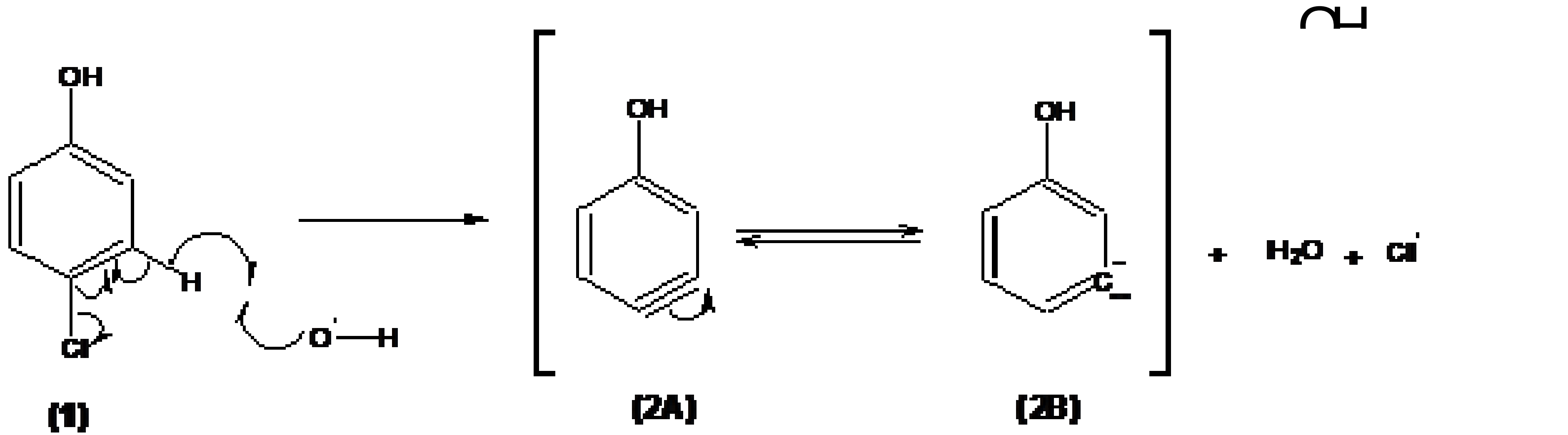
J. Matos et al., J. Mater. Sci., 45 (2010) 4934

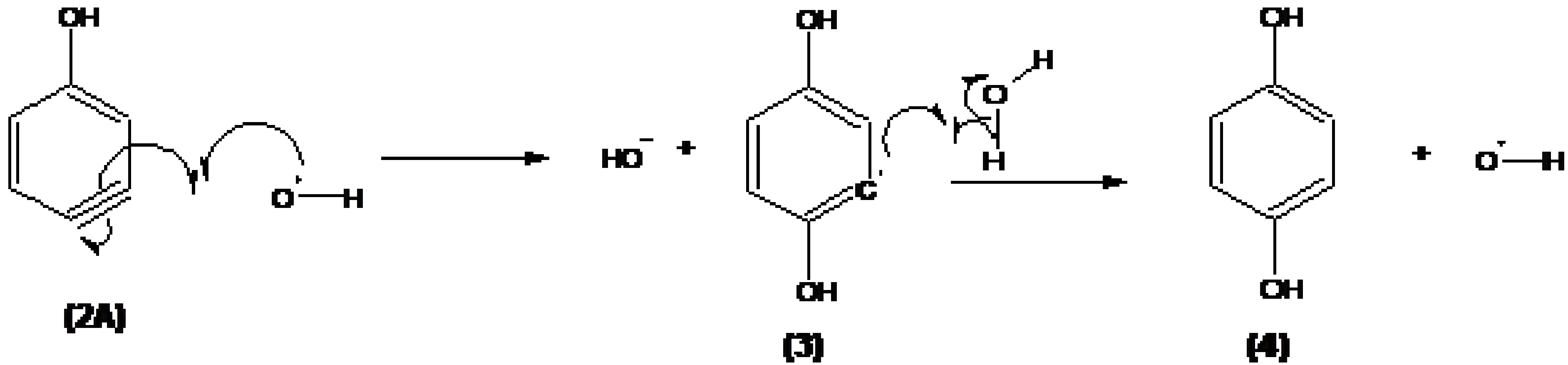
ESR Spectra of DMPO-OH adducts formed after UV-Irradiation of Aqueous Suspensions of TiO_2 and AC



Velazco, Ania, Carmona, Matos, Carbon 73 (2014) 206-221

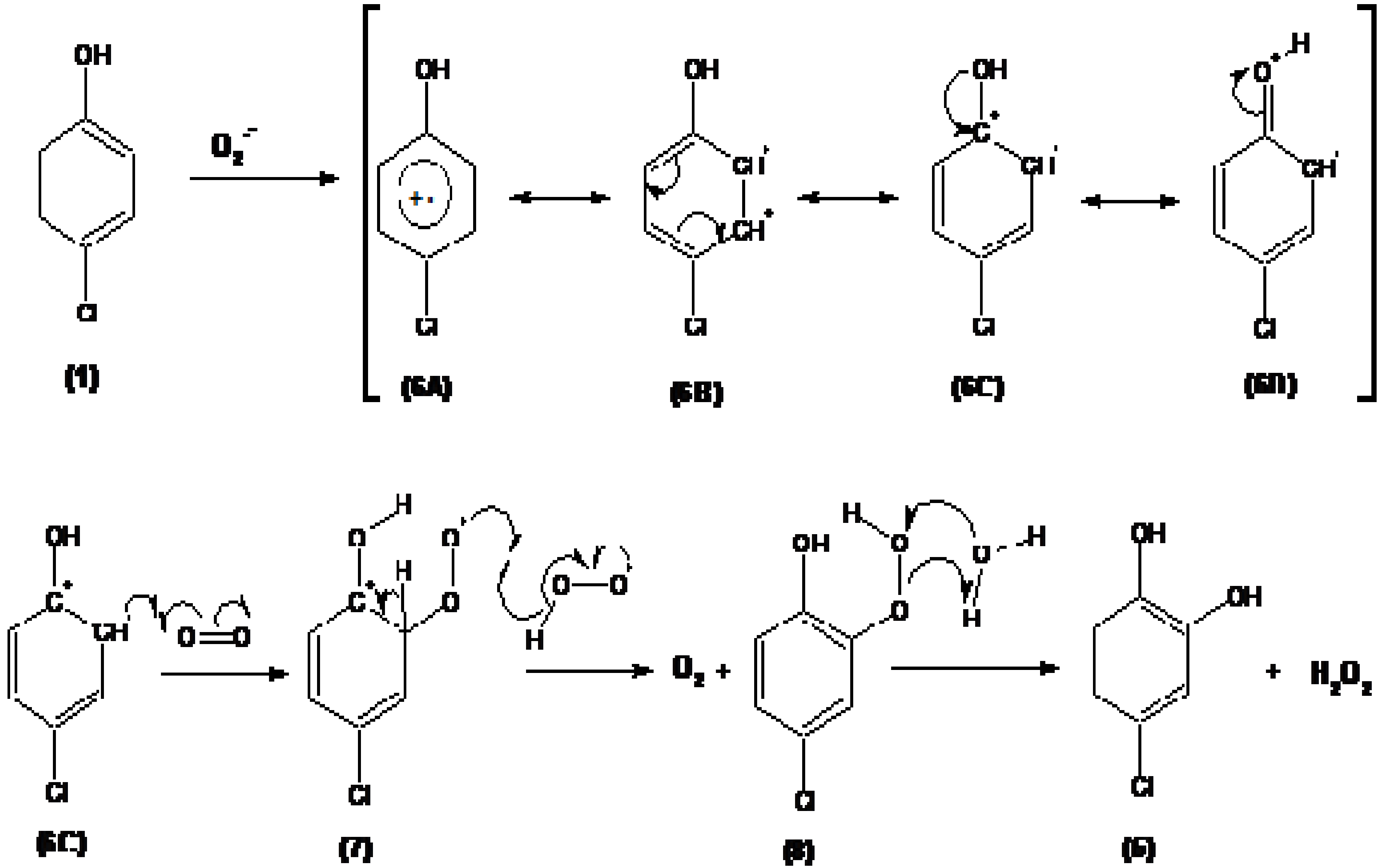
p-hydroxylation mechanism induced by basic surface pHand Close topology of AC





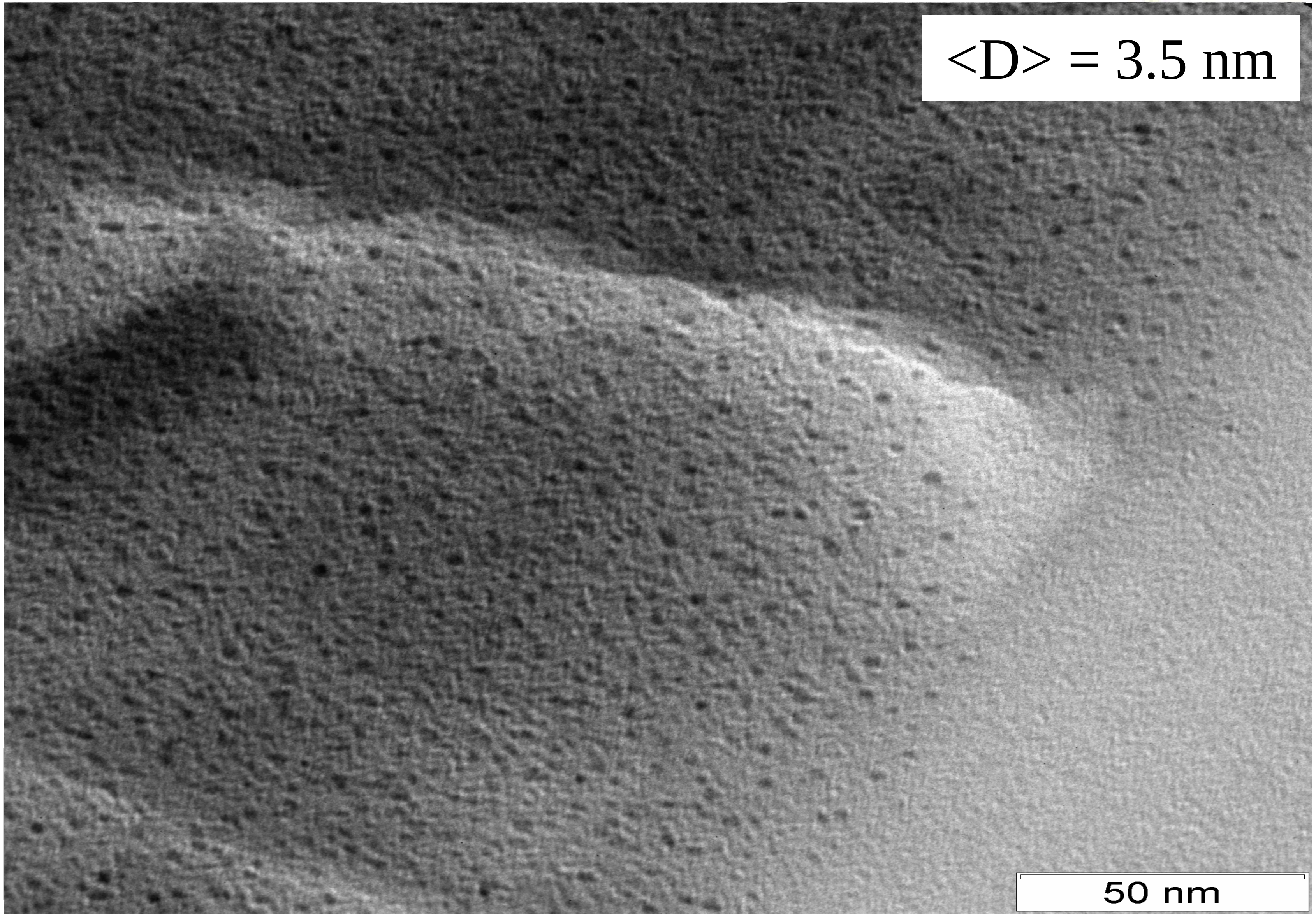
J. Matos et al., J. Mater. Sci., 45 (2010) 4934

o-hydroxylation mechanism induced by acid surface pH and Open topology of AC



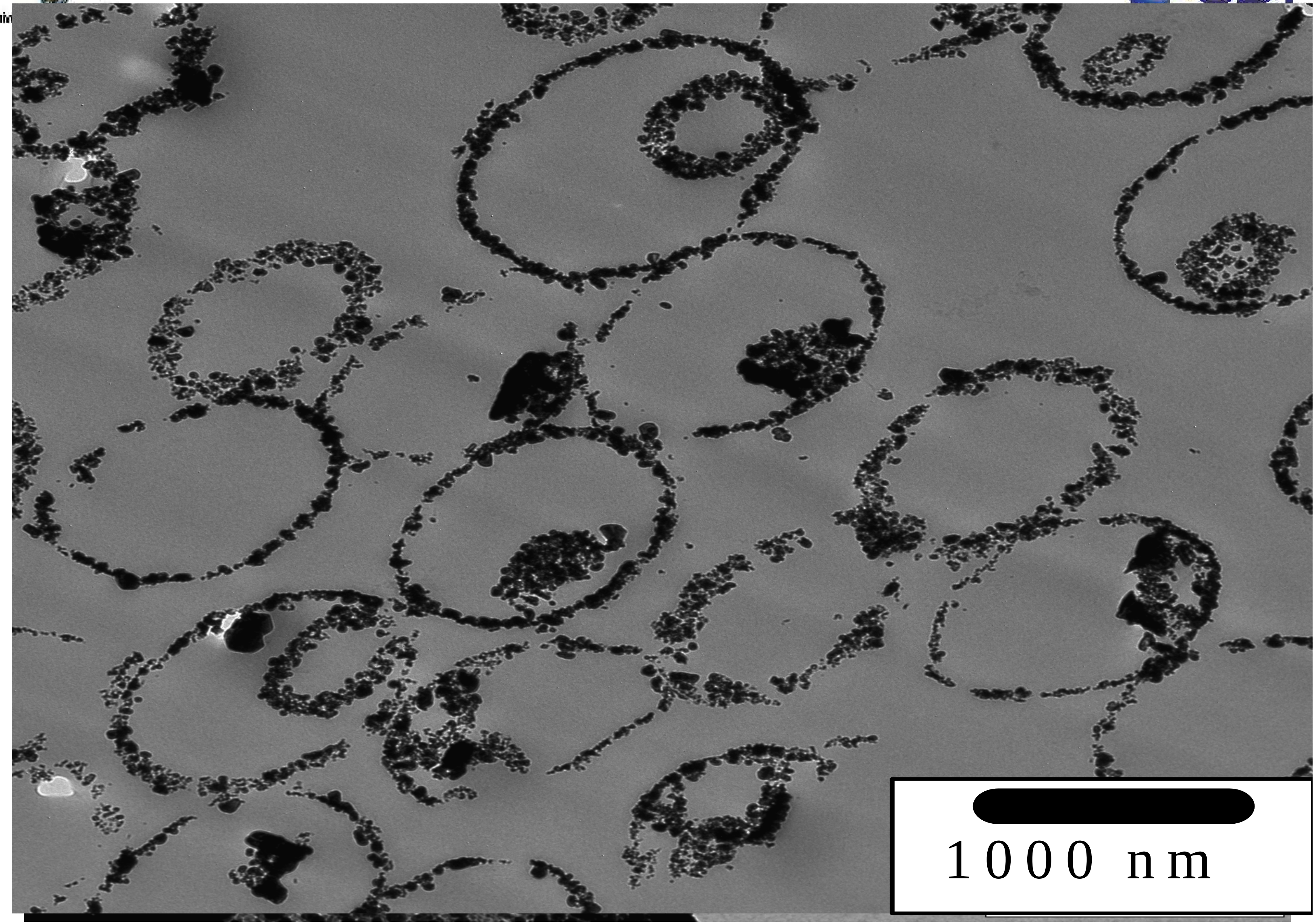
J. Matos et al., J. Mater. Sci., 45 (2010) 4934

SEM and TEM images of Pt-Ru/C



J. Matos, M.M. Titirici, et al., Appl. Catal. A: General 386 (2010) 140-146

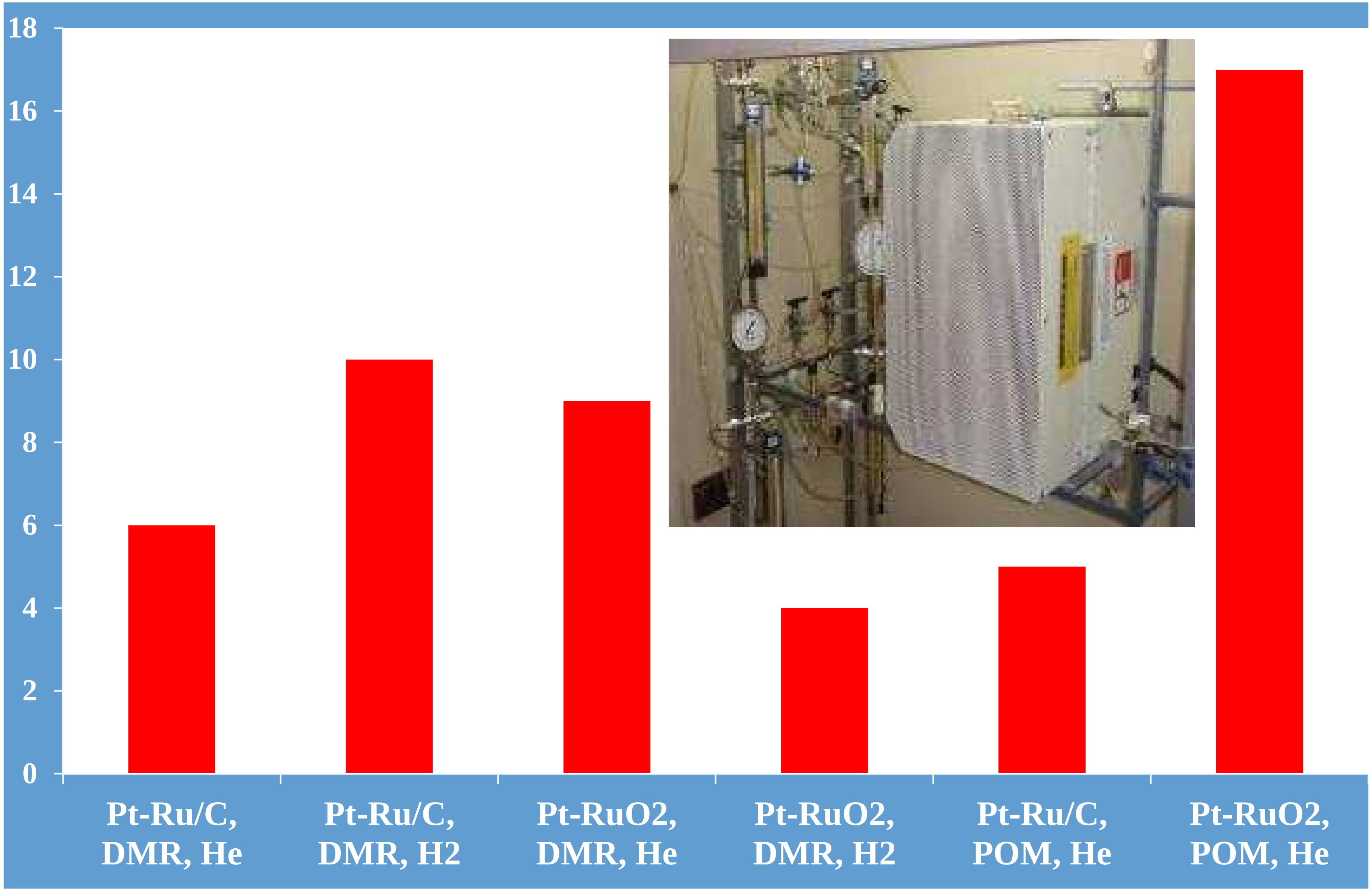
SEM and TEM images of Pt-RuO_2



J. Matos, M.M. Titirici, et al., Appl. Catal. A: General 386 (2010) 140-146

Catalytic Activity (mmoles.g^{-1}.min^{-1})

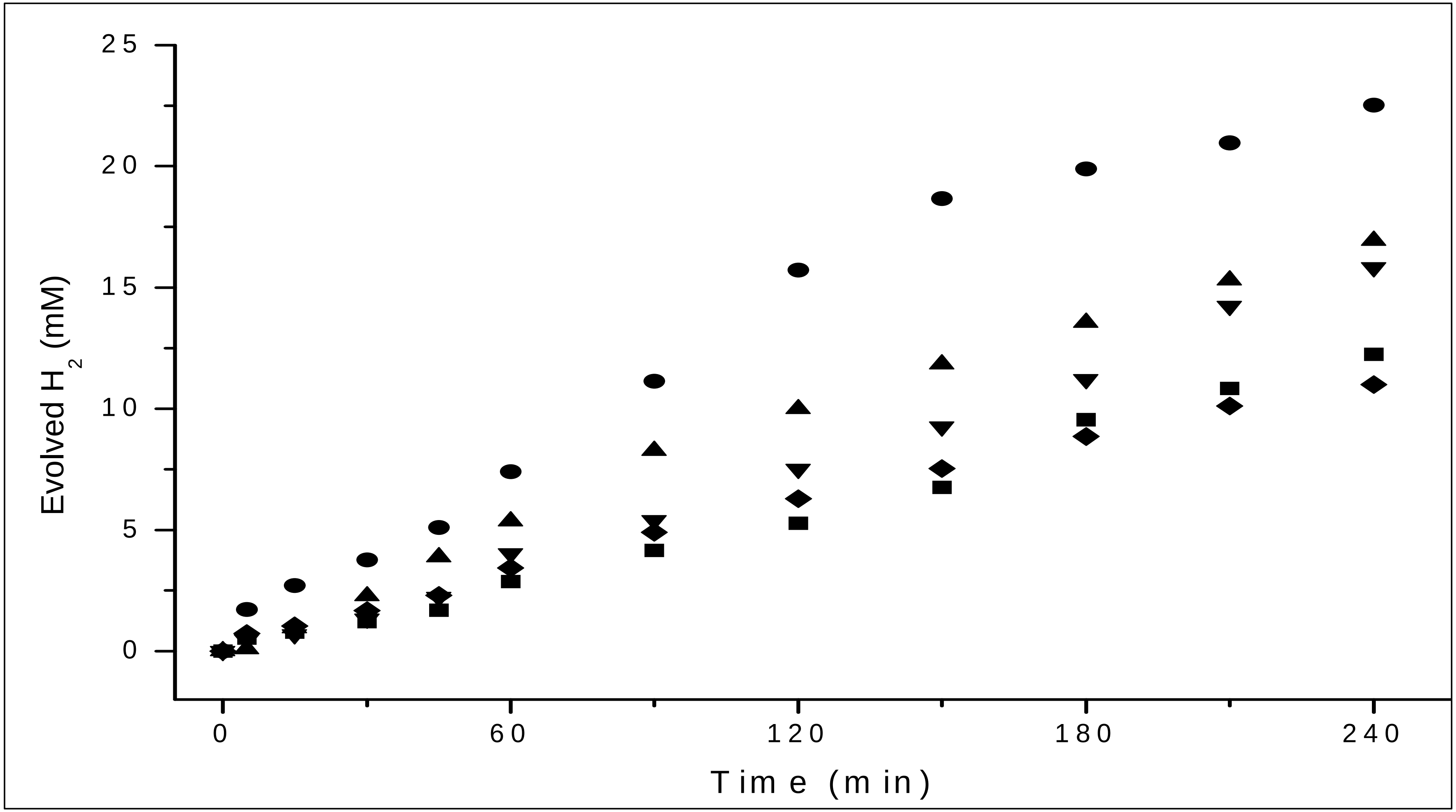
at 650ºC for DMR and POM



J. Matos, M.M. Titirici, et al., Appl. Catal. A: General 386 (2010) 140-146

3. Water Splitting: H_2 Photoproduction under vis-light

■ **Commercial.** ● **Au-S1/C_{H1}.** ▲ **Au-S1/C_{H2}.** ▼ **Au-S1/C_{L1}.** ♦ **Au-S1/C_{L2}**



J. Matos et al., Appl. Catal. A Gen., 417– 418 (2012) 263– 272

H_2 photoproduction on Hybrid Au-TiO_2/C

Universidad de Concepción

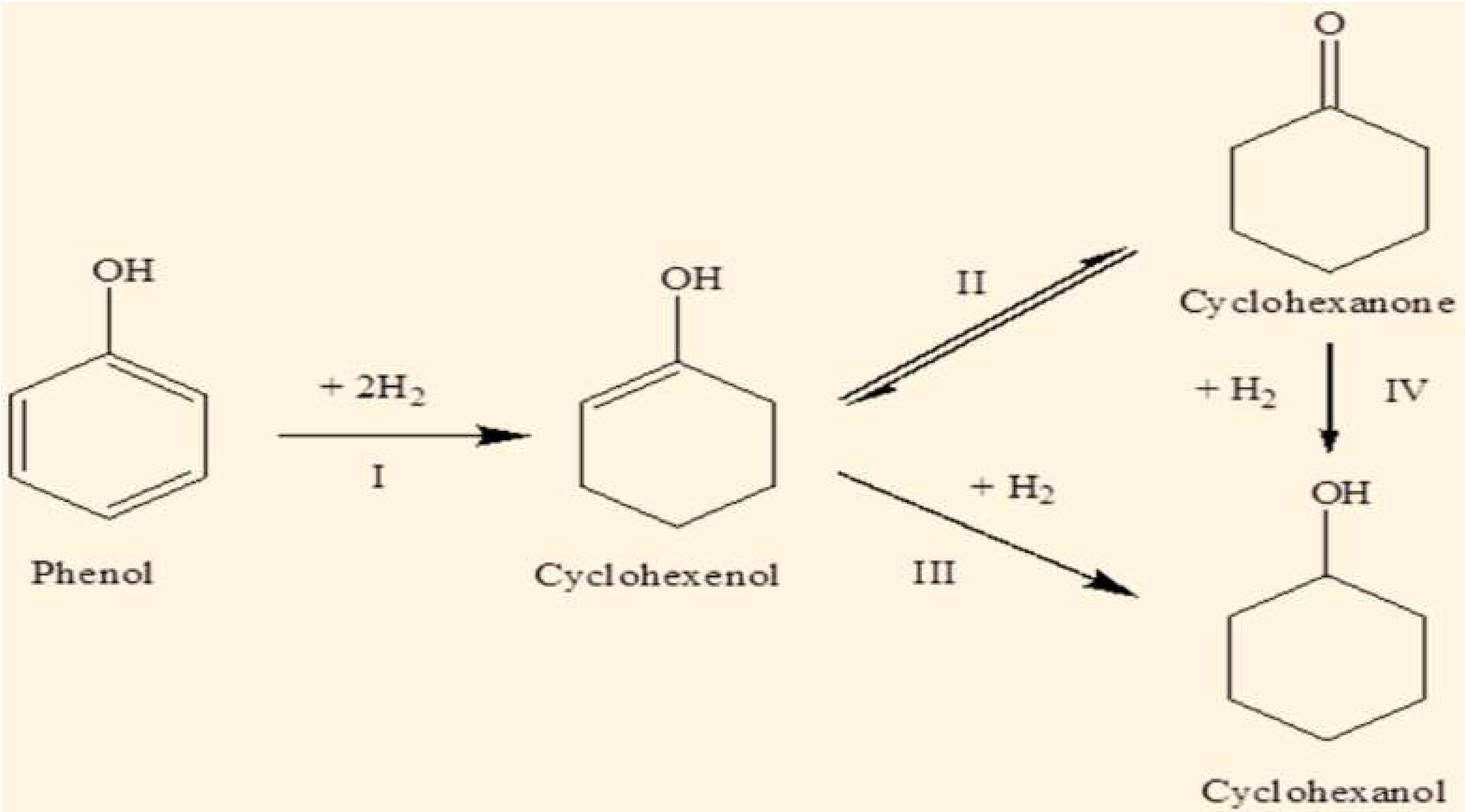
UDT

First-order rate-constants (k_{reac}) for the hydrogen photoproduction

Sample	k_{reac} [a] ($mM.min^{-1}$) UV and visible light	R^2	k_{reac} [a] ($mM.min^{-1}$) Visible light ($\lambda > 385$ nm)	R^2
Commercial	0.392	0.9077	0.044	0.9790
Au-S1/C_{H1}	0.428	0.9143	0.115	0.9840
Au-S1/C_{H2}	0.356	0.9285	0.094	0.9965
Au-S1/C_{L1}	0.240	0.9949	0.062	0.9730
Au-S1/C_{L2}	0.298	0.9617	0.052	0.9890

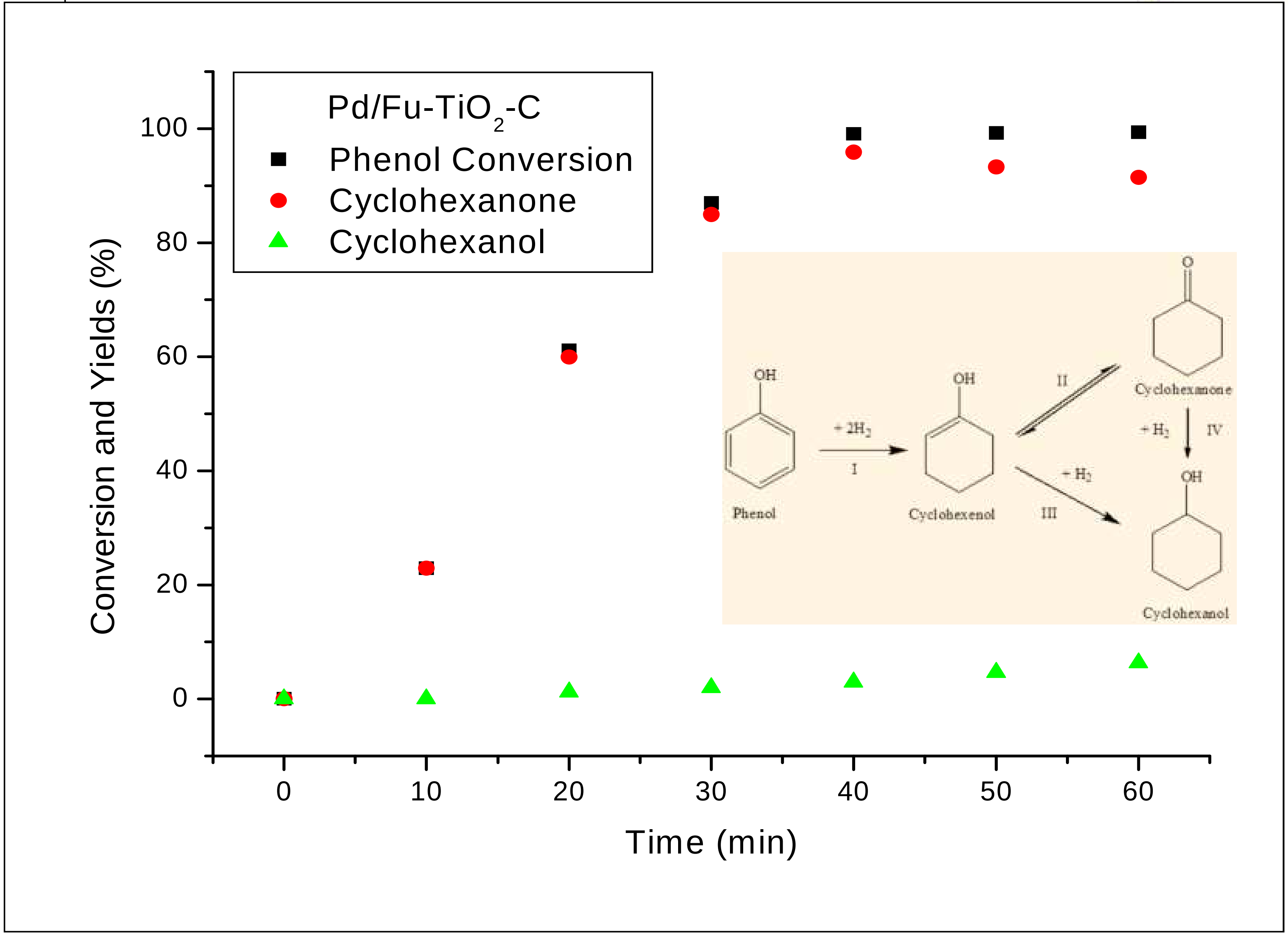
4. Selective Phenol Hydrogenation

HYD produces cyclohexenol as intermediate product (step I) that by consecutive HYD (step III) gives cyclohexanol or by isomerization gives cyclohexanone (step II) which can be converted by HYD into cyclohexanol (step IV)

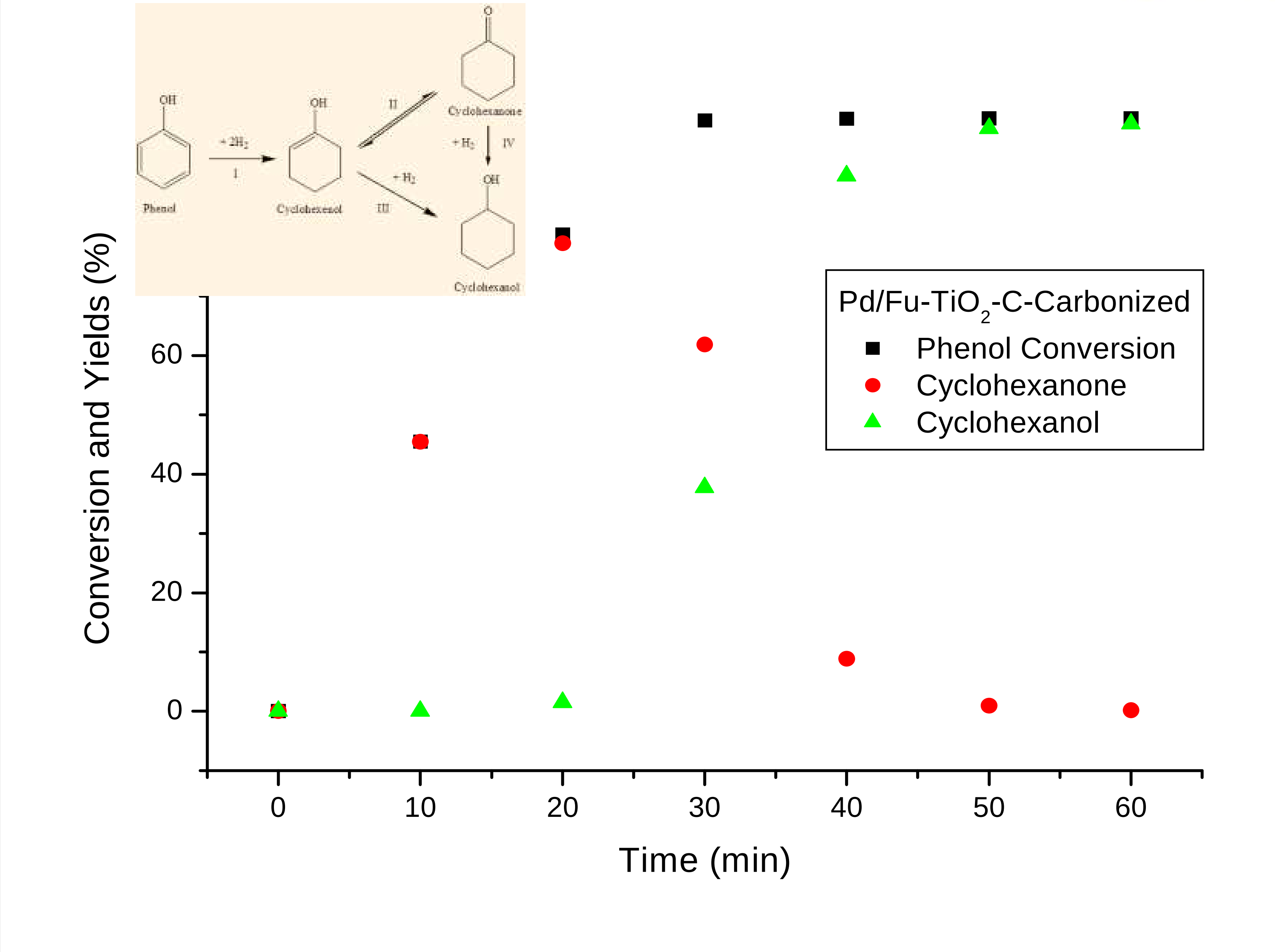


J. Matos, A. Corma. Applied Catalysis A General 404 (2011) 103– 112

Kinetics of Phenol HYD on Pd-based catalysts



Kinetics of Phenol HYD on Pd-based catalysts

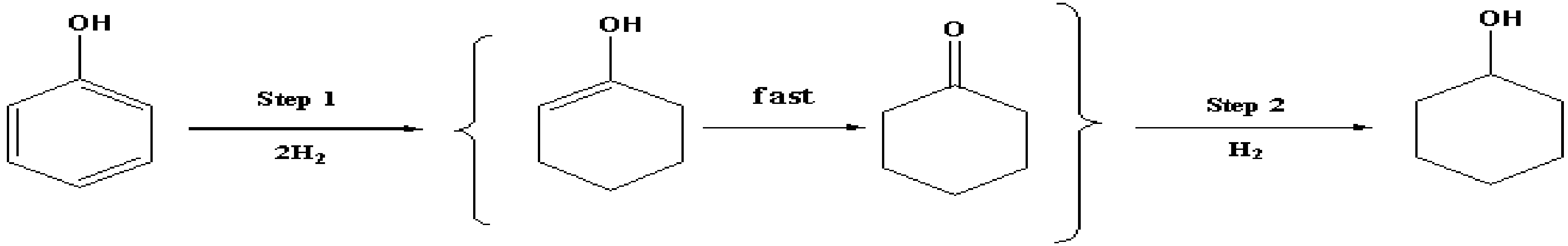


Kinetic results of Ph HYD. Initial activity, maxima Ph conversion (Ph_{conv}), selectivity to cyclohexanone ($S_{C=O}$) and to cyclohexanol (S_{OH})

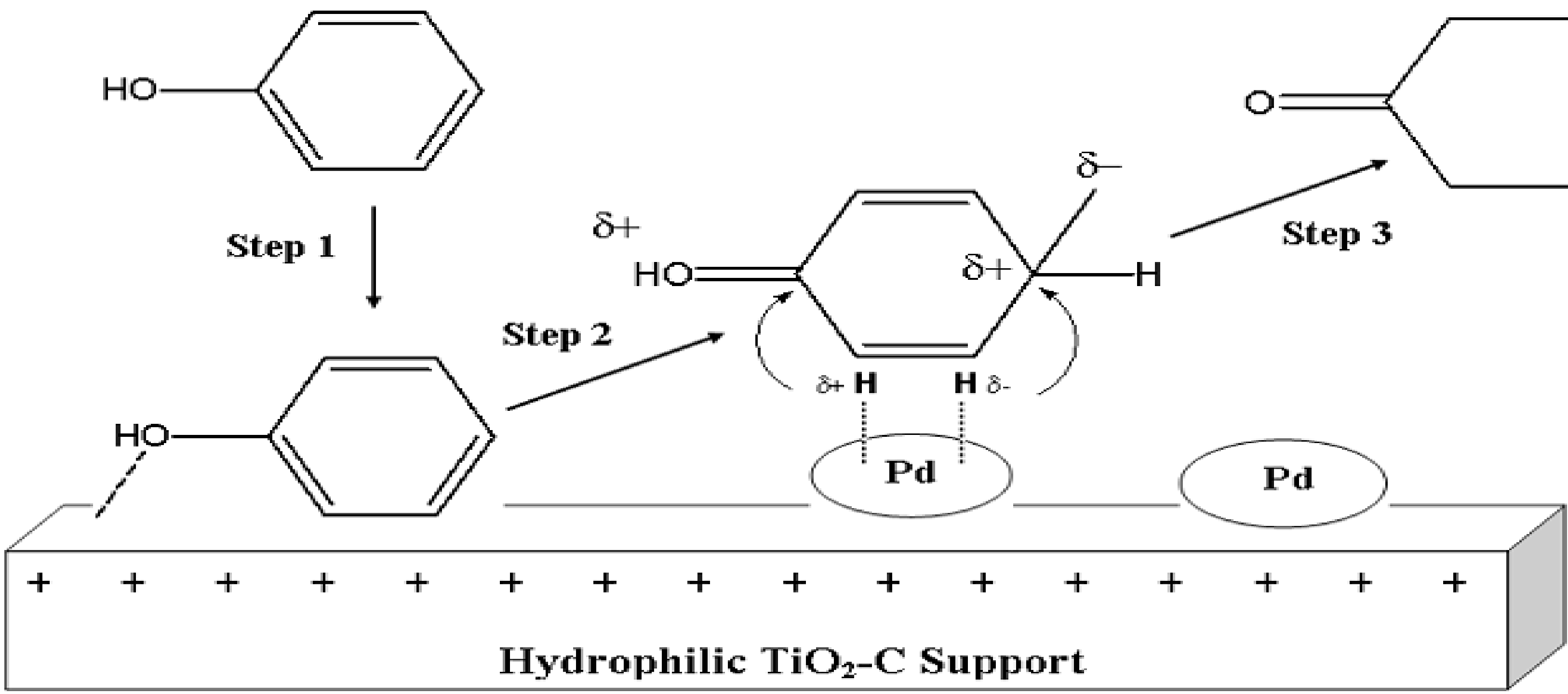
Catalyst	Pd (wt %)	Activity (μmol.gPd^{-1}.s^{-1})	Ph_{conv} (%)	$S_{C=O}$ (%)	S_{OH} (%)
Pd/TiO_2-P25	1.1	45.5	99	98	2
Pd/Fu-TiO_2-C	1.0	71.0	99	97	3
Pd/Sac-TiO_2-C	0.9	40.3	99	93	7
Pd/Fu-TiO_2-C-C	0.9	156.2	99	9	91
Pd/Sac-TiO_2-C-C	1.0	60.8	99	8	92
Pd/TiO_2-AC_{CO2}	0.9	62.1	99	24	76
Pd/TiO_2-AC_{N2}	1.0	48.3	99	19	81
Pd/TiO_2-AC_{ZnCl2}	0.9	91.1	99	96	4
Pd/TiO_2-AC_{H3PO4}	0.9	62.2	99	89	11

Hydrogenation of phenol. (A): General reaction steps. (B): General pathway for selective hydrogenation of phenol to cyclohexanone

(A)

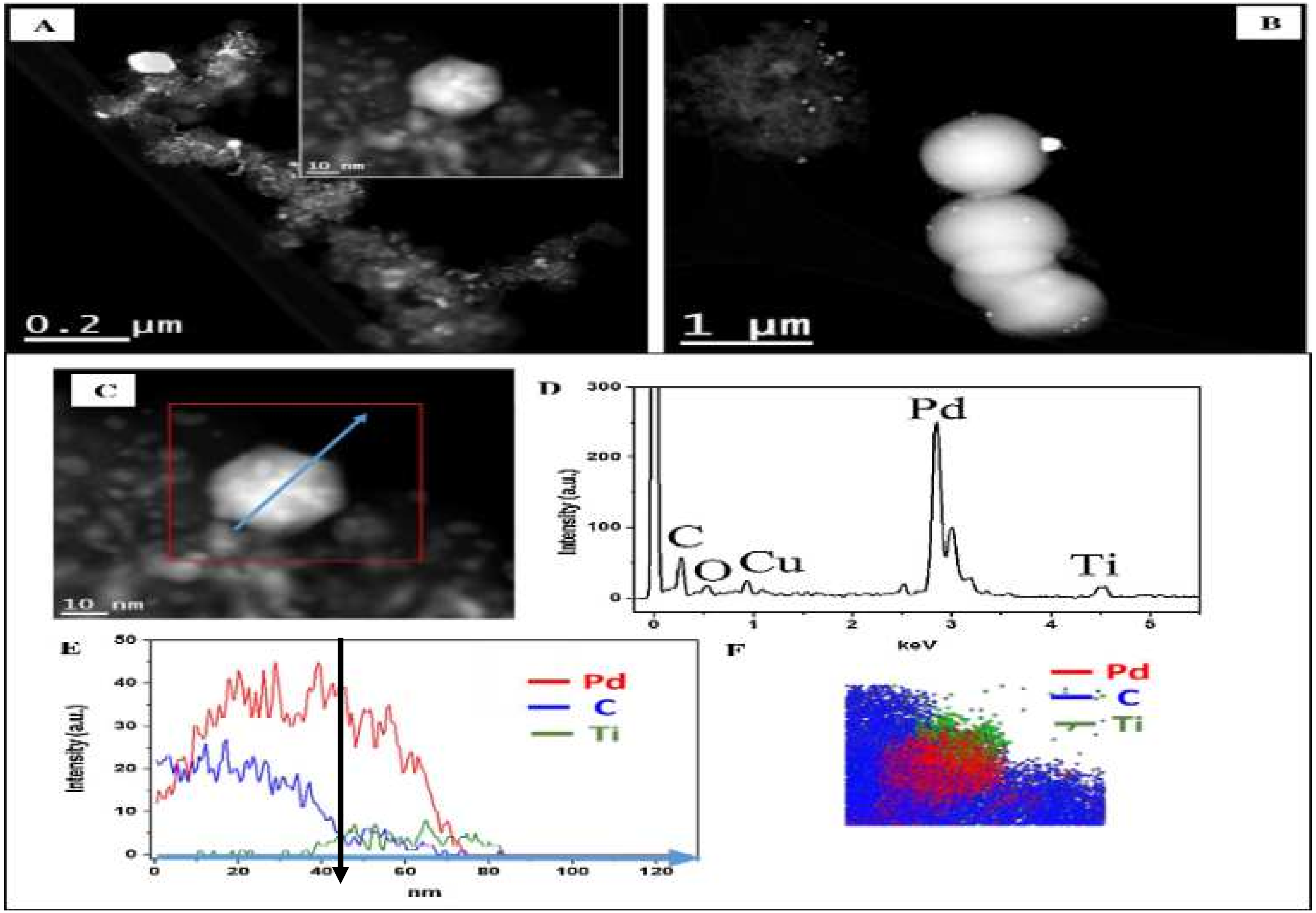


(B)



J. Matos, A. Corma. Applied Catalysis A General 404 (2011) 103– 112

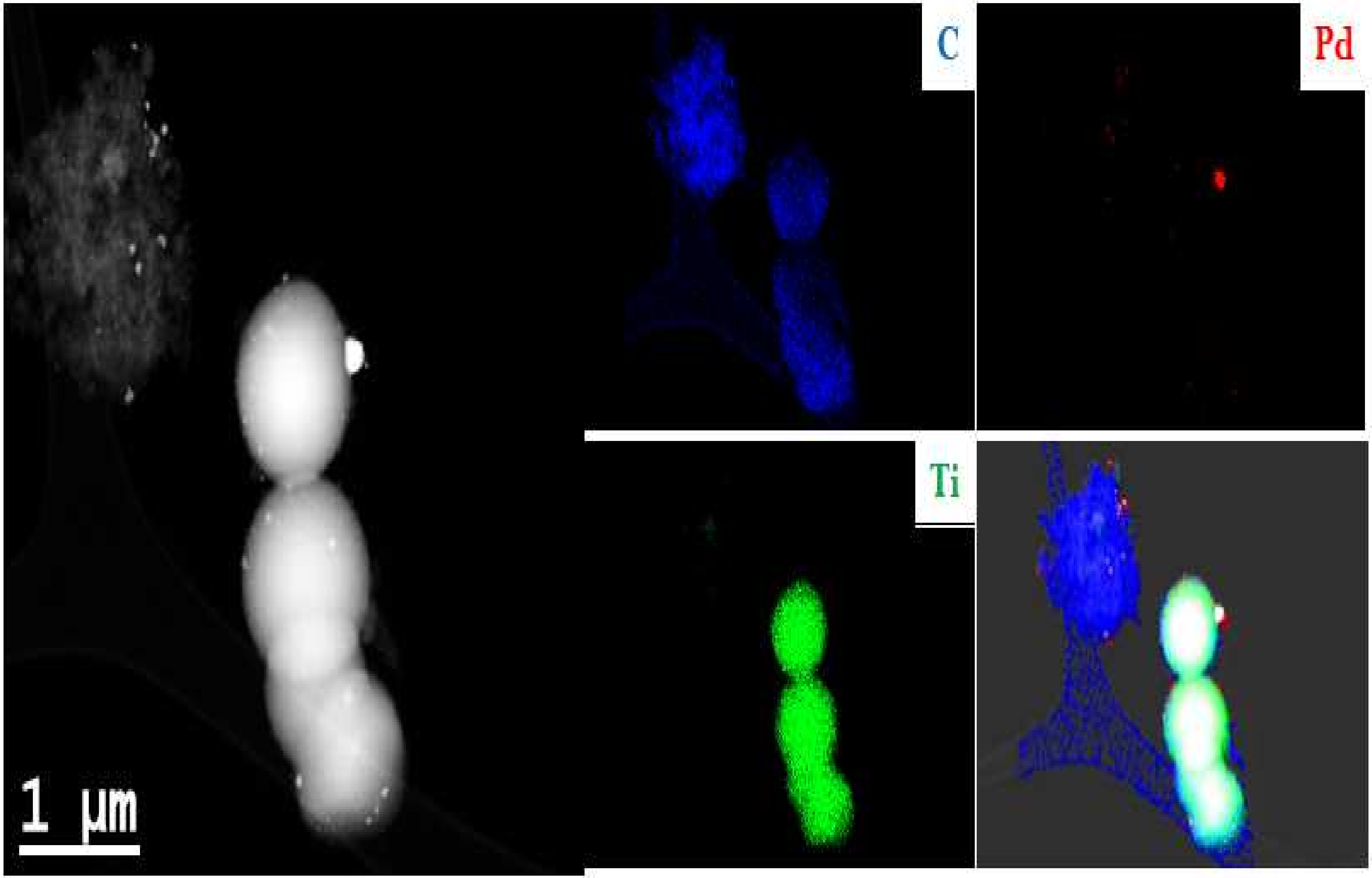
(A-C): STEM-HAADF images of the Pd/Sac-TiO_2-C-C catalysts.
(D): EDX spectra acquired from the selected box area.
(E): Profile of element distribution through a particular arrowed direction.
(F): Elemental distribution map in the box area.



J. Matos, A. Borodzinski, et al., Appl. Catal. B Environ., 163 (2015) 167-178

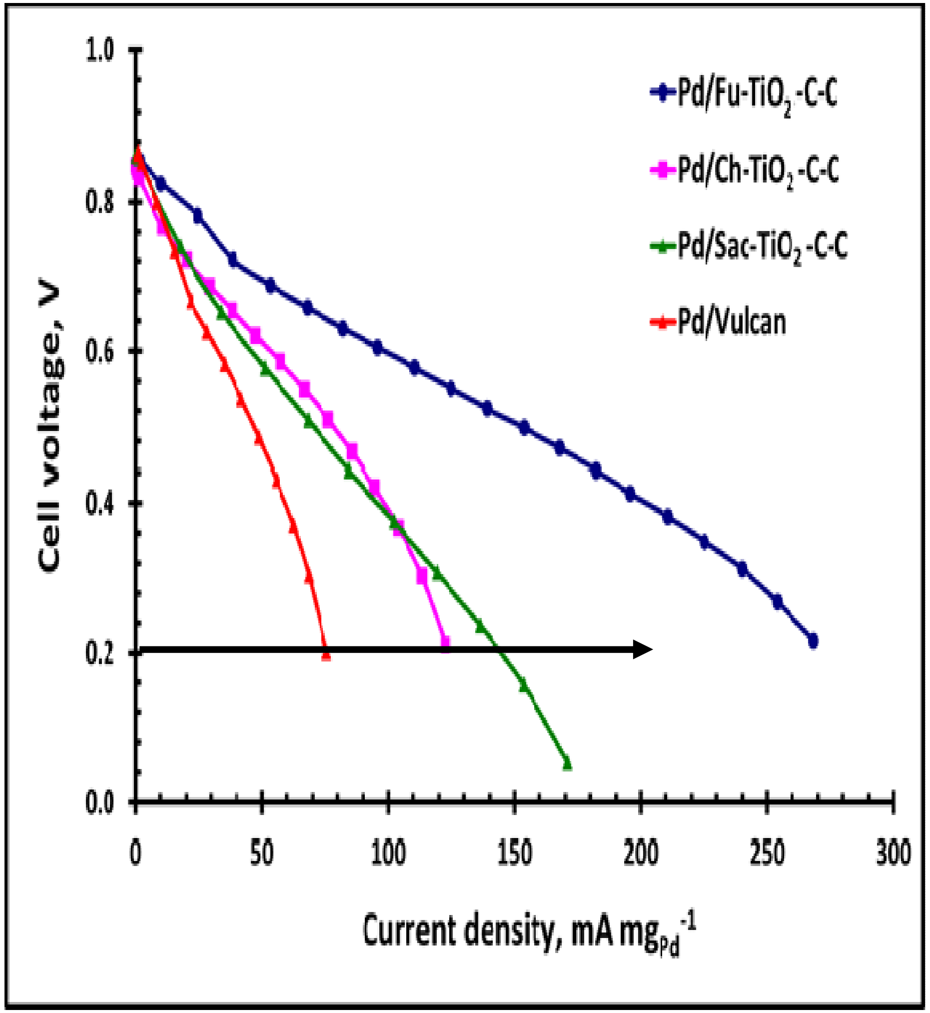
Direct Formic Acid Fuel Cell on Pd/C-TiO_2

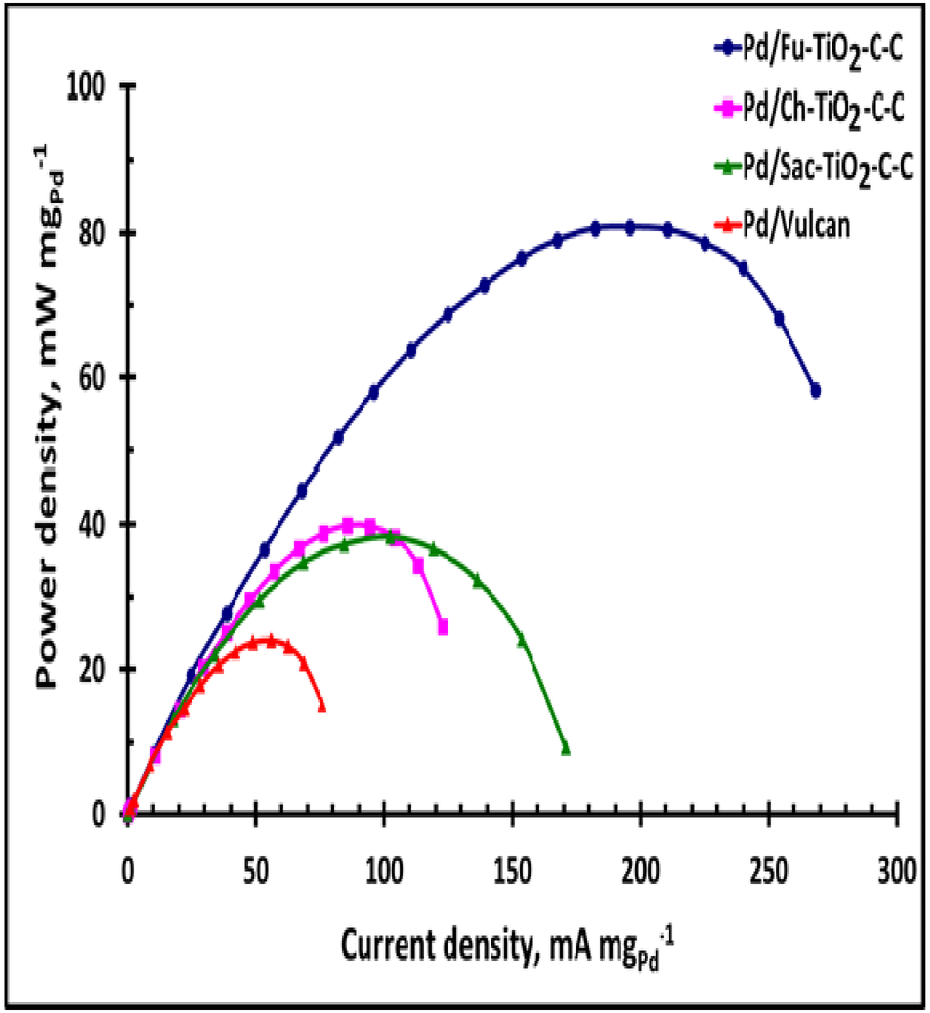
STEM images/Element Distribution on Pd/C-TiO_2



J. Matos, A. Borodzinski, et al., Appl. Catal. B Environ., 163 (2015) 167-178

Cell voltage (left), and Power density (right) as a function of current.





[1] J. Matos, A. Borodzinski, et al., Appl. Catal. B Environ., 163 (2015) 167-178

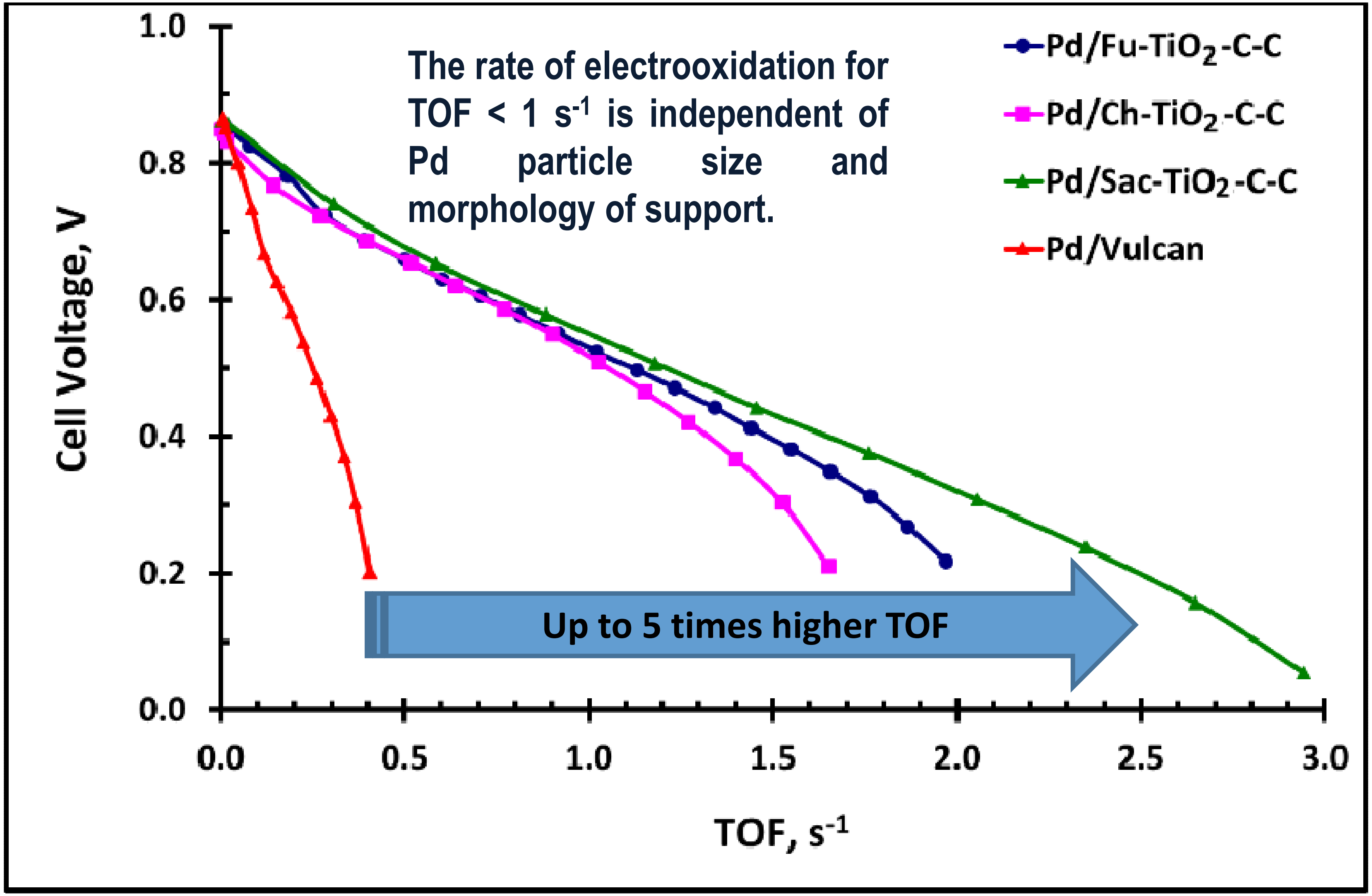
Maxima Power Density for the DFAFC with 20 wt% Pd anodic catalysts on various supports, specific conductivities of respective supports and catalysts measured at 94.2 atm.

Support	Power maxima for Pd catalysts (mW/mg_{Pd})	P_{rel} [a]	Specific conductivity[b] for the supports ($S.g\ cm^{-4}$)	Specific conductivity [b] for the Pd catalysts ($S.g\ cm^{-4}$)
Vulcan XC-72	24	1.00	2.75	2.42
Fu-TiO_2-C-C	80.0	3.34	0.000383	0.342
Ch-TiO_2-C-C	39.9	1.64	0.00215	0.065
Sac-TiO_2-C-C	38.4	1.60	0.00049	0.32

[a] Maxima Power increase relative to Pd/Vulcan catalyst.

[b] Specific conductivity estimated from equation: $\Psi = [(\sigma.\ \gamma) = (m/R.A^2)]$, where Ψ is the product of conductivity and density for the Pd catalysts [$S.\ g.cm^{-4}$]; σ is the conductivity of the sample, [$S\ cm^{-1}$]; γ is the density of the sample [$g\ cm^{-3}$]; m is the weight of the sample [g]; R is the measured resistance of the sample [Ω]; A is the surface area of the cross section surface of the sample (0.49 cm^2).

Relation between cell voltage and TOF for different catalysts

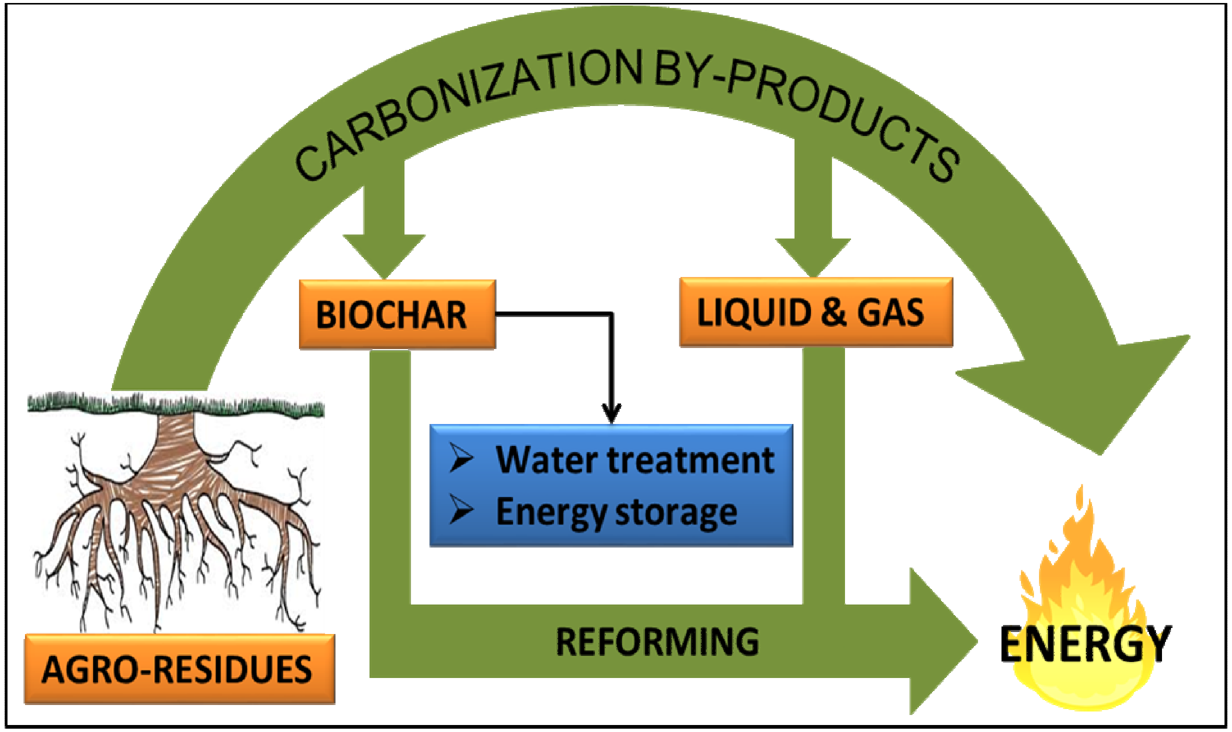


[1] J. Matos, A. Borodzinski, et al., Appl. Catal. B Environ., 163 (2015) 167-178

Summary

1. **Biochar-based materials permit the multidisciplinary study and development of thermal, optical, and photoelectronic processes.**

2. **Efficient harvesting of solar energy is possible for the application in Environment, Health, Selective Catalysis and Photocatalysis, and for the Clean Energy Production and Storage**



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Dr. E. García

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