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Photocatalytic partial oxidation of organic molecules under mild green conditions

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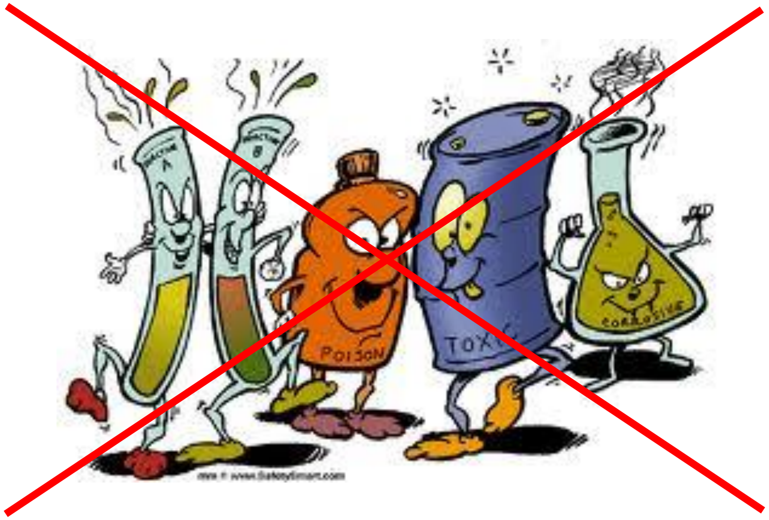
Green Chemistry

1. Better ***prevent*** than treat ***waste***
2. Maximize ***incorporation*** of the used materials into the ***final product***
3. Use and generate substances possessing little or no ***toxicity*** to human health and environment
4. Use and design products preserving ***efficacy of function***
5. Use of ***auxiliary substances*** (solvents, separation agents, etc.) should be avoided or be innocuous
6. Minimize ***energy*** requirements and work at ***ambient temperature*** and ***pressure***
7. ***Raw materials*** should be ***renewable*** wherever possible
8. Unnecessary ***derivatization*** (blocking group, protection/deprotection) should be avoided if possible
9. Use ***catalytic*** reagents (as selective as possible) rather than ***stoichiometric*** reagents
10. Design chemicals so that at their life-end they do not ***persist in the environment***
11. Develop ***real-time monitoring*** to allow for instant alert at formation of hazardous substances
12. Select substances as to ***minimize*** potential for ***chemical accidents*** (e.g. releases, explosions, fires)



P. Anastas, J. Warner, *Green Chemistry: Theory and Practice* (Oxford University Press: New York, 1998)

It is not easy being…green ☺

Green solvents
Water, ethanol, dimethyl carbonate

Degradation of pollutants

Possibility of **solar light** irradiation

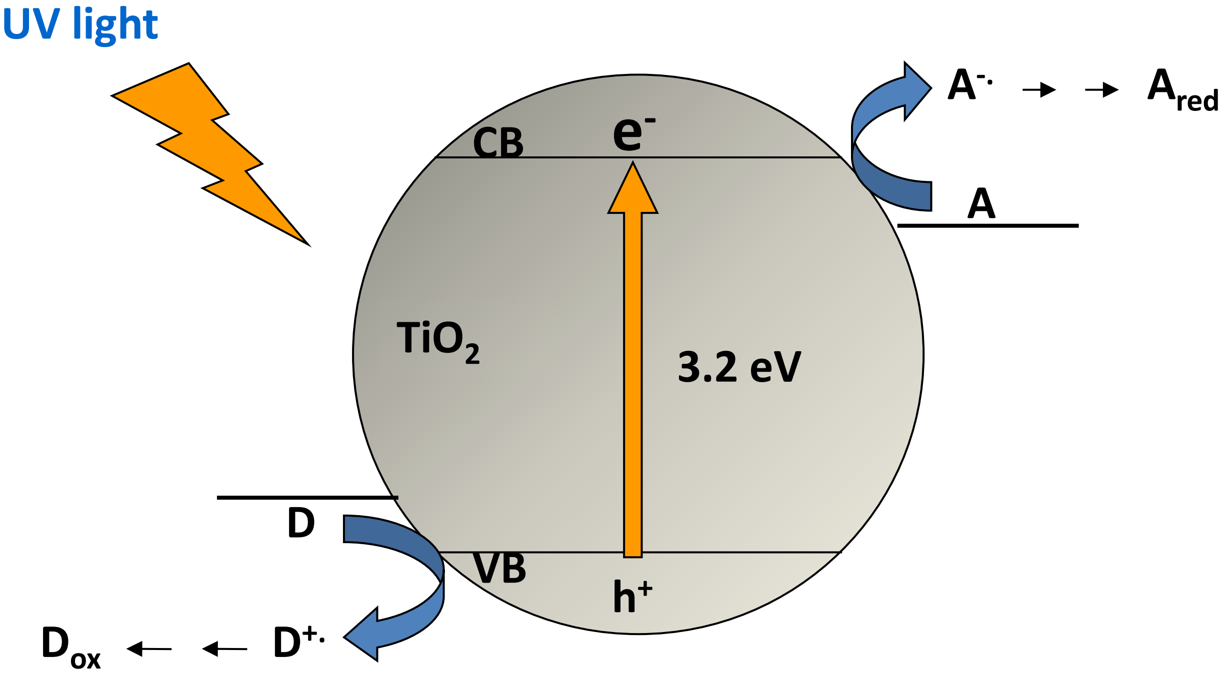
Synthesis of valuable products

Mild operating conditions (room T and P)

TiO_2 is **cheap** and **non toxic**

Radical chain reactions…
low selectivity?

Photocatalytic mechanism



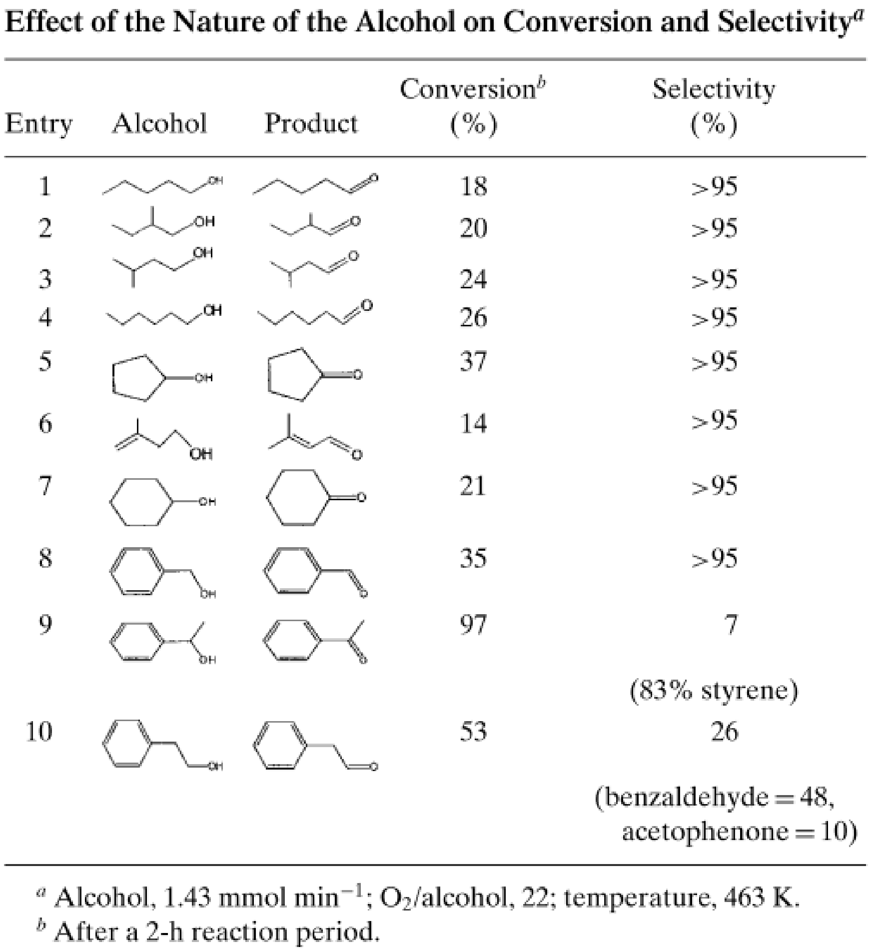
Some examples…

Alcohols to aldehydes

The selective oxidation of alcohols to carbonyl compounds is a process of great industrial importance; generally it is carried out in environmentally ***harmful organic solvents at high temperature and pressure*** by employing ***stoichiometric oxygen donors*** (such as chromate and permanganate) that not only are expensive and toxic compounds but also produce high amounts of ***dangerous wastes***.

Photocatalysis in the presence of TiO_2 is able to yield selective reaction as showed in Table 1.

The table reports results related to photoreactions occurring **in a gas-solid system**.



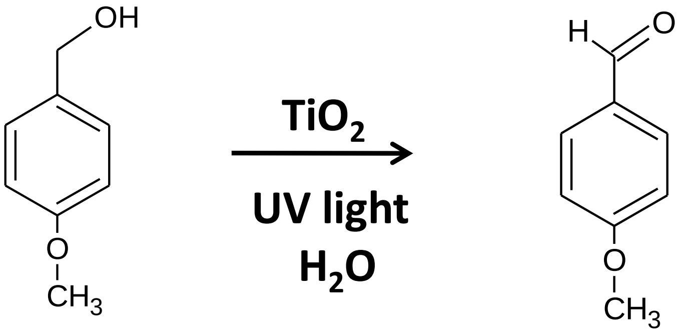
Effect of the Nature of the Alcohol on Conversion and Selectivity[a]

Entry	Alcohol	Product	Conversion[b] (%)	Selectivity (%)
1			18	>95
2			20	>95
3			24	>95
4			26	>95
5			37	>95
6			14	>95
7			21	>95
8			35	>95
9			97	7 (83% styrene)
10			53	26 (benzaldehyde = 48, acetophenone = 10)

[a] Alcohol, 1.43 mmol min^{-1}; O_2/alcohol, 22; temperature, 463 K.
[b] After a 2-h reaction period.

U. R. Pillai, E. Sahle–Demessie., *J. Catal.*, 211 (2002) 434

THE CASE STUDY OF 4-METHOXYBENZYL ALCOHOL



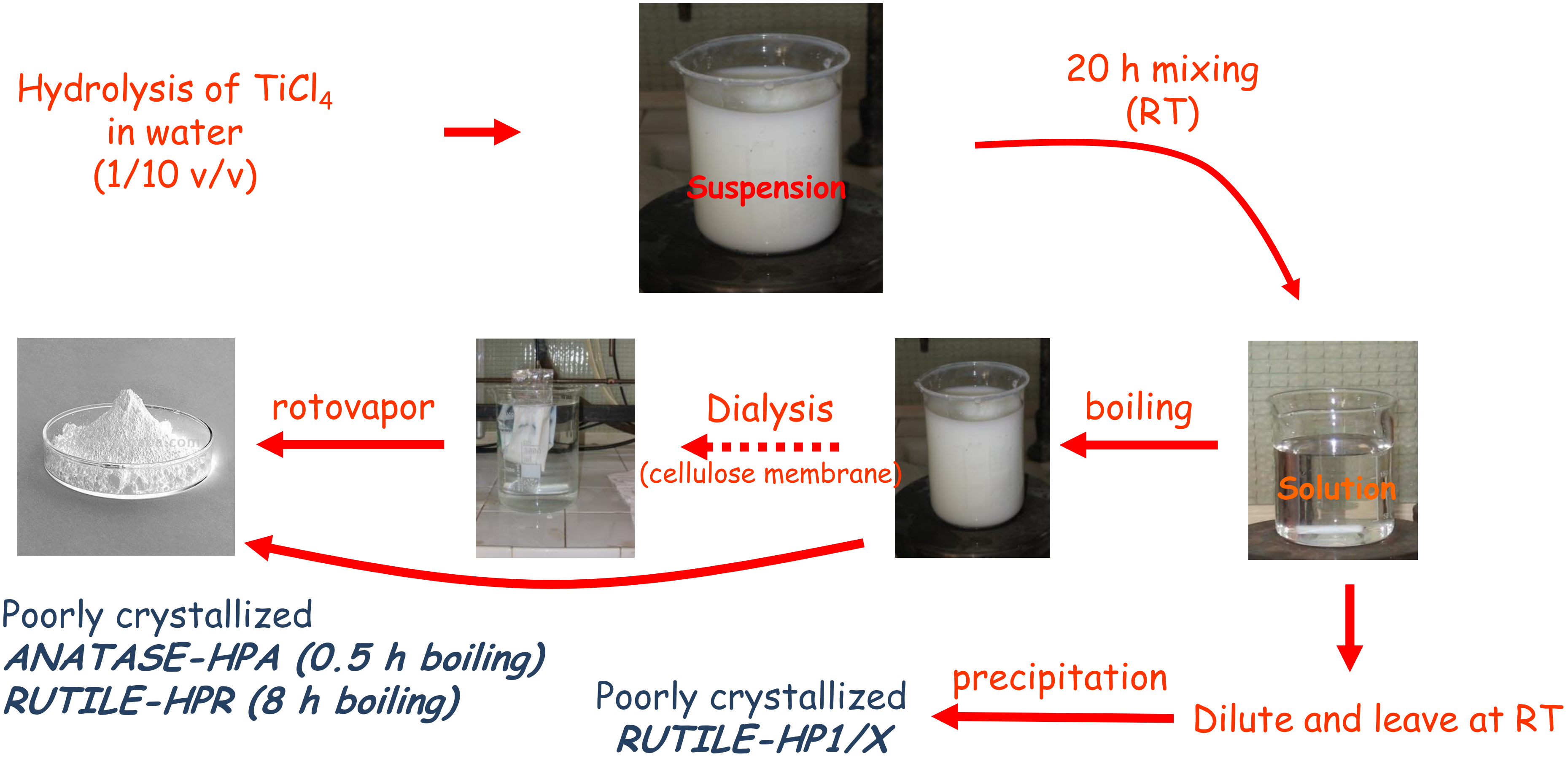
Catalyst	SSA $[m^2/g]$	Crystallite size [nm]	Particle size [nm]	MBA [mM]	$t_{1/2}$ [h] half-life time	Selectivity [% mol]
HPA[a]	235	5	28	1	4.1	31
HPA[a]	235	5	28	10	19.5	39
HPR[b]	107	7	50	1	2.1	58
HPR[b]	**107**	**7**	**50**	**10**	**8.8**	**62**
HPB[c]	82	9	95	1	1.8	39
HPB[c]	82	9	95	10	9.1	50
SA[d]	2.5	52	240	1	2.1	21
Merck[e]	10	60	170	1	2.0	16

[a]Home-prepared anatase, [b]Home-prepared rutile, [c]Home-prepared brookite, [d]Sigma-Aldrich rutile, [e]Anatase

Nanostructured, low crystalline TiO_2 home-prepared photocatalysts ex $TiCl_4$, synthesised under mild conditions, showed high selectivity for the oxidation of 4-methoxybenzyl alcohol to p-anisaldehyde – *in water* – compared with commercial ones. The experiments were carried out in a batch Pyrex cylindrical photoreactor and a medium pressure 500 W Hg lamp was used.

G. Palmisano et al., *Adv. Synth. Catal.*, 349 (2007) 964; S. Yurdakal et al., *J. Am. Chem. Commun.*, 130 (2008) 1568; M. Addamo et al., *Catal. Lett.*, 126 (2008) 58; V. Augugliaro et al., *Photochem. Photobiol. Sci.*, 8 (2009) 663

Home-prepared TiO_2 ex-$TiCl_4$



Hydrolysis of $TiCl_4$
in water
(1/10 v/v)

Suspension

20 h mixing
(RT)

Solution

boiling

Dialysis
(cellulose membrane)

rotovapor

Poorly crystallized
ANATASE-HPA (0.5 h boiling)
RUTILE-HPR (8 h boiling)

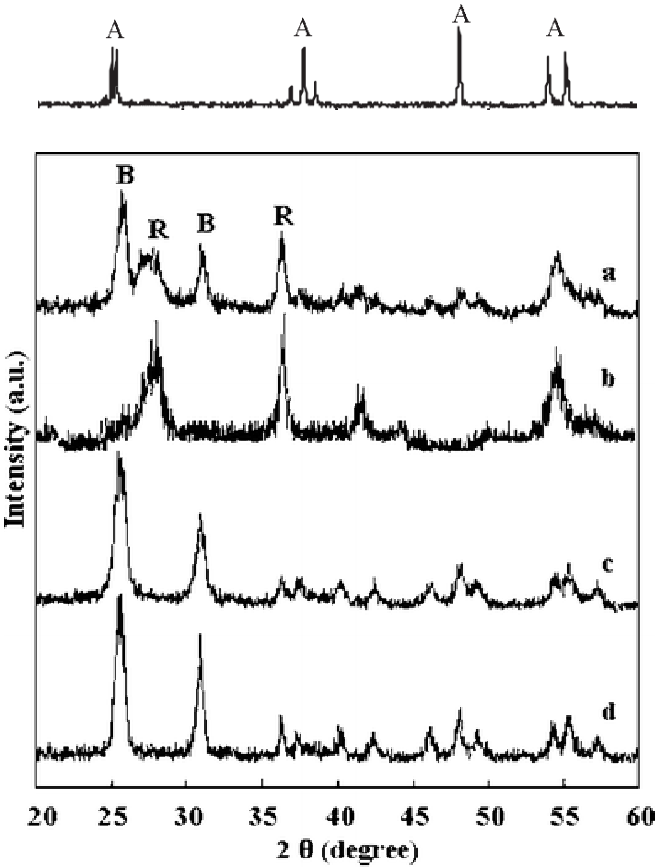
Dilute and leave at RT

precipitation

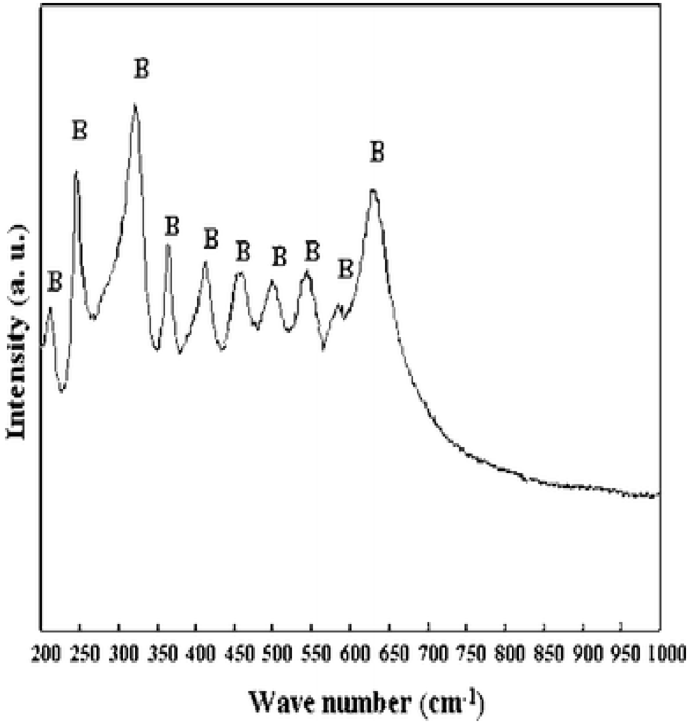
Poorly crystallized
RUTILE-HP1/X

BROOKITE-HPB can be obtained by thermal treatment at 100°C of a $TiCl_4$ solution prepared in a HCl aqueous solution. The clear supernatant is then separated and water is added. The procedure is repeated twice. Finally brookite particles are present in the supernatant, whereas rutile precipitates.

Details are given in: A. Di Paola et al., Coll. Surf. A, 317 (2008) 366



XRD diffractogram of the samples: (a) brookite-rutile mixture; (b) pure rutile; (c) pure brookite; (d) calcined brookite. B = Brookite; R = Rutile



Raman spectrum of a home-prepared pure brookite sample

However, the highest selectivity (up to ***74%***) was obtained by using **rutile** samples prepared under very mild conditions at room temperature.

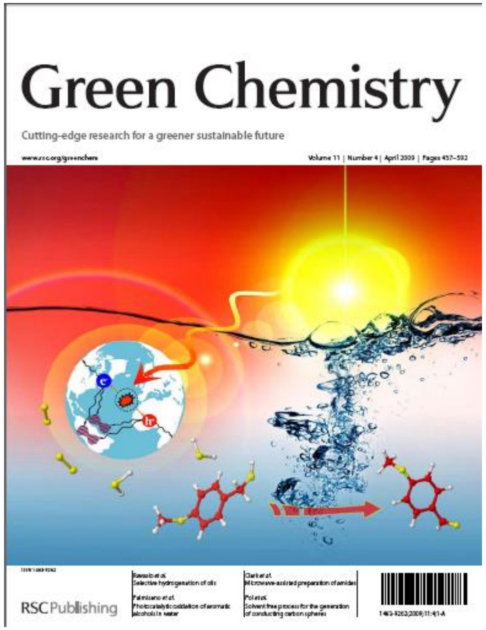
BET specific surface area (SSA), particle size and crystallite size of the photocatalysts

Catalyst	$TiCl_4/H_2O$ v/v ratio	SSA/$m^2\ g^{-1}$	Aging time/days	Time for precipitation starting/days	Agglomerates size/nm	Crystallite size/nm
HP1/20	0.05	129	9	8	286	5.5
HP1/35	0.029	116	6	3	1050	5.6
HP1/50	0.02	118	6	3	719	6.8
HP1/75	0.013	125	4	2	304	7.1
HP1/100	0.01	135	4	2	244	6.1
SA	—	2.5	—	—	240	52

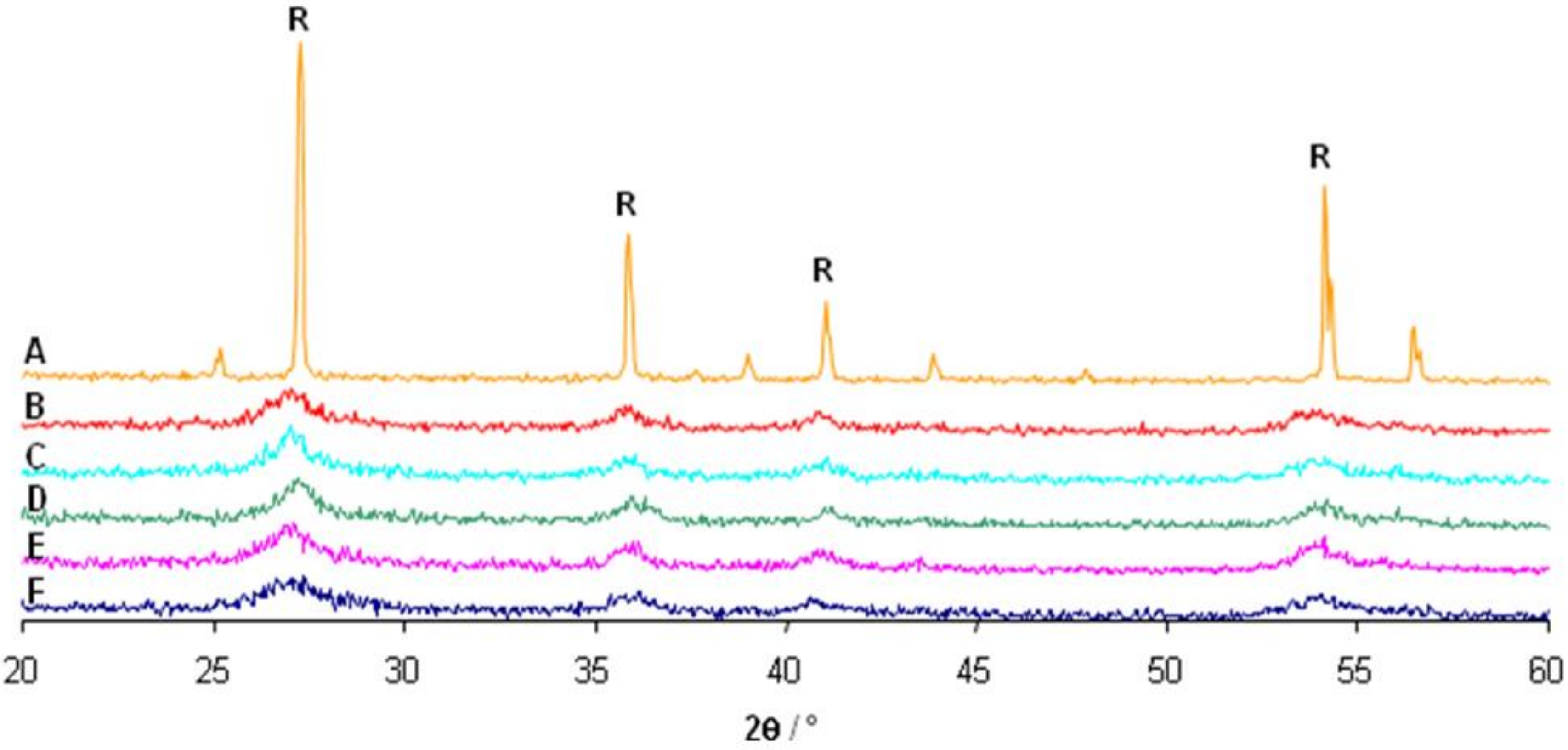
Photocatalysts performance for MBA photo-oxidation to MBAD for 50% conversion

Catalyst	Catalyst amount/g L^{-1}	$t_{1/2}$/h	Selectivity (% mol)	C balance (%)[a]
HP1/20	0.2	2.3	45	91
HP1/35	0.6	3.6	60	96
→ HP1/50	0.2	6.65	74	99
HP1/50	0.6	2.6	72	98
HP1/75	0.2	2.95	55	94
HP1/100	0.2	3.3	61	96
SA	0.4	2.15	21	70

[a] C-balance was obtained as sum of MBA, MBAD and CO_2 concentration.



S. Yurdakal et al., *Green Chem.*, 11 (2009) 510



XRD patterns of HP and commercial TiO_2 samples; A) SA, B) HP1/100, C) HP1/75, D) HP1/50, E) HP1/35, F) HP1/20. “R”: rutile peaks

By increasing the catalyst crystallinity, the selectivity decreases, whereas the activity increases.

The photoreactivity results obtained **by using the three studied TiO_2 phases** as photocatalysts indicate that the aromatic alcohol molecules participate in two parallel oxidative processes on the catalyst surface: the first one is the partial oxidation giving rise to the aldehyde and the second one is the complete oxidation producing eventually CO_2.

In the first pathway the adsorbed aromatic alcohol is transformed into the corresponding aldehyde which desorbs from the surface.

In the second one the substrate is mineralized through consecutive oxidation steps producing species which remain adsorbed onto the surface.

Why the HP samples are much more selective (less oxidant power) than the commercial samples for this reaction?

Are the intrinsic electronic properties important?

Do the surface physico-chemical properties play a role?

In order to answer, although tentatively, to the above questions, a catalyst characterization was carried out in collaboration with the groups of Prof. H. Kisch (Germany) and M.J. López-Muñoz (Spain).

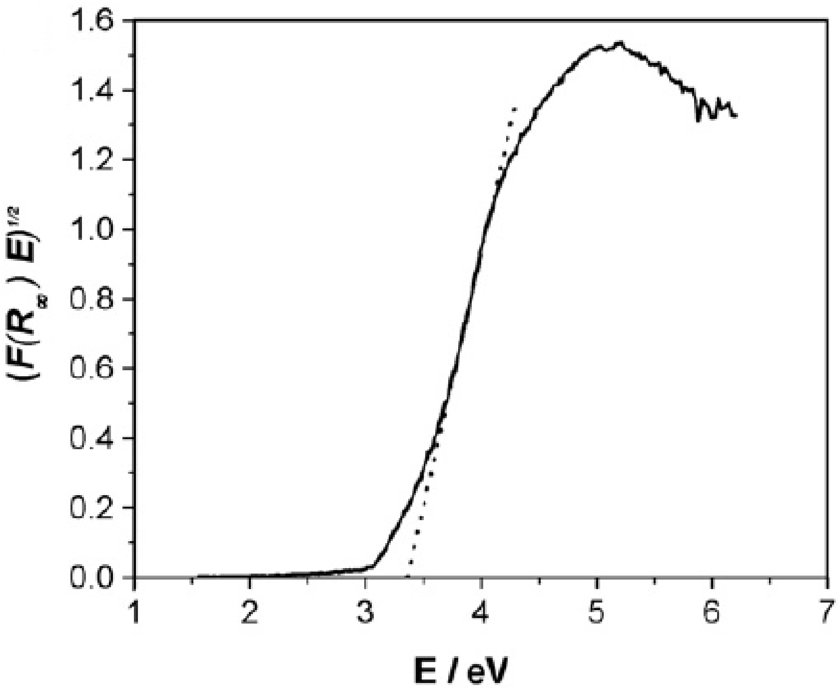
The photoelectrochemical features of some anatase and anatase/rutile samples were determined and an ATR-FTR study was performed.

V. Augugliaro, H. Kisch, V. Loddo, M.J. López-Muñoz, C. Márquez-Álvarez, G. Palmisano, L. Palmisano, F. Parrino, and S. Yurdakal, **Appl. Catal. A** 349, 2008, 189

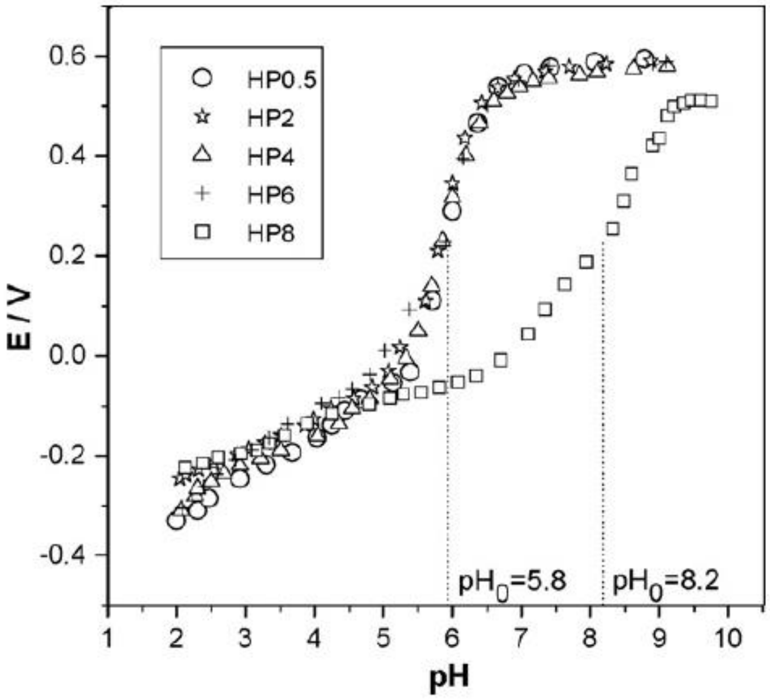
Electronic properties

Some intrinsic electronic properties of home prepared (HP) TiO_2 catalysts were investigated by:

Diffuse Reflectance Spectroscopy



quasi-Fermi Level measurements



Band Gap

+

CB Edge

Roy et al. determined the flatband potential, E_{fb}, of CdS and CdS/Ag_2S (1.5wt%) particles from photovoltage measurements in the presence of the electron acceptor methyl viologen (MV^{2+}). Measurements have been taken whilst irradiating the semiconductor suspensions. This is one of the simplest techniques for the determination of the E_{fb} of semiconductors through the following equation
($E^0_{MV^{2+}/MV^{+\cdot}}$ = -0.45 V vs. NHE; k = 0.059 V)

$$\mathbf{E_{fb} = E^0_{MV^{2+}/MV^{+\cdot}} + k(pH_0 - pH)}$$

By assuming that the difference between the quasi-Fermi level potential of electrons and conduction band edge is negligible, the valence band edge values can be obtained by addition of the band gap energy.

HP0.5, HP2, and HP4 band edge is located at 2.84 V, whereas it is shifted to 2.74 for HP6, which contains a significant amount of rutile, and for HP8, nearly pure rutile.

The values of band gap, valence band and conduction band edges are almost identical for all the HP samples in which anatase phase is predominant, whereas appreciable differences can be noticed for an HP sample containing high amount of rutile phase.

A.M. Roy, G.C. De, N. Sasmal and S.S. Bhattacharyya, Int. J. Hydrogen Energy 20 (1995) 627-630

Catalyst	Band gap (eV)	E_{fb} (pH 7) (V)	VB edge (V)
Degussa P25 (A,R)	3.26	-0.55	2.71
Merck (A)	3.22	-0.43	2.79
HP0.5 (A)	3.36	-0.52	2.84
HP2 (A)	3.36	-0.52	2.84
HP4 (A,R)	3.36	-0.52	2.84
HP6 (A,R)	3.26	-0.52	2.74
HP8 (R)	3.11	-0.37	2.74

Surface Properties

The ATR-FTIR results indicate that HP and Degussa P25 surfaces show a very dissimilar hydrophilicity and different ability for adsorbing benzaldehyde.

HP0.5

The photoactivity results obtained with HP0.5 catalyst show a low oxidation rate of benzyl alcohol but a high selectivity to benzaldehyde.

The surface of HP0.5 catalyst is rich in molecularly adsorbed water, which is able to displace benzyl alcohol (BA) molecules in the dark.
Under irradiation water displaces BA and the produced benzaldehyde more effectively, determining a very low oxidation rate of benzyl alcohol and a higher selectivity.

P25

The reactivity results, in the case of P25 indicate that the mineralization pathway predominates over the partial oxidation.

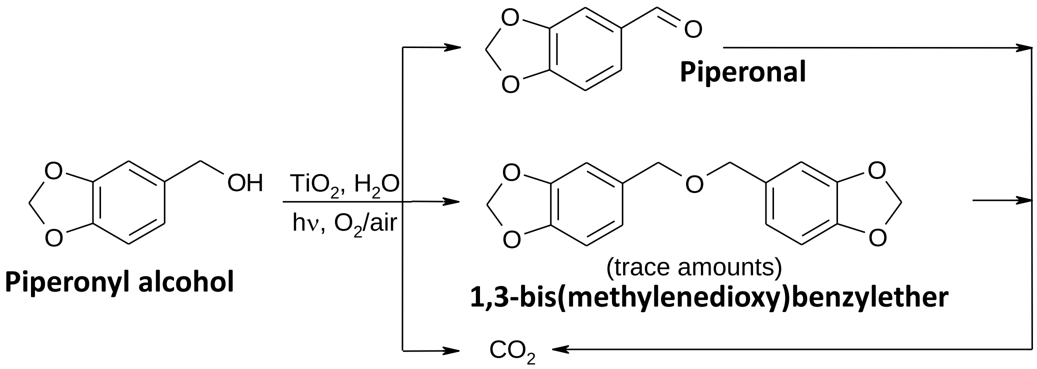
The smaller hydrophilicity of P25 as compared to HP0.5 implies a low ratio between water and benzyl alcohol and, therefore, it is likely that mineralization sites are not preferentially occupied by water molecules.
The displacement of BA and benzaldehyde (before its further oxidation) occurs with more difficulty!

PIPERONAL SYNTHESIS

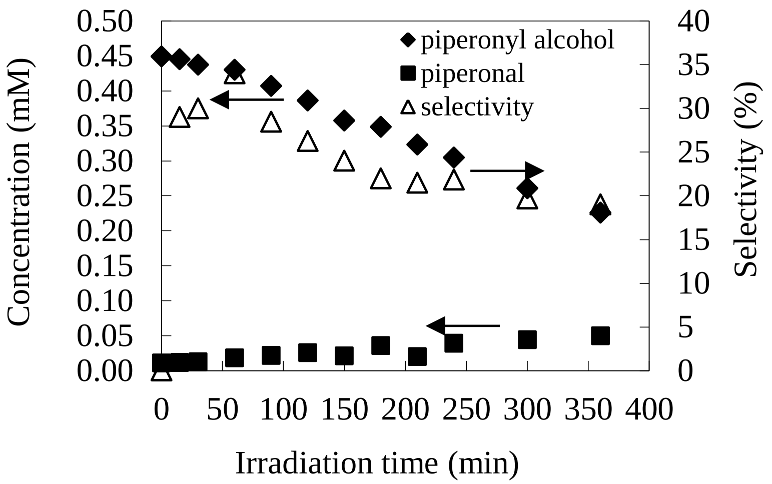
Synthesis of valuable piperonal in aqueous suspensions of home-prepared TiO_2 has been recently performed, followed by separation and characterization of the obtained product.

Piperonal is widely used:

- as basis for the heliotrope-type perfumes and for cosmetic preparations;
- as an intermediate for agrochemical and pharmaceutical products;
- as aroma-therapy since it is able to elevate mood and to impart a general well-being



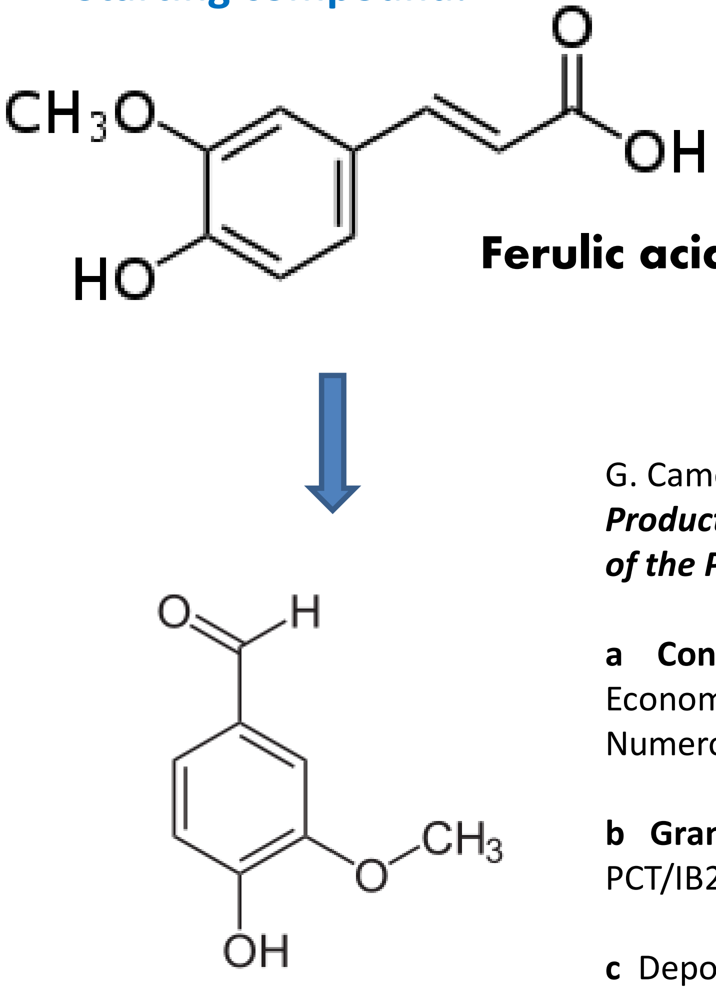
Home prepared poorly crystallized TiO_2 catalysts give ***selectivities*** of about ***19%*** at conversions of 30%, whereas commercial TiO_2 allows to reach selectivities of only ***6%***.



M. Bellardita et al., *Appl. Catal. B*, 144 (2014) 607

Synthesis of vanillin

Starting compound:



Ferulic acid

Vanillin

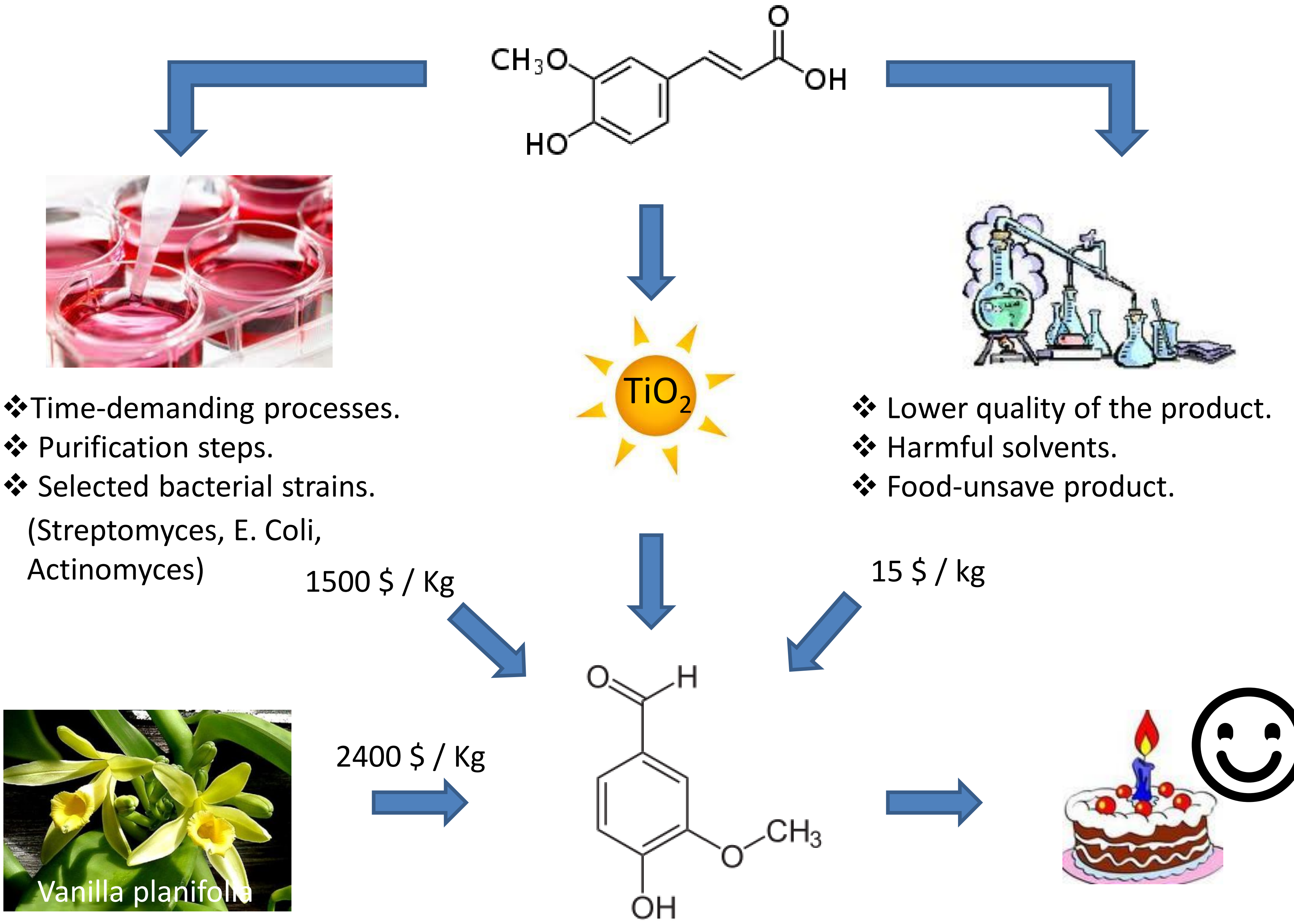
- Component of lignin.
- Cheap and abundant component of waste streams of wood-, paper-, nutraceutical-industries.

G. Camera Roda, V. Augugliaro, V. Loddo, L. Palmisano, G. Palmisano
Production of Aldehydes by Oxidation in Aqueous Medium with Selective Recovery of the Product by Means of Pervaporation

a **Concesso il 16-12-2013** dall’Ufficio Brevetti e Marchi, Ministero dello Sviluppo Economico, Roma. Numero Domanda: RM2010A000319, Tipologia Invenzioni; Numero Brevetto 0001405068. Depositato il 11-06-2010.

b **Granted by USPTO 11-11-2014**. Patent application n. 13/703618, patent number PCT/IB2011/052541. Deposited on 10-06-2011.

c Deposited at the European Patent Office (11729741.6 – 1451) on 10-06-2011.



❖Time-demanding processes.
❖ Purification steps.
❖ Selected bacterial strains.
(Streptomyces, E. Coli, Actinomyces)

1500 $ / Kg

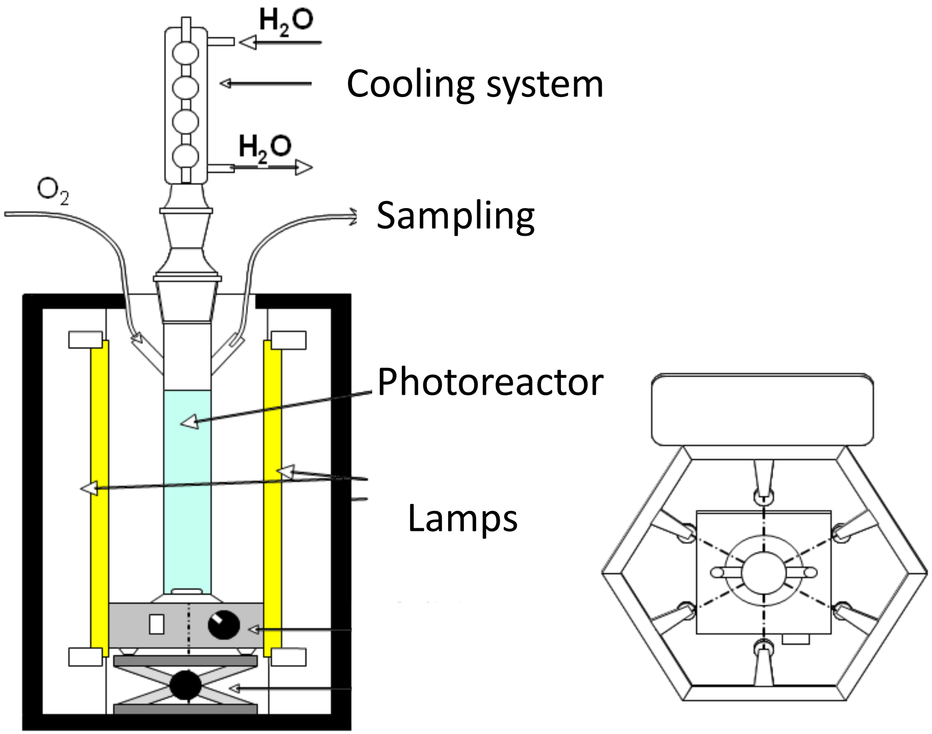
❖ Lower quality of the product.
❖ Harmful solvents.
❖ Food-unsave product.

15 $ / kg

2400 $ / Kg

Synthesis of vanillin in water by TiO_2 photocatalysis – UV irradiation

Starting substrate	t_{irr} [min]	X%	S%
Ferulic acid (Merck)	90	14	12
Vanillyl alcohol (HPC3)	90	15	21
Isoeugenol (Merck)	90	54	12
Eugenol (Merck)	60	20	5

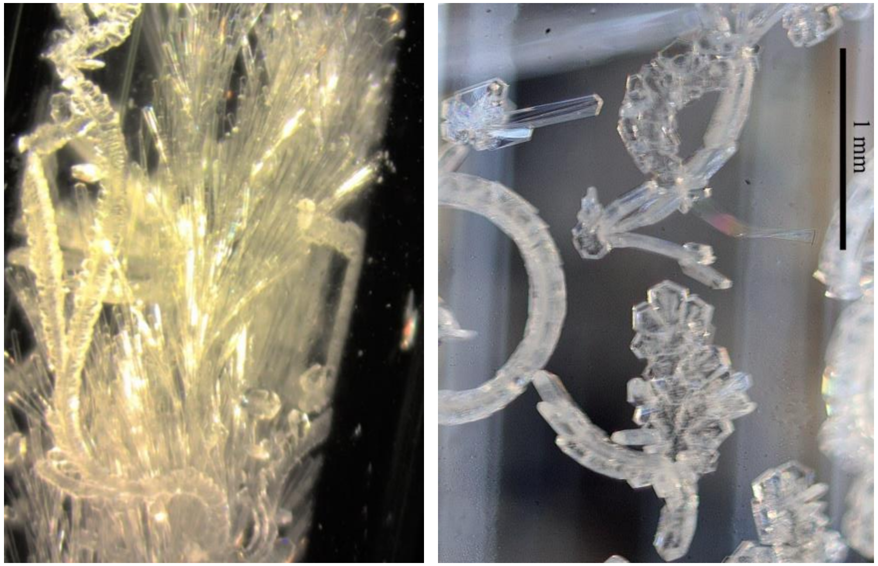


Starting substrate: Ferulic acid			
	t_{irr} [min]	X%	S %
P25	30	11	3
Merck	90	14	12
HPC3	90	42	2
HP0.5	120	96	1.5

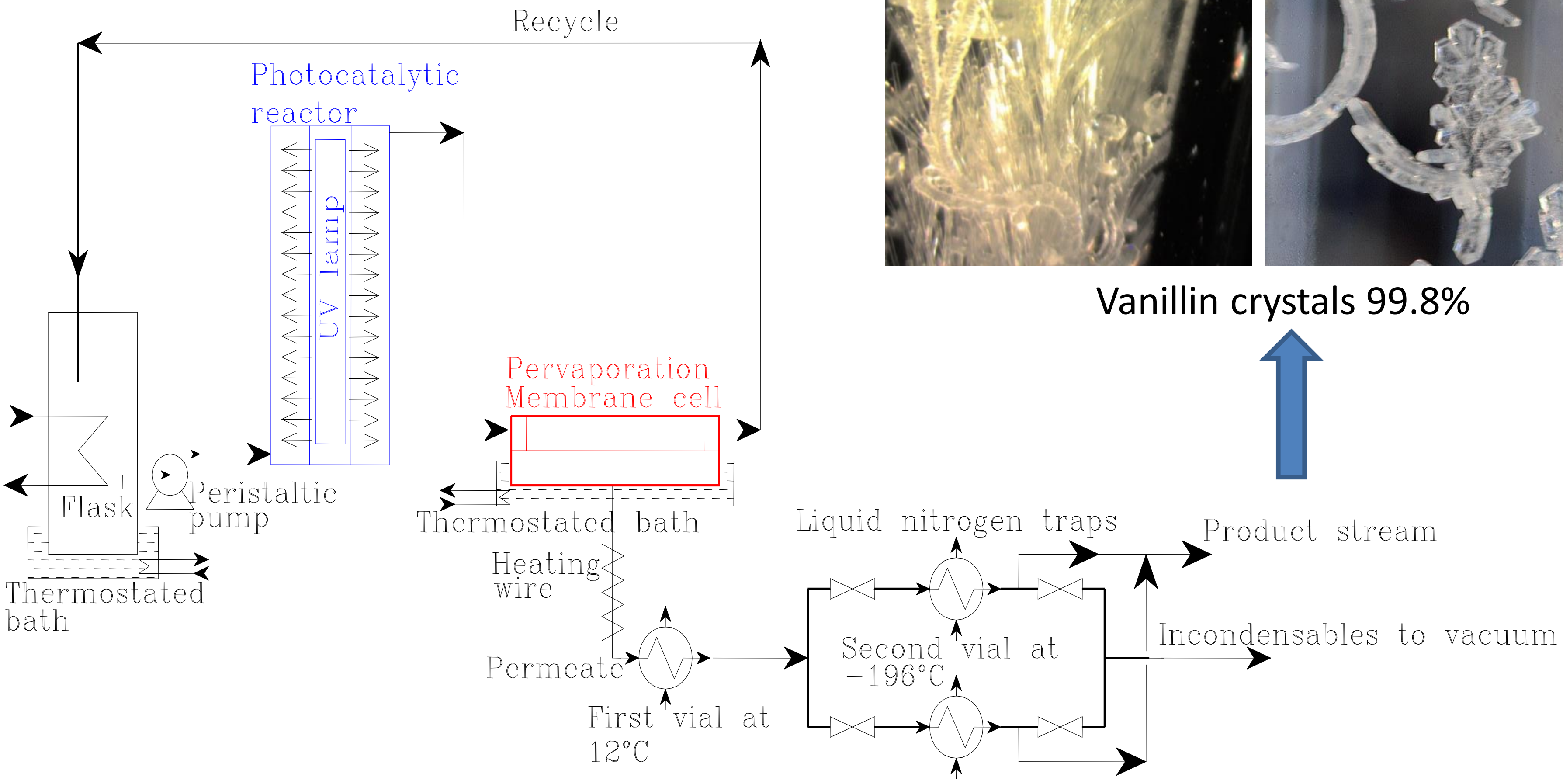
The reported selectivities are the highest obtained

V. Augugliaro, G. Camera-Roda, V. Loddo, G. Palmisano, L. Palmisano, F. Parrino, M. A. Puma, *Appl. Catal. B: Environ.* **111-112**, (2012) 555

Vanillin recovery by **pervaporation**

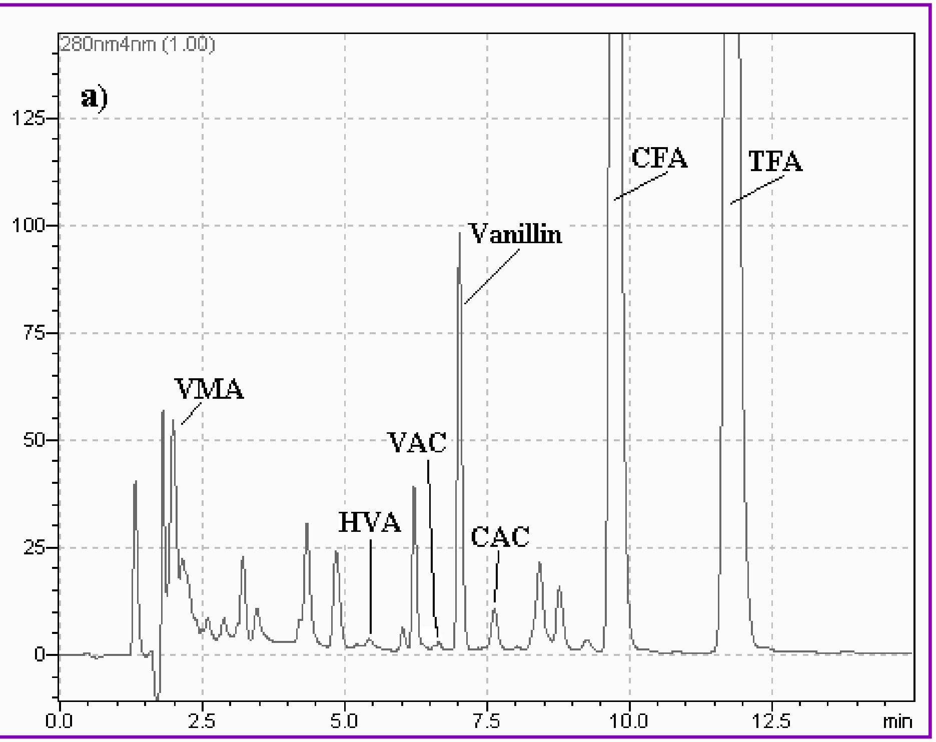


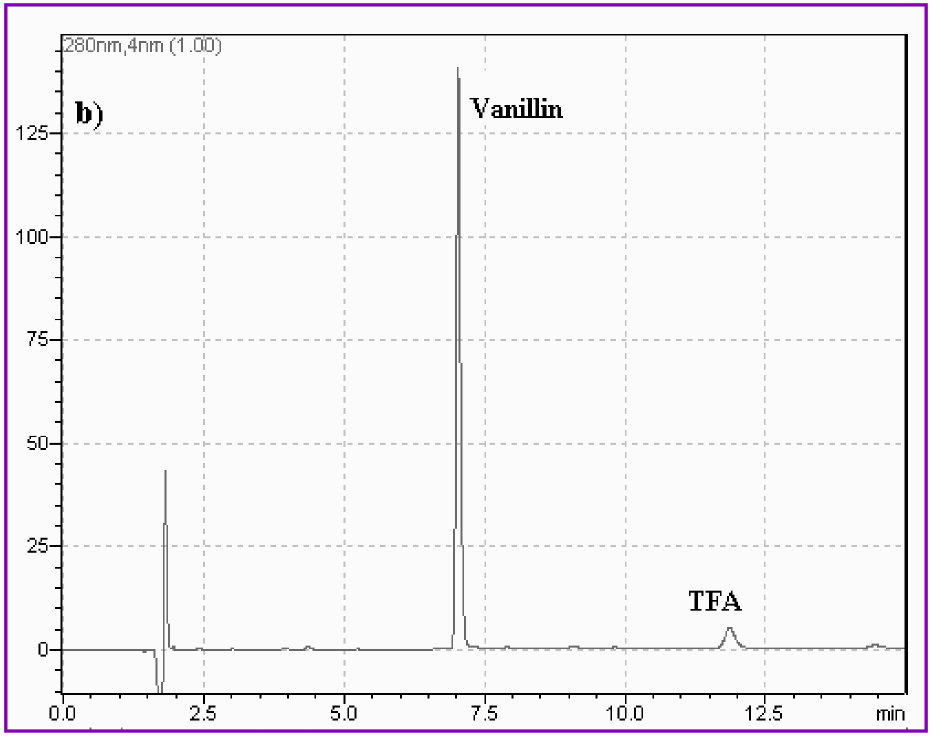
Vanillin crystals 99.8%



The polymeric membrane used is made of polyoctylmethyl siloxane (POMS) or polydimethyl siloxane (PDMDS), commercially available.

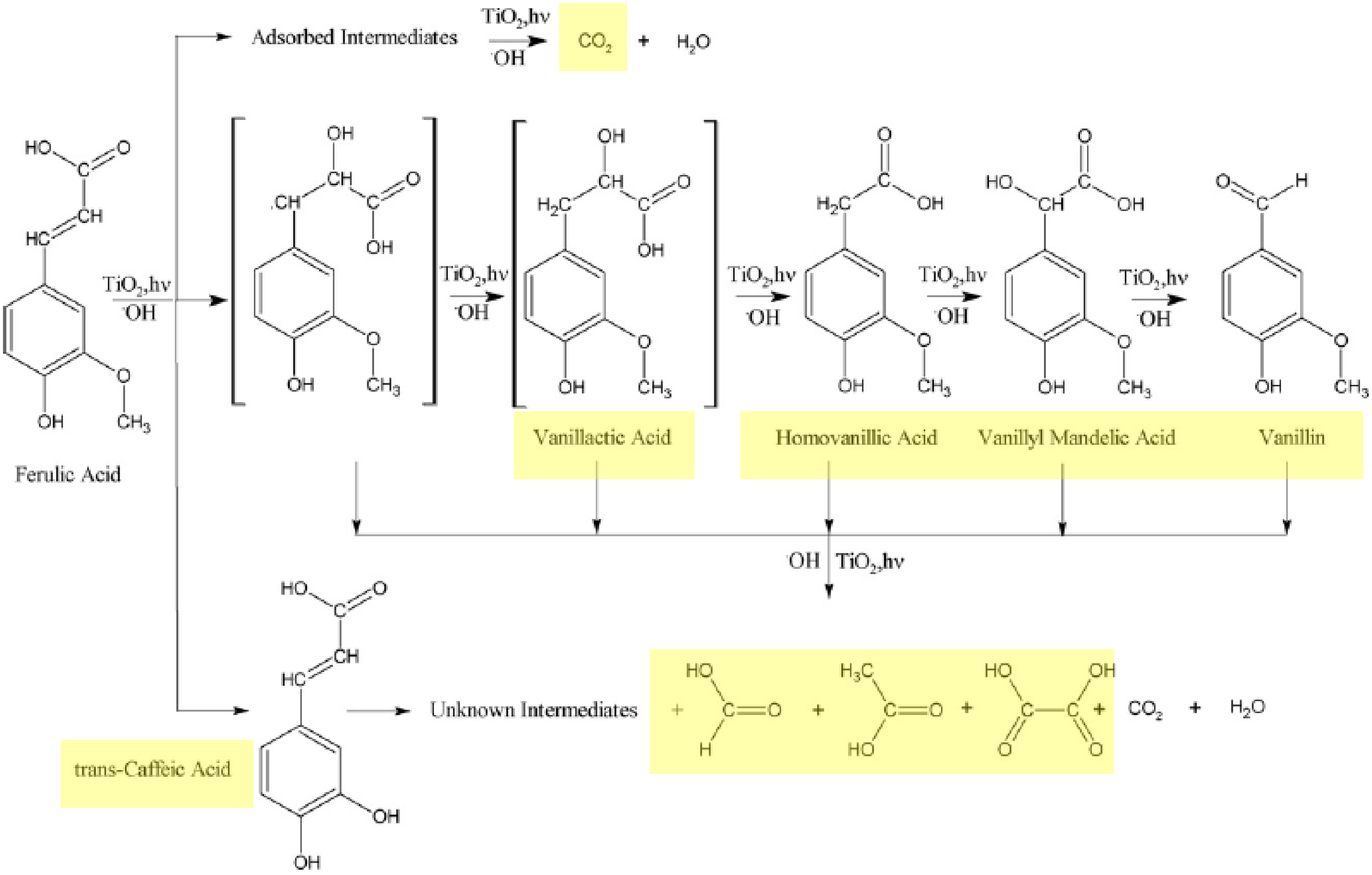
After 2h UV-irradiation…



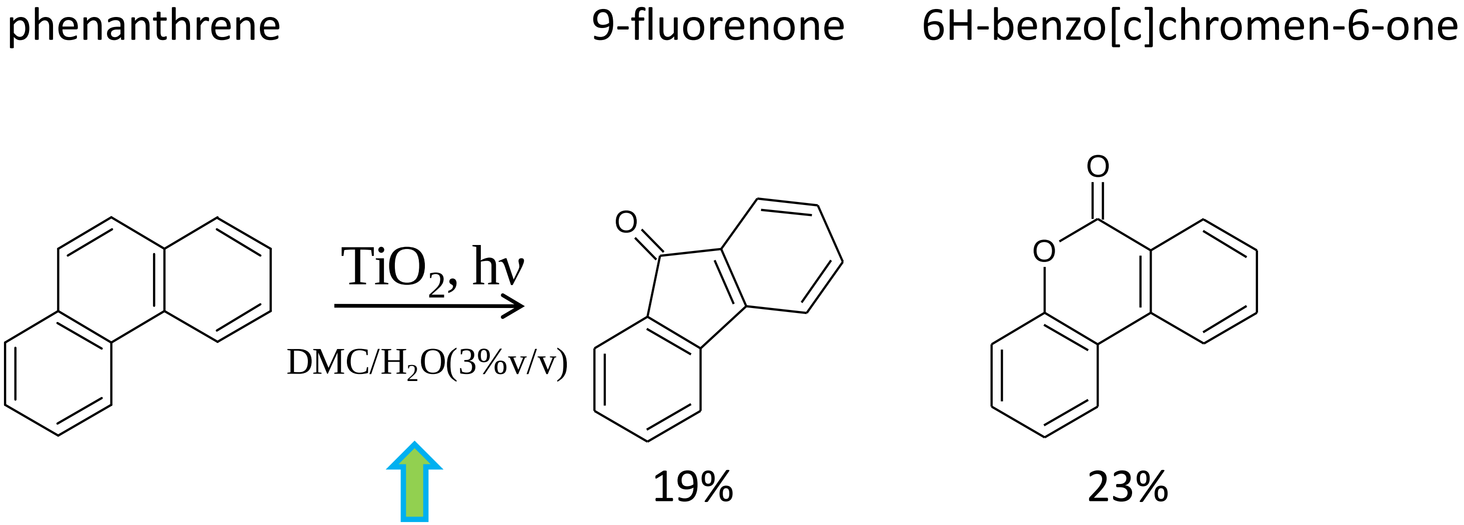


In the reacting solution

In the permeate


Adsorbed Intermediates
TiO2,hv
·OH
CO2 + H2O
Ferulic Acid
Vanillactic Acid
Homovanillic Acid
Vanillyl Mandelic Acid
Vanillin
trans-Caffeic Acid
Unknown Intermediates
CO2 + H2O

Phenanthrene partial oxidation

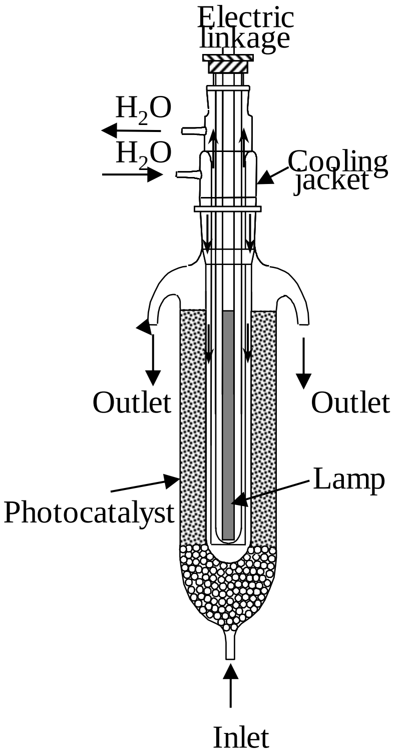


- Genotoxic
- Carcinogenic
- Persistent in the environment

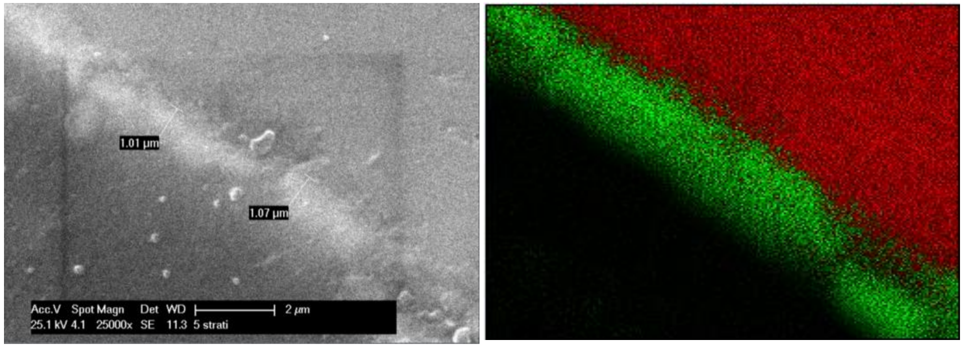
- High value-added products
- Uses: antibiotics and antimalaria drugs, solar cells, display devices.

M. Bellardita, V. Loddo, A. Mele, W. Panzeri, F. Parrino, I. Pibiri, L. Palmisano
Photocatalysis in Dimethyl Carbonate Green Solvent: Degradation and Partial Oxidation of Phenanthrene on Supported *TiO_2*
RSC Adv. 4 (77) (2014) 40859

Experimental set-up



Fixed-bed reactor operating in total recirculation mode



(a)

(b)

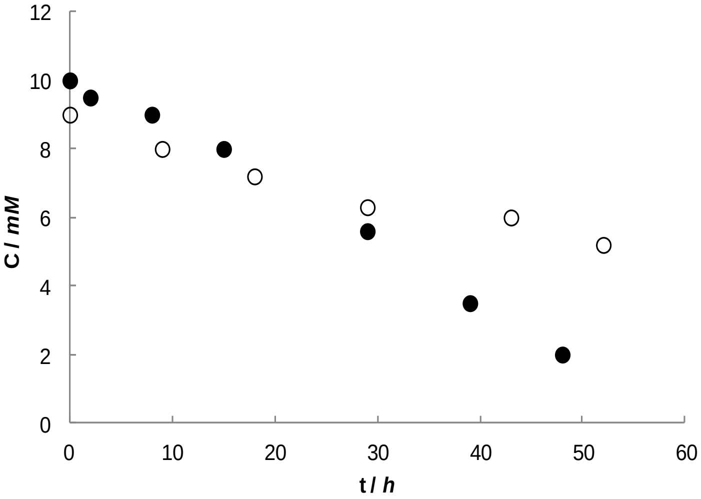
Cross-section micrograph (a) and EDAX (b) mapping of a layer of TiO_2 supported on a glass bead.

Alcohols as solvents/reactants

❖Phenanthrene degradation rate was higher in the presence of water, only using ethanol as the solvent. In the case of propanol the reaction rate was not dependent on the co-presence of water.

❖Alcohols participated to the reaction producing insertion of alkyl and/or alcoholate groups into the aromatic rings **(green entries).**

❖The main oxidation products obtained after ca. 80% conversion of phenanthrene, detected by GC-MS analysis, are listed in the table below.



❖Phenanthrene concentration versus reaction time for runs carried out in the presence of ethanol (empty circles) and ethanol/H_2O(3%v/v) mixture (full circles) as solvents.

$C_{14}H_{10}$	Phenanthrene
$C_{14}H_{12}O_2$	Cis-9,10 dyhidroxyphenanthrene
$C_{14}H_8O_2$	9,10 Phenanhtrenedione
$C_{14}H_{10}O_4$	2-2’-diphenic acid
$C_{16}H_{14}O_4$	2,2'-diphenic acid ethyl ester
$(C_6H_4CO_2C_2H_5)_2$	2,2'-diphenic acid diethyl ester
$C_{15}H_{14}O_2$	2 phenylbenzoic acid ethyl esther
$C_{10}H_{10}O_4$	Phthalic acid ethyl ester
$(C_6H_4CO_2C_2H_5)_2C_2H_5$	Ethyl-2,2'-diphenic acid diethyl ester
$(C_6H_4CO_2C_2H_5)_2OC_2H_5$	Ethoxy-2,2'-diphenic acid diethyl ester
$C_{14}H_{10}O$	3-Phenanthrol
$C_{13}H_{10}$	9H-Fluorene
$C_{13}H_8O_2$	6H-benzo[C]chromen-6-one
$C_{13}H_8O$	9- Fluorenone
$C_{14}H_{12}$	9H-Fluorene, 2-methyl
$C_{14}H_{10}$	9-Methylene-fluorene

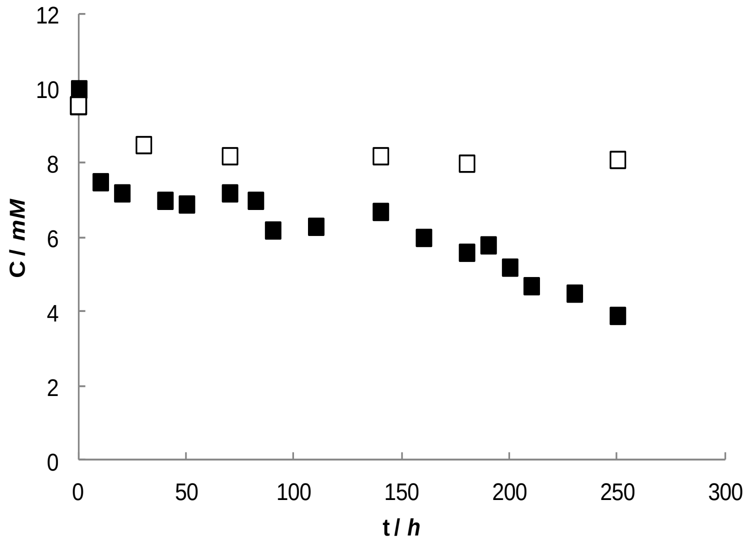
DMC as solvent

❖Phenanthrene degradation rate was higher in the presence of water, possibly because of the higher production of OH radicals obtained through water oxidation.

❖Virtually, DMC does not react with phenanthrene during the run.

❖Most of the oxidation products obtained after ca. 60% conversion of phenanthrene, detected through GC-MS analysis are listed in the table below .

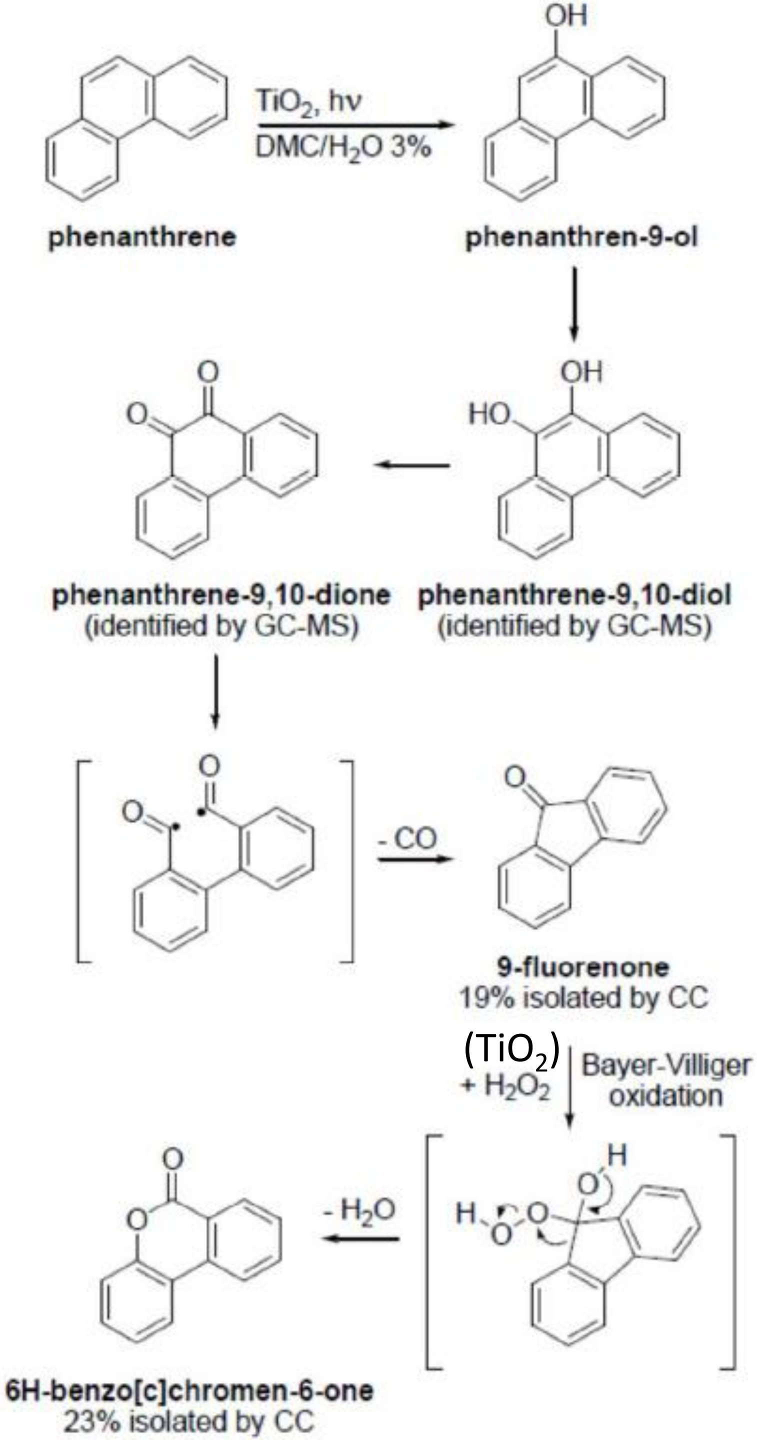
❖Among the oxidation products obtained in a run lasting 250 h (ca. 60% conversion of phenanthrene), **9-Fluorenone and 6H-benzo[c]chromen-6-one were separated by means of preparative column chromatography with a yield calculated on the converted phenanthrene equal to 19% and 23%, respectively.**



Concentration of phenanthrene versus irradiation time in (□) DMC and (■) DMC/H_2O (3%v/v) mixture as solvents.

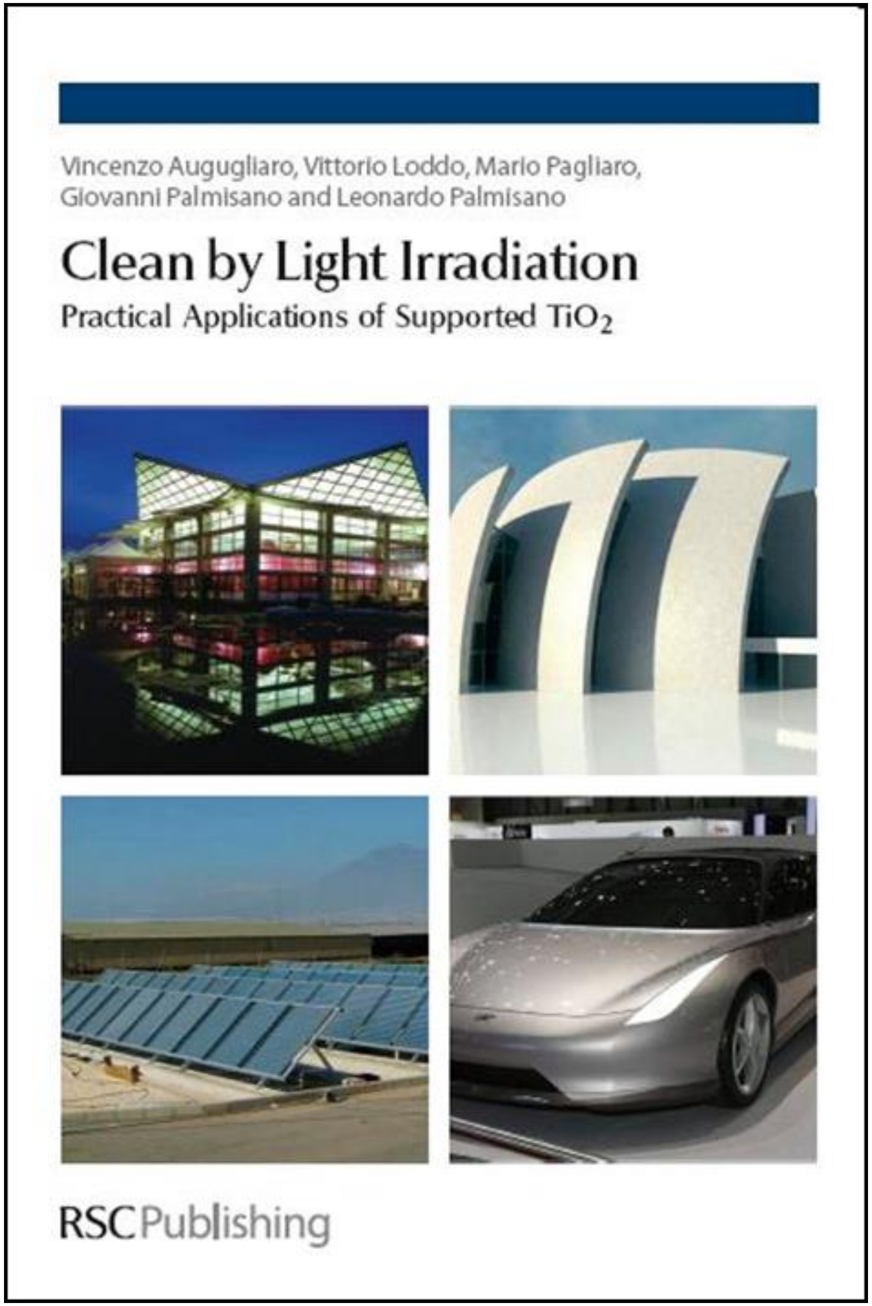
$C_{14}H_{10}$	Phenanthrene
$C_{14}H_{10}O$	9- Phenanthrol
$C_{14}H_{12}O_2$	Cis-9,10 dyhidroxyphenanthrene
$C_{14}H_8O_2$	9,10 Phenanhtrenedione
$C_{14}H_{10}O_4$	2-2’-diphenic acid
$C_{12}H_{14}O_4$	1,2-Benzenedicarboxylic acid, monobutyl ester
$C_{16}H_{22}O_4$	1,2-benzenedicarboxylic acid bis(2-methylpropyl) ester
$C_{24}H_{38}O_4$	1,2 benzenedicarboxylic acid diisooctyl ester
$C_{32}H_{54}O_4$	didodecyl phthalate
$C_{24}H_{38}O_4$	bis(2-ethylhexyl)phthalate
$C_{10}H_{10}O_3$	2-(1-oxopropyl)benzoic acid
$C_{15}H_{26}O$	Farnesol
$C_{15}H_{10}O$	Phenanthrene-9- carboxaldehyde
$C_{13}H_8O_2$	**6H-benzo[c]chromen-6-one**
$C_{13}H_8O$	**9- Fluorenone**

Proposed mechanism



To sum up very briefly…

- Heterogenous photocatalysis can be a powerful tool for synthetic purposes (synthesis of aldehydes, ketones, lactones) in real green conditions.
- It is not possible to generalize the choice of selective photocatalysts.
- To couple photocatalysis and pervaporation membrane technology has proved to be effective for the separation of aldehydes and in particular of vanillin.



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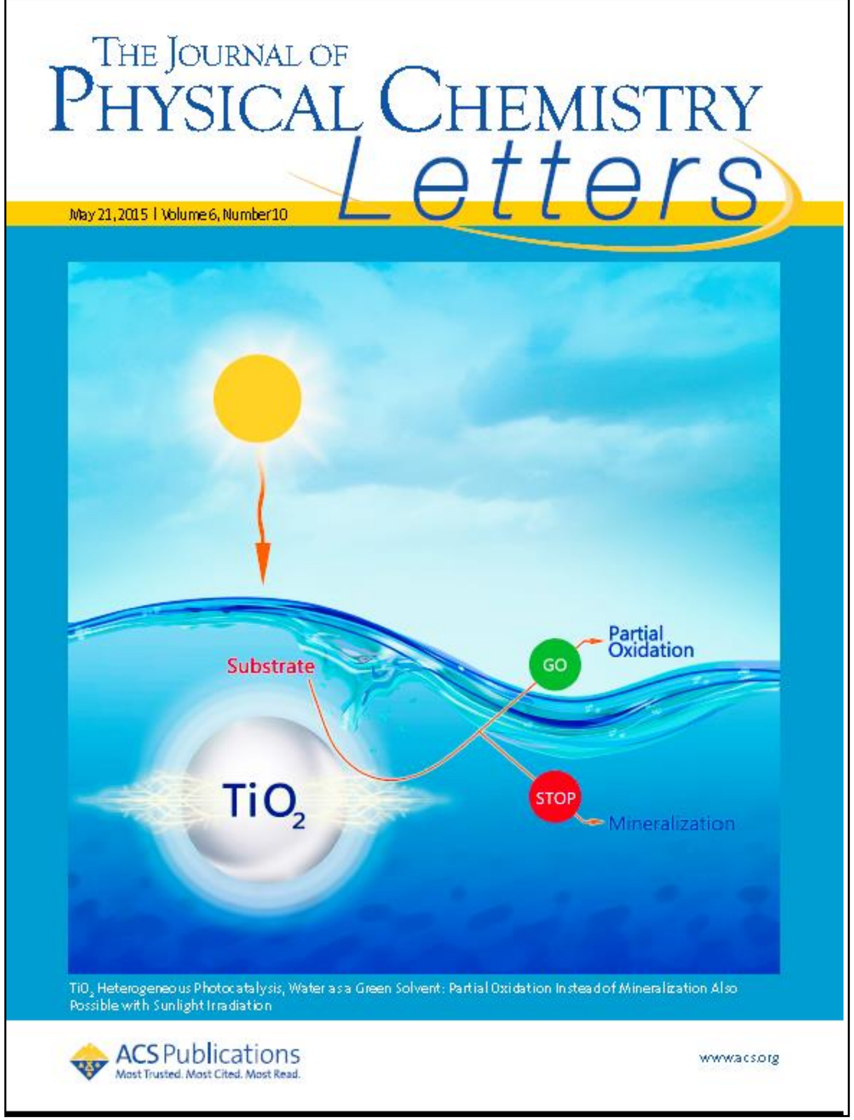

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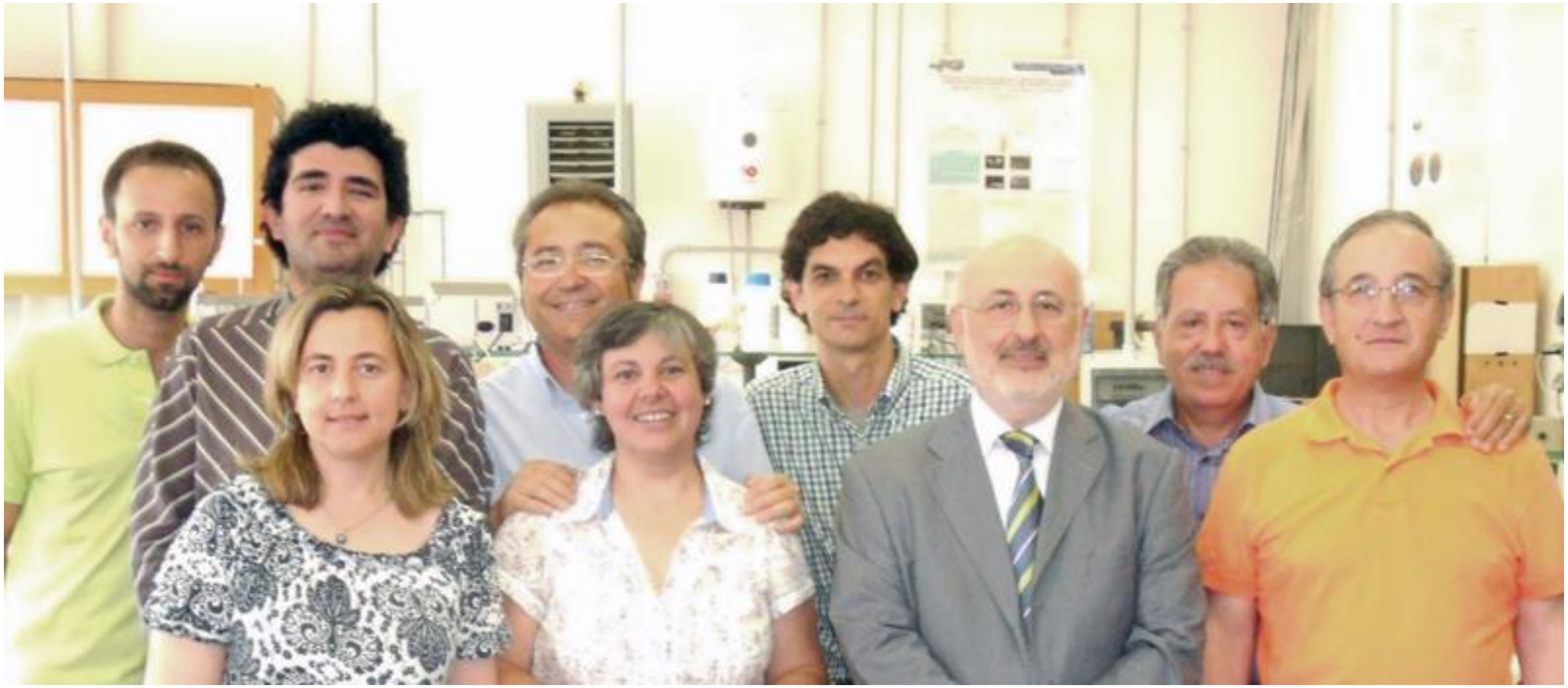
Heterogeneous Photocatalysis and Photoelectrocatalysis: From Unselective Abatement of Noxious Species to Selective Production of High-Value Chemicals

Vincenzo Augugliaro, Giovanni Camera-Roda, Vittorio Loddo, Giovanni Palmisano, Leonardo Palmisano, Javier Soria, and Sedat Yurdakal

J. Phys. Chem. Lett. 6 (2015) pp. 1968-1981.

Perspective article

Thanks for your kind attention



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