

R. R. Bacsa and J. Kiwi, "Effect of Rutile Phase on the Photocatalytic Properties of Nanocrystalline Titania During the Degradation of p-Coumaric Acid", *Appl. Catal. B: Environ.*, **16**, 19-29 (1998).

Background

correlation between

photocatalytic activity (PA) (for what kind of reaction?)
and physical properties of photocatalyst (e.g. TiO₂)
e.g., crystallite phase (structure): polymorph - [amorphous], anatase, brookite, rutile
crystallite size
surface area
etc

a lot of discussion on the effect of crystal structure, especially **anatase** and **rutile** --> ambiguous
many authors claimed the superior activity of TiO₂ with anatase and rutile **mixture**

problem 1: Can we discuss PA by using only crystal phase?
many characteristics are also changed along with crystallite phase
generally rutile crystallite forms larger particle, i.e., smaller specific surface area

problem 2: Is the order of PA applied in any case?
different dependence of PA on physical properties
How can we evaluate PA comprehensively?

fact 1: rutile is thermodynamically stable, and the others are kinetically stable;
transform into rutile by treatments including heating (annealing), braying...

fact 2: XRD (X-ray diffraction) tells us the crystallite phase, **qualitatively**, not quantitatively
very small nuclei of crystallites only gives raman scattering peak, but not appears in XRD

fact 3: several modes of mixing of two crystallite phase are possible

e.g., physical mixture of crystallites
one crystal phase covers others
two phases are attached each other

TEM and electron diffraction can be a possible technique but homogeneity is needed

Photocatalysts

prepared by hydrothermal treatment (250-275 deg, ca. 15-40 atm) of peptized (making clear) sol prepared with hydrolysis of titanium(IV) alkoxides [already reported by **ref. 13** but not interpreted]

Table 1

catalyst	BET surface area/m ²	precursor (alkoxide)	crystal phase	PA/10 ¹⁸ no of mol. sec ⁻¹ m ⁻²	PA/10 ¹⁸ no of mol.sec ⁻¹
A100	109	Ti butoxide	anatase (amor?)	1.6	170
R30	72	Ti isopropoxide	anatase 70/rutile 30	40	2880
R50	68	Ti ethoxide	anatase 50/rutile 50	12	820
R100	9	Ti ethoxide	rutile	1.5	10
P-25	(50)	commercial Degussa	anatase 80/rutile 20	24	1200
CLDO2210	50	commercial Tioxide	rutile	7.7	390

PA: photocatalytic oxidative decomposition of p-coumaric acid (p-CA) into CO₂
H₂O₂ was added

suspension containing

TiO ₂	1g	
p-CA	0.37 mM (in many cases) 55 mg	370 μmol
H ₂ O ₂	3.7 mM (in many cases)	3700 μmol
O ₂	?	?
water	1 dm ³	

cf. Fig. 13 in ref. 11.

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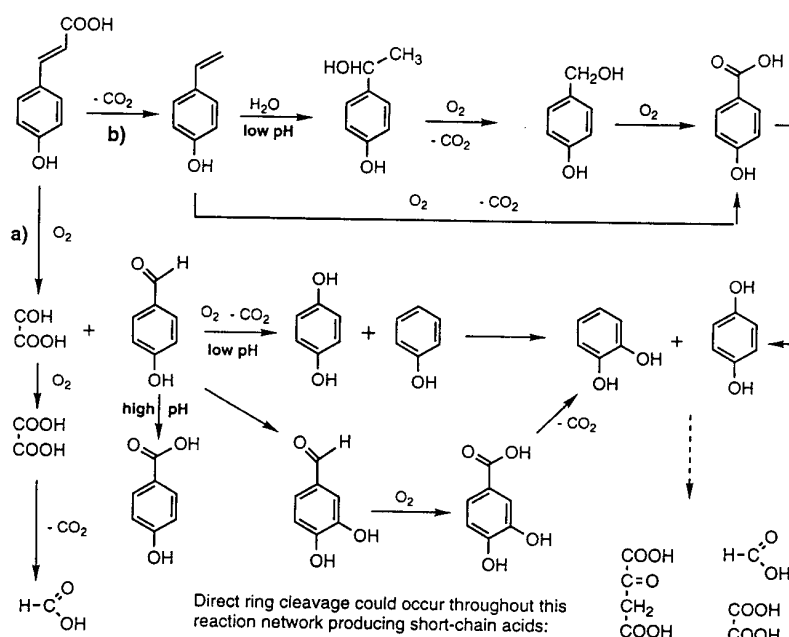


Fig. 13. The proposed reaction network for the oxidation of p-coumaric acid with CuO·ZnO·Al₂O₃ catalyst.

Table 1 (meaning of PA divided by BET area?) if not considered --> right side column extraordinary high activity of R30 and negligible activity of R100.

Fig. 1 unknown how could they evaluate the **rate** of PA decrease --> initial slope? A100, R100, and CLDO2210 were less active; anatase-rutile mixtures were better? PA for R100 and CLDO2210 were similar (? >5 times) --> not influenced by BET area

Fig. 2 effect of irradiation (wavelength? 2.1 kW Suntest lamp (AM1) - Xe arc?) effect of H₂O₂ addition

Fig. 3 (delete "log" of legend of vertical axis) first-order kinetic simulation (how much C₀?) fitted --> what does it mean?
1) rate was determined by diffusion of p-CA from the bulk of solution
2) amount of adsorbed p-CA was proportional to concentration in bulk (Henry type) ratio of rate constant of P-25 ca. 1.6 times, corresponding to what?

Fig. 4 dependence on the initial concentration of p-CA on R30: not so obvious "0.08-0.5 mM" in the figure caption should read 0.18-0.9 mM

assuming C_0 in Fig. 3 was lower than those in Fig. 4,

- 1) light intensity (photon flux) limited rate
- 2) saturation of adsorption at > 0.18 mM p-CA

Fig. 5 dependence of amount of R30 --> rate was increased with the amount but saturated
inner filter effect ? <-- number of absorbed photons might be constant
presumably due to the decreased concentration of adsorbed p-CA

Fig. 6 relation between TOC (total organic carbon) decrease and CO_2 evolution;
almost parallel --> without long-lived intermediate(s) at lower concentration
cf. in Fig. 4, 0.2 mM was the lowest and gave monotonous decrease

Fig. 7 X-ray diffraction

facts: R100 contained small amount of anatase and/or brookite (trace 4)

A100 contained small amount of rutile (trace 1)

cf. ref. 13 reported the preparation of TiO_2 powders

Table 1 in ref. 13

ethoxide, water/alkoxide ratio = 80, BET = 68.0 ---> R50

isopropoxide ratio = 80, BET = 71.8 ---> R30

butoxide, ratio = 80, BET = 107.1 ---> (A100)?

Fig. 2 in ref. 13

above-mentioned three samples giving different XRD patterns

"An estimate of the anatase/rutile is obtained by taking the ratio of the integrated intensities (the intensity ratios are calculated from the integrated area ratios) of the (110) reflection of the rutile to the (101) reflection of the anatase phase. [What was the standard?]

cf. in ref. 13: It is mentioned here that **the peak intensity is a qualitative estimate** of the trend because large differences in the crystallite size are observed in the transmission electron micrographs (TEM, Fig. 1) and hence the rutile concentrations could be less than that shown in Fig. 3.

cf. Fig. 2 in ref. 13

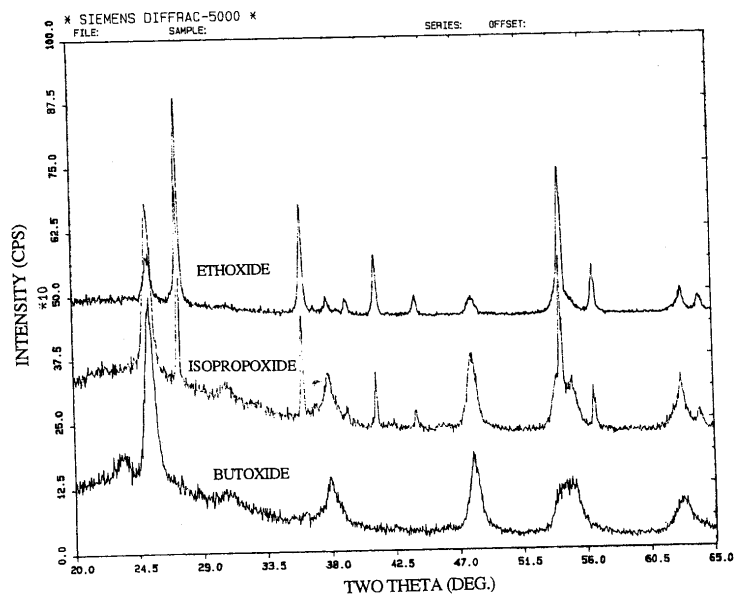


Fig. 2. Powder X-ray diffractograms of titania powders after hydrothermal processing of peptized titania from ethoxide, isopropoxide, and butoxide. Water/alkoxide ratio in all cases is 80.

Fig. 8 TEM of R30 (**completely same as Fig. 1 in ref. 13!**)
sphere (diameter ca. 25 nm) + long prismatic particles (end-to-end length ca. 50 nm)
assignment: ambiguous
cf. in ref. 13 "All the large (55 nm) crystals show the rutile phase..." concluding independent formation of crystallites of anatase (sphere) and rutile (prism)

--> mixing anatase and rutile is **not a reason for higher activity**
--> anatase or rutile crystallites prepared under the condition where both crystallites are included?

Fig. 9 pore size distribution (**partly same as Fig. 4 in ref. 13!**)
characteristic behavior of R50 giving larger pores (mesopore)
maximum pore size was increased with rutile content
rutile crystallites made larger pores --> higher photocatalytic activity?

Fig. 10 electrophoretic mobility: point of zero charge, a pH where mobility is zero
zeeta potential of R30 = +49 mV: preferential adsorption of negatively charged molecules (p-CA)

Conclusion

PA: combination of pore size
pore size distribution
appropriate crystal plane on which adsorption takes place

References ref. 20 should read J. Kiwi, M. Graetzel, J. Phys. Chem., 91 (1987) 6673-6677.

No consideration of electron-hole recombination and effect of physical properties on it.
rutile crystallites with relatively larger surface area (CLDO2210)