CHIMIE « VERTE » : APPLICATION DE LA PHOTOCATALYSE AUX TRAITEMENTS DE L'AIR ET DE L'EAU/ *GREEN CHEMISTRY : APPLICATION OF PHOTOCATALYSIS TO AIR AND WATER TREATMENT*

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Heterogeneous photocatalysis has recently appeared as a new emerging "Advanced Oxidation Process" (AOP), with more than 2000 recent publications on the subject.

1. Principle

When a divided semiconductor is illuminated with photons of energy higher than or equal to its band gap energy, photo-electrons e^- and photo-holes (or positons) h^+ are created. In a fluid reaction medium, reactants can adsorb and react either with electrons (acceptor molecules such as O_2) or with holes (donor molecules). Photocatalysis is based on the double aptitude of the photocatalyst (essentially titania) to simultaneously adsorb reactants and to absorb efficient photons. The 5 main parameters which govern the kinetics are (i) the mass of catalyst, (ii) the wavelength, (iii) the initial concentration (or pressure) of the reactant, (iv) the radiant flux and (v) exceptionally the temperature

2. Water treatment: Types of pollutants removed by photocatalysis

2.1 Inorganic pollutants

Many toxic inorganic ions are oxidized in their harmless upper oxidized state. For example, SO_3^{2-}, HSO_3^-, $S_2O_3^{2-}$, S^{2-} and HS^- are oxidized into innocuous SO_4^{2-} ions whereas PO_3^{3-} is oxidized into PO_4^{3-}. NO_2^- and NH_4^+ ions are oxidized into NO_3^-,whereas CN^- is oxidize into OCN^- and subsequently into NO_3^- and CO_3^{2}. In parallel, heavy metal cations (Ag^+,Hg^{2+},Pd^{2+},Au^{3+},Rh^{3+},Pt^{IV},...) can be reduced by the photoelectrons and then deposited on titania as crystallites without screening its surface.

2.2 Organic pollutants

This is the main field of water photocatalytic decontamination. Most of aliphatic and aromatic pollutants are totally mineralized into CO_2 and innocuous inorganic anions. More complex molecules such as pesticides (herbicides, insecticides, fungicides etc...) or dyes are totally destroyed. In particular, the dangerous organophosphorous are destroyed, as an example, phenitrothion completely disappeared according to the stoichiometry:

$$(CH_3)_2\text{-}P(S)\text{-}O\text{-}C_6H_3(NO_2)\text{-}CH_3 + 13/2\ O_2 \rightarrow 9\ CO_2 + 3\ H_2O + 4\ H^+ + H_2PO_4^- + SO_4^{2-} + NO_3^-$$

Another example of green chemistry is the total degradation of dyes in water with, in particular for the azo-dyes, the 100% selective degradation of the-N=N- azo-group into di-nitrogen N_2.

2.3 Prevention of water pollution by photocatalysis

Water pollution can be avoided by photocatalytic clean, "green" and selective chemistry. For example, an important intermediate in industrial fine (perfume) chemistry (4-tert-butyl-benzaldehyde) is environmentally-hostilely prepared in industry by a stoichiometric oxidation of 4-tert-butyl-toluene by permanganate in a strongly acidic aqueous medium with a lot of (in)organic by-products:

$5\ C_4H_9\text{-}C_6H_4\text{-}CH_3 + 4\ KMnO_4 + 6\ H_2SO_4 \rightarrow 5\ C_4H_9\text{–}C_6H_4\text{-}CHO + 2\ K_2SO_4 + 4\ MnSO_4 + 11\ H_2O$

By contrast, the oxidation of 4-TBT is 100% selective in 4-tert-butyl-benzaldehyde by mere irradiation of titania at room temperature in pure **organic** phase (both in gas or liquid) without using water:

$C_4H_9\text{-}C_6H_4\ CH_3 + O_2\ (air) + TiO_2 + h\nu \rightarrow C_4H_9 - C_6H_4 - CHO + H_2O$

The photocatalytic oxidation of 4-TBT is a typical example of "Green Chemistry" with the use of air and a cheap, stable and recyclable titania catalyst which does not need solvents nor heating but only UV-A light provided by lamps whose technology is permanently improving.

3 Air treatment

All pollutants in the aqueous phase can also destroyed when they are in air phase, especially all the COV's, provided a certain air humidity enabling titania to produce cracking OH° radicals. For chemical engineering reasons, the photocatalyst has to be in a fixed bed, or better deposited on a photo-inert support. This has been done using special AHLSTROM papers on which titania can be also associated with activated carbon to absorb pollution peaks. In these conditions, UV-irradiated titania-based photocatalysis could be successful applied to the elimination of air pollutants, COV'S, solvents, odors, chemicals, etc.

Concerning odors, an anti-odor domestic refrigerator prototype has been validated, patented and industrially produced in a first series at 40,000 examplaries and in a second one at 70,000 units.

Other photocatalytic devices can equip kitchen ventilations, air conditioning systems in rooms or in cars. Some air purification devices are envisaged for the electronics industry, which requires a "molecular" purity of the ambient working atmosphere for better performances of their nano-scale components. It can be noted that silicon-containing VOC's are destroyed, the organic part being mineralized as CO2 and H2O, whereas Si is converted into silica at the surface of titania, silica being transparent to UV-light. Air treatment has to be associated to water and solid wastes treatment because of odors. This is done by covering water treatment ponds or lagunas by rafts on which large sheets of Ahlstrom papers are deposited, supporting associated activated carbon-titania catalysts which destroy odors with solar UV-photons in day time, whereas activated carbon traps odors during the nights before their transfer to titania the next day, the driving force being the very strong concentration gradient between AC and self-cleaning titania. Eventually, C.Guillard from LACE, could eliminate Virus H5N2, a model virus close to H5N1, responsible for the aviar flu. The photocatalytic de-activation of H5N3 was performed in a contaminated air flux of 60 m^3/h in a specialized P3 medical laboratory.

Present researches on air treatment concern possible improvements in coupling photocatalysis with other oxidizing agents or with adsorbents (activated carbon, zeolithes…) or with other processes (cold plasma, sonication,…).