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Heterogeneous photocatalysis: an emerging discipline involving multiphase systems

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Abstract

The influence of the various parameters which govern the kinetics (mass of catalyst, wavelength, initial concentration, temperature, radiant flux, modification of the photocatalyst) has been analyzed. The knowledge of these parameters enables one to determine the best conditions for an optimum quantum yield. The photon appears as a reactant and the light flux as an additional phase (the 'electromagnetic phase'). Several examples of polyphasic photocatalytic systems are described with up to 5 phases working concertedly, especially in the case of pollutant removal from used waters.

1. Introduction

Heterogeneous photocatalysis appears as an emerging technology in the domain of the environnement for air and water treatment. Several books and reviews have been recently devoted to this problem [1–4]. Besides this recent application, heterogeneous photocatalysis is also a typical discipline involving complex multiphasic systems with up to 5 different phases. In all cases, the photonic flux is considered as a full phase as justified further.

1.1. Principle of heterogeneous photocatalysis

When a semiconductor catalyst SC (oxide or sulfide) is illuminated with photons whose energy is equal to or greater than their band-gap energy E_G ($h\nu \geq E_G$), there is absorption of these photons and creation within the bulk of electron-hole pairs, which dissociate into free photoelectrons in the conduction band and photoholes in the valence band. In the presence of a fluid phase (gas or liquid), a spontaneous adsorption occurs and according to the redox potential (or energy level) of each adsorbate, an electron transfer proceeds towards acceptor molecules, whereas positive photoholes are transferred to donor molecules. Each ion formed subsequently reacts to form the intermediates and final products. The photonic excitation of the catalyst appears as the initial step of the activation of the whole catalytic system. Thence, the efficient photon has to be considered as a reactant and the photon flux as a special fluid phase, the 'electromagnetic phase'.

2. Experimental

2.1. Catalysts

Various chalcogenides (oxides and sulfides) were used. However, in all the systems described,

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the catalyst used was non-porous titania (Degussa TiO_2 P-25, 50 m^2/g, mainly anatase), unless otherwise stated. Titania was sometimes modified either by iron doping or by deposition of a metal (Pt, Rh or Ni).

2.2. Photoreactors

Depending on the reaction considered, various microphotoreactors were chosen: fixed-bed photoreactors (differential flowing type for gas phase oxidations or static integral type for isotopic exchange) or slurry batch photoreactors either mechanically or magnetically stirred. Near-UV light was provided by a Philips lamp (HPK 125 watts) placed in front of the optical window of the photoreactor. IR beams were removed by a circulating-water cell. The wavelength was selected with optical filters (fused silica, or pyrex, or Corning glass filters). The radiant flux was measured with a radiometer.

3. Influence of physical parameters governing the kinetics

3.1. Mass of catalyst

Either in static, or in slurry or in dynamic flow photoreactors, the initial rates of reaction were found to be directly proportional to the mass m of catalyst (Fig. 1A). This indicates a true heterogeneous catalytic regime. However, above a certain value of m, the reaction rate levels off and becomes independent of m (Fig. 1A). This limit depends on the geometry and on the working conditions of the photoreactor. It was found equal to 1.3 mg TiO_2 per square centimeter of a cross-section of a fixed bed and to 2.5 mg TiO_2 per cubic centimeter of suspension. These limits correspond to the maximum amount of TiO_2 in which all the particles — i.e. all the surface exposed — are totally illuminated. For higher quantities of catalyst, a screening effect by excess particles occurs, which masks part of the photosensitive surface. For applications, this optimum mass of catalyst has to be chosen in order (i) to avoid an unnecessary excess of catalyst and (ii) to ensure a total absorption of efficient photons.

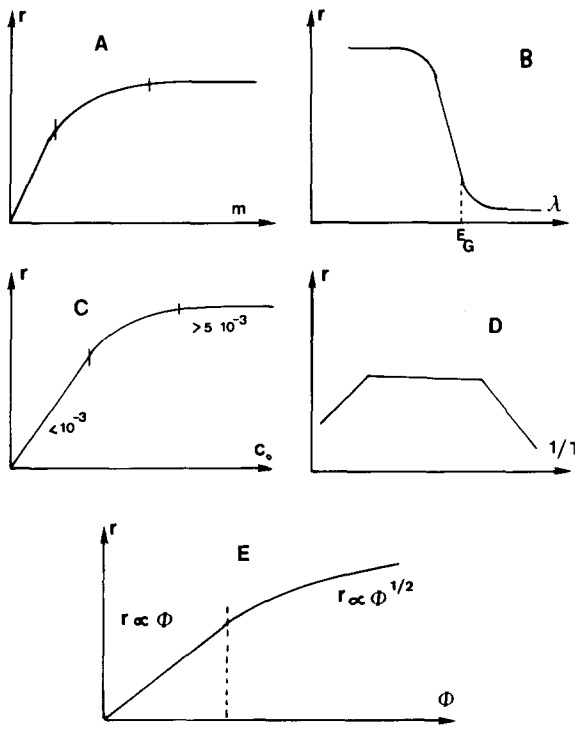

Fig. 1. Influence of the main physicochemical parameters upon the photocatalytic reaction rate. (A) mass of catalyst; (B) wavelength; (C) initial concentration; (D) temperature; (E) light flux.

3.2. Wavelength

The variations of the reaction rate as a function of the wavelength follows the UV-visible absorption spectrum of the catalyst, with a threshold corresponding to its band gap energy (Fig. 1B). For TiO_2 with $E_G = 3.02$ eV, this requires: $\lambda \geqslant 400$ nm. In addition, it must be checked that the reactants do not absorb the light to conserve the exclusive photoactivation of the catalyst for a true heterogeneous catalytic regime (*no homogeneous nor photochemistry in the adsorbed phase*).

3.3. Initial concentration

Generally, the kinetics follows a Langmuir–Hinshelwood mechanism confirming the hetero-

geneous catalytic character of the system with the rate r varying proportionally with the coverage as: $r=k(KC/(1+KC))$. For diluted solutions ($C<10^{-3}$ M), KC becomes $\ll 1$ and the reaction is first order, whereas for concentrations $>$ ca. 5×10^{-3} M, ($KC\gg 1$), the reaction rate is maximum and of the zeroth order (Fig. 1C). Similar Langmuir–Hinshelwood expressions including partial pressures P instead of C have been found for gaseous reactants. In some cases, such as in alcohol dehydrogenation [5], the rate follows a square root variation: $r=k[K^{1/2}C^{1/2}/(1+K^{1/2}C^{1/2})]$. This indicates that the active species react in the dissociated adsorbed state. In other cases, such as in the photocatalytic degradation and mineralization of chlorobenzoic acids [6], a zero kinetic order was found, even at low concentrations. This is due to a strong chemisorption on titania with the saturation of the hydroxylic adsorption sites. For a maximum yield, reactions should be performed with initial concentrations equal to or higher than the threshold of the plateau.

3.4. Temperature

Because of the photonic activation, the photocatalytic systems do not require heating. The true activation energy is nil, in agreement with an experimental activation energy E_a very small (a few kJ/mol as seen in Fig. 1D). Photocatalysis is generally operating at room temperature. At low temperature (<0°C), the activation energy E_a increases and tends to become equal to the heat of desorption of the reaction product. This is exemplified by the case of hydrogen in alcohol dehydrogenation [5] or alkane–deuterium isotopic exchange [7], carried out on bifunctional Pt/TiO_2 photocatalysts. This means that at these low temperatures, the rate-limiting step has become the desorption of H_2 (or HD) from the metallic part of the catalyst.

By contrast, at 'high' temperatures ($\theta\geq 70$°C) for various types of photocatalytic reactions, the activity decreases and the apparent activation energy becomes negative. This indicates that the adsorption of the reactant becomes the rate limiting step [8].

As a consequence, the optimum temperature is generally comprised between 20 and 80°C. This explains why solar devices which use light concentrators require coolers [9]. This absence of heating is attractive for photocatalytic reactions carried out in aqueous media and in particular for environmental purposes (photocatalytic water purification). There is no need to waste energy in heating water which possesses a high heat capacity. Photocatalysis has been presented as competitive with incineration for VOC treatment in air [10].

3.5. Radiant flux

The light power invested is determined by measuring the radiant flux Φ. The total light power emitted corresponds to ca. 20% of the electrical power consumed. It has been shown, for all types of photocatalytic reactions, that the rate of reaction r is proportional to the radiant flux Φ (Fig. 1E). This confirms the photo-induced nature of the activation of the catalytic process, with the participation of photo-induced electrical charges (electrons and holes) to the reaction mechanism. However, above a certain value, estimated to be ca. 250 W/m^2, the reaction rate r becomes proportional to $\Phi^{1/2}$ (Fig. 1E). It can be demonstrated that the rate of electron-hole formation becomes greater than the photocatalytic rate, which favours the electron-hole recombination:

$$e^- + p^+ \rightarrow N + E$$

(N: neutral center; E: energy (light $h\nu' \geq h\nu$ or heat).

The optimal light power utilization corresponds to the domain where r is proportional to Φ.

3.6. Quantum yield

By definition, it is equal to the ratio of the reaction rate in molecules per second (or in mol per s) to the efficient photonic flux in photons per second (or in Einstein per second (an Einstein is

a mol of photons)). This is a kinetic definition, which is directly related to the instantaneous efficiency of a photocatalytic system. Its maximum value is equal to 1. It may vary on a wide range according (i) to the nature of the catalyst; (ii) to the experimental conditions used and (iii) especially to the nature of the reaction considered. We have found values comprised between 10^{-4} and 0.7. The knowledge of this parameter is fundamental. It enables one (i) to compare the activity of different catalysts for the same reaction, (ii) to estimate the relative feasibility of different reactions, and (iii) to calculate the energetic yield of the process and the corresponding cost.

3.7. Modifications of the catalyst by noble metal deposit and ion-doping

As generally observed, the maximum quantum yields are always obtained with titania. In addition, anatase is the most active allotropic form among the various ones available, either natural (rutile and brookite) or artificial (TiO_2–B, TiO_2–H). In photocatalytic reactions involving hydrogen, either as a reactant (deuterium–alkane isotopic exchange [7]) or as a product (alcohol dehydrogenation [5]), the system requires the presence of a metal acting as a co-catalyst necessary (i) to dissociate the reactant (D_2) and (ii) to recombine H and D into dihydrogen (or HD). Additionally, the metal (i) attracts electrons, by photoinduced metal-support interaction (PMSI), (ii) decreases the electron-hole recombination and (iii) maintains the turn-over number constant [11].

Another modification was aimed at extending the photosensitivity of titania to the visible region to harvest cheaper and more abundant solar efficient photons. This was done by ion doping, either n-type (Nb^{5+}, Sb^{5+}, Mo^{6+} Ta^{5+}) or *p*-type (Ga^{3+}, Cr^{3+}, Al^{3+}). Unfortunately, ion doping was found to strongly inhibit the reaction and decrease the quantum yield. This was explained by the fact that both pentavalent donor impurities and trivalent acceptor impurities behave as electron-hole recombination centers. However, this drawback could be turned into advantage by using ion doping as a means of passivating TiO_2-based pigments in paintings and plastics against weathering [12].

4. Examples of multiphase photocatalytic reactions

4.1. Gas–solid–UV light systems

These triphasic reactions were performed in differential flow photoreactors or in batch reactors. They concerned oxidations, gas decomposition and hydrogen involving reactions. In oxidation reactions oxygen or air was used as the oxidizing agent. They mainly concerned the mild oxidation of alkanes, alkenes and alcohols into carbonyl-containing molecules (aldehydes and ketones) [13]. Inorganic gases such as NH_3 or H_2S could be oxidized. Ammonia was oxidized mainly into nitrogen [14]. NO could be photocatalytically decomposed into N_2 at low pressures and into N_2O at higher pressures, whereas the oxygen generated could be used as an oxidizing agent for butanols [15].

Isotopic exchange between alkanes and deuterium was performed on bifunctional Pt/TiO_2 catalysts. By contrast with classical heterogeneous catalysis, the reaction was found not only selective in monodeuteroalkane (propane [16], cyclopentane [7]) but also regioselective (exchange of only one primary hydrogen atom per period of adsorption [14]).

$$CH_3–CH_2–CH_3 + D_2 \rightarrow CH_2D–CH_2–CH_3 + HD$$

4.2. Gas–solid–liquid organic phase–UV light systems

These tetraphasic reactions were performed with a thermostated slurry batch photoreactor with an optimized agitated suspension of 3.5 g TiO_2/l. They concerned the selective mild oxidation of

liquid hydrocarbons (alkanes, alkenes, cycloalkanes, aromatics) into aldehydes and ketones.

For instance, cyclohexane and decaline were oxidized into cyclohexanone (85%) and 2-decalone (86%), respectively [17]. Aromatic hydrocarbons [18] such as alkyltoluenes or *o*-xylenes were selectively oxidized on the methyl group into alkylbenzaldehydes. Pure liquid alcohols were also oxidized into their corresponding aldehydes or ketones. Using a bifunctional M/TiO_2 photocatalyst (with M = Pt, Rh, Ni) and in the absence of air the same alcohols were dehydrogenated with high quantum yields [5].

$$R\text{–}CHOH\text{–}R' \xrightarrow[h\nu]{Pt/TiO_2} R\text{–}CO\text{–}R' + H_2(g)$$

The hydrogen produced could be transferred to an unsaturated molecule added in the medium (case of diphenylacetylene (tolane) hydrogenated in situ into *cis*-diphenylethylene (*cis*-stilbene)) [19].

4.3. Gas–solid–solid–liquid phase–UV light systems

4.3.1. Photocatalytic deposition of noble metals

In aqueous suspensions of illuminated titania, noble metals can be reduced by photoelectrons and deposited as small crystallites according to the reaction:

$$M^{n+} + n/2H_2O \rightarrow M^\circ + nH^+ + n/4O_2(g)$$

with the following relative reactivity pattern: $Ag^+ > Pd^{2+} > Au^{3+} > Pt^{4+} \gg Rh^{3+} \gg Ir^{4+} \gg Cu{=}Ni{=}Fe{=}O$. This reaction was developed in two directions: (i) the noble metal recovery from diluted solutions and (ii) the one-step synthesis of highly divided noble metal catalysts deposited on semiconductors. In the former case, it was shown that a metal abatement to less than 0.1 ppm could be reached and that for high metal loadings, the metal gathers as large crystallites (case of Ag [21]) or as sponge-like agglomerates (case of Pt [20]), thus letting most of the photosensitive surface of titania free to continue to react. Small units for recovering silver from photographic baths have been proposed since titania is able to recover silver from thiosulfate complexes, $S_2O_3^{2-}$ ions being oxidized into SO_4^{2-} [21]. In the photocatalytic synthesis of metal catalysts, a high dispersion can be reached with particle size ranging from $\geqslant 1$ nm for Ir to 3–8 nm for silver [22]. For bimetallic catalysts, alloys could be detected only with metals of similar reactivity (case of Pd–Pt [22]).

4.3.2. Photo-assisted preparation of H_xMoO_3 hydrogen bronze

The illumination in the near UV of a suspended mixture of MoO_3 and TiO_2 in isopropanol in the absence of air produces the formation of a hydrogen–molybdenum bronze $H_{0.93}MoO_3$ [23]. TiO_2 acts as an alcohol dehydrogenation photocatalyst, which necessitates a metal co-catalyst for dihydrogen recombination and evolution (see above). Presently, since TiO_2 is naked, the only issue for H atoms (or protons) formed is the transfer onto MoO_3 particles during collisions in the suspension. H atoms incorporate into MoO_3 and form the bronze. If 0.5 wt.% Pt/TiO_2 is used instead of TiO_2, Pt recombines and evolves H_2, thus preventing the formation of the bronze. These reactions clearly indicate a possible transfer of matter between two solid phases in illuminated suspensions.

4.3.3. Photosensitization of Pt/TiO_2 in the visible by addition of a CdS co-catalyst

Because of its band gap energy E_G equal to 3.02 eV, titania is not active in the visible ($\lambda \leqslant 400$ nm). By addition of powdered CdS — which is photosensitive in the visible ($E_G = 2.4$ eV) — to a suspension of Pt/TiO_2 during methanol dehydrogenation, the triphasic CdS–Pt/TiO_2 mechanical mixture becomes an active photocatalytic system. This means that CdS absorbs the visible light and creates photo-electrons and holes. The holes oxidize isopropanol in acetone and protons, whereas electrons are transferred to TiO_2 and then to Pt. The protons are also transferred onto TiO_2, on which they migrate, by reverse spill-over, to Pt particles where they are reduced in a cathodic-like

process as H_2 molecules. This is an example of a simultaneous electron and hydrogen transfer between two solid phases in suspension.

4.4. Gas–solid–water–UV light systems

This system is the most promising issue for an application of heterogeneous photocatalysis since it is directly connected to water detoxification and to pollutant removal in aqueous effluents. Reactions have been carried out in static or in circulating slurry photoreactors. Some attempts have been made to deposit titania on glass beads and sheets (glass, fused silica, stainless steel) for an easy separation of the catalyst from purified waters. These reactions concern organic and inorganic pollutants.

4.4.1. Inorganic pollutants

Many toxic inorganic ions are oxidized in their upper harmless oxidation state. Hence, SO_3^{2-}, $S_2O_3^{2-}$, S^{2-} and HS^- are oxidized into innocuous sulfate ions. Nitrites are oxidized into nitrates, whereas cyanide ions are oxidized into isocyanate OCN^- and then to NO_3^- and CO_2.

4.4.2. Organic pollutants

This is the main field of water photodecontamination since most of aliphatic and aromatic pollutants are completely mineralized into CO_2 and H_2O. In the laboratory, various types of aromatic pollutants could be eliminated such as chlorophenols, dimethoxybenzene, chlorobenzoic acids, benzamide and nitrophenols [24]. More complex molecules such as pesticides (tetrachlorvinphos [24] and phenitrothion could be totally mineralized into H_2O, CO_2 and innocuous anions (NO_3^-, $H_2PO_4^-$, SO_4^{2-}). For phenitrothion, the overall degradation reaction corresponded to:

$$(CH_3O)_2\text{–}P(S)\text{–}O\text{–}C_6H_3(NO_2)(CH_3) + \frac{13}{2}O_2 \rightarrow 9CO_2 + 3H_2O + 4H^+ + H_2PO_4^- + SO_4^{2-} + NO_3^-$$

It is generally assumed that the oxidizing agent are OH free radicals generated by photoholes ($OH^- + p^+ \rightarrow OH^\cdot$), which hydroxylate the aromatic ring before its degrading opening, leading to aliphatic fragments such as oxalic, acetic and formic acids which subsequently oxidize into CO_2.

5. Reactorless multiphase photocatalytic systems in the environment

5.1. Artificial systems

5.1.1. Cleaning-up of marine oil spills

Through photoxidation on TiO_2 coated hollow glass or glass-ceramic microbeads or cenospheres floating at the air-oil interface [25] have been performed. This polyphasic system actually involves salty water, oil, oxygen from the air, UV-beams from sunlight and supported titania. Oleophilic cenospheres are effective in aggregating oil which then undergoes total oxidation and only white, sand-like particles are left [25].

5.1.2. Purification of air

Besides small air-cleaning apparatus based on illuminated titania for confined atmospheres, titania can be deposited as a ceramic on coated tilings [26]. It was shown that titania can be excited by ordinary domestic fluorescent lamps. Such photosensitive tilings are commercialized in Japan, especially for hospitals since, in addition to its photocatalytic ability of cleaning air, illuminated titania possesses bactericide properties [26,27].

5.2. Natural systems

5.2.1. Natural photo-assisted polyphasic reactions in the atmosphere

Urban atmospheres contain pollutants and solid particles. Some of them originate from soils such as Fe_2O_3 and others such as TiO_2 from human activities (fly ashes). These aerosols are able to chemisorb atmospheric pollutants and to be pho-

toactivated by sun light during day time. Orthoxylene was chosen as a model atmospheric pollutant [28]. In dry conditions, illuminated titania oxidizes *o*-xylene into *o*-tolualdehyde in agreement with the oxidative properties of titania [13,18]. By contrast, in the presence of water which is a constituent of the atmosphere, the oxidation becomes total with the formation of CO_2 and H_2O.

Such a behaviour indicates that some self-cleaning processes can occur spontaneously in the atmosphere.

5.2.2. Natural photo-assisted polyphasic reactions in soils

Crude-oil residues in contact with beach sand and air have been observed to undergo photocatalytic oxidation on exposure to light [29]. The beach sand used contained magnetite and ilmenite as minor constituents. These materials are known to have catalytic properties for hydrocarbon oxidation. These results indicate an other example of environmental photo-assisted 'self-cleaning' process.

6. Polyphasic photoreactors

To perform the various types of photocatalytic reactions described above, different types of photoreactors have been built with the catalyst used under various shapes: fixed bed, magnetically or mechanically stirred slurries, catalyst particles anchored on the walls of the photoreactor or in membranes or on glass beads or on glass-wool sleeves or on small spherical pellets, etc. [1–4]. The main purpose is to have an easy separation of the catalyst from the fluid medium, thence the necessity to support titania and to avoid ultrafine particles filtration.

Various devices have been developed such as TiO_2-coated tubular photoreactors, annular and spiral photoreactors, falling-film photoreactors. Some attempts have been made to use successfully solar energy in long tubular reactors placed at the focus of parabolic troughs or in automatically orientated falling-film solar reactors [3]. A new dynamic reactor has been recently commercialized by a Canadian firm for water pollutant removal [3].

7. Conclusions

An overview has been presented on the various potentialities of heterogeneous photocatalysis, the most promising being water detoxification. This last application appears as a new technology, simultaneously safe (no chemical additives), cheap (air as oxidizing agent, low cost of titania) and simple (no ageing of the catalyst, easy cleaning). From the energetic point of view, the use of photons is not redhibitory, since (i) UV-lamp technology has improved and (ii) a lot of thermal energy can be saved because of the absence of the necessity to heat water known for its high heat capacity. The challenge now exists to develop polyphasic photocatalytic systems working in larger scale with all the parameters described above operating in optimized conditions with an efficient catalyst deposited on an inert support for an easy separation.

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