USUAL FREE NANOPARTICLE PHOTOCATALYSTS: TIME IS OVER?

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Abstract

In order to directly compete with traditional nanoparticle monophasic photocatalysts and probably substitute them, interactive composites photosensitive materials elaborated over macroscopic acceptor supports can be applied. The main requirements for these materials destined to be used in oxidation photocatalysis are discussed in this paper.

Keywords: photocatalysis, nanoparticles, interactive composites, acid-base surface properties.

1. INTRODUCTION

The photocatalytic phenomenon, firstly observed as early as 1938 [1] and later applied for the water-splitting procedure in 1972 [2], is generally considered an effect only in nanosized photosensitive well-crystallized semiconductors having optimal forbidden zones controlling the free charge carrier (FCC) recombination. It is namely “nanosized structure” which stays a keyword of this traditional consideration: taking into account the real distances covered by the FCC during their average lifetime in an individual semiconductor under excitation [3], it is believed that an efficient photocatalyst has to be designed preferentially in the nanoparticle state.

However, some well-known application problems (significant handling difficulties, severe sanitary restrictions, etc.) largely restrain, more and more, the use of the free nanoparticle photocatalysts. That’s why an alternative concept of a nanocomposite photocatalyst manufactured using a macroscopic support playing, at the same time, hosting and immobilization roles for a nanostructured photosensitive active component (PAC), was developed during the 1990s. Nevertheless, the PAC coupling to a macroscopic matrix can’t automatically guarantee a good quality of a composite photocatalyst, even if the handling and the main sanitary problems seem to be resolved.

Instead of traditional monophasic nanoparticle photocatalysts or their joining composite analogues where the PAC and the support phases are chemically independent, we propose using of interactive composite materials (ICM) where well-layered photosensitive active components are covalently bonded to special macroscopic matrix manifesting pronounced acceptor capacities and belonging thus, in their original non-hydrated surface states, to the Lewis acids [4 – 7]. Staying in the framework of this concept allowing, besides other benefits, an efficient managing of the FCC surface repartition, we’ve put forward a list of major requirements to be respected in order the photocatalytic properties of macroscopic photosensitive composites could correspond to the ones of the best nanoparticle photocatalytic products (e.g., Degussa-P25). We consider this way to be promising for partial or even whole substitution of usual free nanoparticle or joining composite photocatalysts by their ICM followers.

2. EXPERIMENTAL PART

The test TiO\textsubscript{2} / SiO\textsubscript{2} composite samples were elaborated at 175 – 350°C by means of Molecular Layering Method (MLM) [8] also known as Atomic Layer Deposition technique (ALD) [9] over pure silica supports (silica gel for column chromatography, pore size – 6 nm, grain size – 0.250–0.315 mm, specific area – 440 m\textsuperscript{2}/g, supplier – ACROS Organics) applying titanium tetrachloride TiCl\textsubscript{4} (supplier – ACROS Organics) as a
volatile PAC’s precursor. The structural properties of titanium dioxide surface deposits were studied using XRD (X-ray diffractometer BRUKER D8 Advance) and UV-Vis DRS (UV-Vis spectrometer SPECORD M40 Carl Zeiss Jena) techniques. All diffuse reflectance spectra have been obtained in differential recording mode: pure SiO₂ was applied as a compensatory absorbance species in order to eliminate a vain signal contribution resulting from silica. The sample morphologic characteristics and their elementary compositions were investigated via environmental mode SEM method coupled with EDX analysis facilities (scanning electronic microscope Quanta 200 Feg). The acid-base properties of the sample surfaces were probed both by Tanabe pH-metric techniques [10] and by Hammett indicator method largely described in literature (see, for instance, [11]). The photocatalytic activities of all elaborated species were measured in humid air (RH₂₅°C = 40%) in dynamic conditions (gas flow rate G₂₅°C = 200 ml/min, gas sojourn time in the reaction zone = 19 s) using a coated wall annular reactor irradiated by a black-light UV lamp (electric power – 6W, measured irradiation intensity – 1500 lux, supplier – PHILIPS). Vaporized toluene C₇H₈ (in-let concentration C₀ = 40 mg/m³) was used as the test compound being at the same time a sacrificial agent of the whole oxidation photocatalytic reaction C₇H₈ads + 14 H₂Oads + 14 h⁺vb → 7CO₂gas + 36 H⁺ads, where h⁺vb is an electronic hole in the PAC’s valence band. A degree of the test compound transformation into the whole oxidation products was examined by GC-FID method (gas chromatograph Finnigan Trace GC Ultra). Two main parameters were controlled: 1 – toluene current in-let and out-let concentrations (on-line valve sampling), 2 – total VOC traces availability in out-let gas mixtures at the detection level of a dozen µg/m³ (solid phase micro-extraction sampling, SPME). A permanent follow of total VOC traces presence in out-let gases allowed concluding on the oxidation reaction performance: if in stationary oxidation process no derivate organic compounds did not exist neither over the sample surface, neither in the gas phase, the test compound transformation into the whole oxidation products was considered to be practically complete.

3. RESULTS AND DISCUSSION

Eighteen interactive composite samples containing titanium dioxide PACs chemically deposited over amorphous silica considered to be a powerful acceptor agent [12] were elaborated. The SEM images of the most representative TiO₂ / SiO₂ composite species with extremely different morphologic characteristics are shown in Fig. 2. As to their surface morphology, all the samples may be divided in three groups: I – PAC dominantly deposited as big aggregates (middle diameter ≥ 1 µm, samples 1 – 7, 12); II – PAC deposited as relatively small aggregates (middle diameter ≈ 100 – 200 nm; sample 8); III – PAC dominantly deposited as a layer (middle layer thickness ≈ 100 – 150 nm, SEM estimation using a cut grain; samples 9, 11, 13, 14, 18).

![Fig. 1. XRD patterns (a) and DRS spectra (b) of three typical composite samples representing all morphological groups: 1 – well-crystallized nanoparticle TiO₂ photocatalyst Degussa P25 (80% mas. – anatase, 20% mas. – rutile; a bench-mark sample); 2 – sample 7, group I; 3 – sample 8, group II; 4 – sample 9, group III (composite samples numbering after Fig. 2). Independently of their morphological features, the PACs of all typical samples are rather few crystallized (Fig. 1 (a)). However, all these species contain anatase crystalline nuclei (maximum absorption at ~ 380 nm, Fig. 1 (b)) having the average diameters calculated from Sherrer equation for anatase phase near to 16 nm.](image)
Fig. 2. SEM images of the most representative elaborated samples (samples 1 – 9, 11 – 14, 18) and an EDX spectrum of the sample 18.
A pronounced homogeneity of the PAC crystalline properties for all morphology sample types may be caused by a strong ordering role of a silica support staying still reach, at moderated temperature conditions applied during the synthesis operations, in Brönsted acid (BA) surface sites involved in the MLM exchange (substitution) reactions. Being in the highest proximity over a well hydrated support surface, neighbour BA sites have to favour at first the anatase phase formation (unit cell “a” parameter = 3.78 Å, Fig. 3), whereas over a partially dehydrated surface the rutile phase has to be preferentially formed (“a” = 4.58 Å, Fig. 3). For example, this is the case for the sample 4 (Fig. 2) elaborated at 350°C in extremely dry nitrogen middle (dew-point below -50°C): in its DRS spectrum the absorption maximum is shifted to 415 nm manifesting thus the fact that the PAC begins to be structured just as the rutile phase.

Contrary to the structural features of their PASc, the acid-base surface properties of the tested samples strongly depend on the morphology factor. The samples attributed

**Fig. 3.** Anatase (left) and rutile (right) unit cells [13].

**Fig. 4.** Acidity surface spectra obtained after Hammett indicator method.
to the first and even to the second morphological group show low PAC surface acidity – both for primary Lewis acid sites (Fig. 4 (a), (b)) and for secondary Brönsted ones (Fig. 5). This circumstance probably justifies a weak interactivity of the concerned species: the electron pump ability of an acceptor silica support is not sufficient for any important contribution in the dissociation degree of the secondary surface active sites (BB ↔ LA + OH⁻, BA ↔ LB + H⁺). The situation begins to change only for the samples constituting the third morphological group (Fig. 4 (b), (c) and Fig. 5), with an exception for the sample 12 formally attributed the first group but due to the particularities of its elaboration method possessing a mixed PAC morphology represented both by aggregate and layer forms. Tab. 1 contains the surface acidity parameters of four samples representing in pairs the Ird and the IIIrd groups. In this table, R is a ratio of the average surface acidities of the concerned species: the electron pump ability of an acceptor silica support.

**Tab. 1. Surface acidity parameters of four samples representing in pairs the Ird and the IIIrd groups.**

<table>
<thead>
<tr>
<th>Sample and its morphology group</th>
<th>1 (I)</th>
<th>6 (I)</th>
<th>9 (III)</th>
<th>13 (III)</th>
<th>R</th>
</tr>
</thead>
<tbody>
<tr>
<td>Measured surface Brönsted and Lewis acidities (BA, LA)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BA after Tanabe (Fig. 5), g-ion H⁺ / L</td>
<td>4.0-10⁻⁴</td>
<td>2.5-10⁻⁴</td>
<td>7.0-10⁻⁴</td>
<td>7.1-10⁻⁴</td>
<td>≈ 2.2</td>
</tr>
<tr>
<td>Average for 1, 6: 3.25-10⁻⁷</td>
<td></td>
<td></td>
<td>7.05-10⁻⁷</td>
<td></td>
<td>(for BA sites)</td>
</tr>
<tr>
<td>LA after Hammett (Fig. 4), mmol / g at pKₐ = 14</td>
<td>6.0-10⁻⁴</td>
<td>6.5-10⁻⁴</td>
<td>15.0-10⁻⁴</td>
<td>18.0-10⁻⁴</td>
<td>≈ 2.6</td>
</tr>
<tr>
<td>Average for 1, 6: 6.25-10⁻³</td>
<td></td>
<td></td>
<td>16.50-10⁻³</td>
<td></td>
<td>(for LA sites)</td>
</tr>
</tbody>
</table>

* This value is not presented in Fig. 4*

acidity between the IIIrd and the Ird sample groups. It may be seen that both Lewis and Brönsted sample acidities arise at the same degree when the aggregate PAC surface morphology (3D) is substituted by the layer one (2D). This fact signify that both Brönsted basic (BB) and Brönsted acid (BA) surface sites of the layer composite samples are deeply influenced by an acceptor support and their dissociation constants are considerably more important. The highest surface acidities are manifested by the samples 11 and 18 (group III; Fig. 2 and Fig. 5). For the sample 11 the RBB ratio arises already to 4.4, whereas for the sample 18 RBA reaches 9.8 (I), always as compared to the average BA acidity value obtained for the samples 1 and 6 (Tab. 1). The surface acidity of a composite oxide material is thus an important criterion of its interactive ability. As to composite oxide photocatalysts, a high interactivity is absolutely required in order to free maximum of LB sites over the PAC surface: in standard conditions, the most of these primary sites being active centres of the photocatalytic oxidation process are transformed into inactive BA-centres which must be therefore destroyed by their forced dissociation assisted by an acceptor support.

The data exposed in Fig. 6 confirm that the highest photocatalytic activities are manifested just by interactive composites samples with the most important surface acidities and the PACs well layered over their supports.
It has to be noted that for interactive composite photocatalysts the PAC’s crystalline structure is not a major factor which stipulates their oxidation capacities, as in the case of monophasic nanoparticle semiconductors.

![Graph](image)

**Fig. 6.** Evolution in time of the out-let toluene concentrations during the photocatalytic activity tests: – – sample 6; – – sample 1; – – sample 9; – – sample 13; – – sample 11; – – sample 18.

### 4. CONCLUSION

Interactive composite materials (ICM) elaborated using acceptor supports with chemically bonded to their surfaces well layered photosensitive active components (PAC) can be applied in order to substitute traditional monophasic free nanoparticle photocatalysts considered being potentially dangerous for human health. The main quality criterion for an ICM photocatalytic species is its high surface acidity. On the contrary, the PAC crystalline features are not determinant ones because in ICM structures the FCC separation efficiency is totally controlled by an acceptor support functioning as a powerful electron pump [4, 5].

### LITERATURE


[13] [http://ruby.colorado.edu/~smyth/min/tio2.html](http://ruby.colorado.edu/~smyth/min/tio2.html)